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T H E S E

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Présentée et soutenue par
Mehwish TANEEZ

Stabilisation d'un sédiment marin pollué en utilisant des résidus de bauxite - Evaluation de la mobilité d'éléments trace

Stabilization of contaminated marine sediment by addition of bauxite residues - Evaluation of potential mobility of trace elements

Thèse dirigée par **Nicolas MARMIER**
Et **Charlotte HUREL**

Soutenue publiquement le 24 Juin, 2016 devant la Commission d'examen composée de:

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Résumé

La contamination des sédiments aquatiques est un problème environnemental mondial. Les activités de l'homme et les caractéristiques hydrographiques sont responsables de l'accumulation de contaminants dans les sédiments d'estuaires, de ports et de zones côtières. Par conséquent, les sédiments marins sont le réceptacle final des contaminants chimiques organiques, les métaux lourds et métalloïdes.

Le dragage des sédiments des ports maritimes est essentiel pour maintenir la profondeur de navigation dans les ports. Près de 50 millions de mètres cubes de sédiments sont dragués chaque année en France. Les sédiments extraits sont parfois fortement contaminés et sont alors considérés comme un déchet qui nécessite d'être traité.. La gestion des sédiments dragués doit suivre les recommandations de la convention internationale OSPAR (1992) pour la protection des milieux naturels marins de l'Atlantique Nord-Est, la Convention mondiale de Londres (1972) sur la prévention de la pollution marine par immersion de déchets, et la convention de Barcelone de 1976. En France, la législation relative aux opérations de dragage et d'élimination des sédiments marins a fait l'objet d'un décret national (14 Juin 2000) dans lequel deux niveaux de concentrations en éléments traces et en PCB dans les sédiments marins et estuariens (N1 et N2) ont été définis afin d'évaluer le degré de contamination des sédiments de dragage , Lorsque le niveau de contamination est en dessous du niveau N1, les sédiments sont considérés comme non contaminés, ils peuvent être ré-immergés et l'impact écologique est considéré comme négligeable. Pour un niveau de contamination compris entre les niveaux N1 et N2, les sédiments sont classés comme contaminés, des analyses chimiques complémentaires sont requises et l'évaluation de l'impact écotoxicologique est nécessaireet. Enfin, si la concentration d'au moins un contaminant dans les sédiments est supérieure au seuil N2, ils sont alors considérés comme hautement contaminés et l'impact écologique peut être très important. Ces sédiments ne peuvent plus être rejetés en mer, ils doivent être traités ou stockés à terre et sont considérés comme des déchets.

De nombreux traitements physico-chimiques ont été étudiés pour permettre la valorisation de ce type de déchets, mais compte tenu des volumes de sédiments contaminés dragués chaque année, les traitements chimiques d'un sédiment dans son ensemble peuvent

s’avérer très coûteux. Ainsi, des pré-traitements tels que la déshydratation, la séparation des particules, le lavage sont réalisés afin de réduire le volume de sédiment à traiter. La partie la plus contaminée du sédiment (fraction fine de diamètre < 0.45µm) est alors vitrifiée ou solidifiée/stabilisée afin de limiter la dissémination des contaminants chimiques dans l’environnement. La solidification/stabilisation a pour but d'immobiliser les contaminants dans une matrice solide en utilisant des matériaux tels que par exemple des cendres, du ciment, de la chaux etc. Cette voie de traitement semble être la plus prometteuse car elle consiste à utiliser des matériaux peu coûteux intégrés simplement dans la matrice sédimentaire. Les matériaux riches en fer (Fe^0, goethite, hématite, et ferrihydrite par exemple) ont montré une bonne efficacité pour la réduction de la mobilité de As, Cd, Cu, Mo, Ni et Zn dans les sols et les sédiments. Cependant les oxydes de fer commerciaux peuvent s’avérer coûteux, c’est pourquoi l’utilisation de sous-produits issus de l’industrie et riches en oxydes de fer pourraient présenter une alternative intéressante.

Dans ce travail de thèse, nous nous sommes intéressés à un sous-produit industriel riche en oxydes de fer et issu de l’extraction de bauxite afin de l’utiliser comme additif minéral pour limiter la lixiviation des contaminants issus d’un sédiment marin. Ce sous-produit industriel (connu également sous le nom de boue rouge) est un matériau alcalin (pH10-13) généré pendant la digestion caustique de la bauxite pour la production d'alumine. Il est de couleur brun rougeâtre avec une fine distribution de taille de particules. Les principaux constituants sont des oxydes ou hydroxydes d'aluminium, de fer, de silicium, de titane. Deux formulations de sous-produits industriels (Bauxaline® et Bauxsol) ont été fournies par l'usine ALTEO (Gardanne, Bouches-du-Rhône, France)et une troisième formulation, composée de Bauxaline® neutralisé avec 5% de gypse a été fournie par l’INERIS. Ces trois formulations ont été utilisées comme additif minéraux dans des expérimentations pilotes de stabilisation chimique d’un sédiment marin menées à l’échelle du laboratoire. Le sédiment marin étudié est issu de la zone portuaire navale de Toulon (Sud-est de la France), collecté à l’issue d'une campagne de dragage réalisée par les autorités portuaires. Après dragage, le sédiment a été composté à terre à proximité de la zone portuaire durant 4 mois. Durant cette période, le sédiment a été retourné mécaniquement et humidifié hebdomadairement. Ce processus de compostage a favorisé l'activité microbienne et une

diminution significative de la concentration en polluants organiques a été obtenue. De plus, l'humidification a permis de réduire la charge saline du sédiment. Les concentrations en éléments traces (Cd, Cu, Zn, Ni, As, Cr et Mo) dans la matrice du sédiment après compostage ont permis de classifier ce sédiment comme étant fortement contaminé puisque le niveau de contamination mesuré pour Cu, Cd, Zn et As était supérieur au niveau admissible N2.

Afin d'évaluer la capacité des sous-produits industriels à adsorber les polluants chimiques issus du sédiment étudié, des tests préliminaires d'adsorption de As et Cd ont été réalisés avec la Bauxaline® et le Bauxsol. Ces essais préliminaires ont permis de confirmer l'efficacité de rétention à pH neutre des matériaux envisagés. Ainsi, deux séries d'expérimentations de stabilisation d'un sédiment marin composté ont été réalisées en plein air à l'échelle pilote pendant trois mois à Nice (France). La première expérimentation pilote a été conduite de Mars 2013 à Juin 2013. Au cours de cette expérimentation nous avons testé l'efficacité de stabilisation de la Bauxaline® et du Bauxsol lorsqu'ils étaient introduits respectivement dans un sédiment à un taux massique de 5%. Au cours de la seconde expérimentation pilote (menée d'avril 2014 à juillet 2014), la Bauxaline®, le Bauxsol et la Bauxaline® neutralisée ont été introduits respectivement dans un échantillon de sédiment marin à un taux massique de 20%. A titre de comparaison avec la première expérimentation, de la Bauxaline® neutralisée a été testée à un taux de 5% dans cette seconde expérimentation. Des évènements de pluies artificielles ont été régulièrement appliqués au cours des deux expérimentations, les eaux de percolation ont été ensuite recueillies et les concentrations en éléments traces (Cd, Cu, Zn, Ni, As, Cr et Mo), le pH, la conductivité électrique et les concentrations en carbone organique dissous ont été mesurés dans tous les échantillons de lixiviats. Des test de toxicité ont été menés sur les lixiviats collectés en utilisant des rotifères marins comme organisme de référence.

Les résultats ont montré que les polluants cationiques (Cu, Cd, Zn) étaient efficacement immobilisés dans la matrice sédimentaire par la Bauxaline® le Bauxsol et la Bauxaline® neutralisée même lorsqu'un faible taux d'additif était introduit (5%). Cependant un faible taux d'additif introduit n'a pas permis de rendre efficace la stabilisation des polluants

anioniques (As et Mo). Les expériences de toxicité n'ont pas permis de mettre en évidence une diminution significative du taux de mortalité des rotifères marins lorsque 5% d'additifs étaient introduits. Lorsqu'un taux de 20% de Bauxaline®, Bauxsol Bauxaline® neutralisée était appliqué, le taux de mortalité des rotifères marins était nettement abaissé. Ceci était en très bon accord avec les réductions significatives des concentrations en polluants cationiques des lixiviats de sédiment. Malgré un taux d'additif de 20%, l'immobilisation de As et Mo ne s'est pas réalisée aussi efficacement que pour les polluants cationiques (immobilisation inférieure à 20%). Néanmoins, les concentrations de l'ensemble des polluants mesurées dans les lixiviats de sédiment ont été considérablement abaissés lorsque 20% d'additifs ont été introduits et répondent aux critères de qualité définis pour les déchets inertes, excepté le Mo.

Ce travail de thèse a permis de mettre en évidence que les sous-produits industriels tels que les résidus de bauxite pourraient être utilisés comme additifs minéraux à faible coût et respectueux de l'environnement pour la stabilisation des éléments traces dans les sédiments marins pollués. L'efficacité de la stabilisation dépend du pH, du taux de matière organique dans le sédiment et la teneur en argile dans le sédiment. . Dans les conditions de ce travail, la stabilisation par additifs minéraux a permis l'amélioration de la qualité chimique et écotoxicologique des lixiviats issus du sédiment contaminé. Des études complémentaires nécessiteraient d'être menées afin d'évaluer l'efficacité à long terme de ce traitement (> 4 mois). Il serait également intéressant d'envisager l'introduction d'autres additifs (tels que les laitiers d'acierie) afin d'augmenter l'efficacité de stabilisation des polluants anioniques.

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List of Acronyms

AFNOR: **A**gence **F**rançaise de **NOR**malisation

CEC: **C**ation **E**xchange **C**apacity

EC: **E**lectrical **C**onductivity

DDT:**Di**chloro**d**iphenyl**t**richloroethane

DOC: **D**issolved **O**rganic **C**arbon

GÉODE: **G**roupement d'**É**tude et d'**O**bservation sur le **D**ragage et l'**E**nvironnement

GEODRISK: Logiciel d'aide à la décision permettant de calculer des scores de risques àpartir des concentrations chimiques en polluants métalliques et PCB.

ICP OES: **I**nductively **C**oupled **P**lasma **O**ptical **E**mission **S**pectrometer

IFREMER: **I**nstitut **F**rançais pour la **R**echerche et l'**E**xploitation des **MER**s

N1: **N**iveau **1**

N2: **N**iveau **2**

OM: **O**rganic **M**atter

ORP: **O**xidation-**R**eduction **P**otential

OSPAR Convention: The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR « **OS**lo-**PAR**is »)

PCBs: **P**oly**C**hlorinated**B**iphenyls

PAHs:**P**olycyclic **A**romatic **H**ydrocarbons

RM: **R**ed **M**ud

RNO**: R**éseau **N**ationald'**O**bservation

TBT**: T**ri**b**utyl**t**in

TCLP: **T**oxicity **C**haracteristics **L**eaching **P**rocedure

US EPA: **U**nited **S**tates **E**nvironment **P**rotection **A**gency

UNEP: **U**nited **N**ations **E**nvironment **P**rogram

General Introduction

Aquatic ecosystems are a valuable ecological resource that covers 70% of earth surface and therefore logically represents key targets of the nation and European policies for resource management. Since the human settlement in coastal areas, many advantages in terms of resource such as food (fishing), transportation (shipping) or commercial (tourism) are offered. Thus, about 3 billion people, nearly half the world's population live within 200 km of coastline and estimations indicate that this figure will double by 2025 (Creel, 2003). Permanent increase in anthropogenic activities (urbanization, industrialization, agricultural) is associated with a strong expansion of discharges of contaminants (organic and inorganic) into the aquatic environment (Depledge and Galloway, 2005). Over time, these free contaminants, can undergo transformations and usually adsorb on fine clay and sand particles that make up marine sediments. Therefore, sediments constitute true reservoirs for contaminants and form important sources of contamination for living organisms (Förstner, 1989; Luoma and Rainbow, 2008). Moreover, sediments serve as habitat to the wildlife and it is therefore important to monitor, evaluate and protect the sediment compartment.

Sedimentation became a real problem when deposited in large quantities in waterways (ports, access channels, estuaries, canals, and rivers), and interferes or prevents the movement of ships, from small pleasure boats to supertankers. Usually, the port structures and their associated industries are established in areas where the water depth is relatively low where it is essential to carry out dredging to allow boats access to the docks. Dredging is not only carried out at the time of construction of the port, but also periodically to remove accumulated sediments in the channels and docks. The dredged volumes are very important and variable depending on the size of ports and their geographical position. Thus, in France the annual maintenance operations in all ports, regardless of their size and purpose (trade, fishing, boating), generate approximately 50 million cubic meters of dredged sediments (Alzieu et al., 1999). The three main ports estuaries (Rouen, Nantes - Saint-Nazaire and Bordeaux) reported an average annual volume of about 25 million cubic meters, including 6.5 million cubic meters of sand, 9.3 million cubic meters of silt in immersion zones and an equivalent amount released in overflow. The five major seaports, Dunkerque, Calais, Boulogne, Le Havre and La Rochelle, dredge an average annual volume of 6.2 million cubic meters, consisting of about 20% sand and 80% silt. The larger

portion of dredged volume from these major ports is discharged in authorized open sea dumping sites. Small volume of dredged sediments from many harbor enclaves can be problematic due to significant contamination by metals/metalloids, organotins, and other organic pollutants (PAHs, PCBs) (Alzieu et al., 1999). These contaminated sediments can severely affect the flora and fauna of the marine environment. According to the risks they pose to the environment, the dredged sediments can be either immersed in authorized areas or deposited on land for storage or treatment.

Before 1992, the dredged sediments were immersed into the sea or stored on land in inert landfills. The physico-chemical analysis of the waste was not imposed. French legislation regarding disposal of dredged materials was revised and the national decree of 14th of June 2000 proposed two threshold levels (N1 and N2) in line with OSPAR convention for trace elements concentrations and PCBs in marine and estuarine sediment to classify sediments according to the risk on the environment. For Non-or little contaminated sediments, immersion into the sea is permitted (N1). The physico-chemical analysis of the waste is not necessary. More or less heavily contaminated sediments pose more complex problems (N2) and discharge into the sea is prohibited. In order to homogenize practices, and provide a common frame of reference to port authorities, consultancy companies, and administrations, the studies and observation group on dredging and environment (GÉODE)was set up to produce a technical guide. This group has defined thresholds content of different compounds (arsenic, metals, PCBs) that can decide the fate of sediments (Alzieu and Quiniou, 2001). In the case where the sediment contamination is intermediate between levels 1 and 2, only analytical results cannot judge the environmental risk posed by their immersion. To facilitate the risk assessment of these sediments, the inter-ministerial group Geode developed software to support the decision, Geodrisk, based on the results of chemical analyzes recommended by the technical instructions regarding sampling and analysis of dredged material in the decree of 14 June2000 (Alzieu, 2003).It is necessary to determine the potential toxicity of sediments undetected by analyzing chemical substance. Several tests (bivalve toxicity and Microtox®) have been proposed for assessing the toxicity of sediments due to their sensitivity and their ability to differentiate various types of contamination (Alzieu and Quiniou, 2001).

The establishment of French sediment quality guidelines in the decree of 14 June 2000 and the appearance of the sediment waste in the European Decree No 2002-540 of 18 April 2002 had a considerable impact on the dredging and sediment management, especially for all operations involving contaminated sediments. As according to the legislations the contaminated sediments are prohibited to be dumped into sea and the "stock" of sediment, which will necessarily be dredged in the next ten years, is estimated about 10 million tons. It is therefore necessary and urgent to provide solutions for the management of dredged sediments. As an initiative, a research project “SEDIMARD 83” was launched by Var General Council in partnerships with ten French and Italian harbor authorities, aiming to propose land management of dredged sediments as alternative to dumping of contaminated sediments. The research program “SEDIMARD 83” experimented different methods of treatment and pre-treatment (composting, calcination, stabilization / solidification, etc.) on a wide range of port sediments, representative of the variability of these matrices (Grosdemange et al., 2008). After the SEDIMARD 83 project, many research programs emerged at national level on treatment (SEDIMATERIAUX) and management of harbor sediments (SEDIDEPOT, SEDIGEST).

In this context, this thesis studies the feasibility of treatment of contaminated marine sediments with stabilization using mineral amendments (bauxite residue). The treatment technique is a geochemical stabilization of the sediment by adding a mineral additive to the sediment in order to increase the sediment retention capacity and thus to limit the dispersion of pollutants into the environment through the percolating water.

This thesis is comprised of three chapters: Chapter I is a literature review and divided into two parts: Part A is devoted to the state of art on key physicochemical characteristics of the sediments, the behavior of trace elements in sediments, and the influential factors controlling trace metal availability. The main pre-treatments and treatment methods for dredged sediment management available on an industrial scale and research and development are described. A regulatory part is also included describing the legislative requirements dealing with dredged materials management in terrestrial and maritime sectors. Part B of this chapter presents literature review on bauxite residue (an alumina

industry by-product), its production and properties. After the adoption of the Water Framework Directive by European Union member states to achieve good chemical and ecological status of water bodies by 2015, and the Barcelona Convention for the protection of the Mediterranean Sea against pollution, the rejection of bauxite residue into the Mediterranean Sea must decrease to 0 million tons by the end of 2015. Owing to rich mineral content of bauxite residue different uses of bauxite residue have been studied and proposed. The review provides an insight to the possible use of the bauxite residue in various environmental media (water, soil and sediment).

Chapter II presents the equipment, materials and methods used in the study. The sediment and mineral amendments were supplied by concerned authorities and physico-chemical properties of these materials were determined using standard protocols. The procedure of pilot experiment to stabilize trace elements marine dredged sediment with mineral amendments was explained and *Brachionus plicatilis* was used as test organism to test toxicity of sediment leachates.

Chapter III is devoted to results and discussion. This chapter includes three articles; the first article describes the interaction of inorganic contaminants (arsenic and cadmium) with bauxite residues (bauxaline® and bauxsol) in aqueous medium. Adsorption tests were carried out under different physicochemical conditions (pH, and concentration). The effects of these conditions and their impact on the capacity and adsorption mechanisms were discussed. The adsorption data is modeled using “ECOSAT” software. The harbor sediments are highly contaminated with trace elements. Chemical stabilization of trace elements (As, Cd, Cu, Mo, Ni, Zn and Cr) in composted sediments using mineral amendments has been studied in two pilot experiments. The first stabilization experiment was carried out outdoor in a pilot device and two amendments (bauxaline® and bauxsol) were applied at 5% rate. The treatment effect was evaluated according to the concentrations of contaminants (trace elements) in the percolating water. Finally, the toxicity of the leachates collected from untreated and treated sediment samples was evaluated using the marine rotifers. This work is published in “Marine Pollution Bulletin”. The 2nd stabilization experiment is performed using higher rate (20%) of bauxite residues

(bauxaline®, bauxsol and neutralized bauxaline®) and the results are discussed. The effectiveness of treatment is assessed by the chemical and ecotoxicological quality of elutriates. The results of the neutralized bauxaline® are presented in an article published in "Chemosphere".

Finally, the manuscript ends with a general conclusion and offers research opportunities listed in the continuity of this work.

Introduction générale

Les écosystèmes aquatiques, ressource écologique précieuse qui couvre près de 70% de la surface de la terre sont des cibles clés des politiques européennes en matière de gestion des ressources. Les zones côtières présentent de nombreux avantages tant en termes de pêche, de transport maritime mais aussi de tourisme. Ces raisons expliquent qu'environ 3 milliards de personnes, soit près de la moitié de la population mondiale vivent à moins de 200 km de côtes. Ce chiffre ne cesse d'augmenter et promet même de doubler d'ici 2025 (Creel, 2003). L'augmentation permanente des activités anthropiques (l'urbanisation, l'industrialisation, l'agriculture) est associée à une forte expansion des rejets de contaminants (organiques et inorganiques) dans le milieu aquatique (Depledge and Galloway, 2005). Au fil du temps, ces contaminants libres, peuvent subir des transformations et s'adsorber sur les argiles et les fines particules de sable qui composent les sédiments marins. Ainsi les sédiments, véritables réceptacles pour les contaminants, constituent des sources importantes de contamination pour les organismes vivants (Förstner, 1989; Luoma and Rainbow, 2008). En outre, les sédiments servent d'habitat à la faune sauvage. Il est donc important de les surveiller, de les évaluer et de les protéger.

La sédimentation est devenue un réel problème pour les infrastructures portuaires. Déposés en grandes quantités dans les cours d'eau (ports, voies d'accès, estuaires, canaux et rivières), les sédiments interfèrent ou empêchent la circulation des navires. Habituellement, les structures portuaires et leurs industries connexes sont établies dans les zones où la profondeur de l'eau est relativement faible, où il est essentiel d'effectuer un dragage pour permettre aux bateaux d'accéder aux quais. Le dragage est non seulement réalisé au moment de la construction du port, mais aussi périodiquement pour éliminer les sédiments accumulés dans les canaux et les quais. Les volumes de dragage sont très importants et variables en fonction de la taille des ports ainsi que de leur position géographique. Ainsi, en France, les opérations de maintenance annuelles dans tous les ports, indépendamment de leur taille et de leur fonction (commerce, pêche, canotage), génèrent environ 50 millions de mètres cubes de sédiments dragués (Alzieu et al., 1999). Les trois principaux ports d'estuaires (Rouen, Nantes - Saint-Nazaire et Bordeaux) font état d'un volume moyen annuel d'environ 25 millions de mètres cubes, dont 6,5 millions de mètres cubes de sables, 9,3 millions de mètres cubes de vases clapées dans des zones d'immersion et une quantité équivalente rejetée en surverse. Les cinq grands ports maritimes (Dunkerque, Calais,

Boulogne, Le Havre et La Rochelle) draguent un volume annuel moyen de 6,2 millions de mètres cubes, constitué d'environ 20% de sable et de 80% de limon. La plus grande partie du volume de dragage de ces grands ports est rejetée en mer dans des sites autorisés. Toutefois, de petits volumes de sédiments dragués peuvent être problématiques en raison de leur contamination significative par les métaux, les métalloïdes, les organoétains, et d'autres polluants organiques (HAP, PCB) (Alzieu et al., 1999). Ces sédiments contaminés peuvent gravement affecter la flore et la faune du milieu marin. Selon les risques qu'ils présentent pour l'environnement, les sédiments dragués peuvent être soit immergés dans les zones autorisées ou déposés à terre pour le stockage ou le traitement.

Jusqu'en 1992, les sédiments dragués étaient immergés dans la mer ou stockées sur terre dans les décharges inertes et l'analyse physico-chimique des déchets n'était pas été imposée. Depuis, la législation française en matière d'élimination des matériaux de dragage a été révisée conformément à la convention OSPAR. Un décret national a été publié le 14 juin 2000 dans le but de classer les sédiments marins et estuariens en fonction du risque sur l'environnement. Pour cela, deux niveaux de seuils ont été établis (N1 et N2) en fonction des concentrations en éléments trace et en PCBs dans les sédiments. Pour les sédiments non ou peu contaminées (concentrations inférieures au niveau N1), l'immersion en mer est autorisée et l'analyse physico-chimique des déchets n'est pas nécessaire. Les sédiments plus fortement contaminés (concentrations supérieures à N2) posent des problèmes plus complexes et ne peuvent être rejetés en mer. Un Groupe d'Etudes et d'Observations sur les Dragages et l'Environnement (GÉODE) a été mis en place pour produire un guide technique afin d'homogénéiser les pratiques, et de fournir un cadre de référence commun aux autorités portuaires, aux sociétés de conseil, et aux administrations. Ce groupe a défini des seuils en différents composés cibles (arsenic, métaux, PCB) qui peuvent décider du sort des sédiments (Alzieu and Quiniou, 2001). Dans le cas où la contamination des sédiments est intermédiaire entre les niveaux 1 et 2, les résultats d'analyse seuls ne peuvent pas déterminer le risque environnemental posé par l'immersion des sédiments. Pour faciliter l'évaluation des risques de ces sédiments, le groupe interministériel GÉODE a développé un logiciel permettant d'appuyer la décision: Geodrisk. Ce logiciel est basé sur les résultats des analyses chimiques recommandées par les instructions techniques concernant l'échantillonnage et l'analyse des déblais de dragage du décret du 14 Juin 2000

(Alzieu, 2003). Toutefois, l'analyse des substances chimiques présentes dans les sédiments ne permet pas de déterminer leur toxicité. Pour cela, plusieurs tests (toxicité du bivalve et Microtox®) ont été proposés en raison de leur sensibilité et de leur capacité à différencier les différents types de contamination (Alzieu and Quiniou, 2001).

L'établissement des directives françaises sur la qualité des sédiments (décret du 14 Juin 2000) et l'apparition des déchets sédimentaires dans la classification européenne (décret européen n ° 2002-540 sur les déchets du 18 Avril 2002) a un impact considérable sur le dragage et sur la gestion des sédiments, en particulier pour toutes les opérations impliquant les sédiments contaminés. Etant donné l'interdiction de les rejeter en mer, le « stock » de sédiment contaminé qui sera dragué au cours des dix prochaines années est estimé à environ 10 millions de tonnes. Il est donc nécessaire et urgent de fournir des solutions pour la gestion de ces sédiments. À titre d'initiative, un projet de recherche "SEDIMARD 83" a été lancé par le Conseil général du Var en partenariat avec dix autorités portuaires françaises et italiennes afin de développer une alternative au rejet des sédiments contaminés. Dans le cadre de ce projet de recherche, différentes méthodes de traitement et de pré-traitement (compostage, calcination, stabilisation / solidification, etc.) ont été expérimentées sur une large gamme de sédiments portuaires afin de représenter la variabilité de ces matrices (Grosdemange et al., 2008). Suite au projet SEDIMARD 83 de nombreux programmes de recherche ont vu le jour au niveau national sur le traitement (SEDIMATERIAUX) et la gestion des sédiments portuaires (SEDIDEPOT, SEDIGEST). Dans ce contexte, cette thèse étudie la faisabilité du traitement des sédiments marins contaminés en utilisant la stabilisation à l'aide d'amendements minéraux (résidus de bauxite). Cette technique de traitement est une stabilisation géochimique des sédiments qui consiste à ajouter un additif minéral dans les sédiments afin d'augmenter la capacité de rétention des sédiments et donc de limiter la dispersion des polluants dans l'environnement à travers l'eau de percolation.

Ces travaux de thèse sont présentés à travers trois chapitres:

Le chapitre I est une revue de la littérature divisée en deux parties. La partie A est consacrée à l'état de l'art sur les caractéristiques physico-chimiques clefs des sédiments, le comportement des éléments traces dans les sédiments et les facteurs influençant la disponibilité des métaux traces. Les principales méthodes de pré-traitement et de traitement

utilisées pour la gestion des sédiments dragués à l'échelle industrielle ainsi qu'à l'échelle de la recherche et du développement y sont décrites. Enfin est inclue une partie décrivant les exigences législatives relatives à la gestion des matériaux dragués dans les secteurs terrestres et maritimes. La Partie B de ce chapitre présente une revue de la littérature sur les résidus de bauxite (produit dérivé de l'industrie de l'aluminium), sa production et ses propriétés. Avec l'adoption par les Etats membres de l'Union européenne de la directive cadre sur l'eau qui vise à atteindre un bon état écologique des masses d'eau chimique d'ici 2015, et la Convention de Barcelone pour la protection de la mer Méditerranée contre la pollution, la gestion des rejets de résidus de bauxite est devenue une priorité. En effet, les états membres de l'union européenne s'engagent à diminuer progressivement le rejet des résidus de bauxite dans la mer Méditerranée jusqu'à complètement disparaitre d'ici la fin 2015. Etant donné leur teneur riche en minéraux, différents usages des résidus de bauxite ont été envisagés. Cette revue fournit un aperçu de l'utilisation possible du résidu de bauxite dans divers milieux environnementaux (eau, sol et sédiments).

Le chapitre II présente les équipements ainsi que le matériel et les méthodes utilisés pour cette étude. Les propriétés physico-chimiques des sédiments et des additifs minéraux fournis par les autorités concernées ont été déterminées en utilisant des protocoles standards. La procédure utilisée pour réaliser les expériences pilote de stabilisation des éléments trace dans les sédiments marins dragués avec des additifs minéraux a été expliquée et *plicatilis Brachionus* a été utilisé comme organisme d'essai pour tester la toxicité des lixiviats de sédiments.

Le chapitre III est consacré à la présentation des résultats et à la discussion. Ce chapitre comprend trois articles; le premier article décrit l'interaction des contaminants inorganiques (arsenic et de cadmium) avec des résidus de bauxite (de Bauxaline® et Bauxsol) dans un milieu aqueux. Des tests d'adsorption ont été réalisés dans différentes conditions physico-chimiques (pH, concentration). Les effets de ces conditions et leur impact sur la capacité d'adsorption et sur les mécanismes d'adsorption ont été discutés. Les données d'adsorption ont été modélisées à l'aide du logiciel "ECOSAT". Les sédiments portuaires sont fortement contaminés par les éléments trace. La stabilisation chimique de ces éléments (As, Cd, Cu, Mo, Ni, Zn et Cr) dans les sédiments compostés en utilisant des

additifs minéraux a été étudié dans deux expériences pilotes. La première expérience de stabilisation a été effectuée en plein air dans un dispositif pilote et deux additifs (Bauxaline® et Bauxsol) ont été appliqués à un taux de 5%. L'effet du traitement a été évalué en fonction des concentrations de contaminants (éléments trace) dans l'eau de percolation. Enfin, la toxicité des lixiviats collectés à partir des échantillons de sédiments traités et non traités a été évaluée en utilisant les rotifères marins. Ces travaux sont publiés dans «Marine Pollution Bulletin". La deuxième expérience de stabilisation est effectuée en utilisant le taux plus élevé (20%) des résidus de bauxite (Bauxaline®, Bauxsol et neutralisé Bauxaline®) et les résultats sont discutés. L'efficacité du traitement est évaluée par la qualité chimique et écotoxicologique des élutriats. Les résultats de la Bauxaline® neutralisé sont présentés dans un article publié dans "Chemosphere".

Enfin, le manuscrit se termine par une conclusion générale et présente les possibilités de recherche envisagées dans le cadre d'une poursuite de ce travail.

Chapter 1

Literature review

The main objective of this research is to evaluate the potential mobility of inorganic pollutants in marine sediment treated with bauxite residue. For this purpose, it is essential to have a good knowledge of the study matrix. The first bibliographic part deals with environmental issues related to the management of contaminated marine sediments. This section allows understanding of more accurately what are sediments and its primary constituents? What are the issues related to dredging of harbors and problems associated with the management of contaminated sediments? This chapter also includes the detail of regulations on dredged materials and different sediment treatment options. The 2nd part of this chapter deals with the extensive review on bauxite residue, its production and properties. The methods used for neutralization of bauxite residue and its application in pollution control (water, soil and sediment).

1-A) 1.Sediment- what is it?

Sediment is the unconsolidated material that settles at the bottom of water bodies such as lakes, rivers, estuaries, and oceans after travelling downstream from their source of origin (US EPA, 1999). Sediment is an integral and dynamic component of aquatic system that provide habitat and food sources for ecological and economical important aquatic species. They also play an important role in nutrients recycling and serve as food source for many species (Chapman, 1989). Sediments should not be considered as problem but can become problematic in three ways (i) erosion from anthropogenic activity (agriculture or construction, etc.) result in excessive sedimentation at the bottom of aquatic systems and cause environmental damage in number of ways (ii) excessive sedimentation in human commerce areas can disrupt ship navigation and requires periodic dredging (iii) and contaminants can easily sorb onto sediment particle and accumulate to the level where they endanger human and ecosystem health (US EPA, 1991). However, the sediments can serve as a sink for contaminants as well as ultimate source of the contaminants. Anthropogenic (dredging activities) and natural events disrupt the natural equilibrium between sediment and water, leading to the remobilization of contaminants from the sediment into overlaying water column increasing potential for environmental damage (Eggleton and Thomas, 2004).

1.1 Marine sediments, origin and types

Marine sediments are heterogeneous in nature and their composition is closely related to their source and geographic location. They originate from the erosion of soil or weathering of rock, the shell and organic matter derived from plant and animals, salt precipitated from seawater, and volcanic eruption products (ash and pumice) (Fig. 1).Mostly sediments are derived from weathering of rocks and ultimately transported by wind, water and ice to great distances. The sediments that come into oceans as particles particularly from disintegration of pre-existing rocks and volcanic ejecta, are dispersed and settle onto sea floor are known as **lithogenous** sediments. This sediment fraction is generally enriched in coastal areas and mainly composed of quartz, calcite, aluminosilicates (feldspars, clays) and oxides of iron and titanium. The lithogenic clays are generally illite, chlorite, kaolinite and smectite. **Hydrogenous** sediments are those that are precipitated out of seawater and

interstitial. These are Fe/Mn oxides or oxyhydroxides, clays (montmorillonite, nontronite, glauconite, zeolite...) and baryte. The Fe/Mn oxyhydroxides minerals are found in deep sea waters. **Biogenous** sediments are formed by organisms or accumulation of skeletal fragments. Major components of biogenic sediments are carbonate (calcite, aragonite), silica (opal), and sulphate (baryte, celestite) and calcium phosphate (teeth, bones and crustacean carapaces)and finally the cosmogenic sediments are of secondary importance made up of debris of meteorite (Seibold and Berger, 1996; Fütterer, 2000).

