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Remediation of dredged sediments by electrokinetic treatment prior to their valorization

Mathilde Betremieux

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IMT NORD EUROPE



UNIVERSITÉ DE LILLE



THESE

présentée en vue d'obtenir le grade de

DOCTEUR

en

Génie-Civil, Chimie, Environnement

par

Mathilde BÉTRÉMIEUX

DOCTORAT DE L'UNIVERSITÉ DE LILLE

DÉLIVRÉ PAR IMT NORD EUROPE

Titre de la thèse :

**Dépollution des sédiments de dragage par traitement
électrocinétique dans la perspective de leur valorisation**

Soutenue le 22 Octobre 2021 devant le jury d'examen :

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A mes parents



Abstract

The exploitation of natural granular resources is necessary to meet the needs of construction and public works stakeholders. However, the ever-increasing needs for aggregates and the lines of conduct adopted until then have led to overexploitation or even to the depletion of certain resources. The use of alternative materials (sediments, demolition waste, fly ash, slag from non-hazardous waste incineration, etc.) to substitute natural granular resources therefore appears to be a sustainable solution to the problems of overexploitation of quarry aggregates. However, for some alternative materials, the environmental issue is significant and determines the modalities of their reuse. This is particularly the case with dredged sediments. Indeed, these materials resulting from soil erosion are deposited in the bottom of waterways and are excavated during dredging operations in order to ensure the navigability of ports and channels. The maintenance of the “Voies Navigables de France” (VNF) generates 6 to 9 million m³ of material each year. However, given the diversity of contaminants encountered in sedimentary matrices, it is imperative to ensure their environmental quality before considering their recycling. Thus, the onshore management process for dredged sediments must make it possible to reduce the level of contamination of the most polluted materials in order to meet the environmental requirements applicable to alternative materials.

The work of this thesis aims to study an electrokinetic remediation process applied to two contaminated sedimentary matrices, with a view to their future valorisation in the field of civil engineering. Two major objectives were pursued: (i) optimize viable electrokinetic treatment protocols that respect the environment, taking care to choose suitable reagents (natural or biodegradable); (ii) evaluate the effectiveness of treatments for the remediation of inorganic pollutants based on their total contents, their leaching behaviour in the sedimentary matrix, and the analysis of effluents.

The results made it possible to highlight the significant influence of electrokinetic processes on the total concentrations, the distribution and the availability of metallic and metalloid trace elements within the sedimentary matrices. The use of acidic reagents (e.g. citric acid) in combination with chelating molecules (surfactants) has helped to optimize the extraction of these contaminants. Finally, it has been shown that the addition of activated carbon particles can modify the electrical conductance of the sediment matrix and lead to the maintenance of a higher electrical intensity during the depollution process. Given the variability of remediation

performance according to the physico-chemical characteristics of river sediments, it seems essential to systematically carry out a treatability study on a laboratory scale in order to develop suitable treatment protocols.

Résumé

L'exploitation des ressources granulaires naturelles est nécessaire pour répondre aux besoins des acteurs du bâtiment et des travaux publics. Cependant, les besoins toujours croissants en granulats et les lignes de conduites adoptées jusqu'alors ont conduit à des surexploitations ou même à l'épuisement de certaines ressources. L'utilisation de matériaux alternatifs (sédiments, déchets de démolition, cendres volantes, mâchefers d'incinération de déchets non dangereux, etc.) en substitution des ressources granulaires naturelles apparaît donc comme une solution durable aux problématiques de surexploitations des granulats de carrières. Cependant, pour certains matériaux alternatifs, la problématique environnementale est prégnante et conditionne les modalités de leur réutilisation. C'est notamment le cas des sédiments de dragage. En effet, ces matériaux issus de l'érosion des sols se déposent dans le fond des cours d'eaux et sont excavés lors d'opérations de dragage afin d'assurer la navigabilité des ports et des chenaux. L'entretien du réseau fluvial des Voies Navigables de France (VNF) génère chaque année 6 à 9 millions de mètres cubes de matériaux. Cependant, compte tenu de la diversité des contaminants rencontrés dans les matrices sédimentaires, il est impératif de s'assurer de leur qualité environnementale avant d'envisager leur recyclage. Ainsi, le processus de gestion à terre des sédiments de dragage doit permettre de réduire le niveau de contamination des matériaux les plus pollués afin de répondre aux exigences environnementales applicables aux matériaux alternatifs.

Les travaux de cette thèse visent à étudier un processus de remédiation électrocinétique appliqué à deux matrices sédimentaires contaminées, dans la perspective de leur valorisation future dans le domaine du génie civil. Deux objectifs majeurs ont été poursuivis : (i) optimiser des protocoles de traitement électrocinétique viables et respectueux de l'environnement, en prenant soin de choisir des réactifs adaptés (naturels ou biodégradables) ; (ii) évaluer l'efficacité des traitements pour la remédiation des polluants inorganiques en s'appuyant sur leurs contenus totaux, leur comportement à la lixiviation dans la matrice sédimentaire, et l'analyse des effluents.

Les résultats ont permis de mettre en évidence l'influence significative des processus électrocinétiques sur les concentrations totales, la répartition et la disponibilité des éléments

traces métalliques et métalloïdes au sein des matrices sédimentaires. L'utilisation de réactifs acides (par exemple de l'acide citrique) en combinaison avec des molécules chélatrices (des tensioactifs) a contribué à optimiser l'extraction de ces contaminants. Enfin, il a été démontré que l'ajout de particules de charbon actif peut modifier la conductance électrique de la matrice sédimentaire et conduire au maintien d'une intensité électrique plus élevée pendant le processus de dépollution. Compte tenu de la variabilité des performances de dépollution en fonction des caractéristiques physico-chimiques des sédiments fluviaux, il apparaît indispensable de procéder systématiquement à une étude de traitabilité à l'échelle du laboratoire afin de mettre au point des protocoles de traitement adaptés.

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Submission envisaged in: Journal of soil and sediment (IF 3.308)

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- Article 2. Mathilde Betremieux & Yannick Mamindy-Pajany (2021) Investigation of a biosurfactant-enhanced electrokinetic method and its effect on the potentially toxic trace elements in waterways sediments, Environmental Technology
DOI: 10.1080/09593330.2021.1936202

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General introduction

It is difficult to imagine the construction industry, or that of public works, without the massive use of gravel or aggregates. The exploitation of these natural resources is necessary to meet social and economic needs, however, the ever-increasing needs and the policies adopted so far have led to the overexploitation or even extinction of certain resources (Tribout, 2010). Stone quarries are often abandoned at the end of their life and have an important risk of collapsing, due to water infiltration which weakens them. In addition, they strongly alter the landscape, creating cliffs and cutting hills. The use of renewable granular resources (sediments, bricks, concrete, mortars, etc.) as a substitute for natural resources therefore appears to be both a sustainable solution to the problems of overexploitation appears to be both a sustainable solution to the issues of overexploitation (Cazalet, 2012), while promoting construction activities. Nonetheless, these granular resources, especially sediment, strongly influence the modalities of reuse in the building and public work sectors due to a significant environmental awareness (Nguyen, 2008).

Dredged sediments are naturally renewable materials, resulting from erosion, and are deposited in the bottom of waterways. In order to ensure the navigability of ports and channels, dredging campaigns are necessary. They consist of removing sediments accumulated on the bed of the waterway, increasing the available water level and thus making transport infrastructures practicable (Lecomte, 2018). In France, the maintenance of waterways is carried out by the “Voies Navigables de France” (VNF) and generates 6 to 9 million m³ of sediment from streams, rivers and canals every year (Poitevin, 2012). In the Nord and Pas-de-Calais departments only, 10 million m³ have been dredged in 20 years (Lemay, 2020), and between 140,000 and 230,000 m³ over the last three years in the Hauts-de-France region.

In September 2015, the “Centre d'Etudes et d'Expertise sur les Risques, l'Environnement, la Mobilité et l'Aménagement” (CEREMA) published an information note in the continuity of the SETRA (2011) guide, providing an approach for assessing the environmental acceptability of alternative materials, made from waste and intended for use in road techniques (in the form of aggregates, gravels, soils, fillers or binding agents). The overall objective of this guide is to demonstrate, for a specific road application, that the emissions of dredged sediments and road material are compatible with the respect of the water quality aimed by the methodological guide (SETRA, 2011). The traditional solutions have often been to deposit or re-suspend continental sediments. Yet, nowadays, the re-suspension

of these materials is scarce because of the regulations regarding the quality and environmental impact (Law text of 9 August 2006) (Lecomte, 2018). Moreover, we know that sediments extracted from their environment see their physico-chemical conditions change and can favour the emission of pollutants. Therefore, extracted sediments are often considered as a polluting source (Cazalet, 2012). This is why most of dredged waterways sediments are managed on land (Lemay, 2020). However, due to the diversity of contaminants found in sedimentary matrices and the variability of their physico-chemical properties, the pollution contained in these materials is analysed of total content (acid digestion test) and mobility (leaching test). The environmental impact of land-based management of these materials has led to an increase regarding recovery researches and techniques.

This thesis was conducted in order to develop viable and relevant recovery pathways for dredged sediments, in order to that these materials can be easily integrated into different sectors, such as construction or public works. More specifically, the research work carried out in this thesis aims to study two contaminated sediment matrices, subjected to the electrokinetic (EK) treatment process, in order to evaluate and understand the mobility of inorganic pollutants.

The EK process appears as a promising remediation method, applicable both *in* and *ex situ*, on low permeability sediments in order to decontaminate them from a wide variety of pollutants. The process is based on the application of a low-intensity electric current in a sediment matrix (Tian, 2018). The current is delivered into the sediment via electrodes, and the electric field creates a differential potential between the electrodes. This result in electrolysis reactions of the water in the direct proximity of the electrodes, as well as transport mechanisms, responsible for the migration of chemical species into the liquid phase (Matteo Masi, Ceccarini, and Iannelli, 2017). This remediation method has the advantage that it can be combined with other treatment or pre-treatment processes, and can be improved by adding additives to the electrode compartments. However, EK remains at the research and development phase and has not yet found a way to industrial development.

This research work lays on the work previously made in the literature (reagents or experimental set-up), but also led to an optimisation of the treatment, by significantly improving the electric current, without increasing the voltage initially delivered. Therefore, our problematic is the following: How can EK remediation be used and optimised to enhance the valorisation of sedimentary waste in road construction?

Four major scientific challenges were investigated in this thesis:

- (i) in this thesis, we wanted to test a novel reagent developed by a research laboratory. The whole set of treatment reagents was chosen with the aim of proposing viable EK protocols with low environmental impact. Natural and biodegradable, they also have the ability to complex with trace elements to optimise remediation performance;
- (ii) we looked to optimise the EK phenomena, by increasing the mobility of inorganic pollutants in the sedimentary matrices studied. Two different matrices were used in this research, in order to evaluate the effect of the matrix in the inorganic elements outcomes, subjected to EK treatment;
- (iii) we were interested in the impact of treatment on matrix transformations. We identified the main mineral phases influencing the mobility and retention of inorganic pollutants in the sediment matrix, using sequential extraction;
- (iv) we have attempted to optimise the EK phenomena of the treatment with an activated carbon amendment.

In order to achieve these objectives, this thesis is structured around four chapters:

Chapter 1: State of knowledge - Review.

This chapter is dedicated to regulatory aspects and brings together all the bibliographic research carried out. It acts as a review of the current literacy. In this chapter is detailed the challenges of the management of dredged sediments, the definition and origin of sediments and pollutants, the different retention mechanisms of pollution as well as the principle of electrokinetic remediation.

Chapter 2: Study of an electrokinetic method reinforced by a novel biosurfactant.

This chapter study a newly developed biodegradable biosurfactant by HTS Bio research laboratory and its impact on EK. We discuss the experimental results and show that further investigations could be considered with this type of electrolyte and that the solubilisation mechanisms of the inorganic elements should be studied in order to improve the removal efficiency of the solid phase. This chapter also present the equipment and the method used to carry out the remediation tests (**Figure 1**). This chapter answer the (i) challenge discussed above.

Chapter 3: Comparison of treatment efficiency on two sedimentary matrices and analysis of pH effect on pollutant mobility.

As stated in the chapter 2, the use of acidic reagents provides a good prospect in order to improve the solubilisation of the elements (**Figure 1**). Thus, in the first instance, two waterways sedimentary matrices were subjected to electrokinetic treatment, with weak acids, in order to measure the impact of pH on the mobility of elements. Leaching tests, under pH control (pH 2 and pH 12), showed that the pH not only had a significant impact on the mobilisation of trace elements, but also on the major elements (constituents of the carrier phases).

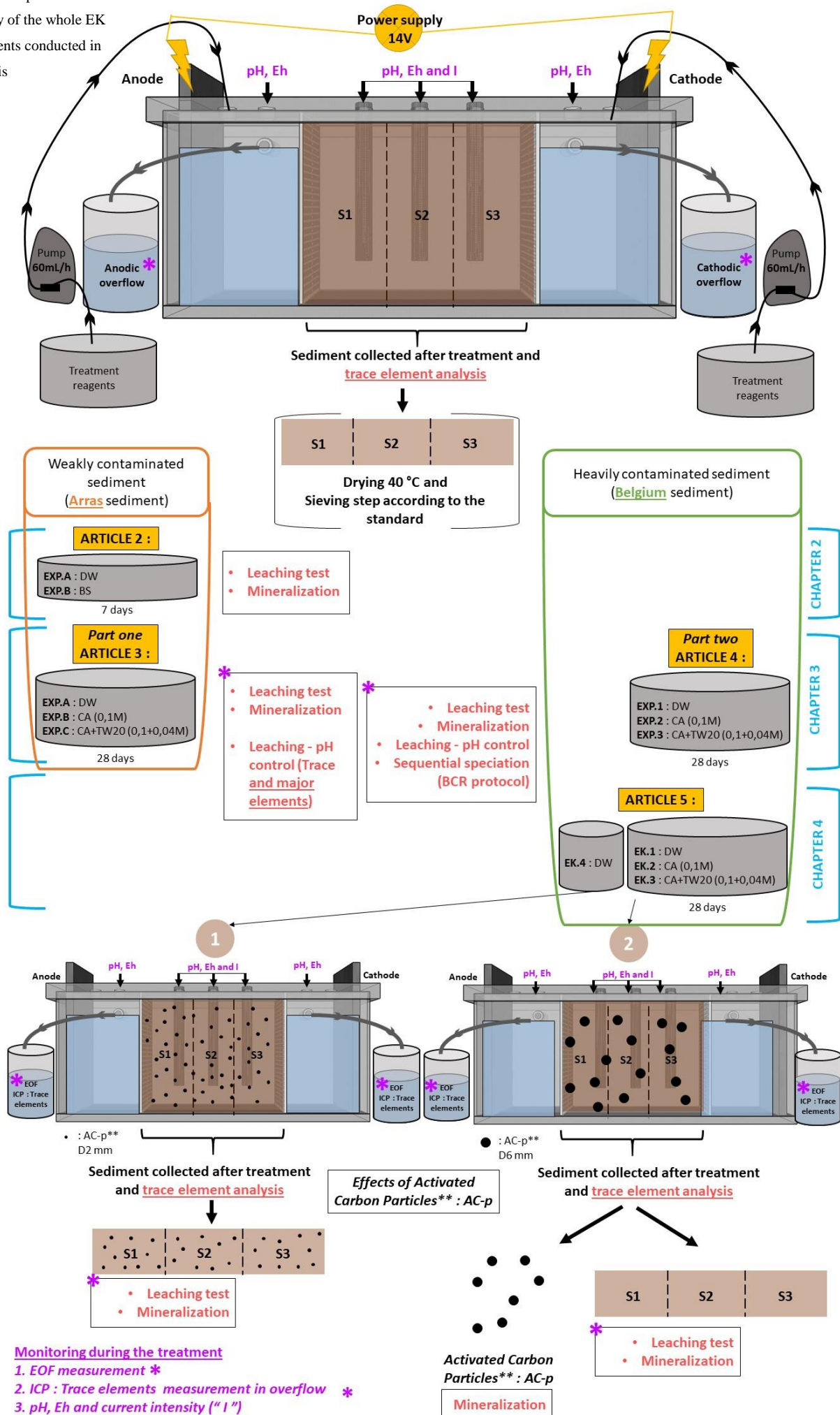
The analysis of the carrier phases was therefore our second line of investigation in this chapter. To this end, a test characterising the sequential extraction of trace elements was carried out on one of the sedimentary matrices studied.

This chapter answer the (ii) and (iii) challenge discussed above.

Chapter 4: Increasing the electric current intensity with activated carbon and measuring the impact on trace element mobility.

This chapter presents a new approach to improve the electric current intensity during electrokinetic treatment, while reducing the operating costs. Two types of activated carbon were mixed with the sediments (**Figure 1**) in order to enhance the transmission of the electric current and thus improve the electrokinetic remediation parameters. This chapter answer the (iv) challenge discussed above.

Figure 1: Experimental summary of the whole EK experiments conducted in this thesis



CHAPTER 1 - STATE OF KNOWLEDGE - REVIEW

A review of electrokinetic sediment remediation:

Highlighting metals retention mechanisms and parameters influencing electrokinetic treatment. Proposal of a treatment protocol using electrokinetics for the valorisation of sediments

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Abstract

Pollution is now a global problem and is becoming an increasing concern. Dredged sediments are known to store large amounts of trace elements, and play an important role in the transformation of chemical elements. Sediment management is therefore a major economic, social and environmental issue for waterway managers. One of the favoured solutions is to be able to reuse these sediments as secondary raw materials, in partial or total substitution of more noble aggregates. However, the presence of pollutants in these sediments prevents their valorisation. A significant amount of research has been carried out on this issue and new valorisation methods are still being studied. This is particularly the case for electroremediation, which is difficult to adapt on a pilot scale. The aim of this article is to review the state of knowledge in electrokinetic treatments apply to sediments and to assess factors that influence its effectiveness. Electrokinetic (EK) remediation is a method involving many interdependent parameters, making its use complex. This method is mainly focus on trace elements remediation, by playing on the variations of pH and oxidation-reduction potential (Eh). The pH is involving in the distribution of trace elements in the sediments, whereas the Eh mainly occurs by modifying the pH values, thus indirectly modifying the distribution of metals.

Keywords: Electrokinetics, Sediments, Remediation, Trace elements, Retention mechanisms

I. Introduction

Large quantities of dredged sediment, often polluted by anthropogenic activities, have become a major economic, health and environmental issue for local authorities. Recovery methods are needed for these materials, which can be used in the construction and public works sectors. Dredged sediments are known to store large quantities of trace elements which are potentially toxic. In the aquatic environment, trace elements are generally distributed as follows: water-soluble species, colloids, suspended forms and sedimentary phases. However, unlike organic pollutants, natural decomposition processes do not remove heavy metals. Rather, they are usually enriched in the sediment by organisms or other compounds (Peng et al., 2009). Nonetheless, heavy metals cannot remain in the sediment for a long period of time. As the physico-chemical characteristics of the water change, some of these metals bound will return to the surrounding water and become available to living organisms. Thus, sediments often act as carriers and potential sources of contamination in aquatic environments (Zoumis et al., 2001). Trace metals generally exhibit significant toxicity to aquatic organisms and subsequently affect human health through the food chain (Ammami, 2013). Interestingly, to alleviate this toxic risk, decontamination treatments have been developed, based on protocols already used for soil treatment. Indeed, there are important analogies between sediments and soils, despite their own particularities. Different treatments exist today. These are listed in several categories: physical, physico-chemical, biological, thermal and chemical. Here are some examples of treatment methods (Kribi, 2005) : Cycloning, attrition, magnetic separation (Gillet, 2003), flotation (Cauwenberg, Verdonckt, and Maes, 1998), ultrasonic decontamination (Chew and Zhang, 1998), and more recently Meegoda and Perera (2001) has improved the method by using ozone nano-bubbles (powerful oxidizing agents). Leaching extraction, complexation extraction, solvent extraction, cation exchange process also called: solidification/stabilization (Song, 2017; Alshawabkeh and Sheahan, 2003), desorption, wet air oxidation, vitrification, incineration, bioleaching (Tyagi et al., 1993) phytoextraction (Licinio, 2017), biodegradation (Gill et al., 2014; Crampon, 2015).

One of these treatment methods is Electrokinetic (EK) remediation. It is a promising method able to depollute low permeability sediments from a wide variety of inorganic (*i.e.* trace elements) and organic pollutants (*e.g.* PAHs, PCB.). EK consists of the use of a weak electric current, introduced into the matrix of the material to be treated in order to extract the pollutants. This method uses several transport mechanisms such as electroosmosis, electromigration or electrophoresis (Mao, Shao, and Zhang, 2019), as well as electrochemical

reactions such as water electrolysis. The literature focuses mainly on the extraction of the total mineral contaminants, however, the standards for sediment valorisation are based on sediment leaching. Reducing the level of pollutants below the levels defined in the legislation can allow their reuse in the fields of civil engineering as well as limiting the risks related to human health and the environment. Although a significant amount of experimental work has been carried out, the diversity of the mechanisms involved, the great complexity as well as the heterogeneity of the sedimentary matrix have sometimes complicated the effectiveness and understanding of electrokinetic treatment (Masi, 2017).

The aim of this bibliography chapter is to establish the state of the art of EK remediation technology for the treatment of sedimentary matrices. This chapter includes:

- (i) The context and issues of electrokinetic remediation, in order to introduce the theoretical and experimental backgrounds of this thesis;
- (ii) A review of the different operations carried out with this method, in order to trace the history of electrokinetics and to understand the evolution of the technique. The electrochemical mechanisms that occur during the EK process are also detailed;
- (iii) An investigation of contaminants, retention mechanisms, and the distribution of chemical elements within the sedimentary material;
- (iv) Factors influencing the EK remediation process.

II. General context on electrokinetic remediation

II.1. History

EK-related phenomena have been known since the early 1800s, when Ferdinand Friedrich Reuss applied a direct current to a mixture of clay and water. He was able to observe a movement of the fluid moving from the anode to the cathode under the influence of the electric current and to note that this phenomenon is in fact a surface phenomenon linked to the existence of the electric double layer (Song, 2017). Reuss became the first to study electro-osmosis and was then credited with this discovery in 1808. Reuss's research had proven significant for combating the many problems of wall dampness caused by water rising through the capillaries (Bolard, 1882).

The physiologist and physicist Hermann von Helmholtz has been the first to provide an analysis of electroosmotic phenomena related to electrokinetics. His theory was then

studied further and deepened by Marian Smoluchowski, leading to a well-known equation: the Helmholtz-Smoluchowski equation (*i.e.* HS equation). This equation is still commonly used to quantify the electroosmotic flux (EOF) of Newtonian fluids (fluid which keeps its fluidity under mechanical stress) (Masi, 2017). The Helmholtz-Smoluchowski equation describes the electrofiltration potential (electrical potential between the sample ends) and assumes that ions of opposite sign of the solid particle of material are concentrated in the electrical double layer at the interface. This equation expresses how a liquid moves at the speed of the ions. In addition it shows that the thickness of the electrical double layer is negligible compared to the grain diameter, so is the case for the surface conductivity compared to the conductivity of the fluid (Crespy and To, 2008).

Then, in the 1940s, Leo Casagrande used electroosmosis to cause consolidation of fine-grained soils (Casagrande, 1949). He developed a model based on the H-S equation to determine electroosmosis in clays by considering the effects of porosity and tortuosity of electroosmotic flows. His model describes the transfer of water in a soil under the action of an electric field. Initially, this phenomenon was mainly used in soil mechanics. The aim was to consolidate soils with low permeability in order to improve their mechanical properties locally (Song et al., 2014).

More recently, environmental concerns have led to the application of electrokinetic phenomena to the remediation of soil and other materials. Since the end of the 80's witnessed the development of successful EK approaches, used to remediate different types of materials (*e.g.* soil / sediment): (Sibel Pamukcu and Wittle, 1992; Probst and Hicks, 1993; Acar and Alshawabkeh, 1993; Ottosen et al., 1997; Alexandra B. Ribeiro and Mexia, 1997; Beaulieu, 2000; Nystroem, Ottosen, and Villumsen, 2005; Gomes, Dias-Ferreira, and Ribeiro, 2012; Ammami et al., 2015; 2014; Ammami, 2013; Tian, 2018)

EK technique has also been applied to different types of wastes, such as treated wood wastes (Ribeiro et al., 2000); mining residues and fly ash (straw and wood) (H. K. Hansen et al., 2001; 2007) ; contaminated fly ash (Ferreira, Ribeiro, and Ottosen, 2005) ; on kaolin (J. Y. Wang et al., 2007); on reactor residues (Jensen et al., 2010) or industrial wastes (mining residues and metallurgical furnace powder), but also to clean up polluted water, and has proved its worth in the remediation of soil and various materials (Chew and Zhang, 1998; Shin-Shian Chen, Yi-Chu Huang, 2010). Interesting innovations in the conventionally experimental set-up can be noted: as example Yan et al. (2018) used activated carbon synthesized from coconut shells as a third electrode, introduced directly into the soil matrix.

The removal of inorganic pollutants (heavy metals) induced by EK treatment has been extensively studied in the literature (Virkutyte, Sillanpää, and Latostenmaa, 2002). This method then naturally extended to organic contaminants, such as phenol (Acar et al., 1995); chlorinated solvents, including tetrachloroethene and trichloroethene, which are among the most common organic contaminants found in soils and groundwater (Mao et al., 2012; Chang, Qiang, and Huang, 2006); petroleum hydrocarbons (Guo et al., 2014; Jeon et al., 2010); herbicides (A. B. Ribeiro et al., 2005; Alexandra B. Ribeiro, Mateus, and Rodríguez-Maroto, 2011); and polycyclic aromatic hydrocarbons (PAHs) (Lima et al., 2011; Bocos et al., 2015).

Since the first works showing that EK can effectively lead to sediment (or other materials) remediation, this field has become very active. In particular, this has led to a real progress in the understanding of the effects of EK in soils, as well as in modelling (Alshawabkeh and Acar, 1996; Masi, 2017) and in the understanding of the factors limiting pilot-scale applications (M. Masi, 2017).

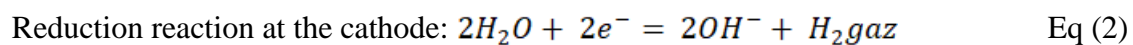
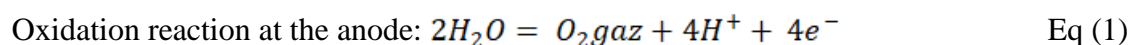
II.2. Basic mechanisms of EK

In order to mobilize pollutants and to extract them from the sediment by electrokinetic, it is necessary to apply a low electric current within the sediment matrix. The current is conducted through the sediment by means of two electrodes located on both sides of the material (at least for laboratory experiments). The positive pole electrode is called the anode, while the negative electrode is called the cathode. For a pilot application, the electrodes are more numerous and are arranged in the middle and around the area to be treated. The electrodes' form can be plate or cylindrical, and their material may also vary according to the study. The potential difference between the electrodes causes physico-chemical and hydrological changes in the matrix, and allows the migration of ions and water to the electrodes (Peng et al., 2009). An essential electrochemical reaction induced by the electric current occurs at the electrodes: water electrolysis (Acar and Alshawabkeh, 1993; K. J. Kim et al., 2011) detailed below.

At the anode, the water is oxidized (Eq 1), producing H^+ ions and gaseous oxygen. The H^+ ions are transported mainly by electrical migration to the cathode. As a result, an acid front is created that moves through the sediment from the anode to the cathode and solubilizes metals and ammonium ions, as well as organic compounds (Yeung and Gu, 2011). This solubilisation, improved under low pH conditions, positively charges the heavy metals,

causing them to migrate in the same direction as H^+ ions. In addition, it makes the pollutants mobile and extractable by electrical migration (Gidakos and Giannis, 2006). Indeed, Ait Ahmed (2016) observes that 90% of heavy metals are generally immobilized in the sedimentary matrix in a form in which they cannot be extracted by the electric field. Consequently, solubilisation is necessary to allow their extraction. This production of H^+ ions at the anode has a direct impact on the pH of the electrolysis solution. The latter becomes acidic when it is enriched by these ions (Song, 2017) and thus allows the trace elements solubilisation.

At the cathode, a reduction reaction takes place (Eq 2), it generates OH^- ions and hydrogen gas. The OH^- ions, as well as anions (e.g. chlorides, fluorides, nitrates and negatively charged organic compounds) move towards the positive pole, despite the movement of the H^+ ions. However, when the trace elements, solubilized by the acid front of the H^+ ions, come into contact with the OH^- ions, this immobilizes them again in the sediment. In addition, the H^+ and OH^- ions react together to form water that neutralizes the advance of the acid front and the base front. Therefore, in order to ensure the correct extraction of heavy metals, the composition of the solutions in contact with the electrodes must be checked regularly. Nonetheless, there are certain organic contaminants, of low polarity, which are difficult (or even not at all) to mobilize by electrokinetics. This is even true in the case of fine-textured soil, such as clay. In these cases, the use of polar chemical compound has an interesting result for EK: hydrophobic compound can be solubilised and can migrate thanks to the induced electric potential difference



Although the migration of ions is induced by the electric current, different transport mechanisms, interdependent, are involved in the EK process (Mosavat, Oh, and Chai, 2012a; Baraud, Tellier, and Astruc, 1999). Combined with the heterogeneous sediment matrix, EK process is difficult to study.

In order to be able to carry out electrokinetic depollution tests, an experimental cell must be built. In the literature, various experimental set-ups have been carried out. These set-ups vary in many terms such as the size of the cells, materials used, flow rate of the pumps. An exhaustive comparison is made in **paragraph III**.

The EK cells generally consists of 5 units: (i) the central chamber, of varying size, contains the sediment or soil to be remediated; (ii) the adjacent chambers will contain the electrolytes and electrodes; (iii) the electrolyte chambers are separated from the main chamber by means of perforated grids and filter paper to prevent contamination of the electrolytes with sediment particles. Ions in solution, transported by the electric current, can progress from the electrodes into the matrix; (iv) the electrolytes are fed into the anode and cathode compartments using a continuous injection system; (v) Finally, an evacuation system (overflow) is also installed in the two injection compartments, in order to maintain a constant electrolyte height in the cell. The cell used in this thesis was introduced in **chapter 2**.

In theory, EK relies mainly on three transport mechanisms (Tang et al., 2021):

- Electrophoresis: transport of charged particles or colloids under the influence of an electric field to the electrode of the opposite charge (Faulkner, 2010). Contaminants bound to mobile particles can be transported in this manner. Electrophoresis becomes important in electrokinetic treatment when surfactants are introduced into the treatment fluid to form micelles (charged particles) with other species (Song, 2017).
- Electroosmosis: movement of a fluid (which can be de-ionized water (DW), an electrolyte or an organic fluid) along a solid surface, induced by a tangential electric field in the diffuse layer (Banerjee et al. 1991).
- Electromigration: movement of ions present in the interstitial water of the soil that move when an electric field is applied (Page and Page, 2002) (Méndez et al., 2012).

From the literature, it appears that these three mechanisms are the most predominant (Kim et al. 2001).

II.2.1. Electromigration

Electromigration is the movement of ionic species, including H^+ and OH^- ions produced by the electrolysis of water, to the oppositely charged electrode and moving through the porous matrix (Kim et al. 2001). The acid front generated by the H^+ ions moves faster than the base front made of the OH^- ions. This is due to the greater mobility of the hydrogen ions, and therefore dominates the chemistry of the sample, which is favourable to the chemical elements solubilisation. Electromigration can be considered as a special case of electrophoresis, when the particle size is close to zero (molecular scale). Ammami (2013)

states in his thesis that electromigration constitutes the conductivity of the porous medium. [Ammami \(2013\)](#) also states that transport by electromigration is only possible when the electro-neutral equilibrium in a system is broken by the exchange of electrons as a result of electrochemical reactions at the electrodes. Electromigration therefore acts to restore the electro-neutrality balance. During electrokinetic treatment, the concentrations of ionic species in the system vary, and therefore the conductivity of the medium varies as well. The voltage and the electrical intensity have interesting an behavior for EK treatment: if the voltage is kept constant: this controls the speed of ion transport and the electrical intensity varie; if the electrical current is kept constant, the total amount of species recovered from the anode and cathode compartments can be controlled ([Alshawabkeh and Acar, 1996](#); [Ammami, 2013](#)). Thus, species move according to their ionic mobility, according to their intensity of the electric field, the charge and ionic concentration, the size of the ions, the diffusion coefficient in the medium and the temperature. The following equation represents the simplified model of electromigration ([Yvon, 2008](#)) :

$$J_{em} = \mu^* \theta C \nabla(-E) \quad \text{Eq (3)}$$

With:

J_{em} : electromigration flow ($\text{mol.s}^{-1}.\text{cm}^{-2}$)

μ^* : effective electric mobility ($\text{cm}^2.\text{s}^{-1}.\text{V}^{-1}$) : $\mu^* = \frac{\mu}{\tau}$; where μ is the electrical mobility and τ the tortuosity

θ : porosity (in saturated zone, otherwise $n\theta$, with n = saturation coefficient)

C : concentration of the species in the interstitial fluid (mol.cm^{-3})

$\nabla(-E)$: electrical gradient (V.cm^{-1})

Consequently, there is no transport by electromigration for non-ionic species. These species are only moved by electroosmotic advection. Their migration's speed and direction are the one of the electroosmotic flow ([Baraud, Tellier, and Astruc, 1999](#)). Finally, it is worth to note that electromigration is a rapid transport that is unaffected by the electrical state of the surface of the solid particles. Nevertheless, changes in polarity and/or solubility of the species can influence the speed of migration by altering ion mobility or even the direction of migration.

II.2.2. Electroosmosis

As mentioned in the introduction, Reuss noted in 1809 that electroosmosis is in fact a surface phenomenon, linked to the existence of the electrical double layer (EDL) (Song, 2017). The EDL is the interface between the charged surface and the electrically neutral liquid layer (Ammami, 2013). The surface of the solid particles has its own electrical charge, and an accumulation of counter ions occurs in the solution in the vicinity of this surface, in order to counteract the surface charges and to maintain the electro-neutrality of the solid/liquid interface. Excess counter ions in the double layer will transmit a greater driving force to the aqueous solution (Figure 1). This is because when an electric field is applied, it induces a net movement of the fluid in the direction of where the counter ions migrate in the diffuse double layer.

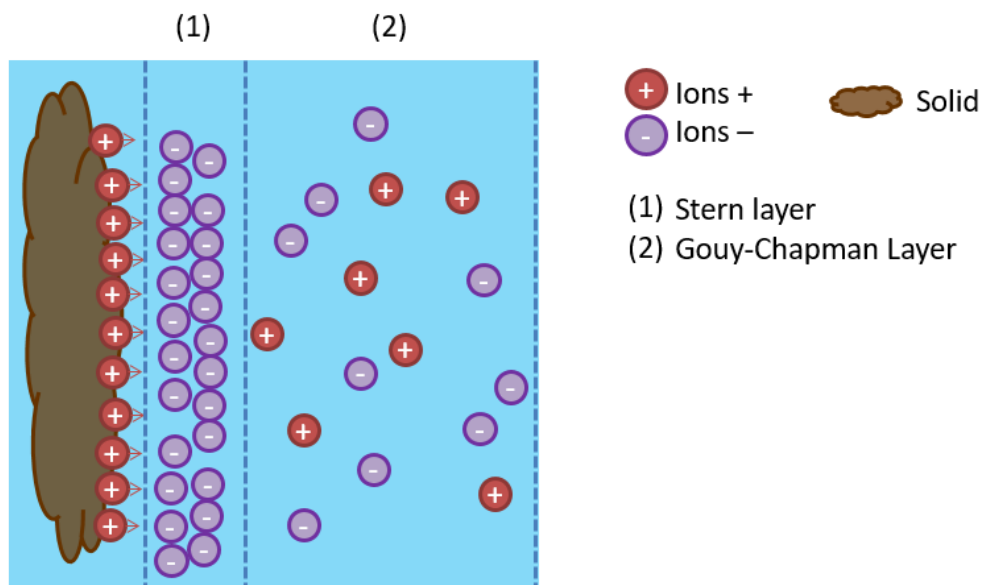


Figure 1 Diagram showing the electrical double layer (EDL)

The following equation represents the simplified model of the electroosmosis phenomenon (Yvon, 2008):

$$J_{eos} = -K_e C \nabla(-E) \quad \text{Eq (4)}$$

With :

J_{eos} : electroosmotic flow ($\text{mol.s}^{-1}.\text{cm}^{-2}$)

K_e : electroosmotic permeability coefficient ($\text{cm}^2.\text{s}^{-1}.\text{V}^{-1}$)

C : concentration of the species in the interstitial fluid ($\text{mol}.\text{cm}^{-3}$)

$\nabla(-E)$: electrical gradient ($\text{V}.\text{cm}^{-1}$)

In the case of clays, which are generally negatively charged, the density of the cations in the solution will be higher near the surface while the anions in the solution will be repelled. The application of electric current causes the cations in excess near the surface to move towards the cathode. This excess associated with water molecules, generates a stress that acts on the interstitial fluid: this creates a shear force due to the viscosity of the fluid in the pores (Iyer, 2001). He summarizes that electroosmosis can be defined as the mass flow due to the pore fluid. The thinner and less permeable a material is, the more interesting electroosmosis becomes, because it allows the transport of water on a molecular scale, even if hydraulic gradient is not very effective.

The efficiency of electroosmosis is strongly influenced by the pH variation, which can change the surface charge state of the solid particles (Iyer, 2001). Indeed, under certain conditions of acidic pH, the clay particles are no longer charged, so there is no longer an electric double layer and the electroosmotic flow becomes zero. In this case, the zeta potential (noted : ζ) of the surface, representing the intensity of the charge of counter ions in the double layer, becomes zero. Incidentally, the zeta potential can be used to predict the direction of an electroosmotic flux (Baraud, Tellier, and Astruc, 1999). The most widely used theory to describe the electroosmotic process has been proposed by Helmholtz-Smoluchowski. Their theory deals with the electroosmotic velocity of a fluid and the zeta potential under an imposed electrical gradient. In the literature, several model of the H-S equation exist. We have selected the following one (Eq 5) from Virkutyte, Sillanpää, and Latostenmaa, (2002) which details all the parameters involved:

$$U_{EO} = \frac{\epsilon\zeta}{\mu} \frac{\partial\phi}{\partial x} \tag{Eq (5)}$$

With:

U_{EO} : electroosmotic speed

ζ : zeta potential

$\frac{\partial \phi}{\partial x}$: effective porosity

μ : viscosity of the fluid

ε : the dielectric constant of the interstitial fluid

Usually:

- If $\zeta < 0$ the flow goes from the anode to the cathode.
- If $\zeta > 0$ the flow goes from the cathode to the anode.
- If, during the electrokinetic treatment, the electrical potential remains constant, all the parameters of the equation remain constant, except for the zeta potential.
- If the zeta potential is zero (*i.e.* zero charge point), there is no more electric double layer and the electroosmotic flux becomes zero.

Zeta plays an important role in the direction of the electroosmotic flow and will therefore influence the efficiency of the electrokinetic treatment of the sediments. Indeed, zeta potential can exceed the zero-charge point in case of strong acidification, and sediment particles will become positively charged. The anion will then be directed towards the anode and will therefore drive the electroosmotic flow in the opposite direction: from the cathode to the anode (Ammami, 2013). Ammami (2013) recommends to maintain pH conditions low enough to ensure the transport of dissolved metal contaminants in the aqueous phase in the anode/cathode direction, but high enough to maintain negative zeta potential (*Cf.* Eq 5). The zeta potential is also a good indicator of the thickness of the electrical double layer: as the absolute value of the zeta potential increases, so does the thickness. Zeta potential is also a function of pH and ionic strength.

II.2.3. Electrophoresis

Vieira-Nunes (2018) identify four types of electrophoresis and show that all the electrophoretic methods are applicable in common electroosmotic installations (*i.e.* a similar device as the EK cell presented in **Paragraph II.2**). This device is made of the cathode and the anode compartments, the separation chamber and the injection system. Vieira-Nunes (2018) shows that differences in mobility's result in various ion velocities: this effect can be used to successfully separate ionic species. This separation principle has been applied in three

main separation techniques, called "Electrophoretic Separation Methods": (i) zone electrophoresis, (ii) mobile boundary (or free solution) electrophoresis and (iii) isotachophoresis.

In other word, electrophoresis can be considered as a flow due to charged particles.

Under the influence of an applied electric field (E), the ionic species move at a velocity (v), given by the following expression (**Eq 6**):

$$v = UE \quad \text{Eq (6)}$$

where U is the effective mobility of the ionic species.

III. Assessment of the application of the EK technique

A comparative study was conducted in order to establish a comprehensive list of laboratory experimental set-up, including the size, the shape or even the tension used. This list is presented in **Table 1**. We also present a comparison of the experimental protocols used in the literature and the effectiveness of the EK-remediation in **Table 2**. The size of the cell, as well as the volume of sediment treated, has a major impact on the remediation ([Masi, 2017](#)). The study mainly focused on the laboratory, pilot and semi-pilot experiments. The end purpose of this study is to provide the community with concise insights regarding experimental variations, the impact of the parameters in EK treatment, as well as raising new scientific problematics.

III.1. Electrokinetic cells

In the literature, the materials commonly used to make the experimental EK cells are acrylic, Teflon and Plexiglas (**Table 1**). The cells are cylindrical or rectangular in shape and electric current is usually injected continuously into the system. Concerning the electrodes, they are mainly made of graphite, titanium or stainless steel. The injection rate of the reagents is not always indicated in the studies. Nevertheless, important variations can be observed. For example, for a similar treatment volume, [Hamed and Bhadra \(1997\)](#) use an injection rate of 1.2 to 7.98 mL/h, while [Lee and Lee \(2001\)](#) inject his reagents at 80 mL/h. One might also think that the tension injected is proportional to the volume of material processed, but this is not necessarily the case. For similar treated volumes (about 260 cm³), ([Song, 2017](#); [Tian, 2018](#); [Ammami, 2013](#)) used a voltage of 14V. [Ait Ahmed \(2016\)](#), for a smaller treated

volume (115 cm³) used a higher voltage and [Yvon \(2008\)](#) for a volume of 160 cm³ used a voltage of 10V.

Some authors, such as [Hamed and Bhadra \(1997\)](#) and [Colacicco et al. \(2010\)](#), have varied the voltage to study its effects on remediation. In the most recent studies, filter paper at 0.45µm, coupled with a perforated grid is the most commonly used solution to separate the reagents from the material. Some authors have used other separation techniques. For example [Pazos et al. \(2013\)](#) and [Colacicco et al. \(2010\)](#) used a porous stone. [Rozas and Castellote \(2015\)](#) a textile and [Hamed and Bhadra \(1997\)](#) perforated electrodes.

The pilot and semi-pilot devices were always rectangular in shape. The treated volume of these device varies from study to study; [Masi \(2017\)](#) treated the largest volume: 150 m³ with a 7 x 15 x 1.25 m set-up.

The pilot device were made of concrete and geotextile for [Masi \(2017\)](#), and woven geotextile for [Tyagi \(2006\)](#), while the semi-pilot cells retained the materials used for the cells made for the laboratory. The voltages used are higher, but still remain in the VLV (Very Low Voltage) range as they do not exceed 120V DC.

The type of electrodes, used in large-scale applications, is similar to those used in the laboratory, except for [Micic et al. \(2001\)](#) who used a steel mesh. However, it should be noted that [Micic et al. \(2001\)](#) did not use electrokinetics as a means of depollution, but rather to consolidate the matrix. The choice of electrode is perhaps guided by this objective.

III.2. Efficiency

Trace elements analysed in these studies are commonly: As, Cd, Cr, Cu, Ni, Pb and Zn (**Table 2**). Treatment times can vary from 1 to 120 days for laboratory experiments, from 3 days to 18 months for pilot scale and from 5 to 56 days for semi-pilot scale. The variation in treatment times suggests that the authors looking for more meaningful abatement results.

Concerning the reagents, some authors decide to use the same reagents in both electrolyte chambers (*i.e.* anodic and cathodic chambers), but others decide to vary them. Demineralised water is often used in studies, and is mainly used as a control in experiments. Citric acid, acetic acid, nitric acid and ethylenediaminetetractic acid (EDTA) are commonly used, as well as surfactants such as Tween 20, 21 and 80. [Tyagi \(2006\)](#) used a mixture of three acids and achieved the highest removal of Cd, Cr and Cu. Although the test conditions were not similar with the other works studied (**Table 2**), it can deduce that the mixture

proposed by [Tyagi \(2006\)](#) strongly acidify the medium and therefore degrade the phases carrying the metals and improving their abatement.

Regarding abatements, the reagent that seems to give the best result in a specific experimentation does not always give optimum abatement results. For example, Song obtains a 60% Pb abatement with EDTA while ethylene diamine disuccinate (EDDS) only offers a 30% Pb abatement. However, it is considered to be the additive that has shown "significant treatment efficiency, leading to a relatively more homogeneous distribution of the residues of the metals in the matrix" ([Song, 2017](#)). Consequently, our study suggests that the effectiveness of the reagent used cannot be only accounted by the abatement rate. Other criteria, such as the chelation capacity or the biodegradability of the products must also be considered.

References	Cell Type	Cell dimensions	Volume processed (cm ³)	Cell Shape	Matter	Separation	Electrode ANODE	Electrode CATHODE	Voltage (V) or current (mA - A)	Current type	Flow (mL/h) or rotation (rev/min)
AIT AHMED (Ait Ahmed, 2016)	Lab	length × Ø int = 12cm × 3.5 cm	115	Cylindrical	Plexiglass	Propylene textile fiber pads		Graphite	25 V	Direct current	72 mL/h
AMMAMI (Ammami, 2013)	Lab	14 x 4.9 x 4.9 cm	260	Cylindrical	Teflon-PTFE	Filter paper (0.45µm) + Perforated grid		Graphite	14 V	Direct/periodic	-
BAHEMMAT (Bahemmat and Farahbakhsh, 2015)	Semi-Pilot	50 x 10 x 10 cm	3,000	Rectangular	Plexiglas	Filter paper (Whatman 42) - 2.5 µm		Graphite	2 V/cm (100 V)	Direct current	-
COLACICCO (Colacicco et al. 2010)	Lab	length × Ø int = 30 x 6.2 cm	292	Cylindrical	Plexiglass	Porous stones		Titanium	60V/60-30V/30-60V	Direct current	-
HAMED (Hamed and Bhadra, 1997)	Lab	length × Ø int = 10.16 × 10.16 cm	830	Cylindrical	Plexiglass	Perforated electrodes to allow drainage		Graphite	10/15/20/25/ 30/50mA	Direct current	1.2-7.98 mL/h
IANNELLI (Iannelli et al. 2015)	Lab	Sediment compartment : 30 x 7 x 7 cm	1,470	Rectangular	Acrylic	nylon grid (2mm mesh) + filter paper	Titanium mesh + mixture of metals Oxide coating	Stainless steel	40 - 20 A/m ² and 40 A/m ²	Direct current	-
KIM et Al (Kim et al. 2001)	Lab	15 x 9 x 9 cm	1,215	Rectangular	Acrylic	Perforated walls (Ø : 0.5cm) + filter paper	Platinum wire (net: 9 x 9 cm)	Titanium plate	0,1 A	Direct current	1-100 rev/min
LEE (Lee and Lee, 2001)	Lab	20 x 8 x 6 cm	720	Rectangular	Plexiglass	Popypropylene filter 30µm		Graphite	40 mA (0,83 mA/cm)	Direct current	80 mL/h
MASI (Masi, 2017)	Lab	30 x 7 x 9 cm	2,200	Rectangular	Acrylic	A nylon grid (2mm mesh) + filter paper	Titanium net + oxidized metal mixture	Same Anode or Stainless steel	40 A/m ²	Direct current	-
MASI (Masi, 2017)	Pilot	7 x 15 x 1,25 m	150 x 10 ⁶	Rectangular	Concrete + Geotextile	-	Titanium mesh coated with mixed metal oxide	Stainless steel tubes of 10 mm Ø and 1.5 mm thick	48 V	Direct current	1 x 10 ⁶ and 3 x 10 ⁶ mL/h
MICIC (Micic et al. 2001)	Semi-Pilot	30.6 x 11.9 x 25.4 cm	5,100	Rectangular	Plexiglas	HDPE geogrid wrapped in geotextile (cathode)		Steel mesh	15/24,8 A/m ²	Periodic current	-
PAZOS (Pazos et al. 2013)	Lab	length × Ø int = 10 × 3.2 cm	80.4	Cylindrical	-	Filter paper + porous stones		Graphite	30 V (3V/cm)	Direct current	-
PEPPICELLI (Peppicelli et al., 2018)	Lab	20 x ? x 6.5 cm	1,000	Rectangular	Acrylic	Filter paper + Perforated grid		Graphite	20 mA (0,4mA/cm ²)	Direct current	-
ROZAS (Rozas and Castellote, 2012)	Lab	-	94	Cylindrical	-	Textile		Titanium	30 V	Direct current	-
SONG (Song, 2017)	Lab	length × Ø int = 14 × 4.9 cm	264	Cylindrical	Teflon-PTFE	Filter paper (0.45µm) + Perforated grid		Graphite	14V	Direct/periodic	5 - 10 mL/h
SONG (Song, 2017)	Semi-Pilot	80 x 20 x 25 cm	24,000	Rectangular	PVC	Filter paper (0.45 µm) + Perforated grid		Graphite	30 V	Direct current	50 mL/h
TIAN (Tian, 2018)	Lab	length × Ø int = 14 × 4.9 cm	264	Cylindrical	Teflon-PTFE	Filter paper (0.45µm) + Perforated grid		Graphite	14V	Direct current	10 mL/h
TIAN (Tian, 2018)	Semi-Pilot	80 x 20 x 25 cm	24,000	Rectangular	PVC	Filter paper (0.45 µm) + Perforated grid		Graphite	30 V	Direct current	50 mL/h
TYAGI (Tyagi, 2006)	Pilot	2.5 x 1 x 1 m	1.5 x 10 ⁶	Rectangular	Woven geotextile -	Woven geotextile - "GEObox"		Graphite and stainless steel	2A	Direct current	1-250 rev/min
YVON (Yvon, 2008)	Lab	15 x 4 x 4 cm	160	Rectangular	Teflon-PTFE	-		Graphite Stainless steel +Particles of activated carbon and iron ions: AC-Fe	10 V (1 V/cm)	Direct current	-

Table 1 Comparison of experimental cells

References	Cell Type	Duration (days)	Targeted pollutants	Matrix	Reagents ANODE	Reagents CATHODE	Reagents appearing to be the best	Reductions (%) - (Best results - all tests combined)	Reductions (%) - (Best reagents)
AIT AHMED (Ait Ahmed, 2016)	Lab	7	Pb	Kaolinite (K) / K + CaCO ₃ / K + NaCl	Citric Acid / EDTA		-	(K) Pb : 57 % - (K + CaCO ₃) Pb : 18.5% - (K + NaCl) Pb : 44.6%	<u>Kaolinite only</u> : Pb : 57 %
AMMAMI (Ammami, 2013)	Lab	7/10/15	Cd, Cr, Pb, Zn, Cu, PAH	Reconstructed and natural estuary	Demineralized Water (DW) / NaCl / HNO ₃ / Citric Acid / SDS / Tween 20		Citric Acid + TW20	<u>Natural sediment</u> : PAH : 55% ; Cd : 38.6% ; Pb : 33.4% ; Zn : 53% ; Cr : 8.5% ; Cu :	<u>Natural sediment</u> : PAH : 55% ; Cd : 35% ; Pb : 28.8% ; Zn : 53% ; Cr : 8.5% ; Cu :
BAHEMMAT (Bahemmat and Farahibakhsh, 2015)	Semi-Pilot	5/10/15/20	Co, Pb	Soil	Demineralized Water	Nitric Acid	Nitric Acid	-	Co : 73.84% / Pb : 62.88%
COLACICCO (Colacicco et al. 2010)	Lab	23/25/27/30	PAH / As / Cd / Cr / Cu / Ni /	Marine sediment	DW / EDTA / Tween 80	DW / EDTA	EDTA	-	As : 84% ; Cd : 28% ; Cr : 62% ; Cu : 38% ; Ni : 44% ; Pb : 32% ; Zn : 32% ; PAH :
HAMED (Hamed and Bhadra, 1997)	Lab	5/25	-	Kaolinite	Demineralized Water		-	<i>Influence of current density and pH. Stopping the tests after decreasing the pH of the effluent. The acid front of the anode has reached the cathode</i>	
IANNELLI (Iannelli et al. 2015)	Lab	14/43/63	Cd, Cr, Cu, Ni, Pb, Zn	Marine Sediment	DW	H ₂ SO ₄ / HNO ₃	Nitric acid	Cr: 20.7 % ; Ni : 16% ; Pb : 22.3 % ; Cu : 17.5 % ; Zn : 10 %	Cr: 20.7% ; Ni: 16% ; Pb: 22.3% ; Cu: 17.5% ; Zn: 9.5%
KIM et al (Kim et al. 2001)	Lab	4	Pb (II) , Cd (II)	Kaolinite (K) and mine tailings (MT)	Sulfuric acid	Sulfuric acid	-	-	Cd(II) : (K): 86% ; (MT): 68% Pb(II) : (K): 75% ; (MT): 50%
LEE (Lee and Lee, 2001)	Lab	1/2/4/6/8	Diesel fuel	Soil	Buffer solution of: Phosphate / Carbonate / Mixed: Phosphate + Ammonia		Phosphate + Ammoniac	Diesel fuel : 60%	Diesel fuel : 60%
MASI (Masi, 2017)	Lab	14/32/43/63/120	Cr, Ni, Pb, Zn, Cu	Marine sediment	DW	H ₂ SO ₄ / Acetic acid / Citric Acid / HNO ₃	Nitric acid	-	Cr : 30% ; Ni : 41.9% ; Pb : 47.8% ; Cu : 40.7% ; Zn : 28%
MASI (Masi, 2017)	Pilot	504	Cd, Cr, Pb, Ni, Zn, As, Cu	Marine sediment		-	Nitric Acid	-	-
MICIC (Micic et al. 2001)	Semi-Pilot	6	-	Marine sediment	Demineralized Water		-	-	<i>Micic did not use EK to depollute, but rather to consolidate the matrix</i>
PAZOS (Pazos et al. 2013)	Lab	15/30	Hydrocarbures pétroliers (TPH) / Zn / Pb	Marine sediment	EDTA + H ₂ O ₂ / Tween 80		EDTA + H ₂ O ₂	TPH : 90% ; Zn : 57.3 % ; Pb : 59.8 % ; Cu : 59.4% ; Hg : 54.5%	TPH : 90% ; Zn : 57.3 % ; Pb : 59.8 % ; Cu : 59.4% ; Hg : 54.5%
PEPICELLI (Peppicelli et al., 2018)	Lab	28	Zn, Pb	Industrial waste (mining residues)	Demineralized Water (DW)		-	-	Pb : (MT): 31% ; (EAFD): 48.8% Zn : (MT): 88.5% ; (EAFD): 53.7 %
ROZAS (Rozas and Castellote, 2012)	Lab	14	Cu, Zn, Cd, Cr, Pb, Ni	Port dredging sediments (Spanish)	DW / citric acid / acetic acid	DW / citric acid / acetic acid / humic acid / EDTA	EDTA and Acetic acid + Citric acid	Cu : 62 % ; Cd : 74% ; Cr : 74 % ; Pb : 63 % ; Ni : 89 % ; Zn : 81 %	EDTA : Cu : 62% / Pb : 63% Acetic acid: Cd : 74% / Ni : 89% / Zn : 81% Citric acid : Cr : 74%
SONG (Song, 2017)	Lab	21	Cr, Ni, Cd, Cu, Zn, Pb, As	Reconstructed and natural estuary	Demineralized Water / Citric Acid / EDTA / EDDS / NTA / Tween 21		EDDS	<u>Natural sediment</u> : As : 35% ; Cd : 40% ; Pb : 60% ; Zn : 35% ; Cr : 53% ; Cu : 50%	<u>Natural sediment</u> : As : 31% ; Cd : 32% ; Pb : 30% ; Zn : 25% ; Cr : 35% ; Cu : 50%
SONG (Song, 2017)	Semi-Pilot	21	Cr, Ni, Cd, Cu, Zn, Pb, As	Estuary natural sediment	Citric Acid (CA)		Citric acid	-	As / Cd / Cr / Cu / Ni / Pb / Zn < 3%
TIAN (Tian, 2018)	Lab	14/28	Cd, Cr, Pb, Zn, Cu, PAH, PCB	Reconstructed and natural estuary	Rhamnolipide / Citric Acid / Tween 20 / Saponine / pure water / EDSS		Citric Acid + Saponine	<u>Natural sediment</u> : PAH : 29.2% ; PCB : 38.7% ; Cd : 14.4% ; Pb : 14.4% ; Zn : 5.8%	<u>Natural sediment</u> : PAH : 29.2% ; PCB : 38.2% ; Cd : 14.4% ; Pb : 4.4% ; Zn : 5.8% ;
TIAN (Tian, 2018)	Semi-Pilot	56	Cd, Cr, Pb, Zn, Cu	Estuary natural sediment	TW20	TW20 + CA	CA + TW20	-	Cd : -3.3% ; Cr : 22.7% ; Cu : 5.3% ; Pb : 9.5% ; Zn : -6.5%
TYAGI (Tyagi, 2006)	Pilot	3	Cd, Cr, Cu, Pb	Sludge - Wastewater treatment plant	Polyester resin + mixture of 3 acids (Tri-fluoroacetic / propionic / sulfonic acid)		-	-	Cd : 75.3% ; Cr : 30.5% ; Cu : 25.7% ; Pb : 36.1%
YVON (Yvon, 2008)	Lab	13/14/17/29	TBT	Doped kaolinite and marine sediment	nitric acid; acetic acid; ascorbic acid; formic acid; NaOH; NaOH +	nitric acid; acetic acid; ascorbic acid; formic acid; Buffer ascorbic-scorbate;	ascorbic acid formic acid	-	<u>TBT</u> : 96 %

Table 2 Comparison of the EK protocols and the efficiency of the reagents used.