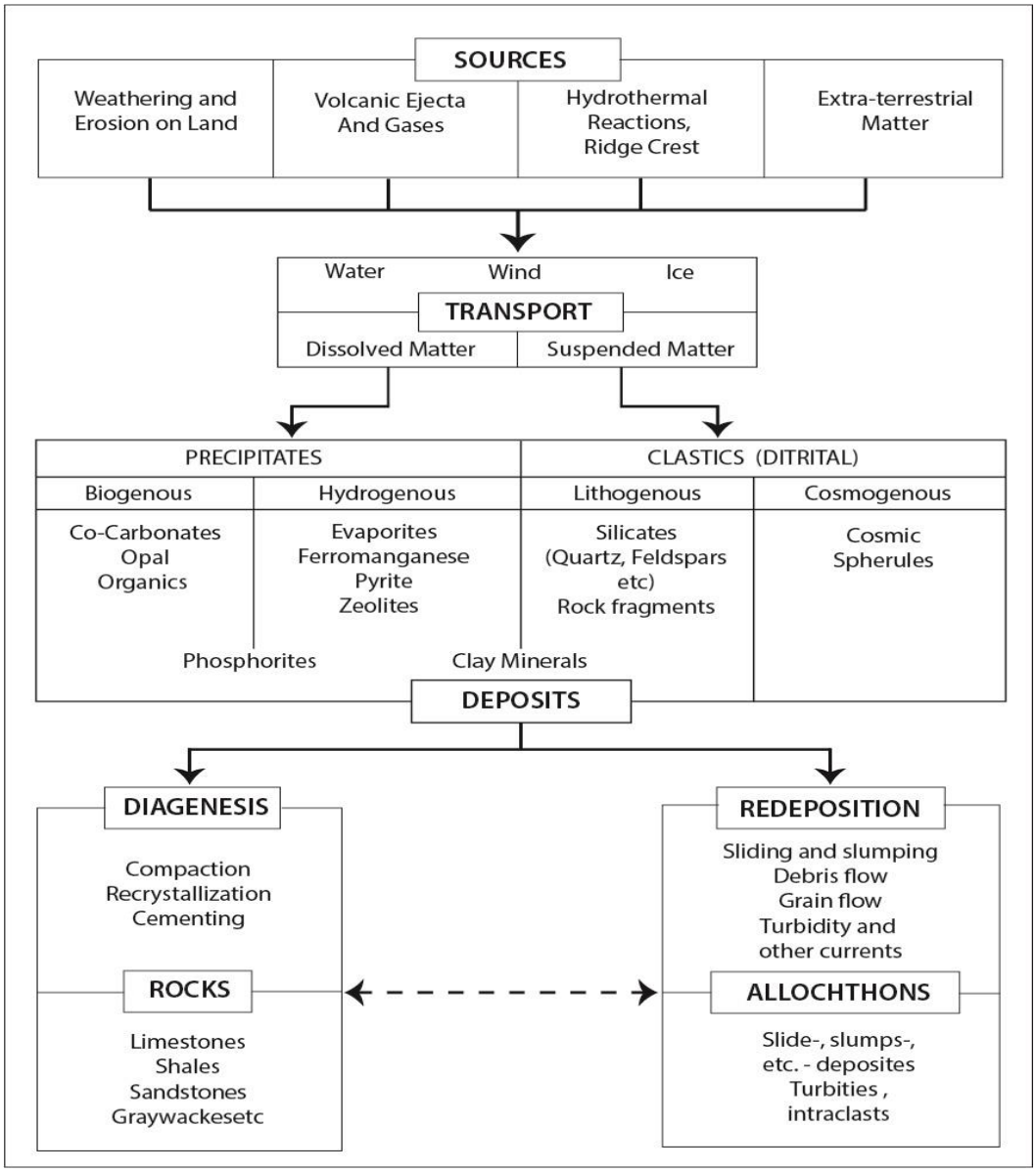

Fig 1 Sources, transport and destination of marine sediments (Seibold and Berger, 1996).

1.2 Primary components of sediment

Major constituents of sediments are mineral particles (clay, silt, sand, and gravel), organic matter and interstitial water (US EPA, 1999).

- **Interstitial water** is the largest component of the sediment occupying 20-90 % of volume by filling spaces between sediment particles (Seibold and Berger, 1996).
- **Inorganic materials** constitute of minerals from the earth's crust and shell debris. These minerals are primarily clays, carbonates and silicates. The size of mineral particles varies from sand to very fine colloidal fraction. The mineral particles are coated with iron and manganese hydroxide and organic substance exhibit high sorption capacity for inorganic and organic contaminants (US EPA, 1991).
- **Organic matter** is another important component of the sediment that occupies from near zero to more than 10 percent of the volume of sediment. Organic material in sediment results from the activities of living organisms. Organic material consists of plant debris while some exist in dissolved form in the water in sediment. The organic matter plays a crucial role to regulate the mobility and bioavailability of large number of contaminants, particularly nonionic organic compounds. Organic matter in the sediment tends to be highly reactive towards ionic and polar contaminants due to the presence of various molecules such as proteins, polysaccharides, lipids, humic and fulvic acids. Among these compounds, humic acids play an important role in the natural ecosystems because they tend to form organometallic complexes in aqueous phase, on the surface of inorganic particles, and thus change the availability of inorganic contaminants. Natural organic matter possesses both hydrophilic and hydrophobic sites, which can strongly affect its sorption and complexation behavior to charged and uncharged trace molecules and inorganic ions. Organic matter can be classified depending on its size as dissolved organic carbon (DOC < 1 kDa), colloidal (1 kDa <COC < 0.22 µm), and particulate > 0.22 µm) (US EPA, 1991; Santschi et al., 1997; Santschi et al., 1999).

1.3 Granulometry

Particle size and their distribution are the fundamental properties of sediments and soils. Sediments vary in their particle size distribution and are generally finer in texture than their source soils. Particle size distribution is used to determine the size of particle constituting the mineral phase of the material.

- Coarse fractions of sediments generally have particle size greater than 63 µm and consist mainly of sand and inorganic silicate materials. Coarser particles are predominant fraction at near shore stations due to re-suspension process caused by surface wave activity. The sandy sediments have low cohesion, a small contact area between particles and therefore less affinity for contaminants. The gravels and cobble are larger than 2000 µm in diameter while sand particles have diameter of between 50 µm and 2000 µm (Ujević et al., 2000).
- Fine sized sediment particles have diameter less than 63 µm and constitute of clays (diameter between 0.2 and 2 µm) and silt (diameter between 2 µm and 63 µm). Fine particles accumulate in quiescent zones where the re-suspension of sediments is negligible (US EPA, 1991; Ujević et al., 2000). The fine grained fractions have larger cohesion, high surface area, and negatively charged surface due to prevalence of clay minerals. These characteristics of the fine size particles give them a great adsorbing power for metallic contaminants. In addition organic matter is also mainly associated with these fine particles, may provide increased cohesion. It consists of heterogeneous macromolecules having hydrophilic sites that allow its adsorption on clay minerals, and complexation with the metal and organic contaminants (Seibold and Berger, 1996).

Table 1. Particle size (Seibold and Berger, 1996**)**

Pebbles	Gravels and cobbles	Sand	Silt	Clay
> 20 mm	>2000 µm	63 µm - 2000µm	2 µm -63 µm	< 2 µm

1.4 Sediments contamination and major contaminants

Sediments have the property of adsorbing contaminants from water and they are considered contaminated when the concentration of chemical substances (toxic or hazardous) is sufficiently available to affect human or environment health (US EPA, 1999). Contaminants are introduced into aquatic system due to anthropogenic and natural activities. Chemical contamination of marine sediments is mainly anthropogenic; it can enter into the sea not only through deliberate routes such as sewage discharge, industrial effluents (pesticides, paints, lather, textile, fertilizers, pharmaceutical), agricultural and urban runoff, deposition of airborne pollutants, dumping of waste and port activities. A great variety of contaminants finds their way into the sea through shipwrecks, lost cargos, from plastic ducks, etc. (US EPA, 1991; Tait and Dipper, 1998). Following are the major contaminants of sediments:

1.4.1 Nutrients

Elevated concentration of nutrients such as phosphorous promote unwanted growth of algae which lead to lower oxygen level in water body, when algae die or decay. High concentration of nitrogen compound such ammonia can be toxic to benthic organisms (US EPA, 1991).

1.4.2 Organic contaminants

Coastal and marine sediments contains numerous substances some of organic contaminants of particular concern include

- Polychlorinated biphenyls (PCBs) used before the end of the 90sas additives in paints, insulators for electrical equipment.
- Polyaromatic hydrocarbons (PAHs) present in environment can be due to the biosynthesis, pyrolysis of organic matter, oil spills or use of fuels fossils.
- Tributyltin (TBT) is an active ingredient of antifouling paints for the protection of ship hulls.
- Other organic compounds such as dioxins, organochlorine and organophosphorous pesticides), and endocrine disruptors are also found in sediments (Alzieu et al., 1999; Rulkens, 2005).

Organic chemicals persist in the environment, through sedimentation, bioaccumulation, and biotransformation, posing a risk to the health of the ecosystem. They can be carcinogenic (PAHs) (Li et al., 2014; Sarria-Villa et al., 2016), neurotoxin (organochlorine and organophosphorous pesticides, carbamates) (Koureas et al., 2012; Saeedi Saravi and Dehpour, 2015), growth or reproductive inhibitors (TBT and drugs) (Antizar-Ladislao, 2008; Haguenoer, 2010).

1.4.3 Trace metals

Trace metals pollution of environmental media is ubiquitous, persistent and complex environmental issue. Generally, trace metals are present at low level as natural constituents of marine and freshwater environment (Ansari et al., 2004). Sediments are known to accumulate metals up to several orders of magnitude higher than in the water (Bryan and Langston, 1992). They are derived from natural sources such as erosion of rock, soil and sediments and can be mainly through human activities (Luoma and Rainbow, 2008). The levels of these trace metals increased due to human activities (Mine drainage, offshore oil and gas exploration, industrial and domestic effluents, agricultural runoff and acid rain) in water systems and eventually incorporated in aquatic sediments (Ansari et al., 2004). At trace levels the elements such as Fe, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, As, Mo, Sn, and Sb are essential for living organisms but toxic in high doses (Bowen, 1979). Other elements (Pd, Ag, Cd, Pt, Au, Hg and Pb) are toxic to living organisms even at their low concentration (Luoma and Rainbow, 2008), and currently have no known biological function with the exception of cadmium which can act as an nutrient under Zn limited conditions in some marine diatoms (Lee et al., 1995). Toxicity of the trace metals depends largely on their physic-chemical forms, and bioavailability. Usually the free or dissolved forms of the metals are the most toxic (Alzieu et al., 1999). They may act by binding to membrane receptors after physiologically active or active transport in the intracellular medium, inactivating the enzyme mechanisms and in particular forming metalloenzymes in place of the essential elements (Goyer and Clarkson, 1996). The contaminants that are mostly monitored due to their intrinsic properties, i.e. toxicity, persistence, bioaccumulation, amount of inputs in coastal environments are usually arsenic (As), cadmium (Cd),

chromium (Cr), copper (Cu), manganese (Mn), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) because of their abundance and toxic effects (Milenkovic et al., 2005).

1.5 Fractionation of trace metals in sediment

The sediment is considered as complex matrix due to its composition (mineral and organic phases, interstitial water), structure, function (as a source of food and habitat), and diversity of contaminants present (Hakanson, 1992). The distribution of trace metal in various sediment compartments and overlaying water is controlled by physical, chemical and biological processes. Trace metals can be associated to various compartments in the sediments in different ways. They are partitioned into five fractions such as exchangeable (F1), carbonates bound (F2, acid-soluble),adsorbed on clay surfaces or Fe/Mn oxyhydroxides (F3, reducible), sulphides or complexed with organic matter (F4, oxidizable), and metals fixed in crystalline phase (F5, residual fraction) (Tessier et al., 1979; Ashraf et al., 2012). Exchangeable fraction of trace metals generally referred to as highly environmentally available component. Carbonate fraction include the trace metals which are precipitated and co-precipitated with carbonates. Their availability is affected by little variation in pH. Metal soluble oxides or hydroxides are associated with Fe-Mn oxides fraction under slightly acidic conditions as well as the metal associated with reducible amorphous Fe-Mn oxyhydroxides. This fraction is sensitive to oxidation-reduction potential (ORP) and can be dissolved with variation in ORP. Organic bound fraction involves the association of trace metals with various forms of organic matter through complexation or bioaccumulation process. This fraction exists in sediment for longer time and can be available with degradation of organic matter. Residual fraction relatively stable can only be available after weathering or decomposition (Salomons, 1998; Peng et al., 2009).

1.5.1Influential factors of trace metal availability

For many species, the major route of exposure is the transfer of these chemicals from sediments to organisms. Contaminants are not necessarily fixed permanently in the sediments. The availability of trace metals greatly depends on particle surface properties, physico-chemical conditions of the environment such as pH, Eh, and salinity and

biological processes (Calmano et al., 1993). However the mobilization of sediment bound contaminants can also occur during bioturbation of benthic animals by sea currents, storms and dredging activities (Eggleton and Thomas, 2004).

1.5.1.1 pH

pH is an important factor responsible for the adsorption and mobilization of inorganic contaminants. In sediments, pH depends on the biological activities as well as the buffering system (carbonates). Reduction of sulfates to sulfides leads to an increase in the pH. Conversely reduction of nitrates to nitrogen (denitrification) decreases pH (Meyer et al., 1994). Oxidation of acid volatile sulfides and degradation of organic matter caused decrease in the pH of sediment from neutral to acidic (pH ~1.2), which results in an increase rate of some trace metal release (Kraus and Wiegand, 2006). During land disposal of sediment, oxidation of zinc sulfide result increased leachability of Zn (Panfili et al., 2005). In acidified conditions, the competition between the H^+ ions and metal cations increases for the adsorption site. It subsequently decreased the adsorption capacity and increased the mobility of metals (Tack et al., 1996; Wang et al., 2015). The mobility of anionic contaminants increases with increasing pH whereas cations are precipitated in the form of metal hydroxide. Potential mobility of each metal is different in sediment at same pH e.g., at pH 4.0 the mobility of metals decrease as follows;
Zn>Cd>Ni>As>Cu>Pb (Salomons et al., 1995; Peng et al., 2009).

1.5.1.2 Redox potential

The redox potential or redox (Eh) is another important factor that determined the possibility of dissolution or precipitation of inorganic compounds in sediments (Salomons et al., 1995).Under reducing condition acid volatile sulfides (AVS) have key role in reducing the mobility of divalent metals by complexation/adsorption. Increase in redox potential facilitates the oxidation process and leads to remobilization of trace elements. This phenomenon is more important in organic rich medium (Calmano et al., 1993; Tack et al., 1996). Moreover, seasonal variations, heavy rains or flooding disturbed sediment conditions and oxidation process enhanced contaminants concentration in overlaying water (Stephens et al., 2001; Zoumis et al., 2001; Piou et al., 2009). Therefore dredging of

aquatic sediments should be done carefully to avoid the oxidation of sediments and contaminant release (Peng et al., 2009).

1.5.1.3 Organic matter (OM)

Considerable fraction of organic matter in sediment exists in particulate form. It plays a vital role in the fate of metals. Generally the solubility of OM determines the bioavailability of metals. High molecular weight OM can reduce metal availability by forming insoluble complexes as compared to low to medium molecular weight OM, which can form soluble metal (Du Laing et al., 2009). Sediment OM is heterogeneously complex component serve as a main geo-sorbent for hydrophobic organic contaminants in sediments and soils (Hong et al., 2010). OM is composed of humic and fulvic acids in natural rivers and lakes. Generally, the complexation reaction between metals and organic matter components determines the speciation and bioavailability of trace metals. The sediment with higher humic substance will have higher metal content (Fernandes et al., 2011). However, it is difficult to predict the reaction type between OM and metals in severely contaminated river system due to OM complexity. Mostly, precipitation, co-precipitation or flocculation plays vital role in heavy metal fixation. Decomposition of higher OM produces humic acid which lead to lower the pH value and increase metal leaching. However, binding of metals to OM is considered relatively stable but it is important to monitor the release of trace metal due to organic matter degradation with time (Peng et al., 2009).

1.5.1.4 Salinity

Similarly, increase in pore water salinity enhances the competition for sorption sites between metals ions and other cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) and decreased the adsorption of metals to humic acids (Du Laing et al., 2009; Peng et al., 2009). For oxyanions such as arsenic, chromium or molybdenum, the same phenomenon is observed in the presence of anions such as carbonates, phosphates, silicates, nitrates and chlorides (Du Laing et al., 2008). High salinity can also inhibit the growth and activity of sulfate reductive bacteria which affect the reduction of sulfate and decomposition of organic matter in sediment, resulting in increase in the bioavailability of metals (Zhang et al., 2014).

1.5.1.5 Quantity and nature of metals present in sediment

Generally, the total concentration of metals in sediment is appeared to the most important parameter which is affected by different physiochemical factors. The proportion of clay minerals and organic phases determined the distribution and reactivity of sediment pollutant (Zoumis et al., 2001). Metal accumulation in aquatic biotas is strongly correlated with its total concentration in the sediment. In sediments, usually their concentration is three fold higher than the overlying water. Metal concentration is also indirect reflection of mineralogy and the origin or nature of sediment (Bryan and Langston, 1992; Zhang et al., 2014). Changes in the physiochemical parameters caused the solubilization of metals. Studies have shown that the adsorption capacity of both sediment and suspended particulate matter increases with increase in the concentration of metals in the water and sediment (De Jonge et al., 2009; Saeedi et al., 2013). Bioaccumulation also increases linearly with increase with the total concentration of metals in sediment. However, no significant correlation between metal accumulation and its pore water concentration was found. The total concentration is not always concerned with its toxicity and bioavailability (De Jonge et al., 2009). Only less than 1 % of the metal contaminants (and other pollutants) are dissolved in the water, while 99% of the contaminants are stored in sediment (Salomons, 1998). Moreover, the bioavailability of metals can be determined by their chemical forms. The metals are generally present in five fractions (exchangeable, carbonate, iron–manganese oxides, organic matter and residual) (Tessier et al., 1979).The distribution of different species indicates the bioavailability and migration of metals in sediment (Huo et al., 2013). The exchangeable, carbonate and Fe-Mn oxides fractions are readily available by organisms due to their weak binding with metals and accompanied by its toxicity (Kelderman and Osman, 2007; Baumann and Fisher, 2011; Campana et al., 2013). However, residue fraction is most stable one and metal complexes with organic matter/ sulfides are stable and metals are immobilized and less available but can mobilize under certain conditions (Peng et al., 2009).

1.5.1.6 Other factors

Although, pH, Eh and OM are the most important environmental factors affecting the metals distribution in sediments. Metal distribution can also be affect by some other factors

such temperature, retention time, cation exchange capacity (CEC). Adsorption of metals onto sediment decreases with Increase in temperature. Difference in CEC of metals their mobility capacity varies correspondingly (Cs > Zn > Cd > Fe >Ag > Co >Mn). Moreover, according to long time kinetic adsorption-desorption behaviors show that the freshly associated metal with particles presents less stable and higher potential bioavailability than those associated for a long time. Due to aging effect there is decrease in exchangeable and carbonate fractions while increase in the refractory fractions (organic and residual phase) (Peng et al., 2009; Zhang et al., 2014).

1.6 Chemical contamination of Mediterranean port sediments and bioaccumulation in living organisms

The Mediterranean is considered to be the most polluted ocean in the world and marine life is heavily threatened by habitat degradation mostly due to human activities, such as fisheries, ship traffic, water pollution, coastal anthropization. According to UNEP (United Nations Environment Program) approximately 650,000,000 tons of sewage, 129,000 tons of mineral oil, 60,000 tons of mercury, 3,800 tons of lead and 36,000 tons of phosphates are dumped into the Mediterranean Sea annually. Mediterranean Sea is so enclosed by land that its warm waters take more than 100 years to clean and renew themselves (Iaccino, 2014).

Mediterranean sediments are hugely contaminated by inorganic contaminants (As, Cu, Cd, Zn, Ni, Hg, Cr and Pb) organometallics, and organic compounds (PAHs and PCBs, DDT) (Andral et al., 2004; Gómez-Gutiérrez et al., 2007; Martín et al., 2009; Tessier et al., 2011; Mamindy-Pajany et al., 2013; Pougnet et al., 2014b). Because of the chemical contamination biodiversity is badly affected in coastal areas. The marine and coastal ecosystems are among the most productive and provide socio-economic benefits for humanity (UNEP/MAP/CP RAC, 2006). Continuous anthropogenic activities increased pollution load in coastal areas which leads to degradation of ecosystem. Organisms living in contaminated habitats are exposed to risks by accumulating pollutants in their tissues via food intake (particulate contaminant), membrane facilitated transport (active dissemination) or passive diffusion (dissolved contaminant). The rate and uptake mechanism of contaminants can vary among and within species. It also depends on the

development stage, season, behavior, sexual condition and history of contaminant exposure. Bioavailability of contaminants, including inorganic contaminants is dependent on speciation / distribution in the dissolved and particulate fraction (Eggleton and Thomas, 2004).

The benthic community structure is an important indicator of the quality of sediments. Exposure of marine organisms to pollution induces accumulation of contaminants in certain tissues, organs or organisms. This phenomenon is known as bioaccumulation and through food chain this factor is amplifying. Contamination of marine environment by trace element causes the fragility of whole food chain: Phytoplankton-Zooplankton-bivalve/ crustacean- fishes-marine top predators (Reinfelder et al., 1998; Rahman et al., 2012). Bivalves are useful environmental indicator organisms and incur a significant risk of exposure due to their sedentary character and filter feeders. They can concentrate both metals and organic contaminants. That's why they have been extensively studied and used as bio-indicator of the quality of natural aquatic environment. They have been used in different international programs such as Mussel Watch (USA) and the RNO (France) (Claisse, 1989; Andral et al., 2004; Casas and Bacher, 2006; Kim et al., 2008; Kimbrough et al., 2008; Hamza-Chaffai, 2014). These programs have demonstrated the important contamination level of global coastal areas likely to affect biota, particularly to induce a health risk because of the bioaccumulation of contaminants in these organisms.

1.6.1 Area of study: Toulon harbor sediments contamination

According to surveys conducted in 1986 to monitor the chemical contamination of different port sediments in France shown that the arsenal port sediments have contamination level above N2 for majority of elements except for Ni and Cr which are lower than N2 (Table 3) (Grosdemange et al., 2008). Arsenal is the military port of French Navy situated in the city of Toulon, southeastern France which is subjected to military and commercial activities. The Toulon bay is located on the north-western part of the Mediterranean Sea. The sediments of the Toulon bay found be contaminated by multitude of metals, metalloids (Tessier et al., 2011; Dang et al., 2014), organometallics (Pougnet et al., 2014), and organic compounds (Andral et al., 2004). In addition to characteristics of area (semi-closed, low tidal amplitude, long water/particle residence time), it is also

submitted to various anthropogenic inputs from historic (bombardments, warship scuttling and raising during and after the 2nd World War) and more recent activities such as Navy, nautical traffic, sewage runoff from Toulon urban area, industries and tourism (Tessier et al., 2011). Great anomalies have been observed in contaminants concentrations in mussels transplanted at Toulon bay (Andral et al., 2004), as well as clear variations in concentration of trace metals both in water and mussel samples was found (Casas et al., 2008).

Periodic dredging of the study site is required to maintain the ship navigation and maritime activities. Dredging of such contaminated sediments causes potential mobility of such contaminants and further risk for surrounding environment after land disposal. Therefore, management of dredged sediments contaminated with trace metals/elements is an important issue.

1.7 Dredging of port sediments

Dredging is a routine activity carried out worldwide that involve the removal of excessive sediments and debris from the bottom of lakes, rivers, harbors, and other water bodies and deposit them to other locations (Brunn et al., 2005; Todd et al., 2014). Dredging of ports and harbors is performed to fulfill the following purposes.

- Navigation: maintenance or improvement of navigation depth in ports, harbors, marinas and shipping channels to ensure the safe passage of ships, and boats. Periodic dredging of ports is also a legal requirement for port authorities.
- To improve drainage and reduce flood risk.
- Construction and reclamation: in support of coastal development or for the provision of foundations for civil engineering works.
- Mining to extract minerals and aggregate materials from underwater locations.
- Beach nourishment: to improve or restore the performance of beach as a sea defense or an amenity
- Environmental: it is also performed to reduce the exposure of aquatic life and people to contaminants and generally for the removal of contaminated sediments to prevent contamination to other areas of water body. This environmental dredging is often necessary because sediments in and around cities and industrial areas are frequently contaminated with a variety of pollutants (IADC/CEDA, 1997).

Dredging plays a vital role in nation's economy. However, after dredging a portion of the sediments remained suspended in the water column, water currents moved suspended sediments from dredging sites, and often retuned to sediment bed through particle settling and deposition. Therefore, the transport and fate of suspended sediments after dredging are of prime importance due to impact on natural resources (USACE, 1983; Smith and Friedrichs, 2011).

In Europe, quantities of dredged sediments vary with size and geographic location of ports. An assessment undertaken within the SedNet European network found that the total amount of sediment dredged in Europe is between 100 and 200 million m^3 per year. In France nearly 50 million $m^3$of sediments are dredged out annually from the main maritime and commercial ports (Alzieu et al., 1999). Previously, dredged sediments were discharged at sea with no precautions regarding contaminations. Increasing concern about pollution has resulted in national regulations enforcing rigorous control and monitoring of contaminated sediments discharge (Caplat et al., 2005). Dredged sediments are often contaminated with organic and inorganic pollutants. After dredging, sediments are disposed on land therefore the fate and effects of sediment contaminants are of particular concern to preserve the environment (den Besten et al., 2003).

1.7.1 Dredged sediments legislation

The management of the dredged sediments complies with the international OSPAR convention (1992) for the protection of marine natural environments of North-East Atlantic Ocean and, the World London Convention (1972) on the prevention of marine pollution by dumping of waste, and the Barcelona convention (1976) for the Mediterranean Sea. These conventions establish guidelines and proposed recommendations concerning the physico-chemical and toxicological evaluation of dumping materials, the positioning of dumping sites and issuance of dumping permits. The member countries of OSPAR convention were recommended to define sediment quality guidelines linked to the action levels for number of contaminants (proposed by OSPAR) (Alzieu et al., 1999).

In France, legislation regarding to the dredging and disposal of marine sediments was revised and completed in June 2000. The national decree of 14th of June 2000 proposed two levels N1 and N2 in line with OSPAR convention for trace elements concentrations

and PCBs in marine and estuarine sediment to assess the impact of dredging on natural environment. Table 2 presents the French sediment quality guidelines (the N1 and N2) for different contaminants in sediments (inferior to 2 mm).

According to this regulation, if the level of contamination is below N1 level, the sediments are considered as uncontaminated and can be successfully submerged into the sea. The ecological impact is considered to be negligible. For the contamination between N1 and N2 levels, the sediments are classified as contaminated and assessment of toxicity is required along with chemical analyses. If at least the concentration of one contaminant is greater than N2 level, the sediments are considered as highly contaminated with potential ecological impacts on the aquatic environment. These kinds of sediments are usually managed on land in controlled landfills. The contaminants are not necessarily permanently immobilized in dredged sediments, and trace elements remobilization from sediment constitutes a potential danger to surrounding environment (Alzieu, 2005)

Table 2. Reference action levels (mg/kg dry sediment) for metals and polychlorobiphenyls according to the decree of 14 June 2000 (Alzieu et al., 1999).

Metals	**Level 1**	**Level 2**
Arsenic	25	50
Cadmium	1.2	2.4
Chromium	90	180
Copper	45	90
Mercury	0.4	0.8
Lead	100	200
Nickel	37	74
Zinc	276	552
Polychlorobiphenyls	**Level 1**	**Level 2**
CB 28	0.025	0.050
CB 52	0.025	0.050
CB 101	0.050	0.100
CB 118	0.025	0.050
CB 138	0.050	0.100
CB 153	0.050	0.100
CB 180	0.025	0.050
Σ PCB	0.5	1

1.7.1.1 Risk assessment related to dredged sediments

In 1986 monitoring surveys were conducted in France to assess the chemical quantity of dredged sediments. Table 3 shows that nearly all the sediments of port have contamination level below level 1. In some basins the level of contaminant concentrations was between level 1 and 2 only a small volume of sediments have contamination level greater than level 2 requiring specific management (Alzieu et al., 1999).

Table 3. Chemical composition of dredged sediments from several Mediterranean ports (Grosdemange et al., 2008).

Pollutants	Arsenal	Bregaillon	Bandol	Cannes	Marseille	St Mandrier	Sanary/ Lavandou	N1	N2
As	196	30	16	21	30	16	34	25	50
Cd	5.9	1	0.4	0.6	3.7	0.3	0.8	1.2	2.4
Cr	94	58	33	46	68	53	51	90	180
Cu	1459	206	95	166	456	48	504	45	90
Hg	111.5	14.9	2.5	54	11.4	0.4	0.5	0.4	0.8
Ni	42	33	14	17	29	26	25	37	74
Pb	1340	278	62	198	1011	37	246	100	200
Zn	3493	488	145	359	2415	93	565	276	552
PCB total	0.89	0.24	0.11	0.75	1.68	0.05	0.48	0.5	1
$Q_{PEC\ m}$	39	6	1	16	7	1	2	–	–
Risk score	2.8	1.8	1	1.7	2.6	0.6	1.9	–	–

To assess the risk of intermediate and highly contaminated dredged sediments on the basis of chemical data (recommended by national decree); French Research Institute for Exploitation of the Sea (IFREMER) and the studies and observation group on dredging and environment (GÉODE) has developed the Geodrisk software. Based on Geodrisk score, it provides a bench mark for the operator to design a management process according to tree

(Fig. 2). It also enables to differentiate dredged sediments according to their contamination level and potential toxicity (Alzieu and Quiniou, 2001).

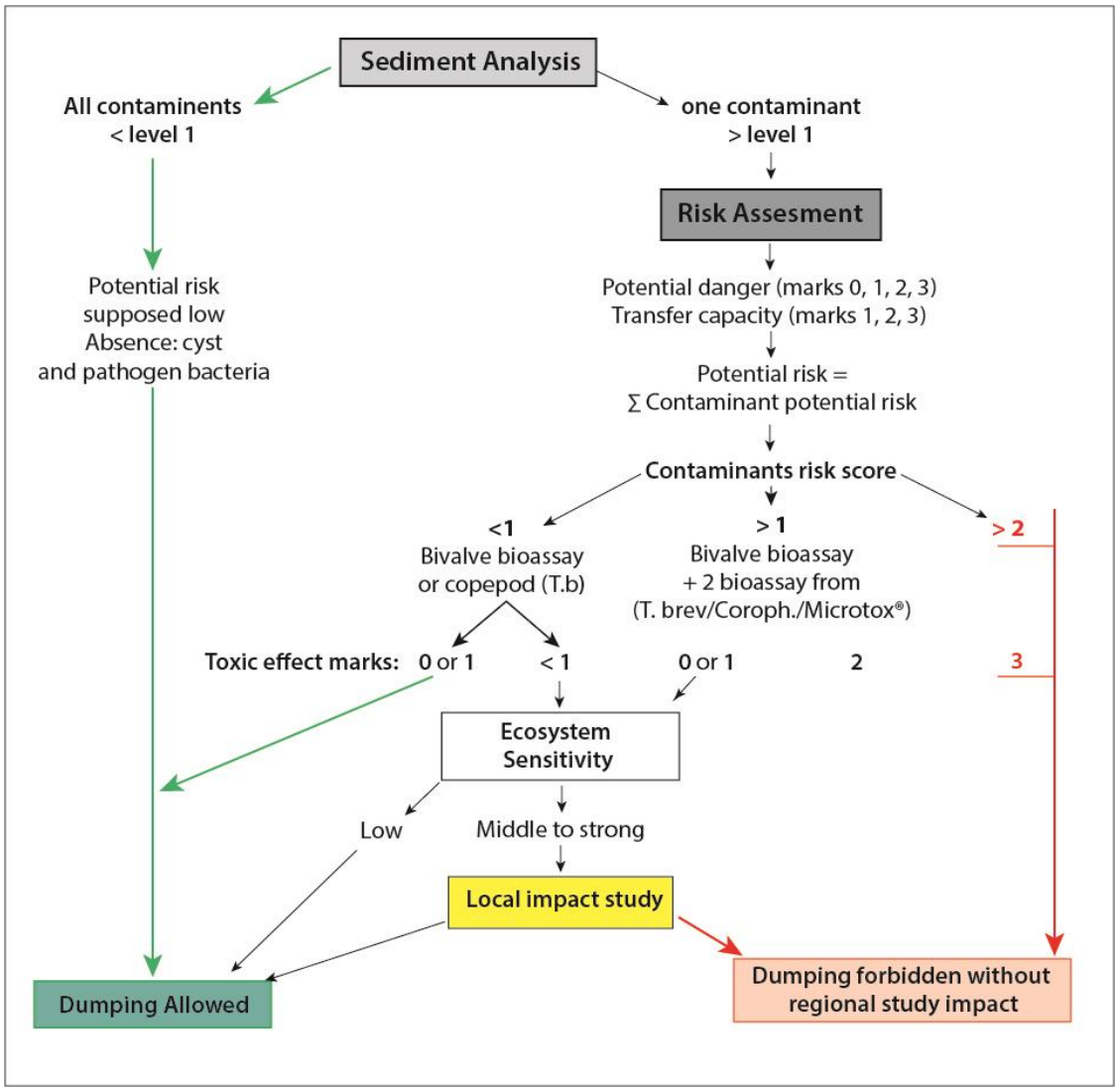

Fig. 2 Geodrisk decision tree(Alzieu, 2003).

1.7.2 Regulation for landfill

In 2002, European council developed criteria and procedures for acceptance of waste for landfills based on leaching and percolation test (European Council, 2002). Depending on the levels of pollutant concentration in water leaching and percolation, sediment waste can be classified into three categories:

- Hazardous waste (Class 1)

- Non-hazardous waste (Class 2)
- Inert waste (Class 3)

Procedure for the acceptance of waste for the landfill depends on the full characterization of the waste for its safe disposal in long term context. Leaching limit values for different contaminants are given in $mg.kg^{-1}$ of dried material (Table 4). Moreover, for the category of inert waste (Class 3) must also follow additional limit values for total content of organic parameters (Table 5).

Table 4. Threshold values of chemical parameters in leachates (L / S = 2, L / S = 10) for the acceptance of waste at waste disposal center. The value of L/S ratio is the ratio of the amount of liquid (in liters) and solid (in kilograms) (European Council, 2002).

Elements (mg/kg)	**Threshold values in leachates for waste acceptance**					
	Class 1		**Class 2**		**Class 3**	
	L/S = 2	L/S = 10	L/S = 2	L/S = 10	L/S = 2	L/S = 10
As	6	25	0.4	2	0.1	0.5
Ba	100	300	30	100	7	20
Cd	3	5	0.6	1	0.03	0.04
Cr	25	70	4	10	0.2	0.5
Cu	50	100	25	50	0.9	2
Hg	0.5	2	0.05	0.2	0.003	0.01
Mo	20	30	5	10	0.3	0.5
Ni	20	40	5	10	0.2	0.4
Pb	25	50	5	10	0.2	0.5
Sb	2	5	0.2	0.7	0.02	0.06
Se	4	7	0.3	0.5	0.06	0.1
Zn	90	200	25	50	2	4
Chloride	17 000	25 000	10 000	15 000	550	800
Fluoride	200	500	60	150	4	10
Sulfate	25 000	50 000	10 000	20 000	560	1 000
Phenol index					0,5	1
Dissolved organic carbon (DOC)	480	1 000	380	800	240	500
Total dissolved solids (TDS)	70 000	100 000	40 000	60 000	500	4 000

Threshold value presented in table 4 for waste acceptance, the inert waste must also meet the following additional limit values for the total content of organic parameters (Table 5).

Table 5. Limit values for the total content of organic parameters(European Council, 2002).

Parameters	Values (mg/kg)
TOC (Total organic carbon)	30 000(*)
BTEX (Benzene, Toluene, ethyl benzene, and xylene	6
PCBs(Poly chlorobiphenly 7 congeners)	1
Mineral oil (C10 to C40)	500
PAHs (Poly aromatic hydrocarbons)	Member States to set limit value

(*) In the case of soils a higher limit value may be admitted by the competent authority, provided the Dissolved Organic Carbon at pH 7 (DOC7) value of 500 mg/kg is achieved.

European waste codes for such waste are

17 05 05* dredging spoil containing dangerous substances

17 05 06 dredging spoil other than those mentioned in 17 05 05

According to the decree of 14 June 2000, if the concentration of one contaminant is greater than N1 level, the sediment is classified as hazardous waste. The hazardous character of such waste is defined in Annex III of waste directive and includes 14 criteria (H1 to H14) distributed among 4 types.

H1 to H3: Physical hazard

H1 H12: Hazard for human health

H13: Hazard following elimination of waste

H14: Environmental hazard

H14 bases on ecotoxicity test seem to be determining criterion to calculate the dangerousness of sediment placed on earth.

1.8 Management of dredged sediments

Dredging of European ports is done for various purposes (flood prevention, navigation, maintenance and capital dredging, and for remediation) and it yields 100 to 200 million m^3 of dredged sediments yearly. Therefore, the methods of management vary with the kind of dredged material. The flow chart in Fig. 3 represents the management options for dredged

sediments. Relatively clean sediments are relocated or immersion into sea. Relocation of non-contaminated sediment is considered to be sustainable solution, as the sediment is integral part of our river basins. The management of contaminated dredged sediments is difficult due to possible danger of the pollution of surrounding environment. The contaminated dredged sediments/materials are either treated ex-situ or in-situ. The term reuse is used for treated and untreated dredged materials, while disposal in a disposal site is not considered to be a beneficial use or reuse.

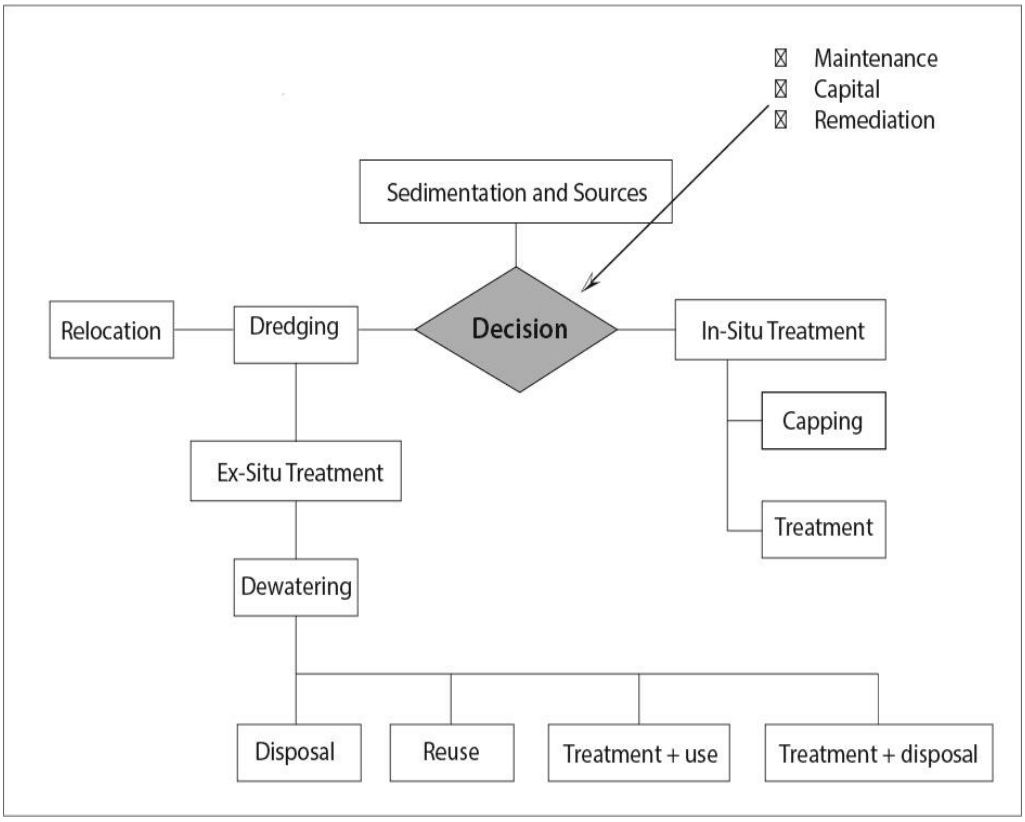

Fig. 3 Flow chart representing the management options leading to the needs for dredging and/or treatment (Bortone et al., 2004).

1.8.1 Treatment types and disposal options

Several treatment technologies are described for dredged sediments. Applicability of each treatment depends on the physical and chemical characteristics of the sediments and the possibilities for use as construction material or beneficial reuse. In Fig. 4, a modified drawing gives an overview on available treatment chains. According to this, all the

sediment cannot be immersed. Immersion is applicable only for those having chemical contamination level below N1. Contaminated sediments can be directly treated in situ or dredged and stored under water. Ex-situ treatments are applicable to average contaminated sediments where dumping is prohibited. The treatment chain is using solidification / stabilization process to use sediments as construction materials. This does not necessarily involve particle separation because the pollutants are immobilized in the sediment by solidification. Particle size separation techniques are applied to separate the uncontaminated sand fraction for construction material and treating the fine fraction for beneficial use or disposal. The processing of fine fraction of contaminated sediments often requires a combination of several techniques (physico-chemical, biological and thermal). Generally, the total cost of the process increases with the level of sediment contamination.

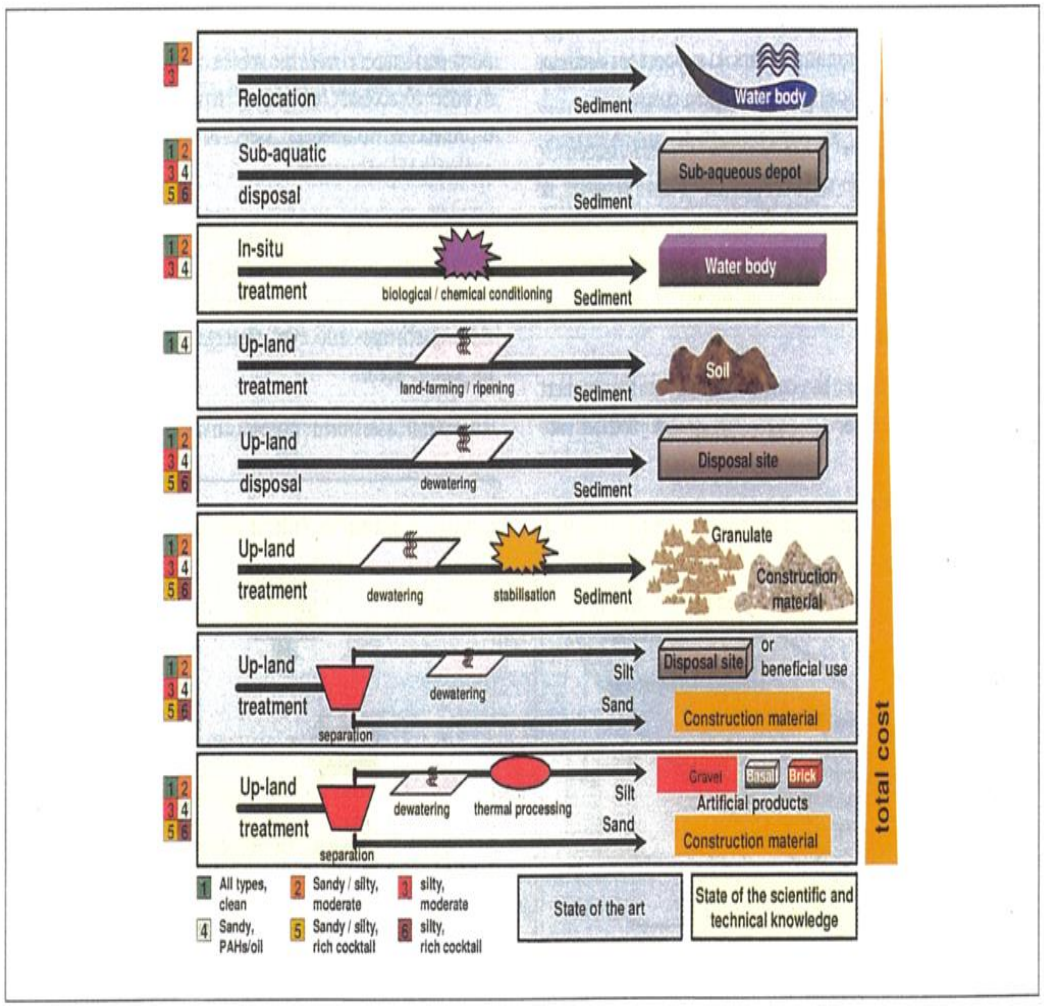

Fig 4. The main available treatment chains in Europe (Bortone et al., 2004).

1.8.2 Dredged sediments treatments methods

Usually, the treatment methods are similar to those used for soil but fewer are feasible for sediments. This limitation is due to difference in the properties of sediments and other matrices. Sediment treatments include pretreatment, physical separation, thermal processes, biological decontamination, Electrokinetics, stabilization/solidification and washing (Mulligan et al., 2001).

1.8.2.1 Pretreatment (dewatering and physical separation)

Pretreatment of dredged sediments is necessary before further treatment processes. Removal of debris and water from dredged sediments is often necessary after dredging to remediate and treat contaminants. Debris (tires, concrete blocks, automobile parts, and rocks) can be removed by backhoes or clamshells while small debris parts are removed by trammel screens or grizzlies.

The quantity of water in dredged sediments depends of the type of dredging used and the technology to be used for its treatment. Mechanical dredged sediments contain more than 50% of water content while hydraulically dredged sediments contain 20% of water. 40% of water content is required for many processes. Dewatering is done by draining of the water in lagoons with or without coagulants and flocculants, or using presses or centrifuges. The material dryness of the waste must be of 30% minimum. Pretreatment is done to give cohesion to the dredged sediments by effecting dehydration of the material through different technical processes (US EPA, 1993; Delort and Grodemange, 2006).

Physical separation includes centrifugation, flocculation, hydrocyclones, screening, and sedimentation to separate smaller contaminated particle. Hydrocyclones applies centrifugal force to separate large particles (10-20 µm) from small particles. Screening is applicable mostly to particles larger than 1 mm. Fluidized bed separation removes smaller particles in the countercurrent overflow in a vertical column by gravimetric settling. Flotation involves the use of special chemicals and aeration which cause to float contaminated particles. Sedimentation or gravity separation is applicable if the contaminated fraction has a higher specific gravity that the rest of the sediment fraction. The grain sorting separates the sandy part from muddy part of the sediment. This separated sand may be washed and used as material (nourishment, roads, concrete ...). This technique is useful when the sediment

contains a significant quantity of sand, since it considerably reduce the volume of sediment. Physical techniques only concentrate the contaminants in smaller volumes and are, thus useful before thermal, chemical or other processes (Mulligan et al., 2001).

1.8.2.2 Main treatments applicable for sediments

Following methods are employed to separate, destroy and immobilize the contaminants in sediments.

(i) Biological decontamination; include the use of microbes. Microorganisms can destroy organic pollutants in contaminated sediments while metallic contaminants can be removed through bioleaching.

(ii) Physico-chemical treatment; can immobilize or transform the contaminants by physico-chemical interaction (adsorption/ desorption, oxidation/reduction, ion-exchange, precipitation/ dissolution).

(iii) Thermal treatment; involves the heating of sediments which destroy the organic contaminants and immobilize heavy metals in sediments (Rulkens, 2005).

The main treatment techniques applicable for sediments are summarized in Table 6

Table 6 Main treatments techniques used for the management of sediments

Biological treatments					
Strategy/Technique	**Principle**	**Contaminants**	**Advantages**	**limitations**	**References**
Bioleaching	Bioleaching can be performed either in sediment slurry or by heap leaching with sulphur oxidizing bacteria	Metals	*Thiobacilli* remove 70-75% of heavy metals (except Pb and As)	Speciation of metals, Water treatment	(Mulligan et al., 2001)
Biodegradation or Bioremediation	Aerobic composting Mixing of dewatered sediment with natural organic materials and placed in an aerial stockpile	Hydrocarbons	Natural process Low cost Reduce volume	Duration	(Rulkens, 2005)
	Bioreactor Stirring the sediment with bacteria under control parameters (pH, nutrients, O_2 content)	Organic	Efficient for sediments consisting of fine particles and organic contaminants	Very expensive	(Mulligan et al., 2001; Rulkens, 2005)
	Land farming Open air spreading of sediment for dewatering and possible activation by adding nutrient or mechanical turnover.	Organic	Natural process Slow ripping of sediment Low cost	Duration Area and alteration of soil	(Rulkens, 2005)
Phytoremediation	Use of special plants to remove or	PAHs, PCBs,	Easy implementation	Applicable to low	(Mulligan et al., 2001;

	destroy contaminants. There are three modifications of the process. Phyto-degradation: degradation of contaminants by root assisted microbes Phyto-extraction: extraction of metals and their subsequent accumulation in plants Phyto-stabilization: immobilization of contaminants with plants	and metals	Green technology Biomass production and its use	and medium contaminated sediments, if the level of contamination is within 100 cm (root access). Slow process Only extractable / available metals	Rulkens, 2005)
Thermal treatments					
Thermal techniques	Incineration: Oxidation of the sediment at high temperature 800-1200 °C destroying organic contaminants, dewatering, and metals are immobilized except for Hg contaminating compounds (Hg, As,and Cd become more leachable like As, Mo and V)	PAHs, PCBs, pesticides, dioxins, and metals	Highly contaminated sediments Valorization Economic value by providing pure Hg	Very expensive Residue elimination is difficult	(Mulligan et al., 2001; Rulkens, 2005)
	Thermal desorption: Use of heat (100-500°C) to vaporization organic contaminants and water	Volatile organic contaminants, some metals	Suitable for volatile substance	Moderate cost Residue treatment	(Mulligan et al., 2001; Rulkens, 2005; Peng et al., 2009)
	Vetrification:	All	End product can be used	Pretreatment is	(Mulligan et al., 2001;

	Complete destruction of organic contaminants and immobilization of metals in sediment at high temperature	contaminants	as building material	necessary, Very expensive	Rulkens, 2005)
	Wet oxidation: Oxidation of wet sediment at high temperature (200-300°C) and pressure (20-100 bars)	Petroleum hydrocarbons , Phenols, PAHs	-	Very expensive	(Kribi, 2005)
	Supercritical oxidation: Modification of wet process-temperature and pressure are above the critical point of water.	PAHs, PCBss	Higher oxidation rate Complete oxidation of PCBs	Special equipment Very expensive	(Rulkens, 2005)
Physico-chemical treatments					
Wet classification	Separation of polluted sediment particles from non-polluted sediment particles. In first step intensive mixing od sediment is carried out. While 2nd step involves mechanical separation (hydrocyclone, centrifuge, flotation etc.)	Inorganic contaminants	Moderate cost	Applicable only to sediments in which contaminants are bound to a certain fraction of sediment that can be easily separated.	(Rulkens, 2005)
Oxidation/reduction	Addition of reducing or oxidizing agent in the sediment, extraction or	Inorganic contaminants	Precipitates are less soluble	Expensive	(Mulligan et al., 2001)

	precipitation of contaminants				
Solvent extraction	Use of organic solvents to extract the contaminants from sediments by mixing sediment with solvent. Solvents can be water soluble or slightly soluble in water	Organic	Applicable to fine fraction of sediment Moderate cost	slow	(Rulkens, 2005)
Chemical leaching/ Sediment washing	Agitation of sediment with water, inorganic acids (HCl, H_2SO_4, HNO_3), chelating agents ((ethylenediaminetetraacetice acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA)) or surfactants.	Metals	Efficient removal of metals Applicable to sand and gravels sized sediments	Expensive Restricted to weakly bound metals Not applicable to fine fraction of sediment	(Rulkens, 2005; Peng et al., 2009)
Electrochemical process	Use of an electric current between two electrodes to allow migration of pollutants towards electrodes	Metals, and organic	Fine fraction	Maintenance cost	(Rulkens, 2005; Peng et al., 2009)
Flotation	Using gas bubble attachments to dispersed phase and floating aggregates can be separated	Metals, valuable mineral ores	Low energy requirement Fine particles (20-50 µm)	Depend on particle size Redistribution of metals	(Peng et al., 2009)
Ultrasonic assisted extraction	Application of ultrasonic coupled with vacuum pressure	Metals	Coarse fraction	Expensive Applicable to low clay content	(Peng et al., 2009)

Main contaminants solidification /stabilization techniques					
Solidification / stabilization	Mixing of sediment with hydraulic or organic binders	Heavy metals and hydrocarbons	Creation of inert waste	Must contain 50% moisture, organic contaminants can interfere, increases volume	(Mulligan et al., 2001; Lafhaj et al., 2008; Chatain et al., 2013)
	Novosol process: hydroxyapatite precipitation by adding phosphoric acid followed by calcination of the material	Metal and removal of organic			

1.8.3 Stabilization of trace elements in marine dredged sediments with mineral amendments

Even until late 20th century sediments were considered as valuable source for human (agriculture) and nature. This perception change drastically when it became clear that sediments not only contain nutrients but serve as a sink for a number of contaminants. Hence the contaminated sediment management is complex and multivariate approach involving Science, politics and economics. Frequently, decontamination techniques are not acceptable economically due to large volumes of contaminated sediments to be processed. In this case, the concept of geochemical engineering can provide effective solutions, sustainable and low cost (Förstner, 2003). The geochemical engineering uses geochemical processes to influence the biogeochemical cycles of contaminants in the sediment. The use of mineral additives to decrease the mobility of pollutants is one of the applications of this concept. The process is named as solidification/stabilization that involves the mixing of dewatered sediment with specific bulk material like fly ash, cement, lime, chemicals, and mineral additives/amendments to limit the leaching of contaminants. Depending upon the contaminants leachability stabilized sediment has to be disposed in a landfill or can be used as construction material. Significant monitoring is required in case of solidification/stabilization process since the solidification process can be reversible. However, the successful stabilization of multi-element contaminated sites depends on the combination of critical elements in the sediment or soil and the choice of amendments (Mulligan et al., 2001; Rulkens, 2005; Kumpiene et al., 2008).

1.8.3.1 Mechanism for the sorption of contaminants on mineral amendments

Mineral amendments decrease leaching of inorganic contaminants and their bioavailability by inducing various sorption processes. The term refers to various mechanism explained below.

- Ion exchange

Ion exchange involves exchange of ionic species present in the solution with the ionic species of attached to solid surface of mineral amendment. The main cations and anions

involved are alkali and alkaline earth, sulphates, chlorides and nitrates (Deneux-Mustin et al., 2003), and the main ion exchanger in soil/ sediment are clays and organic matter (Sigg et al., 2000).

- Surface complexation

Surface complexes are formed by the interaction of an ion with specific functional groups of the surface. This interaction can result in the formation of covalent bonds (inner sphere surface complex) or ion pairs (outer sphere surface complex) mainly due to electrostatic forces (the water molecules of solvation layer remaining around of sorbed ions) (Zhou and Haynes, 2010). The formation of surface complexes is due to the acid-base character of mineral surfaces. In aqueous media the surface groups (denoted ≡S-OH) behave as weak acids. Depending on pH range they can behave as acids or weak bases (i.e., amphoteric). The ionization reactions of the surface are following (≡S-OH represents a surface hydroxyl group):

$$\equiv\text{S-OH}_2^+ \leftrightarrow \equiv\text{S-OH} + \text{H}^+ \quad K_{a1}$$

$$\equiv\text{S-OH} \leftrightarrow \equiv\text{S-O}^- + \text{H}^+ \quad K_{a2}$$

Proton transfer reactions generate a charge that can be positive, negative or neutral depending on pH. Electroneutrality at the charged surface is maintained by indifferent counter ions with a charge equal in magnitude and opposite in sign to surface charge (Stumm, 1992; Sigg et al., 2000).

- Adsorption of cations and anions

The surface sites in the form of ≡S-OH can act as ligand for metal cation (M^{z+}). The mechanism of sorption is then similar to a complexation reaction with proton exchange with formation of monodentate (1) or bidentate (2) complex.

$$\equiv\text{S-OH} + \text{M}^{z+} \leftrightarrow \equiv\text{S-OM}^{(z-1)+} + \text{H}^+ \qquad (1)$$

$$2\equiv\text{S-OH} + \text{M}^{z+} \leftrightarrow (\equiv\text{S-O})_2\text{M}^{(z-2)+} + 2\text{H}^+ \qquad (2)$$

In the case of the adsorption of an anion (L^{y-}) the ≡S-OH surface site will behave as a metal center towards the ligand (L^{y-}). This result in a ligand exchange between (L^{y-}) and

the OH^- ions of the surface site, with the formation of a mononuclear (3) or binuclear complex (4):

$$\equiv S\text{-}OH + L^{(y-)} \leftrightarrow \equiv S\text{-}L^{(y-1)-} + OH^- \qquad (3)$$

$$2 \quad \equiv S\text{-}OH + L^{(y-)} \leftrightarrow 2 \equiv S\text{-}L^{(y-2)-} + 2\ OH^- \qquad (4)$$

- Adsorption of cation in the presence of ligand

Many inorganic and organic ligands are present in aquatic environment. It is possible to consider various type of linkages that are developed between mineral surface (≡S-OH), ligands (L^{y-}) and the metal cations M ($^{z+}$).

In a first case (5), sorption of the cation and ligand will be comparable to that of a single cation, ligand may be fixed in higher pH ranges.

$$\equiv S\text{-}OH + M^{z+} + L^{(y-)} \leftrightarrow \equiv S\text{-}OM\text{-}L^{(z-y-1)-} + H^+ \qquad (5)$$

In the second case (6), the cation behaves like an anion, so the presence of ligand induced an increase in the sorption of the metal cation in more acidic pH range compared to the case where this cation is alone.

$$\equiv S\text{-}OH + M^{z+} + L^{(y-)} \leftrightarrow \equiv S\text{-}L\text{-}M^{(z-y+1)-} + OH^- \qquad (6)$$

The main complex ligands are water molecules (H_2O), hydroxyl (OH^-), carbonate (CO_3^{2-}), chloride (Cl^-) and sulphates (SO_4^{2-}). However, in soils and sediments, metal cations may also bind with cellular ligands containing -OH groups (alcohol), $-NH_2$ (amine), -SH (thiol), as well as organic ligands substances such as humic. There are a multiple complexing sites that may be encountered in the humic substances (Sigg et al., 2000; Zhou and Haynes, 2010).

- Surface precipitation and co-precipitation

Precipitation and co-precipitation are among the main inorganic pollutants retention mechanisms. Surface precipitation is the sorption mechanism that occurs when the surface site become saturated. During precipitation, the composition of surface is modified due to the emergence of new phase whose composition varies between original solid and the precipitated surface solute. Precipitation can result in both pure and contaminated

precipitates (Stumm and Morgan, 1996). The co-precipitation can be defined as the simultaneous precipitation of a chemical agent in conjunction with other elements (Sposito, 1983).Co-precipitation incorporates contaminants into the precipitates by replacing a constituent atom of the mineral. For example, arsenic can co-precipitate with oxides of iron and manganese (Alloway, 2005).

- Isomorphic substitution in the solid phase

Isomorphic substitution is the substitution of one element for another in a mineral in the crystal lattice by diffusion. This mechanism depends on the charge, electronegativity and the ionic radii (Stumm, 1992; Sigg et al., 2000).

1.8.2.2 Mineral amendments used

Mineral amendments have been largely studied for the stabilization of pollutants in contaminated soils (Guo et al., 2006; Kumpiene et al., 2006; Kumpiene et al., 2008a). The most studied mineral amendments are phosphate materials, alumino-silicates (clay,zeolites), alkaline materials and iron bearing compounds (zero-valent-iron, goethite, hematite, and ferrihydrite). Alumino-silicates and iron-based materials are the two groups of additives for immobilizing the larger number of pollutants (Kumpiene et al., 2008a; Komárek et al., 2013; Mamindy-Pajany et al., 2013). Iron bearing amendments shift exchangeable fraction of metals from contaminated matrices to iron oxide fraction (iron hydroxides). In lime addition, contaminants are precipitated as carbonates and hydroxides. Metal are directly adsorbed and fixed in the presence of Fe and Mn bearing materials and alumino-silicate. Phosphate containing compounds (apatite) shift non-residual metal to residual fraction (Peng et al., 2009).

In case of contaminated sediments, the use of mineral additives has been extensively studied for in situ treatment (Förstner, 2003; Qian et al., 2009; Yu et al., 2009). An inventory of the most common minerals used in situ stabilization of sediments is shown in Table 7. These mineral additives were selected for their stability, sorption capacity and low cost (Förstner, 2003).

Table 7. Minerals amendments used for the in situ stabilization of the sediments (Förstner, 2003).

	Mineral amendments	**Contaminant retention**	**Physical/chemical suitability**	**Environmental acceptability**	**Availability/ Costs**
Industrial by-products	Fly ash	Metals	+/- (very fine grained)	- (high equilibrium pH, potential toxicity)	+
	Red mud	Metals	+/- (very fine grained, not stable under reducing condition)	(heavy metals)	+
Natural minerals and rocks	Calcite	Metals, nutrients	+	+	+
	Apatite	Metals	+	+	+/-
	Clays (e.g.bentonite)	Metals	+/- (very fine grained)	+	+
	Zeolites (e.g. clinoptilolite)	Metals	+	+	+

(+) effective (+/-) more or less effective (-) ineffective

Mineral amendments have been widely studied for the in-situ stabilization of contaminated soils and sediments, however, fewer studies were conducted for the stabilization of contaminated sediments after dredging. In the literature, use of mineral amendment mainly concerned with the phyto-stabilization of deposited sediments (Müller and Pluquet, 1998; Panfili et al., 2005; Vandecasteele et al., 2010). However, some limitations were reported in case of As, Mo, and Cr during field application (Seaman et al., 2001). Recently, nano-hydroxyapatite (nHAp) used as amendment to metal contaminated sediments and

significant stabilization of Cd and Pb was achieved. Sequential extraction showed that nHAp could effectively reduce the exchangeable fraction of Pb and Cd in the sediment and significantly reduce the concentration in porewater (Zhang et al., 2010).

Studies on the stabilization of trace elements in contaminated sediments with mineral amendments are few and none have tested the feasibility of such treatment on freshly dredged marine sediments after composting, as these sediments have different physical and chemical characteristics than soils.

Present study aimed to investigate the use of bauxite residue an industrial by-product as amendment to stabilize trace elements in marine dredged sediments.

Following comprehensive review describes the utilization of bauxite reside in various environmental compartments (water, soil, and sediment) as well as use of different neutralization methods to enhance the sorption capacity of material towards contaminants.

Part B) Literature Review

Potential uses of industrial by-product as amendment for environmental media: A sustainable approach for waste management

(Under submission)

Abstract

Red mud is a solid waste of bauxite processing via Bayer process which involves caustic digestion of Al-containing mineral for alumina production. The global inventory of red mud waste reached an estimated 4 billion tons in 2015, increasing by approximately 120 million tons per year. Therefore, its management is becoming a global environmental issue due to increased awareness need for the protection of environment. Although, red mud is not considered to be hazardous material in many countries but its high alkalinity and fine particle size poses significant environmental threat. Red mud was found to be an interesting material for environmental remediation purposes due to its rich iron content. This paper provides a review of possible uses of red mud in various environmental compartments. Recently, red mud was found to be an efficient adsorbing agent for the removal of pollutants from water and stabilization of pollutants in solid phases. Modification of red mud presents novel opportunities for cost effective and efficient removal of metal ions, inorganic anions, dyes and phenols from wastewater and acid mine drainage. Re-vegetation and trace elements stabilization in acidic soils and mine sites presents the usefulness of this material but less research has been done so far to investigate its use in the stabilization of polluted sediments. In addition, leaching and eco-toxicological tests revealed that red mud does not present high toxicity to the environment. Nevertheless, neutralization is recommended for its safe disposal and before its application in any environmental media.

1. Introduction

Metallurgy industry is one of the most important industries in the world. It produces metals and metal alloys using ores and metallic scraps as raw materials. Extraction of metals from ores and metallic scrap generates large amounts of gaseous, liquid and solid by-products (Panias et al., 2001). Global production of aluminum, iron, copper and zinc generates approximately 2,000 megatons of by-products annually. Therefore, metallurgy industry is

regarded as one of the major contributor in the generation of solid by-products. By-products produced during extraction of metals are of no or little economic value depending upon their composition. Solid by-products valorization is necessary and new scientific advances are vital for utilization of by-products in remediation techniques (Zheng and Kozinsk, 1996; Panias et al., 2001; Kumar et al., 2006). Alumina industry is regarded to be one of the major contributors towards the generation of solid by-products and its appropriate management is of increasing environmental concern. Industrial by-products can be classified as hazardous or non-hazardous depending on the possible release of pollutants from the matrix into environmental media (Panias et al., 2001; Kumar et al., 2006). Prior to the decision about industrial by-products management the characterization of solid by-products according to globally accepted protocols and regulations is mandatory (Panias et al., 2001; Siddique, 2014).Over the last few decades, efforts have been made to find cost effective and sustainable solutions for by-products minimization and utilization (Bandopadhyay et al., 2002). Re-use or recycling of industrial by-products has become an attractive alternative since it could reduce the risk of environmental pollution as well as space for their disposal (Siddique, 2014). In this review paper, we attempt to present a critical overview of the uses of an alumina industry by-product called red mud (RM), the different treatments applied to that kind of by-product to make it suitable for specific re-use, its use for treatment of contaminated water, soil and sediment depending on the contaminant types, and finally the ecotoxicity investigations.

2. Properties of by-product from alumina extraction industry

Alumina is industrially extracted from bauxite ore by applying Bayer process. This process consists in digestion of bauxite mineral with concentrated sodium hydroxide under high temperature and pressure conditions. In these alkaline conditions, majority of species containing aluminum is dissolved from bauxite, while residues precipitate. After separation of the residue (by settling and/or precipitation), aluminum trihydroxide ($Al(OH)_3$) is precipitated by cooling the solution and seeding, then washed and calcinated to get pure aluminum. Extraction residue is commonly called red mud (RM) due to its specific reddish brown color. Application of Bayer process to bauxite produces from 0.3 ton to 2.5 tons of red mud per ton of alumina, depending on quality of ore (Wang et al., 2008; Power et al.,

2011). On average, 1-1.5 tons of red mud is generated per ton of alumina, (Genç et al., 2003). Therefore, 120 Million tons of red mud are produced annually worldwide and the global inventory of red mud approaches 4 billion tons in 2015 (Power et al., 2011). Red mud generation is comparatively high to other metallurgical wastes (i.e. 1 ton pig iron produces 300-400 kg of slag) (Kumar et al., 2006). Red mud is a highly alkaline material (pH 10-13), with 90% of particles having a size below 75 µm (Nadaroglu et al., 2010), and a specific surface area (BET) between 10 to 25 m^2/g. Physical, chemical, and mineralogical properties of red mud depend on the bauxite ore source and refining process (table 1). Nevertheless, the main mineralogical fractions present in red mud are hematite (Fe_2O_3) goethite (α-FeOOH), boehmite (ϒ-AlOOH), quartz (SiO_2), titania (TiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$) and gypsum ($CaSO_4.2H_2O$), with a minor presence of calcite ($CaCO_3$), whewellite (CaC_2O_4 H_2O), gibbsite ($Al(OH)_3$) and minor constituents like Na, K, Cr, V, Ni, Ba, Cu, Mn, and Zn (Genç et al., 2003; Brunori et al., 2005; Wang et al., 2008; Palmer et al., 2009; Snars and Gilkes, 2009; Liu et al., 2011).