IV. Inorganic contaminants and retention mechanisms

IV.1. Inorganic pollutants

The [SETRA \(2011\)](#) guide provides an approach to assessing the environmental acceptability of alternative materials made from waste for use in road construction. This guide includes a section dealing with the environmental characterisation of the alternative material and the road material. The overall objective of this section is to demonstrate, for the specific road use, that the emissions (especially in trace elements) from the alternative and road materials are compatible with the water quality objectives. This step considers three levels of investigation: Level 1 is based on carrying out leaching tests and total content analyses; Level 2 is based on carrying out percolation tests and Level 3 is based on producing a specific study. The execution of the Level 1 environmental characterisation is required in order to be eligible for use as a road technique ([SETRA, 2011](#)). The **table 3** is an extract from the guide and lists the trace elements to be considered during valorisation studies, as well as the thresholds to be respected.

Parameters	Cumulative release at L/S = 10 l/kg (leaching test NF EN 12457-2 or NF EN 12457-4)		
	Set of values to be met by at least 80% of the samples (mg/kg dry matter)	Set of values to be met by at least 95% of the samples (mg/kg dry matter)	Set of values to be met by 100% of the samples (mg/kg dry matter)
As	0.5	1	1.5
Ba	20	40	60
Cd	0.04	0.08	0.12
Cr total	0.5	1	1.5
Cu	2	4	6
Hg	0.01	0.2	0.03
Mo	0.5	1	1.5
Ni	0.4	0.8	1.2
Pb	0.5	1	1.5
Sb	0.06	0.12	0.18
Se	0.1	0.2	0.3
Zn	4	8	12
Fluorides	10	20	30
Chlorides (*)	800	1,600	2,400
Sulphates (*)	1,000	2,000	3,000
Soluble fraction (*)	4,000	8,000	12,000

(*) For chlorides, sulphates and the soluble fraction, either the values for chlorides and sulphates or the values for the soluble fraction must be met to be considered compliant.

Table 3. Leaching' maximum values regarding to the acceptability of alternative materials in road techniques, from [SETRA \(2011\)](#).

The majority of studies usually deal with only five to seven trace elements. Therefore to enrich the database, in this work, 11 trace elements were studied. The objective here was to deal with a majority of chemical elements, and in particular those that are problematic from a regulatory and environmental point of view.

IV.2. Retention mechanisms

Some of the trace elements in the sediments are part of the minerals' crystal networks and, by extension, of the rock fragments that constitute the sediments. During the formation of mineral phases, various physico-chemical phenomena occur and are responsible for the retention of heavy metals in the solid phases of the sediment (or soil). **Figure 2** below illustrates the main interactions between an atom and solid matter. It has been adapted from the publications of [Hlavackova \(2005\)](#) and [Achard \(2013\)](#) themselves inspired by the work of [Manceau, Marcus, and Tamura \(2002\)](#).

Metals have multiple ways of associating with the sedimentary matrix. They can, for instance, be co-precipitated or be associated with sediment particles through sorption phenomena depending on the environmental conditions (pH, temperature, etc...). Links between a metal ion and electric charges present on the surface of the particles can be reversible and some metals have a high affinity for the organic fraction of sediments which facilitates their mutual association. Based on the study by [Manceau, Marcus, and Tamura \(2002\)](#), some authors ([Deschamps et al., 2006](#); [Causse, 2009](#)) highlight the following physico-chemical processes to explain heavy metal trapping: Adsorption, precipitation, substitution, inclusion (co-precipitation) and complexation.

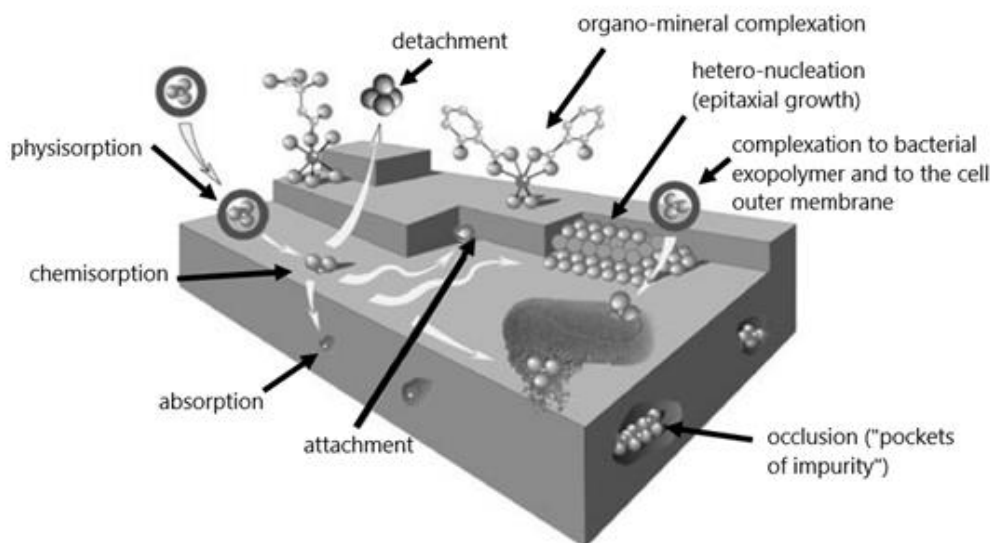


Figure 2 Main interactions between an atom or a molecule and a solid at the solid/liquid interface (from [Manceau, Marcus, and Tamura 2002](#))

IV.2.1. Adsorption

Adsorption occurs when atoms, or molecules, attach themselves to the solid surface by various processes. [Keil and Mayer \(2013\)](#) explain that this phenomenon is influenced by the chemical properties of the mineral and the presence of organic matter (OM). This is mostly the surface chemistry and physical properties (shape, roughness and specific surface area) that influence the adsorption phenomena. For example, clays are excellent adsorbents because of their large specific surface area. Although [Keil and Mayer \(2013\)](#), work on natural organic compounds, these principles are comparable to anthropogenic metals. They are valid for the interaction between OM and the sedimentary matrix.

A distinction is generally made between two types of adsorption: physical adsorption and chemical adsorption. This distinction is made according to the nature of the chemical bonds that are created ([Evans, 1989](#)). It is these chemical bonds that explain the fixation of organic compounds on mineral surfaces. The bonds commonly used to explain this retention are: ligand exchange, cationic bridges, ion exchange, Van der Waals forces and hydrogen bonds.

IV.2.1.a Physical adsorption:

Physical adsorption (physisorption) corresponds to an electrostatic attraction between a polarized surface and a solute, in order to maintain the electro-neutrality of the medium. The binding energies involved are relatively low, which makes physical adsorption reversible, and are therefore considered as a negligible binding mechanisms. The two physical adsorption mechanisms commonly mentioned in the literature are : The "Van der Waals forces" and hydrogen bonds (It should be kept in mind that cation retention by physical adsorption is called "cation exchange capacity": C.E.C. ([Deschamps et al., 2006](#)). This term is often used in electrokinetic depollution literature).

Van der Waals' strengths

Van der Waals forces are intermolecular, low intensity electrostatic interaction forces that result from the orbital motion of electrons and create a similar motion of atoms or molecules in the immediate vicinity of the electrons. An ion (or molecule) in the vicinity of orbiting electrons creates an electric field. This electric field causes a deformation, resulting in a temporary dipole moment (known as an induced dipole moment) that acts on the electronic system of the neighbouring molecule like a fluctuating polarizing dipole ([Keil and Mayer,](#)

2013). A mutual attraction of charges of opposite signs is then created. For instance, a partially positively charged hydrogen atom interacts with partially negatively charged oxygen or carbon atoms (Lützow et al., 2006). One can picture these forces as a vector oriented from the negative charge to the positive charge. However, Van der Waals forces can be exerted between non-polar atoms or molecules as well. Polarity therefore affects the van der Waals forces and influences a number of physical or chemical characteristics. This is why the surface tension of the molecule changes.

Hydrogen bonds

A hydrogen atom of positive partial charge is attracted to an electronegative atom (Lützow et al., 2006). This attraction is purely electrostatic (Élie, 2004), like the Van der Waals forces. The H atom thus provides a bridge, a bond, between itself and an O, N or F atom. The positive poles (hydrogen atoms) can therefore be attracted by negatively charged entities (anion).

IV.2.1.b Chemical adsorption:

Chemical adsorption is the adhesion of molecules to the surface of a solid through ionic or covalent bonds. These bonds generate a monomolecular layer and are only possible between elements with an adapted electronic configuration (*i.e.* they are specific). This is the very reason that makes chemical adsorption hard to revert (Deschamps et al., 2006). In the case of a solid particle, chemical bonds can be formed on its surface with the solution's ions: this is called surface complexation.

Ionic bonds

Ionic bonds are strong intramolecular bonds. They are characterized by the total transfer of one or more electrons to a third element with a large difference in electronegativity (Charrasse, 2013). This is often the case between a metallic and a non-metallic atom. Table salt (NaCl) is an example of an ionic intramolecular bond. The more the ions are charged, the stronger are the bonds. Consequently, the strongest ionic bond will be obtained for the greatest difference in electronegativity.

Covalent bonds

Covalent bonds are strong chemical bonds (Call, 1892), formed when two atoms share a pair of electrons (*i.e.* binder doublet). This type of bond is more likely to occur between neighbouring electronegativity atoms, each of which is both a donor and acceptor of electron(s). The covalent bonds can be "dative" and/or "polarized".

The dative covalent bond (*i.e.* coordination bond) is the pooling of electrons between an atom with a free doublet and another atom with an electron gap. These two atoms have different electronegativity, and it is the more electronegative one that gives an electron pair. Coordination bonds are formed during acid-base reactions.

The polarized covalent bond (also called polar bond) is the pooling of one or more electrons by two atoms of different electronegativity. This difference in electronegativity between the two atoms causes an electron cloud to move towards the more electronegative atom. From this displacement, result a formal or partial charge on the atoms involved in the bond, leading to the manifestation/appearance of a dipole moment.

Ligand exchanges

A ligand is an atom, an ion or a molecule, carrying chemical functions allowing it to bind to one or more central atoms or ions. The metal/ligand interaction is explained by the Lewis acid/Lewis base type. The bond formed is called a covalent coordination bond. Ligand exchanges are therefore special cases of covalent coordination bonds (or organometallic complex if it contains at least one metal-carbon bond). These bonds occur through the linking of the acid functions of organic compounds (carboxylic acids, phenolic acids etc...) with the hydroxyl functions of clay minerals in low pH environments. They induce stable and durable organo-mineral associations (Lützow et al., 2006).

Keil and Mayer (2013) corroborate the finding of Lützow et al. (2006), that the ligand exchange occurs mainly in acidic and oxide-rich soils. Complexation of OM on mineral surfaces via ligand exchange increases with decreasing pH. Lützow et al. (2006), show that, at a pH between 4.3 and 4.7, sorption is theoretically maximal and is linked to the pKa values of the most abundant carboxylic acids in soils.

Cationic bridges

Organic anions are normally repelled from negatively charged surfaces, but cationic bonding occurs when polyvalent cations are present on the exchange complex. Unlike Na⁺

and K^+ , polyvalent cations are able to maintain neutrality at the surface, neutralizing both the charge on the negatively charged surface (e.g. in clay minerals) and the acidic functional group of the organic material, negatively charged (e.g. COO^-). They act as a bridge between the two charged sites.

The main polyvalent cations present are: Ca^{2+} and Mg^{2+} in neutral and alkaline soils, and Fe^{3+} and Al^{3+} in acidic soils. The coordination complexes of Fe^{3+} and Al^{3+} ions are considerably stronger than those of Ca^{2+} . However, the binding of organic matter bound by cationic bridges to phyllosilicates is lower than the binding of organic matter via ligand exchange between the aluminium and iron oxyhydroxide surfaces (Keil and Mayer, 2013).

In sediments, which contain OM, cationic bridges take place between these organic particles and the metal cations responsible for the pollution of these materials. This retention process is similar in functionality to one of the transport mechanisms present in EK remediation (Cf. **section II.2**). Indeed, in electroosmosis, the notion of electrical double layer is involved and is very similar to the retention mechanism by cationic bridges.

Ion exchange

Ion exchange is considered one of the most important binding mechanisms in soils and sediments (Keil and Mayer, 2013). It is characterized by the exchange of ions between a solution and a complex or a surface. In soils and sediments, this phenomenon usually occurs between OH groups, associates on mineral surfaces and carboxyl groups ($COOH$) as well as phenolic OH groups of organic matter, (e.g. Fe-O-C bonds) (Lützow et al., 2006) - (Keil and Mayer, 2013).

IV.2.2. Precipitation

Precipitation is the transformation of a species from a dissolved state to a solid state. Metals can precipitate solid particles from pores or from the surface of water. In the natural environment, they precipitate mainly in the form of hydroxide, carbonates, phosphates or sulphides (Deschamps et al., 2006). Precipitation reactions influence the movement of fluids in a porous medium, so in order to effectively remove contaminants and improve the EK process, it is necessary to avoid precipitation and keep contaminants in a solubilized form (Mosavat, Oh, and Chai, 2012a).

In addition to these adsorption reactions, the precipitation of new mineral phases can occur if the physico-chemical conditions of the pore solution are supersaturated with insoluble precipitates. Evans, (1989) considers that among these secondary minerals, oxides,

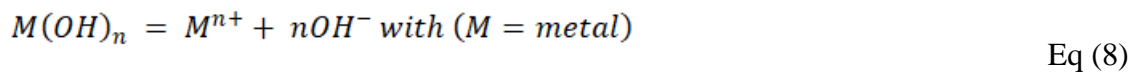
hydroxides, oxyhydroxides and carbonates are the most important; sulphides, phosphates and silicates are considered less important.

Precipitation equilibria are governed by solubility products (K_s). The solubility products is defined by the product of the equilibrium concentrations of hydrated ionic species, as expressed in **Eq 7**:

$$K_s = (A)^x \cdot (B)^y \quad \text{Eq (7)}$$

where (A) and (B) represent the activity of the species in the liquid and x and y their respective stoichiometries (Deschamps et al., 2006). These species' activity is dependent on the temperature, ionic strength and the nature of other dissolved ions. The solid therefore precipitates when the solubility product is exceeded.

Metal hydroxides, being poorly soluble in aqueous aera, create a balance between the precipitate and the undissolved ions in solution (Tatangelo and Tatangelo, 2006), according to **Eq 8**:



The laws of chemical balance apply and the concentration of species is governed by the constant K_s (Tatangelo and Tatangelo, 2006). In the case of metal hydroxide formation, the equilibrium constant is given by **Eq 9**:

$$K_s = [M^{n+}] \cdot [OH^-]^n \quad \text{Eq (9)}$$

IV.2.3. Surface complexation

Surface complexation is a complex method of growing crystals under different conditions. This is the result of polymerization, where heteroepitaxial overgrowths can form on the surface of a solid. Unlike epitaxy, heteroepitaxy grows a crystal with a different chemical composition from that of the support. This process is probably the most important crystal formation process in soil systems (Hlavackova, 2005). Complexation changes the charge of the metal ion and thus its direction of movement under the action of an electric field. In the case of complexation by the conjugate base of a weak acid, the higher the pH, the higher the level of progress of the complexation reaction. The presence of a pH gradient across the width of the experimentation cell allows the metal salt to be present in cationic

form, and therefore free in an acidic medium, or anionic, when complexed at more alkaline pHs. (Vieira-Nunes, 2018)

From a pollution stabilisation context, Deschamps et al. (2006) conclude that the sorption, complexation and precipitation mechanisms contribute to put a metallic element retained on the surface of a material more quickly into a solution. Therefore, their toxicity risks are increased compared at if the element was to be inserted into the crystalline network of the material. However, in the context of EK remediation, where the process mobilizes the ions present in solution, this solubilisation is of great interest.

IV.2.4. Substitution

An atom can be substituted for another in a crystal network. This is only possible if its charge and size are similar (Deschamps et al., 2006). This is, for example, true of a metal ion incorporated into the crystal network during its precipitation, or which diffuses into the solid to fill a void or replace an atom in the solid.

IV.2.5. Inclusion

The inclusion mechanism is in fact a mechanical trapping of various impurities in pores that do not open during mineral growth (Deschamps et al., 2006). This can be in dissolved or solid form.

Although the retention of metals (governed by these different mechanisms) is natural, it poses many problems, particularly in the environmental and health context, as explained in the introductory part of this chapter. However, since electrokinetic remediation is a method of mobilization, it is possible to extract these metals, as well as other organic pollutants, mostly by electrical pulse and many physico-chemical mechanisms.

V. The distribution of contaminants within sediments

The solid phase of sediments contains different mineral and/or organic fractions, with different affinities depending on the trace elements present (Pickering, 1986). The retention mechanisms previously described are essential, but the retention of elements is carried out on the solid particles and therefore on the different fractions constituting of the sedimentary matrix (*e.g.* iron and manganese oxides, organic matter, carbonate and exchangeable fractions, argilo-silicate fraction) (Serpaud et al., 2005).

Environmental quality concerns have encouraged the studies of several divalent metals (Cu, Pb, Zn and Cd) (Eggleton and Thomas, 2004). Several works have identified and

compared the spatial distribution (speciation) of metals (Zoumis et al., 2001; Calmano, Hong, and Forstner, 1993; X. Li et al., 2000; Serpaud et al., 2005) in sediments, and therefore provide valuable insights into the physico-chemical factors influencing metal's environmental availability and toxicity.

According to (Calmano, Hong, and Forstner, 1993), the transformation of trace element binding forms in sediments includes the following main processes:

- sorption and desorption;
- formation and dissolution of carbonate bound metals;
- formation and decomposition of soluble and insoluble metal organic complex compounds;
- formation and dissolution of hydroxides and oxyhydrates;
- sorption and coprecipitation of metals by Fe-/Mn-oxides, particularly in oxidic environments at neutral pH;
- precipitation of metal sulphides in strongly reducing environments and dissolution as sulphates under oxic conditions.

Metal contaminants get associated on particles such as clay minerals, Fe and Mn oxides/hydroxides, carbonates, organic substances (e.g. organic acids) and biological material (e.g. algae and bacteria) (Calmano, Hong, and Forstner, 1993; Eggleton and Thomas, 2004). Research has shown that binding sites depend on the oxidation state of the sediment. Oxides/hydroxides of Fe and Mn as well as organic matter are important binding sites for metals in oxic sediments (Zoumis et al., 2001), whereas under anoxic conditions solid heavy metal compounds are generally stable, especially sulphide forms (Calmano, Hong, and Forstner, 1993).

Table 4 below shows the main trace elements that are problematic from a regulatory point of view for the reuse of sediments, and classifies them according to the retention phases with which they are associated:

Trace elements	Sedimentary fraction	Author(s)
As	Fe oxide *	(Keon et al., 2001; Asaoka et al., 2012)
Ba	Residual *	(Gonneea and Paytan, 2006)
Cd	Organic matter / Residual	(Ahmed et al., 2018)
Cr	Fe/Mn oxides	(López-Sánchez et al., 1996)
Cu	Sulphide / Organic matter / Residual	(López-Sánchez et al., 1996); (Calmano, Hong, and Forstner, 1993); (Li et al., 2000); (Ahmed et al., 2018)
Mo	Organic matter (Oxydable) / Extractible fraction (Labile)	(Yu et al., 2010; Solongo et al., 2018)
Ni	Residual	(López-Sánchez et al., 1996)
Pb	Mn oxide	(López-Sánchez et al., 1996)
Sb	Fe oxide	(Asaoka et al., 2012)
Se	Residual	(Ahmed et al., 2018)
Zn	Sulphide and Fe/Mn oxides	(Li et al., 2000); (Ahmed et al., 2018)

(*) : more specifications in the text

Table 4 Binding sites for trace elements within sediment

Arsenic speciation (« * » in **Table 4**) is complicated to identify. Keon et al., (2001) carried out a study with the aim of testing a sequential extraction procedure designed to differentiate the chemical forms of As according to the mineralogical phase of attachment. Keon et al., (2001) explain that: “In aqueous solutions of neutral pH, arsenate, As(V), is present predominantly as $H_2AsO_4^-$, while arsenite, As(III), is uncharged as H_3AsO_3 . The distribution of As between these species is important due to the higher toxicity and enhanced mobility of As(III). In oxic sediments, As(V) forms strong inner sphere complexes with iron hydroxides or may be present in oxide minerals. Iron-reducing conditions often coincide with the reduction of As(V) to As(III), and studies suggest that As(III) can adsorb onto remaining Fe oxides. In sulfidic environments, As may adsorb onto pyrite, co-precipitate with authigenic pyrite, or form As(III) sulphide minerals. In organic-rich sediments and pore water, humic acid amine groups may also complex As(V) and As(III).”

The results of (Gonneea and Paytan, 2006) indicate that the majority of Ba is associated with the residual fraction (« * » in **Table 4**). However, other studies associate Ba with other phases that may represent 20-40% of total Ba in some sediments.

VI. Factors controlling contaminants mobility within sediments

It is known that environmental factors have influences on the distribution of metals in sediments and therefore on the EK remediation. A simple variation in these factors is sufficient to produce significant changes in metal distribution. Many factors can alter the distribution of metals. pH, redox and OM as the most crucial according [Peng et al., \(2009\)](#). The treatment conditions, the nature of the electrodes, the electrical power used and the treatment time also influence the results of EK remediation.

VI.1. The influence of the pH

Electrolysis of water causes a local change in the pH of the pore solution, so that acidity and alkalinity increase, respectively at the anode and the cathode ([Page and Page, 2002](#)). A further issue is the effect of pH on soil minerals. Soil constituents, including clay minerals, may dissolve due to the change in the composition of the pore solution. The concentration of some ions (*e.g.* Mg, Al and Fe), often increases with an increase in acidity while others ions like Si and Al increase in alkalinity.

The variation in pH appears to be the most important factor in determining trace element mobility. Many authors agree that lowering the pH promotes the mobility of heavy metals, particularly by dissolving metal salts or, when the pH is very acidic, by destroying the retention phase. Conversely, an increase in pH therefore favours metal adsorption on the reducible fraction of sediments (iron and manganese oxides), after exchange of metal cations with H⁺ ions at certain surface sites ([Ciesielski, Guérin-Lebourg, and Proix, 2007](#)).

The natural biodegradation of organic matter encourages the formation of sulphides and are both function of pH conditions (as well as redox reactions). They would then allow interpretation of metal speciation in sediments and their environmental availability ([Serpaud et al., 2005](#)). Indeed, the speciation of a metal changes with pH and influence its fixation on the solid phase ([Hlavackova, 2005](#)). In the context of an electrokinetic treatment, the acidity of the medium generated (or intensified) by the electrolysis of water at the anode can improve the conditions of electroosmosis ([Saichek and Reddy, 2003](#)) and therefore the efficiency of the pollution control treatment by making the metals soluble, and therefore mobilizable. It appears that pH influences the sorption and solubilisation mechanisms, as well as the speciation of contaminants presents in the matrix. However, [Banerjee, Horng, and Ferguson \(1991\)](#) remain more measured about the effects of electrolysis reactions and even talks about "side effects". Electrolysis reactions can change the chemistry of ionic species and the pH of

the pore water. The dissolution of the metal electrodes may even introduce other species into the system ([Banerjee, Horng, and Ferguson, 1991](#)).

High buffering capacity inhibits the advancement of the acid front necessary for desorption and contaminant transport. Conversely, in soils with low buffering capacity, acidification may lead to excessive dissolution of some of their constituents. [Amrate \(2005\)](#) concludes that it is then preferable to use reagents to solubilize metals without further acidification.

In order to measure the impact of pH variations on the adsorption of certain pollutants contained in the surface sediments of a watercourse, [Serpaud et al. \(2012\)](#) carried out a study to measure the adsorption of certain metals, subjected to conditions of varied pH (pH = 5, 6, 7 and 8). They showed that in the case of Cu, Cd and Zn, the adsorption rate increases systematically when the pH increases (Cu: 70/90%; Cd: 75/90%; Zn: 75/95%). However, some metals seem to be less reactive to pH variations. For the case of lead for instance, its evolution is not significant since the adsorption rate varies from 99 to 97%, within the defined pH range. Finally, other works such as [Kim et al \(2005\)](#), [Yuan and Chiang \(2008\)](#) and [Song \(2017\)](#) have observed that some metals show an opposite behaviour. In the case of molybdenum (Mo), arsenic (As) and selenium (Se), their mobility increases with increasing pH. This was further observed for As, due to the easiness of extraction from the matrix at more alkaline pH values. Interestingly, the matrices used in these studies were all different, making these observation consistent. It should be noted, however, that extraction at alkaline pH is not the best option if other metals are to be remediated.

At this stage, and in accordance with [Serpaud et al. \(2012\)](#)'s observation, several conclusions can be drawn:

- H⁺ ions compete less with cationic species.
- An alkaline pH would cause an increase in the number of fixation sites (carboxyl groups in organic matter, hydroxides in oxides and clay minerals).
- At low pH the dissolution of the alumino-silicate compound reduces the effective adsorption surface area.
- Humic compounds in sediments can see their configuration change from aggregates to a more stretched structure, where complexing sites are more accessible.
- The increase in pH favours the precipitation of oxides, hydroxides or hydroxycarbonates and consequently the adsorption on these phases in suspension.

In general when the elements in cationic form are stable (*e.g.* Cd^{2+} , Zn^{2+} , Cu^{2+}) the increase in pH favours the fixation of cations by the soil. When the elements in anionic form are stable, solution increases when the pH increases (Moszkowicz, 2002). The shape of the chemical element thus seems to be related to the pH, and these two parameters work together according to very specific physico-chemical particularities. Furthermore, the parameters that influence EK treatment are all related to each other.

VI.2. The influence of the redox potential (Eh)

The redox potential of sediments has a strong impact on the chemical form of the elements, and therefore influences their availability in the environment. The redox potential results from a natural phenomenon called early diagenesis, which progressively transforms the sediments into sedimentary rock. These transformations are mainly the result of bacterial mineralisation of the sedimentary organic matter and determine the redox level of the sediment (Gorny, 2015). When organic matter is located at the water-sediment interface, mostly in particulate form, it cannot be directly assimilated by bacteria. The degradation process then begins with a phase of extracellular hydrolysis of the macromolecules that make up the organic matter. This hydrolysis is catalysed by extracellular bacterial enzymes (Hoppe, 1983). In this thesis, Bourgeois (2013) detailed the degradation processes of OM in sediments as well as the actors involved. Consequently, bacteria thus play a major role in biogeochemical cycles, but their potential to re-mineralise organic matter depends on the availability of electron acceptors present in the environment.

In anaerobic sediments, acid volatile sulphide (AVS) is naturally present. According to Peng et al., (2009) it is a key component that controls the activities of certain divalent cationic metals. Initially, the majority of AVS in anaerobic sediments are bound to iron in different forms or emerge as free sulphides. However, if divalent metals are present (Cd, Cu, Cr, Pb or Zn), the iron in the iron sulphides is displaced and one of these elements rapidly binds to the AVS with a higher affinity (Hansen et al., 1996). As the Eh in the sediment increases, the rate of oxidation of metal sulphides and the rate of degradation of organic compounds increases accordingly. Both phenomena can accelerate the release of adsorbed/complexed heavy metal (Calmano, Hong, and Forstner, 1993). For this reason, it is common for dredging process to rely on method that avoid oxidation of the sediment, otherwise chemical elements could be released into the environment.

There are three ways in which redox conditions can influence the mobility of the elements (Moszkowicz, 2002) :

- The degree of oxidation of a metallic element: A change in the degree of oxidation can affect the solubility and mobility of the metal, such as the oxidation of Cr(III) to the considerably more soluble Cr(VI);
- The formation or dissolution of phases carrying pollutants: The solubilisation of iron and manganese oxyhydroxides under reducing conditions, at acidic pH, participates in the release in solution of the metals associated with these carrier phases;
- The change in the oxidation state of elements that bind with the metal: The oxidation of sulphides into sulphates, for example, allows the solubilisation of the associated metals. Conversely, the reduction of sulphates to sulphides leads to the precipitation of metal sulphides whose solubility product is very low.

Variations in Eh therefore occur in the natural condition, but also during the EK treatment by the oxidation/reduction reactions produced at the electrodes. Eh, measured in mV, is a complex parameter to measure during the EK treatment, because it requires the use of electric current and therefore disturbs the measurements.

Although this parameter is important in the mobility dynamics of chemical elements, it is, to the best of our knowledge, never studied in the literature. Yet, it is a good indicator of the evolution of the redox potential of the sediments during the EK treatment and can explain certain precipitation or dissolution phenomena in addition to the data on pH.

The oxidation-reduction potential of the environment therefore plays an important role. On the one hand, it directly influences the oxidation state of the heavy metals and thus their mobility, and on the other hand, it influences the sediment components that bind the heavy metals. The redox of the sample can therefore influence the results of EK remediation, but this parameter may also be modified during treatment.

VI.3. The influence of organic matter species

Organic compounds are present in sediments, often in considerable quantities and in particulate form. They play an important role in the transformation of trace elements (Peng et al., 2009). In river sediments, trace elements that bind to organic matter (OM) generally represent the most important part of sediments.

It is the solubility of organic matter that determines the mobility of chemical elements. If metal ions complex with insoluble organic compounds, then their mobility decreases significantly (Peng et al., 2009). Conversely, if soluble metal ions complex with dissolved organic compounds, then their mobility increases. Peng et al., (2009) state that the sediments of rivers or natural lakes contain OM composed mainly of humic and fulvic substances. Charrasse (2013) has shown that insoluble organic matter amount (humins) is considerable for all the sediments studied (marine and river). However, the complexity of the organic matter, the type of reactions between organic complexes and metals are difficult to predict.

Furthermore, because the OH⁻ ions produced at the cathode help some organic molecules to desorb, the pH of a medium and the electrolysis reactions produced during EK treatments influence the desorption of OM (Page and Page, 2002).

VI.4. The influence of the electrical conductivity

As we have seen, EK electroremediation imply a change both in pH and ionic strength. Consequently, non-uniform electrical conductivity and voltage profiles arise quickly (Hamed and Bhadra, 1997; Page and Page, 2002). The majority of EK works apply direct current voltages. Nevertheless, drops in conductivity are observed near the cathode. These drops seem to be linked to the precipitation of trace elements in the form of solid hydroxides (Page and Page, 2002). Then, the value of the measured electric current gradually decreases due to the neutralization of the migrating cationic and anionic ions (Ammami et al., 2014). Cations migrating to the cathode (also including H⁺, due to the electrolysis of water) can be neutralised by anions migrating to the anode (also including OH⁻). As the acid front progresses, the flow of fluid is reduced. But as long as the concentration of ions in solution is sufficient, electromigration remains effective and helps to remove trace elements from the system (Probstein and Hicks, 1993). However, as the ions are removed, the electrical conductivity drops. These drop are more significant near the cathode (Alshawabkeh and Acar, 1996).

Some authors have applied a periodic voltage to the EK remediation process. This periodicity generates electrical conductivity profiles different from the DC voltage. When the voltage is not applied, mass transfers of charged solutes from the soil to the aqueous medium occur, resulting in a higher current when the voltage is reapplied (Maturi and Reddy, 2006; Ammami et al., 2015). This could have beneficial impact on the migration of trace elements and thus their remediation.

VI.5. The influence of sedimentary matrix

Sediment texture and structure are factors involved in the mobility of trace elements. In a structured matrix, the velocity of water and soluble compounds will be greater than in a disordered matrix. When colloids are suspended and then entrained by a flow of water or solution, they play an important role in the mobility and outcome of metals associated with these solids (Hu, 2012). In addition, the particle size and the MO content in the sediment will influence the efficiency of the treatment. Indeed, the richer a sediment is in MO and fine particles, the richer it will be in pollutants. Adsorption phenomena that are difficult to reverse are favored by the OM and the large specific surface area of the fine particles.

The mineralogical composition of the sediment is also a determining factor to be taken into account. The electrokinetic treatment may present totally different abatement results depending on the sediment treated. Indeed, some metals will be more easily associated with certain mineral phases than others (Cf. **Table 4**). Some clay minerals show significant physico-chemical changes, resulting in water loss and thus shrinkage of the material structure (Grundl and Michalski, 1996; Grundl and Reese, 1997). Pore obstruction and flow arrest may result from the deposition of metal hydroxide compounds, conceivably formed by reaction between hydroxyl ions near the cathode and heavy metal contaminants. That is why preventing the precipitation of insoluble metal compounds in the sediment is important.

Moreover, physico-chemical parameters of a sediment, and therefore its reaction to the treatment, seems also linked to other parameters, such as the place of extraction, the age of the sediment, the dredging method or the storage before treatment.

VI.6. The influence of the treatment duration

It has often been concluded in studies that there exists a positive correlation between treatment times and removal results: the longer the time, the better the results (Yuan and Chiang, 2008; Colacicco et al., 2010). Actually, Iannelli et al. (2015) found that extending the treatment time to 60 days produced an interesting accumulation of metals in the cathode compartment. He deduced that this allowed the formation of cationic aqueous complexes favored by the more acidic conditions established in the system.

Tang et al. (2018) varied the treatment time for his tests (48, 96, 144 and 192 h). He indicated that higher treatment times would generally favor the removal of heavy metals, particularly at the section near the anode.

The duration of treatment does not only influence the abatement results. Indeed, [Ammami \(2013\)](#) also observe that the treatment time was related to the efficiency of the drainage of water contained in the dredged sediments subjected to the electrokinetic process. The longer the treatment lasts, the greater the water drainage is, and the more alkaline the pH becomes. It would appear that the pH becomes acidic at the beginning of the experiment, but eventually becomes alkaline and then stabilizes until the end of the treatment.

VI.7. The influence of the nature and the configuration of electrodes

The position of the electrodes does not seem to raise any real questions when the studies are carried out in the laboratory. Indeed, electrodes are often introduced in pairs and are placed on either side of the matrix to be treated. For studies aimed at depolluting larger volumes, the arrangement of the electrodes and the distance between them have an impact on the decontamination rates ([Page and Page, 2002](#)). Large-scale studies are relatively limited compared to laboratory experiments, but [Masi \(2017\)](#) conducted an electrokinetic remediation study on marine sediments using a field-scale pilot (*Cf. Tables 1 and 2*). The electrodes were positioned to create an array of anodes and cathodes distributed over 14 lines. Each line consisted of 6 electrodes of the same polarity, spaced 1.1 m apart. The electrodes of opposite polarity were 1 m apart. Each of the electrodes was placed inside a vertical slit well, placed in the sediment in order to allow electrolyte circulation and ensure electrical continuity between the electrodes and the sediment.

Another implementation of the electrokinetic process was carried out by the US Environmental Protection Agency (US EPA) at the Superfund site in Corvallis, Oregon ([Banerjee, Horng, and Ferguson, 1991](#)). Two configurations were adopted: a hexagonal pattern with 1.5 m electrode spacing and a square pattern with 2.4 m spacing. The hexagonal wells served as cathodes and the central well as an anode. The objective was to obtain a uniform electric field. The authors note that the electrical gradient, which is the driving force for ion migration, is much higher in the immediate vicinity of an anode or a cathode in the centre of the system. This implies that ion migration should be much more efficient in the central region than around the treated area. This conclusion is shared by [Masi \(2017\)](#) and his simulations to evaluate the progression of the acid front and lead migration. He concluded that the acid front progressed faster along the anode/cathode axis. This can be explained by a higher electric field intensity in the anode/cathode axis compared to the domain boundaries. Therefore, the residual Pb concentration followed the same trend and higher levels were

observed along the anode-cathode axis. The simulation also revealed that Pb accumulates in a specific area of the study domain before to move towards the cathode over time. The reason of such a Pb concentration could be the existence of an abrupt pH transition, from acidic to alkaline, known to precipitates Pb.

In the literature, the analysis of the efficiency of the depollution process is usually performed into the space between the two electrodes. However, considering the whole setup could prove even more interesting when it comes to large-scale experiments. Indeed, the area to be treated being larger, it often includes many electrodes. These are usually positioned alternately positive and negative electrodes, with an electronic range more or less important (depending on the intensity of current delivered, the resistance of the material etc). Depending on the configuration of the installation, the chemical elements in the sediment matrix will be distributed differently.

The choice of electrode material also affects the EK remediation process. Yet, in practice, it is limited by cost considerations, simplicity of manufacture and robustness (Page and Page, 2002). In general, graphite electrodes are used (Cf. **Table 1**). They are inert and avoid external contamination by dissolving the material (Banerjee et al., 1991). However, in some cases, reactive anodes, such as iron, have been used. Often for reasons of electrode longevity.

Morefield et al. (2006) have studied the impact of the nature of the electrodes on this treatment process using iron, zinc, copper and aluminium electrodes. Malekzadeh, Lovisa, and Sivakugan (2016) have compiled tables summarising the different types of metal electrodes reported in the literature, with their advantages and limitations. For example, Ammami (2013) has chosen graphite electrodes for depollution purposes because graphite is chemically inert and therefore does not corrode and will not become passivated during the experiments. Titanium, stainless steel and platinum have also been used in other laboratory experiments (Cf. **Table 1**). These three materials have varying degrees of corrosion resistance.

Benamar et al. (2007) compared the efficiency of three electrodes of different materials (aluminium, copper and stainless steel) and was able to highlight their interaction with the environment and their influence on the efficiency of the treatment. Aluminium was found to be the most effective material, probably because it is a good conductor of current. However, Malekzadeh et al. (2016) state that this material interacts with the medium (cathode alteration) and is also a source of contamination as it interacts with the environment. Changes in soil composition were also observed, as well as the production of aluminium hydroxide.

Regarding copper, it seems to have many drawbacks: a high rate of wear, voltage losses at the cathode and therefore a loss of power, and a production of hydrogen; consequently a source of important contamination and a notable risk for the environment. [Alcántara et al. \(2008\)](#) have observed similar results to copper with almost complete organic pollution degradation using either graphite or titanium electrodes.

The literature shows that the choice of electrodes has been studied extensively, seeking to compare the effectiveness of electrokinetic treatment by varying electrode materials. It would seem that most authors agree that electrodes should be carefully selected according to the objective of the study (*e.g.* conductive properties, inert character, corrosion, release of chemical elements into the environment, price...)

VI.8. The influence of the electrolytes

During EK treatment, the use of one (or several) electrolyte(s) is essential. In most electrokinetic studies, the authors vary the reagents' nature in order to measure their impact on the abatement results. The use of acids is widespread: nitric acid, citric acid (CA), EDTA, nitrilotriacetic acid (NTA), sulphuric acid, acetic acid, etc. Demineralised water as well as surfactants (Rhamnolipid, Saponin, Tween 20, Tween 21 and Tween 80) are also commonly used, together with solutions of NaCl, SDS, sodium sulphate, hydrogen peroxide (H₂O₂) and humic and acetic acids. The choice of reagents influences the efficiency of the treatment by having impacts on different parameters (*Cf.* **Table 2**).

The addition of electrolyte additives such as chelating agents and surfactants are essential to improve contaminant removal ([Tian, 2018](#)). The use of surfactant is generally used to mobilise PAHs. [Ammami \(2013\)](#) found that the Tween 20 (TW20) was most effective than anionic surfactant Sodium Dodecyl Sulphate (SDS), as it does not oppose electro-osmotic flow. [Ammami \(2013\)](#) notes that the combination of TW20 with citric acid had only a slight effect regarding the extraction of heavy metals, but the presence of citric acid did not affect the performance of Tween 20. The two products can therefore be used together.

[Tian \(2018\)](#) has also combined TW20 and citric acid in his experiments. Tween 20 was introduced into the electrolytes to promote micelle formation in the interstitial fluid. Citric acid was used at a concentration of 0.1M, which seems to be favourable to the electroosmotic flow. However, his work shows that this combination does not favour the increase of the electrical intensity. Interestingly, the electrical intensity decreases very quickly during the first 100 hours, then stabilizes at the end of the treatment. This means that the ionization of the species in the aqueous phase could be inhibited by the presence of Tween 20

at this concentration (5 g.L^{-1}). The dielectric permittivity of the electrolyte is decreased by the presence of high concentrations of non-ionic Tween 20. [Ammami \(2013\)](#) agrees with this conclusion by stating that in his tests, the addition of Tween 20 did not help to improve the electric current, even compared to demineralised water.

However, [Ammami \(2013\)](#) was able to observe that the non-ionic surfactant (Tween 20) significantly improves the electroosmotic flow compared to the anionic surfactant SDS and demineralised water. This is not the case for [Tian \(2018\)](#) where Tween20 have altered the surface properties of sediment particles, such as charge density, by sorption of the non-ionic surfactant, thus decreasing the surface dielectric constant and decreasing the EOF. This decrease in EOF was also reported when Tween 80 was used in other studies ([Saichek and Reddy, 2003](#)).

The use of the surfactant Tween 20 slightly improved the removal rates of As, Cr, Cu and Pb compared to the experiment conducted with anode deionized water and a 0.1M CA solution ([Song, 2017](#)). In addition, [Ammami \(2013\)](#) reported similar results for Cu, Cd and Pb (Cr and Zn were less well mobilized using the TW20 compared to the demineralized water control experiment). He also noted that the metal compounds are recovered exclusively at the anode in the case of the TW20 treatment. The amounts recovered at the anode remain low, but much higher than in the SDS experiment. The low metal migration can be explained by the appearance of a base front that hinders metal migration to the cathode.

Regarding the use of acids as a processing reagent, citric acid seems to be a good choice. Indeed, it is a natural organic product, biodegradable, inexpensive and therefore easily usable for construction site ladders ([Song, 2017](#)). It allows the pH of electrolyte solutions to be controlled to avoid the formation of certain insoluble salts (PbCl_2) and the production of harmful gases such as Cl_2 when a strong acid is applied. It also allows the formation of citric salts, which are complexing agents that can form soluble complexes with the heavy metals adsorbed on the particle surfaces.

[Kim et al. \(2011\)](#) investigated the suitability of various treatment fluids (EDTA, citric acid, HCl and HNO_3) for the enhancement of the EK of dredged marine sediments contaminated with Ni, Cu, Zn and Pb. Tap water was used as the anolyte and the process fluids were dispatched in a cathodic manner at a concentration of 0.1 M. The experiments were carried out for 15 days. They achieved the best removal rates with citric acid and HCl, showing extraction efficiencies up to 70%.

[Ammami \(2013\)](#) during his study carried out a citric acid/Tween 20 mixture on a natural sediment and on a model sediment. This choice proved to be the best compromise to

extract metals and PAHs simultaneously. However, the heterogeneous and complex sediment matrix did not give the same results as those obtained on the model sediment. This is due (i) to a less heterogeneous constituents of the reconstituted sediment (notably the nature of the organic matter), (ii) the low diversity of the inorganic ions introduced into the aqueous medium (low buffering capacity) and (iii) the low ageing of the model matrix (a few months as opposed to several decades for the natural sediment).

Citric acid has often been presented as a favourable reagent for treatment. It favourably increases the EOF and is a good extractant due to its ability to lower the pH value (*Cf. Table 2*). However, these results are not necessarily shared in other works. The particular characteristics of the river sediments used by [Tian \(2018\)](#), especially their resistance to acidification, as well as the effect of dehydration during electroremediation, were responsible for low removal rates of trace elements, independently of the use of citric acid or EDDS chelating agents. However, citric acid can modify the zeta potential of sediment particles and has a favourable effect on the electroosmotic flux and electric current intensity, which are factors conducive to metal removal. However, increasing the concentration of citric acid did not lower the pH of the sediment sufficiently to make the metals more mobile, as advocated by [Ammami \(2013\)](#).

[Kim et al. \(2011\)](#) and [Masi \(2017\)](#) used dredged marine sediments, yet these two works lead to opposite conclusion. [Kim et al. \(2011\)](#) were in favour of the use of citric acid, while [Masi \(2017\)](#) seems more reluctant to use it due to the massive rainfall at the cathode and its clogging, followed by a drastic increase in tension, therefore limiting large-scale tests. In addition, citric acid increases the resistivity of the material over time. Likewise, the maximum flow rate of the EOF was measured in the citric acid-enhanced experiment and the metal removal was also satisfactory. [Masi \(2017\)](#) noted that acetic acid does not cause precipitation, but the high resistivity increase from the anode could pose design problems at the field scale due to high stress that would be applied. As for nitric acid, it effectively removes metals, did not increase the resistivity of the marine sediment used, and did not precipitate species, preventing clogging.

In conclusion, it is difficult to give general trends on the effectiveness of a specific reagent. Indeed, the treatment efficiency depends on multiple heterogeneous conditions for both the materials and the experiments, which differ from study to study (*e.g.* intensity used, type of electrode, volume of sediment treated).

VII. Conclusion

Most of the trace elements washing into rivers are stored in the sediment and remain available to living organisms for a long time. Remediation of sediments is therefore necessary to preserve the environment. A review of the EK remediation technique as well as research on previous work has been examined in this chapter. This review has shown that some laboratory tests and field/semi-pilot scale applications have proven to be effective, however, there are still many parameters and phenomena to be understood. Deficiencies in large-scale research need to be addressed, especially with numerical models, therefore further laboratory scale research is required. Many questions are still unanswered and require careful analysis for implementation on a larger scale, in particular the understanding and the control of side effects during the treatment. Precipitation, EOF reversals or current reduction for instance are important effects that need to be further studied. Indeed, although the EK remediation process is quite simple in its implementation, the numerous physicochemical processes involved and the material's composition give rise to very complex situations. Moreover, it is important to assess the potential toxicological effects of the surfactants and processing reagents used. Indeed, at the laboratory level, although some reagents are natural and biodegradable, at the end of treatment they are often contaminated with heavy metals (especially effluents recovered from anodic and cathodic overflows). What to do then with these reagents? This problematic also arises for treatments on a field scale or directly *in situ*, because the reagents are directly found in the environment.

The chemistry and the composition of a material has a major effect on the effectiveness of the EK method, so the heterogeneity of the sediments complicates their decontamination. Improvement techniques are mainly aimed at controlling pH and keeping or bringing contaminants into solution (Page and Page, 2002). However, further research is needed to understand EK transport processes and thus improve the technology.

The main focus of future research tends to be the development of hybrid technologies that combine electroremediation with other decontamination processes.

**CHAPTER 2 - STUDY OF A BIOSURFACTANT ENHANCED
ELECTROKINETIC METHOD**

Investigation of a biosurfactant-enhanced electrokinetic method and its effect on the potentially toxic trace elements in waterways sediments

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Abstract

In this study, the biosurfactant-enhanced electrokinetic method was investigated for the removal of potentially toxic trace elements (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn) in waterways sediments. The effect of this method was compared to the removal capacities of deionised water in the same conditions in order to assess its efficiency. After treatment, batch leaching tests have shown that almost toxic elements (As: 81.3 %; Ba: 80 %; Cr: 97.3 %; Cu: 82 %; Zn: 94.5 %; Mo: 13.8 %; Ni: 62.7 %; Se: 66.8 % and Sb: 9.3 %) were less released in waters. On the whole sediment samples, Ba and Cd displayed the highest removal rates (Ba: 71.2 % and Cd: 77.5 %). The use of biosurfactant enhanced the electrokinetic method by improving the trace elements migration and altering pH and Eh locally generated by the system. Overall, the application of this new approach dredged sediments seems to be promising but needed further investigations for industrial applications.

Keywords : Sediment, Biosurfactant, Electrokinetic, Metals, Remediation

I. Introduction

Waterways maintenance produces several tons of sedimentary waste every year (Dubois et al., 2009), posing several environmental and management issues. Meteoritic events facilitate the runoff of both metallic and hydrocarbon pollutions into fluvial and aquifer systems, involving ecological disruptions. Therefore, remediation becomes a major step before the perennial storage of sediments and their valorisation in civil engineering techniques. Different methods leaning on principles as various as densiometric separation, biological degradation, chemical alteration (Xu et al., 2020; Wu et al., 2020), incineration or flotation are currently investigated in this purpose (Amrate, 2005). These techniques may allow the total or partial decontamination of sediment, by isolating and/or chemically altering the problematic compounds (Kribi, 2005). The remediation of the polluted sedimentary matrices can also be conducted with hydraulic binders (solidification/stabilisation) or achieved thanks to vitrification techniques (Mamindy Pajany et al., 2010; Mamindy-Pajany et al., 2013).

The adequate treatment depends notably on sediments nature and the typology of associated contaminants (Kribi, 2005). In civil engineering, highly effective extraction techniques such as bioleaching (R. D. Tyagi et al., 1993; S. Y. Chen and Lin, 2001; Gan et al., 2015), phytoextraction (Licinio, 2017) and ElectroKinetic (EK) treatments (Benamar, Baraud, and Alem, 2007; Ammami, 2013; Song et al., 2014) are usually implemented.

From a historic viewpoint, EK was first postulated in the 1800s after the observation of fluid movement from anodic to cathodic poles under the influence of electric current (Mahmoud et al., 2010; Song, 2017). The understanding of EK principles improved in the following years and the technology has been increasingly implemented for soils and sediments remediation, especially in finely sized materials (T. Li et al., 2009). The method leans on ionic contaminants transportation by electromigration (Yang et al., 2014; H. Zhang et al., 2021), and interstitial non-ionic contaminants movement via electro-osmosis (Acar and Alshwabkeh, 1993; Acar, Alshwabkeh, and Gale, 1993; Shapiro and Probstein, 1993; S Pamukcu and Wittle, 1993; Acar et al., 1995; Cameselle, 2015).

In organo-mineral matrices, the electromigration mobilizes not only free ions such as H^+ and OH^- generated by water electrolysis, it also induces the migration of anthropogenic cations (heavy metals, ammonium etc.). It mobilizes as well, local and allogenic inorganic anions like chlorides, cyanides, fluorides and nitrates, as well as ionisable organic compounds (Mosavat, Oh, and Chai, 2012b; Cameselle, 2015). During water electrolysis, the generated

H⁺ and OH⁻ ions involve pH gradients between the anode and cathode (Acar et al., 1995). Variations of pH may favour inorganic pollutants desorption from organo-mineral matrices and alter their electronic state (Tang et al., 2018). These variations are usually delayed during EK treatment as a result of the high acido-basic buffering capacity of dredging sediments (Yeung and Hsu, 2005; Matteo Masi, Ceccarini, and Iannelli, 2017). Overall, pH variation appears to be the most determining factor regarding the mobility of contaminants (Reddy and Chinthamreddy, 2003; Ottosen et al., 2005). It is now well acknowledged that a decrease in pH promotes trace elements mobility through the dissolution of bearing phases and/or the alteration of redox states (Gidakos and Giannis, 2006). Conversely, high pH near to the cathodic poles of EK systems are detrimental to trace elements migration and favour their adsorption onto mineral phases (e.g. iron and manganese oxides) via cation/H⁺ exchange (Kennou et al., 2015).

Classic chemical reagents used as electrolytes in EK devices may induce secondary soil and groundwater pollution (Gonzini et al., 2010). According to Ammami (2013), electrolytes based on nitric acid for example are toxic and therefore unsuited for in-situ treatment. Similarly, EDTA and EDDS are poorly biodegradable and present Pb-accumulation risks in aquatic environments (Wong, Hicks, and Probst, 1997; Evangelou et al., 2007; Song et al., 2016).

This study uses a new chemical extractant for the remediation of dredged sediment by EK methods. This new compound is an anionic cyclic lipopeptide BioSurfactant produced by bacterial organisms (*Bacillus subtilis*). This eco-friendly BioSurfactant (BS) was chosen on the basis of its biodegradability, and its economic viability. This type of anionic BS lowers the surface tension of water molecules and has good biodegradability rates (W. C. Chen, Juang, and Wei, 2015; Tang et al., 2017). Compared to synthetic surfactants, BS have larger molecular structures and more functional groups (Tang et al., 2021; 2020). Their large specific areas reduce interfacial tensions, and favour the formation of micelles (Tang et al., 2018). Micellar BioSurfactants remove trace metals through electrostatic adsorption or ionic exchange. Thanks to chelating agents they also allow trace elements complexation. As polar groups bind with the metals, the neo-formed ensemble (BS molecule/pollutant) becomes more soluble in water (Tang et al., 2019; Aşçi, Nurbaş, and Sağ Açıkel, 2010). This solubilisation is essential for effective EK remediation. The cationic, anionic or non-ionic nature of the hydrophilic parts conditions contaminants binding capacity and constrain their contaminants removal (Giannis, Gidakos, and Skouta, 2007). Thus, the EK remediation is achieved thanks

to a coordination of factors, among which the redox state of contaminants and the micellar properties of BS are the most preeminent (Gonzini et al., 2010).

The main objective of this study was to identify the contribution of this newly developed BS for the simultaneous removal of 11 frequent trace contaminants (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn) known to be problematic for the environment. Its performances were compared to the yields of Deionised Water (DW) to highlight its advantages in both liquid and solid phases. Indeed, most studies deal with the whole sediment (trace elements distribution within the solid phases) omitting to consider the fate of the contaminants in the aqueous mobile phase. An experimental program was carried out in this purpose, using a pilot-scale cell specially designed to treat large amounts of sediments.

As BS is not well known, these results were used to identify which trace elements it most effectively removed, hence the large number of pollutants studied. This work also aimed to identify the points requiring adjustment for future investigations. The background parameters (electric current, redox potential and pH) were monitored in the pore waters, as well as in the electrolytic chambers in order to identify the effect of the BS on the latter. Moreover, background parameters (pH, Eh and electric current) were also measured to assess their impact on the removing process.

II. Materials and methods

II.1. Sediments sampling

Sediments were collected from the Scarpe River, located in Saint-Laurent-Blangy (Haut-de France, France), using an excavator, and conserved in containers (25 L) at 5 °C. They were thoroughly homogenised before physico-chemical: X-ray Diffraction (XRD), X-Ray Fluorescence (XRF), fire loss, Plasma-Optical Emission Spectrometry (ICP-OES) characterization.

II.2. BioSurfactant and solvents properties

The HTS Bio[®] BioSurfactant implemented in this study bases on surfactin from natural fermentation process. It is an amphiphilic molecule with a hydrophobic lipid part consisting of β -hydroxylated fatty acids (C12 to C15) and a hydrophilic part consisting of heptapeptides. This corresponds to a 25 % of sodium surfactin solution with a density of 1.05. It is majorly anionic and easily biodegradable (90 % in 28 days). Its critical micellar concentration is 0.0003 %, which is 300 times lower than the optimal concentration of

classical surfactant such as Sodium Dodecyl Sulphate (SDS). Solvents implemented after EK treatment were analytical grade nitric acid (65 % v/v), Trace Analysis Grade ($d = 1.18$), hydrochloric acid (37 % v/v) and trace Analysis Grade ($d = 1.42$), nitric acid (> 68 % v/v), all from Fisher[®] Chemical. The deionized and ultra-pure waters were supplied via an Aquadem Veolia[®] system (E500 resin) and an Elga Purelab[®] ultra analytic system respectively.

II.3. Experimental ElectroKinetic system

In this study, a glass-made parallelepipedal system was used as EK cell (**Figure 1**). It consisted of three parts which were: (i) A central compartment for the sediments with three cross sections (S1, S2 and S3) for zoned monitoring and localised analyses after treatment; (ii) Two electrolyte compartments on both extremities as depicted in **Figure 1**.

In most studies, small laboratory cells are used to perform EK treatment on dredged sediments, which limit the scale up of experimental tests. For this purpose a new laboratory pilot cells was designed, to work on important quantities of sediments (4 kg) and to improve the quality of experimental measurements. This allows to test the viability of the method at larger scale. The dimensions (L × W × H) were 200 mm x 100 mm x 160 mm for the sediment chamber and 100 mm x 100 mm x 160 mm for the electrolytic chambers. Graphite plates (100 mm x 10 mm x 200 mm) were implemented as electrodes and two perforated grids (100 mm x 2 mm x 160 mm) were disposed to separate the sediment compartment from the electrolytes' chambers (**Figure 1**).