Table 1. Major constituents (%wt), pH, EC and SSA of bauxite residue generated in different parts of the world

Country	Plant	Fe_2O_3	Al_2O_3	TiO_2	SiO_2	Na_2O	CaO	pH	EC (mS/cm)	S_{BET} (m^2/g)	Ref
Australia	AlCOAKwinana	28.5	24.0	3.11	18.8	3.4	5.26	11.45	2.98	28	(Snars and Gilkes, 2009)
	AlCOAPinjarra	31.7	18.8	3.17	20.2	4.2	4.44	11.63	6.09	25	
	AlCOAWagerup	29.6	17.3	2.65	30.0	3.2	3.64	11.99	2.69	24	
	AlCOAWorsley	56.9	15.6	4.46	3.0	2.2	2.39	12.56	6.28	25	
	Nabalco	34.8	23.2	8.03	9.2	7.1	2.25	12.44	10.75	29	
	QAL	30.7	18.6	7.01	16.0	8.6	2.51	10.22	8.15	29	
	QAL (Bauxsol)	34.05	25.45	4.90	17.06	2.74	3.69	10.00	-	30	(Genç et al., 2003)
USA	Reynolds Metal Company	35.5	18.4	6.31	8.5	6.1	7.73	11.04	3.59	27	(Snars and Gilkes, 2009)
China	Shandong Aluminum Industry Co., Ltd	21	12	1.4	9.4	7.0	3.0	10.8	-	21.6	(Luo et al., 2011)
France	ALTEO Gardanne Bauxaline®	14	50	11.5	6	3.5	5.5	10.60	0.919	23.06	(Taneez et al., 2015)
Turkey	Seydisehir Aluminum Plant	35.04	20.20	4.0	17.29	9.40	5.30	12-13	-	10-25	(Nadaroglu et al., 2010)
India	NALCO	54	13	3.5	7	8	-	11.8	-	31.7	(Sahu et al., 2010)
Brazil		45.6	15.1	4.29	15.6	7.5	1.16	12.21	3.26	15	(Snars and Gilkes, 2009)
Germany		44.8	16.2	12.3	5.4	4.0	5.22	12.08	2.57	23	(Snars and Gilkes, 2009)
Spain		37.5	21.2	11.4	4.4	3.6	5.51	12.58	2.34	21	(Snars and Gilkes, 2009)
Italy	Eurallumina, Sardinia	30.35	9.65	4.13	4.32	5.17	1.04	11.1	8.70	19.5	(Garau et al., 2011)

Considering the legislative requirements about by-products management, alumina industries are facing a challenging environmental issue. Indeed, until 1980 sea dumping and lagooning were considered to be the main options for red mud disposal. Since 1980 dry stacking and dry cake stacking has been used instead of lagooning because it can minimize the potential of leakage to groundwater and land use. However, certain limitations are associated with this method as it is difficult to achieve in areas of high rainfall and low evaporation, and the significant compaction density limits vegetation establishment. In case of North America, land based disposal in lagoons has favored even for refineries on the seaboard (Power et al., 2011). Sea dumping has been practiced in France, UK, Germany, Greece and Japan, but it was stopped in France in 2015 due to a national regulation (article 4.5 of the decree of 24 May 1994). From this date, red mud is adequately stored on land in the industrial site area (Mange Garri Basin) which is large enough to store red mud for 6 years (Dauvin, 2010). US Environment Protection Agency (EPA) evaluated red mud in terms of four hazardous waste characteristics: corrosivity, reactivity, ignitability and extraction procedure (EP) toxicity. All the EP constituents (except selenium) were below EPA regulatory levels and red mud was classified as non-hazardous (US EPA, 1984, 1990). Nevertheless, the Ajka (Hungary) disaster unveiled that some red mud suspensions could be really irritant and corrosive (hazardous properties H4 and H8, respectively, as defined in Directive 2008/98/CE(European Union, 2008).Red mud due to trace element concentrations and caustic nature may be viewed as hazardous waste(Liu et al., 2011).However, in numerous jurisdictions (USA, Canada, and the EU) red mud has been characterized as non-hazardous waste(European Commission, 2000; Klauber et al., 2011).Despite its high alkalinity, red mud appears to be an interesting material due to its mineralogical composition, in particular its high proportion of hematite and, goethite. Indeed, investigations on single minerals have shown that hematite surface sites are able to form strong surface complexes with toxic trace elements such as As and Cd (Giménez et al., 2007; Mamindy-Pajany et al., 2009; Jiang et al., 2013). On the basis of the previous researches carried out on single minerals, red mud has been investigated for toxic metal removal from aqueous and solid environmental media(Lombi et al., 2002b; Brunori et al., 2005; Nadaroglu et al., 2010), but the highly alkaline nature of red mud limited its direct

use and pre-treatment to lower its pH was often necessary. After pH neutralization, red mud can be used for various remedial applications (Wang et al., 2008).

2.1 Neutralization of red mud

Adequate neutralization of red mud is vital to reduce the environmental impact caused due to its high alkalinity and to provide a material that could be used for various applications. A range of methods has been investigated for neutralization purpose such as acid treatment (neutralization or activation), thermal activation, washing with seawater or saline brines, addition of gypsum or phosphogypsum, CO_2sequestration, combination of these treatments, and microbial neutralization. The objectives of neutralization are (i) to lower the initial pH of the material and (ii) to increase the surface area and (iii) to provoke neo-formed phases (Genç-Fuhrman et al., 2004a; Krishna et al., 2005; Santona et al., 2006; Sahu et al., 2010; Lopes et al., 2013; Sahu et al., 2013).

2.1.1 Acid treatment (neutralization or activation)

Acid treatment of red mud with minerals acids such as HCl, HNO_3, H_2O_2, and H_2SO_4 is widely used method. It not only removes alkali metals and inorganic impurities but also organics impurities as well as provokes neo-formed surfaces (Apak et al., 1998; Kirwan et al., 2013). The treatment of red mud with acid can be carried out by two ways: (i) Refluxing of red mud sample with solution of acid (0.1-1.0 M). After the reflux solution was cooled to room temperature, liquor ammonia was added until complete precipitation followed by washing of precipitates with deionized water and dried at 110°C (Pradhan et al., 1998; Genç-Fuhrman et al., 2004a) (ii) Red mud sample was treated or refluxed with solution of mineral acid (0.1-1.0 M). Final residue was washed with deionized water and dried at 100 ◦C. The refluxing time varies from 1 h to 2 h in both cases (Apak et al., 1998; Altundoğan et al., 2002; Altundoğan and Tümen, 2003). Treatment of red mud with concentrated solutions of acids (0.5 M) (hydrochloric, nitric and sulphuric acid) caused the dissolution of sodalite and cancrinite, which increased the availability of metal oxide/hydroxide sites. It also transformed the surface site $\equiv SOH/\equiv SO^-$ to $\equiv SOH^+_2$. However, concentrated acids have a negative effect on adsorption due to the dissolution of these iron and aluminium oxide/hydroxide sites. Sudden changes in pH have shown to

have negative influence on the removal efficiencies (Liang et al., 2014). This is a relatively expensive treatment since large volumes of reagents are required to fully neutralize the red mud, in addition it can increase amount of impurities to the process water stream (for example sulphate in the case of sulfuric acid, chloride in the case of hydrochloric acid). It is therefore likely that the return of any water from the residue deposits to the production process will be unacceptable without further treatment to remove these added impurities (Apak et al., 1998; Kirwan et al., 2013). The time taken to attain equilibrium pH depends on the quantity of acid added, and the degree of dissolution of solid phase alkalinity (calcium hydroxides, carbonates and aluminates, such as tricalcium aluminate- ($Ca_3Al_2(OH)_{12}$). For example, the equilibrium reaction of 5 g of RM slurry (40% solid by weigh) with continuous addition of acid (0.02N HCl) with 5 min interval to attain a pH of 8 took approximately 50 days (Khaitan et al., 2009).

2.1.2 Thermal activation

Red mud is thoroughly washed with deionized water and heated at various temperatures such as 200, 500, 600, 700, 800, 900 and 1000 ^{o}C in an electrical furnace for different time (1h-3h). Thermal treatment destroys organic and unstable compounds and excludes water from mineral phases (Altundoğan et al., 2002; Li et al., 2006; Smiljanić et al., 2011). The main crystalline phase in XRD analysis was found to be hematite (Fe_2O_3), whereas gibbsite and bayerite ($Al(OH)_3$) were identified as Al-bearing minerals. In addition, the peaks originated from sodalite ($Na_8Si_6Al_6O_{24}Cl_2$), calcite ($CaCO_3$) and quartz (SiO_2) were present, as well as of TiO_2 in the forms of both anatase and rutile. In the investigated temperature range quartz, hematite and rutile were not affected by the heating process, however, the improved hematite crystallinity with temperature increase above 600 ◦C, was clearly observed. During heating at 500 ◦C the surface area of red mud increased initially, as the expulsion of water leads to the development of but it was found adsorption of elements decreased on red mud heated above 700°C. This is due to sintering shrinkage of materials due to particle aggregation (Genç-Fuhrman et al., 2004b; Li et al., 2006; Smiljanić et al., 2011).

2.1.3 Seawater neutralization

Washing with seawater is the neutralization treatment that has been widely used in recent years. Seawater neutralization significantly facilitates reduction in pH of red mud without altering the acid neutralization capacity of the material. This treatment involves the use of soluble calcium and magnesium ions from seawater to neutralize red mud through the precipitation of hydrotalcite-like compounds and other Mg, Ca, and Al hydroxides and carbonate minerals. Excessive use of seawater can decrease red mud pH up to 8.5-8.8 and increase surface area to approximately 30-31 m^2/g (Genç et al., 2003; Palmer et al., 2009; Rai et al., 2013; Hanahan et al., 2004).

2.1.4 Gypsum neutralization

Red mud can be neutralized using a soluble calcium source such as gypsum. By gypsum addition (at the rate 5 to 8%), the precipitation of hydroxyl, hydroxoaluminate, and carbonate ions (as $Ca(OH)_2$, tricalcium aluminate (TCA), hydrocalumite and $CaCO_3$) is favored, conferring a buffer capability of red mud and pH was reduced consequently to 8.6 (Gräfe et al., 2011; Burke et al., 2013; Kirwan et al., 2013). After gypsum addition the electrical conductivity (EC) of residue solution increased due to soluble reaction product (like Na_2SO_4) but under adequate drainage conditions salinity can be reduced with water having lower salinity (Gräfe et al., 2011). Gypsum application demonstrates positive effect on red mud re-vegetation and can be applied as self-sustaining re-vegetation technique in the field (Wong and Ho, 1993; Courtney and Timpson, 2005).

2.1.5 CO_2 neutralization

The reaction of red mud with CO_2 results in neutralization through carbonation of the alkaline components of the liquid phase. CO_2 neutralization Involves bubbling of CO_2 through red mud slurry and generates carbonic acid which rapidly reacts with alkaline components of slurry and decreases the pH but it soon rises again due to additional leaching of alkaline material from red mud (Kirwan et al., 2013). The pH of liquid slurry depends on the relative concentration of carbonates species which in turns depends on the partial pressure of CO_2. At sufficiently low pH (i.e. sufficiently high pCO_2), and if held in contact for long enough, solid forms of alkalinity will also react. Most of the literature

regarding carbonation and reactivity of solid phase alkalinity has focused on the reactivity of TCA. The reaction of TCA with carbon dioxide leads to the formation of calcite and amorphous aluminium hydroxide and the kinetics of the solid phase reaction is very slow (Smith et al., 2003). After CO_2 sequestration the intensity of gibbsite was increased prominently and ilmenite ($FeTiO_3$) was formed due to dissolution of minerals (Sahu et al., 2010). Fine and coarse gibbsite powder heated between 350-400^oC showed 80-92 % removal of As(V) (Bhattacharya, 2005). Nano-ilmenite synthesized particles showed high adsorption capacity for methylene blue (Chen, 2011).

2.1.6 Combined treatments

It is evident from the literature that to improve surface properties and to decrease initial pH of red mud, combined treatments have been used. For example seawater neutralized red mud (Bauxsol^{TM}) was subjected to (i) acidification with HCl, (ii) combined acid-thermal treatment, and then treated with ferric sulfate and aluminum sulfate. These treatments further enhance the surface area of material to 130 m^2/g compared to the initial Bauxsol^{TM} which was 30 m^2/g (Genc et al., 2004). Combined treatments such acidification and calcination are frequently used to improve material efficiency for remediation purposes and XRD peaks confirm the following mineral phases: hematite (α-Fe_2O_3), goethite (α-FeO(OH)), gibbsite (Υ-$Al(OH)_3$), calcite ($CaCO_3$), rutile/anatase (TiO_2) and quartz (SiO_2) (Altundoğan et al., 2002; Gupta and Sharma, 2002; Altundoğan and Tümen, 2003; Sahu et al., 2013).

Other modification can also be applied to improve the stability and adsorption capacity of red mud including: sand coating, granulation and pellet making (Han et al., 2002; Genç-Fuhrman et al., 2007; Zhu et al., 2007). Other reagents used for red mud modification are $FeCl_3$, and Cetyltrimethyl ammonium bromide (CTAB) (Zhang et al., 2008; Li et al., 2015). Carbonized red mud was produced by heating red mud sample from room temperature at a rate of 10 ^oC/min under a 20 ml/min flow of $CH_4$and scans were taken at 100 ^oC intervals between 100 and 700 ^oC. The red mud samples having significant carbon growth on them have high surface areas and are magnetic (Pulford et al., 2012). H_2controlled reduction of red mud at 500-600 ^oC produces Fe^0. In addition to zero valent iron, red mud has some oxy/hydroxides of Al, Si, Ti, which upon thermal treatment will

form some thermally stable oxides. These oxides support the reactivity of Fe^0 (Costa et al., 2010). Zirconium hydroxide- modified red mud porous material (Zr-modified RMPM) was prepared as explained in method (Lv et al., 2013). Due to hydrolysis, $ZrOCl_2 \cdot 8H_2O$ formed $Zr(OH)_4$ precipitate under alkaline condition which coated onto the RM surfaces (Lv et al., 2013).

2.1.7 Microbial neutralization

Few researchers investigated microbial mode of neutralization of red mud despite significant results of early researches as microbial treatment significantly reduced the pH of red mud (by 2-3 units) and also helps in promoting plant growth in it. The microbial species used in neutralization are bacteria (*Bacillus, Lactobacillus, Leuconostoc, Micricoccus, Staphylococcus, Pseudomonas, Flavobacterium and Endobacter*) and fungi (*Aspergillus tubingensis*) (Hamdy and Williams, 2001; Krishna et al., 2005). The exact mechanism of microbial neutralization reaction is not fully understood but it is assumed to be a combination of organic acids release by the microbes and a diffusion of the respiratory gasses into solution (Hamdy and Williams, 2001). Microbial neutralization can be considered significant in following aspects: the neutralization is continuously controlled by microorganisms. Buffering of pH (drops from 13.0 to 6.0-7.0) by microbes is more efficient than buffering chemically controlled as long as nutrients are provided to microbes. Presence of microbes improved bulk structure of solid, which improves drainage, nutrient exchange, and the chances for establishing a plant cover. Microbes are intrinsic part of functioning rhizospheres of plants covering mine and residue spoils (Vachon et al., 1994; Hamdy and Williams, 2001; Krishna et al., 2005; Gräfe et al., 2011).

3. Application of red mud in pollution control

Industrial by-products can be used for various applications and the most interesting application is in the field of environment that is the decontamination of wastewater, soil and sediments.

3.1 Water remediation

The main sources of pollutants in water ways is discharge of industrial, sewage effluents, and agricultural runoff. These pollutants include toxic heavy metals, inorganic anions, metalloids as well as organic compounds such as dyes and phenolic compounds (Bhatnagar et al., 2011). Direct discharge of these pollutants into the environment has toxic effects on humans, animals and plants. Various techniques are used for water treatment, among them adsorption is considered to be cost effective and widely employed (Wang et al., 2008). Activated carbon has been recognized as a most promising adsorbent for the removal of different pollutants and it is widely used for water treatment. It has been cited by US Environmental Protection Agency as one of the best available control technologies (Derbyshire et al., 2001). However, high cost associated with the production and regeneration of activated carbon, has necessitated the search for alternative inexpensive absorbents (McKay et al., 1999; Crini, 2006). In order to decrease the cost of treatment, considerable researches have been carried out to find low cost adsorbents. In past years, researchers also focused to valorize the use of industrial by products. The industrial by-product red mud has been largely studied as low cost adsorbent due to its fine granulometry, high porosity and iron oxides richness. Removal capacities of bauxite residue for various pollutants (trace elements, anions, dyes and phenolic compounds) present in waste water are discussed below.

3.1.1Removal of metal ions

Presence of heavy metal and metalloids, and anionic species is unambiguous in nature. Discharge of these contaminants into water systems caused harmful effects on humans, animals and plants (Huang et al., 2010). Mining, metal plating, tanneries, paper and pulp, and petroleum industries are the main sources of water pollution with heavy metals and metalloids (Wang et al., 2008). Several studies have shown that red mud has significant adsorption properties for heavy metals and proven to be effective adsorbent for wastewater treatment due to its properties, that facilitate the adsorption of metal ions, as well as high pH of red mud cause surface precipitation. General influential factors during adsorption process are pH, adsorbent dosage, contact time, initial concentration of contaminant, and existence of other ions.

3.1.1.1 Nickel (Ni)

Despite the fact that wastewaters contain Ni ions in addition to other cations and anions, only a few number of researchers investigated the sorption of Ni ions onto red mud. Red mud was found to be an effective scavenger for Ni ions. Red mud addition to aqueous synthetic solution of Ni caused precipitation of nickel as insoluble hydroxide with simultaneous adsorption of nickel hydroxide and aiding the flocculation/sedimentation of the resultant fine particulate matter (Zouboulis and Kydros, 1993). After pretreatment (8% of gypsum, washing and thermal) an effective removal of Ni ions was obtained (López et al., 1998; Smiljanić et al., 2010). The optimum pH adsorption was 2.0-3.5 and removal capacity of thermally activated red mud was 27.54 mg/g (i.e., 20% higher than inactivated rinsed red mud). Coexisting divalent cations inhibit the sorption process of Ni in the following order Cu >Pb ≥ Zn> Cd>>Ca, while monovalent cations (Na and K) had no influence. Fluoride ions slightly improved sorption which means that fluoride neither form sufficiently stable complex with aqueous Ni, nor exhibit sorption affinity for red mud surface higher than Ni. Reduction of the positive surface charge after sorption of negative anions such as F^- may result in a more attractive surface for Ni sorption. Organic and inorganic anions decreased Ni ions removal in the order of EDTA > chromate > acetate > sulfate. In addition presence of citrate anion decreased retention of Ni on raw red mud due to competition for adsorption sites (Smiljanić et al., 2010; Smiljanić et al., 2011; Smičiklas et al., 2014). The same researcher further treated red mud with HCl solution (0.05-1.0 M) and observed that maximum removal of Ni ions occurred at acidic pH. Moreover, the adsorption kinetic is short (< 24 h), and isotherms followed Langmuir model. Low reversibility of adsorption process showed that Ni is tightly bound to treated red mud surface permitting its safe disposal or reuse (Zouboulis and Kydros, 1993; Smičiklas et al., 2014).

3.1.1.2 Cadmium (Cd)

Red mud is an inexpensive adsorbent and the adsorption of Cd is highly dependent on pH and optimum removal can be obtained in the neutral pH (6.5-7.5) range. When the pH increases to 8.0 precipitation of cadmium hydroxide occurs (Vaclavikova et al., 2005; Khan et al., 2015). For this reason, it is suspected that precipitation is the removal

mechanism instead of sorption at basic pH values (Genç-Fuhrman et al., 2007). In batch studies, satisfactory removal of Cd was obtained on non-treated red mud (Vaclavikova et al., 2005; Santona et al., 2006; Ma et al., 2009), while acid treatment can decrease the capacity of red mud to adsorb metal ions, which is attributed to the dissolution of portion of the cancrinite or other zeolite-type compounds in red mud contributing as adsorption sites (Apak et al., 1998; Santona et al., 2006). However, several studies reported that adsorption rate enhanced by acid neutralization or combination of treatments (thermal, gypsum addition (8%), and formulations such as granulation, ball milling, red mud pellets, etc (López et al., 1998; Gupta and Sharma, 2002; Han et al., 2002; Genç-Fuhrman et al., 2007; Zhu et al., 2007; Luo et al., 2011; Ju et al., 2012; Khan et al., 2015). Furthermore, the adsorption decrease with the increasing temperature showing that adsorption is exothermic in nature, optimum temperature reported to be room temperature, and adsorption isotherms were correlated well with Langmuir and Freundlich models (Apak et al., 1998; Gupta and Sharma, 2002; Vaclavikova et al., 2005; Santona et al., 2006; Zhu et al., 2007; Khan et al., 2015). Saturation of adsorbent in the presence of other cationic pollutants sometimes mobilized the previously retained Cd(Ma et al., 2009).

3.1.1.3 Copper (Cu)

Red mud has great retention capacity for Cu compared to other cations (Zn, and Cd) due to the formation of atacamite ($Cu_2Cl(OH)_3$) due to NaOH, and $CaCO_3$ content present in red mud (Vaclavikova et al., 2005; Ma et al., 2009).

$$2CuCl_2 + CaCO_3 + 2H_2O \rightarrow Cu_2(OH)3Cl + HCl + CaCl_2 + CO_2 \quad (1)$$

$$2CuCl_2 + 3NaOH \rightarrow Cu_2(OH)_3Cl + 3NaCl \quad (2)$$

Favorable removal of Cu can be achieved at pH 5.5 at ambient temperature and above this pH precipitation of Cu was reported due to increase in hydroxyl ion in the solution (Apak et al., 1998; López et al., 1998; Han et al., 2002; Agrawal et al., 2004; Nadaroglu et al., 2010; Grudić et al., 2013). A novel carbonized red mud was produced by catalytic hydrocarbon cracking, which results in a magnetic material of greater surface area. The efficiency carbonized material for the sorption of Cu has been compared with parent red mud and acidified red mud. There is an approximate ten-fold increase in removal of Cu by carbonized red mud compared with acidified red mud (Pulford et al., 2012). The adsorption isotherms best fit with Langmuir model (Apak et al., 1998; López et al., 1998; Nadaroglu

et al., 2010; Pulford et al., 2012). Red mud loaded with Cu can be treated with cement to form durable concrete mass for its safe disposal (Apak et al., 1998).

3.1.1.4 Lead (Pb)

Heterogeneous nature of red mud makes it an inexpensive choice for Pb adsorption from aqueous solution (Vaclavikova et al., 2005; Santona et al., 2006). Combined acid and heat treatment or pellets formulation have shown satisfactorily increased adsorption capacities. The results suggest that optimum pH for removal of lead was 4.0(Gupta et al., 2001; Han et al., 2002; Sahu et al., 2013).Carbonization of red mud result in 10 fold increase of removal rate compared to acidified red mud, due to the phase transformations and appearance of magnetite, wustite, iron carbide, and iron along with graphite (Pulford et al., 2012). The adsorption data of Pb on red mud shown to have best fit with Langmuir model (Apak et al., 1998; Han et al., 2002; Santona et al., 2006; Pulford et al., 2012). Presence of co-existing ions decreased Pb adsorption in the following order: potassium > magnesium > calcium > sodium. The leaching of contaminant was within limits using TCLP test and adsorbent can be easily regenerated under acidic conditions (Vaclavikova et al., 2005; Sahu et al., 2013).

3.1.1.5 Zinc (Zn)

Red mud has shown efficient removal capacity from aqueous medium (Vaclavikova et al., 2005; Santona et al., 2006; Ma et al., 2009). Neutralization (acid, gypsum, CO_2) and heat activation showed increased removal of Zn and preferential retention of Zn was observed at pH 6.0-7.0. Adsorption experiments carried out at high temperature decreased adsorption of Zn (López et al., 1998; Gupta and Sharma, 2002; Sahu et al., 2011). Sequential extraction demonstrate that very low fraction of Zn was adsorbed in the form of water-soluble and exchangeable on red mud while great fraction of Zn was tightly bound to red mud suggesting that it would not be expected to be released readily under natural conditions (Santona et al., 2006). However, saturation of red mud in mixed metal solution (Cu, Cd, Zn) can release previously immobilized Zn in the presence of Cu, which has higher affinity for red mud (Ma et al., 2009).

3.1.2Removal of inorganic anions

3.1.2.1 Arsenic (As)

Most common forms of arsenic present in water are inorganic arsenate (As(V)) and arsenite (As(III)) and under oxidizing conditions arsenate oxyanions are dominant (Mohan and Pittman Jr, 2007). Researcher paid significant attention for its removal. The adsorption of As(V) and As(III) on red mud is pH dependent. As(V) removal is favored at highly acidic pH (1.8-3.5) while As (III) was effective in the range of pH 5.8-7.5 (Altundoğan et al., 2000). Acid treatment helps to leach out sodalite compounds and improve adsorption capacity. The adsorption of As(III) is mainly physical and exothermic in nature while removal process of As(V) is endothermic and by chemical. As(V) was strongly attached to adsorbent and leaching of As(III) expected to be high (Altundoğan et al., 2002; Guo et al., 2014).

Seawater neutralization of red mud produced product named Bauxsol^{TM} having pH 8.4-8.8 and a higher surface area than raw RM. The results showed that Bauxsol^{TM} had higher affinity for As(V) and As(III) suggesting that for favorable removal, As (III) need to be oxidized to As (V) (Genç et al., 2003; Genç-Fuhrman et al., 2004a). Bauxsol^{TM} was further subject to combine acid-heat activation and an approximate removal of As(V) was 100% with or without presence of competing ions (phosphates, bicarbonates, sulphates) (Genç-Fuhrman et al., 2004b). Thermally activated seawater neutralized red mud revealed that seawater provokes the precipitation of hydrotalcites like compounds which in turns facilitates simultaneously the inclusion of arsenate, vanadate, or molybdate anions (Palmer et al., 2009). CO_2 neutralization of RM with thermal activation revealed that the hydroxyl surfaces of Al, Fe, and Ti oxides provides strong adsorption affinity of As (V) by forming inner sphere complexes. Most of the above discussed results suggests optimum pH for As(V) adsorption on bauxsol was 4.0-4.5 (Sahu et al., 2010). Addition of acidic waste materials like phosphogypsum to red mud at an appropriate proportion (RM+25% phosphogypsum) sorbed 3.5 fold higher concentration of arsenic than raw red mud which was due to presence of Ca^{2+} that leads to the formation of ternary complex by altering the charge balance of adsorbent (Lopes et al., 2013). Surface modification with $FeCl_3$ increased the iron content (17.5%) and surface area 192 m^2/g of red mud which ultimately improved the adsorption sites for maximum removal of As(V). The regeneration efficiency

of modified red mud was ≈92.1% using 0.2 mol/L of NaOH (Zhang et al., 2008; Shuwu and Wenchao, 2013).Magnetic Fe_3O_4 nanoparticles were synthesized from red mud and used to remove As(V) from ground water. The results showed that total arsenic concentration of the samples could be efficiently reduced up to 99.2% (Akin et al., 2012). Iron-arsenic co-precipitation and arsenic adsorption was obtained by using ferrous based red mud and this treatment was reported to decrease turbidity of water (Li et al., 2010). In comparison to the Freundlich isotherm model (Akin et al., 2012), the Langmuir isotherm was fitted to the experimental data (Altundoğan et al., 2002; Genç et al., 2003; Genç-Fuhrman et al., 2004a; Zhang et al., 2008; Sahu et al., 2010; Lopes et al., 2013; Guo et al., 2014). Adsorption of arsenic was increased in the presence of Ca ions as it diminishes the negative charges and forming a metal–arsenate complex or a metal-H_2O-arsenate complex, while nitrate had little effect compared to other competitive ions such as bicarbonate and phosphate had reduced adsorption rate (Genç et al., 2003; Genç-Fuhrman et al., 2004b; Zhang et al., 2008; Li et al., 2010). Regeneration possibility of used adsorbent with 0.2 M NaOH was reported to be high (Zhang et al., 2008).

3.1.2.2 Chromium (Cr(VI))

Some researchers have investigated the possibility of using red mud after pre-treatments as adsorbent for the removal of Cr(VI) from water systems. Only (Singh and Singh, 2002) used raw red mud in high adsorbent dose (100 g/L) for complete removal of Cr(VI) from aqueous solution at initial concentration of 10 mg/L at pH 3.0 while heat activated red mud showed better results at pH 2.0 for the same initial concentration of Cr (VI) with 20 g/L of adsorbent dose (Erdem et al., 2004). Acidification, followed by ammonia addition, or heat activation showed that Cr(VI) maximum adsorption was obtained at acidic pH (2.0-3.0) (Pradhan et al., 1999; Gupta et al., 2001; Ma et al., 2014). Remarkable reduction of Cr (VI) in aqueous medium compared to commercial Fe^0 fine powder has been shown by red mud treated by H_2 (Costa et al., 2010). Recently, modified red mud with Cetyltrimethyl ammonium bromide (CTAB) showed favorable removal of Cr(VI) (Li et al., 2015). Moreover, negligible removal was observed at neutral pH and adsorption was negatively influenced with increase in temperature, while effect of competing anions (PO_4^{3-},SO_4^{2-},and NO_3^-) depends on their relative concentration and affinity for the

surface. The adsorption of Cr (VI) was found to be exothermic, and followed Langmuir isotherm model (Pradhan et al., 1999; Gupta et al., 2001; Pulford et al., 2012; Ma et al., 2014; Li et al., 2015).The Cr(VI) loaded adsorbent was solidified with cement and low leaching of elements confirms the effectiveness of stabilization process and could be used as building material. Furthermore the spent red mud can be easily regenerated by simple treatment with H_2 at 600°C (Singh and Singh, 2002; Costa et al., 2010).

3.1.2.3 Phosphates

Dephosphatation with chemical techniques are widely accepted methods. Common precipitants used for phosphate removal are lime, aluminum sulfate, and ferric chloride. However, the cost of metal salts and sludge production are the typical draw backs (Altundoğan and Tümen, 2003; Zhao et al., 2009). Therefore, dephosphatation potential of various low cost adsorbents fly ash, red mud, natural zeolites, slag, biochar etc) from wastewater has been widely explored(Wang and Wu, 2006; Karapınar, 2009; Chen et al., 2011; Liu et al., 2011). Many researchers have promoted the use of red mud as adsorbent for phosphate removal from aqueous solutions.

The adsorption of phosphates on bauxite or red mud and thermal activation was found to be pH dependent and favorable pH was 3.2-5.5. The activation process not only increased surface area of adsorbent but provides additions surface active sites while acidification decreased adsorption capacity due to dissolution of surface constituents. The mechanism of phosphate adsorption onto bauxite was ligand exchange mechanism. Sequential extraction results showed that phosphate retention at pH 4.0 and 7.0 was mainly regulated by two different mechanisms that gave rise to a chemical adsorption on RM phases, and to the formation of metal phosphate precipitates. By contrast, at pH 10.0 the P-sorption was regulated by a chemisorption mechanism on Fe-Al phases of RM (Altundoğan and Tümen, 2002; Altundoğan and Tümen, 2003; Li et al., 2006; Liu et al., 2007; Castaldi et al., 2010). However, with low initial concentration of phosphate (1 mg/L) acid treated red mud and Bauxsol^{TM} exhibited increased sorption than raw red mud (Akhurst et al., 2006; Huang et al., 2008; Baraka et al., 2012). Approximately 80-90% of phosphate removal at constant pH of 5.2 was reported by using precipitated residue obtained after acid activated red mud having a high specific surface are of 249 m^2/g (Pradhan et al., 1998).

Granulates of red mud, bentonite and starch (RMGA) were prepared at different mass ratios and sintering temperature and tested for phosphate removal. The optimum mixture was RMGA-85% and RMGA-95% showed best result for phosphate adsorption at acidic pH 3.0 (Yue et al., 2010). For the first time, powdered-acid-activated-neutralized red mud (Aan-RM), was employed with hydroxypropyl methylcellulose and powdered straw as the main ingredients for granular Aan-RM production for phosphate removal. X-ray photoelectron spectroscopy (XPS) analysis of P 2p peak on granular Aan-RM after phosphate adsorption demonstrated that 79.01 % of the phosphate was adsorbed through precipitation and ion exchange mechanisms with strong chemical bonds, and 20.99 % of the phosphate was adsorbed through surface deposition mechanism with weak chemical bonds (Ye et al., 2015). It was found that adsorption was decreased in the presence of bicarbonate ions due to competing effects and increased in the presence of Ca and Mg ions due to increase in positive sites while chlorides and sulphates had little effect (Akhurst et al., 2006).Regeneration of granulates (RMGA) adsorbent using HCl showed high desorption and low resorption capacities owing to the extraction of effective components from RMGA. In case of NaOH extractant showed relatively better resorption of phopahte due to OH^- amelioration of the chemical composition on the surface of RMGA during desorption process (Zhao et al., 2009).

3.1.2.3 Nitrates and Fluorides

Presence of nitrates in high concentrations in waterways stimulates algal growth and presents a potential risk to public health (Danalewich et al., 1998). Limited researchers tested red mud for nitrate removal. Original and modified red mud (HCl-treated) adsorbents used to remove nitrate from aqueous solution. The adsorption capacity of the acidified red mud was higher than original. The removal mechanism of nitrate was explained due to surface chemical interaction of red mud and metal oxides with nitrate ions (Cengeloglu et al., 2006). Approximately 98 % removal of nitrates was achieved by mixing acid activated red mud mixed with Fe^0 in solution. Nitrate was transformed into ammonium indicating that reaction pathway of nitrate removal is associated with reduction. The enhancing effect of activated red mud was assumed to be the result from scavenging of the reaction precipitate, thereby minimizing passivation of Fe^0 surfaces, and

formation of additional reactive sites (e.g. green rust) for nitrate reduction (Cho et al., 2011). The rate of nitrate removal decreased at pH above 7 due to stronger competition with hydroxide ions on adsorbent surface (Cengeloglu et al., 2006).

Mineral based adsorbents have been used for the removal of fluoride. A study showed the fluoride removal potential of HCl activated red mud was higher than original. This tendency was explained on the basis of the chemical nature and specific interaction with metal oxide surfaces. Maximum removal was obtained at pH 5.5 and decreased sharply above pH 5.5 due to competition with OH^- ions on adsorbent surface. The adsorption of fluorides was also not favored in very acidic pH, which may be due to the formation of weakly ionized hydrofluoric acid. The activated red mud could remove only 77% of 21 mg/L fluoride, leaving 2.7 mg/L fluoride in solution which was still higher than the acceptable levels (Çengeloğlu et al., 2002). Best removal efficiency for fluoride was given by H_2SO_4 treated red mud due to 2 protons being available to protonate the surface hydroxyl groups (Liang et al., 2014). Thermally activated bauxite (TRB) at 300-450 ◦C greatly increased its fluoride adsorptive capacity. The pH 5.5–6.5 was found to be the optimal pH for maximum removal, equilibrium was short (90 min), and adsorption data fitted well with both Langmuir and Freundlich isotherm models. Uptake of fluoride on TRB was not affected by the presence of common interfering ions. NaOH (0.015 mol/L) was used to get complete desorption of fluoride at pH of 11.1 (Das et al., 2005). Defluoridation capacity of Zr-modified RMPM at 3-4 was 0.6 mg/g. After adsorption, the modified material could be regenerated using NaOH solution at pH 12 with over 90% of recovery ratio (Lv et al., 2013). It was found that $Zr(OH)_4$ precipitates known to adsorb gases. acidic gases, can be modified and used to adsorb basic gases (Glover et al., 2012).

Comprehensive summary of adsorption capacity of raw and treated red mud for metal ions, and inorganic anions are presented in table 2 and table 3, respectively. These tables provided valuable information regarding the effect of treatment on surface area of red mud, initial concentration of various contaminants, optimum pH and temperature range, and quantities of adsorptions. Adsorption data followed mostly Langmuir isotherm model than Freundlich. The Langmuir model is a simple model assumes adsorption of molecules on a

monolayer on a homogenous surface with a finite number of similar active sites and no interaction occurs between adsorbed species (Langmuir, 1918). The well-known expression of the Langmuir model is given by the following Eq (3):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (3)$$

C_e (mg/L) is the equilibrium concentration q_m (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is the Langmuir constant.

The empirical Freundlich equation based on adsorption onto a heterogeneous surface having not equivalent adsorption sites (Freundlich, 1906). This model is expressed by the following equation (4):

$$q_e = K_f C_e^{1/n} \qquad (4)$$

where K_f and 1 / n are Freundlich constants related to the adsorption capacity and the adsorption intensity respectively, and C_e (mg/L) is the equilibrium concentration. Both of Langmuir and Freundlich isotherms might adequately describe the same set of liquid-solid adsorption data at certain concentration ranges, in particular if the concentration is small and the adsorption capacity of the solid is large enough to make both isotherm equations approach a linear form.

Table 2. Adsorption capacities of red mud before and after treatment for metal ions

Ions	Red mud& treatments	Initial Conc. (mg/L)	S_{BET} (m^2/g)	T/°C	pH	Isotherm	Adsorption (mg/g)	Ref
Ni(II)	RM-$CaSO_4$	250	58	-	6.9	Langmuir	10.9	(López et al., 1998)
	RM-Rinsed	465	-	-	2.0-3.5	Langmuir	21.8	(Smiljanić et al., 2010)
	RM-heated 600°C	465	-	-	2.0-3.5	Langmuir	27.54	(Smiljanić et al., 2011)
	RM-0.05M HCl	465	-	-	5.0	Langmuir	11.11	(Smičiklas et al., 2014)
Cu(II)	RM	3177	14.2	25	6.0	Modified Langmuir	75.2	(Apak et al., 1998)
	RM-HCl	3177	20.7	25	4.5	Modified Langmuir	35.2	(Apak et al., 1998)
	RM-HCl-hetaed600°C	3177	28.0	25	5.7	Modified Langmuir	65.2	(Apak et al., 1998)
	RM-$CaSO_4$	250	58	-	5.6-6.2	Langmuir	19.7	(López et al., 1998)
	RM-pellets	20	17.33	25	5.64	Langmuir	6.56	(Han et al., 2002)
	RM-acid	190.62	10-25	30	5.5	Freundlich and Langmuir	5.35	(Nadaroglu et al., 2010)
	RM	-	10-15	-	11.5	Langmuir	8.9	(Pulford et al., 2012)
	RM-HCl	-	45-48	-	4.5	Langmuir	3.5	(Pulford et al., 2012)
	RM-carbonized	-	70	-	8.2	Langmuir	25	(Pulford et al., 2012)
Cd(II)	RM	3934	14.2	25	6.0	Langmuir	66.8	(Apak et al., 1998)
	RM-HCl	3934	20.7	25	4.2	Langmuir	46.9	(Apak et al., 1998)
	RM-HCl-hetaed600°C	3934	28.0	25	5.9	Langmuir	66.8	(Apak et al., 1998)
	RM-$CaSO_4$	250	58	-	4.7-6.2	Langmuir	10.57	(López et al., 1998)
	RM-H_2O_2-heated 500°C	100	108	30-50	4.0	Freundlich and Langmuir	11.2-13.0	(Gupta and Sharma, 2002)
	RM-pellets	20	17.33	25	6.15	Langmuir	6.62	(Han et al., 2002)
	RM	100	18.38	-	6.0	Langmuir	68	(Vaclavikova et al., 2005)
	RM	337	18.9	-	5.5-5.9	Langmuir	152	(Santona et al., 2006)
	RM-HCl	337	25.2	-	5.5-5.9	Langmuir	102	(Santona et al., 2006)
	RM-granular	400	15.28	20	6.0	Freundlich	38.2	(Zhu et al., 2007)
	RM-granular	400	15.28	30	6.0	Freundlich	43.4	(Zhu et al., 2007)
	RM-granular	400	15.28	40	6.0	Freundlich	52.1	(Zhu et al., 2007)
	RM-2%cement	10	17.42	30	6.5	Langmuir	9.42	(Ju et al., 2012)
	RM-2%cement	10	17.42	40	6.5	Langmuir	10.19	(Ju et al., 2012)
	RM-2%cement	10	17.42	50	6.5	Langmuir	10.78	(Ju et al., 2012)
Zn(II)	RM-$CaSO_4$	250	58	-	6.9-7.8	Langmuir	12.59	(López et al., 1998)
	RM-H_2O_2-heated 500°C	120	108	30-50	4.0	Freundlich and Langmuir	11.8-14.5	(Gupta and Sharma, 2002)
	RM	100	18.38	-	7.0	Langmuir	133	(Vaclavikova et al., 2005)
	RM	196	18.9	-	5.5-5.9	Langmuir	161.5	(Santona et al., 2006)
	RM-HCl	196	25.2	-	5.5-5.9	Langmuir	104	(Santona et al., 2006)
	RM-CO_2 -heated 500°C	30	68.22		6.0	Langmuir	14.92	(Sahu et al., 2011)
Pb(II)	RM	10360	14.2	25	6.0	Langmuir	165.8	(Apak et al., 1998)
	RM-HCl	10360	20.7	25	4.4	Langmuir	117.3	(Apak et al., 1998)
	RM-HCl-hetaed600°C	10360	28.0	25	5.7	Langmuir	138.8	(Apak et al., 1998)
	RM-H_2O_2-heated 500°C	700	108	30-50	4.0-6.0	Freundlich and Langmuir	66.9-71.3	(Gupta et al., 2001)
	RM-pellets	20	17.33	25	5.68	Langmuir	17.2	(Han et al., 2002)
	RM	621	18.9	-	5.5-5.9	Langmuir	390	(Santona et al., 2006)
	RM-HCl	621	25.2	-	5.5-5.9	Langmuir	160	(Santona et al., 2006)
	RM	-	10-15	-	11.5	Langmuir	133	(Pulford et al., 2012)
	RM-HCl	-	45-48	-	4.5	Langmuir	9.0	(Pulford et al., 2012)
	RM-carbonized	-	70	-	8.2	Langmuir	94	(Pulford et al., 2012)
	RM-HCl-heated 500°C	10	67.10	-	4.0	Langmuir	6.21	(Sahu et al., 2013)

Table 3. Removal capacities of various bauxite residues for inorganic anions

Ions	Red mud & treatments	Initial Conc. (mg/L)	S_{BET} (m^2/g)	T/°C	pH	Isotherm	Adsorption (mg/g)	Ref
As (V)	RM	10		25	3.2	Langmuir	0.38	(Altundoğan et al., 2000)
	RM	10	-	25-70	3.5	Langmuir	0.51-0.82	(Altundoğan et al., 2002)
	RM-HCl	10	-	25-70	3.5	Langmuir	0.94-1.32	(Altundoğan et al., 2002)
	Bauxsol	0.06-2.4	30	23	6.4	Langmuir	1.08	(Genç et al., 2003)
	Activated Bauxsol (AB)	2.58-11.39	130	23	7.1	Langmuir	2.99	(Genç-Fuhrman et al., 2004a)
	Bauxsol coated sand (BCS)	0.54–20.34	130	23	4.5	Langmuir	3.32	(Genç-Fuhrman et al., 2004b)
	Bauxsol coated sand (BCS)	1.16-19.60	7.7	25	7.1	Langmuir	1.64	(Genç-Fuhrman et al., 2005)
	AB-coated sand (ABCS)	0.54-20.34	47.3	25	7.1	Langmuir	1.07	(Genç-Fuhrman et al., 2005)
	RM-$FeCl_3$	2.0-100	192	20	6.0	Langmuir	68.5	(Zhang et al., 2008)
	RM-CO_2- heated 500°C	10	63	25	4.0	Langmuir	55.5	(Sahu et al., 2010)
	75%-RM + 25%-G	7.5-97.4		24	5.5	Langmuir	3.333	(Lopes et al., 2013)
	RM-HCl	0.1-30	89.39	25	7.0	Langmuir	5.16	(Guo et al., 2014)
As (III)	RM	10		25	9.5	Langmuir	0.322	(Altundoğan et al., 2000)
	RM	10	-	25-70	7.2	Langmuir	0.46-0.67	(Altundoğan et al., 2002)
	RM-HCl	10	-	25-70	7.2	Langmuir	0.34-0.88	(Altundoğan et al., 2002)
	Activated Bauxsol	0.15-11.8	130	23	6.8	Langmuir	0.54	(Genç-Fuhrman et al., 2004a)
	RM-HCl	0.1-30	89.39	25	7.0	Langmuir	1.47	(Guo et al., 2014)
Cr(VI)	RM-H_2O_2-heated 500°C	300	108	30-50	2.0	Freundlich and Langmuir	21.1-22.7	(Gupta et al., 2001)
	Heated Bauxite	10	86	20-50	2.0	Langmuir	0.403-0.522	(Erdem et al., 2004)
	RM	-	10-15	-	11.5	Langmuir	1.3	(Pulford et al., 2012)
	RM-HCl	-	45-48	-	4.5	Langmuir	1.7	(Pulford et al., 2012)
	RM-carbonized	-	70	-	8.2	Langmuir	0.0	(Pulford et al., 2012)
	RM-HCl	0.08	-	30	2.0	Langmuir	0.03	(Ma et al., 2014)
	RM-0.5% CTAB	100	25.7	-	2.0	Langmuir	22.20	(Li et al., 2015)
Phosphate	RM-HCl	120	294	30	5.2	Freundlich and Langmuir	23.2	(Pradhan et al., 1998)
	Bauxite	10	11	25	4.5	Langmuir	0.67-0.82	(Altundoğan and Tümen, 2003)
	Bauxite-HCl-heated 600°C	10	86	25	4.5	Langmuir	0.98-2.95	(Altundoğan and Tümen, 2003)
	RM	155	14.09	25	7.0	Langmuir	113.87	(Li et al., 2006)
	RM-HCl	155	19.35	25	7.0	Langmuir	161.6	(Li et al., 2006)
	RM-heated 700°C	155	9.69	25	7.0	Langmuir	345.5	(Li et al., 2006)
	RM	155	14.09	25	7.0	Langmuir	95.86	(Liu et al., 2007)
	RM-HCl-hetaed 700°C	155	21.76	25	7.0	Langmuir	202.9	(Liu et al., 2007)
	RM- hetaed 700°C	155	15.69	25	7.0	Langmuir	155.2	(Liu et al., 2007)
	RM-HCl	1.0	28.48	40	5.5	Freundlich	0.58	(Huang et al., 2008)
	Granular Aan-RM	500	113.54	40	6.0	Freundlich and Langmuir	153.2	(Ye et al., 2015)
Nitrate	RM	5-250	14.2	25	6.0	Langmuir	1.859	(Cengeloglu et al., 2006)
	RM-HCl	5-250	20.7	25	6.0	Langmuir	5.858	(Cengeloglu et al., 2006)
Fluoride	RM	69.5	14.2	25	5.5	Langmuir	0.164	(Çengeloğlu et al., 2002)
	RM-HCl	69.5	20.7	25	5.5	Langmuir	0.331	(Çengeloğlu et al., 2002)
	Heated Bauxite (TRB-1)	5-40	-	27	6.0	Langmuir	3.70	(Das et al., 2005)
	Heated Bauxite (TRB-2)	5-40	-	27	6.0	Langmuir	4.13	(Das et al., 2005)
	Heated Bauxite (TRB-3)	5-40	-	27	6.0	Langmuir	3.91	(Das et al., 2005)
	Zr-modified RM	10-20	-	15-35	3.0	Langmuir	0.5-0.9	(Lv et al., 2013)

3.1.3 Removal of organic pollutants

Dyes are widely used in the industries like textile, leather, paper, plastics, printing etc., in order to color their products along with consumption of substantial amount of water. As a result, considerable amount of colored effluent is discharged. The presence of dyes in wastewater is a main concern due to their adverse effect on aquatic life, inhibition of light penetration as well as dyes are considered as potential toxic, mutagenic , and carcinogenic agents. Other organic pollutants such as phenols and derivatives are highly carcinogenic. These pollutants (dyes, phenols and derivatives) need to be removed from effluents before being discharged into water bodies(Wang et al., 2008). In order to widen the applicability of red mud as low cost adsorbent its feasibility for removal of organic pollutants has been investigated during past years.

Studies on different dyes such as congo red (an anionic dye), acid violet, methylene blue, fast green, rhodamine B, and procion orange have shown that RM has removal capacity for dyes. Effect of different initial dye concentrations, agitation time, adsorbent dosage, and pH were studied. Quantitative adsorption of congo red, acid violet, and procion orange on red mud was obtained at pH 2.0, 4.1, 2.0, respectively. Maximum removal capacities for congo red and acid violet were 4.05 mg/g and 1.37 mg/g respectively and adsorption data obeyed both the Langmuir and Freundlich isotherms. Procion orange adsorption data obeyed Freundlich isotherm model and a maximum removal of 82% of the dye was observed. Desorption studies showed that the adsorption was also mainly due to ion-exchange (Namasivayam and Arasi, 1997; Namasivayam et al., 2001; Namasivayam et al., 2002). Successful removal of rhodamine B, fast green, and methylene blue on H_2O_2 activated red mud was achieved up to 71.1 to 94.0%. The adsorption was found to be exothermic in nature (Gupta et al., 2004b). It was observed that heating of red mud imparts negative effect on adsorption of methylene blue (basic dye) than acidified red mud, and adsorption was found to be endothermic in nature (Wang et al., 2005). Reactive dyes are used in textile dyeing industries due to their superior fastness to the applied fabric, high photolytic stability, high solubility and resistance to microbial attack. Adsorption of a reactive dye, (Remazol Brilliant Blue (RBB)) on H_2SO_4 treated red mud was favored at pH 2.0 to 6.0 from dye-contaminated water. The rate of adsorption increases with increasing

temperature (Ratnamala et al., 2012). Acidified red mud gave good removal of congo red dye in short equilibrium time at neutral pH and adsorption data follow Langmuir model (Tor and Cengeloglu, 2006). Highest percentage of removal was obtained for reactive blue dye 19 with seawater neutralized red mud activated at 400 ^{0}C (de Souza et al., 2013). A $MgCl_2$/red mud system (MRM) was used in the decolorization of dye solution. MRM showed more than 98%of the color removal efficiency at a dosage of 25 g RM/L dye solution and a volume of 1.5 mL $MgCl_2$/L dye solution in the decolorization process of reactive dye, acid dye and direct dye. The color removal efficacy was better than the conventional polyaluminum chloride (PAC)/RM and PAC/NaOH systems. The experimental data was best correlated with Langmuir and Freundlich model (Wang et al., 2009).Thermally activated red mud was evaluated to remove reactive blue 19 dye (RB 19). The adsorption of RB 19 was highest when the pH values were lower than the pH_{PCZ} (7.0). Thermally activated RM exhibited adsorption capacity of 178.4 mg/g in acidic conditions and obeyed Langmuir model (de Jesus et al., 2015). An anionic surfactant, sodium dodecyl sulphate (SDS) was used to modify the surface of red mud. Adsorption data of Safranin-O dye on SDS modified RM showed good fit to the Langmuir model with a maximum monolayer adsorption capacity of 89.4 mg/g at pH 4.4, and 35 ^{o}C. Desorption experiments were carried out by testing several solvents such as water, sulphuric acid, hydrochloric acid and acetic acid and the maximum (93.2%) desorption was found using hydrochloric acid (Sahu and Patel, 2015).

Phenols and its derivatives represent one of the problematic organic pollutants. The main sources of aquatic pollution due to phenolic compounds come from petroleum and petrochemical, coal conversion, paints, pesticides, and polymeric resins industries. Phenols can cause unpleasant taste and odor of drinking water even at low concentrations. They are also regarded as toxic and carcinogenic. For this reason it is necessary to eliminate them from water. Adsorption process is widely used for the treatment of aqueous phases (Calace et al., 2002). Red mud neutralized by distilled water stirring until the equilibrium pH reach 8.0-8.5. The removal studies of phenol from aqueous solutions in the wide pH range of 1-9.demonstrate that equilibrium was attained in 10 h with maximum adsorption capacity of 4.127 mg/g. The Freundlich model represented the measured sorption data well compared to Langmuir. The influence of addition of chloride, sulfate and nitrate salts on phenol

removal depended on the relative affinity of the anions for the red mud surface and the relative concentrations of the anions. The anions followed the affinity order; sulfate > nitrate >>>chloride (Tor et al., 2006). Furthermore, neutralized red mud treated by acid was used and showed two fold increases in adsorption capacity (8.156 mg/g) at pH 6 and 25±1°C. The Langmuir isotherm showed very good fit with the adsorption data. Effect of competing ions on neutralized red mud have shown that presence of chlorides (10 to 50 mg/l) have no significant effect on phenol adsorption but in the presence of nitrates and sulphate (50 mg/l) phenol adsorption decreased from 66 to 32% and 15% respectively. Similar effects of these anions on the adsorption of phenol by activated red mud can be expected (Tor et al., 2009). HNO_3 treatedred mud showed increased removal of phenols in pH range of 3-7 and above neutral pH it declined. Increase in initial phenol concentration decrease the removal percentage. Adsorption results show that equilibrium data follow the Freundlich isotherm, and kinetic data was well described by a pseudo-second-order kinetic model (Shirzad-Siboni et al., 2013).Combined acid(H_2O_2) and heat treatment (500 °C) of red mud showed that the developed adsorbent removed up to 94-97% of 2,4-dichlorophenol and 4-chlorophenol, while the removal of 2-chlorophenol and phenol was up to 50–81%.. The removal took place through particle diffusion mechanism and the order of removal was 2,4-dichlorophenol ≈ 4-chlorophenoln> 2-chlorophenol> phenol. The adsorption endothermic in nature and followed both Langmuir and Freundlich models (Gupta et al., 2004a).

Table 4. Removal of organic pollutants

Pollutants	Red mud & treatmemts	Initial Conc. (mg/L)	S_{BET} (m^2/g)	T/°C	pH	Isotherm	Adsorption (mg/g)	Ref
Congo red	RM	10	-	30	7.3	Langmuir	4.05	(Namasivayam and Arasi, 1997)
Acid violet	RM	20	-	30	4.1	Langmuir	1.37	(Namasivayam et al., 2001)
Procion orange	RM	10	-	30	2.0	Freundlich	-	(Namasivayam et al., 2002)
Rhodamine B	RM-H_2O_2-Heate 500°C	4.8-57.5	108	30	1.0	Langmuir	5.56	(Gupta et al., 2004b)
Fast green	RM-H_2O_2-Heate 500°C	7.65-76.9	108	30	7.0	Langmuir	7.56	(Gupta et al., 2004b)
Methylene blue	RM-H_2O_2-Heate 500°C	32-352	108	30	8.0	Langmuir	16.72	(Gupta et al., 2004b)
Methylene blue	RM	10	21.0	30	5.2	Langmuir	2.49	(Wang et al., 2005)
Methylene blue	RM-heated 800°C	10	10.1	30	5.2	Langmuir	0.48	(Wang et al., 2005)
Methylene blue	RM-HNO_3	10	31.9	30	5.2	Langmuir	1.02	(Wang et al., 2005)
Congo red	RM-HCl	20	20.7	25	7.0	Langmuir	7.08	(Tor and Cengeloglu, 2006)
Remazol Brilliant Blue	RM-H_2SO_4-dired 110°C	30	27.3	20-40	2.0	Langmuir	25.64-27.8	(Ratnamala et al., 2012)
Reactive Blue dye 19	Seawater neutralized-RM	2000	22.6	25	4.0	Langmuir	250.0	(de Souza et al., 2013)
	Seawater neutralized RM-heated 400°C	2000	55.4	25	4.0	Langmuir	416.7	(de Souza et al., 2013)
	Seawater neutralized RM-heated 500°C	2000	45.4	25	4.0	Langmuir	38.6	(de Souza et al., 2013)
Safranin-O dye	RM-SDS (sodium dodecyl sulphate)	50	67.10	35	4.4	Langmuir	89.4	(Sahu and Patel, 2015)
Phenol	RM-water neutralized	25	14.2	25	6.0	Langmuir	4.127	(Tor et al., 2006)
Phenol	RM-water neutralized	25	14.2	25	6.0	Freundlich	0.513	(Tor et al., 2006)
Phenol	RM-HCl	60	20.7	25	6.0	Langmuir	8.156	(Tor et al., 2009)

3.2 Red mud application in soil and sediment treatment

Nowadays heavy metals originating from anthropogenic and natural activities have contaminated both soils and sediments. The remediation of soil and sediment is necessary to protect the human health and environment. The choice of most appropriate remediation method for soil and sediment depends on the site characteristics, contaminants types and concentration, and the end use of contaminated medium. The potentially available remediation options for contaminated soils and sediments are either in-situ or ex-situ. Physical, chemical and thermal treatments are frequently used methods. These methods involve physical separation, isolation, sediment/soil washing, extraction, vitrification, and solidification/stabilization (Mulligan et al., 2001). Inexpensive mineral amendments such as apatite, zeolites, clays, beringite, and other iron bearing materials (e.g. zero-valent-iron, goethite, hematite, ferrihydrite) and industrial by-products such as fly ash, and red mud have shown satisfactory performances to reduce trace elements mobility in multi-contaminated soils and sediments (Kumpiene et al., 2008b; Peng et al., 2009). Although, red mud may contain traces of trace elements but bioavailable fraction is low due to their strong binding on red mud. Therefore, red mud has been investigated by numerous researchers as soil amendment and recently for contaminated sediments (Liu et al., 2011; Taneez et al., 2015).

3.2.1 Stabilization of trace elements in soil

Chemical stabilization of trace elements (Cd, Cu, Ni, Zn, Pb, As, Cr, V) in soils using red mud has been assessed. Application of red mud mixed at 2 and 5% rate increased the pH of soil which played dominant role in reducing the metal concentrations soil pore water and metal fluxes. Red mud converted exchangeable fraction of metals to Fe-oxide fraction, decreased the bioavailability of metals at low pH, and specific chemisorption, and diffusion of metals into oxide particles could be the possible mechanism of metals fixation (Lombi et al., 2002a; Lombi et al., 2002b; Lee et al., 2009; Lee et al., 2011). Though, the labile fractions of Cd, Zn, and Cu were reduced in amended soil but it is important to investigate the effects of pH changes on leaching of these trace elements. Re-acidification of amended soil showed that the leaching was always lower than untreated soils across the

range of pH values tested. However, acid leaching of amended soils showed increase As and Cu mobility compared to untreated. Cu is mainly associated to organic matter and addition of alkaline red mud increased the concentration of dissolved organic matter in soil pore water and pH variation affected exchangeable and soluble fraction of Cu. Presence of DOM also decrease the retention of As on goethite (Lombi et al., 2003; Lombi et al., 2004). Field and pot experiments gave similar results than those of Lombi et al., (2002a) but reported to have increased the ammonium nitrate-extractable As, Cu, Cr, and V in soil. Extractable As and V exceeded the trigger value for water quality and thus should be removed from red mud. Cr lability remains unaffected. Red mud application had also increased the mobility of Cu, while toxicity of Cu appeared to be reduced as indicated by the higher corn biomass production. Red mud is promising soil amendment in terms of reduction Cd, Zn, and Ni bioavailability. However, large labile concentrations of As, Cr, and V may limit its application (Friesl et al., 2003; Friesl et al., 2004). In further field investigations it was concluded that if red mud was applied approximately 15 cm below the soils surface it can reduce ammonium nitrate-extractable Cd, Zn, and Pb up to 99% but deeper application may be needed to reduce plant metal uptake (Friesl et al., 2006). Finally, it was concluded that red mud in combination with gravel sludge (a fine-grained waste product of the gravel industry) and metal excluding barley cultivar (*Hordeum distichon* ssp. L.) performed most effectively as a stabilizer for the metal-contaminated soil (Friesl-Hanl et al., 2009). Moreover, red mud was reported to be optimal additive for Cd contaminated agricultural soils due to reduction in water extractable fraction (Feigl et al., 2012; Feng et al., 2013). Red mud amendment in soil can transform 22% of non-specifically adsorbed As to the Fe/Al oxide-bound or specifically absorbed As fractions (Yan et al., 2013). Combined treatment of limestone and red mud (each applied at 2% rate) decreased sufficiently the $Ca(NO_3)_2$-extractable fraction of As, Cd, Pb, and Zn by 58%, 98%, 98%, and 99%, respectively. These results suggest that iron-rich industrial by-products could be used for remediation of soils co-contaminated with metals and arsenic (Lee et al., 2011). In sub-acidic mine soils long term application of red mud had increase in soil pH, decrease of total organic carbon and a significant increase of water-soluble C, N and P. Sequential extraction of amended soil samples indicated a decrease of water soluble As, and a remarkable increase of the residual (non-extractable) arsenic fraction (Garau et

al., 2011). They further reported that after amendment of seawater neutralized red mud in mine contaminated and chromated copper arsenate (CCA) contaminated soils leachability of As, and Pb was increased. This was most likely due to the organic matter degradation and formation of soluble complexes of As and Pb with the low molecular weight organic fractions. On the other hand, the amendment had a more positive response in reducing As and Cu leachability in (CCA) contaminated soil which was probably due to the changes in physical and chemical properties of soil after the addition of sorbents(Silvetti et al., 2014). Transformed red mud (TRM) was used as reactive barrier (RB) placed near the anode of an electrokinetic (EK) system for the removal of chromium or arsenic contaminated clayey soil, and favoring entrapment. The outcome of treatment was beneficial in case of Cr(VI) than As (V). Presence of the anodic TRM RB that suppressed formation of an acidic front, thus decreasing the adsorption capacity of the soil for Cr(VI) oxyanions, increasing the rate of electromigration towards the anode, and limiting Cr(VI) reduction in the soil. Increased mass of TRM in the RB, was shown capable of entrapping all mobilized Cr(VI) before it entered the anolyte, thus preventing contamination of the latter. Conversely, combined treatment was much less effective on As contaminated soil, at least under the operative conditions applied. Low initial As concentration and interference with iron oxides in the soil were likely the reasons underlying low efficiency while attempting As decontamination (Cappai et al., 2012). The efficiency of soil amendments depend on soil conditions, contaminants source and perhaps most importantly the environmental endpoint considered.

3.2.1.1 Trace element uptake by plants and re-vegetation

Red mud treatment not only reduced the labile fraction of trace elements in soils but also significantly increased the soil biomass and four crop species (oilseed rap, wheat, pea and lettuce) were successfully grown in pots (Lombi et al., 2002a; Lombi et al., 2002b). The amendment has positive effect on soil microbial biomass and growth of ryegrass (Lombi et al., 2003; Lombi et al., 2004). Plant uptake was also reduced by 38-87% (Cd), 50-81% (Zn), and 66-87% (Ni) as compared to the control (Friesl et al., 2003). Similar results were found in acidic soil after treatment with red mud and other additives. Particularly, red mud reduced heavy metal uptake of pea and wheat by 60-34% (Pb), 79-80% (Cd), and 93-64%

(Zn) respectively (Castaldi et al., 2009). After red mud amended in microcosm (2 year) study reported decrease in Cd ad Zn uptake of Sinapisalba test plants by 18-29% (Feigl et al., 2012). Red mud can stimulate the growth of Pakchoi plant as well as reduced accumulation of Cd was observed in plan edible part (Feng et al., 2013). In addition to reduced trace element uptake by lettuce (Lee et al., 2009; Lee et al., 2011), and *Festucarubra*, plant enhanced soil microbial activities (soil respiration, urease, and dehydrogenase activity) were significantly increased as well as a dramatic shift in the culturable bacterial population from Gram positive to Gram negative forms in red mud amended soils (Lee et al., 2009; Lee et al., 2011). Phosphorous application with red mud deceased Pb concentration but not total uptake of Pb in *Festucarubra* compared to red mud alone (Gray et al., 2006). Despite the high rate of contaminants mobility, most of the soil microbial and biochemical activities were significantly higher in the RM-soil. Bean germination was almost inhibited in RM-soil while wheat growth was similar to that of the control (Garau et al., 2011; Garau et al., 2014). The effect of soil amendments was more evident when metal uptake by plants was considered. Trial pot showed that the treatments with seawater neutralized red mud in aerobic condition were able to decrease the plant uptake of As by 34 and 57% in Soil-1 (mine contaminated), and by 88 and 87% in Soil-2. Uptake of Cu from Soil-2 (CCA contaminated) reduced (by 68 and 86%) and of Pb from Soil-1 (by 52 and 34%) as a result of amendment (Silvetti et al., 2014).

Besides trace elements stabilization in contaminated soils, red mud can also be used for phosphorous retention and re-vegetation after amendment. Bauxite residue (red mud alone and neutralized with gypsum) can increase phosphorous retention in sandy soil catchment (Summers et al., 1993; Summers et al., 2001), improve pasture growth (Summers et al., 1996), increases soil pH and lower P availability (Snars et al., 2004). A field studied evaluated gypsum as ameliorant at (0, 2, 5, and 8% rate) for vegetation on bauxite residue deposits with two grass species. The research showed that gypsum is an effective ameliorant to reduce the pH, electrical conductivity and significantly enhanced the growth of the two grass species (Wong and Ho, 1993). They also used sewage sludge as another ameliorant for red mud for re-vegetation. Leachate and soil analyses revealed that gypsum was effective in reducing the pH, EC and exchangeable sodium percentage (ESP) of red mud, while sewage sludge gave additional reductions in EC, Na and ESP. In addition,

sewage sludge increased dry weight yield and provided sufficient nutrients for plant growth except K. No heavy metal accumulation was observed. Sewage sludge can also significantly reduce soil bulk density (25%), particle density (9%) and increase the total porosity of red mud (8%) as well as hydraulic conductivity (from 1.5 to 23×10^{-5}m/s) (Wong and Ho, 1994). Similar results were reported by (Xenidis et al., 2005)While most promising results achieved with the combine gypsum and sewage sludge, calcium phosphate application into red mud which further improved plant growth.

3.2.2 Red mud as sediment amendment

Just like soil remediation, in-situ and situ strategies have also been adopted for remediation of contaminated sediments with trace elements. Fewer studies have been reported so far for the use of bauxite residue as amendment for contaminants stabilization in sediments. Pot and field experiments were conducted using red mud and other amendments (sludge from drinking-water treatment, lime, bog iron ore, unused steel shot and steel shot waste) for the immobilization of Cd and Zn in dredged sediment from seaport. The pH and CEC were little influenced by the treatments. In the pot experiments, NH_4NO_3extractable amounts of Cd and Zn in the treated samples were reduced by 50% (DTPA: -20%) while plants uptake was reduced by 20-50%. Conversely, in field trial Cd and Zn were immobilized in the soil to a certain extent, but less effect was observed on the concentrations in plants and soil extracts. Red mud and sludge from drinking water treatment were found to be effective treatments in terms of metal immobilization. Although use of red mud is questionable whether it can be applied in practice as it contains high amounts of Cr and Al ions (Müller and Pluquet, 1998). Stabilization of multi-contaminated marine dredged sediment was evaluated by using two bauxite residues (bauxaline® and bauxsol) at 5% rate. The results revealed that after 3 months of treatment, pH of leachate decreased from 42±3 mS/cm to 12±3 mS/cm and pH remained constant around 8.2, cationic trace elements (Cd, Cu, and Zn) were effectively immobilized but no significant efficacy was observed for anionic pollutants (As and Mo) (Taneez et al., 2015). Increased leaching of anionic pollutants could be limited by addition of higher quantities of amendments. Further investigation by applying neutralized bauxaline® (bauxaline® treated with 5.88% of gypsum) at the rate of 5% and 20% showed relatively better results in case of anionic pollutants. The available

fraction of contaminants in case of 5% neutralized bauxaline® was as follows: Cu (26.5%), Cd (24%), Zn (35%), As (9.6%), Cr (19.1%), and Mo (2.2%). Whereas with 20% neutralized bauxaline® Cu (40%), Cd (55%), and Zn (71.2%), were predominantly stabilized as compared to leaching from control sediment whereas Mo (11.7%). and As (5.2%) were less immobilized. pH was around 8.2, and EC reduced from 44±2 mS/cm to 12±4 mS/cm in the leachates collected during 3 months of experiment (Taneez et al., 2016).

3.3 Leaching and ecotoxicological studies of red mud

US EPA developed a protocol called Standard Toxicity Characteristics Leaching Procedure (TCLP) which is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multi-phase wastes. The intent of this leachate procedure is to simulate the conditions that may be present in a landfill where water may pass through the land- filled waste and travel into the groundwater carrying the soluble materials with it. Standard Toxicity Characteristics Leaching Procedure (TCLP) has been used by many researchers to assess the leaching behavior of trace elements from red mud. Leachability of Cr and Fe from reacted waste using TCLP showed low level of leaching. Cr (VI) loaded waste was treated with Portland cement to minimize further leaching. The results showed further decrease in Cr and Fe leaching confirms the effectiveness of stabilization process (Singh and Singh, 2002). TCLP test of used adsorbents Bauxsol (seawater neutralized RM) and Activated Bauxsol (AB) revealed leached amount of arsenate were very small and below the limits (Genç et al., 2003; Genç-Fuhrman et al., 2004a). Similarly, reduced leaching from RM was observed before and after metal removal using TCLP test shown that red mud is an environmentally compatible material that could be used for the wastewater treatment (Vaclavikova et al., 2005). Environmental compatibility of Bauxsol^{TM} using three different eco-toxicological tests (Microtox™, ASTM microalgae toxicity and sea urchin embryo toxicity test) showed no toxic effects. The treated Bauxsol^{TM} showed high metal trapping capacity and low leachability at pH 5 of trapped As, Cd and Cu (<6 %), but higher (10-30 %) in the case of Mn and Zn (Brunori et al., 2005). Acute toxic effect of metal loaded Bauxsol^{TM} reagent (MLBR) containing more than 6450 mg/kg of bound metal, on the earthworm *Eiseniafetida* was investigated. The

results showed good motility and no mortality of *E. fetida*, bioavailable fraction of metals were low, bioaccumulation of metals in the worms and bioaccumulation factors (BAFs) were below than the reported toxicity thresholds to cause mortality (Maddocks et al., 2005). Red mud addition to soil polluted with heavy metals (Lombi et al., 2002a; Garau et al., 2007; Castaldi et al., 2009), and As (Garau et al., 2011; Lee et al., 2011)showed encouraging results in terms of enhanced plant growth, improve biochemical properties of soils and increased microbial biomass. Moreover, (Pagano et al., 2002) reported toxic effects of red sludge and other solid residues from bauxite manufacturing plant (Turkey, France, Greece and Italy) on sea urchin. These effects were attributed to high concentration of Al and pH. However, striking variability appeared in bauxites by-products in their toxicities. The variable environmental effects are related to variable ore composition and manufacturing process. Fluvial sediments collected from a catchment, western Hungary after accidental red mud spill showed that red mud appear to induce an increase in the density of aerobic and facultative anaerobic bacterial communities when compared with unaffected sediments and reference sites while Lemna minor appears to be a particularly sensitive test organism to the effects of red mud deposition (Klebercz et al., 2012). A more recent study showed that soluble vanadium from red mud spill causes genotoxic and cytotoxic effects in higher plants (Mišík et al., 2014). Marine dredged sediment stabilized by 5% of bauxaline® and bauxsol were not sufficient to lower toxicity of the sediment leachates against marine rotifers (Taneez et al., 2015), while increased the rate of amendment (20%) showed reduction in rate of rotifers mortality up to 36% (Taneez et al., 2016).