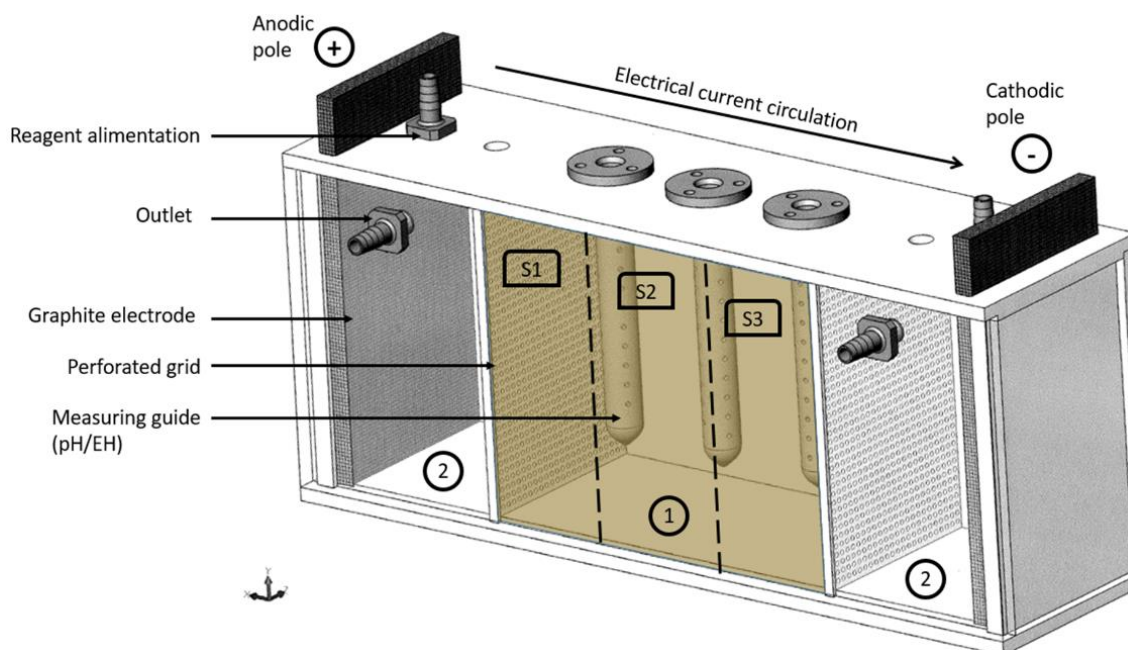


Figure 1 Schematic representation of the experimental device (Electrokinetic cell). (1) Central compartment for sediments; (2) Lateral compartments hosting the electrolytic solutions; S1, S2 and S3 correspond to the cross sections for zoned monitoring.

After each experiment, the EK cell was cleaned with demineralized water and nitric acid (65 % v/v). The probes for redox and pH measurement were carefully calibrated before each EK-run. The complete experimental dispositive comprised a DC power supply, a solution tank, two membrane pumps for reagents circulation ($60 \text{ ml}\cdot\text{h}^{-1}$), a multimeter for electric intensity measurement, and two overflow tanks receiving the excess of solution. In order to avoid the contamination of the anode and cathode chambers, filter papers were sided to the perforated grids. On a chronologic viewpoint, the central chamber was first filled with 4 kg of sediment, and then the electrolytic reagents were added into the two lateral chambers before 72 h of rest time. This resting time had the goal to optimise sediments saturation and to establish a chemical balance. The graphite electrodes were consecutively inserted into the anode and cathode chambers, and connected to the DC power supply.

II.4. Setting during the Electrokinetic tests

As recapitulated in **Table 1**, a 14 V current was injected continuously for 7 days. This setting allows an average voltage gradient of $1 \text{ V}\cdot\text{cm}^{-1}$. It is a voltage frequently used in EK studies (Ammami, 2013; Song, 2017).

For the first experiment, DW was used as anolyte and catholyte (EXP.A), and the BioSurfactant ($0.6 \text{ g}\cdot\text{l}^{-1}$) was implemented during the second experiment (EXP.B). The cell

was covered (aluminium foil) to prevent microorganism contaminations and BS photodegradation. Electrical current, pH and redox, were measured twice a day (on morning and evening) in triplicates using a calibrated multi-probe device (pH/redox), and copper wires connecting the sediment to a multi-meter were implemented for current intensity measurements.

	Current (V)	Duration (Days)	Anolyte and catholyte
EXP.A	14	7	DW
EXP.B	14	7	BS (0.6 g.l ⁻¹)

Table 1 EK experimental conditions (DW: Deionized Water; BS: BioSurfactant).

At the end of each EK-run (168 h), the sediment sample was divided into 3 equal sections, from anode to cathode, according to the three sections S1, S2 and S3 depicted in **Figure 1**. This allows the verification of the preferential migration of studied trace metals. The three sections S1, S2 and S3 were removed from the cell using a sediment shovel and dried (40 °C) before quantifying inorganic elements' concentrations (ICP-OES). Trace elements were quantified with a standard range (concentrations 0, 10, 20, 50, 100, 200 µg.l⁻¹) obtained by diluting standard solutions. Each sample was analysed three times, which allowed the evaluation of a Relative Standard Deviation (%RSD). 10 blanks were used for the analysis sequence.

The efficiency of inorganic elements removal was calculated as following Equation (1).

$$\%R = \frac{C_i - C_f}{C_i} \times 100\% \quad \text{Eq (1)}$$

With :

%R : The removal, expressing the depollution of a given trace element;

C_i : The initial concentration of a given trace element;

C_f : Its final concentration (after EK treatment);

Trace elements partition coefficient K_d representing the fractionation between the solid and liquid phases, was calculated following Equation (2):

$$Kd = \frac{c_s}{c_L} \quad \text{Eq (2)}$$

With :

c_s : Concentration of element in solid phase ($mg.kg^{-1}$)

c_L : Concentration of element in liquid phase ($mg.kg^{-1}$)

II.5. Analytical conditions

Sediments samples were dried at 40 °C before performing standardised measures of redox/pH and trace elements assessments on both solid matrix and leaching solutions.

- *Water content assessment*

150 g of sediment sample was used for water content measurements through weight loss (105 °C), according to the normed protocol NF EN 14346 (French standard).

- *Eh and pH measurement*

Eh and pH were measured on sieved (2 mm) and dried (40 °C) samples with solid/liquid ratio of 1:5. Samples were stirred during 60 min and rested during 60 min before measurement as recommended in the ISO 10390 standard.

- *Fire loss assessment*

Fire loss was measured on sieved (200 µm) and dried (40 °C) samples. Beforehand, ceramic crucibles were calcined at 550 °C during 20 min. 3 g of sediment were then calcined in the ceramic crucibles for 1 h at 550 °C, after which the crucibles were cooled via a desiccator and mass coherency was checked. Each assessment was conducted in triplicate.

- *Leaching*

Trace elements were measured within the leachate of sieved (4 mm) and dried (40 °C) samples with solid/liquid ratios of 10 L.kg⁻¹. Aqueous samples were agitated (vertical rotation) for 24 h and have rested during 15 min, as recommended in the NF EN 12457-2 standard (French norm). Eh, pH, EC and temperature measurements were carried out in the eluates. Chemical assessments were performed using a 5110 model of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) coupled to an SPS4® autosampler (Agilent technologies®) after samples filtration (0.45 µm). Free anions (F⁻, Cl⁻ and SO₄²⁻) were assayed using an ICS-3000 DC model of Ionic Chromatograph (IC) from Dionex®.

- *Solid phase analysis*

Acid digestion was carried out via microwave (Mars®, CEM Corporation) by a successive introduction of 0.5 ml of ultra-pure water, 1 ml of HNO₃ (> 68 % v/v) and 3 ml of HCl (37 % v/v) on 0.250 g of sieved (250 µm) and dried (40 °C) sediment samples for trace elements

evaluation. Samples were collected in accordance with the NF ISO 12914 standard, completed up to 100 ml with ultra-pure water and filtered at 0.45 μm .

III. Results and discussion

III.1. Physico-chemical properties of the raw sediments

X-ray diffraction analysis performed on the raw sediment underlined strong occurrences of quartz, muscovite, albite and kaolinite (**Figure 2a**), which were very likely the erosive outcome of the Scarpe river watershed. The organo-mineral assemblage displayed three main mass losses during their thermogravimetric analysis (TGA) characterization (**Figure 2b**), probably as a result of organic matter (OM) and carbonates pyrolysis. Ignition loss also suggested the high occurrence ($11.91 \pm 0.005 \%$) of these two phases. A few discrepancies between ignition loss and TGA data were observed probably as a result of samples heterogeneities. Although homogenisation steps were undertaken before drying and analysing, OM and carbonates are indeed heterogeneously distributed within this natural matrix. Regarding TGA results; the dehydration of hydrous minerals and early OM pyrolysis induced very likely a first shift in mass loss (3.36 %) , while a second one (2.80 %) fitting rather with tardive OM ignition ([Mahamat Ahmat, Mamindy-Pajany, and Nadah, 2021](#)) and carbonates denaturation ([Tribout, 2010](#)) was observed between 350 and 650 °C. The late mass loss (5.85 %) over the thermal range between 650 °C and 900 °C fitted with the destabilisation of thermally recalcitrant structures likely sulphates and silicates.

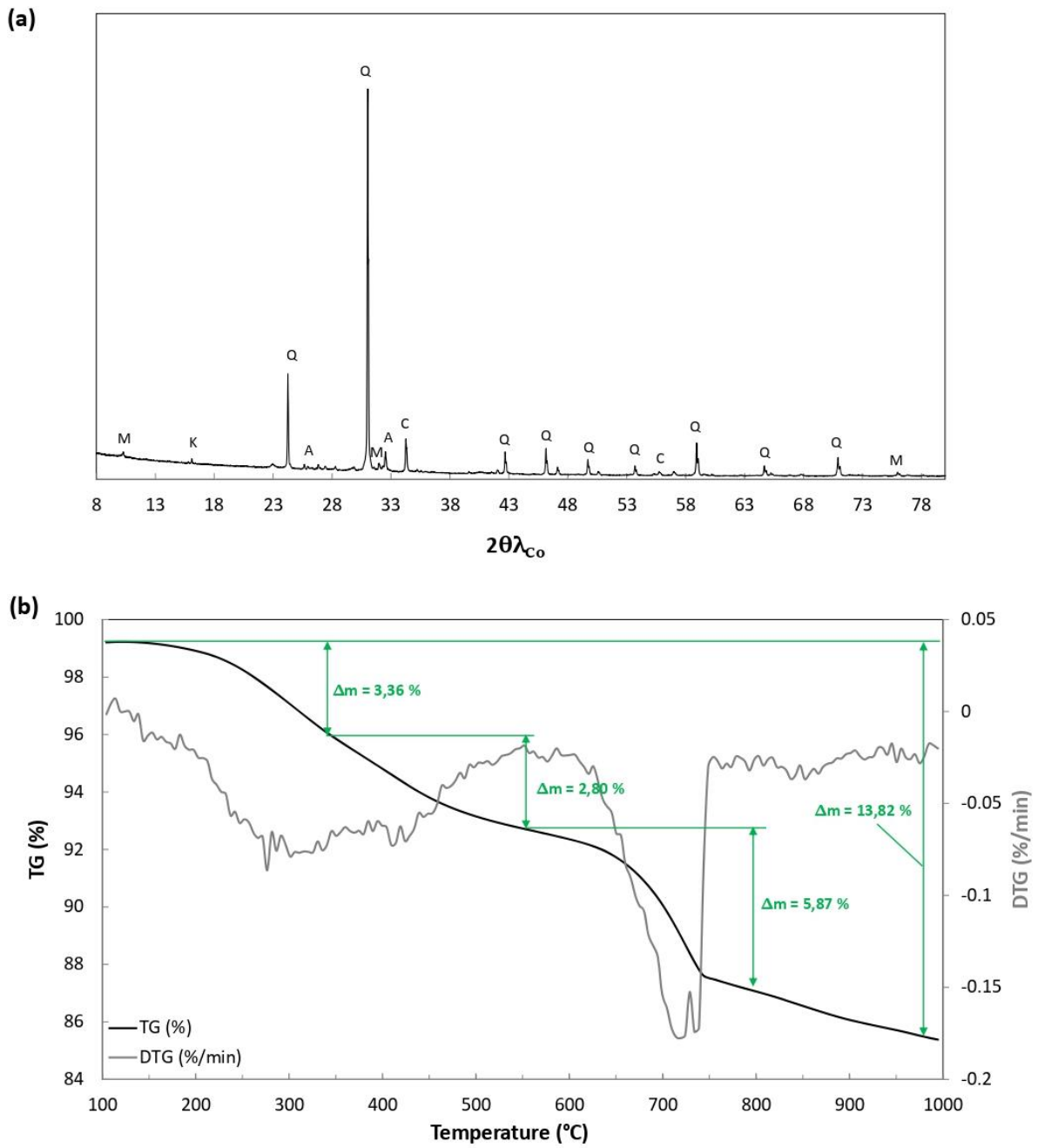


Figure 2 (a) XRD characterization of the raw sediment with Q: Quartz; C: Calcite; A: Albite; M: Muscovite; K: Kaolinite; (b) Thermal behaviour of the sediment (TGA) before electrokinetic treatments.

Raw sediments' chemical content determined through X-Ray fluorescence (**Table 2**) have shown the predominance of SiO₂ as a probable result of the strong representation of silicates like quartz, albite, muscovite and kaolinite (**Figure 2a**). The same assessment showed a good representation of Al (8.6 %), Ca (7.3 %) and Fe (3.3 %) among the major elements. The latter are known to be carried by Al and Fe oxides as well as carbonates, clays, OM and sulphides in sedimentary contexts (Priadi, 2010; Poitevin, 2012). The organo-mineral ensemble presented a pH of 7.48 ± 0.02 before EK treatments and 58.64 ± 0.001 % of water content. Its concentrations of leachable anions namely F⁻, Cl⁻ and SO₄²⁻ were 49.33 ± 4.99 , 104.67 ± 1.25 and 780 ± 8.16 mg.kg⁻¹ respectively.

	Trace elements		Major elements (Oxides)	
	Leaching concentration (mg.kg ⁻¹)	Solid phase concentration (mg.kg ⁻¹)	Oxides	(%)
As	0.19 ± 0.01	6.78 ± 0.27	Na ₂ O	1.1
Ba	1.21 ± 0.01	406.31 ± 1.40	MgO	0.7
Cd	0.01 ± 0.01	0.67 ± 0.05	Al ₂ O ₃	8.6
Cr	0.07 ± 0.01	44.17 ± 0.80	SiO ₂	75.0
Cu	0.60 ± 0.01	41.75 ± 0.69	P ₂ O ₅	0.6
Mo	0.24 ± 0.01	1.30 ± 0.01	SO ₃	0.1
Ni	0.22 ± 0.01	19.33 ± 0.23	K ₂ O	2.1
Pb	0.02 ± 0.01	56.19 ± 1.82	CaO	7.3
Sb	0.12 ± 0.01	2.75 ± 0.15	TiO ₂	0.8
Se	0.14 ± 0.02	1.85 ± 0.01	Fe ₂ O ₃	3.3
Zn	0.96 ± 0.02	333.24 ± 10.60	ZrO ₂	0.1

Table 2 Trace element (ICP-OES) and major elements (XRF) assessed in the raw sediment.

III.2. Evolution of the background parameters (pH / redox), and electric currents during the treatment

III.2.1. Electric current

The electric charges of total chemical species in movement generate an electric intensity which varies as a function of the entire system's resistances (Gao et al., 2013). The circulation of the H^+ and OH^- ions, as well as inorganic elements ions is linked to the magnitude of electric intensity. Its evolution during the treatment with DW (EXP.A) as displayed in **Figure 3a** exhibited high values in the first 48 h before reaching a more stable state around 8-9 mA similar to the results of Maturi and Reddy (2006) and Colacicco et al. (2010) while the experiment with BS (EXP.B) showed an opposite trend. An examination per sections showed that S1 and S2 had close behaviours (rise until 72 h), and a strong decrease at the end of the treatment. S3 conversely, displayed a more pronounced lowering compared to the other sections with average values around 6.5 mA.

As shown in **Figure 3b**, electric current in EXP.A was lower than in EXP.B, suggesting that the use of BS improved electric current circulation within the sedimentary matrix, probably as an effect of micelles formation and emulsification process. For both experiments, the section S2 presented higher current intensity compared to the other sections, suggesting mobile ions electromigration from the anode towards the centre of the EK cell. The electric intensity lowering at the cathode was very likely favoured by localised ions precipitation as shown by Ammami et al. (2014) and Bahemmat and Farahbakhsh (2015).

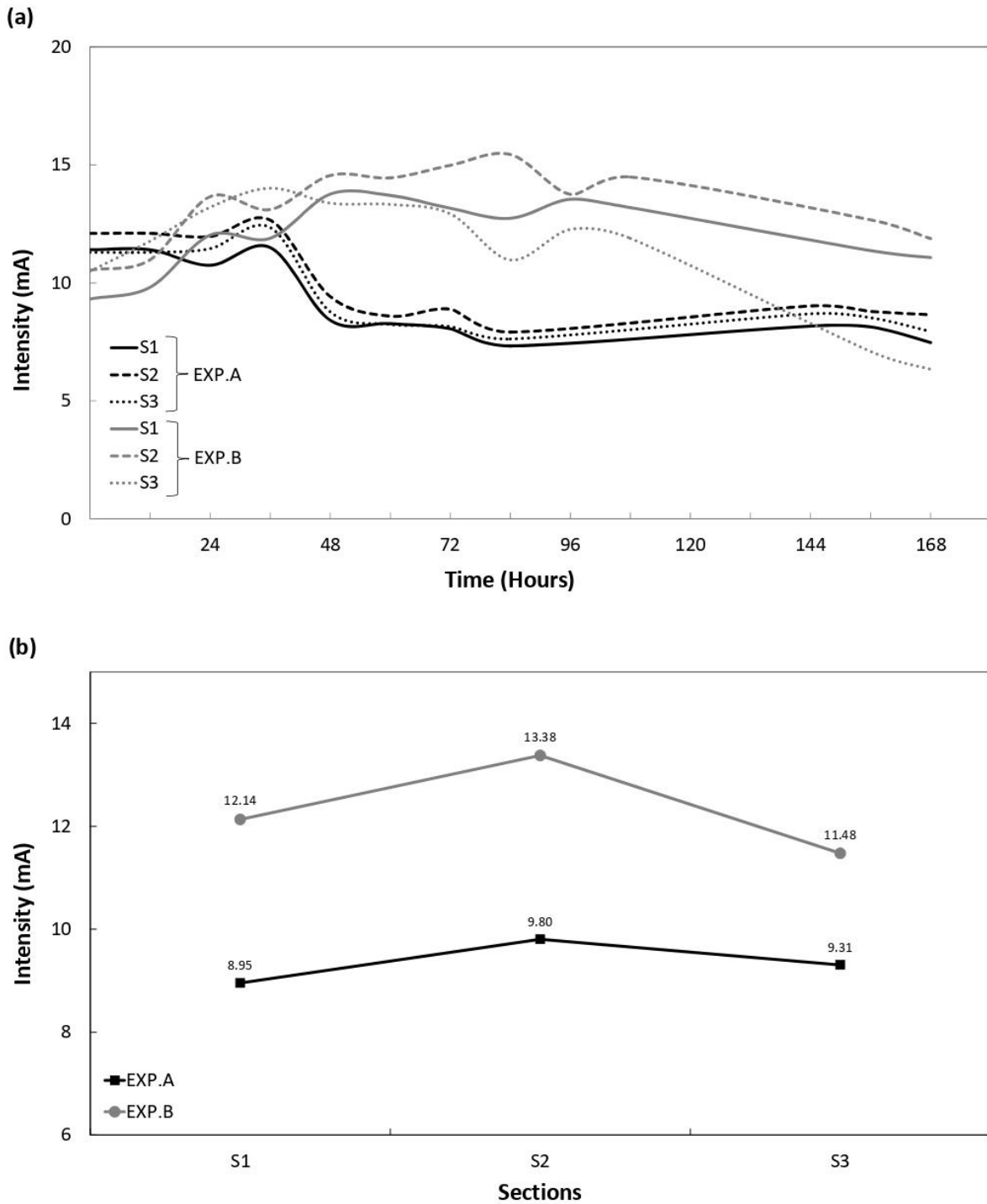


Figure 3 (a) Electrical conductivity evolution during the EK experiments conducted with Deionized Water (EXP.A) and BioSurfactant (EXP.B) as electrolytes. S1, S2 and S3 are cross sections realized from the anode to the cathode; (b) Average electrical intensity in the three sections (S1, S2 and S3) during the EK treatment with both electrolytes.

The electrolytic reduction reactions and pH increase occurring near to the cathode area confer high resistances to precipitated phases. The pH of the pore solution is also an important parameter to consider when analysing the mobility of inorganic elements. Salt solubilisations are acknowledged to involve high pH values at the beginning of EK treatments (Saichek and Reddy, 2003; Bahemmat and Farahbakhsh, 2015), but ions depletion decrease interstitial pH and tends to stabilize it over time (Grundl and Michalski, 1996; Saichek and Reddy, 2003). Stable current is mostly involved by the conductivity of pore solutions (Ait Ahmed, 2016) and reflects the electrical resistance of the treated matrix. Here with BS, values decreased at the end of treatment, but a remaining low intensity suggested that the conductive ions were not completely consumed. Intensity evolutions similar to this trend were reported in several previous EK approaches (Colacicco et al., 2010; Rozas and Castellote, 2012; Song et al., 2016; Tang et al., 2018). The gradual neutralization of migrating cationic and anionic ions is recognized as triggering factors for such evolutions. Cations migrating towards the cathodic pole neutralize indeed, with anions migrating in the reverse direction (Ammami et al., 2014). This not only impacts trace elements displacements but also the movement of H⁺ and hydroxyls ions produced by water electrolysis (Jeon et al., 2010). The pH changes occurring during the treatment are known to be partly responsible for such electrical intensity evolutions (Tanaka et al., 2016; Z. Zhang et al., 2021). In fact, the precipitation of non-conductive solids at high pH values, results in a strong decrease in mobile ionic species (Colacicco et al., 2010), while precipitates dissolution promotes an increase in the electrical intensity (Ammami et al., 2014). Such changes in pH generally lead to changes in the local value of particles surface charges (Kornilovich et al., 2005). The electrokinetic experiment of Tang et al. (2018) obtained peak values of 101 mA and 12 mA in the first 4 h using Sophorolipids, while here the use of BS (EXP.B) induced a relatively small peak (15 mA) within the first 72 h. The increase in intensity was more gradual and less important at the beginning of the experiment with BS compared to Tang et al. (2018) results. Overall, the bibliographical values (ranging between 5 and 10 mA) matched the oscillations observed here with DW and BS as electrolytes.

III.2.2. Evolution of pH

The monitoring of pH magnitudes in pore water and the two electrolyte compartments (anodic and cathodic) is recapitulated in **Figure 4**. In the anodic compartment, it decreased during the treatment with both electrolytes (**Figure 4a**). The use of DW as electrolyte (EXP.A) induced values ranging between 6.35 and 4 while BS (EXP.B) induced oscillations between 7.44 and 5.64, suggesting plausible oxidations at the anode (Chang, Qiang, and Huang, 2006; Mosavat, Oh, and Chai, 2012b; Moghadam et al., 2016). For the cathodic compartment, the pH increased from 8.01 to 9.47 during the first 72 h as a probable effect of OH⁻ income from water electrolysis (Gidakos and Giannis, 2006; Zhou, Zhu, and Wei, 2019), before decreasing to 7.74 at the end of the EXP.A. For EXP.B, it varied in an alkalisation trend with values ranging between 8.33 and 11.22. Regarding pore water pH, a slight decrease was observed during EXP.A (**Figure 4b**), whereas EXP.B exhibited increasing values, especially near to the cathode. Such alkaline pHs usually prevent inorganic elements solubilisation and migration (Acar, Alshawabkeh, and Gale, 1993; Virkutyte, Sillanpää, and Latostenmaa, 2002). Dissolved metal ions adsorbed on the sediment particles finally precipitate as hydroxides, carbonates and other compounds in the high pH zone near to the cathode. Alkaline conditions promote carbonates precipitation and contribute therefore to the buffering capacity of the sediment (Singh, Tack, and Verloo, 1998).

In EK systems, OH⁻ ions lack of mobility compared to H⁺ induces the gradual appearance of an acidic front (Mosavat, Oh, and Chai, 2012b; Ayyanar and Thatikonda, 2020). However here, the pore water pH measured in both experiments was rather neutral, which suggested an absence of acidification and carbonates solubilisation during the treatment. This may have noteworthy implications regarding the fate of the studied trace elements, since carbonates promotes background alkalisation (Hlavackova, 2005).

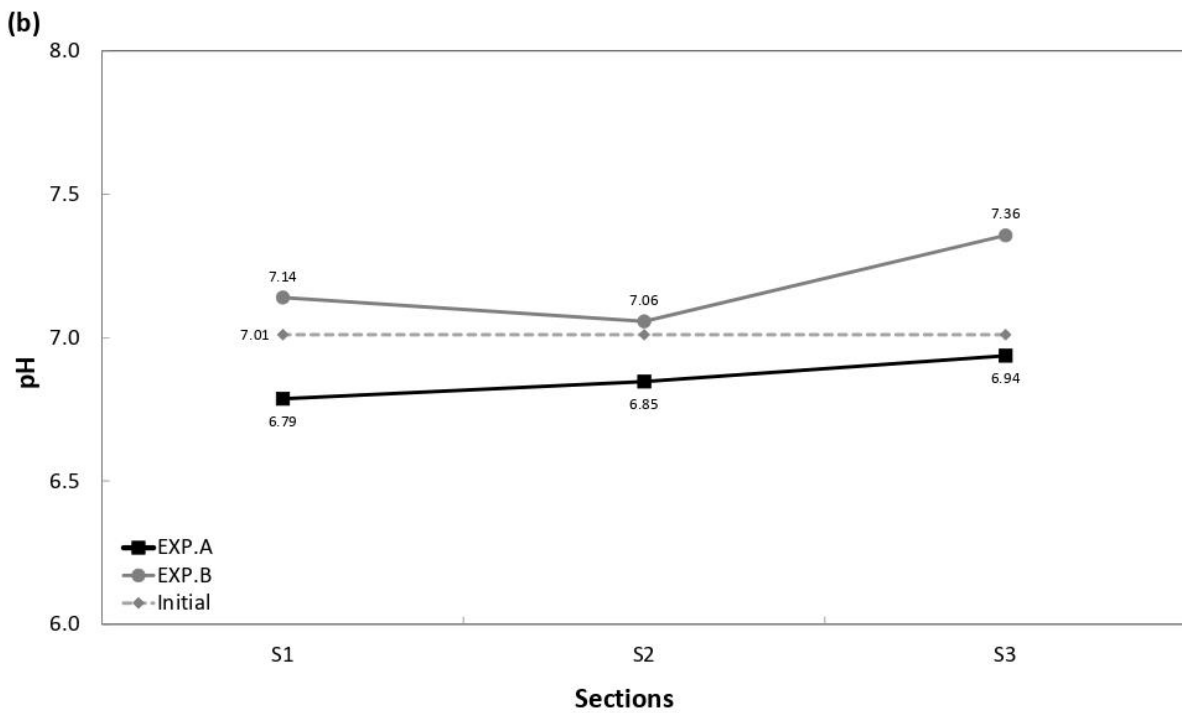
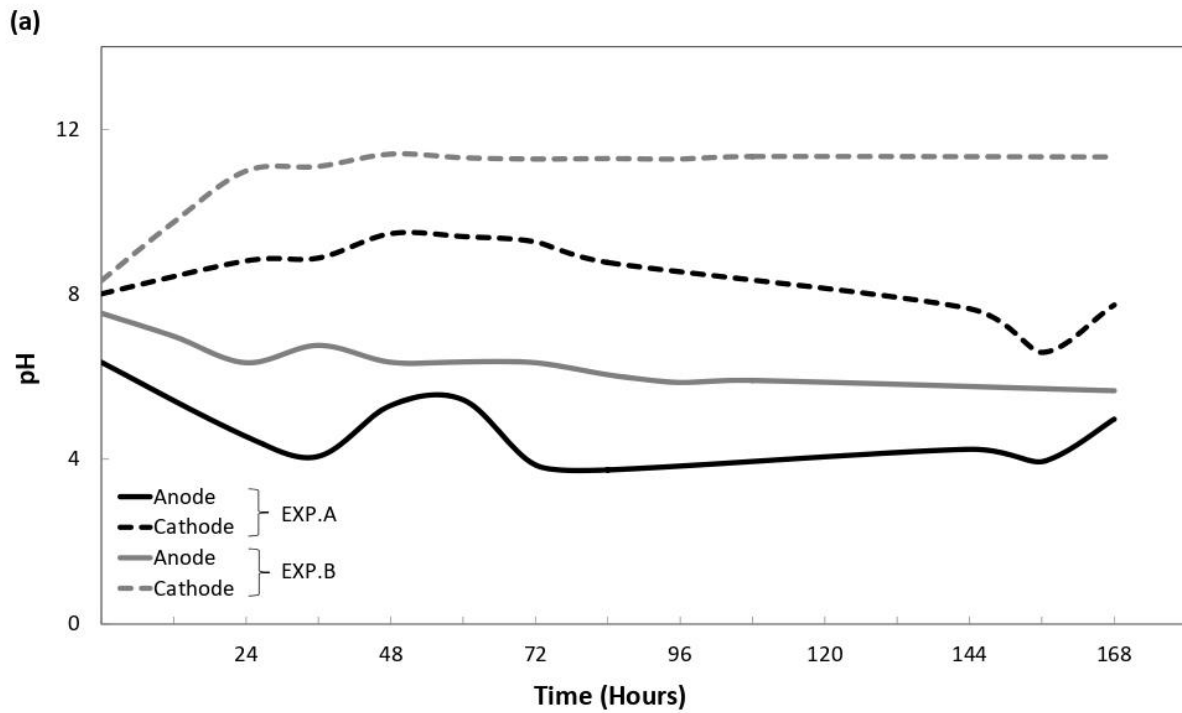


Figure 4 (a) pH evolution within the reagents chambers (anode and cathode) during the EK experiments; (b) Average of pore waters' pH measured within the 3 sedimentary sections (S1, S2 and S3) during EK treatment.

III.2.3. Redox potential

BS (EXP.B) allowed an important redox reduction in both anodic and cathodic poles (**Figure 5a**). In the sedimentary matrix, DW involved an oxidizing medium near to the anodic pole and a reducing environment close to the cathode compartment, whereas BS induced a more homogeneous reduction in the pore waters nearing both poles. Indeed, with BS as electrolyte (EXP.B), redox monitoring results (**Figure 5b**) indicated reducing properties for pore water with pronounced values in the sections near to the cathode (-84 mV). Demineralised water (EXP.A) did not allow such reduction of the medium and showed a more pronounced redox delta between the three sections (**Figure 5b**). Besides, more reducing conditions were observed near to the anode (-54.7 mV), rendering this zone more favourable to the occurrence of reduced mineralogical phases i.e. sulphides (Singh, Tack, and Verloo, 1998).

Previous studies suggested that redox potential increases in the anode regions and decreases at the cathode as an effect of water electrolysis (Ammami, 2013). Low pH combined with high redox potential increases inorganic elements desorption from sediments and improves electrokinetic yields, (Singh, Tack, and Verloo, 1998; Nystroem, Ottosen, and Villumsen, 2005). Although pore water did not change significantly here, the depollution rates remained quite satisfactory within the sedimentary matrix (*Cf.* elements evolution described in the next sections).

Conversely, a decrease in the redox potential promotes minerals precipitation and notably sulphide formation (Tack, Lapauw, and Verloo, 1997). Their gradual oxidation releases associated elements as As, Zn, Cd, Pb (Lions et al., 2007). Oxidizing conditions therefore favour the neoformation of secondary phases, and contaminants co-precipitation or adsorption (Gäbler, 1997; Tack, Lapauw, and Verloo, 1997; Lions et al., 2007; 2010; Isaure, 2012). Secondary phases such as amorphous iron and aluminium (hydro-oxides), have large specific surface areas and play an important role in metals and metalloids retention processes (Meima and Comans, 1998; Dijkstra, Meeussen, and Comans, 2004) but are usually less stable than primary phases which tends to eventually increase the global background solubility (Calmano, Hong, and Forstner, 1993; Morse and Luther, 1999; Achard, 2013).

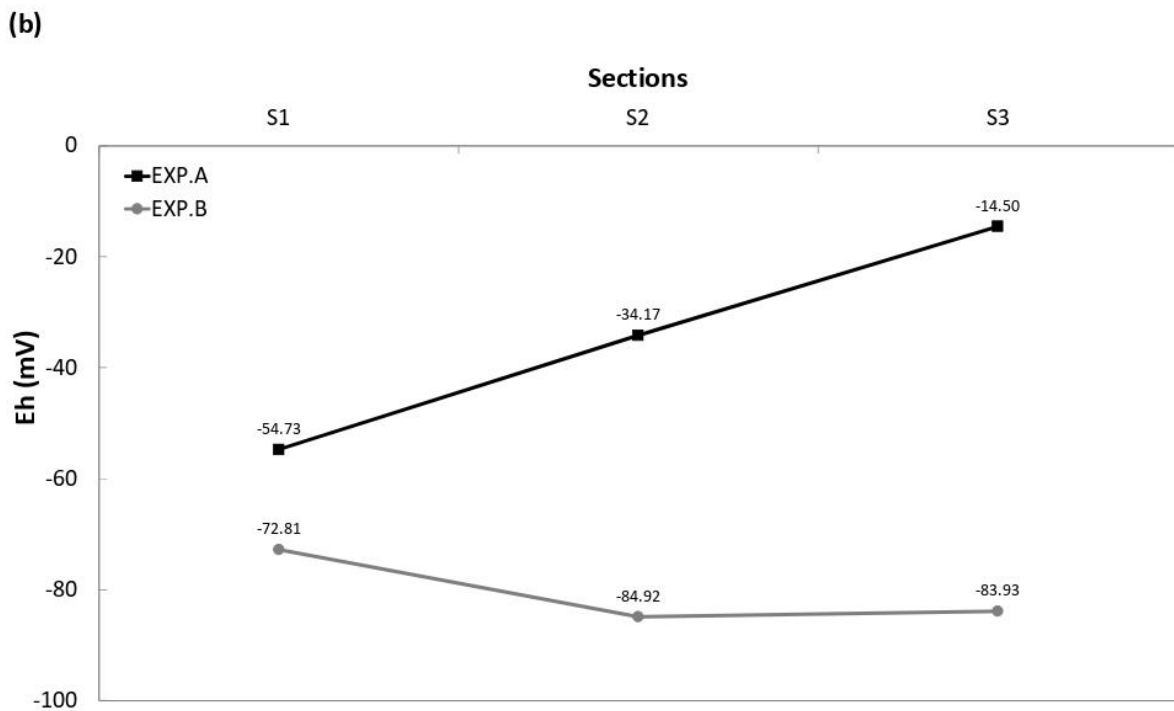
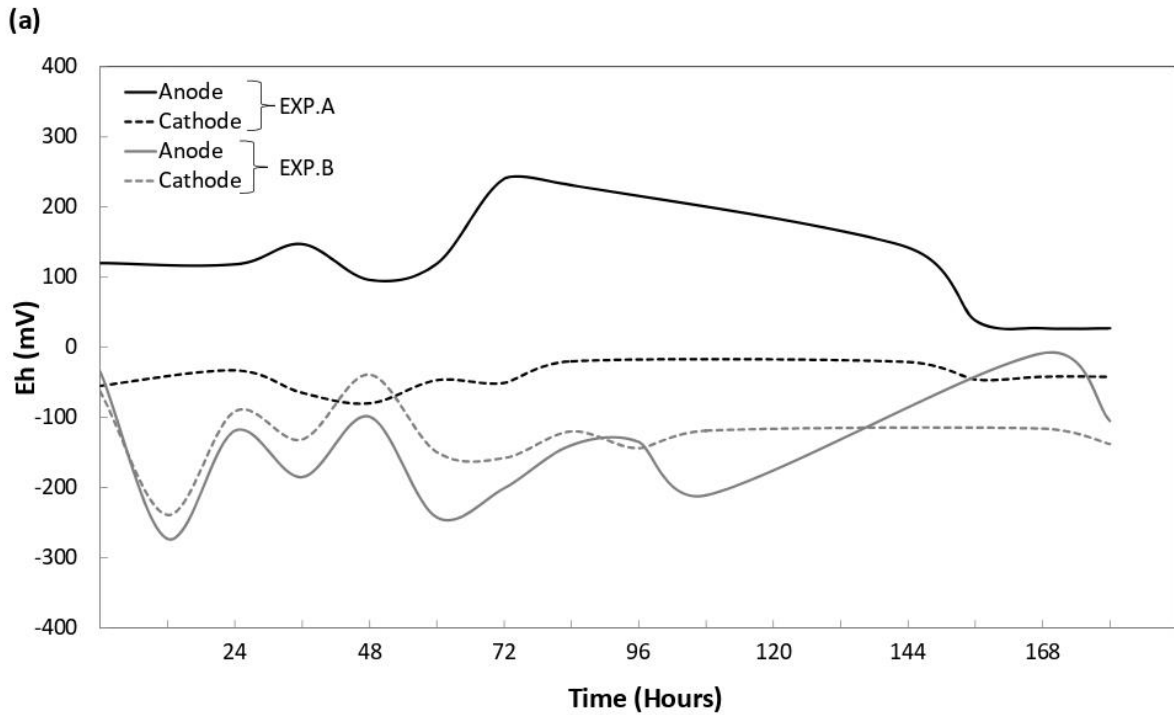


Figure 5 (a) Redox evolution at both anodic and cathodic poles during the EK treatment; (b) Average pore water redox values within sediment sections (S1, S2 and S3) during the treatment.

III.3. Trace elements evolution in the solid phase

III.3.1. Behaviour with Deionized Water as electrolyte (EXP.A)

The studied trace elements (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn) and removal rate (%R) from the solid phase, calculated via **Eq 1**, are presented in **Figure 6** as a function of sediments cross sections. Regarding Zn, poor extractions were observed when DW was used as electrolyte (EXP.A). Similar trends were reported by [Song et al. \(2014\)](#) which suggested that Zn behaviour was driven by high precipitations in the section nearing the anodic pole. The fate of Zn is constrained by its easy thermodynamic evolution from exchangeable to residual fractions ([Song et al., 2014](#)) which lowers the *in fine* yields during EK treatment. Here, Zn appeared difficult to remove from the solid phase, and exhibited greater enrichment tendencies near to the anode (-12.9 %). But on a closer examination, Zn partition coefficient (K_d) suggested rather good trends of solubility (**Table 3**). This data calculated through equation 2 characterize pollutants fractionation between the sedimentary matrix and the mobile aqueous phase. High K_d values of a given trace element suggest in fact, low concentrations in the aqueous phase.

For Cd, Sb and Mo, K_d values were lower in the treated sediments compared to the raw matrix ($K_{d \text{ initial}}$), suggesting a good mobilisation of their labile states and therefore, a lowering trend for their solid phase concentration. Their removal percentages (%R) were 45.4, 56.4 and 53.8 % for Cd, Sb and Mo respectively, which confirmed the solubilisation trend deduced from K_d evolution between the raw state and the EK-treated state. Regarding Ba, partitions were higher in the treated sediment compared to the raw matrix which indicated an EK-driven solubilisation trend. This was corroborated by the removal performances which reached a value of 69.5 % (S2). This good yield was probably favoured by the evolution of redox conditions, since the reducing configuration predominating during the EK-run (**Figure 5b**) is acknowledged to favour the dissolution of Ba-bearing phases ([Cappuyns, 2018](#)).

For Cu, Ni, Pb and Zn, precipitation/complexation phenomena of free forms were very likely involved in the enrichments observed after treatment as suggested by [Isaure \(2012\)](#). Note that the relatively high %R values for Cu may result from the corrosion of copper wires implemented for electrical intensity measurements. Thus, these Cu removal yields were plausibly doped by this potential experimental bias.

As, Cu, Cr, Ni, Pb and Zn had low removal yields and presented punctual enrichments within the solid phase. Eh and pH spatial evolutions as a function of distance from the polar extremities drove very likely these particular behaviours. Cu enrichments were higher in the

section S3, consistently with cations global migration towards the cathode (Ammami et al., 2014). However Ni and Zn were enriched in section S1 i.e. closer to the anode. According to the general directions of cation migration in EK systems (Ammami et al., 2014), they should have migrated to the cathode and therefore provoked more enrichment in the section S3 instead of S1. A plausible explanation for this incoherency is the drying phase (40 °C) inherent to our analytical design. Indeed, this oxidizing pre analytical step could have involve the measured enrichments.

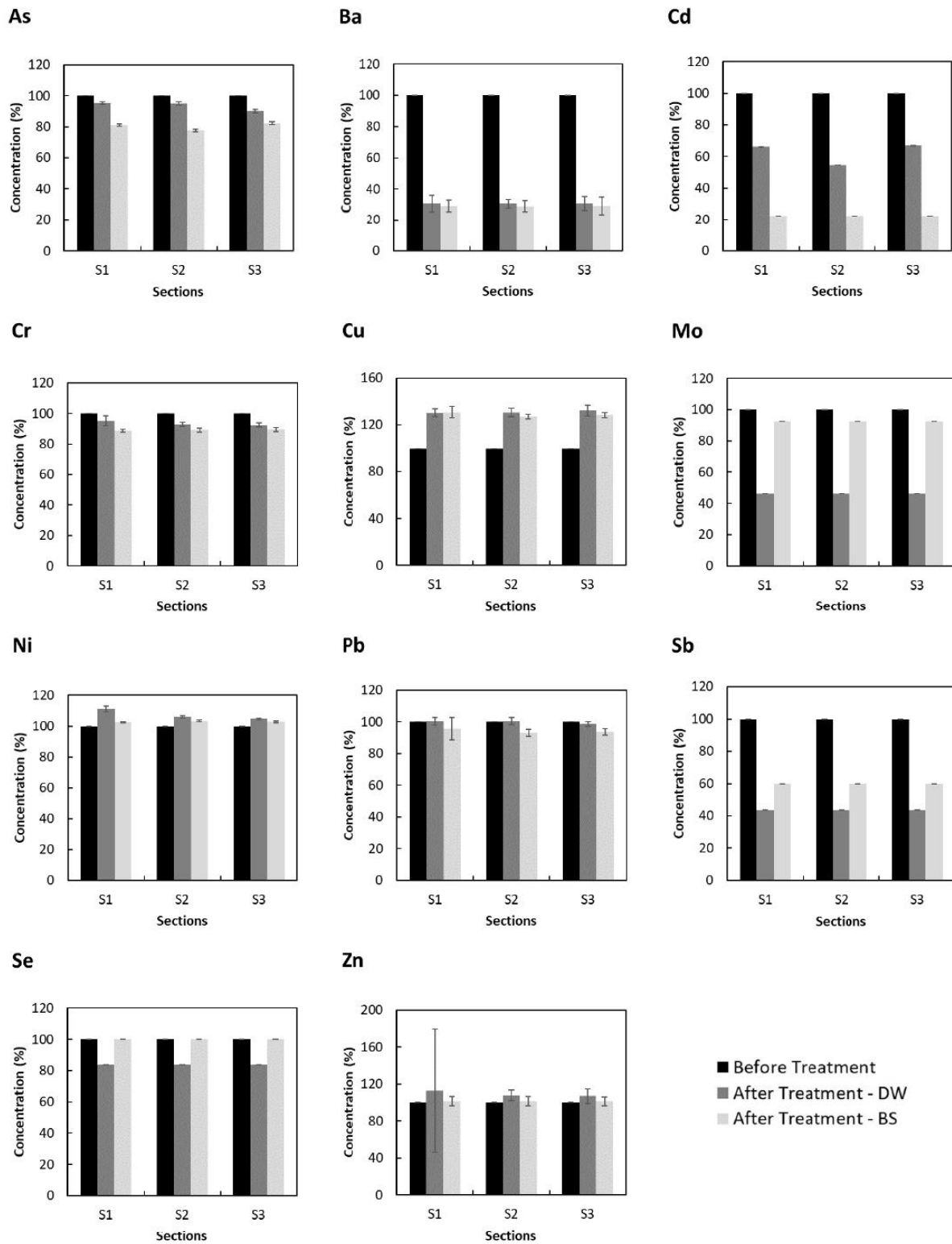


Figure 6 Solid phase concentrations of the studied trace elements in the three sections (S1, S2 and S3) of the EK device before and after treatment, with Deionized Water (DW) and BioSurfactant (BS) as electrolytes.

	EXP A				EXP B		
	K _{dinitial}	K _{dS1}	K _{dS2}	K _{dS3}	K _{dS1}	K _{dS2}	K _{dS3}
As	35.19	71.11	161.17	51.00	152.61	64.84	63.71
Ba	337.08	415.33	412.71	408.86	491.90	443.77	433.76
Cd	222.22	176.00	145.71	178.13	30.00	30.00	30.00
Cr	597.39	8 412.67	8 199.78	8 170.22	19 602.78	19 677.78	19 752.78
Cu	69.52	362.80	286.78	315.34	504.96	369.47	429.32
Mo	5.38	2.93	2.99	3.08	5.76	5.70	5.59
Ni	87.44	237.20	172.86	231.45	228.10	208.43	240.52
Pb	2 809.33	4 176.67	4 181.23	4 107.53	1 918.45	1 868.65	1 878.57
Sb	22.73	9.49	10.43	10.00	12.54	14.85	15.03
Se	13.20	32.98	32.98	32.98	39.78	19.15	16.40
Zn	348.65	3 724.36	2 587.67	3 005.65	4 479.16	6 068.22	6 442.53

Table 3 Evolution of the partition coefficient between the raw sediment (K_{dinitial}) and the treated sediment (K_{dS1}, K_{dS2} and K_{dS3}). The partition within the treated sediment was assessed according to the three delimited sections (S1, S2 and S3).

III.3.2. Elements behaviour in the solid phase using the BioSurfactant as electrolyte (EXP.B)

Although trace elements removals were globally higher with the BioSurfactant (EXP.B) than Deionized Water (**Figure 6**), data underlined a few disparities following elements nature. Ba and Cd for instance, displayed respectively 71.2 % (S2) and 77.5 % (S1, S2 and S3) of abatement, while Se concentrations appeared poorly affected.

For Cd, Sb and Pb, the partition coefficients (K_d) were higher before the treatment (**Table 3**) suggesting EK-aided mobilisations via desorption mechanisms and/or the dissolution of bearing phases'. The micellar properties of BioSurfactants are indeed acknowledged to enhance desorption/solubilisation mechanisms ([Ammami et al., 2015](#); [Xuhui Mao et al., 2015](#)). For Mo, Sb and Se on the other hand, the use of the BioSurfactant did not improve the removal yields significantly (**Figure 6**). This was a result of oxyanion forms of molybdenum, selenium and antimony lack of favorability for micellar interactions. The

anionic BS is indeed known for having a good affinity with cationic pollutants (Xuhui Mao et al., 2015), which could explain the good yields observed for cations such as Cd (77.5 %).

The use of BS induced the hierarchy Cd>Ba>Sb>As>Cr>Co>Mo>Pb>Zn>Ni>Cu, which was probably governed by elements predisposition to interact with the micellar compound. In contrast to EXP.A, %R in the different sections did not vary significantly, which suggested that the elements mobilization here was homogeneous and independent from the distance to the polar compartments.

Ammami (2013) observed Cd, Cu, Pb and Zn strong accumulations in the central section of the treated matrix due to basic pH variations. In his approach, the most important abatements were found under the configurations with the highest current intensities, which was consistent with our study. Indeed, the use of BioSurfactant (EXP.B) led to higher electrical intensity (**Figure 3a and 3b**), and higher elemental abatements compared to the experimental design implementing DW as electrolyte (EXP.A). As previously observed in EXP.A, here also significant Cu enrichments were noted after treatment. The enrichment magnitudes were quasi similar in the two experiments and were probably both doped by the copper wires implemented for intensity measurements.

III.4. Trace elements evolution in the liquid phase

III.4.1. Metals' evolution in the liquid phase with DW as electrolyte (EXP.A)

After treatment with DW as EK electrolyte, pH values in the leachates were 7.12, 7.21 and 7.22 in S1, S2 and S3 respectively, which were quasi equal to the raw sediment pH (7.48). The same measuring spots exhibited redox magnitudes of 189, 197 and 195 mV respectively. The examination of trace elements behaviour underlined better removal yields in the sections near to electrolyte compartments (S1 and S3). Despite relatively basic pH conditions, high depollution rates with the following order Cr>Zn>Ba>Cu>Ni>As>Se>Pb were observed, and poorer yields for Mo, Cd, Sb under the DW experimental configuration. Solubilisation phenomena appeared predominant although the pH of pore waters remained globally neutral (pH \approx 6, 7). Considering As for instance, initial K_d was inferior to K_d after treatment, which suggested EK driven mobilisations (**Table 3**). For this element, removal rates in the solid matrix (**Figure 6**) were lower than in mobile liquid phase (**Figure 7**), corroborating the trend deduced from the partition data. Overall, the high %R measured in the leaching approach (**Figure 7**) indicated effective elimination for trace metals such as Cr (93.2 %), Zn (89.4 %) and Ba (75 %).

Metal removal from the liquid phase depends particularly on background pH. [Ammami et al. \(2015\)](#), showed for instance, that Zn precipitates under hydroxide species at $\text{pH} > 7$, while the precipitation of elements such as Cr, Cu and Pb requires more acidic conditions ($\text{pH} > 4-5$). Our pH conditions (**Figure 4b**) tended to favour Zn cationic state, which is admitted more labile. For, Cr, Pb and Cu, the acido-basic conditions here were theoretically unfavourable to mobile forms and fitted rather with sedimentary immobilization. However, with an average interstitial water pH of 6.86, good removal rates were observed for these elements: Cr (93.2 %); Cu (75 %); Pb (32.5 %). Previous studies attested that acidic and reducing conditions are the most favourable configurations for metal solubilisation, with higher effects of pH compared to the influence of redox potential ([Chuan, Shu, and Liu, 1996](#)). [Chuan, Shu, and Liu \(1996\)](#) for instance, showed that metal solubility increases with lowering redox. Removal results here (**Figure 7**) under evolving conditions suggested that both redox and pH have a significant influence. In addition to pH and redox, the difference of electric potential is also evoked to explain ionic species migration. Electrophoresis is known to confer surface charges onto solubilized colloidal particles ([Vieira-Nunes, 2018](#)). The particle in this case is not immobilized in an electric field, but carried towards the electrodes.

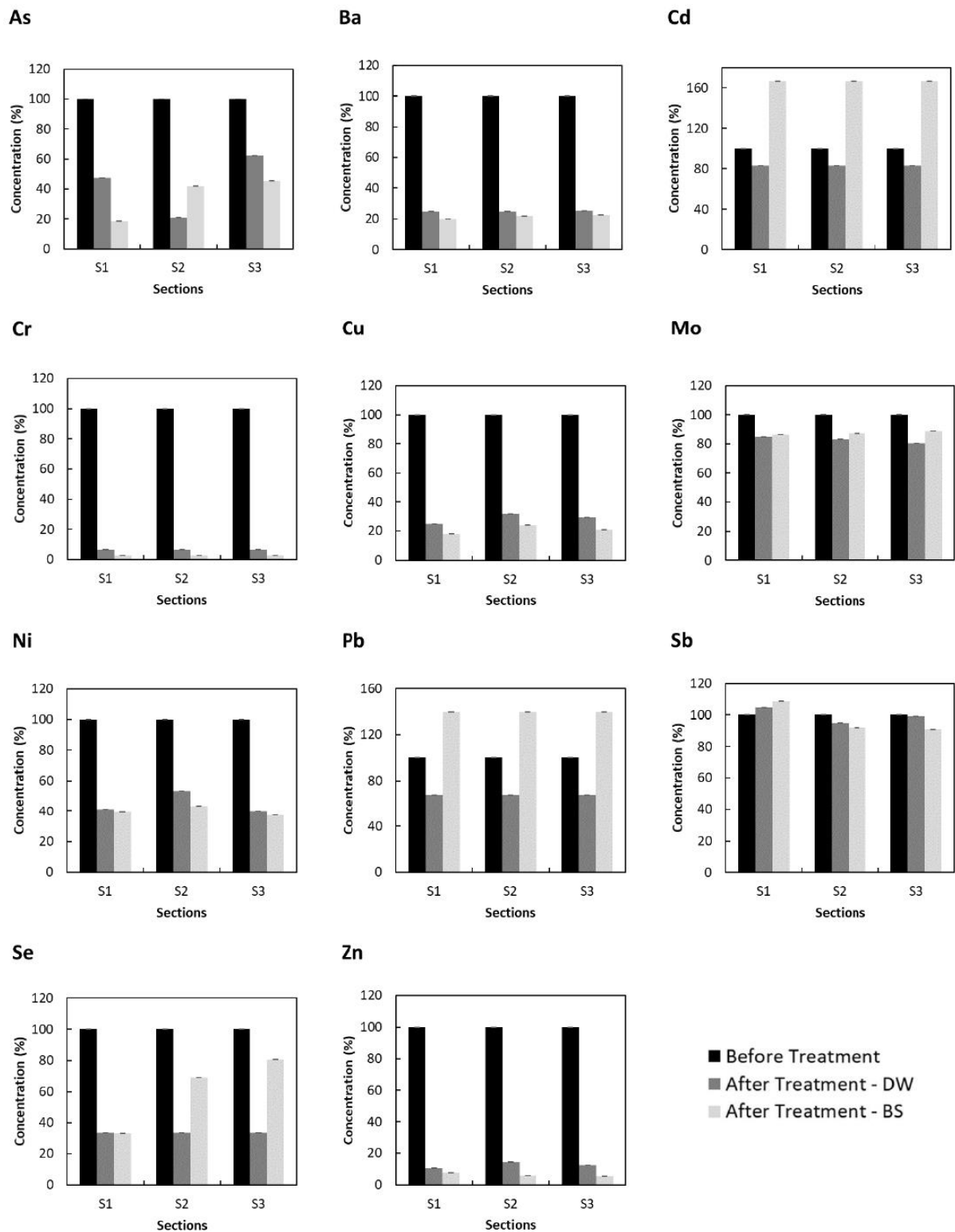


Figure 7 Liquid phase evolution of the studied trace elements after treatment with Deionized Water (DW) and BioSurfactant (BS) as electrolytes. Data for the sedimentary cross sections S1, S2 and S3.

III.4.2. Evolution in the liquid phase with the BioSurfactant as electrolyte (EXP B)

Leachates' pH in S1, S2 and S3 after treatment with BS were 7.27, 7.37, 7.26 respectively, which corresponded to the raw sediment pH (7.48). In the same way, the redox potential was 206, 205 and 205 mV, which also corresponded to the redox value of the raw sediment (205 mV). Despite non-acidic interstitial water (pH = 7.19), most elements (As, Ba, Cu, Mo, Se) were depolluted in greater quantities in S1, and a few (Cd, Pb and Sb) exhibited enrichment trends. As previously mentioned, cations preferentially migrate towards cathodes (Ammami et al., 2014), but here micellar interactions with BS allow the formation of anionic groups that can migrate towards the anodic pole. Data showed that the BioSurfactant caused elements migration mainly from S1 and S3 (Figure 7). Except for As, Ba, Cu, Mo, Se, which were mainly removed in S1, elements as Ni, Sb and Zn had higher yields in S3, with respective %R values of 62.7, 9.3 and 94.5 % (Figure 7).

Cd, Pb and Sb enrichments (respectively 67, 40 and 9 % enrichments) probably as an effect of Eh increase. Sulphides oxidation and secondary phases dissolution are known to involve the rise of aqueous concentrations (Meima and Comans, 1998; Lions et al., 2007). Achard (2013) evoked similar phenomena to explain the increase K, As, Mo, Ni and Zn, in pore water concentrations after EK treatment through probable dissolution and desorption. Cappuyns and Swennen (2005) also reported that elements as As can be released into pore waters through sediments oxidation. Such oxidation mechanism involves Fe-mono-sulphides and pyrite whose alteration leads to the release of associated trace metals. Furthermore, oxidation tends to decrease pH values, which also may affect trace elements' mobility (Satawathananont, Patrick, and Moore, 1991).

According to the technical report of HTS Bio Laboratory, the BioSurfactant implemented for this study precipitates in acidic pH ranges and may involve solid formations in presence of metal salts (Mg^{2+} and Ca^{2+} based salts). Here the treatment induced foamy precipitations in the anodic and cathodic compartments (Cf. appendix a) indicating the probable occurrence of such mechanisms. As a result, the pH decreased from 7.54 to 5.64 in the anodic compartment and rose from 8.33 to 11.22 in the cathodic compartment (Figure 4a). These precipitations suggested Mg^{2+} and Ca^{2+} migrations from the sediment to the cathodic compartment where they plausibly accumulated. Therefore, the anionic forms of BS very likely helped metals electro-migrations under counter-ionic states towards the anodic pole. Such mechanisms could explain the high remediation observed for Ba^{2+} at the anodic side.

The lowering trend observed here for Zn, Cu, and Ni were also stressed out by [Mulligan \(2009\)](#) using similar anionic electrolytes (Saponin, and other BioSurfactants) on contaminated sediment. Batch washing steps included in the [Mulligan \(2009\)](#) study very likely drove the difference in magnitude between their data and the trends observed here with BS. Their highest removal for Zn (33 %) and Pb (24 %) were achieved with 30 g.l⁻¹ of saponin at pH 5. Similarly, their highest Cu removal (84 %) was achieved with 2 % rhamnolipids (pH 6.5). Here the BioSurfactant combined with the EK method was more effective at lower concentrations. 94.5 % of Zn was indeed, removed at 0.6 g.l⁻¹ of BS. The removal of Cu (82 %) was comparable to the rate measured by [Mulligan \(2009\)](#).