The Gardanne alumina refinery (France) is the first site in the world where alumina was manufactured with the Bayer industrial process formulated a scientific committee in response to the State's regulations to ensure an independent evaluation of bauxite residue discharge on the structure and functioning of bathyal ecosystem in the Cassidaigne canyon (north-western Mediterranean Sea). The committee summarizes the main results obtained during sea campaigns from 1999 to 2007. Variation in test response depends on the variable composition of the bauxite ore, and manufacturing process as mentioned above (Pagano et al., 2002). No accumulation of trace elements (Al, Cr, Cu, Fe, Pb, Mn, V and Zn) was found in dominant fish species and showed no accumulation of the element

showing no potential health risk due to consumption. No relationship was also found between measured concentration of toxic metals Cr, and V and the pipe's proximity, reinforces the idea of low potential danger from the red mud in this area. Nevertheless, the scientific committee has proposed feasible approaches to valorize Bauxaline® when the residue discharge stops at the end of 2015. They also recommended that the Gardanne alumina refinery conduct a long-term eco-toxicological survey of sediment collected in at least six sampling sites during the next campaign in 2012 (Dauvin, 2010).

Table 5. Ecotoxicological results (Dauvin, 2010)

Bioassay	Substrate	1997	1999	2002	2007
Microtox	Organic extract	N	-	-	-
	Interstitial water sample	-	N	-	-
	Lixiviated sample	N	N	N	N
	Sediment contact	-	P	N	N
Larval development (sea urchin/mussel/oyster)	Sediment contact	P*	N	N	N
	Lixiviated sample	P**	N	N	N
Ames test	Lixiviated sample	N	-	-	-
	Organic extract	N	-	-	-
Acute toxicity	Sediment contact	N	N	-	-
	Elutriated sample	N	-	-	-

N = negative; P = positive; - = not measured
* Maximum larvae anomaly (38.9%)
** Maximal larvae anomaly = (20.1%)

All of the above investigations showed application of red mud have applications in various environmental media (water, soil and sediments) suggest that after red mud sorbent after waste water treatment exhibits low leaching of its components. Similarly, use of red mud in acidic metal polluted soils, retention of phosphorus in sandy soil and trace elements stabilization in sediment also showed fruitful results. Addition of cement material further stabilizes the waste and it can be employed as brick production or disposed in nonhazardous landfills without causing significant environmental toxicity. Neutralization of red mud is very important to limit possible environmental impacts.

4. Conclusions

Red mud, a by-product from alumina industry contains Fe, Al and Ti oxides which can be used for environmental applications. Conversely, the disposal of red mud in landfill poses

environmental risk due to highly alkalinity and possible leaching of its content. It is critical to find a new cost-effective way to manage this waste product. In the past years red mud can be used as alternative to expensive adsorbents for wastewater treatment. Generally, combined acid and thermal treatment have been widely used methods for improving physico-chemical properties. Large volume of acid required for large scale application which add cost to the product. Among other neutralization methods, the most suitable method which not only improves surface area but also provokes the formation of neo-formed surface without losing acid neutralization capacity of red mud is seawater neutralization. It appears from the literature that red mud works better after neutralization. Increased adsorption capacity of treated red mud for metal ions, anions and organic pollutants from wastewater was reported. It can increase the stabilization rate of trace elements in soil and sediments with optimum quantity of amendment. Chemical stabilization combined with re-vegetation is an innovative remediation technology that focuses on reducing the mobility of elements in soil rather than removing them by converting the fraction of trace elements in non-water extractable or non-bioavailable forms. On the basis of leaching test it was confirmed that spent red mud pose that no serious secondary contamination will occur and ecotoxicological studies demonstrate that red mud is not toxic to many species test. However variation in test response depends on different factors such as high pH and Al content, variation in bauxite ore composition and manufacturing process.

Use of red mud as soil or sediment amendment can consume its large volume. The efficacy of red mud depends on its amendment amount, the type of waste (soil/sediment), and contaminants to be addressed. Despite this red mud remains a valuable stabilizing agent for cationic in soils. However, few investigations have been conducted in case of sediments and it is recommended that more research should focus in this area. In-situ capping with neutralized red mud should be investigated for the long term effectiveness of this process in case of cationic pollutants. Research on mechanism of immobilization should be intensively conducted to promote the process eco- friendly application.

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Chapter 11

Materials and Methods

This chapter explains materials and methods used in this study. The sediment and mineral amendments were characterized and physico-chemical properties (pH, EC, CEC, TOC etc) of these materials were determined following standard procedures. To assess the level of pollution in sediment sample total content of trace elements was analyzed. The adsorption potential of amendments was determined and then these amendments were tested at different rates to stabilize trace elements in pilot device. Leachates toxicity was also measured using *Brachionus plicatilis* as test organism.

1. Sediment and Mineral amendments

1.1 Sediment sample

Dredging is the common practice to prevent accumulation of sediment in harbors and to improve navigation. Sediments are known to accumulate contaminants up to several orders of magnitude higher than in the water. Contaminants can be easily adsorbed onto particles, deposited and accumulated in the sediments, making sediments a sink and an ultimate source of contaminants. Contaminants can be released back into water column during natural events and anthropogenic processes (dredging, dredged disposal and fishing) that provoke little variations of pH or redox potential of interstitial water. Dredging activities generate huge quantity of sediments and these sediments need to be managed according to legislative requirements. Generally, dredging operations are carried out by port authorities. Similarly, port authorities conduct periodic dredging at the arsenal port of Toulon city, southeastern France which is subjected to military and commercial activities. The sediments of the Toulon bay found to be contaminated by multitude of metals, metalloids, organometallics and organic compounds (Mamindy-Pajany et al., 2011; Tessier et al., 2011; Pougnet et al., 2014).

In a previous work, a sediment sample from the navy harbor area of Toulon has been studied. The X-ray diffraction (XRD) data of crude sediment sample indicates the presence of calcite, feldspar, quartz and illite minerals. Mineralogical analysis of the fraction inferior to 2 µm has shown that the clay proportion of sediments contains illite, kaolinite and smectites in a relative proportion of 73%, 19% and 8% respectively (Mamindy Pajany et al., 2010). Chemical analyses has shown that the sediment sample was highly contaminated with inorganic (As, Cd, Cu, Zn, Pb, and Hg) and organic contaminants (PAHs, PCBs and TBT) (Mamindy Pajany et al., 2010; Mamindy-Pajany et al., 2011). To assess the risk of contaminated marine dredged sediments on the basis of chemical data (recommended by national decree); Ifremer and the Geode inter-ministerial group have developed the Geodrisk software that provides a benchmark for the operator to design a management process following a decision tree (see chapter 1, Fig. 2). It also enables to differentiate dredged sediments according to their level of contamination and potential toxicity. According to French sediment quality guidelines two levels named N1 and N2 are fixed for contaminant concentrations in whole sediment. If the level of contaminants is

below N1 then the sediments are considered uncontaminated and can be dumped back into sea. If the level of contaminants is higher than the permissible level N2, this means that the sediment cannot be immersed back into the sea and it should be managed on land. Direct land disposal of such sediments poses risk to environment due to possible leaching of contaminants. If the calculated Geode risk is greater than 2 it means that the dumping of such sediment is forbidden and local impact study should be carried out (Alzieu and Quiniou, 2001). Mamindy-Pajany et al. (2011) reported that the sediment sample had a Geode score of 2.8, meaning that the dumping of such sediment is forbidden and the ecotoxicity of sediment should be investigated. The estimated toxicity of elutriates from composted sediments (navy harbor area and commercial port) by several bioassays (embryo-toxicity test, Microtox® solid phase test, LuminoTox, phytotoxicity tests and genotoxicity test) suggest that sediment from Navy harbor area was highly toxic. Bioassay responses are not clearly correlated with chemical contamination in the whole sediment and vary as a function of tested organisms. It was observed that other parameters such as particle size and organic carbon content should be taken in account at the time of mixture preparation by port authorities as well as composted samples need further treatments for trace element stabilization prior to beneficial re-use or landfill. In a pilot scale study different mineral amendments (hematite, zero-valent iron and zeolite) were applied at different rates, commercial hematite and zero-valent iron were found to be the best mineral additives to stabilize trace elements in marine dredged sediment and decreased the toxicity of sediment (Mamindy-Pajany et al., 2013).

The matrix of this study was formulated from a previous project “SEDIMARD 83” (Grosdemange et al., 2008), and the sediment samples were provided by French port authorities from Navy harbor area Toulon. After dredging the sediments samples were stored on a land designated for dredged sediments management, and actively composted for 4 months. This composting procedure consists in humidification with tap water and mixing of the sediment once per week, to promote microbial degradation, lower salt and organic matter content. Two sub samples were collected in 2 different containers and brought back to the laboratory to perform the experiment.

Use or recycling of the industrial by-products has become an attractive alternative to commercial materials for environmental applications. Bauxite residue (commonly known

as “red mud”) is generated as by-product during alumina extraction from bauxite ore. Generally, for 1 tons of alumina production, 1-1.5 tons of bauxite residue are generated (Genç et al., 2003). Therefore, this by-product is a growing focus of research in recent years due to its huge global production of 120 Million tons per year (Power et al., 2011).

In this study we investigated the use of bauxite residues (bauxaline®, bauxsol, and neutralized bauxaline®) as amendments to immobilize trace elements in composted marine dredged sediments, and to decrease the toxicity of sediment by limiting the leaching of available fraction of trace elements.

1.2 Mineral amendments (Bauxaline®, Bauxsol and Neutralized bauxaline®)

The mineral amendments have been largely studied for the stabilization of trace elements in soils due to their chemical composition and properties. Present study used bauxite reside as mineral amendment to stabilize trace elements in the marine dredged sediment. Bauxite residue is highly alkaline in nature (pH 10-13), reddish brown in color and fine particle size distribution. It is mainly composed of fine particles containing aluminum, iron, silicon, titanium oxides and hydroxides (Nadaroglu et al., 2010).

For this study, bauxite residues (bauxaline®, bauxsolwere provided by ALTEO plant (Gardanne, Bouches-du-Rhône, France) that supplies specialty alumina since 1893. It is the world’s first Bayer Plant and largest producer of specialty alumina. Bauxaline® was neutralized with 5% of plaster (net content of gypsum is 5.88%) by INERIS. This mixture was hydrated and equilibrated for 7 days with Milli-Q water and then the slurry was air-dried. The samples of bauxaline®, bauxsol and neutralized bauxaline® were then supplied to the laboratory. Mineralogical composition of the bauxaline®, bauxsol were provided by ALTEO, and composition of neutralized bauxaline® was provided by INERIS.

Table 8(a). Composition of bauxaline® and bauxsol

	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	SiO_2 (%)	CaO (%)	Na_2O (%)
Bauxaline®	14	50	11.5	6	5.5	3.5
Bauxsol	14	50	11.5	6	5.5	3.5

Table 8(b). Composition of neutralized bauxaline®

Hematite 42 (%), Goethite 27 (%), Cancrinite$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$ 11 (%), Calcite 6 (%), Rutile 4 (%), Katoite $Ca_{2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}$ 4 (%), Gibbsite 2 (%), Quartz 2 (%), Portlandite 1 (%), Boehmite 1 (%), Anatase (traces)

These mineral additives were first tested to investigate their sorption potential for (As(V)), and cadmium (Cd(II) in batch experiments. Later the amendments were applied at different ratios in marine dredged sediment to stabilize trace elements.

1.3 Determination of physicochemical parameters of sediment and mineral amendments

1.3.1 pH and Electrical Conductivity (EC)

pH of sediment, bauxaline®, bauxsol and neutralized bauxaline® samples was measured according to ISO standard method in a 100 g/L suspension of solid in Milli-Q pure water (Milli-Q Academic A10, France) using pH meter (Consort bvba, Belgium), equipped with a combined pH electrode, calibrated using buffer solutions at pH 4.00, 7.01 and 10.00 at room temperature.

The electrical conductivity (EC) indicates the amount of soluble (salt) ions in soils. EC values of sediment and bauxite residue samples (bauxaline®, bauxsol and neutralized bauxaline®)were determined in suspensions (100 g/L) of solid in Milli-Q pure water with (EC) meter (Crison, Barcelona, Spain).

1.3.2 Cation Exchange capacity (CEC)

The cation exchange capacity (CEC) represents the ability of the soil or sediments to absorb or release cations, and consequently is an important parameter in sites contaminated by metals (Ashraf et al., 2012).The cation exchange capacity (CEC) of the sediment and bauxite residue samples (bauxaline®, bauxsol and neutralized bauxaline®) was measured as specified in the ISO standard method (ISO 23470, 2007). This method measures the CEC and content of exchangeable cations(Al^{3+}, Ca^{2+}, Fe^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+) in soils using hexamine cobalt trichloride (Sigma Aldrich ≥ 99%)solution as extractant.

1 g of each sample was placed in 25ml of Cohex solution (0.005M) and agitated for 3 hours at room temperature. After agitation, samples were centrifuged for 10 minutes and filtered using 0.45µm membrane filter. The concentration of cobalt (Co) in solution was determined by measuring the absorbance of cobalthexamine at 476 nm wavelength using a spectrophotometer.

1.3.3 Analysis of total inorganic pollutants

The sediment, bauxaline®, bauxsol and neutralized bauxaline® were mineralized according to US EPA 3050b method for acid digestion of sediments, sludges and soils using hotplate (DigiPREP HT, SCP Science, Quebec, Canada). Digestion was carried out in DigiPREP tubes using samples weighing 0.5-1.0 gram (dry weight) with repeated additions of concentrated nitric acid (HNO_3Fluka, ≥69.0%) and hydrochloric acid (HCl Fluka,≥ 37.0%) and continuous heating at 95°C until no more brown fumes are generated. The mixture was allowed to evaporate and the digested sample was diluted to 50 ml with milli-Q. A 10-ml aliquot of the mineralized samples was filtered using 0.45µm filters and analyzed for total inorganic pollutants (As, Cd, Cu, Mo, Ni, Cr, and Zn) by inductively coupled plasma optical emission spectrometry ICP-OES (Optima 7300, Perkin Elmer Corporation, Massachusetts, USA).

1.3.4 Total organic carbon (TOC) and Dissolved organic carbon (DOC)

Total organic carbon in sediment, bauxaline®, bauxsol, and neutralized bauxaline® was determined according to AFNOR protocol based on sulfochromic oxidation (AFNOR NF ISO 14235, 1998). This method involves spectrometric determination of organic carbon in soils or sediment samples.0.2-0.5 gram of sample was mixed with 5.0 ml of $K_2Cr_2O_7$ (Fluka,≥99.5%) and 7.5 ml of concentrated sulphuric acid (H_2SO_4Sigma Aldrich,≥ 95-97%). The samples were then heated at 147 ^{o}C for 30 min. Then the sample was diluted up to 100 ml with Milli-Q water and centrifuged for 15 min. Supernatant was analyzed with UV spectrophotometer (Metertech UV/VIS SP8001, Taipei, Taiwan) at 585 nm.

Leachates samples collected during experiments were also analyzed for dissolved organic carbon concentration. DOC was measured in leachates using total organic carbon analyzer (TOC-V_{CPH} Shimadzu Corporation, Kyoto, Japan*)*.

1.4 Adsorption experiments

1.4.1 Adsorption protocol and reagents

Adsorption experiments of arsenate (As(V)) and cadmium (Cd(II)) on bauxaline® and bauxsol were carried out according to the US EPA protocol based on batch type adsorption tests (US EPA, 1991). The entire reagents used in adsorption experiments were of analytical grade. All solutions were prepared in high purity water provided by Milli-Q Academic A10, France). Stock solutions (1 g/L) of As(V) and Cd(II) were prepared using $AsHNa_2O_4.7H_2O$ (Fluka, ≥ 98.5%), and Cd $(NO_3)_2.4H_2O$ (Sigma Aldrich, ≥ 99%) in Milli-Q water. The solutions were acidified with 1% HNO_3 (Fluka, ≥ 69.0%) to avoid precipitation or complexation of metal ions. To perform adsorption experiment dilute solutions were prepared from these stock solutions. Sodium nitrate (0.01 M) was used as background electrolyte prepared from $NaNO_3$ (Acros Organics, ≥ 99%). For pH adjustment, micro volumes of solutions of 1M nitric acid and 1M or 0.01M sodium hydroxide (NaOH Fluka, 98%) were added.

1.4.2 Batch experiments

The adsorption batch experiments were carried out at room temperature in polypropylene tubes (50 ml) as function of mass to liquid ratio, contact time, pH and initial adsorbate concentrations. pH adjustment was done using 1M HNO_3 or NaOH solutions. At the end of each experiment the suspensions were centrifuged at 5000 rpm for 10 min. The supernatant was then separated through 0.45 µm cellulose acetate filters. Before measuring final concentrations of As(V) and Cd(II) on ICP-OES, filtrates were acidified (1%) with concentrated HNO_3.

1.4.2.1 Adsorption as function of mass to liquid ratio

In order to determine the adsorption capacity of both solids (bauxaline® and bauxsol) for As(V) and Cd(II), several mass to liquid ratios (0.125, 0.25, 0.625, 1.25, 2.5, and 5.0 g/L) were tested. For this solid mass ranging from 10 mg to 200 mg were weighed separately (for arsenate and cadmium) in polypropylene tube (50ml) and 40 ml of solutions containing desired concentrations of arsenate (1.0 mg/L) and cadmium (5.0 mg/L) were added at fixed ionic strength (0.01 M) using $NaNO_3$ and pH was fixed at neutral value

(6.86-7.0 ± 0.1) by adding previously prepared acid and base solutions. The suspensions were agitated on rotator at 50 rpm for 24 h, and then centrifuged at 5000 rpm for 10 min. The supernatants were filtered, acidified, and analyzed. The percentage of adsorbed As(V) and Cd(II) were calculated separately according to the formula:

$$\%\, adsorption = \frac{Ci - Cf}{Ci} \times 100$$

Where Ci (mg/L) is the initial arsenate or cadmium concentration and Cf corresponds to concentration in supernatant (mg/L).

1.4.2.2 Adsorption as function of time

In order to determine the equilibrium time adsorption kinetic was performed. A constant mass (10 mg) of each solid (bauxaline® and bauxsol) was put in contact with 40 ml of As(V) = 1 mg/L and Cd(II) = 5 mg/L solution in polypropylene tube at neutral pH (7.0) and at constant background electrolyte condition. Then the suspensions were shaken for different times (from 30 min to 24 h). One tube corresponds to one stirring time. After centrifugation, the supernatant was filtered, analyzed and percentage of adsorption was calculated according to above mentioned formula.

1.4.2.3 Adsorption as a function of initial concentration and pH

The adsorption experiments were carried out at neutral pH using mass to liquid ratio of 1.25 g/L of bauxaline® and bauxsol. The initial concentration of As(V) varied from (0.5 mg/L 1 mg/L) while for Cd(II) it varied from 5 mg/L to 50 mg/L. The suspensions were shaken for 2 h (equilibrium time), then centrifuged, filtered and analyzed. The quantities of adsorbed As(V) and Cd(II) in mg/g were calculated as follows:

$$Q = \frac{(Ci - Cf)V}{m}$$

where Q (mg/g) is the adsorption capacity of As(V) and Cd(II) at equilibrium, Ci (mg/L) corresponds to the initial concentrations, Cf (mg/L) is the concentration in the supernatant at equilibrium, m is the amount of adsorbent (g) and V is the volume of solution (L).

Furthermore, effect of pH values between 2 and 10 was investigated. The mass to liquid ratio was 1.25 g/L for both solids. The concentration for Cd(II) was 5mg/L, and 50 mg/L.

1.5 Stabilization of trace element in marine dredged sediment

Solidification/stabilization technique using three mineral amendments was applied to stabilize trace elements in marine dredged sediment. For this purpose two pilot experiments were performed in Nice, France for the period of 3 months. The first pilot experiment was conducted from March 2013 to June 2013 and second one from April 2014 to July 2014. In the first experiment two amendments (bauxaline® and bauxsol) were mixed at 5% rate with first subsample of sediment. Three treatments were prepared: (1) untreated sediment (as control), (2) Sediment + 5% bauxaline®(S + 5% BX), (3) Sediment + 5% bauxsol (S + 5% BS) as shown in (Fig. 5). In second pilot experiment, five treatments were prepared using 2ndsubsamples of sediment: (1) untreated sediment (as control), (2) Sediment + 20% bauxaline® (S + 20% BX), (3) Sediment + 20% bauxsol(S + 20% BS), (4) Sediment + 5% neutralized bauxaline® (S + 5% GBX), (5) Sediment + 20% neutralized bauxaline® (S + 20% GBX). For each experiment 6 kg of sediment was placed in wooden boxes of equal size (40×40×20 cm). Bauxaline®, bauxsol, and neutralized bauxaline® were applied as mineral amendments at the rate of 5% (i.e. 300 g for 6 kg of sediment) and 20% (i.e. 1,200g for 6 kg of sediment). Each box contained a square plastic mesh at the bottom to allow leachates collection. A geotextile cover was placed in the inner surface of each box to prevent the loss of fine particles.

To simulate artificial rainfall two liters of tap water was poured on the top each box during 3 months in the following steps: (1) 1 L of tap water was sprayed homogeneously, (2) using garden shovel, materials were aerated manually, and (3) 1 L of tap water was sprayed again onto materials. Leachates were then collected in plastic containers placed under each box after1 h drainage through the materials. During 3 months experiment, leachates were collected 3 and 2 times in the first and second week respectively. Afterwards, this draining and mixing was repeated weekly. Considering the average annual

rainfall in Nice (approx 740 mm/yr), this corresponds to an average rainfall measured during 3 months. The experimental setup is present in fig 1for both pilot tests.

Trace elements (Cu, Cd, Zn, Ni, As, Cr, and Mo) were measured in filtered leachates (0.45 µm membrane filter) after acidification at 1% with HNO_3 (69 %) by ICP-OES. pH, organic content and electrical conductivity were also monitored in leachates.

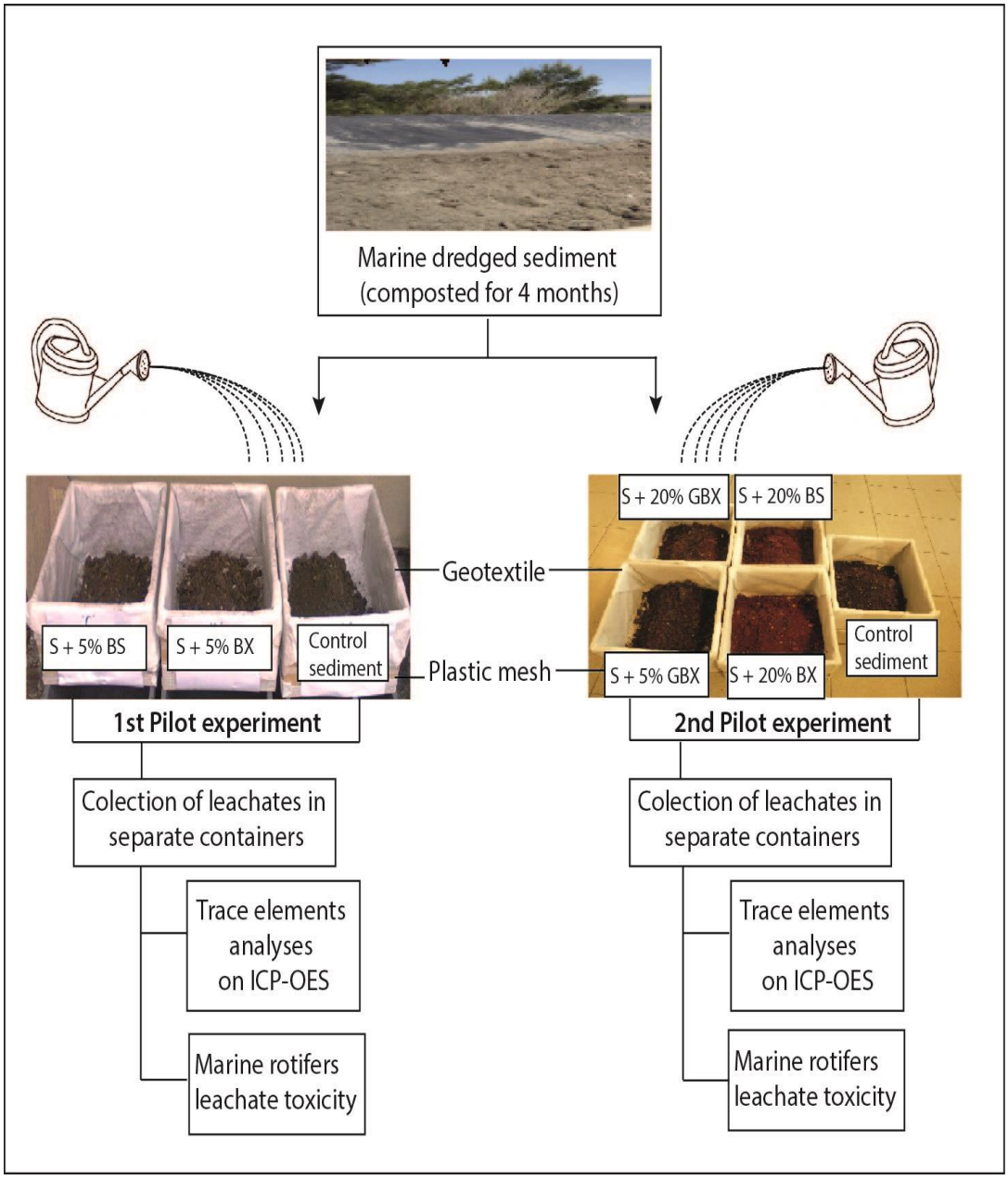

Fig 5. Experimental set up

1.5.1 Leachates toxicity

Toxicity test is considered to be one of the important tools and current regulations imply toxicity test to assess the potential impacts of sediment disposal after dredging. We chose *Brachionus plicatilis* as test organisms because these marine rotifers are able to tolerate wide range of salinity e.g., (5-35 PSU). Since the successive leaching with tap water during stabilization experiments decreased the salinity, *B. plicatilis* appeared to be the most suitable organism to be tested according to our experimental protocol. All the leachates collected during 3 months of both (1st and 2nd pilot) experiment were subjected to toxicity test with *B.plicatilis*. Commercially available Rotoxkits M were purchased from Microbiotest Inc., Belgium. Rotoxkit M is based on 24 h to 48 h mortality bioassay and sensitivity to particular chemicals or mixtures increased substantially with exposure time of 48 h. Hatching of rotifer cysts were made in standard seawater of reduced salinity (20 PSU) at 25 ^{o}C under continuous illumination of 3000–4000 lux for 28 h. Within 2 h of hatching the neonates were transferred to multi-well test plate containing leachate samples. After transferring 5 rotifers into each well the plates were covered with paraffin film and incubated at 25 ^{o}C in darkness. The number of dead rotifers in each well was counted after 24 h and 48 h incubation. Hence, mortality after 24 h and 48 h can be estimated. Rotifers are considered dead if they do not exhibit any internal or external movement in 5 seconds observation. For the rotifers test to be valid, control mortality in standard seawater (35ppt) must not exceed 10%. For this test, potassium dichromate was used as reference toxicant.

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Chapter III

Sorption & Stabilization of trace elements in contaminated marine sediment

The objective of this chapter is to present the results of sorption experiment conducted using synthetic solutions of As and Cd on bauxite residues. Afterwards, the results from stabilization experiments were presented. The addition of bauxite residues in the process of stabilization of contaminated port sediment helped to improve the quality of leachates from sediment. Literature review helped to demonstrate the complexity of the study matrix (sediment) and effectiveness of stabilization process depends on the characteristic of sediment.

1. Summary of article 1: Adsorption of inorganic pollutants on bauxite residues: an example of methodology to simulate adsorption in complex solid mixtures

1.1 Introduction

Presence of inorganic pollutants such as arsenic (As) and cadmium (Cd) in water, soils and sediments has become a worldwide problem in the past decades (Smedley and Kinniburgh, 2002; Luo et al., 2011). Exposure to theses pollutants causes significant health problems due to consumption of contaminated food and drinking water (Diazbarriga et al., 1993; Ke et al., 2015). The fate of toxic elements in the environment is controlled by sorption processes and speciation. In natural waters As is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Arsenate generally exhibits a low mobility compared to Cd which is highly mobile in nature (Smedley and Kinniburgh, 2002; Luo et al., 2011). Al and Fe (hydr) oxides present a strong affinity for As and Cd (Silva et al., 2010; Jiang et al., 2013), and much attention has been paid to the sorption reactions and speciation in immobilizing materials for remediation (Luo et al., 2011). Adsorptive removal of toxic inorganic pollutants on different mineral based materials has been extensively studied and found to be a cost effective and environmentally friendly approach. One of the important mineral additives is bauxite residue produced during alumina extraction in large quantities. Bauxite residue is rich in Fe and Al oxides and has shown a significant affinity for various pollutants from aqueous and solid media (Liu et al., 2011). In this context, interaction of As(V) and Cd(II) using two bauxite residues (bauxaline® and bauxsol) from aqueous solution was studied. Adsorbent properties were determined and the adsorption data was modeled using a surface complexation model. The preliminary determination of adsorption potential was done in order to test these materials for the stabilization of trace elements in the marine sediments.

1.2 Results and conclusion

The results of physicochemical parameters showed that bauxaline® has a higher pH and CEC value than bauxsol but the composition and isoelectric points of both solids were

found to be similar. High adsorption percentages (arsenic and cadmium) were obtained for both solids, and removal rates increased when solid to liquid ratios were increased. Maximum removal of arsenic was obtained at neutral pH with initial concentration of 1.33E-05 molar (M), and solid to liquid ratio of 1.25 g/L. Adsorption of arsenic decreased with the further increase of pH (9.74) indicating that negatively charged surface of the solids had not favored the adsorption and that from this pH desorption of arsenic could occur. Adsorption data were modeled using 2-pK/Double Layer Model (ECOSAT software) considering that only Fe oxides and Al oxides surface sites from bauxite residues were involved in adsorption of As and Cd. Hence, to get a model as simple as possible, the equilibrium and constants associated to acido-basicity of the solid and surface complexation were extracted from the literature considering that iron and aluminium oxy-hydroxides from the bauxite residues could be considered as equivalent to ferrihydrite and gibbsite. A total of 6 adsorption equilibria (3 for ferrihydrite and 3 for gibbsite) for As (V) were necessary to obtain a good fit of experimental data. In these calculation conditions, except for the specific surface area of the ferrihydrite and gibbsite, no data adjustment was necessary to correctly predict the adsorption data.

Experimental data obtained for adsorption of Cd were modelled as described below considering the adjusted specific surface areas for ferrihydrite and gibbsite and 2 adsorption equilibria (1 for ferrihydrite and 1 for gibbsite) for Cd(II). Bauxaline® and bauxsol exhibited the same chemical reactivity towards Cd. The modelling results were in good agreement with experimental data except when high initial concentration of Cd was considered. This suggested that in the presence of solid the precipitation of $Cd(OH)_2$ occurred at a lower pH (i.e. 2 pH units lower). Thus, a supplementary equilibrium corresponding to the solubility product of $Cd(OH)_2$ has been incorporated and fitted in the model to obtain a better correlation of experimental data. Finally, the predictive capacity of the model was evaluated by simulating the adsorption of Cd at various pH values, considering a high solid concentration (1.26 g/L) and a low solid concentration (0.26 g/L) of bauxaline® and bauxsol. When high solid concentration was considered, the sorption edge is well predicted by model until pH 6.0. At low solid concentration, the predicted values were correctly correlated up to pH 8 (corresponding to surface complexation).

Above pH 8, the predicted values were higher than experimental values in the case of bauxaline. For bauxsol the sorbed fraction was closer to the model when the solubility product of pure $Cd(OH)_{2(s)}$ was considered. This behavior was found to be consistent with the high sensitivity of homogeneous/heterogeneous precipitation processes. Depending on supersaturation ratio, solids amount and surfaces type, cations could precipitate in solution or form surface precipitates whose stability constant is not well-defined. Thus, simulations based on the presented models lead to an envelope of experimental results in the pH-range where this phenomena occurs. The precipitation can be avoided for high solid quantities, low cadmium concentration, low pH or a combination of these parameters.

2. Article 1: Adsorption of inorganic pollutants on bauxite residues: an example of methodology to simulate adsorption in complex solids mixtures

(Under submission)

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Abstract

Bauxite residues (bauxaline® and bauxsol) rich in iron and aluminum oxide are good adsorbing materials for the inorganic pollutants. Composition and physic-chemical parameters of bauxite residues were measured. The adsorption of arsenic and cadmium on bauxaline® and bauxsol from aqueous solution was studied as function of solid to liquid ratio, pH, and initial adsorbate concentrations. Both solid showed optimum removal at neutral pH range. Adsorption data was modeled using 2-pK/Double Layer Model. It has been shown that the reactivity of these residues, characterized by a complex composition, can be simplified in a binary mixture of iron oxide and aluminum oxide. Using published values of surface constants of both solids for acido-basicity and surface complexation of As(V) and Cd(II) ions, this approach has been demonstrated to be predictive. Adsorption mechanism was found consistent with the formation a surface complex along with surface precipitation for cadmium.