IV. Conclusion

In this research, the electrokinetic method enhanced with biosurfactant was investigated for the removal of 11 potentially toxic trace elements in waterways sediments. The main findings of this study can be recapitulated as below:

- The use of the biosurfactant in the EK treatment modified the physico-chemical parameters of sediment samples (pH, Eh and electric current) during and after treatment (leaching behaviour of metals and their total contents)
- The characterisations of the whole sediment for metals removal have shown contrasted results. The highest extraction rates were reached for Cd (77.5 %), Ba (71.2 %), Sb (40 %) and As (22.5 %), whereas the lowest ones were obtained for Cr (11.2 %), Mo (7.7 %) and Pb (6.9 %).
- The leaching behaviour of metals in treated sediments were influenced by the biosurfactant and reduced for the most trace elements: As (81.3 %); Ba (80 %); Cr (97.3 %); Cu (82 %); Zn (94.5 %); Mo (13.8 %); Ni (62.7 %); Se (66.8 %) and Sb (9.3 %).
- Overall, BS tended to depollute more efficiently, the section close to the anodic pole compared to other areas of the EK Cell, probably as a result of the formation of anionic micelles in this area of the experimental device.

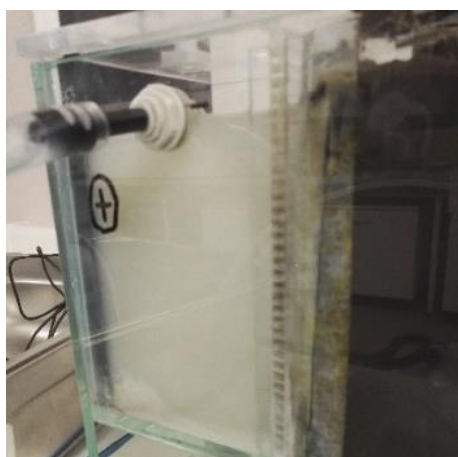
This new electrolyte was promising, and future investigations can be considered with Biosurfactant with a special focus on the mechanisms of inorganic elements solubilisation in presence of this type of foamy compound. The solid phase speciation should be investigated in order to elucidate the metals distribution through the sediment matrix. Another main

enhancement point would require the use of more acidic reagents in order to promote the dissolution mechanisms of minerals phases carrying the contamination.

Acknowledgements

The authors would like to thank the Arras Urban Community for collecting sediment samples in Scarpe waterways (Saint-Laurent Blangy, Hauts-de-France region) and Mr. Jean Philippe Dos Santos, for the BioSurfactant furniture. We are also grateful to Johana Caboche and Damien Bertrancourt (IMT Lille-Douai) for their analytical contributions.

Supplementary data



(a)



(b)

Appendix a White precipitate in the anode compartment (a); White precipitate in the cathode compartment with accumulation at the separation grid (b).

**CHAPTER 3 - COMPARISON OF TREATMENT EFFICIENCY
ON TWO SEDIMENTARY MATRICES AND ANALYSIS OF PH
EFFECT ON POLLUTANT MOBILITY.**

First part

In the **chapter 2**, we investigated how to improve the electrokinetic treatment using the anionic properties of the biosurfactant. It was concluded that this new electrolyte was promising in the removal of the targeted 11 trace elements, and future investigations can be envisaged. The study also showed that a particular attention should be brought to the solubilisation mechanisms of the inorganic pollutant to optimize the removing yields of this type of reagent.

Therefore, the use of more acidic reagents that would enable the dissolution of carrier phases appeared to be a promising axis of investigation. Implementing such reagents could promote the transfer of the metallic and metalloid contamination from the carrying minerals to the aqueous phase, and allow in such manner their evacuation from the sedimentary system thanks to the electromigration. In order to test this possibility, citric acid and Tween 20 were chosen as electrolytes on a bibliographical basis (*Cf: Chapter 1*). We experimented on longer durations, namely 28 days, since the background metrics (pH, Eh and electric current intensity) monitored in the previous study did not show clear stabilisations at the end of the experiments.

The resulting behaviour of contaminants will be examined with regards of contaminants dynamic in extreme pH conditions (pH2, pH12) performed under batch conditions. In this chapter, the efficacy of the treatment will be evaluated also in the overflow exiting the system from the cathodic and the anodic outlets. This will be undertaken, not only to precisely determine the yields of the acidic reagents under a new experimental setting, but also to characterize the preferential pathways of evacuation.

Efficiency of citric acid and Tween20 on the remediation electrokinetic processes of potentially toxic trace elements in waterway dredged sediments.

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Abstract

The behaviour of inorganic compounds was studied in waterways sediment matrix submitted to the electrokinetic treatment with acid reagents. In order to check the efficiency of chemical reagents to remove potentially toxic trace elements, the mobility of chemical elements and their total content in solid phase were measured after electrokinetic treatments. The use of citric acid and tween20 as electrolyte led to the acidification of pore solution with subsequent influence on redox conditions, electrical intensity and trace elements mobility. These parameters are also influenced by electrokinetic processes which provide specific physical-chemical environment near the electrodes. In addition, the electroosmotic flow and the electrical intensity showed an interesting correlation, concomitant to the electroosmotic migration of the elements in the anode and cathode overflows. Remediation efficiency based on the leaching test showed that As was removed by 51% to 79% for the experiment conducted with demineralised water; from 46% to 74% for the experiment with citric acid and up to 55% for the combination of citric acid and tween20. In the latter test, the mobility of As was increased from 91% to 243% in the sediment sections near the electrodes; and by 97% in the section near the anode when the acid was used alone. The observed enrichments reflect an increased mobility of a specific element. They are mainly explained by the partial or total dissolution of some mineralogical phases, which is confirmed by the high solubility of major elements after the electrokinetic treatment. The efficiency of the treatment is influenced by the extractants (nature of the electrolytes), by the electrokinetic conditions (imposed pH, flux, colloids...), but also by the characteristics of the sediment (pollutant fixing phases).

Keywords : Waterway sediment, electrokinetic remediation, potentially toxic trace elements, citric acid, tween20, leaching test

I. Introduction

Electrokinetic (EK) remediation is known to be effective in treating complex matrices such as sewage sludge, soils, sediments, clay soils etc, (Wang et al. 2007, Yang et al. 2014, Tang et al. 2021). Various studies have focused on problematic trace metals (Cameselle & Pena 2016, Soon-Oh et al. 2001), and organic pollution (Pazos et al. 2010) while other investigated the remediation of both types of pollution (Colacicco et al. 2010, Ammami et al. 2014) and using spiking approaches (Tingzong et al. 1997, Yuan & Chiang 2008). In most cases, the natural matrices were highly contaminated. Although interesting for understanding the phenomena, the doping methods do not always reflect real-life situation, mostly because the principle of ageing is neglected yet it is known to consolidates the pollutant-particles bonds. In other cases, few studies have focused on matrices with low overall contamination. However, it would be interesting to visualise the behaviour of trace elements subjected to EK phenomena in this type of matrix, because regulatory limits that must be respected for a whole range of inorganic and organic pollutants (Lecomte, 2018). If the matrix is weakly contaminated as a whole, it is not excluded that some chemical elements exceed the limits required for any future valorisation of the dredged material.

The efficiency of the EK technology depends on a large number of parameters (*e.g.* nature of the matrix, pH, redox, volume of the experimental cell, electrical intensity), and in particular the type of treatment solution used. The electrolysis of water, generated during the EK treatment, produces H^+ ions at the anode pole and OH^- at the cathode pole. The production of OH^- ions leads to the precipitation of metals near the cathode (Ammami, 2013). Therefore, acids have often been used in the cathode compartment, as they enhance solubilisation of trace elements and their electromigration to the cathode (Gidarakos & Giannis 2006, Ammami et al. 2015). In the literature, a large number of acids have already been used in EK experiments (Kornilovich et al. 2005, Rozas & Castellote, 2012, Iannelli et al. 2015, Ayyanar & Thatikonda, 2020). The aim here was to undertake a treatment with a low environmental impact, using natural and/or biodegradable reagents. Deionised water (DW) was used as a reference for the experiments, while Citric Acid (CA) was used as an acidifying reagent.

Non-ionic surfactants are reportedly better at combining with metals than their anionic analogues (Ammami et al. 2013) and can be thus used to enhance EK treatment (Pazos et al. 2010, Song 2017). Although the feasibility of metal uptake on neutral surfactants is debated (due to the unfavourable character of neutral micelles to bind metal cations (Ammami et al,

2014)), the addition of a neutral surfactant in combination with an acidifying agent can be interesting with regard to the desorption mechanisms of the solid phase (Benamar et al. 2020). Indeed, the Tween20 (TW20) used in our experiments is mainly used with the aim of decreasing interfacial tensions and improving desorption processes. This would release the pollutants into the liquid phase and allow their removal from the system through the electromigration process.

Most of the studies have been carried out on a laboratory scale (Ribeiro & Mexia 1997, Ryu et al. 2011, Ribeiro et al. 2011, Song et al. 2014, Guedes et al. 2014, Song et al. 2016), with small volumes of polluted matrices, and few studies have developed this process on a larger scale (industrial pilot type) (Costarramone et al. 1998, Rosestolato et al. 2015, López-Vizcaíno et al. 2016, Mao et al. 2019). The work here concerns a sediment model on which no contaminant doping has been carried out: we wanted to stay as close as possible to complex natural matrices. The tests were conducted with cells wide enough (400 x 100 x 200 mm) to allow the treatment of large volumes of sediment.

Our work proposes an analysis of the EK remediation of river sediment, weakly contaminated by heavy metals. The effectiveness of this method was measured in the solid and liquid (leaching) phases of the sediment, but also in the effluents recovered during treatment. Daily monitoring of various parameters was carried out in order to verify the evolution of the latter. The aim of this paper is to assess the impact of pH on the mobilization of pollutants, both in the solid and leaching liquid phase of natural sediment, weakly contaminated, subjected to an EK treatment conducted in a medium-sized pollution control cell. Acidifying treatments have a direct impact on the sedimentary matrix: they degrade the carrier phases and thus contribute to the solubilisation of trace elements. To understand the results obtained with trace elements, the major elements (constitutive of the retention phases) were also analysed.

II. Materials and methods

II.1. Sediments origin

Sediments were collected with a mechanical shovel, from the Scarpe River, located in Saint-Laurent-Blangy (Haut-de France, France). They were stored in hermetic containers and kept at 5°C to reduce the self-degradation actions of trace element and Organic Matter (OM) (Song et al. 2014). Sediment samples were carefully homogenized before performing the EK-test.

II.2. Experimental ElectroKinetic system

Three EK tests were conducting under a 14 V current, injected continuously during 28 days. For the first experiment, Deionised Water (DW) was used as the anolyte and catholyte (EXP.A). To enhance EK effects (*Cf. Chapter 1 and ARTICLE 2 conclusion*), Citric Acid (0.1 M) were used (EXP.B), and for the last one, 0.04 M of Tween20 combine with 0.1 M of Citric Acid was used (EXP.C). The injection speed of this reagents is $60 \text{ ml}\cdot\text{h}^{-1}$, injected by two pumps. A uniform sediment sample was placed in compartment (i) (presented in **Figure 1**), reagents are also inserted in compartment (ii). The saturation of the cell lasted 72 hours to allow sediments natural deposition and chemical balance establishment. Measurements of pH, redox, and electrical intensity were performed daily in the cell, by means of probe-guides as displayed in **Figure 1**. The ElectroOsmotic Flows (EOF) at the anode and cathode were calculated by the difference between the inlet and outlet flows at the cell outlet (**Figure 1**) and the effluents were collected for chemical analysis. In a previous study ([Betremieux and Mamindy-Pajany, 2021](#)), it was suggested that the copper wire used for current measurements had corroded and enriched the solid phase. To overcome this problem, the copper wire was replaced by a circular graphite rod.

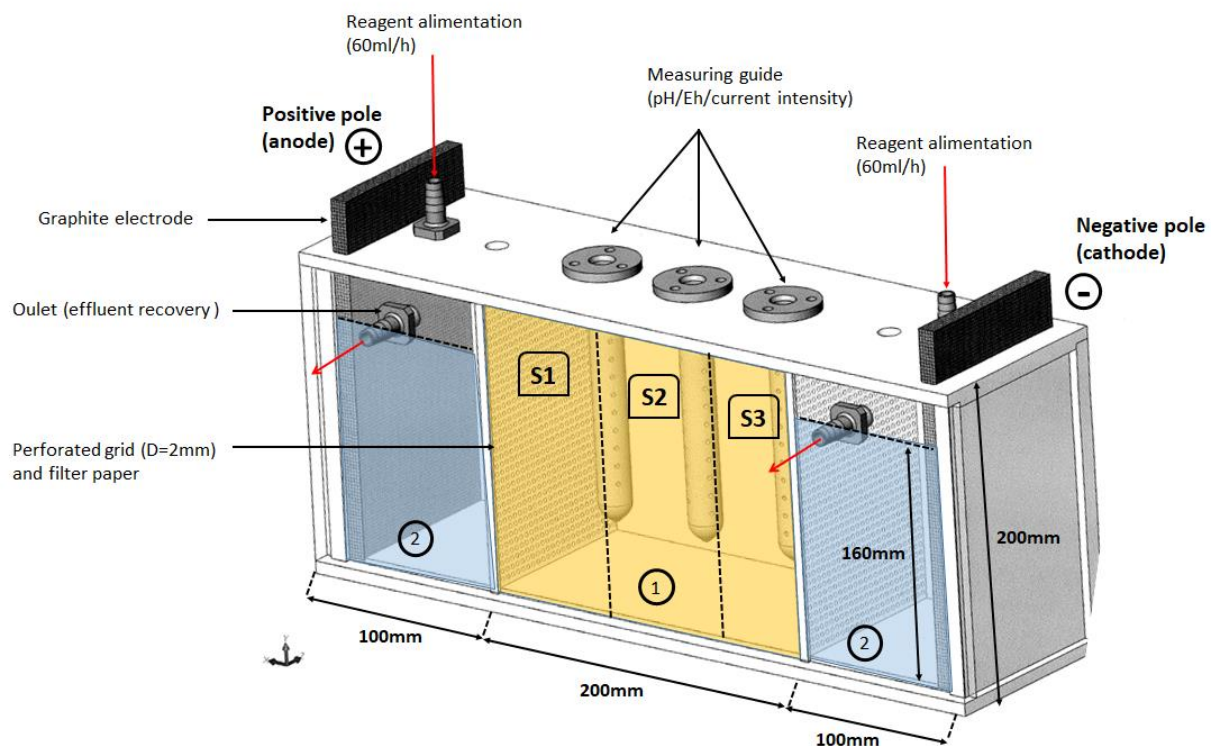


Figure 1 Schematic illustration of the EK-Cell. (1) Sediment's compartment; (2) Electrolytic solutions compartments. Sections S1, S2 and S3 correspond to the cross sections for zoned monitoring ([Modified from Betremieux & Mamindy-Pajany \(2021\)](#)).

Redox and pH were also measured in the anode and cathode compartments to monitor their evolution as a consequence of water electrolysis. Three values of each parameter were measured morning and evening in the cell, throughout the duration of the treatment (28 days). At the end of the experience, the sediment sample was equally divided into 3 sections from anode to cathode (from S1 to S3). Sediment samples were dried at 40 °C for heavy metals quantifications. The removal efficiency of 11 frequent trace contaminants (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn) was calculated as following:

$$\%R = \frac{C_i - C_f}{C_i} \times 100\% \quad \text{Eq (1)}$$

With:

%R : The removal, expressing the depollution of a given trace element;

C_i : The initial concentration of a given trace element;

C_f : Its final concentration (after EK treatment);

II.3. Analytical conditions

The sediment samples were prepared before the standardised tests of Water content assessment (NF EN 14346), pH and Eh measurement (ISO 10390), fire loss assessment (NF EN 12879), leaching (NF EN 12457-2) and solid phase analysis (NF ISO 12914) as detailed [Betremieux & Mamindy-Pajany \(2021\)](#).

A leaching with pH control was performed in this work adapted to the standard NF EN 14997. The sediment was dried at 40 °C, then sieved to 1 mm. 15 g of sample was introduced into 250 ml bottles, the tests were carried out in triplicate. Solutions of nitric acid (2 M) and sodium hydroxide (1 M) were introduced into the flasks to obtain the targeted pH values (pH = 2 and 12). pH measurements were performed at five different timestamps (*t*₀, *t*_{0+2h}, *t*_{0+4h}, *t*_{0+44h} and *t*_{0+48h}) in the eluate before filtration (0.45 µm) at *t*_{0+48h}. The eluate is then analysed by ICP-OES.

II.4. Raw sediments' physico-chemical properties

The sediment used in this work is the same as in [Betremieux & Mamindy-Pajany \(2021\)](#). For a comprehensive description, see [Betremieux & Mamindy-Pajany \(2021\)](#) (ARTICLE 2). Table 1 summarises the chemical characteristics of the sediments tested.

	Trace elements (mg.kg ⁻¹)		Major elements (mg.kg ⁻¹)	
	Dissolved concentrations after leaching test *	Total concentrations in sediment **	Dissolved concentrations after leaching test *	Total concentrations in sediment **
As	0.19 ±0.01	6.78 ±0.27	Al	2.18 ±0.16
Ba	1.21 ±0.01	406.31±1.40	Ca	635.08 ±4.84
Cd	0.01 ±0.01	0.67 ±0.05	Fe	3.73 ±0.12
Cr	0.07 ±0.01	44.17 ±0.80	K	97.33 ±0.72
Cu	0.60 ±0.01	41.75 ±0.69	Mg	31.35 ±0.24
Mo	0.24 ±0.01	1.30 ±0.01	Mn	1.30 ±0.01
Ni	0.22 ±0.01	19.33 ±0.23	Na	79.62 ±1.13
Pb	0.02 ±0.01	56.19 ±1.82	P	17.06 ±0.35
Sb	0.12 ±0.01	2.75 ±0.15	S	426.42 ±5.75
Se	0.14 ±0.02	1.85 ±0.01	Si	74.53 ±0.48
Zn	0.96 ±0.02	333.24 ±10.60		

Table 1 Trace and major elements (ICP-OES) in the raw sediment, after leaching test (NF EN 12457-2)* and after the solid phase analysis (NF ISO 12914)**, adapted from [Betremieux & Mamindy-Pajany \(2021\)](#).

To determine the chemical elements' concentration in solid phase, acid digestion were carried out via microwave Mars[®], CEM Corporation. Chemical assessments were performed using a 5110 model of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) coupled to an SPS4[®] autosampler (Agilent technologies[®]) after samples filtration (0.45 µm).

III. Results and discussion

III.1. Background conditions (pH, Eh, current intensity, EOF)

III.1.1. Variation of electric current and electroosmotic flow during electrokinetic treatment

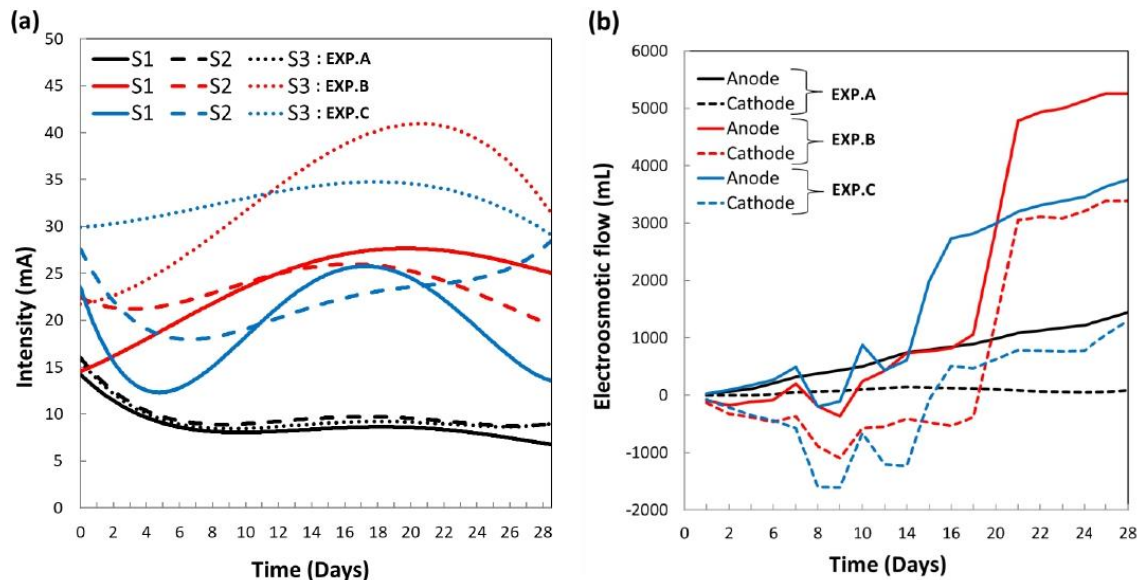


Figure 2 (a) Current intensity (mA) measured within the 3 sections (S1, S2 and S3) during EK-tests; (b) Fluctuations of electroosmotic flow during EK remediation, at the anodic and cathodic overflow.

The electric current evolution during EK treatment, in the three sections of the sediment sample (S1, S2 and S3) for the three experiments (EXP.A, EXP.B and EXP.C) were smoothed with a polynomial of degree 4 (**Figure 2a**).

With Deionised Water as electrolyte (EXP.A), the electric current intensity at the start of the EK-run was respectively 14.87, 17.25 and 16.72 mA for sections S1, S2 and S3. It then decreased to 7.55, 8.92 and 8.26mA after 10 days of treatment, before reaching a stable state for the rest of the treatment. Overall EXP.A showed similar trends in the three sections analysed, and much lower current values than the acid experiments. [Song et al. \(2016\)](#) also noted that the values acquired with DW were the lowest.

Indeed, the intensity with Citric Acid (CA) as electrolyte (EXP B) increased gradually in all three sections over the first 19 days, to values up to 32.43, 28.60 and 44.31mA in S1, S2 and S3 respectively. This probably reflected a desorption of metal ions, which may lead to the rise of ions conductivity in the porous medium ([Ayyanar and Thatikonda, 2020](#)). Once these

peak values are reached, values gradually decreased to 26, 19.6 and 32.2 mA at the end of the treatment (**Figure 2a**).

EXP.C, using CA and Tween20 (TW20) showed a homogeneous behaviour for section 2. Overall, the electric current intensity decreased to 11.74, 21.39 and 29.10 mA in S1, S2 and S3 respectively, during the first 7 days of treatment. Then for S1, the section close to the anode, the electric current increased until a peak at 34.39 mA on day 17, then decreased again until the end of the treatment. For S2, the central section, after day 7, the values simply increased gradually until the end of the treatment to 27 mA. For S3, the section near the cathode, the electric current increased to 40.18 mA at 15 days of treatment and then decreased. The evolution of the curves in S2 and S3, have two variations in their plot whereas S1 have three. Overall, TW20 added to citric acid (EXP.C) did not result in higher electrical intensity values than treatment with citric acid (EXP.B). This seems to reflect a lower mobility of the metal complexes, probably less mobile due to their large size.

The fluctuations in electrical current over time do not correlate with the results of other researchers ([Tang et al. 2018](#), [Ayyanar & Thatikonda 2020](#)). These authors find a significant increase in the first moments of the tests, and then, a gradual decrease in electrical intensity until the end of the EK treatments. [Ammami et al. \(2014\)](#) found for the DW, CA and CA+TW20 treatments, that the electrical intensity values were relatively constant throughout the tests. The lowest value of electric current was observed for DW and did not exceed 10 mA. For our DW treatment, the same trend was observed, but not for the CA treatment and CA+TW20. Matrices' heterogeneity may be the cause of these variations. Indeed, recent studies have shown that the remediation efficiency is particularly dependent on the specific interactions between the pollutants and sediment constituents ([Kirkelund et al. 2010](#), [Hahladakis et al. 2016](#), [Masi et al. 2017](#)). Limiting factors include the high heterogeneity of the sediment matrix and the strong non-linearity of the processes occurring during the application of the electric field ([Alshawabkeh, 2009](#)).

The electric current intensity as well as the electroosmotic flux (EOF) increase when citric acid was used as an enhancer (**Figure 2**). [Ammami et al. \(2015\)](#) noted that the overall EOF to the cathode increased particularly when TW20 was mixed with increasing concentrations of CA. Their observation has not been substantiated in our study, therefore we suppose that this phenomena is governed by other mechanisms. In our work, the EOF was calculated at the anode and cathode outlet (**Figure 2b**) of the cell in order to characterize its dynamic. The electroosmotic flow is the result of the electrochemical interaction of the electric field, soil particles and interstitial fluid. [Cameselle \(2015\)](#) explains this transport

mechanism very well in his paper. The citrate' presence in the pore fluid overall promoted EOF, and even more so on the anode side. The benefits of citrate in EOF were described by [Cameselle \(2015\)](#) who reported the improvement of EOF in an agricultural soil sample with 0.1M citric acid ([Cameselle and Pena, 2016](#)). Citric Acid is known to enrich interstitial solutions with citrate ions, and to increase the current intensity ([Amrate 2005, Ammami 2013](#)). In general, the EOF is from anode to cathode due to the negatively charged solid surface and the greater migration of H^+ than OH^- ([Mosavat et al. 2012](#)). However, high acidification can lead to a positive zeta potential (*Cf. Chapter 1, Eq 5* for more detail) , and reverse the direction ([Yoo et al. 2015](#)). [Ayyanar & Thatikonda \(2020\)](#) stipulate for instance, that a high concentration of H^+ ions in the sediment with an increase in zeta potential, favours a high EOF towards the cathode.

Overall, the flux calculated in all three experiments was greater at the anode compartment (**Figure 2b**). For EXP.A the direction of flow appeared conventional, i.e. from the anode to the cathode. For EXP.B and EXP.C the flux measured at the anode compartment increased progressively to reach high values at the end of the experiment: 5254 mL and 3758 mL respectively. Their flux measured at the cathode pole was initially negative for 14 days (reflecting a reversal of the flow). This decreasing trend has been seldom observed in the literature, yet [Masi \(2017\)](#) noted that in the nitric acid tests, the direction of the EOF reversed towards the anode after approximately 10 to 20 days of treatment. He attributed this reversal to the increased reduction in pH of the pore solution: the progressive acidification of the sediments would have increased the positive surface charge, causing the flow to reverse direction. The acidification of the pore water was indeed observed in our experiments to a certain extent, especially in the section the anode (S1). In this work, pH did not seem to play a significant role in reversing the direction of flow. Although this reversal appears to be specific to the reagent where citric acid is used, it is possible that OH^- ions, produced by the electrolysis of the water at the beginning of the tests, migrated from the cathode to the anode in the first moments of the tests. This migration affects the direction of the EOF and explains the decreasing results up to 14 days in the cathode compartment. OH^- ions electromigration was probably facilitated by the high electric current measured in the S3 (**Figure 2a**).

In the study of [Cameselle \(2015\)](#), the voltage gradient largely affected EOF sustainability and the use of organic acids, in particular citric acid, and induced a large and regular electroosmotic flux. One can correlate this results to ours (**Figure 2a**), since quasi concomitant peaks in electrical intensity and EOF were observed. For example, the section S1 of the experience using CA as electrolyte (EXP.B), displayed an increase in electrical

intensity from about 0 to 20 days, with a peak at day 20. The anodic EOF also has a significant augmentation at day 20. The EOF curves are asymptotic at the moment of the electrical intensity peak, for the experiments conducted with the acidifying reagent (EXP.B and EXP.C). The analysis of S1 in **Figure 2a** with the anode compartment in **Figure 2b** and the analysis of S3 (**Figure 2a**) with the cathode compartment (**Figure 2b**), showed a concomitant correlation in time. Indeed, when the peak intensity is reached, a significant increase in EOF occurs at the same time. However, despite the decrease in electrical intensity, the EOF continues to increase progressively until the end of the treatment. The EOF here is more closely related to the electrical intensity than to the variation of the pH.

III.1.2. Evolution of pH

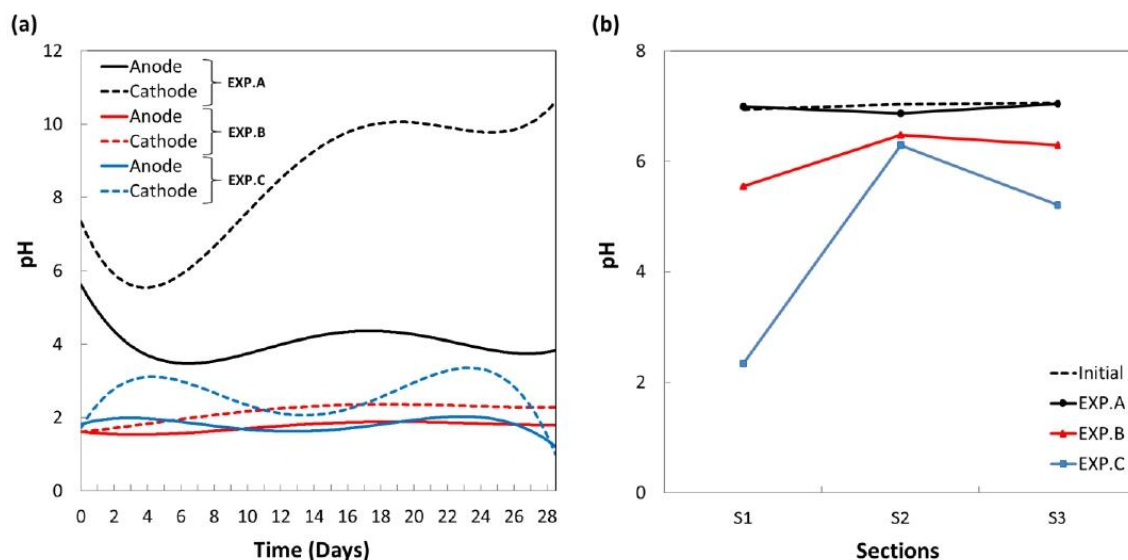


Figure 3 (a) pH evolution within the reagents chambers (anode and cathode) during the EK-tests; (b) evolution of pore water pH in the three sediment analysis sections, comparison with the initial state.

The pH evolution within reagents chambers were smoothed with a polynomial of degree 4 (**Figure 3a**). The pH changes shown in **Figure 3a** were measured in the electrolytic chambers, while those shown in **Figure 3b** illustrate the difference in pH status in the pore water at the beginning and end of the EK treatment (28 days).

The production and mobilization of H^+ and OH^- ions during EK-runs tend to changes the pH of the sediment. Due to the smaller ionic radius, H^+ ions move almost twice as fast as OH^- ions (Acar et al. 1995, Guedes et al. 2014, Ayyanar & Thatikonda 2020), which causes a

wider acidic front compared to the basic one. This acidic front favours the dissolution of heavy metals carried by sediment particles (Mosavat et al. 2012).

For EXP.A, the DW did not reduce the pH of the cathode pole. It increased from 7 to 10 due to the production of OH⁻ ions. The pH at the anode pole decreased rapidly during the first 3 days, from 7 to 3 due to the production of H⁺ ions, and then remained constant at about 4 until day 25, before decreasing slightly at the end of the treatment (Figure 3a).

When CA (EXP.B) was used as enhancer, the pH of the electrolytic chambers remained acidic, close to 2 throughout the test. The boost with TW20 (EXP.C), led to less constant profiles on the cathode side (Figure 3a). Nevertheless, the pH in the anode chamber remained very acidic and close to 2 as well.

The pH of the pore water, saturated with CA (EXP.B), varied from 7 to 5.55 for S1, from 7 to 6.47 for S2 and up to 6.29 for S3 (Figure 3b). pH decrease remains low in the pore water, probably due to the high buffering capacity and the presence of carbonates in quantity (Singh et al. 1998). When TW20 was added to the citric acid (EXP.C), pH at the anode decreased significantly. As previously observed (Figure 2a), the sediment conductivity increased in S1, resulting in an increased in electricity consumption after day 16. This high current consumption in the section near the anode led to a higher production of H⁺ ions, which strongly reduced the pore water pH in this section. This is consistent with observations made by Ayyanar & Thatikonda (2020), who obtained low current consumptions when the concentration of H⁺ ions in the sediment were low. Conversely, they obtained higher current consumptions when the H⁺ ion concentration was higher.

Ammami et al., (2014) reported that an acidic pH contributing to high values of electric current, which allows metal contaminants to remain in aqueous phase. This study also suggests the possibility of EOF inversion at low pH. This inversion inhibits cationic species electromigration and is therefore detrimental to the decontamination process. Ammami et al., (2014) discussed the necessity to maintain a pH low enough to keep metal contaminants dissolved but high enough to maintain a negative zeta potential in order to avoid EOF reversal. Their use of citric acid, being a weaker acid and having a buffering capacity, led to a stabilization of the pH from anode to cathode, between 3.0 and 3.5.

The sediment matrix used here did not allow a great pH reduction in the sediment column, as measured in (Ammami et al., 2014). In particular, the latest study (Betremieux and Mamindy-Pajany, 2021), underlined the strong buffering capacity of the sediment studied here, preventing the reduction of the pH in the pore water. The reagents modifications acidified the sediment matrix, and the combination with the TW20 surfactant (EXP.C)

allowed an important acidification in the section near the anode. The acidic reagents contained in both electrolyte chambers have modified the pH conditions into the column through S1 and S3, but obviously could not change S2 (**Figure 2b**).

III.1.3. Redox potential

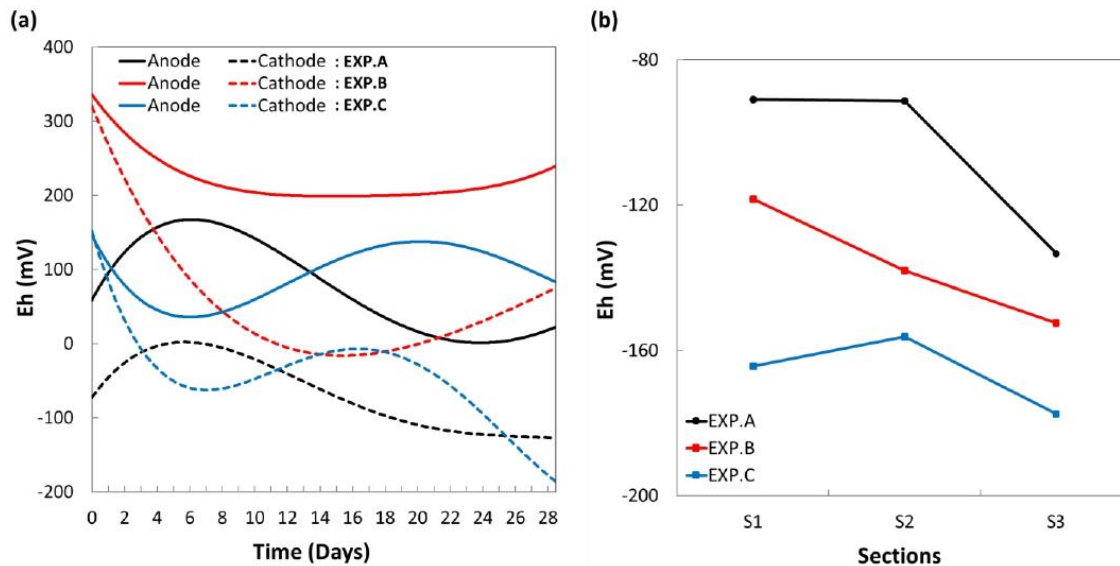


Figure 4 (a) Redox evolution at both anodic and cathodic poles during the EK treatments; (b) Average values within pore water during EK-tests into the three sections (S1, S2 and S3).

The Eh evolution within reagents chambers were also smoothed with a polynomial of degree 4 (**Figure 4a**).

Overall, for all three experiments (EXP.A, EXP.B and EXP.C), the redox measurements of the anodic chamber revealed oxidizing values in agreement with the oxidation reactions produced at the anode (water electrolysis) (Ammami, 2013). The same is true with the cathodic compartment, which for all three experiments showed a reducing environment (**Figure 4a**).

Overall, demineralised water (EXP.A) did not allow much reduction of the sediment porous medium compared to the acid experiments. The most reducing conditions were observed near the cathode (S3) for all three experiments, making this area more favourable for the appearance of reduced sulphide mineralogical phases (Singh et al. 1998). Indeed, a decrease in the redox potential favours the precipitation of minerals and in particular the formation of sulphides (Tack et al. 1997). The DW further reduced the side near the cathode, with a plateau for sections 1 and 2 (**Figure 4b**): -91 mV for S1 and S2 and -133 mV for S3.

CA alone (EXP.B) produced a more reducing environment the closer to the cathode compartment: -120 mV S1, -141 mV for S2 and -155 mV for S3 (**Figure 4b**).

In the sediment matrix, CA combined with TW20 (EXP.C) showed a much more reducing environment than the other EK tests, with a significant reduction in redox in the two sections close to electrodes S1 and S3: -165 and -177 mV respectively (**Figure 4b**).

[Chuan et al. \(1996\)](#) state that a low pH combined with a low redox potential increases desorption of inorganic elements from sediments and improves ElectroKinetic efficiencies.

III.2. Effect of electrokinetics treatment on trace elements

III.2.1. Trace elements evolution in the solid phase

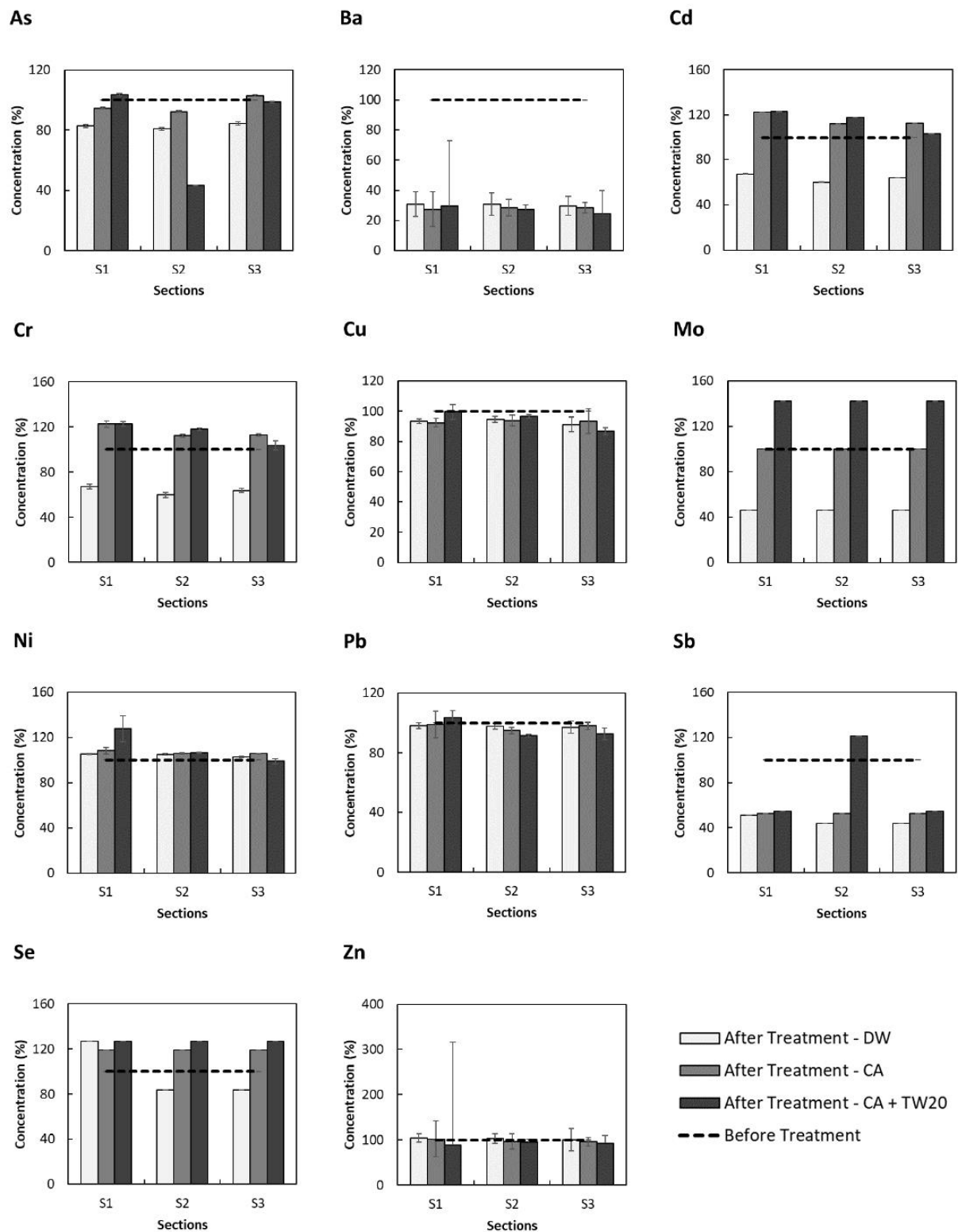


Figure 5 Evolution of solid phase concentrations (%) of trace elements, measured in the three sections (S1, S2 and S3), after treatment with DW, CA and CA+TW20. Data are available in *Appendix A*.

The solid phase removal rates (%R), calculated via Equation 1, are presented graphically in **Figure 5** as a function of sediment cross-sections. The trace elements studied are: As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn.

As in our previous work [Betremieux & Mamindy-Pajany, \(2021\)](#), Zn showed low removal in the EK-run conducted with DW as electrolyte (EXP A). The removals' percent (%R) for Cd, Sb and Mo were 40, 56 and 54% respectively. Ba showed the best removal performance, attaining a value of 70% close to the negative pole of the EK device (S3). These efficiencies were probably favoured by the background reducing conditions, whose magnitudes were favourable to aqueous Ba ([Cappuyns, 2018](#)). Overall, the trends observed for the experiment conducted at the DW are the same as those observed in [Betremieux & Mamindy-Pajany, \(2021\)](#).

For the experiments with citric acid (EXP.B) and TW20/Citric acid (EXP.C); Cd, Cu, Ni and Se showed enrichments across the 3 sedimentary sections. Note that Mo enrichment occurred in EXP.C only. Other punctual enrichments also occurred in EXP.A and B, probably as a result of spatial evolution of Eh and pH as a function of distance from the polar ends (**Figures 3 and 4**). Precipitation/complexation phenomena of free forms were very likely involved in the enrichments observed after treatment ([Isaure, 2012](#)).

III.2.2. Trace elements evolution in the liquid phase (leaching test)

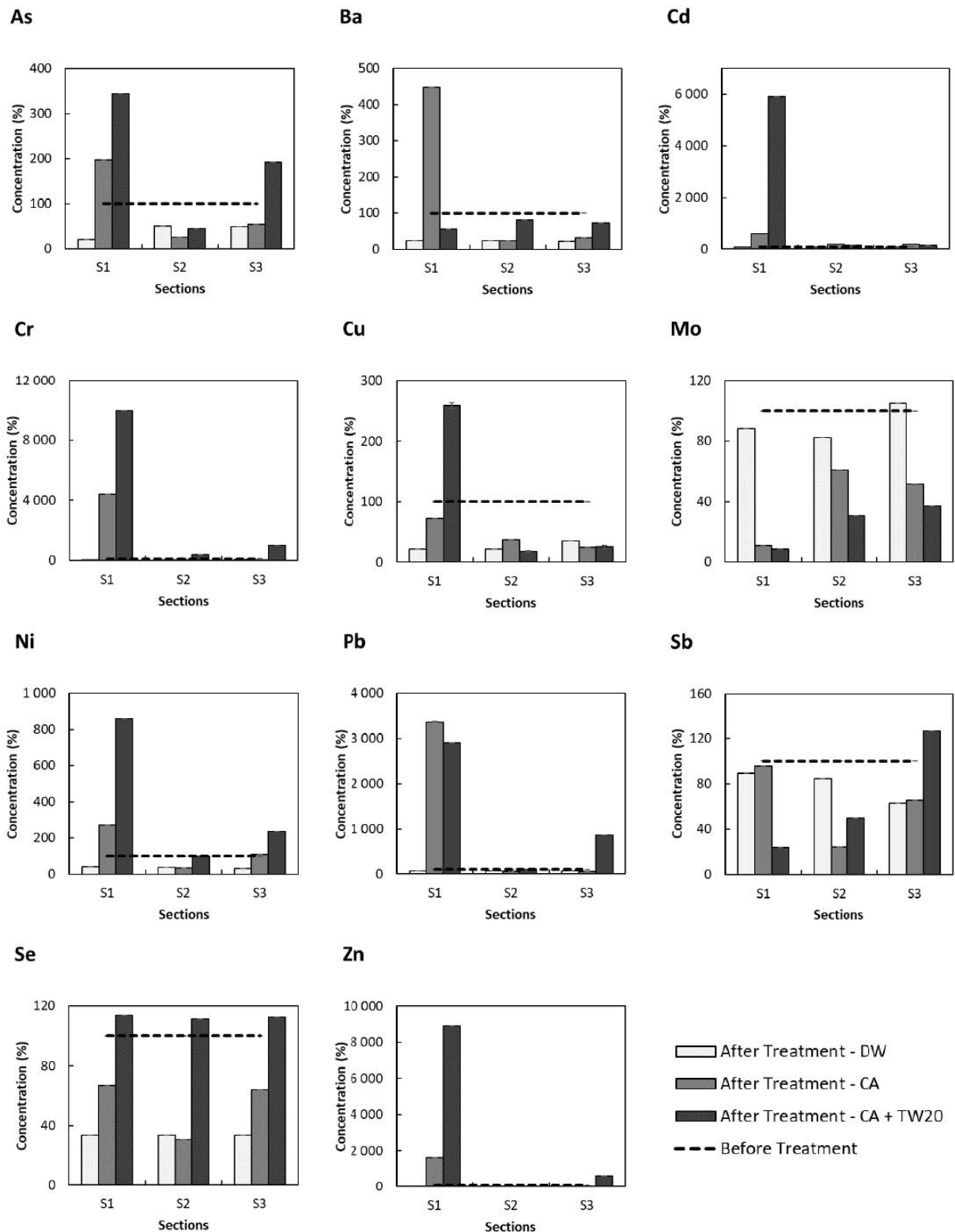


Figure 6 Evolution of leached trace elements concentrations (%), measured in the three sections (S1, S2 and S3), after treatment with DW, CA and CA+TW20. Data are available in *Appendix B*.

The studied trace elements and removal rate (%R) from the liquid phase (leaching), calculated via **Eq 1**, are graphically presented in **Figure 6** as a function of three sediments sections (S1, S2 and S3).

The deionised water (EXP.A) showed better trace elements remediation in the sections near to the electrolyte compartments (S1 and S3) compared to the central section (S2). Despite neutral pH conditions, relatively high remediation percentage were observed, with the following hierarchy (based on the average of the three sections): Zn>Ba>Cu>Cr>Se>Ni>As>Pb>Sb>Cd>Mo. The high %R measured in the leaching approach (**Figure 6**) indicates efficient removal for trace metals such as Zn (95 %), Ba (78 %), Cu (78 %) and Cr (93 %).

The use of citric acid in EXP.B improves the rate of depollution in the liquid phase, by decreasing the pH of the bottom and thus favouring the solubilisation mechanisms. The elements that were best remediated (compared to DW test) were Mo, Pb and Sb, with a remediation rate (%R) of 89 % for Mo (in S1); 40 % for Pb (in S2 and S3); and 76 % for Sb (in S2). Some enrichments has been observed for this experiment, especially in S1 (near the anode). Nevertheless, even though enrichments occurred, the other sections showed interesting %R. For instance, As, with significant enrichment in S1 (**Figure 6**), shown remediation rates (%R) of 74 % in S2 and 46 % in S3. This is also true for Zn, which shown enrichments in S1, but a remediation of 96 % and 69 % in S2 and S3 respectively.

For EXP.C (CA and TW20), Mo and Ba were mobilized in all 3 sections, with stronger remediation in the section near the anode (91 %, 69 % and 63 % of Mo were remediated in S1, S2 and S3 respectively; 44 %, 19 % and 28 % of Ba were remediated in S1, S2 and S3 respectively). Overall, S2 is the section with the highest removal rates. For instance, S2 has a remediation rate of 56 % for As, whereas both S1 and S3 became richer. It is also the case for Zn: S2 has a remediation rate of 28 %. Like EXP.B, enrichments are observed in EXP.C. These enrichments are probably due to the use of citric acid, which increased the mobility of heavy metals. [Yoo et al. \(2015\)](#) found an accumulation of trace elements in the anode section in the presence of citrate. [Song, \(2017\)](#) concluded that EK treatments of sediments using citric acid, which favours an increase in the current intensity value, can improve EOF flux and ions migration, but also cause a higher accumulation of some trace elements. This is consistent with what is observed in our experiments.

The citrate in citric acid mobilised the metals by forming negative complexes which were able to migrate from the cathode to the anode, thus leading to the significant enrichments measured in S1 (**Figure 6**); This observation is supported by [Ammami \(2013\)](#).

Migration of citrate complexes and electromigration of metal cations should normally be opposite to each other and lead to an accumulation of metals in the centre of the soil sample (Cameselle and Pena, 2016). In our experimentations, the accumulation is mainly concentrated in the section near the anode (S1) and to a lesser extent in the section 3 near the cathode (Figure 6).

For instance, when Zn^{2+} combined with citrate dissolves in water, four complexes can be formed, as shown by the equations in the Cameselle & Pena (2016): the relative abundance of Zn^{2+} and neoformed complexes depends on the pH of the. Zn^{2+} is the most abundant state at very acidic pH 1-2, which is noticed for EXP.C in the acidic S1 (pH=2) (Figure 6). Cameselle & Pena (2016) also suggest that a positive complex $[ZnH_2L]^+$ appears at $pH < 3$; and a neutral complex $[ZnHL]$ appears in the range of $pH = 3-4,5$. Then, at $pH > 4,5$, Zn complexes and forms a negatively charged species $[ZnL]^-$.

According to the species distribution suggested by Cameselle & Pena (2016) and because S1 from EXP.C is confronted with a very acidic pH of 2, Zn would be under divalent cation state or a positive citrate complex, which are both suited for electromigration towards the cathode. When the pH is above pH 4.5, as it was the case for S2 and S3 in EXP.C, Zn was expected/observed to form a negatively charged complex which can migrate toward the anode. These opposing Zn flows can possibly meet in S1.

$[ZnL]^-$ complexes possibly formed in S2 and S3 cannot migrate in areas where the pH is below 4. Such pH magnitudes constraint the element to adopt Zn^{2+} or $[ZnH_2L]^+$ states and to favour a migration toward more alkaline conditions. Similarly, the cationic species formed in S1 are not predisposed to migrate further than the S1 section. Indeed, the high pH environment in S2 and S3 (Figure 3b) inhibit the cations progression. Thus, Zn tended to accumulate in the pore liquid of S1, where the pH was acidic. Furthermore, in the neutral pH range (S2), Zn would be in anionic form, which leads to its electromigration and concentration towards the anodic side (Benamar et al., 2020). As mentioned above, our results showed that the majority of heavy metals were recovered in the regions close to the electrodes after the CA+TW20 treatments (particularly in S1, the section close to the anode).

Zn was taken as an instance, because its overabundance implies risks for human health (e.g. stomach cramps, skin irritations, vomiting, respiratory disorders) and for the environment (e.g. negative influence on the activity of micro-organisms, acidification of soil). It is also the most abundant element in the matrix studied, however, the other elements cannot be ignored.

The numerical approach of [Yuan et al. \(2016\)](#) estimated the forms of Ni, Cu, Cd, Zn and Pb, during the EK treatment using Visual MINTEQ. The existing forms of trace elements condition their migration during the EK process. The simulation showed that most of the Cd, Zn and Pb remained as free ions at pH 3-5. However, when the pH increased to about 4.5, most of the Ni and Cu formed negatively charged citrate complexes, which were moved from the cathode to the anode by electromigration ([Yuan et al. 2016](#)). The analysis conducted by [Yuan et al. \(2016\)](#) joined that of [Cameselle & Pena \(2016\)](#). This can therefore explain the majority of our experimental results, which seemed to follow the same trend: Cu enriched S1 while S2 and S3 were remediated (82 % and 75 % respectively); Ni further enriched S1, as well as Pb and Cd. Only Ba and Mo were depolluted from the liquid phase efficiently and in all three sections (EXP.C).

Overall, the TW20/CA experiment (EXP.C) showed higher accumulations rates than in the other experiments, especially compared to the experiment with citric acid as electrolyte (EXP.B). These enrichments were undoubtedly helped by the emulsifying properties of surfactant which is known to decrease interfacial tension ([Alcántara, et al. 2008](#)) allowing the increase of trace elements concentration in the aqueous inter-pore phase. Furthermore, this process was probably aided by the reducing conditions (prevailing especially in S1 and S3) favourable to the solubilisation of trace elements (**Figure 4b**). The pH delta measured in the different sections did not ensure sufficient removal and metal mobilization was from evacuation through the electrolyte compartments and outlets. The pH value in the matrix must therefore be homogeneous in all sections, to ensure effective depollution.

III.2.3. Trace elements measured in the outlets (anode and cathode)

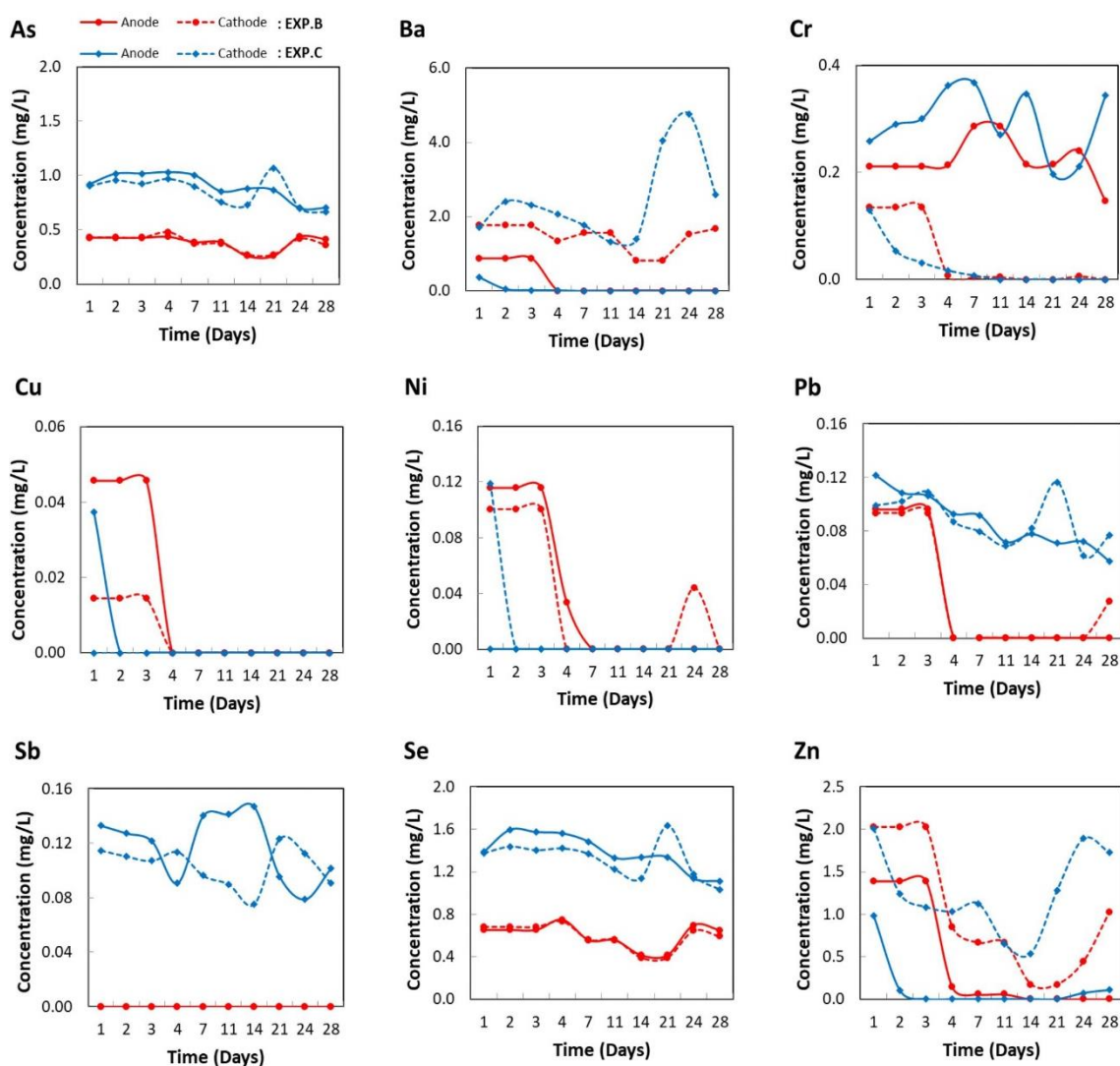


Figure 7 Concentration of metals (mg.L^{-1}) measured in outlet liquid effluent (anodic and cathodic compartment) for experiment with citric acid (EXP.B) and citric acid and tween20 (EXP.C).