Keywords: Surface complexation model; red mud; iron oxide; aluminum oxide

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1. Introduction

Arsenic (As) and Cadmium (Cd) are ones of the priority toxic pollutants present in the environment. Elevated concentrations of both trace elements can be detrimental to living systems. The main sources of arsenic contamination are geological, industrial and agricultural use of arsenal pesticides (Müller et al., 2010; Silva et al., 2010). Significant health problems are reported due to As contamination in environment. Inorganic forms of arsenic such as As(III) (arsenite) and As(V) (arsenate) are present in water supplies. Under aerobic environment, arsenate is more stable and dominant over a wide pH range and occurs as oxyanions of arsenic acid ($H_2AsO^-_4$ and $HAsO^{2-}_4$). US-EPA set maximum concentration level of 10 ppb (0.01 mg/L) for As in drinking water. However, many countries including China and Bangladesh have retained the old WHO guideline of 50 ppb as their standard (EPA, 2001).

Cadmium is a highly toxic element that enters in to environment mainly through anthropogenic industrial effluents (Luo et al., 2011). The regular exposure of cadmium cause serious human health problems such as lung cancer and kidney failure. US EPA set permissible limit of 5.0 ppb (0.005 mg/L) for Cd in drinking water due to its carcinogenic effects (ATSDR, 1997; Järup, 2002). Thus, it is imperative to identify remediation technologies for the contaminated environments. Commonly employed methods to remove trace elements from water are chemical precipitation, adsorption, ion-exchange, reverse osmosis, electrochemical reduction, etc. Adsorption is being the most commonly used method for the treatment of contaminated media (Papandreou et al., 2007). Industrial by-products received considerable attention as alternative adsorbents to activated carbon due to their low cost and mineralogical composition. Bauxite residue (red mud) is aluminum industry waste generated in huge quantities (1 ton of alumina production generates 1-1.5 tons of red mud). Raw bauxite residue is highly alkaline in nature (pH 10-13) due to large amounts of sodium hydroxide and sodium carbonate. It is mainly composed of oxides of Fe, Al, and Ti. Neutralization of bauxite residue is required for safe disposal and utilization purposes. Common neutralization methods involve addition of acids, hard groundwaters, magnesium and calcium chloride salts, saline brines, or seawater (Genç et al., 2003). Bauxite residue is a promising adsorbent for the removal of trace elements from water,

and/or wastewater. It is often utilized as amendment in contaminated soils to immobilize trace elements (Lombi et al., 2002; Santona et al., 2006; Wang et al., 2008). Modelling the adsorption mechanisms has been made in a few works. The reactivity of the surface has been modelled assuming a single homogeneous surface for the sake of simplicity (Genç-Fuhrman et al., 2004; Güçlü and Apak, 2003, 2000) with one amphoteric site >S-OH following a 2-pK approach. A non-electrostatic model has been chosen to fit heavy metal complex-bound EDTA adsorption on red mud (Güçlü and Apak, 2003, 2000). On Bauxsol, a Diffuse Layer Model has been used to fit As(V) adsorption (Genç-Fuhrman et al., 2004). Even though the complexity of the mixture composing the bauxite residues makes difficult to characterize and describe separately the reactivity of every surface, the simplicity of the published approach can be questionable. Thus, four adsorption constants for As(V) have been used in the model (Genç-Fuhrman et al., 2004), correlated to four different surface complexes ($>SH_2AsO_4$, $>SHAsO_4^-$, $>SAsO_4^{2-}$, $>SOHAsO_4^{3-}$) to fit the experimental data. Another interpretation could be to consider a smaller number of arsenate geometries but several different surface sites, connected to different mineral surfaces, as usually assumed in the modelling of mixtures (Lützenkirchen and Behra, 1997). Moreover, the predictive capacity of these works (Genç-Fuhrman et al., 2004; Güçlü and Apak, 2003, 2000) has not be shown, since their objective was to fit experimental sorption data. However, building surface complexation models has two purposes: (1) a speciation purpose where possible structures of surface complexes were tested, and (2) an application purpose where surface complexation constant can be used in a reactive transport model.

In the present work, two bauxite residues (bauxaline® and bauxsol) were investigated for their sorption potential of As(V) and Cd(II) and for their possible use as immobilizing agent for inorganic pollutants in sediments. Moreover, modeling of these inorganic pollutants sorption on bauxite residues was performed using a surface complexation model based on the mixture of the most reactive phases, with the aim of evaluating the predictive possibilities of such model using data from literature for individual phases.

2. Experimental

2.1. Bauxaline and Bauxsol

Bauxaline® and Bauxsol were provided by ALTEO Gardanne plant, (France) that supplies specialty alumina. The pH and electrical conductivity (EC) values of Bauxaline® and Bauxsol were measured in suspension of (100g/L) using pH (Consort bvba, Belgium) and electrical conductivity meter (Crison, Barcelona, Spain) respectively. ISO standard BET method was used to determine the specific surface area (ISO 9277, 2010). Hexamminecobalt trichloride solution was used to determine the cation exchange capacity (CEC) of solids (ISO23470, 2007). Properties of adsorbent materials are presented in Table 1.

Table 1. Properties of adsorbents

	Bauxaline®	Bauxsol
Suspension pH [a]	10.60	9.40
Electrical conductivity (mS/cm) [a]	0.915	1.187
Cation exchange capacity (meq/100g) [a]	6.18	4.15
Specific surface area$_{(BET)}$ (m^2/g) [a]	23.06	31.1
Isoelectric point [b]	6.9	6.9

[a](Taneez et al., 2015), [b]*this study*

2.2. Sorption experiments

All the chemical used in adsorption experiments were of analytical grade. Adsorption experiments were carried out according to the US EPA protocol based on batch type adsorption tests (EPA, 1991). Influence of liquid to solid ratio, pH and initial adsorbate concentrations was studied. Stock solutions of As(V) and Cd(II) (1 g/L) were prepared using $AsHNa_2O_4.7H_2O$ (Fluka ≥ 98.5%), $Cd(NO_3)_2.4H_2O$ (Sigma-Aldrich, ≥ 99%) in Milli-Q pure water (Milli-Q Academic A10, France). The solutions were acidified with 1% HNO_3 (Fluka, ≥ 69.0%) to avoid precipitation or complexation of metal ions. For sorption experiments dilute solutions were prepared from these stock solutions. The experiments were conducted at room temperature in polypropylene tubes (50 ml) with different mass to liquid ratio ranging from 10 mg to 200 mg in 40 ml of solutions containing desired concentrations of Cd (II) or As (V) at constant ionic strength (0.01 M) of $NaNO_3$ (Acros Organics, ≥ 99%) and fixed neutral pH (6.9-7.0 ± 0.1). pH of the

suspensions were adjusted in experiments (between pH 2 to 10) by adding 1M HNO_3 or 1M NaOH solutions. The suspensions were agitated on rotator at 50 rpm for 24 h, and then centrifuged at 5000 rpm for 10 min; supernatants were separated using 0.45 µm cellulose acetate filters. Before measuring final concentrations of Cd (II) and As (V) on ICP-OES (Optima 7300, Perkin Elmer corporation, Massachusetts, USA), filtrate solutions were acidified (1%) with HNO_3. Furthermore, the sorption of Cd (II) and As (V) as a function of contact time, pH (between 2 to 10) and different initial concentrations on both solids was studied.

2.3.Modelling procedure

The software ECOSAT 4.9 (Keizer and Van Riemsdijk W.H., 2009) has been used, with thermodynamic database for aqueous species and minerals. Details about modelling procedure are given in the Results and Discussion part.

2.4.Characterization of solids

Bauxaline® and bauxsol have been characterized to determine their composition. Several analyses have been made: loss on ignition, element analysis by Inductive coupled plasma – Optical emission spectrometry (ICP-OES) end X-ray diffraction.

3. Results and discussion

3.1. Determination of a reference composition

The first step of the modelling was to determine a reference composition of the mixture of solids composing bauxaline® and bauxsol. From XRD, the main phases have been selected (Table 2). From the elemental composition of these phases and the amount of $CO_{2(g)}$ and $H_2O_{(g)}$ released during the ignition, the composition of the mixture has been determined. The values given in Table 2 have been fitted to lead to the smallest difference with element analysis (to – 1.3% for Ca to +9% for Si) and loss on ignition (difference of -9.5% with measured value). Some details about this calculation have been given in Supporting Information part.

Table 2. Composition of Bauxaline® from analysis results

Phase	Solid type	g/g Bauxaline®
Hematite	Oxide	0.31
Goethite	Hydroxide	0.088
Boehmite	Oxide	0.016
Gibbsite	Hydroxide	0.089
Rutile	Oxide	0.081
Calcite	Carbonate	0.028
Quartz	Oxide	0.0078
$Ca_3AlFe(SiO_4)(OH)_8$	Zeolite	0.052
$Na_2O.Al_2O_3.1.68SiO_2:1.73H_2O$	Zeolite	0.14

The second step was to select the solids whose surface reactivity is predominant. First, the zeolites are not expected to present a high affinity for cadmium ions in presence of high concentrations of other cations. Calcite presents an affinity for several anions and oxyanions, but it has not been considered in the modelling for several reasons: (1) its specific surface area is usually lower than those of metal (hydr)oxides, (2) the incorporation mechanism is slower than surface complexation, (3) the modelling of surface complexation is more complex than those of metal (hydr)oxides and its predictive capacity is lower. High amounts of M (III) (with M = Al or Fe) oxides, oxy-hydroxides and hydroxides are present. The huge reactivity of the surface of these phases toward As(V) and Cd(II) has been shown in dozens of articles (see for example published reviews (Giles et al., 2011; Liu et al., 2014)). More interesting for our work, is that the surface properties of M_2O_3, MOOH and $M(OH)_3$ are close, as isoelectric point. Thus, median values of published data were found to be 8.5, 8.9, 8.9 for Al_2O_3, AlOOH, $Al(OH)_3$ respectively, and 8.2, 8.4, 8 for Fe_2O_3, FeOOH and hydrous ferric oxide, respectively (Kosmulski, 2001). For this observation, to simplify the description of the surfaces, M_2O_3, MOOH and $M(OH)_3$ have been merged into goethite for Fe, and gibbsite for Al. Finally, the last phases present in low amount, i.e. rutile (10%) and quartz (1%) have been excluded from reactive surfaces. Thus, this selection would lead to the same composition for both approaches to calculate the composition, i.e. 0.398 g goethite + 0.105 g gibbsite / g Bauxaline®, since the reactivity of remaining phases (0.497 g) is low enough to be negligible. The other solid

used as a sorbent is bauxsol which is bauxaline® partially neutralized by sea water or brine. No effect on iron and aluminum (hydr)oxides is expected, and the composition of the solid is mainly unchanged (precipitation of small amounts of zeolites is expected). The next step is to use this model mixture to simulate and predict the adsorption of As(V) and Cd(II).

3.2.Modelling

For thermodynamic predications of solution chemistry, precipitation/dissolution reactions, and redox processes, software's using thermodynamic values compiled in databases are become a usual tool for chemists. Despite several works, driven by the necessity to simulate the migration of radioelements in geosphere to the safety assessment of a radioactive waste disposal (see (Lee et al., 2011) and references herein), the same approach remains difficult for sorption reactions. Several reasons can explain this problem (see (Kulik, 2009) for example), but the major ones is the variability of characteristics of the solid for a same phase (surface acidity constants for example) and the variety of models used to determine thermodynamic values from experimental data. This last point means that the compilation of sorption data coming from literature should include a first step where all experimental data are fitted using the same model. Such an effort has been made in two books (Dzombak and Morel, 1990; Karamalidis and Dzombak, 2011), which dealt with hydrous ferric oxide (HFO) and gibbsite, respectively. As described above, our model mixture consists in gibbsite and goethite. Thus, we have used sorption data for gibbsite given in (Karamalidis and Dzombak, 2011). For goethite, it can be assumed that the affinity of surface for As(V) and Cd(II) is close to those of hydrous ferric oxide. This assumption is supported by a work (Dixit and Hering, 2003) showing the very close adsorption constants for As(V) onto goethite and HFO. So, sorption data for HFO was used to mimic goethite reactivity. Characteristics of both solids are listed in Table 3, and adsorption equilibria have been given in Table 4.

Table 3. Characteristics of surfaces

Solide	HFO (Dzombak and Morel, 1990)	Gibbsite (Karamalidis and Dzombak, 2011)
Site density (nm^{-2})	ca. 10	ca. 10
pK_+, pK_- (pzc)	7.29, 8.93 (8.11)	7.17, 11.18 (9.18)
Electrostatics	Double Layer Model	Double Layer Model

Table 4. Adsorption equilibria of As(V) and Cd(II) on ferrihydrite (Dzombak and Morel, 1990) and gibbsite (Karamalidis and Dzombak, 2011).

Adsorption equilibria	pKc
$>FeOH + AsO_4^{3-} + 3\ H^+ = >FeH_2AsO_4$	29.3
$>FeOH + AsO_4^{3-} + 2\ H^+ = >FeHAsO^-$	23.5
$>FeOH + AsO_4^{3-} = >FeOHAsO_4^{3-}$	10.6
$>FeOH + Cd^{2+} = >FeOCd^+ + H^+$	0.47
$>AlOH + AsO_4^{3-} + 3\ H^+ = >AlH_2AsO_4$	26.9
$>AlOH + AsO_4^{3-} + 2\ H^+ = >AlHAsO_4^-$	21.8
$>AlOH + AsO_4^{3-} = >AlOHAsO_4^{3-}$	6.4
$>AlOH + Cd^{2+} = >AlOCd^+ + H^+$	-2.73

To apply this model to bauxaline®, several assumptions have been made; even though some of them will be reconsidered later in this work. First, from the composition of the mixture, no effect of resuspension in solution at different pH is expected (no dissolution/precipitation of reactive phases, no release of ions competing with As(V) and Cd(II)). Second, the specific surface area of solids is assumed to be the same that the mean specific surface area of bauxaline®. Third, the isoelectric point of oxides in bauxaline® is the same that those given in (Dzombak and Morel, 1990; Karamalidis and Dzombak, 2011). Fourth, the presence of carbonate ions (experiments carried out in presence of air) has no effect on the As(V) sorption, as previously observed (Kanematsu et al., 2013).

Using the software Ecosat (Keizer and Van Riemsdijk W.H., 2009), the application of this model has been made to simulate experiments of sorption of As(V) on bauxaline®, with different concentrations in adsorbate and solid, and different pH (Table 5). The values obtained in this case (called model 1) present a deviation for experiments with low solid concentrations. From the simulation, it appears that the density of As(V) is around the maximum usually experimentally found, i.e. 2.5 nm^{-2} for goethite, and 1.6 nm^{-2} for

gibbsite. The fact that the simulated sorbed amount is too low could be explained by an underestimated specific surface area (SSA). Indeed, the SSA for bauxaline was used (10 m^2/g), but in this mixture, some low SSA particles, like quartz and calcite, are present. So, the SSA of goethite and gibbsite is likely to be higher than the mean value. The model has been modified according to this conclusion, and the SSA has been fitted to be closer to measurements. A value of 25 m^2/g has been found to lead to a satisfactory result (model 2), and the order of magnitude of this SSA is consistent with this type of particles.

Table 5. Experimental fraction of As(V) sorbed onto Bauxaline®, along with results of models (model 1: SSA = 10 m^2/g, model 2: SSA = 25 m^2/g).

pH	$[As]_0$ (M)	solid (g/L)	Adsorbed fraction		
			measured	model 1*	model 2
7	1.33E-05	0.125	0.45	**0.16**	0.38
7	1.33E-05	0.25	0.78	**0.31**	0.70
7	1.33E-05	0.625	0.79	0.70	1.00
7	1.33E-05	1.25	0.98	0.99	1.00
7	6.68E-06	1.25	0.98	1.00	1.00
9.74	6.68E-06	1.25	0.40	**0.18**	0.38

* in bold: strong discrepancy with experimental value

The same model has been used to simulate the experiments using Bauxsol.

Table 6. Experimental fraction of As(V) sorbed onto Bauxsol along with results of model 2.

pH	$[As]_0$ (M)	solid (g/L)	Adsorbed fraction	
			measured	model 2
7	1.33E-05	0.125	0.46	0.38
7	1.33E-05	0.25	0.67	0.71
7	1.33E-05	0.625	0.73	1
7	1.33E-05	1.25	0.83	1
7	6.68E-06	1.25	0.96	1
9.47	6.68E-06	1.25	0.69	0.69

Application of model 2 coming from experimental values obtained on bauxaline® to bauxsol leads to values closed to experimental ones. Thus, as expected, the treatment of

bauxaline® by brine appears not to change the surface reactivity of the solids. This result is in line with the absence of any difference of isoelectric point between both solids (Table 1). The other pollutant which has been investigated is cadmium (II). Several experiments to determine the effect of solid concentration, adsorbate concentration and pH have been performed and compared to the simulation (Table 7). The calculations have been made using adsorption constant listed in Table 4. The results of simulation are in good agreement with experiments, with the exception of the amount sorbed at neutral pH high Cd concentration.

Table 7. Experimental fraction of Cd(II) sorbed onto Bauxsol along with results of models (see text for details).

Experiment	pH	$[Cd]_0$ (µM)	solid (g/L)	Adsorbed fraction		
				measured	model 2*	model 3
Low concentration, high pH	9.31	8.90	0.25	0.98	1	1
	9.73	8.90	0.62	1	1	1
	9.77	8.90	1.26	1	1	1
	9.73	8.90	2.5	1	1	1
	9.72	8.90	5	1	1	1
Medium concentration, neutral pH	6.82	52.4	0.14	0.23	0.18	0.18
	7.02	52.4	0.26	0.35	0.36	0.36
	6.97	52.4	0.62	0.68	0.74	0.74
	7.01	52.4	1.26	0.89	0.97	0.97
	7.16	52.4	2.52	0.97	1	1
	7.30	52.4	5.03	0.99	1	1
Isotherm, medium to high concentration	7.63	46.6	1.26	1	1	1
	7.12	88.9	1.3	0.85	0.91	0.91
	7.1	193	1.26	0.63	0.52	0.52
	6.84	292	1.25	0.49	0.34	0.34
	7	530	1.27	0.32	0.21	0.21
High concentration, pH edge	2.34	489	1.25	0.03	0	0
	4.24	489	1.26	0.09	0	0
	6.49	489	1.26	0.19	0.20	0.20
	7.15	489	1.26	0.49	**0.23**	0.49
	9.63	489	1.25	1	0.96	1
	11.93	489	1.29	1	1	1

* in bold: strong discrepancy with experimental value

In Fig. 1A, the sorption amounts due to surface complexation and $Cd(OH)_2$ precipitation have been plotted. The value of solubility product of amorphous $Cd(OH)_2$ has been added

in the model, using database of Medusa software (Puigdomenech, 2010), according to the following equilibria:

$Cd^{2+} = 2\ H^{+} + Cd(OH)_{2,am}$ pKs = 13.7 (1)

A blank experiment has been made to measure the precipitation of Cd^{2+} as a function of pH, and the experimental values are found in good agreement with calculated ones using Eq. 1. (Fig. 2). However, the experimental values found in presence of bauxsol suggest that the precipitation occurs at a lower pH. Such a behavior has been previously observed for the $Ni^{2+}/CoFe_2O_4$ and $Co^{2+}/NiFe_2O_4$(Martin Cabañas et al., 2011), where the formation of a precipitate occurred about 2 pH units lower in presence of solid. Thus, the pKs has been fitted to obtain a better agreement with the experimental value at pH 7.15. Using a pKs of 17.5, the pH edge of sorption is correctly simulated (fig. 1B).

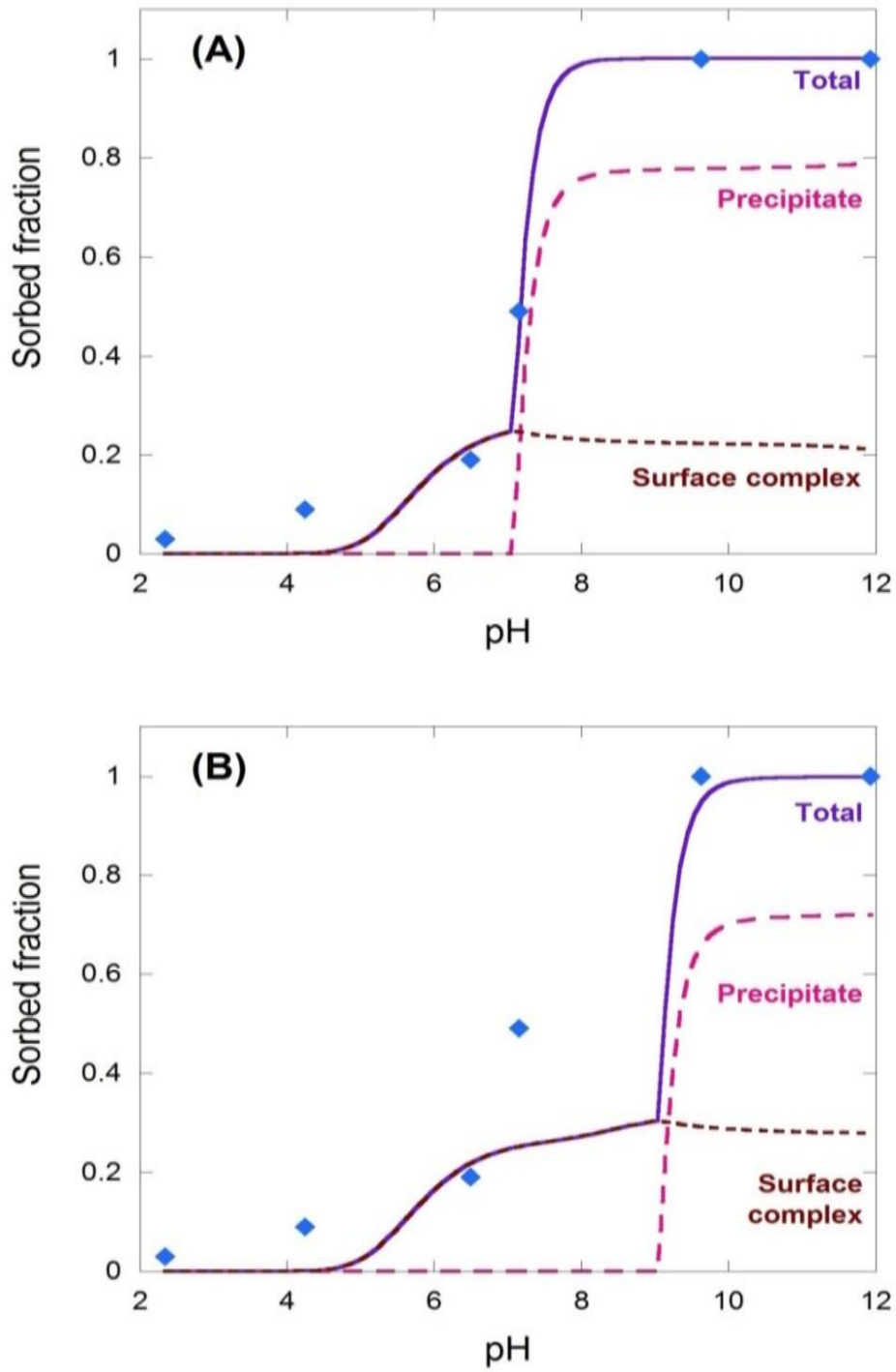

Fig. 1. Experimental data (◆) and simulation (lines) for sorbed Cd(II) onto Bauxsol with different values of pKs ($Cd(OH)_2$): (A) 13.7 (model 2 in the text) and (B) 17.5 (model 3 in the text)

Thus, this first series of experiments has allowed to build a model of reactivity of bauxaline® and bauxsol based mainly on surface complexation parameters of pure

hydroxides present in these complex solids. To evaluate the predictive capacity of this model, a second series of sorption measurements have been made of Cd(II) on these two solids.

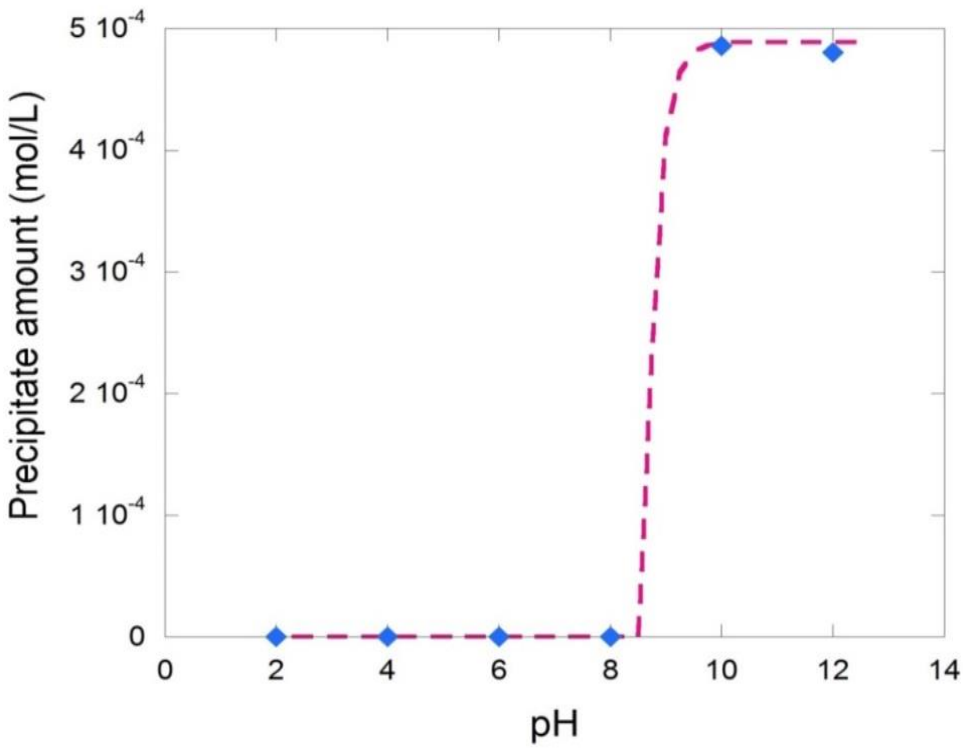

Fig. 2. Experimental data (◆) and simulation for pKs ($Cd(OH)_2$) = 13.7 for solution of Cd(II) without sorbent (---)

The first measurements consisted in evaluating the sorption when only surface complexation is expected, i.e., using a high solid concentration (Fig. 3A). The sorption edge is well predicted by model, with the exception of high pH values. The sorbed fractions measured on both solids are the same, showing that their surface reactivity is very close. The other experiment consisted in a pH edge with a low solid concentration (Fig. 3B). The predictions of models 2 and 3 are shown. Up to pH 8, in the range corresponding to a surface complex, the measurements are the same for both solids, and the model prediction is correct. Above this value, a higher sorbed fraction is obtained for Bauxaline,

but the experimental values remained below the predicted values. For Bauxsol, the sorbed fraction is closer to the model 2, i.e. with the solubility product of pure $Cd(OH)_{2(s)}$.

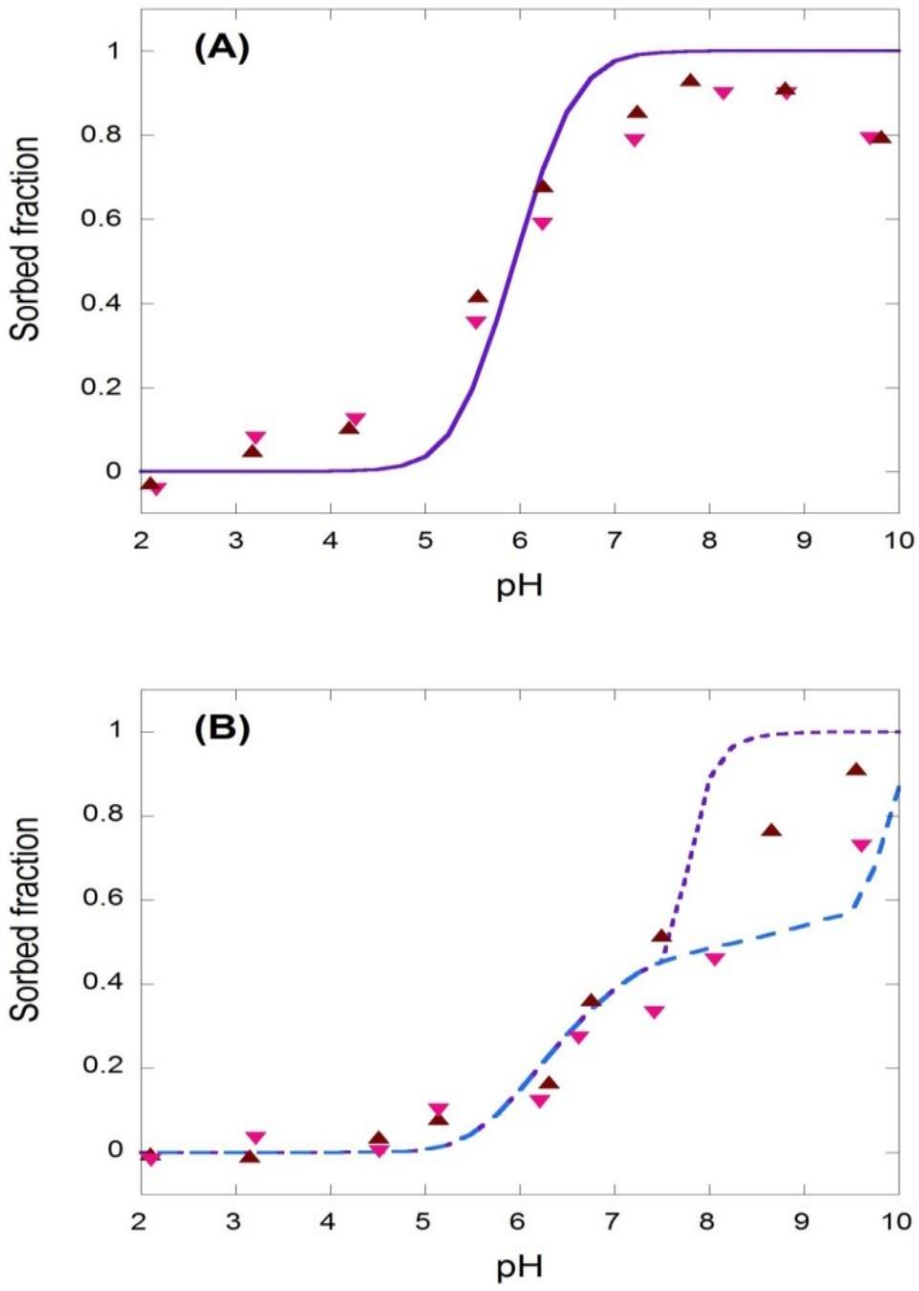

Fig. 3. pH-edges on Bauxsol (▼) and Bauxaline® (▲) for Cd(II) from initial concentration of 45µM (A) 1.26 g/L and (B) 0.26 g/L solid. Lines correspond to model 3 (⋯) and model 2 (---).

This behavior is consistent with the high sensitivity of homogeneous/heterogeneous precipitation processes. Depending on supersaturation ratio, solids amount and surfaces type, cations could precipitate in solution or form surface precipitates whose stability constant is not well-defined. Thus, simulations based on models 2 and 3 lead to an envelope of experimental results in the pH-range where this phenomena occurs. However, several parameters define this precipitation range, and it can be avoided for high solid concentration, low cadmium concentration, low pH, or a combination of these parameters.

4. Conclusion

Modelling sorption of As(V) and Cd(II) on mixtures of solids as bauxaline® and bauxsol have been performed using a predictive approach based on data of pure phases. Chemical analyses of the solid and thermodynamical calculations have allowed to determine the composition of the Bauxaline mixture. Based on the assumption of a reactivity coming from the oxides phases of iron and aluminum, a first additive model has been built. The comparison with experimental values of arsenate adsorption has shown that two parameters should be indirectly estimated, the surface specific area and the isoelectric point. Using As(V) as a probe, the values of these two parameters have been fitted based on experimental sorption values. This first model has been found to be consistent with Cd(II) sorption for a set of chemical parameters (pH, Cd concentration, solid concentration) where surface precipitation is excluded. For conditions where precipitation is likely to occur, the behavior of Cd(II) itself appears to be variable and experiments and simulations led to two extreme possibilities: either a bulk $Cd(OH)_{2(s)}$ precipitation along with the formation of a surface complex, or the formation of a surface precipitate characterized by a low solubility. This work has shown the possibility to apply a surface complexation model to bauxite residues, more realistic than the assumption of a homogeneous surface reactivity. This model is able to simulate and predict the adsorption of pollutant species on bauxite residues, and could be extended to modelling of adsorption to complex mixtures of minerals.

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Adsorption of inorganic pollutants on bauxite residues: toward a methodology to simulate adsorption in complex solid mixtures

Supporting information

1. Calculation of bauxaline composition from XRD analysis

XRD analysis of bauxaline has shown the main crystalline phases. Some traces of portlandite have been seen, but the amount was low enough to neglect it, allowing simplifying the system. Table 1 presents the stoichiometry of each phase, and the mass of CO_2/H_2O lost when oxide is formed on ignition. Calculating the composition consists in solving a system of several equations with 9 unknowns (mass of each phase given in last column of the table). It can be seen that rutile, SASH and calcite are the only phases for a given element (Ti, Na and C, respectively), so their amounts is directly obtained. The remaining 6 unknowns have been determined using 5 equations from elemental analysis and LOI using Excel solver, with the constraint of positive values. The obtained results are close to experimental ones with a maximum of 9.5% between experimental and calculated values (for LOI).