Several samples were collected during the treatment process at both anodic and cathodic outlets. **Figure 7** shows the concentrations of trace elements obtained with EXP.B (Citric Acid) and those obtained with EXP.C (CA+TW20). These results illustrate the evacuation of trace elements over time, as well as their predominant migratory direction. Regarding EXP.B carried out with CA, different migratory trends appear depending to the trace elements' nature. Indeed, some as As and Se are evacuated in a homogeneous way in the two compartments (**Figure 7**). Zn, Pb, Ni, Ba were more strongly extracted at the end of the treatment, while Mo, Cd and Sb were not assayed in the exiting flux for the entire duration of the EK-run. Regarding Ba^{2+} , Pb^{2+} and Zn^{2+} , their evacuation was more pronounced at the

cathodic outlet and seemed thus to be in accordance with the general direction of electromigration. Moreover, concentration peaks were observed in cathodic outlet, occurring at approximately the same time as the electrical and EOF peaks measured during the treatment (**Figure 2a and 2b**). These concentration peaks concerned: As, Ba, Zn, Ni and Se. It should be noted that the highest intensity peaks presented at the **Figure 2a** are those measured in the section near the cathode (S3). The increase in electrical intensity, as well as the acceleration of the EOF, therefore seems to favour the extraction of these trace elements towards the cathode compartment.

Similar observation can be made with EXP.C, conducted with citric acid and TW20 as electrolytes (**Figure 7**). The peak extraction to the cathode chamber occurs on day 14. This corresponds exactly to the period of acceleration of the EOF and the electrical intensity peak measured in S3 (**Figure 2a and 2b**). The elements As, Ba, Pb, Sb, Se, Zn are concerned by these peaks. This synchronous evolution suggests that the electrical intensity and the EOF have a significant influence on the migration of the metallic elements. Zn and Ba were the elements with the most significant delta of concentrations (**Figure 7**). These two elements were majorly extracted at the cathodic side for both EXP.B and EXP.C. The negative citrate complexes ($M\text{-Citrate}^-$) formed, should have promoted the migration of these elements towards the anode. However, as seen previously, the pH measured in these areas is not conducive enough to promote migration the complexes. The extraction must have been carried out in the direction of the EOF, *i.e.* towards the cathode, which explains why significant quantities of elements in the cathode overflow compartment were present.

It is interesting to note that, during EXP.C, the trace elements' concentrations in overflows were much higher than those remaining in the raw and treated matrix leachates. In total, As was extracted in the anode overflow at 8.97 mg.kg^{-1} . In the liquid phase, 0.66 mg.kg^{-1} of As remained in S1, a value higher than what was initially present in the raw matrix liquid phase (0.19 mg.kg^{-1}).

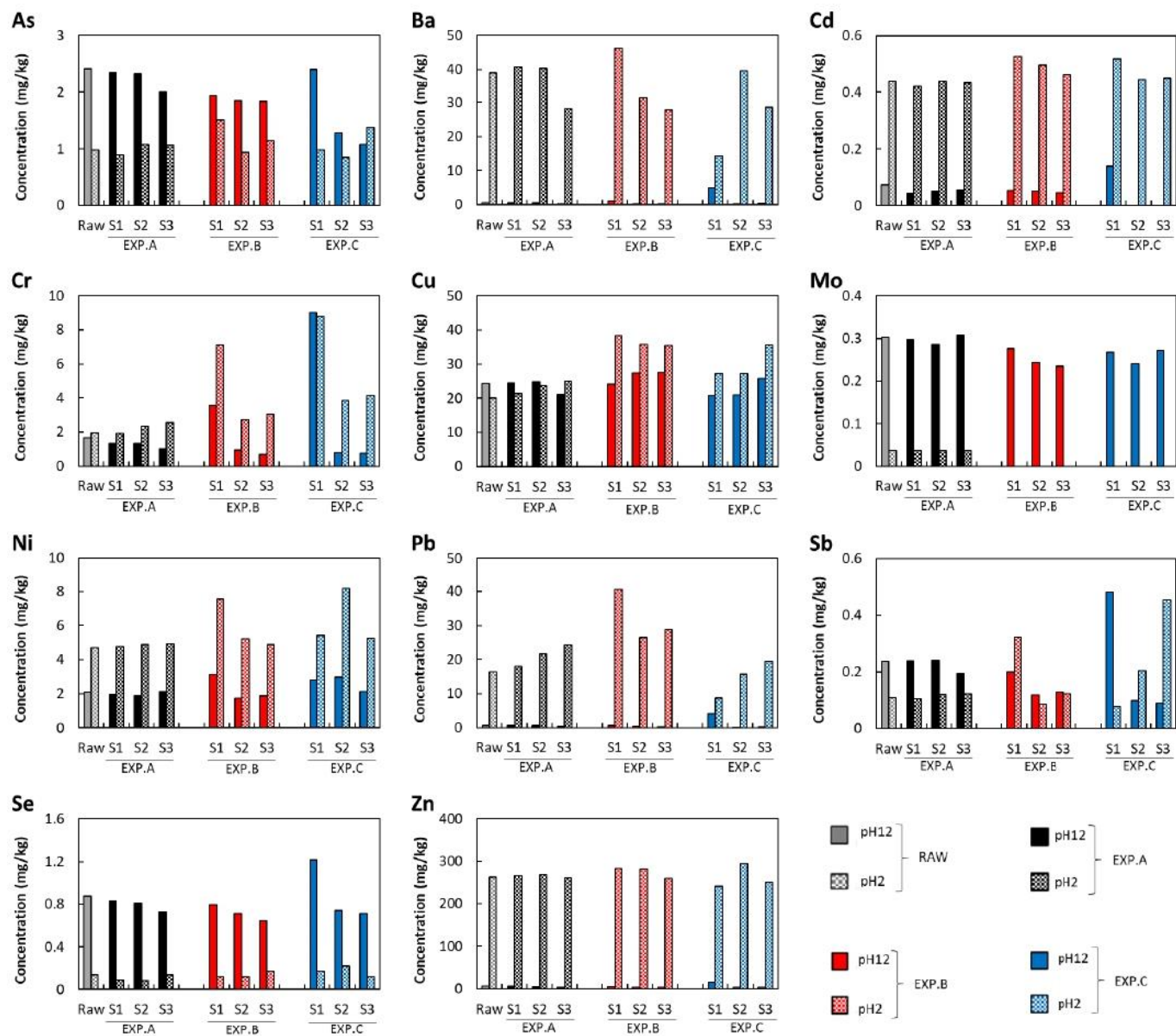
For EXP.A (DW), analyses of the outlets' effluents were carried out in the last week of treatment. No trace elements were found in the anode and cathode overflows, except for Ba, which was only present at the cathode. The EK treatment allows the extraction of metallic elements, towards the electrolytic chambers, in non-negligible quantities when acidifying reagents are used (**Figure 7**). We observe that citric acid contributes to the increase the mobility of the elements, and even more so when a surfactant is added (here TW20). The acidity of the medium, provided by citric acid, contributes to increasing the solubilisation of

elements, while the TW20 lowers the surface tension, and participates in the mobilisation of the elements, even when the pH is not acid.

The initially unavailable trace elements were probably made accessible in an aqueous medium, in particular by the reducing conditions of the bottom and pH conditions, which are suitable to the solubilisation of these elements. In aquatic systems, metals are available in many forms. They can be found in the dissolved or solid phase, adsorbed on the surface of particles, or include more deeply in the mineralogical structure of crystals (Priadi, 2010). This pollution potentially included in the crystals was made available by the EK treatment and therefore migrated into the liquid phase. This explains the enrichments found in the liquid phase for the EXP.B and EXP.C. However, the enrichments observed can be attributed to depollution; depollution that occurred at a deeper level and was due to the degradation of the solid matrix by the EK treatments. The different pH profiles found in the three sections did not allow an efficient migration and led to an enrichment. In order to verify the influence of pH on the migration of pollutants and on the degradation of the carrier phases, leaching tests with pH control were performed.

III.3. Assessment of EK treatment efficiency under acidic (pH2) and basic (pH12) conditions

(a)



(b)

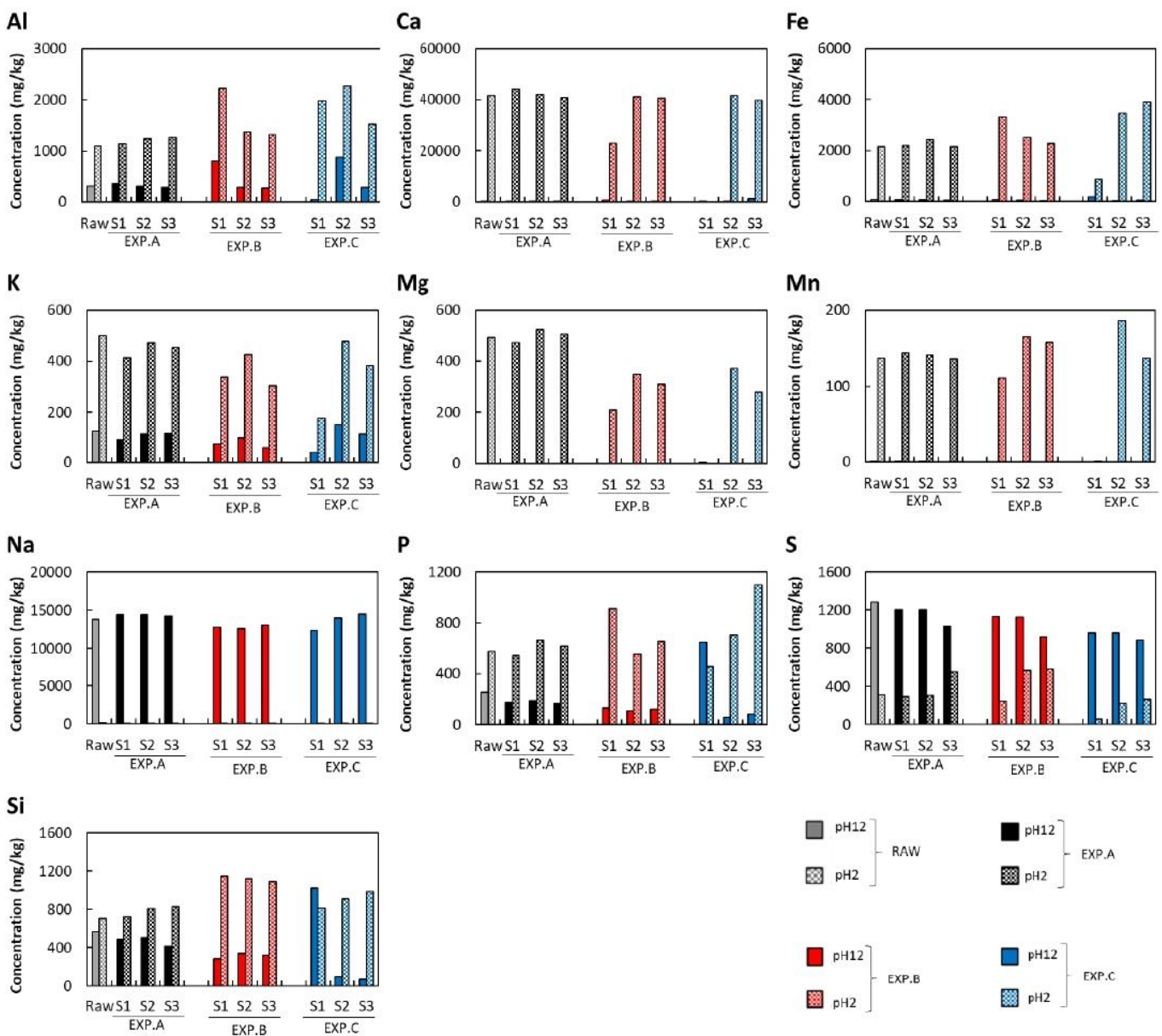


Figure 8 (a) Trace elements behaviour under two pH ranges (pH2 and pH12) for EXP.A, EXP.B and EXP.C treatments measured into S1, S2 and S3 sections; **(b)** Behaviour of leached major elements for pH2 and pH12, for the 3 EK tests and the 3 sections.

To further understand the effect of pH variation on the mobility of trace and major elements during the EK treatments, raw and EK-treated sediments were leached as a function pH under batch configuration. **Figure 8** shows the results of the leaching tests under acidic and basic pH control, presented in the "Analytical conditions" section. It shows the results of trace (**Figure 8a**) and major (**Figure 8b**) elements for the section near the anode (S1), for the 3 EK experiments (DW, CA and CA+TW20), as well as for the raw matrix (Complete data in **Appendix C and D**).

III.3.1. Elements behaviour under acidic conditions (pH 2)

III.3.1.a Trace elements

Overall, cationic elements were better mobilized at acidic pH compared to the anionic contaminants (**Figure 8a**). The hierarchy in the raw matrix and EXP.A, EXP.B and EXP.C was predominantly as follows: Zn>Ba>Cu>Pb>Ni>Cr>Cd (**Appendix C**). The patterns varied slightly in particular with the section and the reagent used.

The results (**Figure 8a** and **Appendix C**) showed that Ba, Cd, Cr, Cu, Ni, Pb, Zn were the most mobile elements at acid pH. Zn in particular is known to be the most mobile trace element ([Hlavackova, 2005](#)). It was found in very high quantities (average 268 mg.kg⁻¹ - **Appendix C**) in the eluates of the batches. Some studies show that Zn does not complex with organic matter but rather by ionic exchange ([Hlavackova, 2005](#)) which would explain its great mobility. When an acidifying reagent is used, the solid matrix was overall depleted in Zn (**Figure 5**), and to a greater extent in S1 of EXP.C with %R = 11.7. In the liquid phase without pH control, Zn was enriched in the sections close to the anode (EXP.B and EXP.C). In S1 of EXP.C, where the pH of this section was very acidic (pH = 2.34) (**Figure 3b**), this enrichment is even more significant. The mobility of zinc increases as the pH of the medium decreases, certainly causing enrichments of the aqueous medium.

In acidic environments, copper retention is not the result of precipitation mechanisms ([Hlavackova, 2005](#)). [Hlavackova \(2005\)](#) and studies therein consider that the retention mechanisms of copper are mainly complexation (on OM) and ion exchange (on clays). As previously shown, copper is mobilized in liquid phase for all the EK tests (**Figure 6**). Nevertheless, the EXP.C, conducted with citric acid and TW20, showed in the acid section (S1) an enrichment in Cu. The pH controlled leaching tests showed that Cu was present in dissolved form. Cu would therefore also be more mobile in an acidic environment as shown in EXP.B with an average of 36.50 mg.kg⁻¹ (**Appendix C**) for all three sections combined. TW20 added to the CA (EXP.C) did not significantly improve the mobility of Cu compared to EXP.B.

Pb has two oxidation states: the tetravalent state (a very strong oxidant, rather uncommon in the environment); and the divalent state ([Salvarredy Aranguren, 2008](#)). In an acidic environment, Pb is associated with sulphates PbSO₄ ([Salvarredy Aranguren, 2008](#)). As Pb sulphate is not very soluble, this explains the low concentration (8.79 mg.kg⁻¹ - **Appendix C**) of lead found in the acidic section (S1) of EXP.C. At neutral pH (**Figure 3b**) as Pb is no

longer associated with sulphates, EXP.B and EXP.A recovered greater amounts of Pb, and even more so in EXP.B where citrate complexes could be formed, improving the mobility of Pb. This is also consistent with what was observed in leaching tests performed without pH control (**Figure 6**), the Pb²⁺ cation appeared to migrate under the action of citrate complexes from sections 2 and 3 to the section near the anode, where it accumulated.

[Kinniburgh et al. \(1976\)](#) evaluated the selectivity sequence for 50 % retention of heavy metal cations as follows (pH indicated between parenthesis): Pb (3.1)>Cu (4.1)>Zn (5.4)>Ni (5.6)>Cd (5.8). Their observation suggests that a medium with a lower pH than those indicated in brackets would improve the desorption mechanisms. This is consistent with our results showing that these trace elements (Cd, Cu, Pb, Ni and Zn) were more rapidly released at pH2 (**Figure 8a**), with specific efficacy in S1, EXP.C where the pH was particularly acidic.

Consequently, pH, redox and treatments reagents all participate to the mobility of the chemical elements. The concentrations found in the leachates of the samples treated with EK are globally higher after treatment (**Appendix C**) and prove the benefits of the EK on the trace elements removal.

III.3.1.b Major elements

The major elements are constitutive elements of the phases carrying the pollution. Quartz (SiO₂); calcite (CaCO₃), albite (NaAlSi₃O₈) were the principal mineral phases highlighted through XRD analysis ([Betremieux and Mamindy-Pajany, 2021](#)). Studying the behaviour of the major elements constituting these phases under two extreme pH ranges (pH2 and pH12) could provide further insights on the fate of the investigated trace elements.

At pH=2, the most concentrated mobile elements were: Al, Ca, Fe, K, Mg, Mn, P and Si (**Figure 8b** and **Appendix D**). We establish the following classification according to the concentrations found in the eluates (**Appendix D**): Ca>Fe>Al>Si. Mn and Na were systematically at the end of the classification with the lowest concentrations. This classification varies according to the sections and the type of reagent used. The most notable variation was observed for S1 for the experiment conducted with CA and TW20 as electrolytes (of EXP.C).

According to [Tack et al. \(1996\)](#), the buffering capacity of carbonates is largely influenced by the particle-size distribution and reactive surface area of solid phase carbonates. Coatings and/or precipitated ions in calcitic materials also affect the dissolution kinetics of carbonates ([Tack et al. 1996](#)). At pH = 1, [Tack et al. \(1996\)](#) showed that the acidity of the system allowed a rapid reaction with the carbonates. The solubility of Ca thus increases

linearly with decreasing pH. This can be related to the high concentrations of Ca found in the pH = 2 range. Also, Fe, Al and Si ions were found in high concentrations at pH2, suggesting their aqueous availability under this magnitude of pH (**Appendix D**). As iron was dissolved in large quantities, it is plausible that cationic elements as Ba, Cu, Pb or Zn which have bond onto iron phases (e.g. iron oxide) were also release in the aqueous medium.

The concentrations of these majors' elements (Ca, Fe, Al and Si) were higher after the EK experiments (EXP.A, EXP.B and EXP.C) compared to the raw sediment, suggesting that the treatment had significantly dissolved the main mineral phases. For example, the raw sediment submitted to the leaching test at pH2 allowed the release of 1104 mg.kg⁻¹ of Al. The average values of the three sections in EXP.A, EXP.B and EXP.C were 1217, 1641 and 1923 mg.kg⁻¹ respectively (**Appendix D**), emphasizing the effect of the electrolytic reaction on the major elements release.

The instability of oxides under acidic conditions ([Mamindy Pajany et al. 2010](#)) and reducing backgrounds ([Ammami, 2013](#)) are a well-known phenomenon. Especially for iron and manganese oxides; and also for other minerals phases, such as clays or calcium carbonates. This can then be accompanied by re-solubilisation of the adsorbed trace metals, which can then adsorb onto other components of the sediment, such as organic matter, clay and sulphides ([Tack et al. 1996](#)), probably causing the enrichments in the solid phase (**Figure 5**).

III.3.2. Elements behaviour under basic conditions (pH 12)

III.3.2.a Evolution of trace elements

The extraction of a few elements as Cu was successful at pH12 (**Figure 8a**). As shown in **chapter 1**, it is acknowledged that high pH favours the dissolution of organic matter, implying a release of carried elements ([Hlavackova, 2005](#)). For high pH values (pH>8), Pb tends to precipitate in hydroxide forms. This acid-base behaviour may explain the low release of Pb observed in our experiment performed at pH12 (**Appendix C**).

In addition, it is known that Pb²⁺ complexes with carbonates when the pH range from 6 to 8 ([Salvarredy Aranguren, 2008](#)), thus reducing its concentration in the liquid phase. This is verified experimentally in our study, since the sections of experiments A and B concerned with this pH range (**Figure 3b**) showed a depletion of Pb (**Appendix B**) in the liquid phase.

Generally, it is accepted that the sorption of As onto solid phase components is limited in an acidic environment (pH < 5.5), since the majority of bearing phase become unstable in an acidic environment ([Mamindy Pajany et al., 2010](#)). Here, As dissolved at basic pH (**Figure**

8a). It could be that the solubility of chemical elements decreases as the pH increases, passes through a minimum, and then increases when the element is in anionic form (Deschamps et al. 2006). The As was probably in anionic or oxyanionic form. This is consistent with Salvarredy Aranguren (2008), which showed that arsenic was mainly present in aqueous media in this form. Overall, As, Mo, Se and in some cases Sb were extracted mainly at pH12, probably as a consequence of their presence under oxyanionic states. The results obtained with the controlled leaching and batch leaching tests seem consistent. Indeed, As was best extracted at pH12 (**Figure 8a**), and when the pH was more acidic, it tended to enrich the liquid phase (**Appendix B**). This was the case for sections S1 of EXP.B and C, and S3 of EXP.C. In contrast, for more neutral pH (**Figure 3a**), the liquid phase was reduced in this element (EXP.A).

III.3.2.b Dynamic of major elements

The major elements dissolved in significant quantities at pH12 were Na and S. Na was dissolved at an average concentration of 14377 mg.kg⁻¹ for EXP.A (all sections combined), 12810 mg.kg⁻¹ for EXP.B and 13617 mg.kg⁻¹ for EXP.C. The average concentrations for S were 1146, 1060 and 935 mg.kg⁻¹ for EXP.A, EXP.B and EXP.C respectively.

The pattern of dissolved elements at pH12 in the raw sediment was as follows: Na>S>Si>Al>Ca>P>K>Fe>Mn>Mg (**Appendix D**). As a trend, in all the experiments, it is the Na and S elements that are dissolved in large quantities in this pH range.

Tack et al. (1996) suggested that in reduced sediments, the retention of trace elements is controlled by sulphides. It is then possible that the retention mechanics here are controlled by the sulphides, due to the reducing environment (**Figure 4**). Because S was dissolved at pH12, it is plausible that Cu was associated with it as it was found in significant quantities in this pH range (**Appendix C and D**). However, while all the concentrations of Cu found in the solid phase increased, all the concentrations in the liquid phase decreased (%R of **Appendix A and B**). However, the reverse should have been observed because the sulphide has been dissolved, Cu should have enriched the liquid phase. Similarly, the Cu recovered in the overflows is not significant enough to explain its elimination by electroosmosis (**Figure 7**). This finding does not support that trace elements are mainly controlled by sulphides as suggested by Tack et al. (1996), and suggests that Copper is carried by another phase. If the cationic elements were associated with the iron oxides, in this pH range, the dissolution of these oxides did not appear to be effective due to the low proportion dissolved found in the controlled tests at pH12 (**Figure 8b, Appendix D**).

III.3.3. General observations

The trends observed in the liquid and solid phases can be linked to the results obtained after leaching at controlled pH. It is recognised that pH is the most important parameter in solubilisation and precipitation phenomena. Thus it is necessary to visualise the behaviour of trace elements and major elements under specific pH ranges in order to understand their behaviour during EK treatment.

Indeed, it was suggested that major elements could provide additional information on the fate of trace elements inside the solid matrix. The major elements are constitutive elements of the main phases carrying the pollution, and the results obtained could indicate the correct operation of the acidifying EK treatments. The aim was to acidify the matrix in order to solubilise the trace elements as well as possible.

This work highlighted a high mobility of trace elements in the solid and extractible phases (leaching). Precipitation/complexation phenomena may be at the origin of the Cd, Cu, Ni, Se and Mo accumulation, observed in the solid phase for EXP.B and EXP.C. The pH controlled leaching results showed that the EK treated matrices undergo a slight increase in Cd, Cu, Ni and Se concentrations when the pH = 2 (**Figure 8a**). This is particularly true when acid reagents were used (EXP.B and EXP.C).

A very acidic pH (pH2) of the medium could therefore initially solubilise the elements that are easily mobilised, then in a second time, the acidic pH combined with the effect of the EK could mobilise elements that are not initially available. This would increase the concentration of available trace elements, which could enhanced the mobility in the liquid phase (**Figure 6**). These elements could then complex with other mineral and/or organic phases, enriching the total content in the same time (**Figure 5**). These enrichments are particularly observed in the liquid phase and when the pH is very acidic (S1 of EXP.C), but also when the pH is more neutral and/or slightly acidic ($5.5 < \text{pH} < 7$) (**Figure 3b**). This is the case for EXP.A and B.

The examination of the major elements under acidic controlled pH (**Appendix D**) shows that the elements Ca, Fe, K, Mg, Mn, Na and S have strongly decreased for S1 of EXP.C (pH=2.34) (**Figure 3b**) suggesting a digestion of the constituent carrier phases of these elements. This could explain the high mobility observed in the liquid phase (**Figure 6 - Appendix B**). The trace elements were then dissolved, and the pH differentials of the pore water did not allow an efficient electromigration to the anodic and/or cathodic compartments, enriching the S1 acid section of this experiment. The highly reducing environment (**Figure 4b**) of EXP.C also contributed to the mobility of trace elements.

For EXP.B, the pH measured in the pore water was generally neutral (**Figure 3b**). However, enrichments were also found, mainly in S1 (**Figure 6 - Appendix B**). The pH controlled leaching tests showed that in the acidic environment the major elements Ca, K, Mg, Mn, Na and S decreased, which may indicate enrichment in this liquid phase section. However, as the pH was less acidic and the environment less reducing (**Figure 4b**) than in EXP.C, the enrichments observed were less important.

The fact that EXP.A showed no overall enrichments in the solid and liquid phase indicates that the citrate complexes formed in EXP.B and EXP.C played an important role in the outcome of the pollutants and that a pH from 5.55 to 2 contributes to the solubilisation of the elements.

IV. Conclusion

The use of acidifying reagents in these EK remediation treatments had the objective of degrading the carrier phases of the pollution, thus making the trace elements mobile and available. The main results of this study can be summarized as below:

- The EOF and electrical intensity showed an interesting correlation. The EOF accelerated significantly whenever a peak of electrical intensity was measured, causing electroosmotic migration of elements into the anode and cathode overflows. This is confirmed by the overflow analysis. Furthermore, this effect was favoured by the use of acidic electrolytes (CA and CA+TW20).
- The leaching behaviour of trace elements in the treated sediments showed that the use of citric acid tended to increase the mobility of elements. This mobility is higher in S1 (near the anode) of EXP.3, and therefore causes some enrichment in this section. The negative citrate complexes formed probably causes the migration of elements from sections 2 and 3 to the positive electrode (S1).
- The leaching tests under acidic pH control (pH2) showed that most cations were dissolved in this pH range. At basic pH (pH12), oxianions were mainly found in the eluates.

A study of the sequential extraction of trace elements should be carried out, in order to visualise the spatial distribution of the elements within the matrix, but also to visualise the influence of the EK treatments on the phases carrying the pollution.

	%R in solid phase								
	EXP.A			EXP.B			EXP.C		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	17.4%	19.3%	15.7%	5.3%	7.7%	-2.8%	-3.4%	56.5%	1.4%
Ba	69.2%	69.2%	70.4%	72.5%	71.5%	71.5%	70.4%	72.6%	75.6%
Cd	32.9%	40.2%	36.2%	-22.6%	-12.3%	-12.8%	-22.9%	-18.0%	-3.5%
Cr	6.6%	5.5%	8.8%	7.5%	6.1%	6.6%	0.5%	3.4%	13.2%
Cu	-28.0%	-27.0%	-24.3%	-20.5%	-15.0%	-26.1%	-26.8%	-16.6%	-20.5%
Mo	53.8%	53.8%	53.8%	0.0%	0.0%	0.0%	-42.3%	-42.3%	-42.3%
Ni	-5.4%	-5.0%	-2.8%	-8.3%	-6.1%	-5.7%	-27.8%	-6.4%	0.9%
Pb	2.1%	2.5%	3.0%	1.2%	5.2%	2.0%	-3.6%	8.6%	7.2%
Sb	49.1%	56.4%	56.4%	47.3%	47.3%	47.3%	45.5%	-21.3%	45.5%
Se	-27.0%	16.2%	16.2%	-18.9%	-18.9%	-18.9%	-27.0%	-27.0%	-27.0%
Zn	-4.0%	-2.7%	-0.2%	-2.1%	3.8%	4.1%	11.7%	4.5%	8.2%

Appendix A Removal (%R) in the solid phase. Negative values correspond to the enrichments, reflecting a retention of elements on the particles.

	%R in liquid phase								
	EXP.A			EXP.B			EXP.C		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	79.2%	49.7%	51.2%	-96.8%	74.0%	46.3%	-243.9%	55.5%	-91.2%
Ba	75.9%	76.8%	78.4%	-348.3%	76.3%	67.9%	43.8%	19.0%	28.1%
Cd	16.7%	16.7%	16.7%	-506.7%	-100.0%	-100.0%	-5806.7%	-50.0%	-50.0%
Cr	93.2%	93.2%	32.4%	-4318.4%	85.1%	48.5%	-9902.4%	-279.8%	-926.3%
Cu	78.4%	78.4%	65.0%	27.8%	62.9%	75.8%	-158.5%	82.2%	74.7%
Mo	11.7%	17.7%	-5.1%	89.0%	39.3%	48.7%	91.3%	69.3%	62.9%
Ni	60.4%	63.8%	68.6%	-171.0%	64.4%	-9.6%	-759.6%	0.6%	-136.4%
Pb	32.5%	32.5%	32.5%	-3267.0%	40.0%	40.0%	-2804.5%	-12.5%	-767.0%
Sb	10.7%	15.7%	37.2%	4.8%	75.6%	34.5%	76.4%	50.1%	-26.4%
Se	66.5%	66.5%	66.5%	33.3%	69.0%	35.8%	-13.5%	-11.1%	-12.5%
Zn	95.4%	92.7%	92.0%	-1519.0%	96.0%	69.1%	-8812.1%	28.3%	-509.1%

Appendix B Removal (%R) in the liquid phase. Negative values correspond to the enrichments, reflecting increased mobility.

	(mg/kg)		EXP.A						EXP.B						EXP.C					
	Raw sediment	SD	S1	SD	S2	SD	S3	SD	S1	SD	S2	SD	S3	SD	S1	SD	S2	SD	S3	SD
pH 12	As	2.41 ± 0.03	2.35 ± 0.01	2.32 ± 0.02	2.00 ± 0.03	1.94 ± 0.04	1.85 ± 0.02	1.84 ± 0.01	2.40 ± 0.03	1.28 ± 0.01	1.08 ± 0.02									
	Ba	0.60 ± 0.01	0.51 ± 0.01	0.52 ± 0.04	0.13 ± 0.001	1.01 ± 0.003	0.15 ± 0.01	0.12 ± 0.001	4.93 ± 0.07	0.16 ± 0.001	0.43 ± 0.01									
	Cd	0.07 ± 0.001	0.04 ± 0.002	0.05 ± 0.001	0.05 ± 0.001	0.05 ± 0.005	0.05 ± 0.001	0.04 ± 0.01	0.14 ± 0.002	<0,01	<0,01									
	Cr	1.65 ± 0.02	1.33 ± 0.01	1.35 ± 0.01	1.00 ± 0.001	3.56 ± 0.10	0.94 ± 0.01	0.70 ± 0.01	9.01 ± 0.09	0.81 ± 0.01	0.75 ± 0.01									
	Cu	24.31 ± 0.11	24.54 ± 0.44	24.90 ± 0.17	21.10 ± 0.06	24.17 ± 0.49	27.42 ± 0.02	27.65 ± 0.04	20.85 ± 0.19	20.94 ± 0.17	25.83 ± 0.21									
	Mo	0.30 ± 0.02	0.30 ± 0.01	0.29 ± 0.01	0.31 ± 0.01	0.28 ± 0.002	0.24 ± 0.01	0.23 ± 0.003	0.27 ± 0.004	0.24 ± 0.01	0.27 ± 0.01									
	Ni	2.11 ± 0.03	1.93 ± 0.01	1.89 ± 0.01	2.14 ± 0.01	3.13 ± 0.10	1.73 ± 0.01	1.87 ± 0.01	2.79 ± 0.02	2.98 ± 0.01	2.12 ± 0.01									
	Pb	0.66 ± 0.18	0.66 ± 0.001	0.67 ± 0.02	0.51 ± 0.01	0.73 ± 0.04	0.43 ± 0.01	0.37 ± 0.01	4.07 ± 0.08	0.19 ± 0.02	0.30 ± 0.01									
	Sb	0.24 ± 0.01	0.24 ± 0.02	0.24 ± 0.003	0.20 ± 0.001	0.20 ± 0.01	0.12 ± 0.004	0.13 ± 0.01	0.48 ± 0.002	0.10 ± 0.01	0.09 ± 0.01									
	Se	0.87 ± 0.02	0.83 ± 0.02	0.81 ± 0.01	0.73 ± 0.01	0.79 ± 0.04	0.71 ± 0.01	0.65 ± 0.01	1.21 ± 0.003	0.74 ± 0.002	0.71 ± 0.01									
Zn	6.70 ± 0.14	6.15 ± 0.09	5.97 ± 0.17	4.49 ± 0.01	5.75 ± 0.29	4.08 ± 0.02	3.47 ± 0.01	15.24 ± 0.40	3.38 ± 0.07	3.54 ± 0.03										
pH 2	As	0.98 ± 0.06	0.89 ± 0.01	1.08 ± 0.01	1.07 ± 0.03	1.51 ± 0.01	0.94 ± 0.04	1.15 ± 0.03	0.99 ± 0.01	0.85 ± 0.06	1.38 ± 0.03									
	Ba	39.05 ± 0.77	40.69 ± 0.06	40.27 ± 0.10	28.27 ± 0.26	46.24 ± 0.21	31.32 ± 0.19	27.89 ± 0.20	14.28 ± 0.04	39.53 ± 0.62	28.69 ± 0.10									
	Cd	0.44 ± 0.01	0.42 ± 0.01	0.44 ± 0.005	0.43 ± 0.003	0.53 ± 0.001	0.50 ± 0.01	0.46 ± 0.01	0.52 ± 0.001	0.45 ± 0.004	0.45 ± 0.01									
	Cr	1.98 ± 0.30	1.92 ± 0.01	2.32 ± 0.02	2.56 ± 0.05	7.13 ± 0.02	2.75 ± 0.11	3.05 ± 0.09	8.80 ± 0.05	3.87 ± 0.05	4.15 ± 0.04									
	Cu	20.03 ± 2.67	21.26 ± 0.18	23.65 ± 0.29	24.96 ± 0.36	38.28 ± 0.08	35.77 ± 0.23	35.46 ± 0.82	27.29 ± 0.26	27.18 ± 0.12	35.59 ± 2.19									
	Mo	<0,04	<0,04	<0,04	<0,04	<0,08	<0,08	<0,08	<0,08	<0,08	<0,08									
	Ni	4.70 ± 0.07	4.76 ± 0.05	4.89 ± 0.004	4.92 ± 0.05	7.57 ± 0.04	5.22 ± 0.01	4.89 ± 0.07	5.43 ± 0.03	8.16 ± 0.02	5.23 ± 0.05									
	Pb	16.45 ± 5.22	18.04 ± 0.37	21.65 ± 0.09	24.21 ± 0.41	40.46 ± 2.44	26.41 ± 1.65	28.80 ± 0.23	8.79 ± 0.74	15.62 ± 0.71	19.58 ± 0.58									
	Sb	0.11 ± 0.02	0.10 ± 0.01	0.12 ± 0.01	0.12 ± 0.01	0.32 ± 0.02	0.09 ± 0.01	0.12 ± 0.01	0.08 ± 0.01	0.21 ± 0.01	0.45 ± 0.01									
	Se	0.14 ± 0.01	0.09 ± 0.01	0.09 ± 0.004	0.14 ± 0.02	0.12 ± 0.01	0.12 ± 0.01	0.17 ± 0.03	0.17 ± 0.01	0.22 ± 0.01	0.12 ± 0.01									
Zn	263.59 ± 9.60	265.84 ± 0.28	269.33 ± 0.35	261.34 ± 2.72	282.85 ± 0.64	282.47 ± 1.47	259.54 ± 1.88	240.59 ± 1.21	294.71 ± 3.18	250.99 ± 0.19										

Appendix C Concentration (mg.kg⁻¹) of trace elements founded in the eluate of the pH controlled leaching tests (pH2 and pH12). All three sections are analysed (S1, S2 and S3) for EXP.A, EXP.B and EXP.C. The concentrations obtained for the raw sediment are also reported.

		(mg/kg)		EXP.A					EXP.B					EXP.C						
Raw sediment		SD	S1	SD	S2	SD	S3	SD	S1	SD	S2	SD	S3	SD	S1	SD	S2	SD	S3	SD
pH 12	Al	± 0.98	307.31	± 169.29	359.09	± 146.42	310.53	± 132.17	805.12	± 12.98	280.51	± 0.09	269.75	± 0.06	52.30	± 0.32	877.67	± 0.77	283.60	± 1.24
	Ca	± 2.32	260.00	± 3.86	241.69	± 6.53	179.28	± 0.30	581.63	± 27.34	176.23	± 3.33	163.56	± 1.88	98.26	± 0.47	231.75	± 1.07	1,206.88	± 0.96
	Fe	± 0.31	86.52	± 0.80	70.46	± 5.08	71.91	± 0.47	83.12	± 2.96	52.84	± 0.08	34.98	± 0.20	170.28	± 6.07	26.32	± 0.33	53.48	± 0.19
	K	± 1.23	125.36	± 0.5	92.33	± 2.96	115.89	± 0.69	75.63	± 0.86	99.93	± 0.13	62.28	± 0.11	41.14	± 2.62	152.63	± 1.35	114.37	± 1.34
	Mg		<0,15	± 0.01	<0,15	± 0.01	<0,15	± 0.01	<0,18		<0,18		<0,18		5.41	± 0.01	<0,18		<0,18	
	Mn	± 0.01	1.11	± 0.03	0.64	± 0.06	0.59	± 0.01	<0,064		<0,036		<0,036		<0,036		<0,036		<0,036	
	Na	± 90.95	13,845.49	± 33.57	14,441.20	± 82.01	14,425.55	± 141.55	12,747.60	± 115.45	12,651.01	± 15.18	13,031.14	± 308.27	12,370.13	± 117.79	14,003.52	± 250.67	14,476.08	± 55.20
	P	± 0.44	252.66	± 1.27	174.78	± 0.50	186.04	± 0.52	132.40	± 1.76	111.69	± 0.22	121.96	± 0.35	648.13	± 2.92	56.70	± 0.66	82.63	± 0.07
	S	± 8.08	1,283.05	± 20.66	1,203.95	± 9.11	1,204.01	± 21.24	1,129.97	± 9.57	1,129.52	± 11.50	921.14	± 0.39	960.87	± 7.00	961.85	± 1.18	882.13	± 4.20
Si	± 6.21	569.95	± 2.69	485.01	± 17.22	505.92	± 1.44	283.67	± 6.88	341.57	± 1.12	320.23	± 0.15	1,024.07	± 9.31	99.88	± 0.01	73.76	± 0.13	
pH 2	Al	± 106.67	1,104.42	± 10.97	1,142.54	± 13.86	1,267.92	± 23.53	2,227.09	± 17.61	1,372.69	± 6.98	1,322.10	± 2.23	1,973.97	± 4.18	2,273.55	± 36.16	1,522.02	± 8.10
	Ca	± 1,833.26	41,584.22	± 106.44	44,233.76	± 38.24	40,849.76	± 363.08	23,047.29	± 19.34	40,983.81	± 129.90	40,477.39	± 370.80	<0,9		41,669.87	± 252.90	39,779.03	± 11.25
	Fe	± 151.06	2,132.77	± 15.75	2,190.00	± 2.61	2,423.67	± 45.55	3,304.48	± 12.02	2,511.78	± 83.78	2,276.35	± 30.71	878.01	± 2.78	3,470.89	± 73.70	3,892.65	± 12.32
	K	± 10.28	499.83	± 1.12	411.86	± 0.47	454.55	± 1.23	336.78	± 0.20	426.07	± 3.05	303.91	± 1.95	177.10	± 0.79	478.45	± 4.00	382.38	± 2.63
	Mg	± 5.42	492.41	± 3.43	471.85	± 6.01	505.03	± 2.13	208.60	± 3.63	348.77	± 1.85	310.76	± 1.68	<0,18		372.95	± 8.17	279.20	± 0.50
	Mn	± 3.01	136.71	± 0.48	144.20	± 0.58	136.52	± 0.23	111.47	± 0.70	165.18	± 0.68	157.46	± 1.42	1.07	± 0.01	186.47	± 0.40	136.80	± 1.02
	Na	± 6.20	164.64	± 1.92	102.55	± 2.40	124.87	± 1.05	57.40	± 2.68	92.20	± 0.80	76.04	± 0.43	19.81	± 0.37	70.01	± 1.06	61.61	± 0.53
	P	± 71.85	575.64	± 7.14	544.79	± 9.74	662.42	± 0.93	913.47	± 4.27	555.51	± 30.26	651.74	± 14.81	454.36	± 1.82	706.74	± 12.98	1,095.96	± 3.26
	S	± 13.09	309.72	± 2.71	289.92	± 0.26	303.46	± 2.53	242.05	± 1.35	566.82	± 0.83	578.31	± 3.59	58.83	± 0.23	219.37	± 0.34	265.36	± 3.05
Si	± 45.24	709.12	± 8.00	730.12	± 20.94	810.89	± 28.92	1,147.76	± 12.24	1,122.07	± 11.94	1,095.84	± 5.69	816.48	± 3.57	910.43	± 18.07	986.68	± 1.83	

Appendix D Concentration (mg.kg⁻¹) of major elements founded in the eluate of the pH controlled leaching tests (pH2 and pH12) for EXP.A, EXP.B and EXP.C, and also for the raw sediment.

Second part

It was concluded in the previous part (**Article 3 in Chapter 3 “first part”**) that the use of citric acid combined with Tween 20 surfactant in the EK treatments further modified the physico-chemical parameters of the sediment samples during treatment. After treatment, the trace metals leaching results in the sediments showed that the use of citric acid had a tendency to significantly increase the mobility of chemical elements, especially in the section near the anode. We made the following hypothesis: the formation of negative citrate complexes, favoured by the pH conditions, causes the migration of trace elements towards the positive electrode, and the large differences in pH measured in the three analysis sections does not allow their removal.

Leaching tests with pH control have been carried out. These leaching tests, under acidic pH control (pH2), showed that most cations were dissolved in this pH range. At basic pH (pH12), oxianions were mainly found in the eluates. The major elements were also analysed in order to understand the influence of pH on the phases carrying the pollution and on the dissolution mechanisms. Furthermore, the intensity of the electric current showed significant peaks, correlating with the acceleration of the electroosmotic flow and the increase in the concentration of trace elements found in the anode and the cathode overflows. The analysis of the effluents recovered from the overflows showed the migration of metal cations in the theoretical direction, namely from the anode to the cathode. We have suggested that a careful study of the sequential extraction of trace elements should be conducted. This study would allow the verification of the hypotheses previously formulated with the pH-controlled leaching tests, and to conclude on the association of trace elements with the different mineral and/or organic fractions, carriers of the pollution.

The next article (**Article 4**) will therefore focus on the study of sequential extraction, carried out on a new sedimentary matrix, highly contaminated with Zinc. The analytical protocol will remain essentially the same, in order to visualise the variations that can occur with different matrices. Indeed, the heterogeneity of sedimentary matrices has often been pointed out as a factor blocking the adaptability of the EK method at large scale. After the EK treatments, the sequential extraction will be carried out with the protocol of the European Community Bureau of Reference (BCR), carried out for 4 pollution carrier fractions.

Electrokinetic treatments conducted with citric acid and Tween20 in order to observe the influence of the treatments on the sequential extraction of trace elements in waterways sediments, strongly contaminated in Zinc.

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Abstract

The sequential extraction of 11 trace elements (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn) before and after electrokinetic remediation is analysed in this work. The tests were conducted in the laboratory, on river sediments coming from Belgium, strongly contaminated with zinc (according to the French decree of 2014/12/12 on ISDI), in a pilot electrokinetic cell. The use of citric acid as electrolyte led to an effective acidification of the pore water, promoting the mobility of the chemical elements. Citric acid buffering maintained an acidic pH profile throughout the experiments, presumably causing partial digestion of the residual fraction, releasing pollution that was inaccessible in the initial state. From this release results a high mobility of chemical elements in the leached phase (aqueous), and an effective decrease of the pollution in the solid phase. Up to 56% removal is observed for As, 67.8% for Cd, 39.6% for Cr, 47.7% for Pb and 88.7% for Zn. Significant quantities of trace elements were found in the electrolytic chambers, despite a reversal of the electroosmotic flow. This suggests that EK treatment could be improved to favour an electroosmotic flow in the conventional direction, thus limiting the accumulations found in the liquid phase and improving removal rates.

Keywords: River sediment, electrokinetic, trace elements, remediation, sequential extraction, citric acid, Tween 20

I. Introduction

The sediment is a complex matrix with many possibilities of association with contaminants (Bonnet, 2000). The remobilization of the associated trace elements depends on their distribution within the mineralogical components (speciation) and is therefore strongly conditioned by the reactivity of these carrying mineral phase (Wernert, 2004). Speciation is controlled by physical, chemical or biological processes (Tack, Callewaert, and Verloo, 1996; Gäbler, 1997). In the aqueous fraction, contaminants may be present in dissolved or complexed form. Thereafter they may be associate with the solid phase by precipitation, complexation or adsorption on particles (Kribi, 2005). For the particulate fraction, resuspension-sedimentation processes can modify the chemical state of associated contaminants. Contaminants can thus return to the aqueous phase under the effect of physical (*i.e.* diffusion) or chemical (*i.e.* desorption) processes (Bonnet, 2000).

El Mufleh et al. (2010) suggested that to accurately determine the behaviour of trace elements, considering the solid phase as a whole is not sufficient. The characterization of elements distribution following mineralogical phases nature with adequate physico-chemical methods (Cornu and Clozel, 2000) is an important prerequisite to understand the dynamic of the contamination within the sedimentary system. Among the methodological options, sequential extractions are frequently used to study contaminants speciation in solid matrices. The protocol initially proposed by Tessier et al. (1979) is the most often implemented. It is frequently adjusted with different reagents following experimental settings (Flores-Rodriguez, Bussy, and Thevenot, 1994; Leleyter and Probst, 1999; Gómez Ariza et al., 2000; Van Herreweghe et al., 2003; Jamali et al., 2009; Ahmed et al., 2018).

The Community Bureau of Reference (BCR) has proposed a three-step operational scheme applicable to sediments and certified reference materials (El Mufleh et al. 2010). The steps allows to target different fractions carrying of the pollution: the first fraction, known as the "extractable fraction", corresponds to the trace elements weakly linked to clays, amorphous phases and carbonate fractions; the second fraction, called "reducible", comprises metal oxides; the third fraction, called "oxidizable", includes organic matter. The remaining fraction is called "residual fraction" and can also be analysed.

The aim of this paper is to study the carrier phases of trace elements in a river sediment subjected to an ElectroKinetic (EK) remediation methodology. A comparison of the

sequential extractions will be made from the results obtained on the raw matrix, and on the matrices treated by different EK remediation methods. The aim is to define the distribution of trace elements in the different solid phases of the material, and to visualize the influence of the EK treatment. The results of the sequential extractions will be complemented by leaching analyses and mineralized samples (acid digestion). The main physico-chemical parameters controlling the distribution of contaminants in the sediments are pH and redox potential (Tack, Callewaert, and Verloo, 1996; Bonnet, 2000; Kribi, 2005). They will therefore be studied, especially because the EK treatment is known to alter these parameters during the process. The Electroosmotic Flux (EOF) as well as the intensity of the electric current also influence the mobility of the trace elements, and therefore will be presented in this article as well.

II. Materials and methods

II.1. Sediment and standards used

The sediments were provided by the Belgian waterways, homogenized and stored at 5°C. The pH and redox potential values were measured according to the French standard NF ISO 10390. The fire loss assessment, which gives an indication of the level of organic matter present in the sediment, was measured according to NF EN 15169. Water content and electrical conductivity were measured according to NF EN 14346 and NF ISO 11265, respectively. These analytical methodologies were described in a previous work (Betremieux and Mamindy-Pajany, 2021).

II.2. Electrokinetic experiments

The ElectroKinetic set-up involved three compartments: two electrode reservoirs and a central compartment, filled with the sediment to be treated. Two graphite electrode plates were placed in anodic and cathodic compartments, which were separated from the sediment by perforated grids and filter papers. Two pumps were filling each electrode reservoir with aqueous solutions with a low flow-rate (60 mL.h⁻¹). **Figure 1** schematically reproduces this setting:

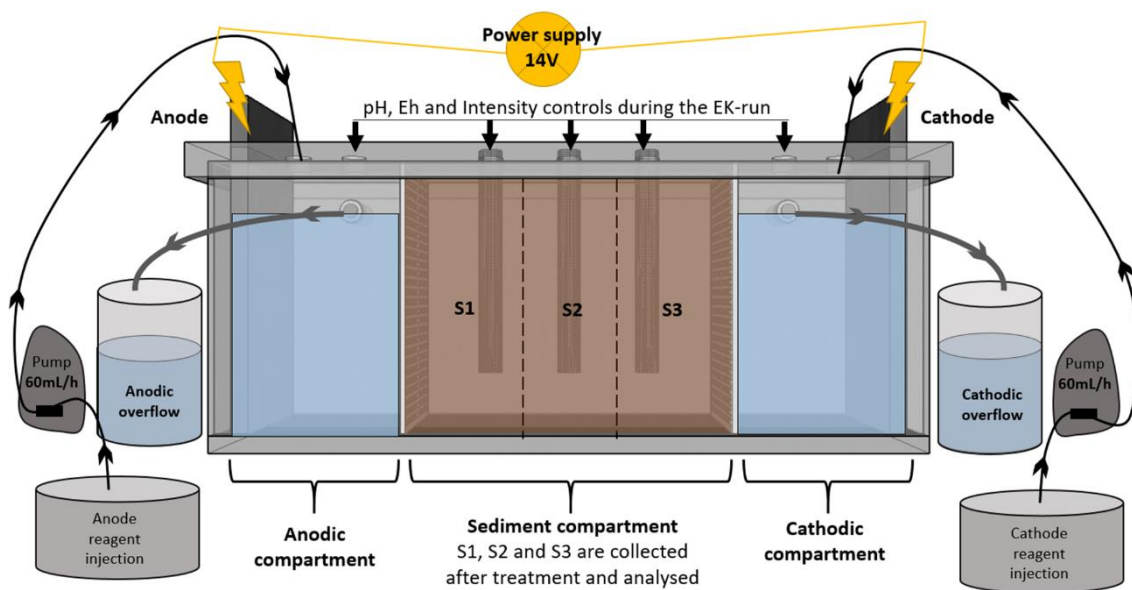


Figure 1 Schematic representation of the electrokinetic tests and the experimental cell installation

Three experiments were conducted in this study for 28 days: EXP.1 conducted with deionized water (DW), EXP.2 using citric acid (0.1 mol.L^{-1}) and EXP.3 conducted with citric acid and tween 20 (CA+TW20) in 0.1 mol.L^{-1} and 0.04 mol.L^{-1} respectively. These reagents were chosen on the basis of the literature (Ammami, 2013; Song, 2017; Tian, 2018), and have shown their benefits in the depollution of dredged sediments by ElectroKinetic (EK) method.

II.3. Sequential extraction

In order to evaluate metals' occurrence following the mineralogical components of the sediment, sequential extraction was performed using the BCR method, as described in El Mufleh et al. (2010), this method includes a 4th step. Sequential extraction was made in duplicate, with 1 g of dried sediment ($40 \text{ }^{\circ}\text{C}$) for each section: S1, S2 and S3 (Figure 1), before and after EK treatment (EXP.1, EXP.2 and EXP.3). The sequential extraction was conducted in 4 steps.

In the first step (exchangeable fraction (F1)), sediment sample was introduced into a 100 ml polypropylene tube with 40 ml of acetic acid CH_3COOH (0.11 mol.L^{-1}), shaken (90 rpm) for 16 h and centrifuged (15 min, 5000 rpm). The supernatants were then filtered ($0.45 \text{ }\mu\text{m}$) and acidified for ICP-OES (HNO_3) analyses.

In the second step (reducible fraction (F2)), the residue from step one was mixed with 40 ml (0.1 mol.L^{-1}) of hydroxylamine hydrochloride $\text{NH}_2\text{OH}\cdot\text{HCl}$ (adjusted at pH2 with

nitric acid), shaken for 16 h and centrifuged according to the procedure described in step one.

In step 3 (oxidisable fraction (F3)), the residues from step 2 were mixed in 10 ml of H₂O₂ (8.8 mol.L⁻¹) and shaken for 1 h at room temperature. A second volume of H₂O₂ (10 mL) was added at 85 °C in shaken water bath for 1 h. The content was evaporated to a small volume (2 ml) then, 50 ml of ammonium acetate C₂H₇NO₂ (1 mol.L⁻¹, adjusted to pH 2 with nitric acid) was added to the cool residue, and then shaken for 16 h and centrifuged.

In step 4 (residual fraction (F4)), the residue from previous step was digested with *aqua regia* which allows to do an assessment of the extraction. The quality of the analyses was controlled by analysis of a reference sediment BCR-701 (lake sediment), submitted to the same procedures. Blanks were also realized for each series, for the evaluation of As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn concentrations.

II.4. Batch leaching experiments

Sediments samples from the 3 sections (S1, S2 and S3, Cf. **Figure 1**), were dried (40 °C) before performing standardised leaching tests (French standard NF EN 12457-2). Batch leaching experiments were carried out in polyethylene tubes (250 ml) at liquid/solid ratio (L/S) of 10 L.kg⁻¹. For each experiment, 15 g of sieved (4 mm) and dried (40 °C) sediment sample was placed in deionised water (150 ml) for 24 h. Samples were shaken (90 rpm) in the mechanical shaker at room temperature (25 ± 2 °C). Supernatants were filtered (0.45 µm) and acidified (HNO₃) before the quantification of trace and major elements concentration. Chemical assessments were performed using a 5110 model of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) coupled to an SPS4 autosampler (Agilent technologies®).

II.5. Solid phase analysis

Solid phase analysis according to the standard NF ISO 12914, consists of an acid digestion. It was carried out via microwave (Mars®, CEM Corporation) by a successive introduction of 0.5 ml of ultra-pure water, 1ml of HNO₃ (> 68 % v:v) and 3ml of HCl (37 % v:v) on 0.250g of sieved (250 µm) and dried (40 °C) sediment samples for trace elements evaluation. Samples were collected in accordance with the NF ISO 12914 standard, completed up to 100 ml with ultra-pure water and filtered at 0.45 µm.

II.6. Leaching with pH control

A leaching with pH control adapted to the standard NF EN 14997 was performed in this work. The sediment was dried at 40 °C, then sieved to 1 mm. 15 g of sample was introduced into 250 mL tubes, and leached in triplicates. Solutions of nitric acid (2 mol.L⁻¹) and sodium hydroxide (1 mol.L⁻¹) were used to obtain the targeted pH values (pH = 2 and pH = 12). pH measurements were performed at t₀, t₀+2h, t₀+4h, t₀+44h and t₀+48h in the eluates before filtration (0.45 µm) and ICP-OES quantifications.

III. Results and discussion

III.1. Observation of the initial state of the sediment (Composition and trace elements)

OM is an important soil constituent for this high content of functional groups, primarily carboxyl COOH, renders OM capable of forming strong complexes with elements (Kumpiene, 2005). After analysis, our retrieved sediments contain a high organic matter (OM) concentration (23.38 %), therefore making it an interesting sample to study.

The water content of the raw sediment was 11.21% and the pH, redox and electrical conductivity are respectively: 6.51, 190.5 mV and 2225 µS.cm⁻¹.

In addition, chemical analysis of the material indicated very significant Zn contamination (**Table 1**), either after analysis of the mobile fraction (liquid phase) conducted by batch leaching tests or by pH control, or in the total fraction (solid phase). The methodology of these tests was presented previously in the sections "Batch leaching experiments", "Solid phase analysis" and "Leaching with pH control".

Examination of the solid phase shows a high concentration of Zn, Pb Ba, Cu and Cr (3253.2, 573.4, 412.4, 165.6 and 152 mg.kg⁻¹ respectively), while the elements Sb, Mo and Se are present in low concentrations (5.58, 3.30 and 1.45 mg.kg⁻¹ respectively). The mobility of the elements in the liquid phase was low for all the trace elements, with a lower concentration of 1 mg.kg⁻¹, except for Zn (32.14 mg.kg⁻¹) which is present in significant quantities. The examination of mobility with pH controlled reveals that the cationic elements have a higher mobility in an acidic pH environment (pH2). Conversely, a basic environment (pH12) improves the mobility of anions or oxyanions such as As, Mo and Se.

	Solid phase (mg/kg)	Leached phase (mg/kg)	Leaching test (pH12) (mg/kg)	Leaching test (pH2) (mg/kg)
As	37.2 ±0.40	0.04 ±0.01	14.86 ±0.03	3.86 ±0.88
Ba	412.4 ±7.34	0.39 ±0.02	-	5.70 ±0.04
Cd	72.8 ±1.17	0.94 ±0.01	0.39 ±0.02	74.90 ±0.55
Cr	152.0 ±3.90	0.01 ±0.001	0.64 ±0.01	28.45 ±2.04
Cu	165.6 ±2.73	0.26 ±0.01	23.15 ±0.51	110.39 ±0.72
Mo	3.3 ±0.01	0.44 ±0.01	1.32 ±0.01	0.03 ±0.01
Ni	90.0 ±1.67	0.89 ±0.01	1.45 ±0.01	40.55 ±0.04
Pb	573.4 ±12.82	0.07 ±0.01	0.49 ±0.02	260.62 ±9.76
Sb	5.58 ±0.23	0.03 ±0.01	0.17 ±0.01	0.30 ±0.07
Se	1.45 ±0.01	0.09 ±0.03	1.30 ±0.01	0.34 ±0.04
Zn	3,253.2 ±12.20	32.14 ±0.82	14.65 ±0.15	2,978.14 ±23.99

Table 1 Summary of physico-chemical characteristics of the tested sediment

III.2. Observation of the chemical elements' behavior to the electrokinetic elimination.

III.2.1. Removal in overflow

Samples were collected during the EK treatment process at the anode and cathode outlets. **Figure 2** and **Figure 3** show the trace elements concentrations obtained with the EXP.1 (DW); EXP.2 (CA) and EXP.3 (CA+TW20) experiments. These results allow the monitoring of trace element removal over time, as well as their migratory orientation.

The concentrations collected for the treatment using demineralised water (EXP.1) are relatively low ($< 1 \text{ mg.L}^{-1}$) for all trace elements analysed (**Figure 2**), except for Zn, which is already highly present in the initial state (**Table 1**). Trace elements are recovered mainly in the anode compartment. An extraction peak is frequently measured on day 11, and then the concentration gradually decreases until the end of the treatment (28 days). This trend is observed for the elements Cd, Cr, Cu, Ni and Zn. As for Pb extraction stabilises from day 11 to day 22, then it decreases (**Figure 2**). As, Ba, Mo and Se are extracted earlier in the EK depollution process, since the extraction peak is measured on day 6. For As and Ba, a stabilisation is also noticed (from day 6 to day 22). Only Sb was not recovered in the anode and cathode tanks.

Figure 3 presents the results obtained with the experiment using citric acid (EXP.2) and citric acid/Tween20 (EXP.3). It shows much higher quantities extracted than EXP.1, up to 2398 mg.L⁻¹ for Zn. The elements are extracted mainly at the anode pole, but mobility happens also towards the cathode pole. An extraction peak is also observed on day 11 in the anode compartment, although the maximum peak is measured at the beginning of the treatment (day 2 and 3). This trend concerns the elements As, Ba, Cd, Cr, Mo, Ni, Pb, Sb, Se and Zn. In the cathodic compartment, a slight peak occurs from day 8 to day 22, also with a maximum at day 11 (**Figure 3**). The elements Ba and Se show a stabilisation before decreasing until the end of the treatment.

For the EXP.3 the trends are almost the same as those observed for EXP.2 (**Figure 3**), but the majority of the extraction is performed in the cathode compartment. This change is probably due to the added surfactant. And finally, the quantities of extracted trace elements are slightly lower than those found in EXP.2.

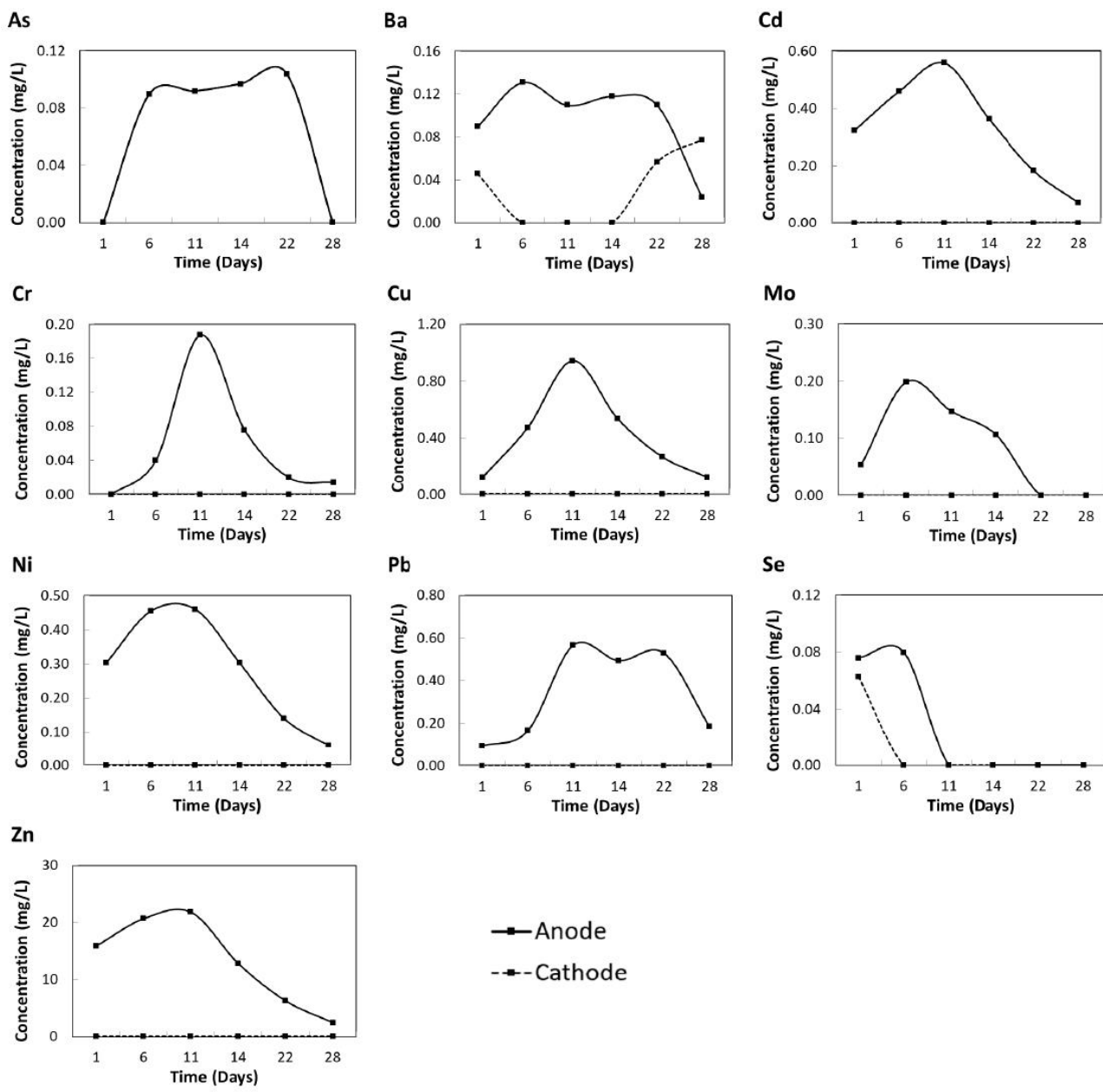


Figure 2 Concentration of trace elements (mg.L^{-1}) measured during each EK treatment, in outlet liquid effluent (anodic and cathodic compartment) for experiment with DW (EXP.1).

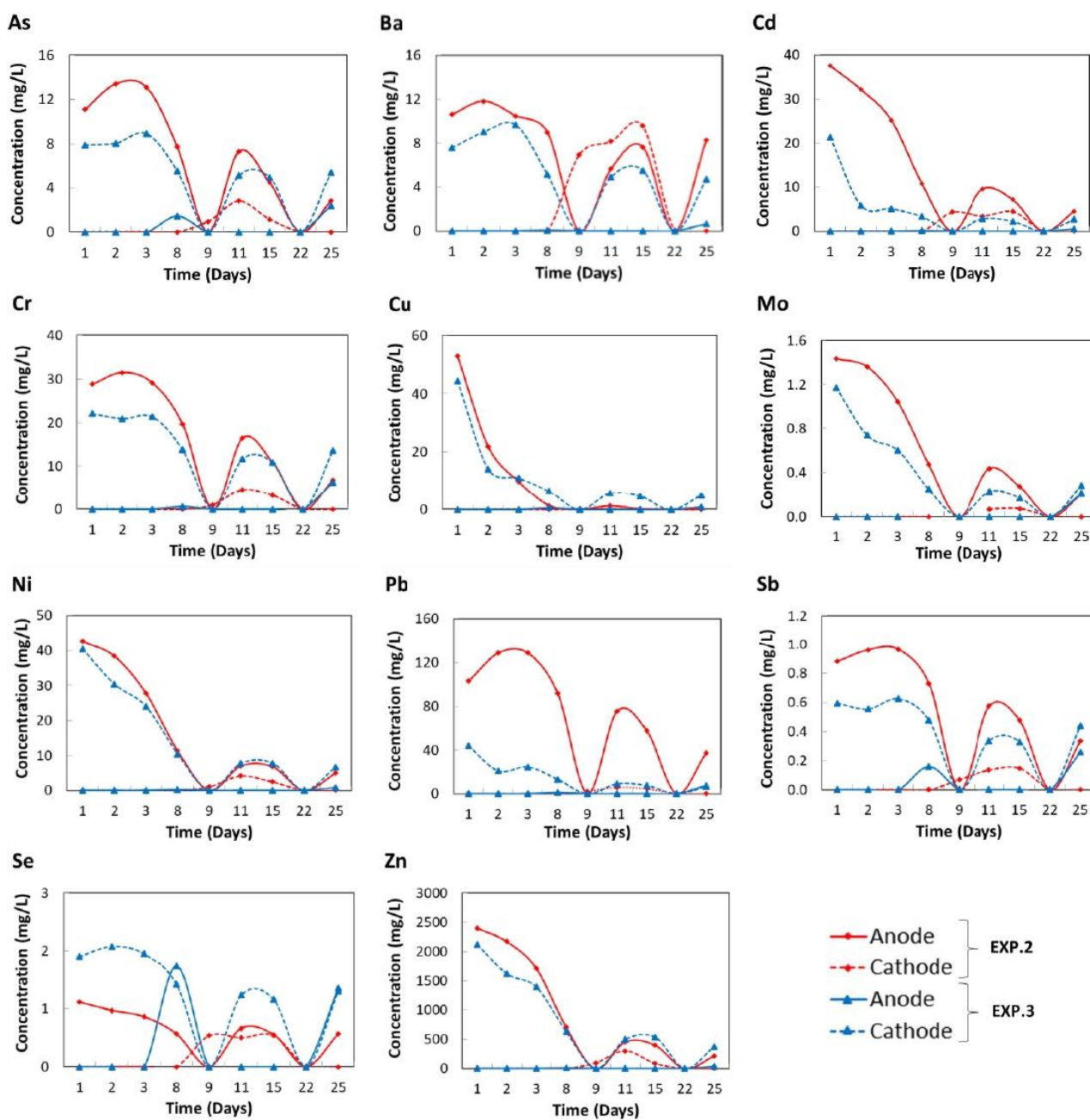


Figure 3 Concentration of trace elements ($\text{mg}\cdot\text{L}^{-1}$) measured after each EK treatment, in outlet liquid effluent (anodic and cathodic compartment) for experiment with citric acid (EXP.2) and citric acid and tween 20 (EXP.3).

III.2.2. Removal in solid phase

Table 2 presents the solid phase removal rates (%R), obtained according to **Eq (1)** below. EXP.1, EXP.2 and EXP.3 are presented, as well as the three analytical sections S1, S2 and S3 (marked in **Figure 1**). Negative values correspond to an accumulation in the solid phase after treatment.

$$\%R = \frac{C_i - C_f}{C_i} \times 100\% \quad \text{Eq (1)}$$

	EXP.1 - DW			EXP.2 - CA			EXP.3 - CA+TW20		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	4.3%	4.8%	2.7%	56.3%	34.4%	49.8%	50.4%	23.7%	23.0%
Ba	16.1%	18.8%	18.7%	10.3%	9.5%	20.1%	13.6%	17.8%	16.8%
Cd	5.2%	3.6%	1.9%	62.0%	37.6%	53.5%	67.8%	32.6%	30.1%
Cr	13.2%	14.7%	14.6%	38.4%	28.5%	36.8%	39.6%	32.4%	34.1%
Cu	-5.6%	-4.5%	-5.4%	4.8%	-8.5%	1.5%	30.1%	-1.8%	-3.9%
Mo	-2.4%	65.2%	65.2%	47.0%	47.0%	47.0%	47.0%	47.0%	47.0%
Ni	7.8%	7.6%	2.7%	41.0%	25.7%	36.4%	45.6%	28.1%	21.3%
Pb	13.5%	11.4%	16.2%	47.7%	27.7%	46.8%	26.2%	19.8%	19.7%
Sb	-5.4%	8.6%	17.6%	32.3%	27.2%	34.1%	31.5%	17.6%	25.1%
Se	-3.4%	-3.4%	-3.4%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%
Zn	9.3%	7.4%	5.1%	77.3%	51.9%	67.5%	88.7%	43.7%	41.5%

Table 2 Results of removal (%R) in the solid phase. Negative values correspond to the enrichments.

Concerning the experiment conducted with DW (EXP.1), a general trend cannot be established because some metallic cations are extracted in higher concentration in the section close to the anode (S1). This is the case of Cd, Ni and Zn, while others are extracted more predominantly in the central section (S2) or near the cathode (S3).

Overall, CA (EXP.2) gave better %R than DW (**Table 2**), especially near the electrodes (S1 and S3). Zn shows a %R of 77.3% (S1) versus 9.3% for EXP.1. The hierarchy is as follows: Zn>Cd>Mo>As>Pb>Cr>Ni>Sb>Ba>Cu>Se.

EXP.3 (CA+TW20) did not on average achieve better %R than the experiment conducted with citric acid alone, with the exception of Ba and Cu (**Table 2**). It seems that the surfactant had a beneficial impact on the removal of the element Cu (31.54%) next to the anode (S1). In addition, it should be noted that the surfactant is non-ionic, but nevertheless

provided better removal rates in the section near the anode (S1). For example, S1 is 88.7% free of Zn, while S2 and S3 are only 43.7% and 41.5% free respectively.

Overall, the acid treatment reagents (CA and CA+TW20) improved the %R of trace elements contained in the solid phase, compared to those obtained with DW.

III.2.3. Removal in liquid phase

Batch leaching tests were used to estimate the water soluble fraction of trace elements before and after EK treatment. **Table 3** shows the %R (**Eq 1**) measured in the leachates of the treated matrix.

The DW experiment (EXP.1) shows reductions in trace element concentration, but also highlight increased motilities, reflected in higher concentrations (**Table 3**). The mobility of As, Cr, Cu, Mo and Sb was enhanced in all 3 sections (S1, S2 and S3). The mobility of Ba was enhanced in S1 only. For the other elements, a depollution was observed in all the sections, with the most important rate measured in S3 for Zn (%R=99.5%).

In general, whether it is a depollution or an increased mobility, the phenomenon takes place in the section near the cathode (S3). The same is true for EXP.2, where the elements are more mobile near the cathode section. The mobility of the elements (in EXP.2) is more important than in EXP.1, but less important than in EXP.3.

It seems that the acidic reagents had a significant impact on the mobility of the elements and caused accumulations in the liquid (leached) phase. Only the concentration of Mo seems to have been reduced (**Table 3**) by this type of reagent (EXP.2 and EXP.3).

The pH-controlled leaching tests were used to estimate the mobility of trace elements as a function of the acidity of the medium. An acidic (pH2) and basic (pH12) range was tested. **Figure 4** presents the concentrations (mg.kg^{-1}) of trace elements, present in the 3 sections for the three experiments (EXP.1, EXP.2 and EXP.3).

Overall, an acidic medium (pH2) allows a better mobility of cationic elements. Conversely, a basic medium (pH12) improves the mobility of anionic elements, as is the case for As, Mo and Se (**Figure 4**). The S3 in EXP.1 presents lower concentrations of As, Cr, Cu, Mo, Pb, Sb and Se than in the neighbouring sections. However, S3 has a very high concentration of Ba. The acid experiments (EXP.2 and EXP.3) reduced the mobility of As,

Cd, Cu, Ni, Pb, Se and Zn. Indeed, the recovered concentrations are lower than EXP.1 which has been conducted with demineralised water (**Figure 4**).

Regarding to the initial concentrations (*Cf.* **Table 1**), it appears that the acid-treated matrices (EXP.2 and EXP.3) show lower concentrations at pH2 for the elements Cd, Cr, Cu, Ni, Pb and Zn (**Figure 4**). This is also the case for the anions As, Mo and Se at pH12. However, this behaviour was not observed in the experiment conducted with demineralised water (EXP.1).

The acidity provided by the treatment reagents have presumably allowed the mobilisation of trace elements, during the EK treatment. This is why the concentrations measured after treatment are lower than the quantities found in the raw sediment.

	EXP.1 - DW			EXP.2 - CA			EXP.3 - CA+TW20		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	-184.6%	-227.3%	-783.7%	-3412.2%	-5372.0%	-7629.3%	-9667.1%	-13356.1%	-15109.8%
Ba	-20.6%	0.9%	56.8%	-1959.2%	-941.6%	-3580.6%	-4235.3%	-4510.5%	-4817.4%
Cd	69.3%	80.2%	98.6%	-109.9%	-128.3%	-426.9%	-1249.5%	-827.6%	-992.3%
Cr	-173.3%	-358.3%	-1886.7%	-144500.0%	-100016.7%	-175183.3%	-481966.7%	-336000.0%	-260200.0%
Cu	-20.9%	-11.7%	-203.3%	-858.2%	-781.1%	-2455.4%	-2403.2%	-2574.5%	-3289.6%
Mo	-59.7%	-40.7%	15.8%	51.7%	-2.7%	40.2%	50.2%	19.7%	4.8%
Ni	56.3%	70.7%	79.4%	-71.7%	-86.4%	-448.2%	-290.4%	-612.9%	-1252.1%
Pb	80.3%	80.3%	80.3%	-23863.3%	-14490.4%	-53587.5%	-121811.0%	-115037.9%	-127760.1%
Sb	-111.9%	-106.7%	-163.9%	-505.3%	-377.2%	-598.2%	-964.9%	-849.1%	-835.1%
Se	59.4%	59.4%	59.4%	54.4%	14.4%	-38.3%	-89.9%	-49.8%	-96.5%
Zn	68.2%	87.8%	99.5%	-118.9%	-139.7%	-504.9%	-488.8%	-1306.4%	-1060.0%

Table 3 Results of removal (%R) obtain after the leaching test. Negative values correspond to the enrichments, reflecting a high mobility of the elements.

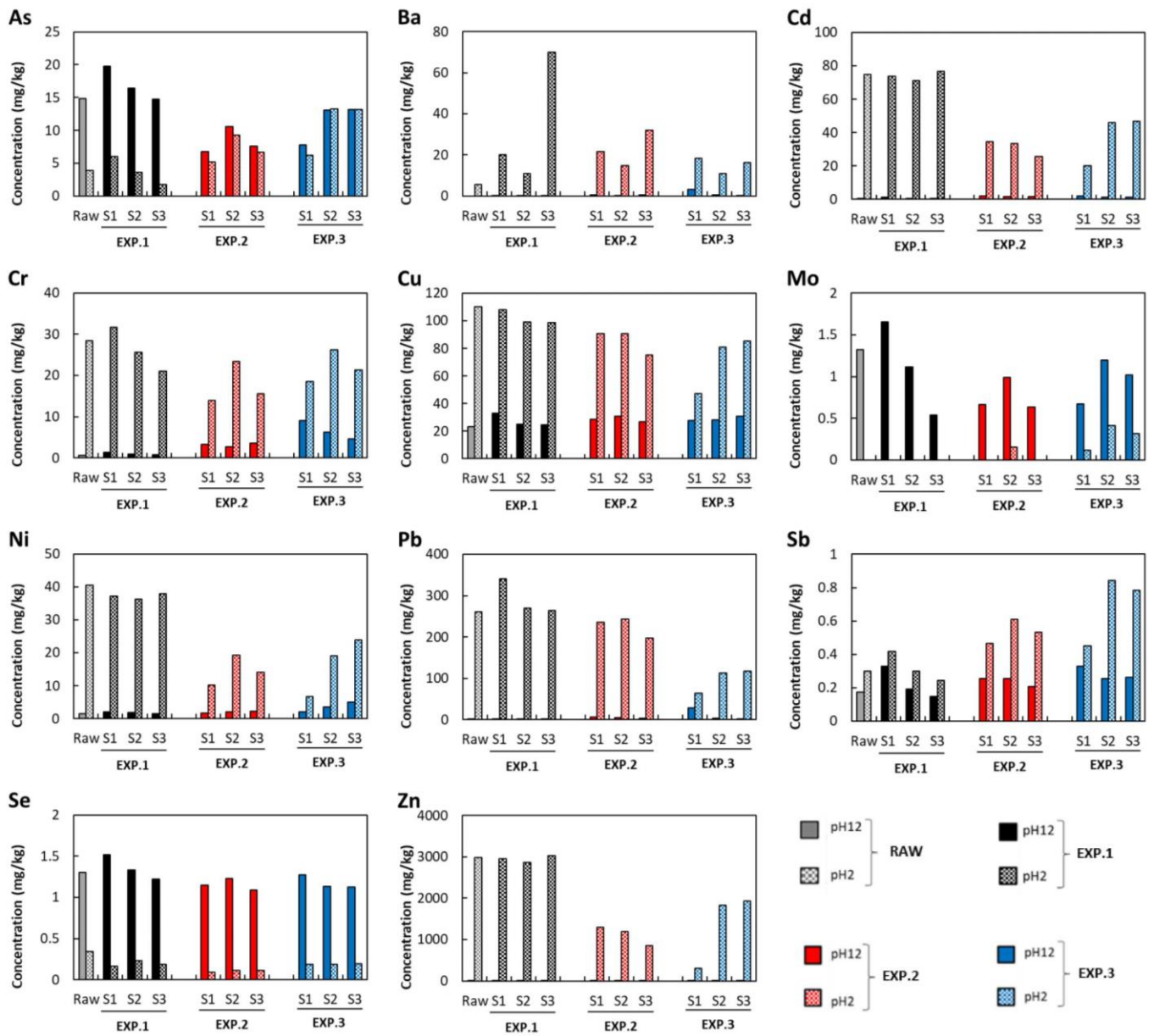


Figure 4 Trace elements found in leachates from 3 EK-tests conducted under pH control, for the 3 sections (S1, S2 and S3).

III.3. Sequential extraction of trace elements in the treated sediment

Sequential extraction was conducted in order to identify and quantify the different fractions, in which a chemical element is present in the solid material. A state of speciation before (*i.e.* initial state) and after EK treatment is presented in **Figure 5**. The enrichments or depletions of the trace elements are measured from the initial concentrations.

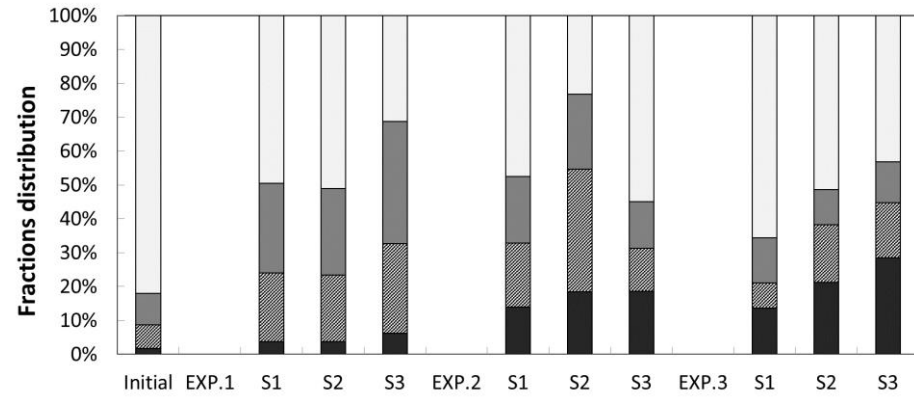
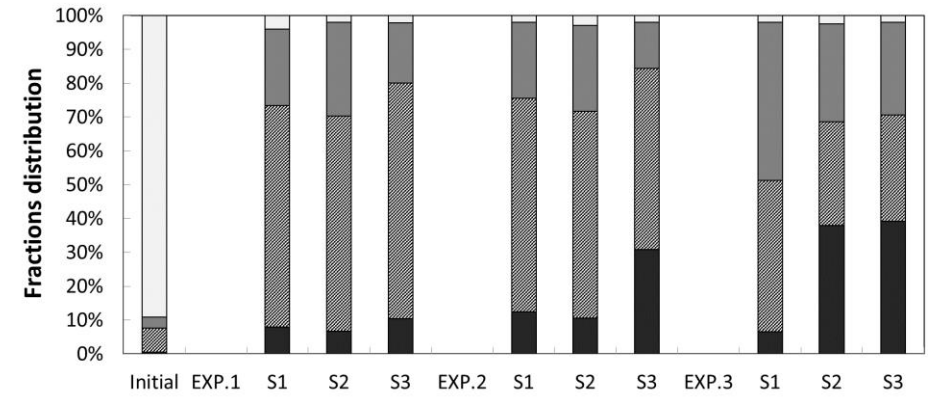
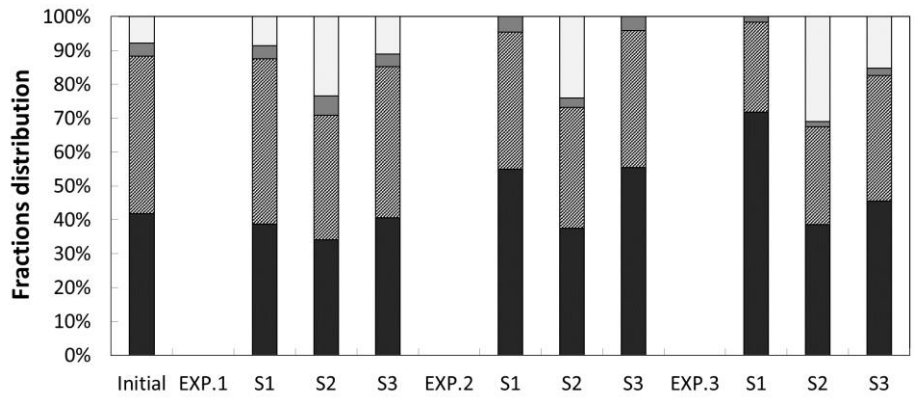
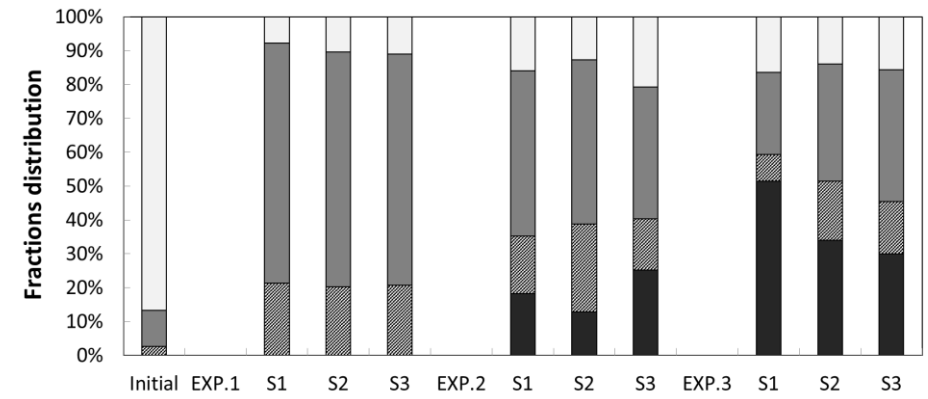
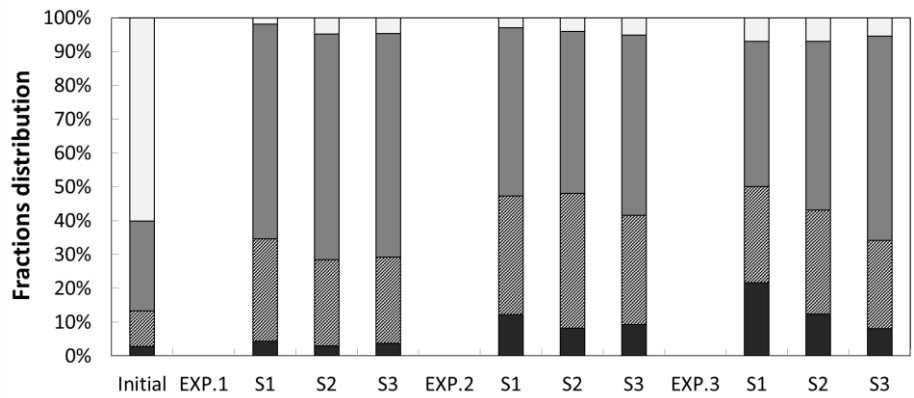
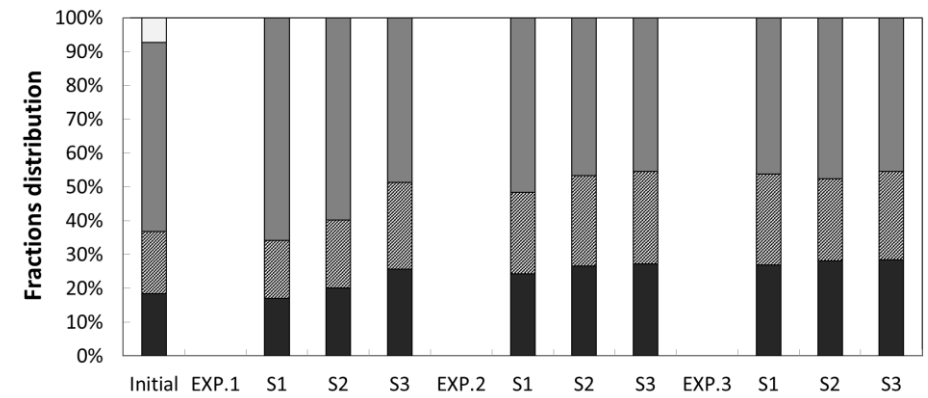
Compared to the initial concentrations, it is shown that in general EK had a significant effect on the residual fraction (F4) for all elements, sections and experiments. The elements As, Ba, Cr, Cu, Ni, Pb and Zn are practically no more found in this fraction after the EK treatments (e.g. EXP.1, EXP.2 and EXP.3). In the initial state, F4 has much higher trace element concentrations than the other fractions. For example, the raw sediment contains 238 mg.kg⁻¹ of Ba in F4, whereas F1, F2 and F3 contain only 1.38, 19.20 and 8.55 mg.kg⁻¹ of Ba respectively.

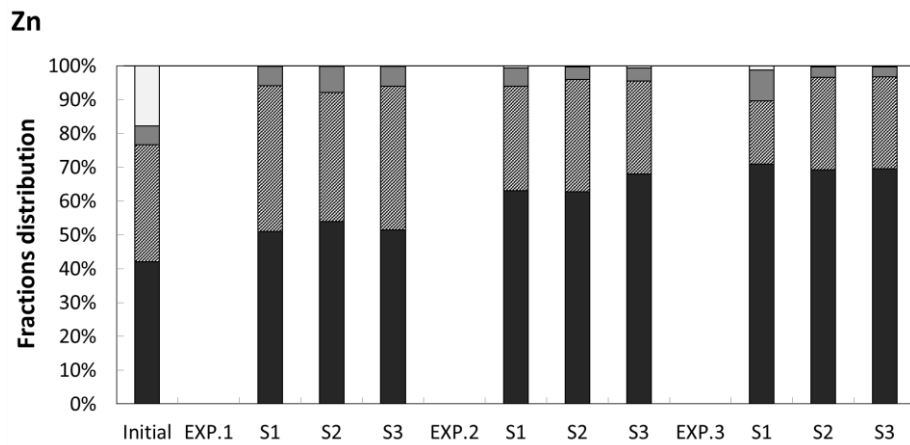
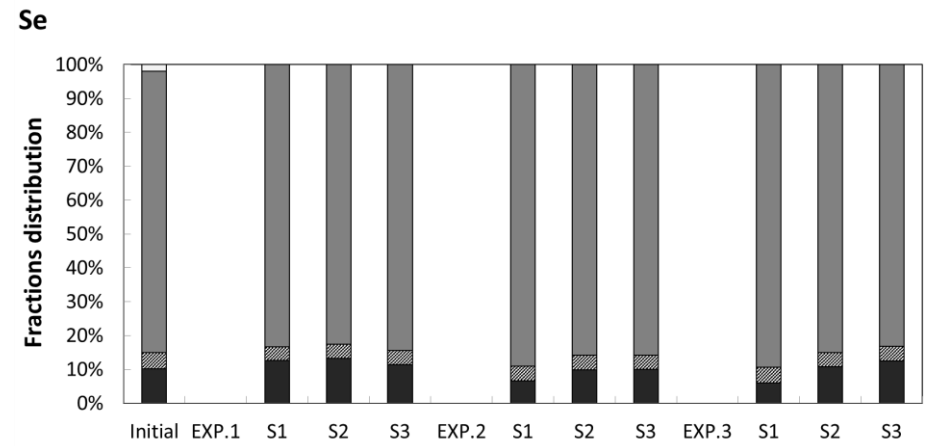
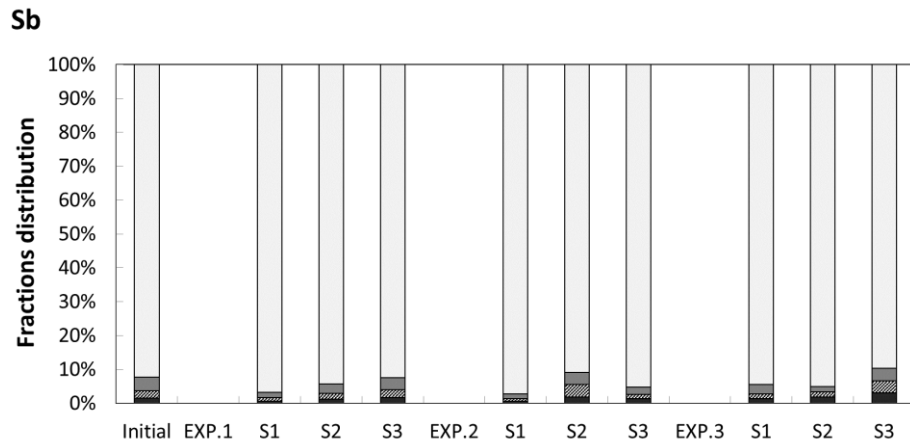
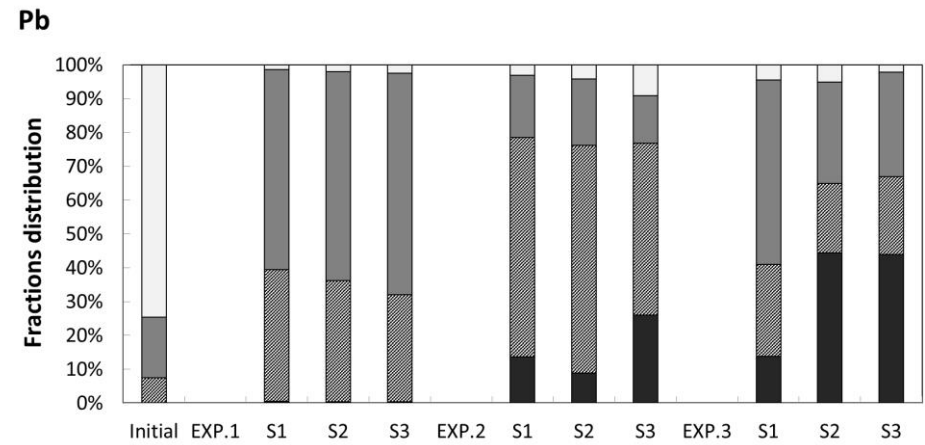
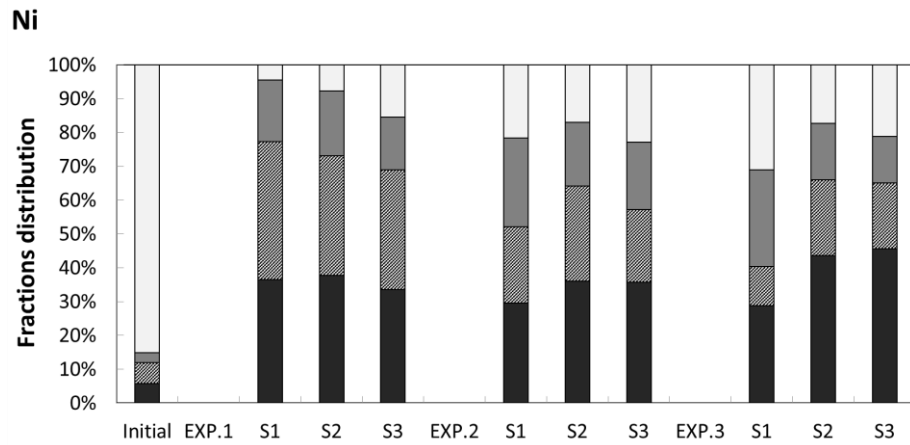
EXP.1 (DW) highlights an increase in the overall concentrations (in all three sections) of As, Ba, Cd, Cr, Cu, Ni, Pb for the oxidisable (F3) and reducible (F2) fractions. The extractable fraction (F1) was enriched in Ba, Cd, Ni, Se and Zn. Some elements enriched the matrix locally, either only in S1 or S3 (**Figure 5**).

EXP.2 (CA) reduced the concentrations of Cd, Mo, Ni, Sb and Zn in all 4 fractions. The concentrations of all trace elements in F3 were reduced, except for Se. Enrichments were observed in F1 for As, Cr, Cu, Pb and Se. F2 was enriched in Cu and Pb, and finally, the element Ba was found in higher quantities than in the initial state in F1, F2 and F3.

In contrary to EXP.2, EXP.3 (CA+TW20) allowed a reduction of Ba in F2. Citric acid and TW20 also reduced the concentrations in F1, F2 and F3 of Cd, Mo, Ni and Zn. In general, S1 had lower concentrations levels than the other sections. This is probably due to the TW20 surfactant used.

We have seen that some fractions were enriched after the EK treatments, while others were reduced. However, the most notable effect was for F4.

As**Ba****Cd****Cr****Cu****Mo**



- F4 : Residual fraction
- F3 : Oxidizable fraction
- ▨ F2 : Reductible fraction
- F1 : Extractible fraction

Figure 5 Trace elements 4 fractions variations (F1, F2, F3 and F4) before and after the electrokinetic remediation treatments (EXP.1, EXP.2 and EXP.3).

III.4. Influence of electrokinetic treatments on speciation and mobility of trace elements.

III.4.1. *Mobility during the treatment*

The analysis of the effluents recovered at the anode and cathode overflows gives an indication on the trace elements' depollution. Indeed, the measured concentrations testify to an efficient migration through the sedimentary matrix of soluble chemical elements or complexed with other elements (citrates for example). We previously shown that acid reagents (EXP.2 and EXP.3) allowed better extraction of trace elements (**Figure 3**). The EXP.1, conducted with demineralized water allowed only small extractions ($< 1 \text{ mg.L}^{-1}$). The low pH of the medium probably played an important role in the solubilisation and mobilization of the elements towards the anode and cathode extremities, as the significant decrease in the pH of the pore water (**Figure 6f**) implies. From an initial pH of 6.50, the values decrease on average for EXP.2 to 3.61, 4.22 and 3.89 for sections S1, S2 and S3 respectively and 2.62, 3.38 and 3.86 for EXP.3. This decrease is mainly due to citric acid used. The electrolysis of water, which occurs in any EK system, produces hydroxide anions OH^- at the cathode and H^+ protons at the anode. Without pH control by acidifying reagents, the pH of the medium would evolve in the same way as in EXP.1. The pH went from 6.51 to 7.59, 8.37 and 10.35 for the S1, S2 and S3 respectively. The mobility of H^+ ions is greater than OH^- ions, so they migrate faster but are then more quickly removed from the sedimentary matrix to the anodic and cathodic effluents. [Ammami \(2013\)](#) explains that this difference in mobility would tend to create a first global acidification of the medium leading to an increase of the pH from the cathode region due to the production of OH^- ions. This trend is observed in EXP.1 (**Figure 6e**), which did not received pH control. The pH of the sections is stabilized by the production of H^+ ions for 5 days. Then, these ions are then eliminated from the system and OH^- ions became the majority, therefore gradually increasing the pH to rather basic values.

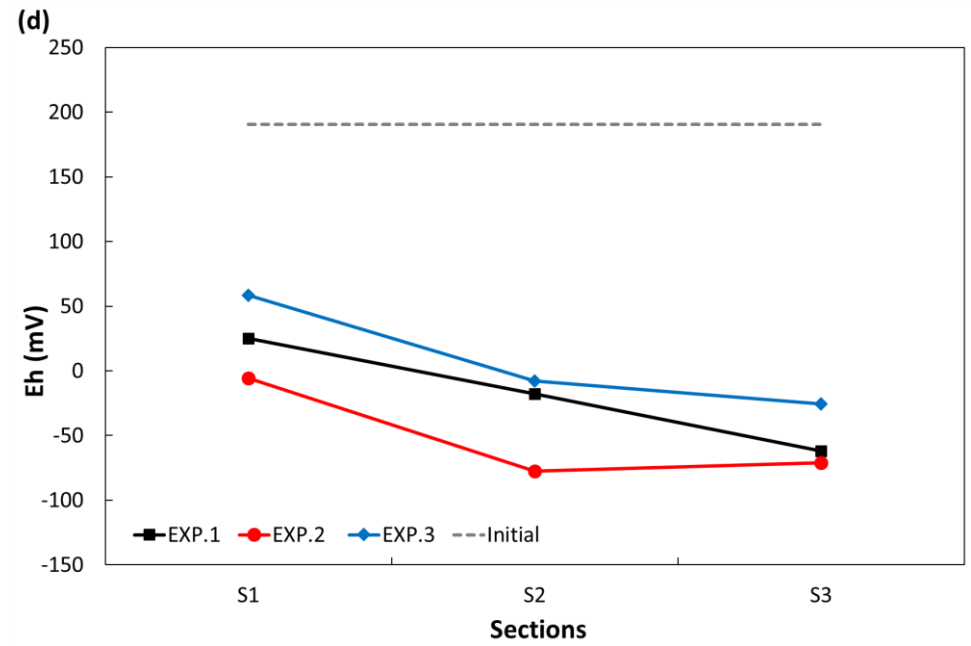
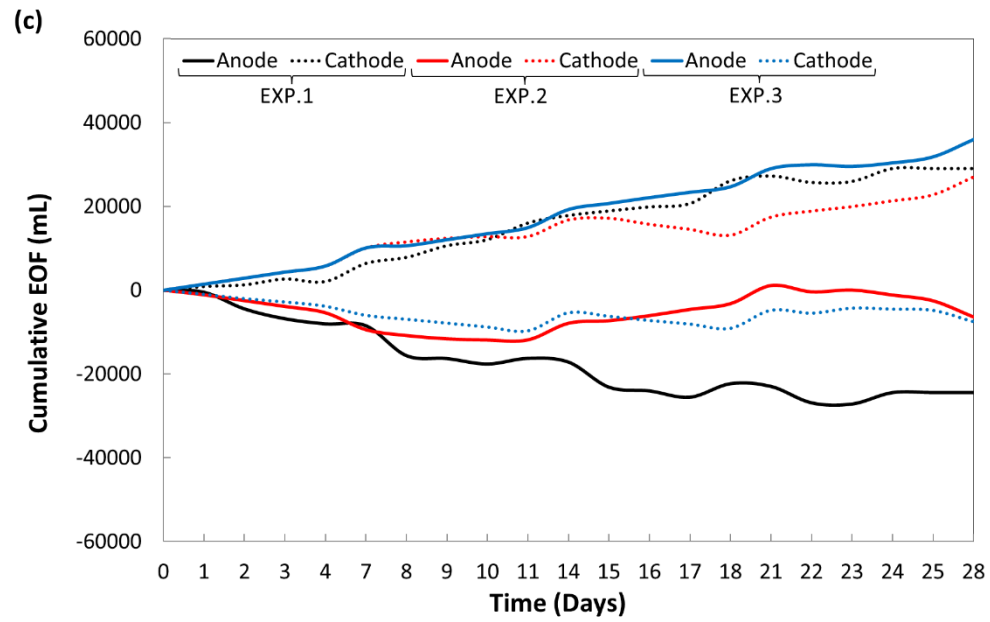
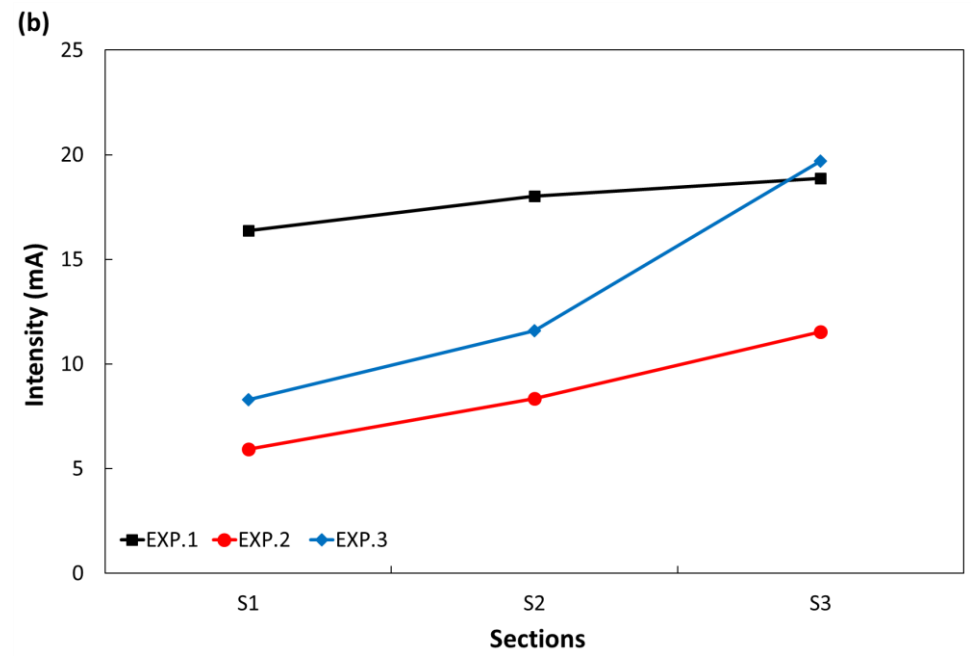
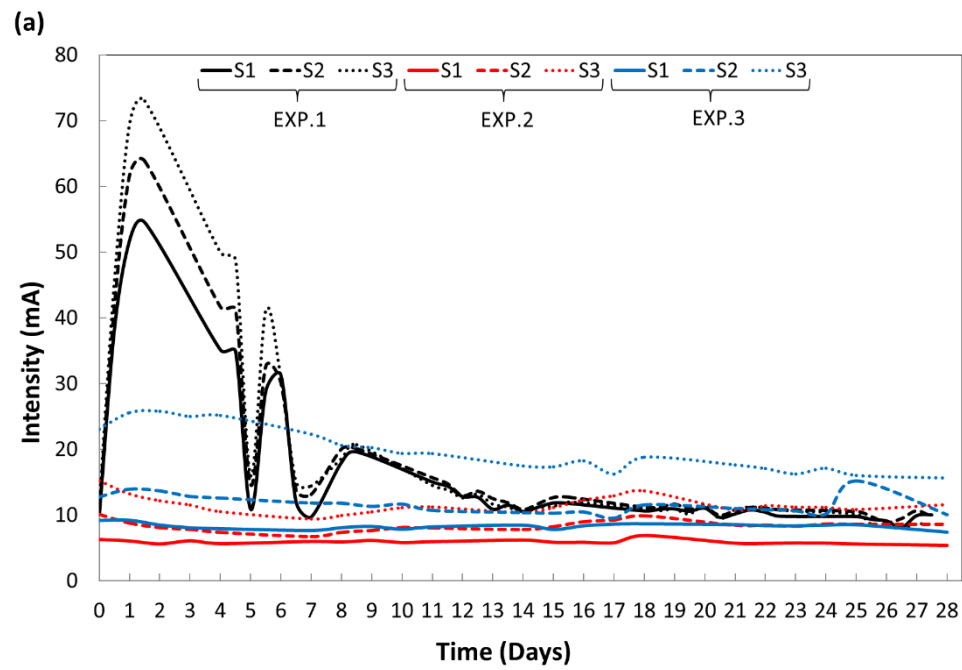
Interestingly, the peaks of extractions observer the 11th day in our previous study (**ARTICLE 2**) does not seem, this time, to be correlated with a peak of electrical intensity or an EOF acceleration. Indeed, the evolutionary curves of these parameters are relatively constant and don't have any particularity at 11th day (**Figure 6a, 6b, 6c**). This can come from the heterogeneity of the matrices studies, or the very acidic pH that dominates the effect of EOF or electrical intensity.

However, it is important to note that depending on the type of reagent used, the migratory orientation of the trace elements will be different. For instance, in EXP.1 (DW) and EXP.2 (CA), the extractions are mainly done on the anode side, while in the EXP.3 (CA + TW20) they are made towards the cathode. For these two first experiments, the migration of metal cations seems to happen in the opposite direction to the conventional direction of migration (Song 2017, Tian, 2018). Indeed, the EOF measured at **Figure 6c** seems to confirm that the direction of the flow at cathodic side of EXP.1 and EXP.2 is carried out in the conventional direction, since the curves are positive (Ammami, 2013). Comparatively, for the EXP.3, the EOF does not show any positive curve at the cathodic overflow. It would seem that Tween20 can potentially reverse the movement's direction with EOF. Significant amount of elements found in the overflows suggests that the effect of the EOF is inferior compared to the effect of electromigration. This observation is also made by Reddy & Chinthamreddy (2003), since they considered that electromigration has been the most dominant transport process for contaminant migration into the electrode reservoirs. Ait Ahmed (2016) is also in accordance with our observation as he explains that for inorganic contaminants, electromigration dominates during transport of ionic species when concentrations are high, while electroosmosis is more effective at low concentrations.

Compared to EXP.2, the TW20 of EXP.3 might have slowed the chelating effect of citrates with the elements, allowing free cations to migrate to the cathode a little more easily. Ammami (2013) notes, as in EXP.2, that a part of the metal cations is recovered at the anode and that this phenomenon is accentuated when using CA. Regarding EXP.2, the elements As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn (**Figure 3**) react with CA to form migrating anionic complexes towards the anode. CA is known not only for its buffering power, allowing to keep an acidic environment, suitable for EK pollution control, but also for its chelating properties with divalent metals (Leštan et al. 2008). The citrate of CA mobilized the metals which may have migrated from the cathode to the anode, thus resulting to enrichments of the aqueous medium measured in S1 (**Table 3**). This hypothesis is also shared by Ammami (2013). The migration citrate complexes and the electromigration of metal cations can be opposed and lead to an accumulation metals (Cameselle and Pena, 2016).

The overabundance of Zn in the sedimentary matrix leads us to take it as an example. Zn also presents many risks to human health and the environment (**ARTICLE 2**). Cameselle & Pena (2016) explains that when the Zn^{2+} combined with citrate dissolves in water, four complexes can be formed. Zn^{2+} is the most abundant state at very acidic pH, which was the

case for the acid tests EXP.2 and EXP.3 (**Figure 6f**). [Cameselle & Pena \(2016\)](#) also suggest that a positive complex $[\text{ZnH}_2\text{L}]^+$ appears at $\text{pH} < 3$; that a neutral complex $[\text{ZnHL}]$ appears in the range of $\text{pH} = 3 - 4.5$; that a negatively charged species $[\text{ZnL}]^-$ is formed by Zn complexes at $\text{pH} > 4.5$. Therefore the section submitted to a very acidic $\text{pH} < 3$ (*i.e.* S1 - EXP.3), would allow Zn to be in a state of divalent cation or in the form of a positive citrate complex, both of which are suitable for electromigration to the cathode. This is what we observed since this element has mainly enriched this cathode section (S3) (**Table 3**). When the pH is greater than 4.5 (S1, S2 and S3 - EXP.1), Zn forms a negatively charged complex which can migrate towards the anode (*Cf.* **Figure 2**). As for all the sections of EXP.2 and S2, S3 of EXP.3 ($\text{pH} 3-4.5$), clays and organic matter, both negatively charged, may have faced a partial dissolution in the aqueous phase by CA which greatly lowered the pH (**Figure 6e and 6f**). Clays contain various minerals ([Ducasse, 2019](#)) that can be degraded by the acidity of the environment, such as quartz, oxides and iron hydroxides, iron sulphides (pyrite) in a reducing medium in particular, carbonates and matter organic. These dissolved phases therefore migrate towards the anode, entraining the complexed metal cations. For EXP.3, the mobility of the complexes formed would have been lower than that of the cations free metal, the migration of trace elements therefore remained preferentially in the direction of the cathode during the EK progress.



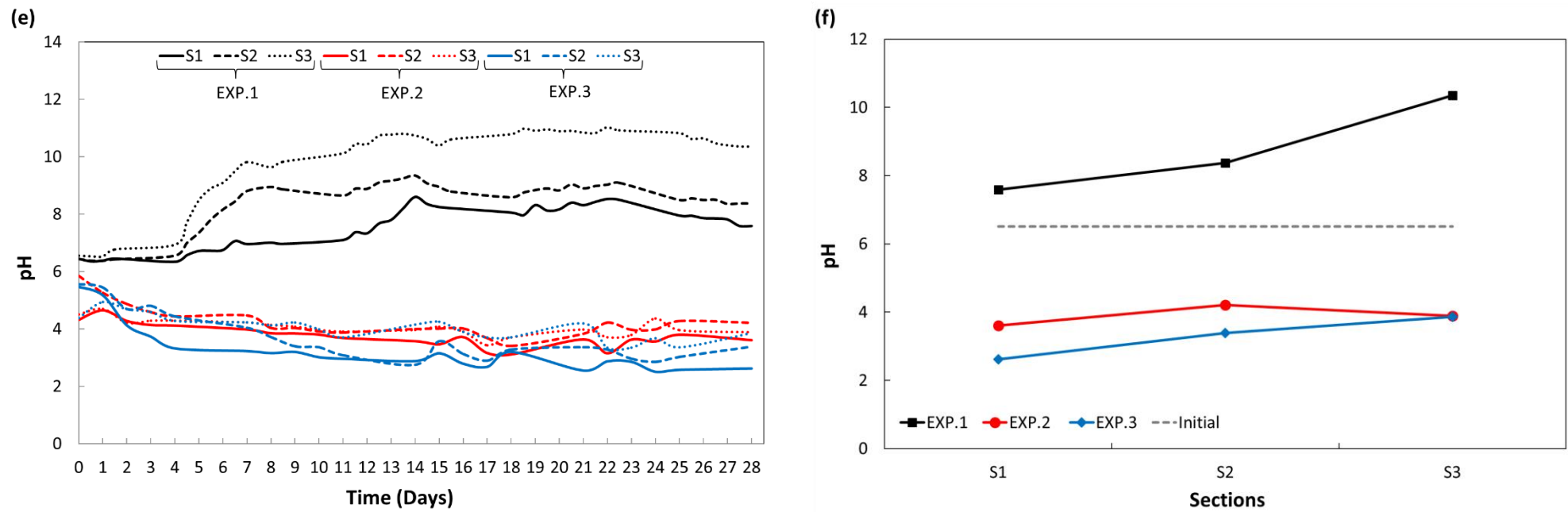


Figure 6 (a) Evolution of the electrical intensity spread in the sedimentary matrix during EK treatment. The results of sections S1, S2 and S3 of the 3 experiments are shown; (b) Average representation of the electrical intensity measurements of sections S1, S2 and S3 for the 3 experiments; (c) the cumulative electroosmotic flux, calculated for the three experiments at the anode and cathode poles; (d) Average representation of the redox potential (Eh), measurements into the pore water of the sections S1, S2 and S3 for the 3 experiments; (e) Evolution of the pH variations in the pore water of the sediment, during EK treatment. The results of sections S1, S2 and S3 of the 3 experiments are shown; (f) Representation of the pH measured on the last day of treatment (28th day). The three sections for the three experiments are shown.

III.4.2. Mobility and speciation of trace elements after the EK-tests

The hypothesis concerning the partial dissolution of the mineral and organic phases, subject to acid treatments (EXP.2 and EXP.3), can be verified by the sequential extraction test. This test is used to determine which mineral or organic fraction the trace elements are associated with. As shown in **Figure 5**, the residual fraction (F4) had been particularly affected by the electrokinetics for all the experiments (**Figure 5**). Indeed, a significant decrease in the concentration of the elements listed below was noticed in F4: As, Ba, Cr, Cu, Mo, Ni, Pb, Se and Zn. Additionally, the concentration of the elements Mo, Ni and Zn, decreased in the fractions 1, 2 and 3 for the acid experiments (EXP.2 and EXP.3). This means that there has been a mobilization of these associated elements or a partial digestion of the mineral phases, leading to a release of associated trace elements. The **Figure 6f** shows that the three analysis sections (S1, S2 and S3) experienced a significant decrease of the pH, which can therefore cause the digestion of the phases carrying these elements. The residual solid (F4) contains predominantly primary and secondary minerals that trap trace metals in their structures crystalline ([Kennou et al. 2015](#)). Therefore, if the minerals are degraded by the acidity of the environment, then they release pollution not initially accessible. The mobilization of this fraction therefore provoked an enrichment in the aqueous medium (**Table 3**), and a decrease in the concentrations in the solid fraction (**Table 2**). It is notably the case for the elements Ni and Zn.

Phenomena of re-deposition, precipitation or complexation may occur during the EK treatment. Indeed, if the concentration of a chemical element decreases for a given fraction, but increases in another fraction, this can mean that the element has first been solubilized, and then associated with a new mineral phase, due to the pH and redox (**Figure 6d**) medium conditions. Two cases can then occur as a result of this phenomenon: The first being that this phenomenon is accompanied by an increase in the concentration in the mobile liquid phase, the second would be that an increase in the solid phase is observed. If the solid phase concentrations increase, precipitation and precipitation reactions complexation then occurred. [Tessier et al. \(1979\)](#) noticed in their study that the results obtained for fractions 3 and 4, indicate that these phases have a very strong trace elements trapping action, disproportionate to their own concentration. This seems to be consistent to the enrichments we observed in F3 for the elements As, Ba, Cd, Cr, Cu, Ni, Pb, Se, Zn of EXP.1 (**Figure 5**). The elements Ba and Se of EXP.2 and EXP.3 also enriched F3. In addition, EXP.2 and EXP.3 mainly enriched in

metal F1, while the EXP.1 caused enrichments in F2 and F3 mainly (**Figure 5**). F1 linked to carbonates, clays and amorphous phases is known to contain significant concentrations of trace elements (Kennou et al., 2015). Blanchard (2000) explains that the dissolving carbonates reactions favour the trapping of metal ions in crystalline forms. This explanation can be used to interpret the increase of the trace elements in F1. Although carbonates are generally dissolved in low pH, F1 was enriched in trace elements, for the two experiments (EXP.2 and EXP.3) (**Figure 5**). A acidic solution (pH = 5) seems sufficiently effective to dissolve calcites and dolomites and thus cause metals bound, without dissolving organic matter, oxides and clay mineral particles (Blanchard, 2000). It could then be that the metals were associated rather with the clay phases of this fraction. The increase in the concentrations in F2 and F3 for the EXP.1, would probably be due to the alkaline pH, measured in the different sections of the sediment (**Figure 6f**). The basic pH would have caused the precipitation of these metals and their association with these phases.

The leaching carried out under pH control allows to verify the mobility of the elements according to an acidic (pH2) and alkaline (pH12) environment. Besides, metal cations were mainly mobilized in this range of pH. This pH = 2 is close to that measured in the sediment for EXP.2 and EXP.3 (**Figure 6f**), then allowing significant mobilization of trace elements. This is also what we observed at the overflows (**Figures 3 and 4**): the elements were mobilized in high quantity. Nevertheless, enrichments were still observed in the liquid phase (**Table 3**), which stipulate that the elements have could not be extracted efficiently during EK processing. It would then be appropriate to look for a way to improve performance of transport with an amendment increasing the electric current, which would improve the EOF (**ARTICLE 2**), electroosmosis being the second most influential mechanism in electrokinetic treatments. This could therefore allow an efficient migration of pollution within the matrix and greater elimination in overflows, thus decongesting the liquid phase and limiting enrichments.

IV. Conclusion

The electrokinetic experiments carried out in this work were conducted on a fluvial sedimentary matrix highly contaminated with Zinc. These experiments aimed to define the distribution of trace elements in the different solid phases of the material, but also to visualise the influence of the EK treatment on these phases. The results of the sequential extractions were complemented by leachate analyses and analyses conducted on mineralised samples (acid digestion), in order to support our hypotheses.

Analysis of the mineralogical fractions showed that trace elements were no longer associated with the residual fraction (F4) after the EK treatments, and that the nature of the treatment reagents was not important in the outcome of this fraction. Indeed, the experiment conducted with DW showed a decrease in trace element concentrations similar to the experiments conducted with acid. Although the association of elements with F4 decreased significantly, other fractions (F1, F2 or F3) were sometimes enriched, reflecting the re-deposition of chemical elements.

Furthermore, our experimental results showed that electrokinetic remediation had a significant impact on F4. We also showed that, coupled with an acidic pH of the medium, there had probably been a partial digestion of this mineralogical phase, releasing the chemical elements which were associated into the aqueous medium. Residual fraction is known to contain a significant quantity of chemical elements, and this release tended to enrich the liquid phase. Conversely, the total content pollution in the solid fraction had decreased and even more so when the acidic reagents were used. The surfactant used, here TW20, did not show any improvement in the rate of pollution removal in the solid fraction, compared to the experiment conducted under acid alone.

Unfortunately, due to the large quantity of elements that enriched the mobile liquid phase, the EK treatment was not able to effectively mobilise these elements and remove them from the system through the anode or cathode overflows. The amounts collected in these electrolytic chambers were, however, significant when the acid reagents were in place. The electromigration of ionic elements was favoured by the suitable environmental conditions (pH and redox), throughout the sedimentary matrix.

Consequently, it would be interesting to look at improving the transport mechanisms. This could be done for instance by adding an amendment, allowing to increase the electric current and therefore accelerating the EOF in the conventional direction, beneficial to the

transport of the pollution. Since electroosmosis is the second most influential mechanism in electrokinetic treatments, it could allow an efficient migration of the pollution within the matrix and a greater elimination in the overflows, thus decongesting the liquid phase and limiting the enrichments observed.

General discussion on chapter 3

It is known that the composition of the sediment matrix is an important parameter in the behaviour of pollution during EK treatment, and in the fate of trace elements. This is why this general discussion will be a comparative interlude between the two matrices studied during this thesis. The sediment noted as “Sed 1” corresponds to the fluvial sediment dredged in the Scarpe river at Saint-Laurent-Blangy (Haut-de-France, France), also described in **chapter 2 (ARTICLE 2)**. The sediment “Sed 2” is the fluvial sediment dredged in Belgium and is involved in **chapter 3 (2nd part - ARTICLE 4)**.

The purpose of this part is to visualize the impact of the physico-chemical differences of the matrices on the efficiency of the EK treatment, as well as on the monitoring parameters (pH, redox and current intensity). Thus, a comparison of the raw matrices will be carried out in a first step. The physico-chemical parameters will be compared as well as the total content of the pollution, and the leached part. Secondly, the changes induced on the monitoring parameters, measured during treatment, will be analysed. Three experiments (presented in chapter 3) conducted with DW, AC and a mixture of AC and TW20 will be presented for each matrix. Finally, we will visualize the impact of similar EK treatments, applied to the both sedimentary matrices, in the mobilisation of trace elements. Removal rates are calculated after carrying out the leaching tests, recommended by the SETRA guide, for the recovery of waste in road techniques, and also by acid digestion tests with *aqua regia*.

I. Comparison of raw matrices

The chemical content of the matrices is presented in **Table 1**. It shows the in elements and oxides found in the sediments after X-ray fluorescence.

Oxides and hydroxides of iron, manganese and aluminium are the most commonly found (Hlavackova, 2005). They are also good pollution retention elements (Ammami, 2013). We can notice that alumina (Al_2O_3) and Fe(III) oxide (Fe_2O_3) are in the majority in Sed 2, which can therefore adsorb chemical elements having a particular affinity with these oxides. In addition to Fe and Al (hydro) oxides, silica and Ca are predominant in sediments (Kribi, 2005). We can see that Sed 1 contains more silica than Sed 2. According to Ammami (2013) silica has a low specific surface area, which limits its capacity to exchange with cations. Overall, the adsorption sites (Oxides and hydroxides of Fe, Mn and Al) are more numerous in sediment 2.

Carbonates are present mainly in the form of calcite (CaCO_3), but they are also found in other forms. Their dissolution balance partially controls the pH. A high carbonate presence can explain the basicity of the medium, and too large a quantity of carbonates is problematic since they promote all modes of trace element fixation on the carbonate surface. Indeed, the very reactive surface of

carbonates is the site of metal ions sorption phenomena by precipitation, adsorption or even inclusion in their crystalline mesh (Blanchard, 2000; Kribi, 2005). **Table 1** shows that the element Ca is present in significant quantities in the raw sediments and is also present in the form of calcium oxide (CaO). This suggests that the sediments contain carbonate phases, which are more numerous in Sed 1.

Elements (%)	Sediments		Oxides (%)	Sediments	
	Sed 1	Sed 2		Sed 1	Sed 2
O	51.6	46.4	Na₂O	1.1	0.7
Na	0.6	0.4	MgO	0.7	1.4
Mg	0.6	0.8	Al₂O₃	8.6	23.6
Al	5.8	10.0	SiO₂	75.0	44.7
Si	29.0	22.5	P₂O₅	0.6	0.2
P	0.4	0.8	SO₃	0.1	traces
S	0.4	1.0	K₂O	2.1	3.9
K	1.9	2.6	CaO	7.3	1.4
Ca	6.3	4.6	TiO₂	0.8	0.8
Ti	0.5	0.5	Fe₂O₃	3.3	5.6
Mn	traces	0.2	Br	-	1.1
Fe	2.6	9.2	ZrO₂	0.1	traces
Zn	traces	0.5	Total	99.6	83.6
Pb	traces	0.1			
Total	99.7	99.6			

Table 1 Summary of the elemental and oxide composition (%) of the two study sediments.

The estimated organic matter (OM) content is more abundant in Sediment 2: $23.38 \pm 0.01\%$ (Sed 2) and $11.91 \pm 0.01\%$ (Sed 1). These values are obtained after achieving an ignition loss at 550 °C on the sedimentary matrices, in accordance with standard NF EN 15169.

The origin of OM can be anthropogenic or natural and results from the decomposition of living organisms in the water column or from the rivers runoff. A distinction can be made between particulate organic matter and organic matter dissolved by filtration (Lecomte, 2018). Natural OM generally has many affinities with trace elements, which it can then complex, reducing their availability. However, chemical elements can be released as a result of OM degradation or pH change (Achard, 2013). The affinity of trace elements for the particulate phase is strong, with concentrations that are several orders of magnitude higher than those observed in the dissolved phase. Sediment 2 therefore contains adsorption sites in greater quantity than in sediment 1. This statement is also confirmed by the particle size distribution presented in **Figure 1**. The purpose of these curves is to compare the two matrices and to visualize which one contains the greatest proportion of fine particles. Indeed, the finest particulate fraction fixes the trace elements more easily than the gross fraction (Agostini, 2006). The curves show a similar appearance from one sediment to another. However, the

largest particles obtained (300 μm) are measured for sediment 1. We note that 50% of the particles have a diameter equal to 23 μm for Sed 1 and 12 μm for Sed 2.

The greater proportion of the retention phases contained in the Belgian sediment (Sed 2) are potentially problematic since they can trap pollution in a more or less irreversible manner. The availability of the adsorbed trace elements will therefore depend on the physicochemical conditions (the pH in particular) of the medium when the EK treatments are carried out. The high availability of reactive surfaces can cause re-deposition phenomena of the elements solubilized on other mineralogical phases, and therefore interfere with electromigration and reduce the effectiveness of EK remediation.

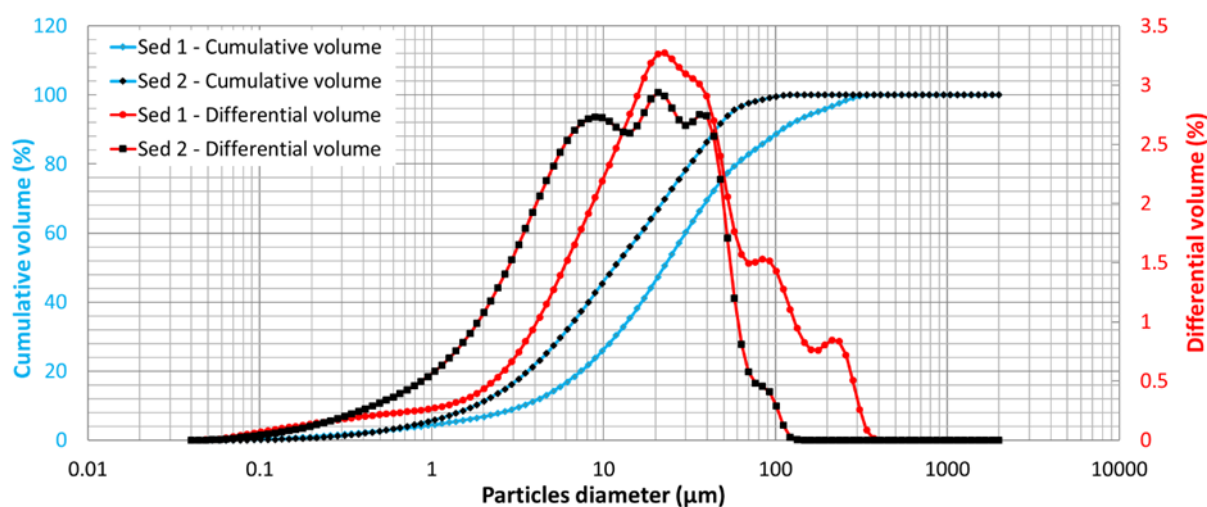


Figure 1 Particle size distribution (Laser particle size distribution: ISO 13320-1) of the raw sedimentary matrices studied. Obstruction 25%.

Table 2 shows the concentrations ($\text{mg}\cdot\text{kg}^{-1}$) obtained in trace elements and in major elements after leaching (NF EN 12457-2) and acid digestion (NF ISO 12914) tests, carried out on raw matrices.

Sediment 2 has a much higher overall (total content) trace element pollution than Sediment 1. However, the leached pollution is overall less important than for Sed 1 (except for Cd, Mo, Ni and Zn. For Zn, Sed 2 is highly contaminated with Zn, the leached proportion is therefore proportionately greater). This can be explained by the many retention phases seen previously. These combine with the solubilised elements and thus lower their availability in the environment.

Concerning the major elements, their total concentration is greater in Sed 2 (except for Ca). For the leached elements, the concentrations of the elements Al, Fe, Na, Si are approximately the same from one matrix to another. Conversely, the elements Ca, Mg, Mn and S are predominant in Sed 2, while K and P are in Sed 1.

The major elements are constituent elements of the mineralogical phases and therefore of the phases carrying pollution. **Table 2** shows that some major elements can still be leached in non-

negligible concentrations (in particular Ca and S for Sed 2) and therefore release the pollution which was associated with it. However, weakly leached trace elements showed that the dissolved major elements were able to adsorb these free metal ions on their surface sites.

Trace elements (mg.kg ⁻¹)				
	Sed 1	Sed 2	Sed 1	Sed 2
	Dissolved concentrations after leaching test *		Total concentrations in sediment **	
As	0.19 ±0.01	0.04 ±0.01	6.78 ±0.27	37.2 ±0.40
Ba	1.21 ±0.01	0.39 ±0.02	406.31±1.40	412.4 ±7.34
Cd	0.01 ±0.01	0.94 ±0.01	0.67 ±0.05	72.8 ±1.17
Cr	0.07 ±0.01	0.01 ±0.001	44.17 ±0.80	152.0 ±3.90
Cu	0.60 ±0.01	0.26 ±0.01	41.75 ±0.69	165.6 ±2.73
Mo	0.24 ±0.01	0.44 ±0.01	1.30 ±0.01	3.3 ±0.01
Ni	0.22 ±0.01	0.89 ±0.01	19.33 ±0.23	90.0 ±1.67
Pb	0.02 ±0.01	0.07 ±0.01	56.19 ±1.82	573.4 ±12.82
Sb	0.12 ±0.01	0.03 ±0.01	2.75 ±0.15	5.58 ±0.23
Se	0.14 ±0.02	0.09 ±0.03	1.85 ±0.01	1.45 ±0.01
Zn	0.96 ±0.02	32.14 ±0.82	333.24 ±10.60	3,253.2 ±12.20

Major elements (mg.kg ⁻¹)				
	Sed 1	Sed 2	Sed 1	Sed 2
	Dissolved concentrations after leaching test *		Total concentrations in sediment **	
Al	2.18 ±0.16	2.50 ±0.01	25,767.80 ±591.00	52,367.60 ±1,232.10
Ca	635.08 ±4.84	3,324.93 ±47.53	41,137.53 ±628.00	28,921.00 ±1,439.71
Fe	3.73 ±0.12	2.76 ±0.01	19,341.54 ±299.00	61,034.40 ±334.64
K	97.33 ±0.72	60.24 ±0.13	5,599.07 ±100.00	15,683.00 ±503.98
Mg	31.35 ±0.24	216.31 ±2.50	3,612.57 ±58.00	6,388.40 ±132.56
Mn	1.30 ±0.01	42.14 ±0.48	295.66 ±4.29	896.600 ±13.28
Na	79.62 ±1.13	79.41 ±1.10	534.51 ±37.00	1,834.60 ±37.47
P	17.06 ±0.35	2.03 ±0.19	2,217.90 ±53.00	4,502.60 ±98.03
S	426.42 ±5.75	2,712.17 ±3.49	1,889.67 ±44.00	4,931.80 ±122.11
Si	74.53 ±0.48	60.80 ±4.05	151.39 ±34.00	614.40 ±56.81

Table 2 Summary of the chemical composition (mg.kg⁻¹) of sedimentary matrices in trace elements and major elements. Leaching (NF EN 12457-2) and acid digestion (NF ISO 12914) tests are presented.

II. Comparison of monitoring parameters

Sediment 1 was subjected to the EK process varying the processing reagents. These tests are detailed in **ARTICLE 3**. Three tests were thus carried out: EXP.A (DW), EXP.B (CA) and EXP.C (CA + TW20). Sediment 2 was subjected to the same tests (**ARTICLE 4**), noted: EXP.1 (DW), EXP.2 (CA) and EXP.3 (CA + TW20).

The monitoring parameters: pH, electric current intensity and redox, were measured during the EK treatment (method detailed in **chapter 2** - (Betremieux and Mamindy-Pajany, 2021)). **Figure 2**

shows the average results, calculated over the 28 days of treatment. It is reminded that three measurements of each parameter were measured twice a day throughout the duration of the tests.

Regarding pH, the values indicate a relatively neutral pH for the experiments carried out with sediment 1, whatever the reagent used (except for S1 of the EXP.C). It has been seen in **Tables 1 and 2** (total content) that the carbonate phases are predominant in Sed 1. Carbonates tend to buffer the pH in more alkaline ranges (Blanchard, 2000; Tian, 2018). This would explain the relatively neutral pH values.

In the Sed 2 experiments, the reagents succeeded in varying the pH of the sediment pore water in all three sections. These variations are due to the electrolysis reactions of water at the level of the electrodes (Chapter 1). They reduced the pH in the section near the anode (S1) and increased it in the section near the cathode (S3) when no acid reagent was added. The acid reagents added to EXP.2 and EXP.3 lowered the pH, and even more when citric acid was used alone (EXP.2). The mineralogical composition of Sed 2 did not buffer the pH of the pore water.

Regarding the intensity of the electric current, the treatment reagents have a significant importance because they add ions to the solution, thus increasing the intensity of the electric current. However, **Figure 2** shows that the matrices also have an impact on this parameter. For example, for the experiments carried out with citric acid alone (EXP.B for Sed 1 and EXP. 2 for Sed 2), the EXP.B shows much higher electrical intensity values than Sed 2. The same is true for the experiments with the acid and the surfactant (EXP.C and EXP.3). Conversely, with DW, the values measured for Sed 2 are higher than for Sed 1. Overall, the differences in electrical intensity measured for an experiment carried out with the same reagent, but with a different matrix, are relatively large. A difference of 7.43 mA is observed if we compare the S1 of the EXP.A and EXP.1 (DW), 16.88 mA of difference for the EXP.B and EXP.2 (CA) and finally, 11.20 mA of difference for the EXP .C and EXP.3 (CA + TW20). Sediment 2 showed that trace elements had a less mobile leaching behaviour than sediment 1 (**Table 2**), which is why the soluble ions of Sed 1 were able to increase the intensity of the electric current by enriching the liquid phase. In addition, the higher quantity of the retention phases in Sed may have retained the chemical elements on the solid particles and thus reduce the concentration of elements present in the liquid phase (S Pamukcu and Wittle, 1993).

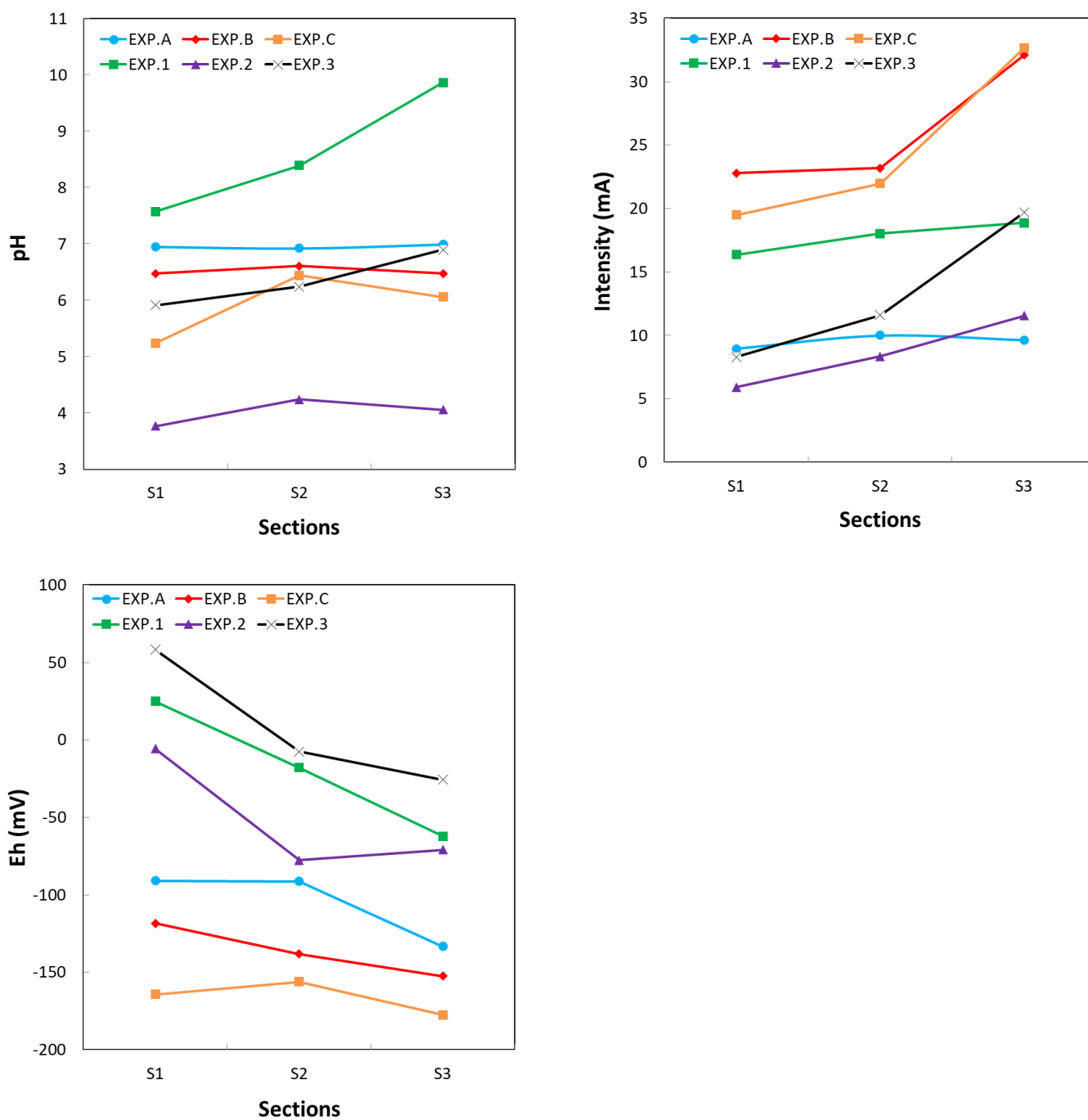


Figure 2 Comparison of EK monitoring parameters (pH, current intensity and redox). The monitoring parameters were measured on three sections (S1, S2 and S3), for three electrokinetic experiments: EXP.A, EXP.B and EXP.C for sediment 1 and EXP.1, EXP.2 and EXP.3 for sediment 2.

Concerning the redox potential values (Eh), all experiments showed a reducing medium during the EK tests for Sed 1. This is generally the case for Sed 2, except in S1 of EXP.1 and EXP.3. As for the intensity of the electric current, the measured variations are important. For example, for the S1, a difference of 115.92 mV is observed if we compare the EXP.A and EXP.1, 112.73 mV difference for the EXP.B and EXP.2 and finally, 222.61 mV difference for the EXP.C and EXP.3.

The redox potential gives an idea of the speciation of chemical elements (their chemical form). Moreover, [Pamukcu and Wittle \(1993\)](#) explain that for As, its availability increases when it is in the form of arsenite (As (III)) in a reducing medium and at basic pH. When the redox potential is high (oxidizing state), the majority of As is in the form of arsenate (As (IV)) making it less soluble than As (III), and tends to retain it on surfaces of oxides of clay minerals.

Reducing conditions can lead to the dissolution of iron and manganese oxyhydroxides, releasing the pollutants bound to them ([Davranche and Bollinger, 2000](#)). It would then appear that the more reducing conditions measured in the sediment 1 experiments are favourable to an efficient electromigration of the soluble ions, associating less well with the retention sites.

III. Comparison of leaching and total trace element removal results

Table 3 shows the results of removal (%) trace element for the two sedimentary matrices, according to the three analysis sections and the three experiments carried out. The upper part shows the results after leaching tests, while the lower part shows the results after acid digestion.

Concerning the total content (acid digestion) pollution, it can be seen that the trace elements were better mobilized from the solid phase for Sed 2, with greater removal rates (**Table 3**). The enrichments observed in the solid phase for the experiments conducted with Sed 1 are less important than with the Belgian matrix (Sed 2).

If we compare the solid phase removal rates of EXP.A and EXP.1 (DW), we notice that the elements As, Ba, Cd, Mo, Sb and Se were more efficiently mobilized from Sed 1 by the treatment EK. It should be noted that trace elements are present at lower concentrations in Sed 1. However, the results seem to support the remark made previously. The pH of the medium in EXP.1 has not decreased enough to attack the carrier phases (due to the electrolysis reactions of the water) and therefore the many retention sites have retained the pollution, not allowing for more interesting removal rates than the EXP.A.

For EXP.B and EXP.2, the pH having been significantly reduced during EXP.2, this made it possible to reduce the total content of the elements As, Cd, Cr, Cu, Mo, Ni, Pb and Zn more efficiently than in EXP.B. The carrier phases have been deteriorated, thus releasing the pollution associated with

them. Dilute acids partially solubilise the trace elements associated with exchangeable fractions, carbonates, oxides of iron or manganese and on organic matter (Blanchard, 2000).

For EXP.C and EXP.3, although the pH of the medium was not sufficiently acidic for both experiments, EXP.3 obtained better removal rates than EXP.C, despite the more numerous adsorption sites (Table 1). This is probably due to the complexing properties of citric acid and tween 20. The TW20 made it possible to lower the surface tension of the solid particles, while the citric acid complexed with the soluble elements, thus enriching the liquid phase (Table 3). The more heavily contaminated sediment 2 therefore released more pollution, thus further enriching the liquid phase compared to Sed 1.

Concerning the abatement rates obtained after the leaching tests, it can be seen that there is an increased mobility of trace elements for Sed 2 (Table 3). The enrichments observed in the liquid phase are greater when the acidic and complexing reagents are used (EXP.2 and EXP.3). This increased mobility of the elements tends to prove that the retention phases have been solubilized by the acidic pH of the medium (Figure 2) or that the reagents (citric acid and tween 20) have complexed the chemical elements. The TW20 lowers the surface tension of solid particles (Ammami et al., 2013), thus making the elements more mobile. Therefore, liquid phase mobility is often increased when this reagent is used (Table 3).

Leaching tests	Sed 1									Sed 2								
	EXP.A			EXP.B			EXP.C			EXP.1			EXP.2			EXP.3		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	79.2%	49.7%	51.2%	-96.8%	74.0%	46.3%	-243.9%	55.5%	-91.2%	-184.6%	-227.3%	-783.7%	-3412.2%	-5372.0%	-7629.3%	-9667.1%	-13356.1%	-15109.8%
Ba	75.9%	76.8%	78.4%	-348.3%	76.3%	67.9%	43.8%	19.0%	28.1%	-20.6%	0.9%	56.8%	-1959.2%	-941.6%	-3580.6%	-4235.3%	-4510.5%	-4817.4%
Cd	16.7%	16.7%	16.7%	-506.7%	-100.0%	-100.0%	-5806.7%	-50.0%	-50.0%	69.3%	80.2%	98.6%	-109.9%	-128.3%	-426.9%	-1249.5%	-827.6%	-992.3%
Cr	93.2%	93.2%	32.4%	-4318.4%	85.1%	48.5%	-9902.4%	-279.8%	-926.3%	-173.3%	-358.3%	-1886.7%	-144500.0%	-100016.7%	-175183.3%	-481966.7%	-336000.0%	-260200.0%
Cu	78.4%	78.4%	65.0%	27.8%	62.9%	75.8%	-158.5%	82.2%	74.7%	-20.9%	-11.7%	-203.3%	-858.2%	-781.1%	-2455.4%	-2403.2%	-2574.5%	-3289.6%
Mo	11.7%	17.7%	-5.1%	89.0%	39.3%	48.7%	91.3%	69.3%	62.9%	-59.7%	-40.7%	15.8%	51.7%	-2.7%	40.2%	50.2%	19.7%	4.8%
Ni	60.4%	63.8%	68.6%	-171.0%	64.4%	-9.6%	-759.6%	0.6%	-136.4%	56.3%	70.7%	79.4%	-71.7%	-86.4%	-448.2%	-290.4%	-612.9%	-1252.1%
Pb	32.5%	32.5%	32.5%	-3267.0%	40.0%	40.0%	-2804.5%	-12.5%	-767.0%	80.3%	80.3%	80.3%	-23863.3%	-14490.4%	-53587.5%	-121811.0%	-115037.9%	-127760.1%
Sb	10.7%	15.7%	37.2%	4.8%	75.6%	34.5%	76.4%	50.1%	-26.4%	-111.9%	-106.7%	-163.9%	-505.3%	-377.2%	-598.2%	-964.9%	-849.1%	-835.1%
Se	66.5%	66.5%	66.5%	33.3%	69.0%	35.8%	-13.5%	-11.1%	-12.5%	59.4%	59.4%	59.4%	54.4%	14.4%	-38.3%	-89.9%	-49.8%	-96.5%
Zn	95.4%	92.7%	92.0%	-1519.0%	96.0%	69.1%	-8812.1%	28.3%	-509.1%	68.2%	87.8%	99.5%	-118.9%	-139.7%	-504.9%	-488.8%	-1306.4%	-1060.0%

Acid digestion tests	Sed 1									Sed 2								
	EXP.A			EXP.B			EXP.C			EXP.1			EXP.2			EXP.3		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	17.4%	19.3%	15.7%	5.3%	7.7%	-2.8%	-3.4%	56.5%	1.4%	4.3%	4.8%	2.7%	56.3%	34.4%	49.8%	50.4%	23.7%	23.0%
Ba	69.2%	69.2%	70.4%	72.5%	71.5%	71.5%	70.4%	72.6%	75.6%	16.1%	18.8%	18.7%	10.3%	9.5%	20.1%	13.6%	17.8%	16.8%
Cd	32.9%	40.2%	36.2%	-22.6%	-12.3%	-12.8%	-22.9%	-18.0%	-3.5%	5.2%	3.6%	1.9%	62.0%	37.6%	53.5%	67.8%	32.6%	30.1%
Cr	6.6%	5.5%	8.8%	7.5%	6.1%	6.6%	0.5%	3.4%	13.2%	13.2%	14.7%	14.6%	38.4%	28.5%	36.8%	39.6%	32.4%	34.1%
Cu	-28.0%	-27.0%	-24.3%	-20.5%	-15.0%	-26.1%	-26.8%	-16.6%	-20.5%	-5.6%	-4.5%	-5.4%	4.8%	-8.5%	1.5%	30.1%	-1.8%	-3.9%
Mo	53.8%	53.8%	53.8%	0.0%	0.0%	0.0%	-42.3%	-42.3%	-42.3%	-2.4%	65.2%	65.2%	47.0%	47.0%	47.0%	47.0%	47.0%	47.0%
Ni	-5.4%	-5.0%	-2.8%	-8.3%	-6.1%	-5.7%	-27.8%	-6.4%	0.9%	7.8%	7.6%	2.7%	41.0%	25.7%	36.4%	45.6%	28.1%	21.3%
Pb	2.1%	2.5%	3.0%	1.2%	5.2%	2.0%	-3.6%	8.6%	7.2%	13.5%	11.4%	16.2%	47.7%	27.7%	46.8%	26.2%	19.8%	19.7%
Sb	49.1%	56.4%	56.4%	47.3%	47.3%	47.3%	45.5%	-21.3%	45.5%	-5.4%	8.6%	17.6%	32.3%	27.2%	34.1%	31.5%	17.6%	25.1%
Se	-27.0%	16.2%	16.2%	-18.9%	-18.9%	-18.9%	-27.0%	-27.0%	-27.0%	-3.4%	-3.4%	-3.4%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%
Zn	-4.0%	-2.7%	-0.2%	-2.1%	3.8%	4.1%	11.7%	4.5%	8.2%	9.3%	7.4%	5.1%	77.3%	51.9%	67.5%	88.7%	43.7%	41.5%

Table 3 Removal rates calculated for the three experiments of the two matrices studied, according to the three sections (S1, S2 and S3) of sediment. Leaching (NF EN 12457-2) and acid digestion (NF ISO 12914) tests are presented. Negative values represent enrichments in total content, and an increase in leaching mobility.

IV. Conclusion

Despite identical experimental conditions (duration of treatment, intensity delivered, treatment reagents), the physico-chemical difference of the sedimentary matrices showed important differences in the fate of trace elements. Indeed, this impacted parameters such as the pH, the intensity of the electric current and the Redox of the medium during the EK experiments. These parameters are essential in controlling the mobility of the elements, but also in the effectiveness of the EK treatment (**Chapter 1**).

Sed 2, which presents a higher overall pollution than Sed 1 (and in particular in Zn) actually contains more adsorption sites; such as oxides of Fe and Al but also a higher MO content. The particle size is also finer and then more easily retains trace elements due to its large specific surface. However, the matrix is less rich in carbonate elements. This allowed greater pH variations throughout the sedimentary matrix (In S1, S2 and S3). These pH variations allowed the dissolution of the carrier phases when the acid reagents were used, greatly increasing the mobility of the elements in the liquid phase (leached). The solid phase is thus devoid of pollution, with quite interesting removal rates. Up to 88.7% reduction for Zn, 67.8% for Cd, 56.3% for As... However, for the EXP.3, the pH measured during treatment is not as acidic as for the EXP.2, but the mobility of the elements has been greatly improved. This is probably due to the complexing properties of citric acid and tween 20. The TW20 lowered the surface tension of the solid particles, while the citric acid complexed with the soluble elements, thus enriching the liquid phase.

Sed 1 with its greater quantity of carbonate phases, did not reveal pH variations as great as those measured for Sed 2. Carbonates, with their buffering capacity, did not allow an efficient acidification of the medium. The carrier phases were therefore not solubilised and therefore reduced the mobility of the elements in leaching compared to Sed 2.

In conclusion, we were able to highlight the impact of the physicochemical characteristics of the sedimentary matrix. In addition, the heterogeneity of the sediments is a characteristic to be kept in mind when interpreting the results.

**CHAPTER 4 - INCREASING THE ELECTRIC CURRENT
INTENSITY WITH ACTIVATED CARBON AND MEASURING
THE IMPACT ON TRACE ELEMENT MOBILITY**

Activated carbon coupled with electrokinetic method, using citric acid and Tween20 in enhancing the remediation of trace elements waterways sediment

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Abstract

Trace metals, from anthropogenic pollution, are leached by rainwater, run off with eroded particles and are then trapped in river and marine sediments. These contaminated materials then pose many problems and challenges, from an environmental, health, economic and legislative perspective. This article focuses on the ElectroKinetic (EK) remediation technique, enhanced with activated carbon. Two particle sizes (D2 mm and D6 mm) of activated carbon particles (AC-p), mixed with a contaminated sediment matrix, were used as a third electrode. Leaching and total content analysis was performed on the carbon particles (D6 mm), but also on the EK treated sediment.

The results showed that AC-p had a positive effect on the electric current intensity, with an increase in electric current of 250% for D2mm AC-p and up to 1169% for one of the experiments with D6mm AC-p. In addition, the D6mm AC-p increased electro-osmotic flow (EOF) rates and promoted flow in the conventional direction when acid reagents were used. Overall, the difference in particle size of the AC-p showed significant differences on the EK parameters. The larger particle sizes (D6 mm) showed higher efficiency on: pH (more acidic), redox (less reducing), electric current intensity and EOF. Nevertheless, the remediation results (%R) obtained in the solid and liquid phase were sometimes more interesting when the 2mm carbon particles were used. Using the conductivity of activated carbon could be an interesting economic alternative, to use less electric current in EK tests. However, a large variety of sediments, activated carbons and reagents (citric acid and surfactants) should be tested in order to identify the optimal conditions.

Keywords : River sediment, electrokinetic, inorganic pollution, remediation, activated carbon

I. Introduction

Although ElectroKinetic (EK) remediation is recognized as an effective method in the literature, the previous chapters have shown that the method sometimes seems to show limitations in its ability to mobilise trace elements from the aqueous phase (**ARTICLE 2 and ARTICLE 3**). Indeed, EK transport mechanisms do not seem to be strong enough to remove pollutants from the leachable phase. It is therefore necessary to try to improve these transport mechanisms during the treatments, in order to allow an efficient removal of the pollution in the anodic and cathodic overflows. As electromigration is considered to be the dominant mechanism in the literature ([Benamar et al. 2019](#)), an improvement in electroosmosis could combine with the effects of electromigration and thus be beneficial to treatment. Furthermore, the results of a previous study (**ARTICLE 2**) highlighted the link between the electrical intensity of the medium and the mechanisms of electromigration and electroosmotic flow (EOF). In order to optimise EK treatments, a third electrode, in the form of activated carbon particles (AC-p), was developed in this work. Due to the conductive properties of the carbon the electric current would be better distributed in the sediment matrix and could have a direct influence on the increase of the electric current intensity, and probably an influence on the removal rates by promoting the flow and elimination of elements in the anodic and cathodic overflows.

In other circumstances, activated carbon has already been used in the literature to the treatment of organic and inorganic substances from industrial wastewater ([Xiong & Karlsson 2002](#), [Wang et al. 2007](#), [L. Yan et al. 2011](#), [Neti & Misra, 2012](#)), but also in soils ([Yan et al. 2018](#), [Xie et al. 2021](#)) and even electronic waste ([Zhang, 2021](#)). However, few studies have been applied to electrokinetic treatment of dredged sediments. Activated carbon is often used in plate form rather than granular form. It is also used as an adsorbent barrier in the literature and the impact of its conductive properties is not highlighted.

The aim of this work is therefore to use activated carbon particles (AC-p) as a 3rd electrode, in order to improve the transport mechanisms under the immediate influence of the electric current, and thus to limit the accumulation of elements that can occur. Two grain sizes (D2 mm and D6 mm) were mixed with a sedimentary matrix particularly contaminated with zinc. A characterisation of leached (liquid phase) and mineralised (solid phase) trace elements was carried out on the carbon particles (D6 mm only), but also on the sediment treated by the

EK method. Monitoring of the physico-chemical parameters during treatment was also conducted, as well as analysis of the effluents recovered from the anode and cathode overflows.

II. Materiel and method

II.1. Materials and chemical

The activated carbon particles (AC-p) were purchased from Europrix, located in Lens (Haut-de-France, France). This carbon is suitable for use in contact with weak acids, in order to avoid its disintegration during treatment. The sediment sample is particularly contaminated with Zinc and was collected in a waterways from Belgium. It was stored in sealed bags at 5 °C. All chemicals used in this study were of analytical quality, and the water used in the experiment was deionised. More specific information is given in a previous work (**ARTICLE 2**).

II.2. ElectroKinetic remediation experiments

The setup used for the EK experiments is shown in **Figure 1**, and is exactly the same as that presented in a previous study ([Betremieux and Mamindy-Pajany, 2021](#)). This setup consists of two main parts: the central chamber, for processing the sediment and the side compartments for electrodes. The central chamber was divided into 3 equal sections (S1, S2 and S3) from anode to cathode. Graphite plates were used as the electrodes at the anode and cathode, while activated carbon particles (AC-p) were used as the third electrode and mixed with the sediment matrix. After being sieved through a standard 6 mm sieve, the AC-p was mixed into the 2 mm sieved sediment matrix using a laboratory agitator. Carbon particles were added to the sediment volume at 10 % of the dry volume, and then the mixture was inserted into the EK treatment cell (**Figure 1**). The mixture was left for 72 h in contact with the treatment reagents, before starting the depollution tests. After the remediation tests, the sediment is divided into 3 sections as shown in **Figure 1**.

Three experiments were conducted for this work using 6 mm diameter of AC-p size, under a continuous voltage of 14 V and an injection flow rate of 60 mL.h⁻¹ for the treatment reagents. The reagents used for these tests were: demineralised water (DW) for EK.1, citric acid (CA : 0.1 mol.L⁻¹) for EK.2 and citric acid combined with Tween20 (CA+TW20 : 0.1 +

0.04 mol.L⁻¹) for the last experiment EK.3. For fine carbon (D2 mm), one test were conducted, using DW (EK.4). **Figure 1** shows the experimental protocol used.

After the treatment, the sediment is sieved to 5 mm so that the 6 mm AC-p can be collected and analysed separately from the sediment at the end of the treatment. The results presented in this article can be compared with those reported in a previous work (**ARTICLE 3**), as the experiments are the same, except that the sediment was not mixed with AC-p.

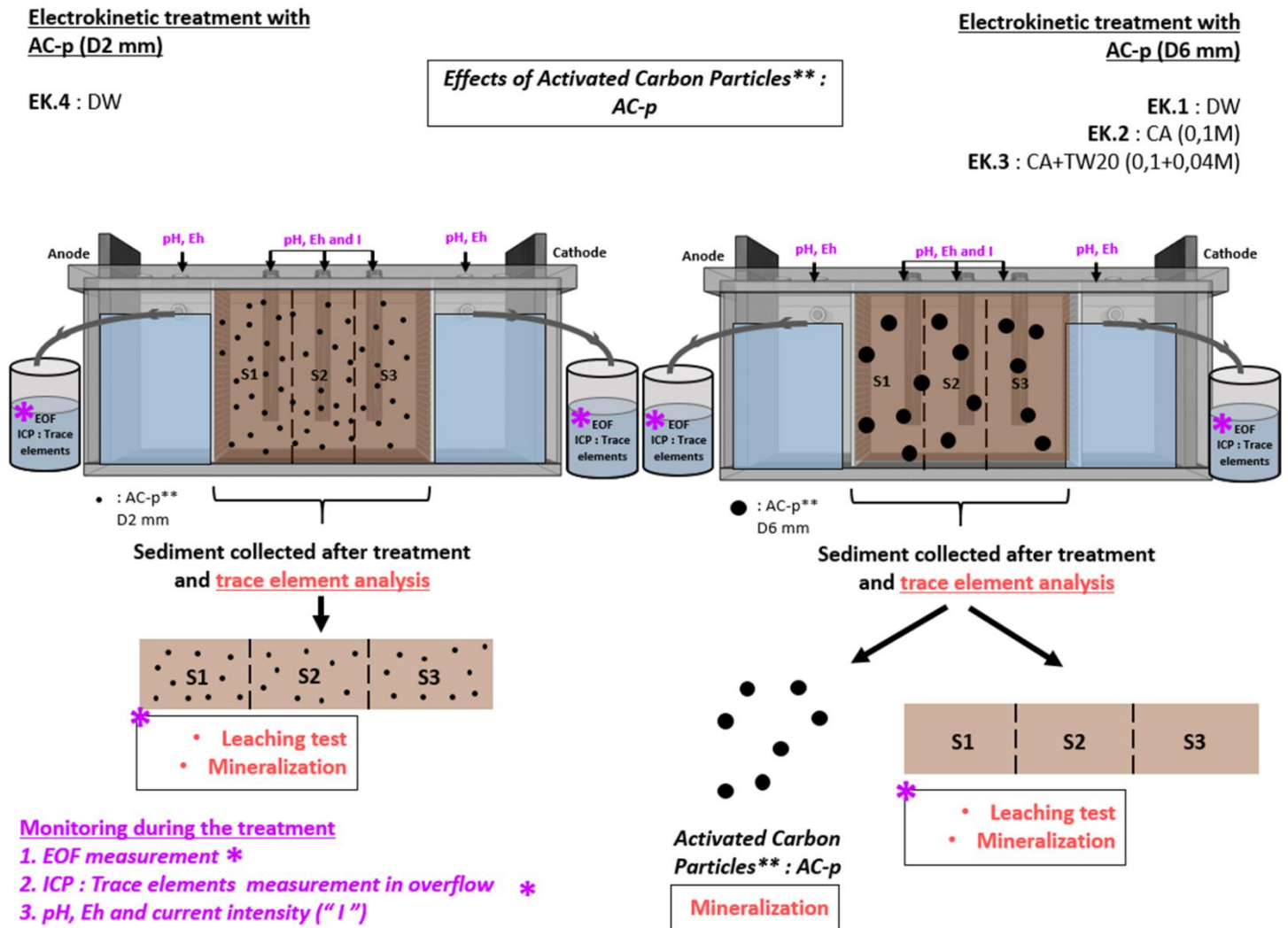


Figure 1 Schematic representation of the electrokinetic tests and the experimental cell installation. (Adapted from the **Figure 1** presented in "General introduction").

II.3. Analytical methodology

Electric current, pH and redox were measured in the sediment during the EK treatment. The composition of catholyte and anolyte were characterized as function of test

duration with the 5110 model of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) coupled to an SPS4® autosampler (Agilent technologies®). Total and leached concentrations of trace elements (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn) were carried out by microwave (Mars®, CEM Corporation) and ICP-OES respectively. The efficiency of inorganic elements removal was calculated as following Equation (1) :

$$\%R = \frac{C_i - C_f}{C_i} \times 100\% \quad \text{Eq (1)}$$

With:

$\%R$: Removal rate, expressing the depollution of trace elements;

C_i : Initial concentration;

C_f : Final concentration (after EK treatment);

III. Results and discussion

III.1. Initial state

III.1.1. Raw sediment

The elementary composition of the sediment was determined and is shown in **Table 1** below. The sediment used has a moisture content of 11.2 % and an indicative organic matter (OM) content of 23.38 %, as determined by the loss on fire test at 550 °C. X-ray fluorescence analysis (**Table 1**) shows that the sediment contains a large amount of Silica (silicon dioxide) at 44.73% and alumina at 23.63%. Iron oxide and potassium oxide are also present in significant proportions. These tests are detailed in the article by [Betremieux & Mamindy-Pajany \(2021\)](#).

	Mineralization* (acid digestion)		Leaching test** pH = 6.8		Major elements (oxides)	
		SD		SD	Mass	Oxides percentages (%)
As	37.20	±0.40	0.04	±0.01		
Ba	412.40	±7.34	0.39	±0.02	Na₂O	0.70
Cd	72.80	±1.17	0.94	±0.01	MgO	1.39
Cr	152.00	±3.90	0.00	±0.01	Al₂O₃	23.63
Cu	165.60	±2.73	0.26	±0.01	SiO₂	44.73
Mo	3.30	±0.01	0.44	±0.01	P₂O₅	0.25
Ni	90.00	±1.67	0.89	±0.01	K₂O	3.93
Pb	573.40	±12.82	0.07	±0.01	CaO	1.43
Sb	5.58	±0.23	0.03	±0.01	TiO₂	0.81
Se	1.45	±0.01	0.09	±0.03	Fe₂O₃	5.62
Zn	3,253.20	±12.20	32.14	±0.82	Br	1.13

Table 1 Summary of physico-chemical characteristics of the tested sediment, adapted from Betremieux and Mamindy-Pajany (2021) – **ARTICLE 3**, after the acid digestion analysis with *aqua regia* (NF ISO 12914)* and batch leaching test in DW (NF EN 12457-2)**.

III.1.2. Raw activated carbon

The elemental composition of the 6 mm raw activated carbon was studied and is presented in **Table 2** below. Knowing the initial state of the activated carbon particles prior EK remediation will reveal the proportion of chemical elements adsorbed onto the carbon particles. For the fine AC-p (D2 mm), acid digestion analysis and leaching tests showed concentrations below the quantitative limit (<QL) for the 11 trace elements studied. Therefore, the data are not presented in **Table 2**.

Leaching tests were carried out with other reagents such as citric acid (0.1 mol.L⁻¹) and citric acid and tween20 (0.1 + 0.04 mol.L⁻¹), to visualise the impact of acidifying reagents on the carbon particles. The acidic reagents permitted a better mobility of trace elements and more so when the TW20 surfactant was used.

Granulometric curves were carried out on the two types of activated carbons (**Figure 2**), in order to calculate the D10 and D60. These two values are used to define the Cu (Uniformity Coefficient) according to the French standard NFP 18-540 ([Thior et al., 2019](#)). The Cu of the 6mm AC-p is 1.349 and the Cu of the 2mm carbon is 1.455. If the uniformity coefficient is less than 3, the grain size is considered uniform ([Thior et al., 2019](#)).

	Mineralization* (acid digestion) (mg.kg-1)	<i>SD</i>	Leaching** with DW pH = 8.05 (mg.kg-1)	<i>SD</i>	Leaching with CA (mg.kg-1)	<i>SD</i>	Leaching with CA+TW20 (mg.kg-1)	<i>SD</i>
As	4.4	± 0.01	0.11	± 0.01	0.55	± 0.01	0.99	± 0.02
Ba	55.7	± 2.49	0.81	± 0.02	6.59	± 0.38	6.81	± 0.12
Cd	0.4	± 0.01	0.01	± 0.01	0.02	± 0.01	0.03	± 0.01
Cr	2.7	± 0.37	0.00	± 0.01	0.06	± 0.01	0.08	± 0.01
Cu	3.1	± 0.48	0.02	± 0.01	0.41	± 0.03	0.52	± 0.01
Mo	3.5	± 0.01	0.09	± 0.01	0.09	± 0.01	0.09	± 0.01
Ni	5.3	± 0.73	0.05	± 0.01	0.10	± 0.01	0.10	± 0.01
Pb	24.9	± 2.57	0.03	± 0.01	1.53	± 0.03	1.60	± 0.09
Sb	2.3	± 0.01	0.06	± 0.01	0.06	± 0.01	0.06	± 0.01
Se	3.3	± 0.01	0.08	± 0.01	0.54	± 0.02	1.22	± 0.01
Zn	34.5	± 1.22	0.11	± 0.05	5.06	± 0.18	6.58	± 0.24

Table 2 Behaviour of 6 mm raw activated carbon particles, after the acid digestion analysis (NF ISO 12914)* and after leaching test (NF EN 12457-2)* and QL correspond to “Quantitative Limit”.

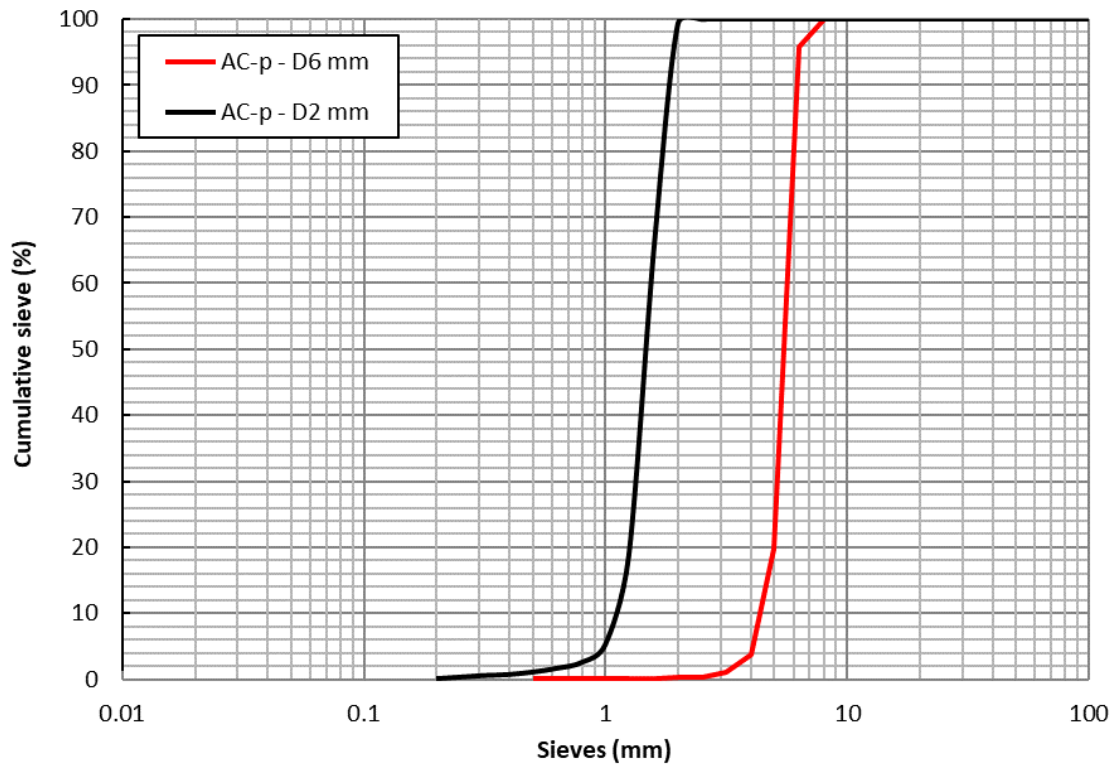


Figure 2 Granulometric curves of both AC-p (D2mm and D6 mm).

III.2. Monitoring: evolution of background parameters with the added amendment

III.2.1. Sediment pH and Eh during EK treatments

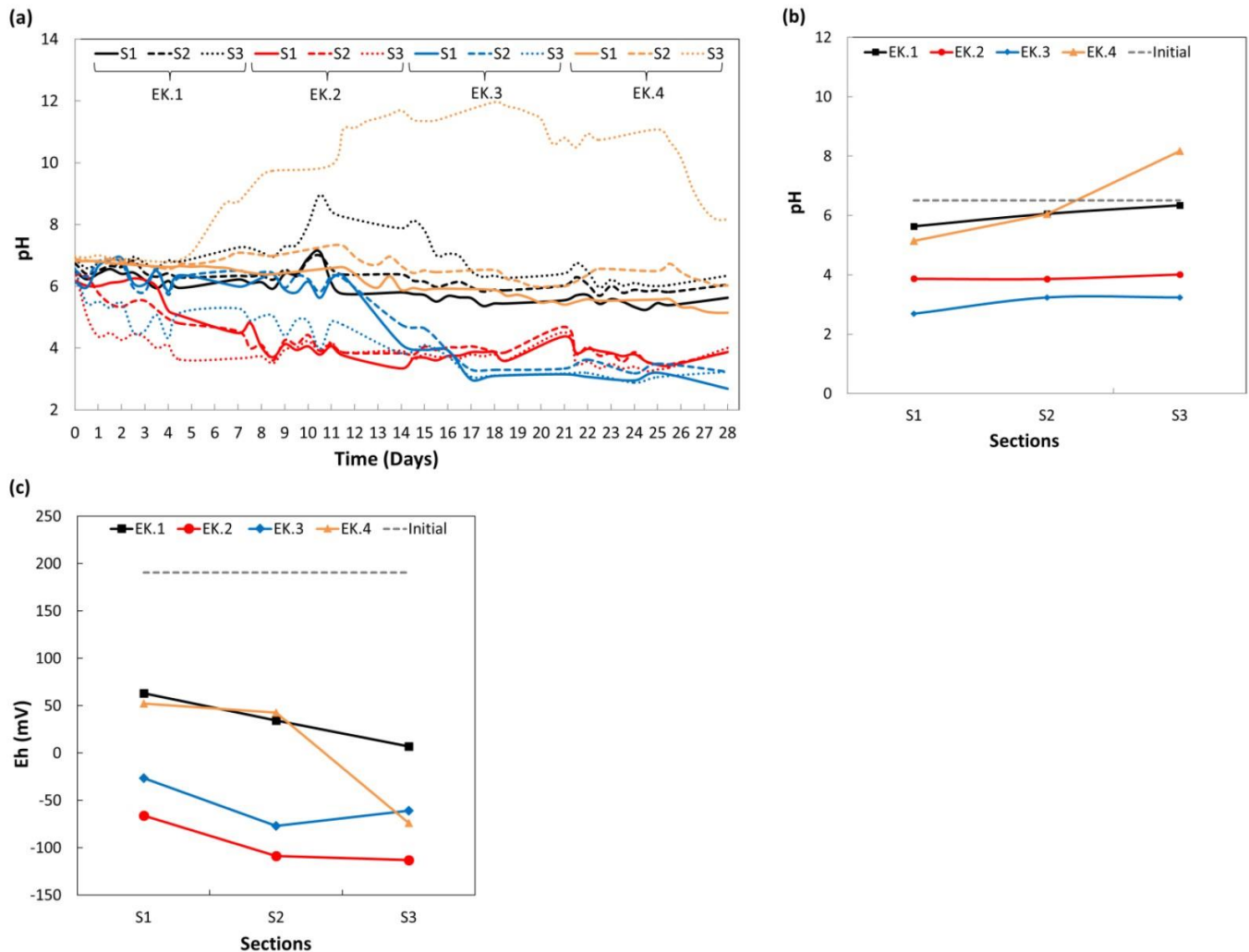


Figure 3 Distribution of pH value along the sediment specimen (S1, S2 and S3) during the EK tests (a), pH values at the end of EK tests into the three sections (b), and average representation of the redox potential (Eh), measurements into the pore water of the sections S1, S2 and S3 for the 3 experiments (c).

Figures 3a and **3b** show that without acid additive (test EK.1 and EK.4), water electrolysis generated H^+ ions in the anode compartment, which decreased the pH of the sediment pore water (**Figure 3b**) from 6.51 to 5.63 and 5.14 for EK.1 and EK.4 respectively in the section close to the anode (S1). At the same time the OH^- ions generated in the cathode compartment did not allow a significant increase of the pH in S3 compared to the initial pH

value for the 6 mm carbon experiment (EK.1). However, for fine AC-p (D2 mm), the effect of pH was more marked in S3. The pH increased from 6.51 to 8.2 at the end of the treatment (EK.4).

When citric acid (CA) was added (tests EK.2 and EK.3), a decrease in pH affected the whole medium (S1, S2 and S3). Contrary to some authors (Song et al., 2016, Benamar et al., 2019), acidification was effective in all sections (Figure 3b), even those in the center of the sample and close to the cathode. The main purpose of acidification of sediments by the use of additives is to dissolve cationic trace metal contaminants. Indeed, pH was found to be the main factor determining the solubility of trace metals (Chuan, Shu, and Liu, 1996). At low pH, contaminants are desorbed from the surface of solid particles, dissolved in the pore fluid and efficiently transported through the sample by electromigration and electroosmotic advection (Yeung and Hsu, 2005). Benamar et al. (2019) used a concentration of citric acid twice as much (0.2 mol.L^{-1}) as that used in this study. However, acidification of the whole sample was not achieved and the pH value ($\text{pH} = 7$) was too high to solubilise the heavy metals. In our study, the pH of the experiments conducted under acid was quite low (Figure 3b): 3.87, 3.86 and 4.01 in S1, S2 and S3 respectively for EK.2 and 2.68, 3.24 and 3.24 for EK.3; it would then appear that the conditions are favourable for efficient solubilisation of metal cations. This difference with the work of Benamar et al. (2019) can be explained by the difference in the study matrix and the heterogeneity of the sediments. A high buffering capacity, produced by the presence of carbonates, delays the acidification of the sediment sample. It was concluded that a longer treatment time could overcome this problem.

Figure 3a shows that time does indeed have a significant impact on the progression of pH differentials within the sediment matrix. For EK.1 conducted under DW, the pH of S3 increases strongly from day 10, then decreases again from day 17 towards a pH close to S1 and S2. The experiment conducted with the fine AC-p (EK.4) globally showed stabilised pH curves in S1 and S2 throughout the test (Figure 3a) and quite close to the values found for these same sections in EK.1 (Figure 3b). However, for S3, although the beginning of the experiment is similar to the EK.1, from the 5th day of treatment, the pH increases strongly until the 18th day (from 7.10 to 12). The pH of the medium in S3 was much more basic in EK.4 conducted with the fine carbon particles (D2 mm). It can be assumed that the bigger AC-p allowed a better migration of H^+ ions to the cathode, enriching S3 earlier in the treatment, and thus cancelling the effect of OH^- ions. The fine carbon particles did not allow enough H^+ ions to migrate to S3 to lower the pH of this section. Only towards the end of the treatment (day 25) did the pH decrease (Figure 3a). In EK.2, which was treated with CA, the

pH decreased significantly during the first 10 days of the test (and even more for S3), before stabilising overall until the end of the treatment. EK.3, conducted with a mixture of citric acid and TW20, shows that the pH profiles in S1 and S2 are stable until day 11, then decrease sharply until day 17 before stabilising until the end of the treatment (28 days). Like EK.2, the pH profile in S3 decreases more sharply in the beginning of the test, before returning to values close to the neighbouring sections. It would then appear that a treatment period of approximately 20 days is the minimum required for EK treatment of sediments. However, longer treatment times seem to be necessary in some cases, particularly when the material contains a large amount of OM and carbonates (Benamar et al. 2019, Betremieux & Mamindy-Pajany, 2021).

If we compare the present data with our previous work (ARTICLE 3), it can be concluded that the AC-p added to the sediment matrix as the 3rd electrode had a significant impact on the reduction of the pH of the sediment pore water for the experiment conducted with the DW. Indeed, the pH was reduced (average calculated over the 3 sections) by 2.8 points for EK.1 and 2.3 points for EK.4. In contrast, the AC-p did not influence the evolution of the pH for EK.2 (CA). Finally, the AC-p reduced the pH of EK.3 (CA+TW20) by 0.23 points. The largest decreases occurred in the section near the cathode. As mentioned above, the comparisons were calculated on the base of a previous work by comparing experiments with the same type of reagent, in order to measure the impact of carbon particles only.

Concerning the redox potential, measured daily (morning and evening), EK.1 showed rather oxidative values, and more so in S1. Values of 63, 35 and 7.2 mV were registered in sections S1, S2 and S3 respectively (Figure 3c). EK.4 (AC-p D2 mm) shows oxidising values in S1 and S2 but reducing values in S3: 53, 43 and -74 mV respectively. The assumption made above seems to be correct, that the bigger carbon particles optimised the progression of H⁺ ions through the cathode because the most reduced environment was measured in S3 of EK.4.

EK.2 and EK.3 showed a reduced environment throughout the sediment sample. EK.2 using CA had the most reduced values (Figure 3c): -66, -109 and -113 mV respectively in the anode to cathode sections, compared to -26, -77 and -61 mV for EK.3 with CA and TW20. The environment is further reduced in the proximity of the cathode (S3), where the reduction reaction takes place during the EK processes. In the same way as with pH, the impact of AC-p was calculated for redox potential using results from a previous study (Betremieux & Mamindy-Pajany - ARTICLE 3). The environment oxidised by an additional 53 points for EK.1 (DW) using carbon particles as the 3rd electrode. It reduced by 45 points for EK.2 and

63 points for EK.3. EK.4 oxidised on S1 and S2 by 27 and 61 points, while S3 reduced by a further 12 points. The AC-p, which conducts electric current, has a significant influence on the redox of the medium. The granulometry of the carbon particles also seems to be important in the EK mechanisms.

III.2.2. Electric current intensity during the EK treatments

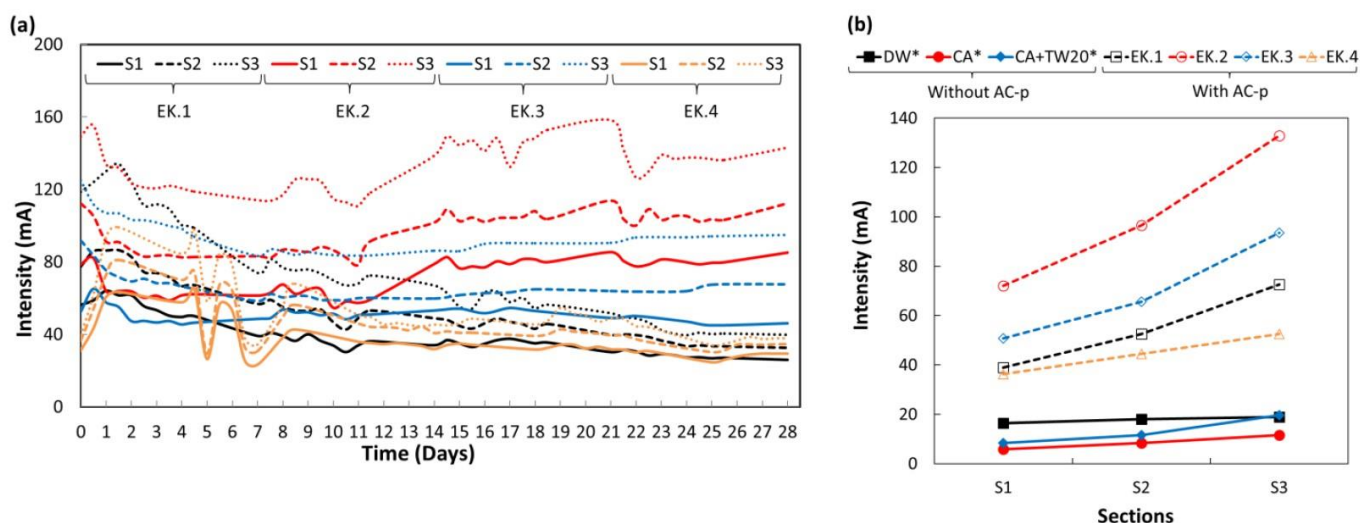


Figure 4 Distribution of electrical intensity along the sediments (S1, S2 and S3) during the EK tests (a), and mean of electric current intensity during the 4 EK tests with AC-p (b). To compare the interest of activated carbon particles on electrical intensity parameter, 3 EK-run (*) from Betremieux & Mamindy-Pajany (**ARTICLE 3**) were added (b).

The overall evolution of the electric current intensity during the EK treatments (**Figure 4a**) showed higher values when acid reagents were used, especially near the cathode (S3) and more when CA was used alone. The current intensity in EK.1 (DW + AC-p D6 mm) decreased overall more rapidly at the beginning of the experiment (until approximately day 10) before reaching more stable values and decreasing gently until the end of the treatment. EK.4 (DW + AC-p D2 mm) showed fluctuations at the beginning of the tests, but the curves stabilized around day 9 and then evolved in essentially at the same manner as EK.1. The test EK.2 (CA + AC-p D6 mm) shows a decrease in electrical intensity in the first two days, (**Figure 4a**) then stabilises until day 11, then increases quite strongly from day 11 to 15, before stabilising again until the end of the treatment. The experiment with TW20 (EK.3) shows a decreasing trend in the electrical intensity curves until day 8 of treatment, then stabilises until the end of the test (day 28).

Figure 4b shows that the average value of the electric current recorded in S1 during the 4 tests was the lowest, and that the closer to the cathode, the higher the current intensity. The electric current values were also higher in the experiments with CA. Indeed, this reagent introduced ionic species into solution and therefore increased the electric current values. In the case of the CA+TW20 mixture, the measured electric current is higher than that of DW but lower than that of CA alone. This is also found by [Ammami et al., \(2014a\)](#) in their work.

In the EK treatments, the electrical intensity values tend to be lower near the cathode chamber, due to a more basic medium generated by the production of OH⁻ ions or the formation of hydroxide or carbonate precipitates near the negative pole ([Colacicco et al., 2010](#)). Here, the cathodic section seems to be more concentrated in soluble ionic species, probably favoured by the acidic pH of the medium (**Figure 3b**) measured in the whole sample for EK.2 and EK.3. However, the neutral pH (pH = 6.34) in S3 of EK.1 and the basic pH (pH = 8.16) of Ek.4 does not seem to correspond to an environment favourable to the solubilisation of ionic species. However, the intensity is also higher than in the other sections. This electromigration could have been favoured by the AC-p. We had seen that the carbon particles had probably improved the migration of H⁺ ions towards the cathode after the analysis of the curves of pH and Eh (**Figure 3**). The evolution of the intensity curves (**Figure 4b**) confirms a little more our hypothesis, that the 6 mm carbon particles promote the electrical transport and the migration of the elements towards the cathode.

Moreover, [Yan et al. \(2018\)](#) have said that the introduction of too many electrode particles caused the formation of numerous small electric fields, which cluttered the electrolyser, thus hindering the electromigration of ions as a whole and thereby reducing the removal efficiency. They make the hypothesis that the excessive addition of electrode particles may result in a short-circuit current and increase the resistance during particle mass transfer, which would lead to a lower removal ratio. Therefore, since small charcoal particles (D2 mm) are more numerous than 6 mm particles, the effect observed would be the same as that deduced by [Yan et al. \(2018\)](#).

A comparison with a previous study shows, on the one hand, that AC-p has a notable interest in the improvement of the electric current within the sedimentary matrix (**Figure 4b**) and, on the other hand, that the experiments carried out with citric acids (EK.2 and EK3) have in this study, presented higher electric intensity values than those measured in the experiment carried out with DW. By comparing experiments conducted under the same type of reagent and on the same sedimentary matrix (**ARTICLE 3**), we obtain a gain of 307 %, 1169 %, 530 % and 250 % of the electrical intensity delivered in the matrix. These values are calculated

over an average of 28 days. This corresponds to about 3, 12, 5 and 2.5 times more than what is measured in the experiments without AC-p (for EK.1, EK.2, EK.3 and EK.4 respectively) (**Figure 4b**).

The electrical intensity would have shown an interesting correlation in a previous study (**Chapter 2**), with notably an acceleration of the EOF in the anodic and cathodic overflows, which have promoted trace elements remediation. For this reason, we have studied these parameters in the next section.

III.2.3. EOF evolution and overflow remediation during the EK treatments

The cumulative EOF curves, presented in **Figure 5**, have for some an increasing trend indicating an overall direction of EOF from the anode to the cathode, while others show a decreasing trend, indicating a reverse direction. This reversal phenomenon was also found by [Benamar et al., \(2019\)](#). The EOF measured at the cathode for EK.1 and EK.4 shows a decreasing trend, while for EK.2 and EK.3 an increase is indicated. In the previous study (**ARTICLE 3**), the EOF of the TW20 experiment was oriented in the opposite direction. The AC-p, combined with CA of the EK.2 and EK.3 experiments, oriented the EOF in the conventional direction.

Although there are increases in the conventional direction, the increase seen for EK.3 is very smooth (**Figure 4a**). The TW20 surfactant then appears to have inhibited the progression of the flux. The addition of TW20 made the reagent more viscous, thus decreasing the porosity of the sediment. This more compact structure therefore slowed the EOF ([Pazos, et al. 2011](#)).

Some authors certify that the EOF is dependent on the electric current ([Hamed & Bhadra 1997](#), [Yuan et al. 2016](#), [Tang et al. 2020](#)), and a previous study showed that EOF was correlated with electric current intensity (**ARTICLE 2**). High electric current, coupled with high EOF, was responsible for solubilized ion migration to the anodic and cathodic overflows. Looking at the cathodic electroosmotic flow rates ($\text{mL}\cdot\text{h}^{-1}$) obtained for each of the experiments, it appears that the activated carbon improved the EOF rate significantly, compared to the experiments in the work of **Chapter 3 (ARTICLE 3)** conducted without the carbon particles. EK.1 improved the electroosmotic flow rate by 1806 %, EK.2 by 1714 % and EK.3 by about 30 %. In contrast, small AC-p did not improve flow rates in the EK.4. The EK.3 performed with TW20 shows a significantly lower flow rate than those obtained in the

other experiments, and reinforces the hypothesis that TW20 inhibits EOF progression, probably due to the viscosity of the reagent.

The improvement in EOF, coupled with the increase in electrical current delivered to the matrix, would normally improve the extraction of trace elements from the system overflows and thus improve removal rates. This hypothesis will be discussed in the following paragraphs.

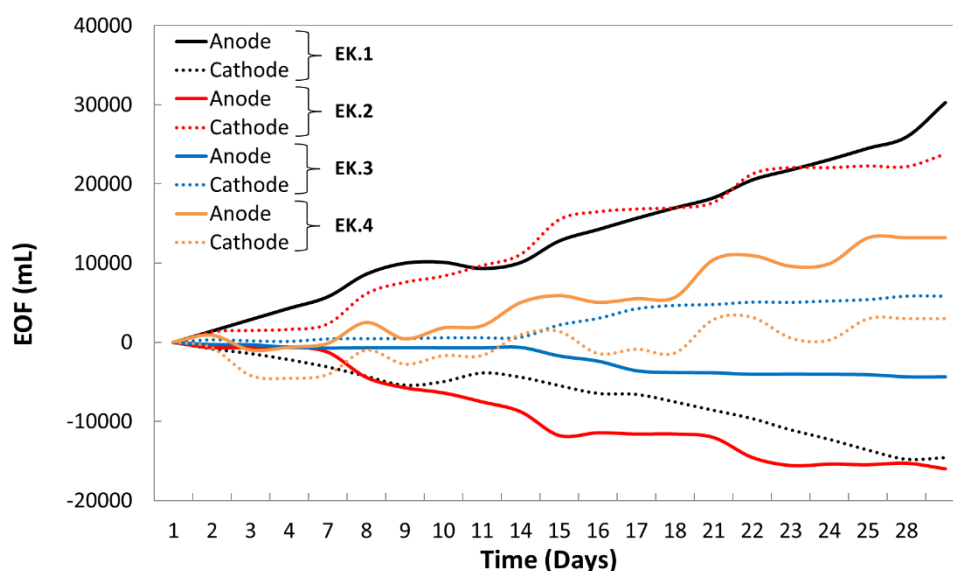


Figure 5 Time evolution of the cumulative EOF into the electrolyte compartments (anode and cathode), for the 4 Ek-tests.

Figure 6 shows the concentrations of the 11 trace elements studied in the liquid effluent (anode and cathode) during each EK treatment. EK.1 and EK.4 did not allow a high extraction of trace elements. However, for the experiments with CA, the extractions were more efficient. Indeed, EK.2 (CA + AC-p D6 mm) shows significant extractions, mainly in the anode compartment: Zn>Pb>Cr>Cu>Ni>Cd>Ba>As>Se>Mo>Sb. Extractions peaks are generally measured around day 10 and 22 (**Figure 6**), coinciding with the increase in electrical intensity (**Figure 4a**) and the decrease in pH (**Figure 3a**).

For EK.3, larger extraction peaks are measured on day 15 in the anode compartment: Zn>Pb>Cr>Cu>Cd>As>Ni>Ba>Se>Mo>Sb. This time is consistent with the significant decrease in pH observed in **Figure 3a**. However, the principal migration of trace elements is not occurring in the direction of the EOF. Indeed, the flow of EK.2 and EK.3 is rather towards the cathode (**Figure 5**), and the concentrations recovered in the overflows are predominantly on the anode side. This can also be observed in a previous work (**ARTICLE 3**). It would

seem that the migration of trace elements takes place in the opposite direction of the electroosmotic migration.

Calcium ions can be released from the surface of the activated carbon during the remediation process. These added calcium ions strongly increase the adsorption of metal pollutants and neutralise the negative charges of the functional groups on the surface of the carbon, but also the negative charges from the elements already adsorbed, thus improving the adsorption yields of anionic micropollutants on activated carbon (Mazet et al. 1988).

When a constant voltage is applied, the semi-conducting behaviour of carbon (Zanjani et al. 2012) increases the temperature in the medium by lowering the resistivity. Temperature is an important parameter that can influence the electrokinetic remediation process, affecting conductivities, ionic mobility's, electro-osmosis and sorption reactions in a way that can enhance or delay pollutant removal (Baraud et al. 1999). Baraud et al. (1999) have experimentally shown that increasing temperature enhances cationic transport as well as anionic movement. Increasing the temperature would increase the adsorption capacity of carbon (Marzal et al. 1996). However, it seems that the increase in electrical intensity in the sediment can increase the temperature of the medium and cause dehydration, unfavourable to the EK treatment (Tian, 2018). Nevertheless, despite the increase in electrical intensity, no dehydration was observed in this study.

The AC-p did not allow to the trace elements studied to be removed to a greater extent. Indeed, when compared with the **ARTICLE 3**, the concentrations found in the anodic and cathodic outlet reservoirs were lower than in the experiments conducted without the addition of particles. It is possible that this decrease is due to the adsorbent properties of the activated carbon, having adsorbed the chemical elements and thus decreased the available quantity that could electromigrate to the electrolytic chambers. A study of the chemical concentrations was carried out on the sediment, but also on the 6 mm AC-p after the EK treatment, in order to verify if the AC-p was effective in the removal of trace elements.

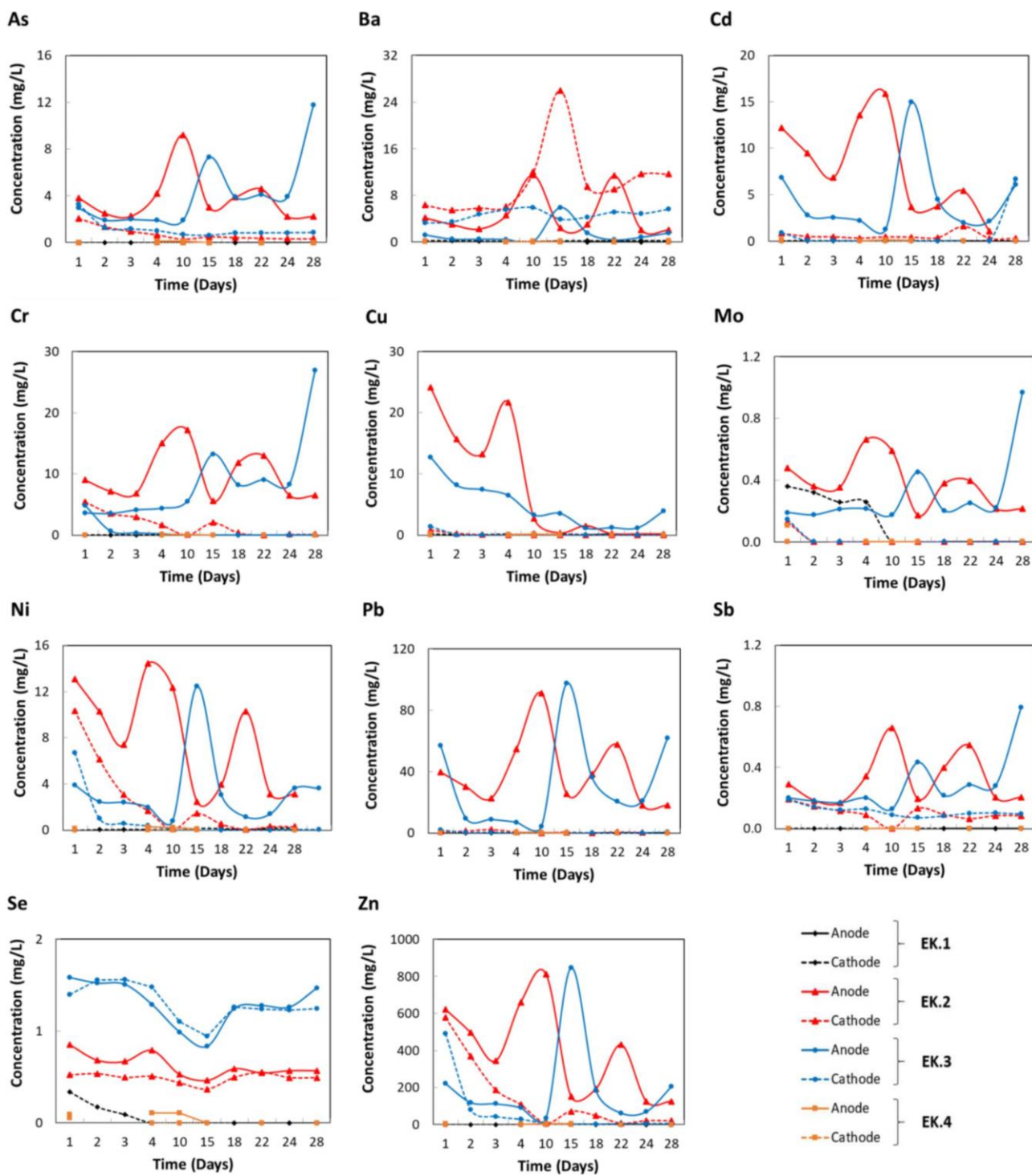


Figure 6 Concentration of trace elements ($\text{mg}\cdot\text{L}^{-1}$) measured during each EK treatment, in the effluents of the anode and cathode overflows.

III.3. Chemical elements' behavior to the electrokinetic remediation

III.3.1. Trace elements adsorbed on 6 mm AC-p

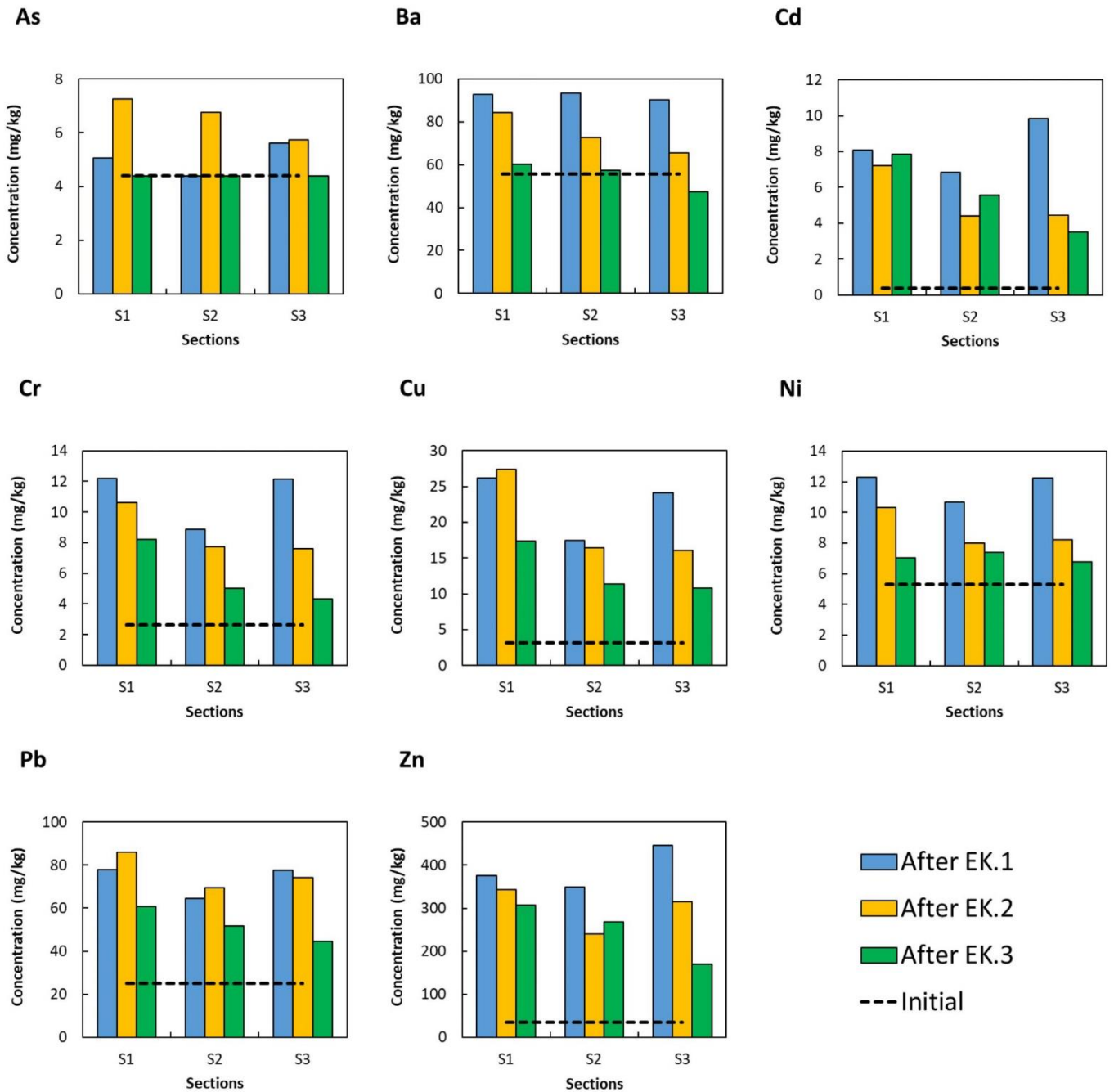


Figure 7 Total concentrations (NF ISO 12914) of trace elements adsorbed ($\text{mg}\cdot\text{kg}^{-1}$) on 6 mm AC-p after EK treatments. The concentration adsorbed during the EK tests can thus be deduced by subtracting the initial concentrations (proportion above the initial line).

The adsorption of chemical elements on the AC-p was investigated in order to verify if the trace elements were adsorbed onto it, thus decreasing the quantity found in the overflows.

Figure 7 shows the total concentrations of the studied trace elements adsorbed on the 6 mm AC-p according to the three sections S1, S2 and S3. The initial concentrations (AC-p Raw) are also shown in order to visualise the proportion of elements that adsorbed during the EK treatment (Visualised by the part of the histogram above the initial line). The elements that were most strongly adsorbed on the AC-p during the EK.1, EK.2 and EK.3 treatments are the cationic elements, and particularly Cd>Zn>Cu>Cr>Pb>Ni (**Figure 7**). However, depending on the reagents used, the adsorption rate is greater or lesser. For example, an additional 1961% of Cd was adsorbed during the EK.1 (DW) process onto the AC-p (averaged over all sections, compared to the initial content of the raw carbon particles). 1236% of Cd is adsorbed on the AC-p during EK.2 (CA) and 1308% during EK.3 (CA+TW20). The adsorption on the carbon particles also differs depending on the analysis section (**Figure 7**). It appears that for EK.1 the elements are more easily adsorbed onto the carbon particles located in the sections close to the electrodes (S1 and S3). For EK.2 and EK.3, the elements are mostly adsorbed in S1, close to the anode. This observation is consistent with that made in **Figure 6**, where the migration of chemical elements was predominantly in the anode evacuation compartment for EK.2 and EK.3. The carbon particles located in S1 were then able to adsorb a greater quantity of trace elements that migrated into this compartment. The anionic elements Mo, Sb and Se do not appear to have been adsorbed onto the AC-p for the three EK tests. The detection limit of ICP did not allow quantitative determination of these elements in the raw carbon particles neither after the EK treatments. The observations made in the study by [Mazet et al. \(1988\)](#), that the adsorption efficiencies of anionic micro-pollutants on activated carbon are enhanced by the release of calcium ions, cannot be verified here because the concentrations of these elements are too low. Finally, acidic reagents did not appear to improve adsorption rates on AC-p compared to DW.

III.3.2. Effect of activated carbon in the removal of 11 trace elements in the liquid and solid phase

The removal rates (%R), calculated according to equation 1, are summarised in **Table 3** for the 3 EK-tests conducted with the 6mm AC-p and for the 3 sections S1, S2 and S3. **Table 3a** shows the results obtained after the leaching test, while **Table 3b** shows the results obtained after matrix mineralisation.

In a previous study (**ARTICLE 3**), the analysis of sequential extraction showed that trace elements were no longer associated with the residual fraction (F4) after the EK treatments, regardless of the reagent used. However, other fractions (F1, F2 or F3) were sometimes enriched, indicating a possible re-deposition of chemical elements. Furthermore, the results showed that an acidic environment had certainly caused partial or total digestion of F4, releasing the chemical elements associated with it into the aqueous medium. As F4 is known to contain a large quantity of chemical elements ([Kennou et al. 2015](#)), this liberation tended to enrich the liquid phase. In order to counteract the enrichments found in the liquid phase, AC-p was added to the sediment matrix to try to improve the EK transport mechanisms.

The %R measured in the leachates, show overall an increased mobility in the liquid phase (**Table 3a**). Nevertheless, compared to similar experiments (**ARTICLE 3**), the AC-p reduced the enrichments found in the liquid phase for EK.1 and EK.3. The CA experiment (EK.2) did not show a benefit in %R. However, the benefit of activated carbon particles does not seem to have a sufficient impact on the removal rates. Indeed, it rather shows a significant mobility of the pollution, without succeeding in extracting it entirely from the system through the anodic or cathodic overflows. Despite a favourable environment (Current intensity, pH and Eh) for the solubilisation and therefore for the migration of chemical elements, the EK seems to have difficulties in removing pollutants from the mobile phase.

The EOF does not appear to be the most influential mechanism for trace element migration. It is possible that the dissolution of the carrier phases in solution favoured the creation of negatively charged complexes (or colloids), where the cationic metals could adsorb on the surface, and then electromigrate to the anode through electrophoresis. Complexes with anionic elements may also have occurred and participated in the migration of these elements.

(a)	AC-p : D6 mm						AC-p : D2 mm					
	EK.1 (DW)			EK. (CA)			EK.3 (CA+TW20)			EK.4 (DW) - D2 mm		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	-34.1%	-34.1%	-322.0%	-8653.7%	-11775.6%	-12740.2%	-6936.6%	-6661.0%	-14256.1%	-3.7%	-3.7%	-608.3%
Ba	4.3%	2.1%	26.2%	-2069.0%	-1659.8%	-3971.8%	-1855.7%	-1301.7%	-6073.6%	19.2%	15.0%	60.1%
Cd	55.8%	36.4%	93.5%	-332.2%	-315.9%	-663.9%	-542.1%	-404.0%	-878.6%	-12.4%	16.8%	99.6%
Cr	33.3%	33.3%	-500.0%	-145950.0%	-126766.7%	-176933.3%	-238000.0%	-111266.7%	-167733.3%	16.7%	16.7%	-2271.7%
Cu	12.5%	-0.8%	-50.8%	-1124.4%	-1009.2%	-2268.9%	-3212.6%	-1382.9%	-2518.6%	96.5%	96.5%	57.2%
Mo	0.9%	-15.6%	-20.8%	2.1%	-12.6%	48.3%	-1.7%	-19.4%	65.4%	49.3%	-29.5%	37.2%
Ni	64.5%	15.4%	74.1%	-181.6%	-190.5%	-892.2%	-362.9%	-756.2%	-1332.9%	7.6%	-13.6%	95.3%
Pb	78.3%	78.3%	78.3%	-39780.4%	-40972.7%	-94916.3%	-37802.2%	-26728.1%	-116510.7%	80.3%	80.3%	80.3%
Sb	0.0%	0.0%	0.0%	-568.4%	-586.0%	-726.3%	-436.8%	-412.3%	-908.8%	-1.8%	-1.8%	-127.5%
Se	54.4%	54.4%	54.4%	54.4%	54.4%	-89.4%	-90.5%	-110.8%	-204.6%	59.4%	59.4%	-10.1%
Zn	63.5%	28.6%	97.3%	-393.3%	-358.8%	-1165.9%	-660.7%	-583.2%	-1193.4%	2.2%	-10.7%	100.0%

(b)	AC-p : D6 mm						AC-p : D2 mm					
	EK.1 (DW)			EK.2 (CA)			EK.3 (CA+TW20)			EK.4 (DW) - D2 mm		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
As	-10.5%	-7.0%	-2.4%	25.3%	20.1%	39.8%	19.9%	14.2%	37.3%	11.3%	11.8%	12.4%
Ba	0.8%	28.2%	28.2%	3.8%	26.8%	42.1%	16.5%	24.8%	34.8%	23.0%	25.7%	27.8%
Cd	15.1%	-10.0%	-9.8%	24.5%	26.0%	47.3%	11.9%	14.3%	41.4%	19.0%	7.1%	8.5%
Cr	0.2%	25.7%	26.2%	25.8%	38.7%	49.0%	27.0%	12.1%	46.0%	19.3%	24.2%	23.3%
Cu	-7.7%	-7.7%	-5.0%	-22.1%	-0.5%	13.0%	-15.6%	1.7%	21.1%	5.0%	3.9%	3.0%
Mo	47.0%	47.0%	47.0%	47.0%	47.0%	47.0%	47.0%	47.0%	47.0%	11.4%	15.8%	65.2%
Ni	14.9%	4.7%	5.0%	24.2%	26.6%	37.4%	21.4%	5.4%	31.6%	23.6%	0.7%	7.1%
Pb	-8.9%	-5.7%	-3.0%	22.1%	16.6%	39.8%	8.8%	11.0%	28.4%	23.3%	22.6%	21.1%
Sb	-15.9%	20.5%	20.0%	14.0%	26.5%	42.7%	7.4%	8.6%	30.1%	12.2%	19.4%	10.0%
Se	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%	-13.8%	-3.4%	-3.4%	-3.4%
Zn	40.4%	0.1%	-3.1%	44.3%	41.2%	59.2%	32.2%	3.2%	49.5%	39.1%	-1.1%	11.9%

Table 3 Removal rate (%R) calculated according to equation 1, after the leaching test (NF EN 12457-2), negative values correspond to a high mobility of trace metals (a); Removal rate after the analysis by acid digestion (NF ISO 12914), negative values correspond to a high retention of trace elements on the solid phase (b)

The removal rates (%R) of trace elements in EK.1 and EK.4 (DW) are quite low in the solid phase (**Figure 5b**). This can be explained by the pH and redox conditions of the medium. The relatively neutral pH (**Figure 3a**) did not allow solubilisation of the elements, and the reduced medium (**Figure 3c**) may have favoured the formation of metal-sulphur complexes, known to be immobile in these reduced sediment fractions (Benamar et al., 2019). This could explain the few retentions (negative values) observed in the solid phase (**Table 3b**). CA was used in EK.2 and EK3 to prevent an alkaline front in the sediment. Benamar et al. (2019) used this weak acid but its capacity to chelate and solubilise metals was not convincing, even when the CA concentration in the electrolyte was increased. Here, the use of CA in combination with a surfactant (TW20) as an additive (EK3) improved the removal of trace elements compared to the EK.1 reference test (**Table 3b**). However, this improvement remained limited and overall lower than the results obtained by EK.2. Overall, the CA was effective in desorbing elements associated with solid particles from the sediment matrix, except for Mo and Se. Indeed, these elements do not seem to have been impacted by the change in treatment reagents (**Table 3b**).

Zinc is taken as an example here, and is used as a marker to verify the interest of 6 mm activated carbon particles in experiments EK.1, EK.2 and EK.3. In addition, it is the element present in the majority in this matrix. A removal rate of 13% was measured for EK.1, whereas 48% and 28% of Zn were desorbed from the solid phase for the experiments conducted under acid (EK.2 and EK.3 respectively) (**Table 3b**). It should be noted that the S3 section (close to the cathode) for EK.2 and EK.3 has the best %R, probably due to the migration of chemical elements during the EK treatment, oriented towards the anode compartment (**Figure 6**). This migration is favoured by the acidic pH of the medium (**Figure 3a**). Furthermore, it may seem surprising that all the cations migrated towards the anode. Comeselle & Pena, (2016) showed that trace metal elements [M] can combine with citrates from the CA, can dissolve in the water and form differently charged complexes depending on the pH: A positive [Citrate-M]⁺ complex appears at pH < 3; a neutral complex in the range of pH = 3 - 4; and finally at pH > 4.5, a negative [Citrate-M]⁻ complex appears. The pH curves shown in **Figure 3a** indicate that for EK.2, the pH was > 4.5 until about day 7 of treatment, and until day 13 for EK.3.

These conditions were favourable to the formation of [Citrate-M]⁻ complexes, which encouraged the migration towards the anode. This almost coincides with the extraction peaks measured in the anode compartment (**Figure 6**). Indeed, it was shown that a first extraction peak

appeared around the 10th day of treatment for EK2 and around the 15th day for EK.3. As the S1 zone was free of available ions, it was necessary to wait until the 22nd (EK.2) and 24th (EK.3) days for the anode compartment to extract higher concentrations of chemical elements once again (**Figure 6**). This probably corresponds to the migration time of the elements from S2 and S3. As for EK.1, since the DW did not reduce the pH of the medium, desorption of metals is more chaotic across sections and does not necessarily follow a logical migration according to the charge states of the cations and anions analysed.

Comparing the Zn results with those of **Chapter 3 (ARTICLE 3)**, it is highlighted that the AC-p (D6 mm) did not allow a better mobilisation of Zn in the solid phase for the experiments under CA (EK.2 and EK.3). Conversely, the %R was better for EK.1 (DW), and even better for EK.4 despite the fact that the AC-p (D2 mm) could not be removed from the matrix at the end of the experiment (**Table 3b**). In general, the fine carbon particles allowed a better mobilisation of the elements in the solid phase compared to the experiment conducted with DW in **Article 3**.

IV. Conclusion

Activated carbon particles, used in an EK remediation system, has permitted:

- Significantly increase the propagation of electrical intensity within the sediment matrix. Up to 307 % (EK.1), 1169 % (EK.2), 530 % (EK.3) and 250% (EK.4) increases in electrical intensity delivered on average during 28 days of treatment.
- Increasing electroosmotic flow rates and favouring a flow in the conventional direction when acid reagents were used (EK.2 and EK.3). The flow rates were improved by about 1806 % (EK.1), 1714 % (EK.2) and 30 % (EK.3).

The difference in particle size of the AC-p showed significant differences on the EK parameters. The larger particle sizes (D6 mm) showed higher efficiency on: pH (more acidic), redox (less reducing), electric current intensity and EOF. Nevertheless, the remediation results (%R) obtained in the solid and liquid phase were sometimes more interesting when the 2mm carbon particles were used.

Here as well, the acid reagents strongly increased the mobility of chemical elements in the liquid phase, thus enriching the leachate. However, these removal results are interesting because

they suggest that these elements enriched the liquid phase through the degradation of the carrier phases, due to the particular physicochemical conditions produced by the EK treatment.

Using the conductivity of activated carbon could be an interesting economic alternative, to use less electric current in EK tests. But its use has yet to be optimised. Moreover, although the carbon particles adsorbed a certain degree of chemical elements, it would appear that this adsorption was not sufficient to capture the residual pollution. This residual pollution was released into solution by the degradation of the carrier phases caused by the acidic pH of the medium. The migration of elements does not appear to be in the direction of the EOF, but rather in the opposite direction, suggesting that the EOF is not the most interesting transport mechanism for depolluting materials, even though electroosmotic flow rates have been improved.

It is known that the nature of the sediment matrix plays a major role in the effectiveness of the remediation treatment. It is necessary to act on the matrix with alternative methods (use of specific reagents or addition of an amendment to optimise the characteristics of the EK). Thus, a large variety of sediments (marine, river), activated carbons and reagents (citric acid and surfactants) should be tested in order to identify the optimal conditions. The idea would be, for activated carbon, to be able to vary its source (different pre-treatments), but also its concentration (v/v %) and its granulometry.

General conclusion

We performed for this research work, a study of EK remediation conducted on two waterways sediment matrices with different physico-chemical characteristics and contamination levels. The aim was to highlight the effects of the granular and chemical composition of the sediment matrices on the treatment efficiency. The trace elements As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn were chosen because current European regulations and texts define them as problematic from an environmental point of view. Therefore, the behaviour of this wide range of inorganic pollutants has been analysed in this thesis. In order to optimise the EK remediation process, we wanted to maintain a constant level of electrical intensity throughout the EK treatments. We therefore developed a process to improve this parameter by incorporating activated carbon particles into the matrix. The impact of this improvement was studied.

As a first step (**Chapter 2 - Article 2**), we wanted to expand the literature by using a novel biosurfactant (from HTS Bio laboratory). Biodegradable and resulting from a bacterial process, this biosurfactant has proven to be effective for the complexation of the 11 targeted trace elements and proved its efficiency in the EK depollution process. Indeed, the leaching behaviour of metals was effectively reduced (%R) for the elements: As (81.3%); Ba (80%); Cr (97.3%); Cu (82%) and Zn (94.5%). The solid matrix analysis, however, showed a less interesting remediation of the total content. We demonstrated that, the complexation of the biosurfactant molecules with the trace elements had a beneficial impact on their mobility for a low-contaminated sediment matrix.

In a second step, we analysed two waterways sediment matrices: one with low contamination and one with high contamination. These matrices were then subjected to an EK treatment process. Consequently, we decided to divide **Chapter 3** into two parts and to conclude with a general discussion to highlight the impact of each matrix. The reagents were selected on the basis of the literature, and were considered to be the most promising, or providing good compromises regarding efficiency and environmental impact in a large-scale use (*Cf. Chapter 1*). In this third chapter, we presented interesting results, highlighting significant differences

regarding the reagents used (*i.e.* DW, CA and CA+TW20) as well as differences generated by the effect of the matrices on the EK parameters.

More precisely, for the **first part of Chapter 3 (Article 3)**, the experimental results allowed us to demonstrate that the use of CA (CA alone or in combination with TW20) would have favoured the transfer of metal contamination from the carrier minerals to the aqueous phase. Indeed, it has been suggested that citric acid citrates' form negative complexes, favoured by our pH conditions, and would have caused the migration of cationic trace elements towards the positive electrode. Unfortunately, our system showed significant pH differentials in all three-analysis sections, so removal to the overflows could not be effective. The increased mobility in the liquid phase leads us to consider the mechanisms of dissolution of the carrier phases. This appeared to be a promising line of investigation. Consequently, the major elements were analysed in order to understand the influence of the pH on the phases carrying the pollution and on the dissolution mechanisms. Furthermore, the intensity of the electric current showed a behaviour in correlation with the acceleration of the electroosmotic flow and the increase in the concentration of trace elements found in the anodic and cathodic overflows. Therefore, we can highlight the interest of the electric current in the efficiency of the EK process. These points are discussed in a separate chapter (*Cf.* **Chapter 4**).

The analysis of the carrier phases was therefore our third line of investigation. A study of the geographical orientation (sequence speciation) of the trace elements was carried out in the **second part of Chapter 3 (Article 4)**. This study was carried out on a sedimentary matrix heavily contaminated with Zn. The effect of heterogeneity of sedimentary matrices, often announced as the factor blocking the adaptability of the EK method on a large scale ([M. Masi, 2017](#)) could thus be appreciated. The sequential extraction test was conducted according to the protocol of the European Communities Bureau of Reference, (BCR), allowing for the analysis of 4 pollution carrier fractions. The analysis of the mineralogical fractions showed that the nature of the treatment reagents was not important in the fate of the residual fraction (F4) and that overall, the trace elements were no longer associated with this fraction after the EK treatments. However, other fractions (F1, F2 or F3) were sometimes enriched, indicating possible re-deposition of chemical elements.

Furthermore, we have shown that electrokinetic remediation, coupled with an acid pH of the medium, would allow the partial digestion of this mineralogical phase (F4). This digestion is consistent with the results obtained on the solid fraction. The conditions of the medium therefore permitted the liberation of the chemical elements associated with F4 in the aqueous medium. This liberation caused enrichments of chemical elements in the liquid phase. These enrichments had already been observed in the previous studies (**Article 2** and **Article 3**). Due to the large amount of elements that enriched the mobile liquid phase, the EK treatment was not able to effectively mobilise these elements and remove them from the system through the anode or cathode overflows.

Consequently, the **Chapter 4 (Article 5)** was conducted with the aim of optimising the EK parameters. We were particularly interested in the intensity of the electric current delivered to the matrix during the treatment. Indeed, we had highlighted in article 3 that this parameter had a significant impact on the efficiency of the EK, by allowing increased mobility of the chemical elements. We therefore set up a process to maintain the electric current throughout the tests.

Activated carbon was chosen as an amendment to the treatments, as its good conductivity. Two types of activated carbon were used for the treatments conducted with DW. These carbons were chosen for their difference in granulometry (D2 mm and D6 mm). The aim here was to measure their reactivity to electrical intensity, and to observe if the current was maintained during the tests. We therefore mixed activated carbon particles (AC-p) into the sediment matrix. Carbon with the largest grain size (D6 mm) could be removed from the sedimentary matrix by sieving at the end of the treatment. The recovery of the AC-p may also have an advantage in the recycling of these particles in the EK treatments (keeping the particles for multiple reuse). The experimental results showed an overall increase in electrical intensity for all the tests performed. For example, up to 1169% increase was measured for the treatment using citric acid (average over 28 days). Furthermore, it seems interesting to note that the electrical intensity profiles remained constant throughout the tests.

We have also shown that the carbon has had a significant impact on other physico-chemical characteristics (*i.e.* pH, Eh and EOF). Nevertheless, even if the conditions seemed favourable, we note a residual pollution in the liquid phase. These elements were released in

solution by the degradation of the carrier phases, caused by the acid pH of the medium, and could not electromigrate efficiently towards the anodic or cathodic overflows.

Moreover, we found that the migration of trace elements was not carried out in the direction of the EOF, but rather in the opposite. This suggests that the EOF is not the most interesting transport mechanism to removal the matrices studied, even if the electro-osmotic flow rates were improved by the addition of AC-p (up to 1806% for the demineralised water treatment).

Perspectives

This thesis demonstrated significant effects of EK treatments on polluted sedimentary matrices. For instance, the nature of the sedimentary matrix plays a major role in the effectiveness of the depollution treatment. Our work shows that it is necessary to act on the matrix with alternative methods, such as the use of specific reagents or addition of an amendment to optimise the EK characteristics.

The results of **Chapter 5** strongly encourage further research in order to refine the results obtained. The use of AC-p in an Ek remediation approach is an interesting perspective. In addition, the study of the most influential parameters of the sediment matrix, such as pH or electric current intensity, should be further investigated.

Periodic voltage EK treatments have been promising in regards to its potential to better remove trace elements from sediments ([Ammami, 2013](#)). In order to verify the techno-economic efficiency of the treatment, studies should be conducted combining the effects of a periodic voltage with the effects of activated carbon. We have highlighted that AC-p increases the electric current intensity in the sediment matrix without increasing the delivered voltage. Using large size carbon particles, these can be used for several EK experiments. This amortizes the acquisition of carbon particles and saves money. The periodic voltage combined with the use of AC-p firstly saves electricity consumption, and secondly improves the efficiency of elimination. Thus, a large variety of sediments (marine, river), activated carbons and reagents (citric acid and surfactants) should be tested in order to identify the optimal treatment conditions. The idea would be, for activated carbon, to be able to vary its source (different pre-treatments), but also its concentration (v/v %) and its granulometry.

Waterways sediment matrices are multi-contaminated with trace elements (heavy metals) ([Samara, 2007](#)) but also with organic pollution (total hydrocarbons "TPHs" and polycyclic aromatic hydrocarbons "PAHs"). Some reagents are known to treat these organic contaminants, so it would be interesting to investigate their behaviour in EK processes ([Ammami, 2013](#)).

Finally, there are still many scientific questions about this remediation process. ADEME has drafted a guide on the treatability of polluted soils ([ADEME, 2009](#)). The objective of the feasibility tests mentioned in this guide is to verify the suitability of the pre-selected techniques to achieve the imposed treatment objectives. The results of these tests will make it possible to assess

the feasibility and applicability of the pre-selected techniques and to provide a comparative summary of the performance of the treatment techniques applicable to the materials to be rehabilitated. The guide includes a characterisation phase which is essential for the selection of the treatment method.

For electrokinetic remediation technology, since a given reagent (carbon particles and/or chemical reagents) will not react in the same way from one sediment matrix to another, nor impact in the same way on the elements (speciation), a treatability study would therefore be essential in order to propose a relevant EK-treatment protocol according to the study matrix. The idea here would be to evaluate the performances in the laboratory before proceeding with a relevant methodology and in fine resulting in a study programme ensuring the monitoring of the parameters but also the consequences of the EK treatment, for a future application at an industrial scale.

Finally, our work is part of a much larger context than EK remediation. United Nations Organization (UNO) has defined a call named: (Sustainable Development Goals (SDG) good practices » to highlight examples of good practices, including those that could be replicated or scaled-up by others across the globe. The work carried out in this thesis is consistent with various challenges set by the UNO.

Challenge 6, ensures the availability and sustainable management of water and sanitation for all. Sub-section 6.3 proposes that by 2030 it should be: « *improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally*»

Our work is a contribution to this great challenge by proposing a treatment method that limits the runoff of pollution into the environment. This limits the contamination of surface water and groundwater. In addition, our work permits the remediation of a material, considered as waste, with the aim of reusing it in various valorisation channels.

Challenge 8, a sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all. Subsection 8.4 highlights the urgency of improving by 2030 « *global resource efficiency in consumption and production and endeavour to decouple economic growth from environmental degradation, in accordance with the 10-year framework of*

programmes on sustainable consumption and production, with developed countries taking the lead»

Our work is also part of this challenge. Indeed, the EK remediation allows to remediate sedimentary matrices and to use these materials as a replacement of noble aggregates in the civil engineering fields. The aim is to participate in the circular economy while preserving the environment.

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Titre en français

Dépollution des sédiments de dragage par traitement électrocinétique dans la perspective de leur valorisation

Résumé en français

L'exploitation des ressources granulaires naturelles est nécessaire pour répondre aux besoins des acteurs du bâtiment et des travaux publics. Cependant, les besoins toujours croissants en granulats et les lignes de conduites adoptées jusqu'alors ont conduit à des surexploitations ou même à l'épuisement de certaines ressources. L'utilisation de matériaux alternatifs (sédiments, déchets de démolition, cendres volantes, mâchefers d'incinération de déchets non dangereux, etc.) en substitution des ressources granulaires naturelles apparaît donc comme une solution durable aux problématiques de surexploitations des granulats de carrières. Cependant, pour certains matériaux alternatifs, la problématique environnementale est prégnante et conditionne les modalités de leur réutilisation. C'est notamment le cas des sédiments de dragage. En effet, ces matériaux issus de l'érosion des sols se déposent dans le fond des cours d'eaux et sont excavés lors d'opérations de dragage afin d'assurer la navigabilité des ports et des chenaux. L'entretien du réseau fluvial des Voies Navigables de France (VNF) génère chaque année 6 à 9 millions de mètres cubes de matériaux. Cependant, compte tenu de la diversité des contaminants rencontrés dans les matrices sédimentaires, il est impératif de s'assurer de leur qualité environnementale avant d'envisager leur recyclage. Ainsi, le processus de gestion à terre des sédiments de dragage doit permettre de réduire le niveau de contamination des matériaux les plus pollués afin de répondre aux exigences environnementales applicables aux matériaux alternatifs.

Les travaux de cette thèse visent à étudier un processus de remédiation électrocinétique appliqué à deux matrices sédimentaires contaminées, dans la perspective de leur valorisation future dans le domaine du génie civil. Deux objectifs majeurs ont été poursuivis : (i) optimiser des protocoles de traitement électrocinétique viables et respectueux de l'environnement, en prenant soin de choisir des réactifs adaptés (naturels ou biodégradables) ; (ii) évaluer l'efficacité des traitements pour la remédiation des polluants inorganiques en s'appuyant sur leurs contenus totaux, leur comportement à la lixiviation dans la matrice sédimentaire, et l'analyse des effluents.

Les résultats ont permis de mettre en évidence l'influence significative des processus électrocinétiques sur les concentrations totales, la répartition et la disponibilité des éléments

traces métalliques et métalloïdes au sein des matrices sédimentaires. L'utilisation de réactifs acides (par exemple de l'acide citrique) en combinaison avec des molécules chélatrices (des tensioactifs) a contribué à optimiser l'extraction de ces contaminants. Enfin, il a été démontré que l'ajout de particules de charbon actif peut modifier la conductance électrique de la matrice sédimentaire et conduire au maintien d'une intensité électrique plus élevée pendant le processus de dépollution. Compte tenu de la variabilité des performances de dépollution en fonction des caractéristiques physico-chimiques des sédiments fluviaux, il apparaît indispensable de procéder systématiquement à une étude de traitabilité à l'échelle du laboratoire afin de mettre au point des protocoles de traitement adaptés.

Mots-clefs :

Dépollution ; Valorisation ; Eléments traces ; Traitement électrocinétique ; Sédiments de dragage

Titre en anglais

Remediation of dredged sediments by electrokinetic treatment prior to their valorization.

Résumé en anglais

The exploitation of natural granular resources is necessary to meet the needs of construction and public works stakeholders. However, the ever-increasing needs for aggregates and the lines of conduct adopted until then have led to overexploitation or even to the depletion of certain resources. The use of alternative materials (sediments, demolition waste, fly ash, slag from non-hazardous waste incineration, etc.) to substitute natural granular resources therefore appears to be a sustainable solution to the problems of overexploitation of quarry aggregates. However, for some alternative materials, the environmental issue is significant and determines the modalities of their reuse. This is particularly the case with dredged sediments. Indeed, these materials resulting from soil erosion are deposited in the bottom of waterways and are excavated during dredging operations in order to ensure the navigability of ports and channels. The maintenance of the "Voies Navigables de France" (VNF) generates 6 to 9 million m³ of material each year. However, given the diversity of contaminants encountered in sedimentary matrices, it is imperative to ensure their environmental quality before considering their recycling. Thus, the onshore management process for dredged sediments must make it possible to reduce the level of contamination of the most polluted materials in order to meet the environmental requirements applicable to alternative materials.

The work of this thesis aims to study an electrokinetic remediation process applied to two contaminated sedimentary matrices, with a view to their future valorisation in the field of civil engineering. Two major objectives were pursued: (i) optimize viable electrokinetic treatment protocols that respect the environment, taking care to choose suitable reagents (natural or biodegradable); (ii) evaluate the effectiveness of treatments for the remediation of inorganic pollutants based on their total contents, their leaching behavior in the sedimentary matrix, and the analysis of effluents.

The results made it possible to highlight the significant influence of electrokinetic processes on the total concentrations, the distribution and the availability of metallic and metalloid trace elements within the sedimentary matrices. The use of acidic reagents (e.g. citric acid) in combination with chelating molecules (surfactants) has helped to optimize the extraction of these contaminants. Finally, it has been shown that the addition of activated carbon particles can modify the electrical conductance of the sediment matrix and lead to the maintenance of a higher electrical intensity during the depollution process. Given the variability of remediation performance according to the physico-chemical characteristics of river sediments, it seems essential to systematically carry out a treatability study on a laboratory scale in order to develop suitable treatment protocols.

Mots clefs en anglais

Remediation ; Valorization ; Trace elements ; Electrokinetic treatment ; Dredged Sediments