		Stoichiometry								
Solid*	Molar mass (g/mol)	Fe	Al	Ti	Si	Ca	Na	C	LOI (g/mol)	Calculated amount (mmol/g bauxaline)
Hematite	159.6	2								1.94
Boehmite	60		1						9	0.27
Quartz	60.1				1					0.13
Calcite	100.1					1		1	44	0.28
Rutile	79.9			1						1.0
Gibbsite	81		1						27	1.1
Goethite	88.8	1							9	1.0
CAISH	431.2	2	1		1	3			72	0.12
SASH	296.108		2		1.68		2		31.14	0.5
Measured**		4.99	2.31	1.01	0.98	0.643	0.97	0.28	0.085	
Calculated		4.99	2.46	1.01	1.07	0.635	0.97	0.28	0.077	
Error		0.1%	6.6%	0%	9.0%	-1.3%	0%	0%	-9.5%	

* CAISH: Calcium aluminium iron silicate hydroxide. SASH: sodium aluminium silicate hydrate. ** elemental analysis results (mmol/g bauxaline) or LOI (g/g bauxaline)

3. Testing of bauxite residues as amendment for trace elements stabilization in marine dredged sediments in outdoor experiments

The preliminary determination of adsorptive potential of bauxite residues (bauxaline® and bauxsol) towards toxic elements (As and Cd) suggests that both solids can be low cost adsorbent for the removal of toxic pollutants from aqueous phase (article 1).Favorable removal of As and Cd was attained in the neutral pH range. Based on these initial results, bauxite residues were used for stabilization of multi-contaminated marine dredged sediment collected from Toulon Navy harbor area. In this study, two sub-samples of sediment after composting were used and the concentrations of contaminants were compared to French regulatory levels (N1 and N2) for dredged sediments.

The total content of trace elements after mineralization of sediment sub-samples is presented in table 9. The concentrations of As, Cd, Cu and Zn were greater than the permissible level N2 suggesting that this kind of sediment cannot be immersed back into the sea and it should be managed on land. Direct land disposal of such kind of sediment poses risk to environment due to possible leaching of contaminants. The calculated Geode risk scores for the two sub-sediment samples were 2.6 and 2.4 respectively meaning that the sediment samples require further treatment to limit the leaching of contaminants prior to dumping (Alzieu and Quiniou, 2001). The difference in total trace element concentrations indicates the heterogeneity of sediment sample. It was previously reported that the concentration of Cd can vary10-fold in sediments when collected at 100 m intervals (Alary and Demougeot-Renard, 2010). Similarly, data variability remained high despite care has been taken in homogenizing dredged sediment before land disposal and at each sampling time (Piou et al., 2009).

Table 9. Trace elements present in two sub-sediment samples

Elements (mg/kg)	1st sub-sediment sample	2nd sub-sediment sample	French Regulatory levels	
			N1	N2
As	150	201	25	50
Cd	4.69	4.8	1.2	2.4
Cu	1721	1880.9	45	90
Mo	9.08	7.4	-	-
Ni	27.36	21	37	74
Zn	1869	3068.5	276	552
Cr	59.11	43	90	180

The first pilot experiment was performed using 1st sub-sediments sample (from March 2013 to June 2013) and the results of the study are present in following article 2. The other sub-sediment sample was used in the 2nd pilot experiment which was conducted from April 2014 to July 2014. The results are present presented in the following articles and chapter.

3.1 Summary of article 2) Ex-situ evaluation of bauxite residues as amendment for trace elements stabilization in dredged sediments from Mediterranean Sea: A case study

3.1.1 Introduction

The Mediterranean Sea is regarded as most polluted sea in the world due to potential human development activities (Iaccino, 2014). The rate of accumulation of contaminants in Mediterranean costal sediments is high due its semi-closed environment low fresh water inputs (Zoumis et al., 2001; Tessier et al., 2011). Sediment management in the Mediterranean Sea is closely related to the need of periodic dredging to ensure sufficient depth for navigation. Thus, the dredged sediment must be evaluated according to French regulatory levels and managed depending upon their level of contamination. Direct land disposal of dredged material increased the risk of pollution to groundwater. Therefore, various sediments treatments are possible but stabilization of multi-contaminated sediments with mineral additives is a promising and alternative technique to the high cost treatments. This process involves mixing sediments with materials (fly ash, cement, minerals or chemicals) aiming to immobilize contaminants in solid matrix (Mulligan et al., 2001). In this context, we evaluated the use of alumina industrial by-product which is composite mixture of minerals phases. In this study sediment sample collected from the Navy port (arsenal of Toulon) was stabilized with mineral based additive such bauxite residue. Two bauxite residues (Bauxaline® and Bauxsol) were mixed to the sediment in order to trap the pollutants and limit their bioavailability. The stabilization experiments were carried out in wooden boxes (see Fig. 1 of article 2) under external conditions for the period of three months. The sediment sample was moistened with tap water and aerated on a weekly basis in order to promote the oxidation of the sediment (see details in article 2). Concentrations of Cd, Cu, Ni, Zn, As, Cr and Mo were monitored and compared with the regulatory levels defined for inert waste for trace elements in liquid to solid ratio of 2L/kg by European Commission. Finally, the leachates were incubated with marine rotifers to assess the toxicity of sediment.

3.1.2 Results and conclusion

The sediment was found to be highly contaminated with As, Cd, Cu and Zn as their total content was higher than N2 permissible limit while the concentration of Ni and Cr was below N1 level. The concentrations of Cu, Cd, Zn, Ni, As, Cr and Mo were measured in leachates over the period of 3 months (see Fig 2 of Article 2). Both amendments (at 5% rate) were found to be effective in immobilizing cationic trace elements, while they remained inefficient in case of As, Cr, and Mo. The pH of sediment matrix remained unchanged after the addition of bauxite residues due to buffering capacity of sediments, which in turn was not suitable for the stabilization of anionic elements. All the trace elements were found to be within regulatory levels at 2 L/kg defined for inert waste except for arsenic. The cumulative release of pollutants (see Fig 2 (h) of Article 2) showed that the amendments reduced overall rate of trace elements leaching less than 1% except for Mo. Nevertheless the 5% amendment rate of Bauxaline® and Bauxsol in the sediment was not sufficient to decrease the toxicity of the leachates within 48 h of contact. Higher rates of amendments should be tested in order to decrease the leachates toxicity by increasing immobilization rate of trace elements, as well as supplementary acute tests to confirm toxicity. The stabilization technique allows durable and inexpensive management of contaminated marine dredged sediments.

3.2 Article 2: Ex-situ evaluation of bauxite residues as amendment for trace elements stabilization in dredged sediments from Mediterranean Sea: A case study

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Ex-situ evaluation of bauxite residues as amendment for trace elements stabilization in dredged sediment from Mediterranean Sea: A case study

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ABSTRACT

Stabilization of marine dredged sediments contaminated with multi-elements is a challenging task in choosing the appropriate sorbent and application dosage. The present study investigates the possibility of using bauxite residues (Bauxaline® and Bauxsol) as amendment for the treatment of contaminated sediment. A pilot scale experiment was conducted for three months to stabilize trace elements in composted contaminated sediment sample using 5% by-product amendment. The results showed that after 3 months of treatment, cationic trace elements were effectively immobilized but increased leaching of anionic pollutants was observed. Increased leaching of anionic pollutants could be limited by addition of higher quantities of amendments. The total content of available pollutants decreased in stabilized sediments but this treatment has no effect on the classification of waste. The leachates were then evaluated for acute toxicity using estuarine rotifers *Brachionus plicatilis*. Bauxite residues can be inexpensive choices for the stabilization of cationic pollutants in dredged sediments.

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1. Introduction

Sediments polluted by heavy metals and organic compounds are a worldwide problem since sediments serve as a sink for various pollutants (Förstner, 1989). Anthropogenic and natural events disrupt the natural equilibrium between sediment and water, leading to the remobilization of chemicals from the sediment (Eggleton and Thomas, 2004). The regular dredging of ports is necessary to maintain maritime navigation. Approximately 600 million m^3 (Boutin, 1999) of sediments in the world and 50 million m^3 in France (Alzieu et al., 1999) are dredged out annually from the main maritime and commercial ports. The management of the dredged materials complies with the international OSPAR convention (1992) for the protection of marine natural environments of North-East Atlantic and, the World London Convention (1972) on the prevention of marine pollution as a result of dumping waste. Thus in France, sediment quality guidelines (named N1 and N2) were fixed concerning the total concentrations of trace elements in the fine fraction of sediments (inferior to 2 mm). If the level of contaminants in whole sediment is below N1, it is assumed that the ecological impact is negligible, and the sediment can be immersed back into the sea. Assessment of toxicity is required along with chemical analyses if the concentrations of pollutants are between N1 and N2 levels. These dredged sediments cannot be dumped back into the sea due to their high levels of contamination. If at least the concentration of one contaminant in sediments is superior to N2 threshold, sediments are considered as waste and it is assumed that the ecological impact can be significant (Alzieu, 2005). Then sediments must be considered according to the levels defined by the European council for inert waste before landfill. These leaching limit values were defined for chemical compounds (e.g. As, Cd, Cu, Cr, Ni, Zn, Mo) to help the authorities for solid waste management (European Council, 2002). These levels were defined according to the concentration of trace elements measured in the liquid fraction, after leaching experiment according to the AFNOR protocol (AFNOR XP X 31-210, 1998). When the chemical concentrations are below the regulatory levels, the solid waste is considered as acceptable for landfill. Depending on the contamination level of sediments, their management can be only submitted to the guidelines defined for sediments or be submitted to both the sediment quality guidelines and the European council standards for solid inert waste. For highly polluted sediments, stabilization or treatment is necessary before storage in a solid waste disposal site (Alzieu et al., 1999). Thus, the management of polluted sediments on land is a significant issue due to the elevated concentrations of anionic and cationic pollutants in a large volume of dredged sediments.

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In the recent years several technologies have been used for ex-situ treatment of polluted marine sediments. Therefore, the management practices are site-specific (Bortone et al., 2004). Ex-situ treatment techniques are usually applied for heavily polluted sediments. Treatment methods used for dredged sediments are similar to the ones used for contaminated soils but due to the differences between matrixes, treatment efficiency can vary. Remedial techniques applied for excavated or dredged sediments include dewatering, particle separation, washing, vitrification and solidification/stabilization (Miller and Orbock Miller, 2007). Stabilization involving extraction, thermal treatments, co-precipitation of pollutants with chemical reagents has shown to be quite efficient especially for cationic trace metals. Novosol process by Solvay Company uses a combined chemical-thermal treatment. Firstly sediment is treated with phosphoric acid (2–3.5%) to precipitate pollutant as phosphate complexes and secondly sediment is calcinated to degrade organic compounds. Even if this technique has shown to be very efficient for stabilization of cationic pollutants, an increased leaching of anionic trace elements (As, Mo, Cr) was highlighted and field application reveal to be hugely expensive considering the large quantity of sediments to be treated (Seaman et al., 2001; Zoubeir et al., 2007). In this context cost effective stabilization of contaminants in sediments is a challenging task and the use of mineral based amendments could be a promising choice to decrease metal leaching and availability in polluted sediments due to their high cation exchange capacity and low cost (Peng et al., 2009). Mineral amendment has been largely studied for soil remediation to stabilize heavy metals (Lombi et al., 2002; Guo et al., 2006). These additives amplify the rate of stabilization by enhancing adsorption, precipitation and complexation reactions onto sediments components (Peng et al., 2009). The most studied mineral based amendments include alumina-silicates (clays, zeolites), iron-bearing compounds (zero-valent iron, goethite, hematite, ferrihydrite) (Mamindy-Pajany et al., 2013), and phosphate compounds such as apatite (Guo et al., 2006; Kumpiene et al., 2008).

Bauxite residue (commonly known as red mud) is the alkaline (pH10–13) by-product generated during caustic digestion of bauxite for aluminium production. The major components of the bauxite by-products are iron and aluminium oxides. These by-products have been shown to have a great potential to remove pollutants (arsenic, cadmium, copper, lead and phosphates) from various environmental media (water, wastewater, acid mine drainage, soil, sediments) (Summers et al., 1993; Apak et al., 1998; Müller and Pluquet, 1998; Doye and Duchesne, 2003; Genç-Fuhrman et al., 2004; Gray et al., 2006; Huang et al., 2008; Nadaroglu et al., 2010). In the current research, we tested the use of bauxite residues (Bauxaline® and Bauxsol) as low cost additives to limit the leaching of contaminants from composted navy harbor sediment in a landfill storage context. For that, we monitored organic content, pH, electrical conductivity, and the concentration of chemicals leached from (i) the sediment and (ii) the amended sediment with Bauxaline® and Bauxsol for 3 months in a pilot scale device. To evaluate the toxicity of the leachates collected from the pilot scale experiment, we chose as test organism a marine rotifer (*Brachionus plicatilis*) able to survive in a large range of salinity (5–35 ppt). Indeed, salinity variation due to successive leaching should not influence significantly survival of the organisms (Snell and Persoone, 1989).

2. Materials and methods

2.1. Sediment and bauxite residue samples

The sample is polluted sediment from the French Mediterranean coast collected by using a Shipek grab during a dredging mission performed by the harbor authorities. It was collected in a marine area between Marseilles and Cannes cities (SE of France) with high military activities and French Navy vessels navigation. After dredging, the sediment was stored in a specific area devoted to dredged sediments management, and actively composted by port authorities during 4 months. This composting procedure consists in humidification with tap water and mixing of the sediment once per week, to promote microbial degradation, lower salt and organic matter content. After composting, the sample was ready for pilot experiments. Sub samples of sediment were collected and brought back to the laboratory for pilot scale experiments. Bauxaline® and Bauxsol (sea water neutralized Bauxaline®) were provided by an international company ALTEO Gardanne plant, (France) that supplies specialty alumina.

The pH of the sediment, Bauxaline®, and Bauxsol suspensions (100 g/L) were measured by a pH meter (Consort bvba, Belgium), equipped with a combined pH electrode, calibrated using buffer solutions at pH 4.00, 7.01 and 10.00 at room temperature. Electrical conductivity values were determined in suspensions (100 g/L) with (EC) meter (Crison, Barcelona, Spain). Specific surface areas were determined by using the international standard method (ISO 9277, 2010 (E)). Cation exchange capacities of solids were measured by hexaminecobalttrichloride according to the international standard method (ISO 23470, 2007). AFNOR protocol (AFNOR NF ISO 14235, 1998) based on sulfochromic oxidation was used to determine organic carbon in the solid phases. Dissolved organic carbon was measured in leachates using total organic carbon analyzer (TOC-V_{CPH} Shimadzu Corporation, Kyoto, Japan). Total inorganic pollutants (As, Cd, Cu, Mo, Ni, Cr, and Zn) were determined by ICP-OES (Optima 7300, Perkin Elmer corporation, Massachusetts, USA). Before ICP-OES analysis, sediment, Bauxaline®, and Bauxsol samples were digested according to USEPA method 3050B using hot plate (DigiPREP HT, SCP Science, Quebec, Canada).

2.2. Experimental design and treatments

The experiment was conducted for a period of three months (from March 2013 to June 2013) to monitor the leaching behavior of trace elements. Three boxes of equal size (40 × 40 × 20 cm), each containing 6 kg of sediment were used. Bauxaline® and Bauxsol were applied as mineral amendments at the rate of 5% (i.e. 300 g for 6 kg of sediment). Each box contained a square plastic mesh at the bottom to allow leachates collection. The inner surfaces of the vats were covered with geotextile to limit the loss of fine particles. Three treatments were prepared: (1) untreated sediment (as control), (2) Sediment + 5% Bauxaline®, (3) Sediment + 5% Bauxsol as shown in (Fig. 1).

Two liters of tap water was poured on top of each box in the following steps. (1) 1 L of tap water was sprayed homogeneously, (2) using garden shovel, materials were aerated manually, and (3) 1 L of tap water was sprayed again onto materials. Leachates were then collected in plastic containers placed under each box after 1 h drainage through the materials. During 3 months experiment, leachates were collected 3 and 2 times in the first and second week respectively. Afterwards, this draining and mixing was repeated weekly.

Trace elements concentrations were measured in filtered leachates (0.45 μm membrane filter) after acidification at 1% with HNO_3 (65%). pH, organic content and electrical conductivity were also monitored in leachates.

2.3. Toxicity test

Toxicity test was performed on leachates collected during three months experiment against marine rotifer (*B. plicatilis*). Leachates

Fig. 1. Experimental setup.

were obtained after tap water pouring above the marine sediments. This provokes a decrease of salinity as far as tap water is added, but salinity did not reach values under 5 ppt during the experiment. In order to be able to account for the decrease of salinity, *B. plicatilis* rotifers were used due to their tolerance up to 5 ppt salinity. Rotoxkits were purchased from microbiotest Inc., Belgium. Rotifer cysts were incubated for 28 h in standard seawater of reduced salinity (20 ppt) at 25 °C under continuous illumination of 3000–4000 lux. The new born rotifers were collected within 2 h after hatching and transferred to multiwell test plate containing the leachates. 5 rotifers were transferred in each well. The test plates were incubated at 25 °C in darkness and after 24 and 48 h, number of dead rotifers in each well was determined. For the rotifers test to be valid, control mortality (as is the rule in aquatic toxicity tests) must not exceed 10%. Potassium dichromate was used as reference toxicant in this test.

3. Results and discussions

3.1. Sample characterization

The physico-chemical parameters concerning the studied materials and the French regulatory levels from sediments quality guidelines (N1 and N2) are presented in Table 1.

The sediment has a pH and EC which are near to sea water pH and EC. The pH of Bauxaline® suspension is highly alkaline due to the chemical process used for alumina extraction from bauxite. On the other hand, Bauxsol is sea water neutralized Bauxaline®, with a lower pH. Electrical conductivity of Bauxaline® and Bauxsol are low, the EC of Bauxsol being slightly superior to Bauxaline® due to neutralization.

Bauxsol has higher surface area (31.1 m^2/g) than Bauxaline® (23.06 m^2/g) due to lower pH and neutralization effect. CEC of dredged sediment, Bauxaline® and Bauxsol are 10.53 6.18 and 4.15 (meq/100 g) respectively. The total organic matter measured in the solid phase of sediment sample was 66.17 g/kg. Just after dredging the organic matter content was 102 g/kg (Mamindy-Pajany et al., 2010). The organic matter from the solid phase decreased significantly during composting before pilot scale experiments.

To evaluate the quality of dredged sediment sample, the total concentrations for As, Cd, Cu, Mo, Ni, Zn and Cr in the whole sediment were measured. These concentrations were compared to N1 and N2 regulatory levels defined for sediments (Table 1). Trace elements concentrations in Bauxaline® and Bauxsol were also measured before mixing with sediment (Table 1). Results showed that sediment has higher concentrations of As, Cu, Cd, and Zn than the permissible maximum level (N2). In Bauxsol and Bauxaline® total concentration of trace elements are below N1 level except for chromium concentration, which is higher than the recommended N2 level. The risk score of the sediment sample was computed using GEODRISK software (Alzieu and Quiniou, 2001), the score result is higher than 2, meaning that this kind of sediment cannot be immersed back into the sea and must be considered as a waste. Table 2 presents the regulatory levels defined for inert waste by European council for trace elements concentrations at liquid/solid ratio of 2 L/kg. According to leachate concentrations, only As concentration in the raw sediment is higher than the regulatory levels. According to the sediment quality guidelines, the sediment sample is highly polluted with As, Cu, Cd, Zn, its immersion into the sea is prohibited and it has to be considered as a waste and submitted to European council regulation for waste. Pilot scale experiments were then carried out considering Bauxsol and Bauxaline® as mineral additives able to limit the leaching of trace elements.

3.2. Pilot scale experiment

Sediment treatment with Bauxaline® and Bauxsol resulted in decrease of electrical conductivity from 42 ± 3 mS/cm to 12 ± 3 mS/cm during the first 20 days. After 20 days, the electrical conductivity remained stable around 12 ± 3 mS/cm. Thus, repeated leaching resulted in lowering of EC values to acceptable limits for land fill. No significant change was noticed for the pH value for Bauxaline® and Bauxsol treated sediment. The pH values remained constant around 8.0 ± 0.2 throughout the experiment. Bauxaline® and Bauxsol being alkaline solids and the buffering capacity of the sediment due to its high carbonate content are responsible of the pH stability during the experiment duration. Fig. 2 presents Cu, Cd, Zn, Ni, Mo, As, and Cr concentrations in the leachates during the experiment. For all the elements, we observed a rapid increase of metal released during the first 20 days, which is linked to the rapid decrease of EC value during the same period of time. During the 20 first days of experiment, the labile fraction of the elements is leached. Amendments with Bauxaline® and Bauxsol significantly decrease the rate of cationic metals mobilization (Cu, Cd, Zn, Ni), in comparison with the control sediment. Bauxaline® addition reduced the bioavailability of metallic species at the following rate: for Cu (9%), Cd (35%), Zn (26%), Ni (10%), Mo (5.6%). Similar behavior of leaching was observed in case of 5% Bauxsol for Cu (27%), Cd (35%), Zn (24.6%) and Ni (8%). Bauxite residue treatment of contaminated soil resulted in an increase of soil pH, decreased metal concentration (Cd, Cu, Pb, Zn) in soil pore water and promoted growth of metal tolerant grass (Gray et al., 2006).

On the other hand, As and Mo mobility is increased in both treatments in comparison with the control sediment. The pH of the materials remained stable around 8.0 ± 0.2. At this pH value, adsorption of cationic species on bauxite residue (made up of iron oxides) is favored (Apak et al., 1998; Nadaroglu et al., 2010), while adsorption of anionic species such as As-Mo is favored on acidic pH value (Goldberg et al., 1996; Genç et al., 2003). Cr release was higher after Bauxaline® and Bauxsol amendment. Indeed, total Cr

Table 1
Physicochemical properties of sediment and bauxite residue samples.

Parameters	Units	Sediment	Bauxaline®	Bauxsol	N1	N2
pH		8.18 ± 0.01	10.60 ± 0.02	9.40 ± 0.02		
Water content	(%)	15.6				
EC	(mS/cm)	7.44	0.915	1.187		
CEC	(meq/100 g)	10.53 ± 0.08	6.18 ± 0.09	4.15 ± 0.12		
Specific surface area	(m^2/g)	3.5	23.06 ± 0.15	31.1 ± 0.2		
Fine particles (a < 63 μm, b < 80 μm)	(%)	21.8[a]	90[b]	90[b]		
Total organic carbon	(g/kg)	66.17	<DL	<DL		
Chloride	(mg/kg)	11,750	–	–		
Al_2O_3	(%)	–	14	14		
Fe_2O_3	(%)	–	50	50		
TiO_2	(%)	–	11.5	11.5		
SiO_2	(%)	–	6	6		
CaO	(%)	–	5.5	5.5		
Na_2O	(%)	–	3.5	3.5		
As	(mg/kg)	150 ± 3.2	<DL	<DL	25	50
Cd	(mg/kg)	4.69 ± 0.12	0.689 ± 0.3	0.582 ± 0.18	1.2	2.4
Cu	(mg/kg)	1721 ± 42	20.23 ± 4	14.4 ± 2.4	45	90
Mo	(mg/kg)	9.08 ± 0.22	<DL	<DL	–	–
Ni	(mg/kg)	27.36 ± 0.63	7 ± 0.11	7.15 ± 0.13	37	74
Zn	(mg/kg)	1869 ± 49	13.04 ± 3.7	7.03 ± 0.86	276	552
Cr	(mg/kg)	59.11 ± 2.15	1864 ± 25	1579 ± 6.2	90	180

Table 2
Comparison of trace elements concentrations (As, Cd, Cu, Mo, Ni, and Zn) measured in leachates from sediment samples with regulatory levels defined for inert waste at liquid to solid ratio of 2 L/kg.

	Regulatory level	Units	Raw sediment	5% Bauxaline®	5% Bauxsol
As	100	μg/kg	133	149	143
Cd	30	μg/kg	15.69	10.08	8.64
Cu	900	μg/kg	736	788	534
Mo	300	μg/kg	225	269	262
Ni	200	μg/kg	11.5	9.65	9.86
Cr	200	μg/kg	29.37	34.7	39.7
Zn	2000	μg/kg	546	374	385

in Bauxaline® and Bauxsol were found to be equal to 1864 ± 25 mg/kg and 1579 ± 6.2 mg/kg respectively (Table 1), while Cr found in the sediment sample (59.11 ± 2.15 mg/kg) was below the N1 regulatory level. In pilot scale experiments, an increased leaching rate of Cr was observed when 5% of Bauxaline® and 5% of Bauxsol were added to sediment. Considering the Cr concentrations found in bauxite residues (Table 1), the Cr amounts measured in the leachates during the pilot experiments are due to leaching from Bauxaline® and Bauxsol. Nevertheless, XPS analyses data (not shown) depicted that Bauxaline® and Bauxsol samples contained Cr (III) which is much less toxic than Cr(VI). Despite the increased mobility of Cr from stabilized sediment, the Cr concentrations measured in leachates remained below the regulatory level for inert waste (Table 2).

Compared with the total concentrations of trace elements in the sediment sample, the leached amount is low meaning that the bioavailable fraction of trace elements is low. After 3 months of treatment, the total concentrations of leached elements were calculated (Fig. 2h). From this figure, it clearly appears that amendment of sediment with bauxite residues reduced the total leaching of pollutants. The rates of trace elements mobilization as compared to their total concentrations in the dredged sediment sample (Table 1) were as follows: As (0.2%), Cd (0.6%), Cu (0.14%), Mo (9.5%), Ni (0.1%), Zn (0.04%) and Cr (0.01%). For As, Cd, Cu, Ni, Zn and Cr, the leaching rate remained inferior to 1% of the total concentration except for Mo. The rates of metal mobilization were of the same order of magnitude; Cd (0.37%), Cu (0.1%), Ni (0.08%), Zn (0.03%) in case of stabilized sediment with 5% Bauxaline® and Bauxsol whereas in case of As and Mo, no change in rate of mobilization was observed. Higher rates of Mo leaching were also observed during the management of multi-contaminated sediments in previous studies. It was observed that Mo was transformed into water soluble forms after air drying (Fox and Doner, 2002; Mamindy-Pajany et al., 2013). Humidification of dredged sediment leads to release of amplified amount of Mo during the experiment.

Dissolved organic carbon measured in the collected leachates varied from 115 mg/L to 131 mg/L from the beginning to the end of the pilot scale experiments respectively. In comparison with the organic matter found in the solid phase of the sediment it corresponds to a very low leaching rate of 0.03%. Considering the literature data (Peng et al., 2009) and the leaching rate of Cd, Cu, Ni and Zn it is obvious that these elements are strongly bound to organic matter (OM) in the sediment. Leaching rates of As and Mo were higher compared to control sediment. Due to their low affinity with organic matter we can expect that leaching experiments resulted in higher bioavailability of these elements. Dissolved organic matter can compete with As for sorption sites and displace both As(V) and As(III) from iron oxides (Redman et al., 2002).

It has been shown that the larger fraction of metals is usually bound to particulate organic matter from sediments and bioavailability of trace elements depends on solubility of organic matter (Peng et al., 2009). In the present study, the solubility of organic matter was very low compared to its total concentration. The bioavailable fraction of pollutants during the duration of the experiment remained low compared to their total concentrations in whole sediment.

The studied sediment is subjected to European council standards for inert waste (European Council, 2002). Leached trace elements (As, Cd, Cu, Cr, Mo, Ni and Zn) concentrations from control sediment and stabilized sediments are presented in Table 2. The regulatory levels defined for inert waste were also added in Table 2 for L/S (L kg^{-1}) ratio of 2. In the pilot experiment this ratio was achieved during the first 20 days of successive leaching with tap water. The studied sediment sample is highly contaminated with four elements (As, Cd, Cu and Zn), on the basis of sediment

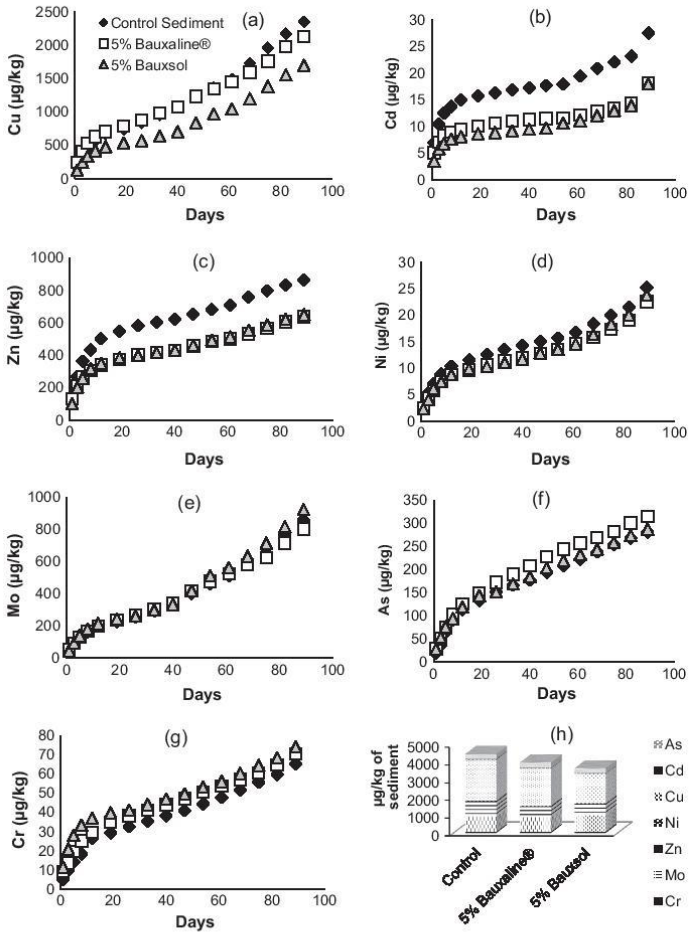

Fig. 2. Amounts of trace elements released from control and stabilized sediments after 3 months for Cu (a), Cd (b), Zn (c), Ni (d), Mo (e), As (f), Cr (g) and total quantities of pollutants released after three months from control and stabilized sediments (h).

quality guidelines, whereas leached concentration of all the trace elements are below the regulatory levels of European council concerning inert waste management except for Arsenic. Mineral amendment with Bauxaline® and Bauxsol can be effective to stabilize waste containing cationic pollutants. Application of amendments at the rate of 5% has no effect on waste classification.

3.3. Toxicity of sediment

Leachates were collected by tap water pouring over the samples during 3 months of experiment. Incubation of leachates with marine rotifers (*B. plicatilis*) was performed for 24–48 h to assess the acute toxicity of leachates. Prior to toxicity experiments, we checked that no osmotic stress was observed on *B. plicatilis* in salinity range from 7.7 ppt to 30.2 ppt (data not shown). As no mortality was observed, the salinity of the leachates was not adjusted before toxicity tests. Rate of mortality in the leachates was compared with rate of mortality in standard seawater (35 ppt) (Table 3). Results showed that in standard seawater as well as in all the leachates samples, rate of mortality remains 0% during the first 24 h of contact. This means that sediment as well as amended sediment with Bauxaline® or Bauxsol has no toxic effects for short contact time (inferior to 24 h). As the contact time increased (48 h) the rate of mortality reached up to 85–88% in leachates of control sediment and amended sediment. Leachates samples collected during the first 20 days of stabilization experiment exhibited mortality up to 82 ± 3% due to rapid increase in dissolved trace elements concentrations. No significant change appeared in rate of mortality for all the leachates samples collected after 20 days. The toxicity data

Table 3
Average toxicity of all leachates .

Mortality (%)	Standard seawater	Control sediment	Sediment + 5% Bauxaline®	Sediment + 5% Bauxsol
Mortality (%) after 24 h	0 ± 0	0 ± 0	0 ± 0	0 ± 0
Mortality (%) after 48 h	0 ± 0	88 ± 9.8	87 ± 11.8	85 ± 11.5

revealed that mortality of *B. plicatilis* was significant only after 48 h. These toxicity data demonstrate that assessment of acute toxicity after 48 h is more appropriated than acute toxicity after 24 h, in the case of sediment leachates.

The 5% amendment rate of Bauxaline® and Bauxsol in the sediment was not sufficient to decrease the toxicity of the leachates within 48 h of contact. Higher rates of amendments should be tested in order to decrease the leachates toxicity, as well as supplementary acute tests to confirm toxicity.

4. Conclusions

Sediment pollution with trace elements and their management is a global issue. In France, dredged sediments are subjected to two guidelines depending on their levels of contamination. Even if stabilization with mineral amendment cannot be considered as a sediment remediation technique, it is still a promising and low cost approach to limit the leaching of trace elements from polluted sediments.

The pilot scale experiments performed in this study have shown that the total leaching of cationic trace elements was significantly reduced when Bauxaline® or Bauxsol were added to the sediment. Bauxaline® and Bauxsol were effective to limit the leaching of cationic trace elements in dredged sediment but no significant efficiency was observed for anionic pollutants (As and Mo).

According to N1 and N2 regulatory levels from French sediment quality guidelines, the studied sediment sample cannot be immersed back into the sea and field management was required. By investigating mineral amendments we showed that cationic pollutants were significantly immobilized in the solid phase. After 3 months of pilot experiments, classification of the sediment samples according to sediment quality guidelines (N1 and N2) was unchanged (since ca. 99% of the total amounts of trace elements remained in the solid phase) but the labile fraction was significantly lowered and met the quality criteria defined for inert waste at 2 L/kg for all elements except As. Nevertheless, 5% of amendment rate was not sufficient to lower toxicity of the leachates. A higher quantity of Bauxaline® and Bauxsol additives or combination with other mineral materials (gypsum for example) should be tested in order to enhance immobilization of anionic pollutants (e.g. As) to reach quality criteria for inert waste and to reduce toxicity of the leachates. Further studies should be investigated to evaluate in a long-term experiment (1 year) the effect of organic matter degradation on trace elements bioavailability.

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3.3 Summary of article 3) Use of neutralized industrial residue to stabilize trace elements (Cu, Cd, Zn, As, Mo, and Cr) in marine dredged sediment from South-East of France

3.3.1 Introduction

In our previous study(article 2) we found that the amendments rates (5%) were not sufficient to stabilize anionic contaminants present in sediment samples (Taneez et al., 2015). To improve the rate of stabilization for anionic elements along with cationic species, bauxaline® was first neutralized with an acidic mineral (i.e. gypsum).In this study, the 2ndsub-sediment sample collected from highly polluted Navy harbor site was mixed with neutralized bauxaline® and the trace elements immobilization was studied for a period of three months. The leached trace elements concentrations, pH, electrical conductivity and dissolved organic content were monitored. The toxicity of leachate samples was tested using a rotifer: *Brachionus plicatilis*.

3.3.2 Results and conclusion

Neutralized bauxaline® (5% and 20%) was mixed with sediment sample and the concentrations of trace elements (Cu, Cd, Zn, As, Cr and Mo) in leachates were measured regularly during pilot experiment. Ni was below detection limit in the leachate samples. The amendments had no effect on pH but the electrical conductivity was decreased due to successive leaching. The neutralization process increased the efficacy of material to stabilize trace elements compared to raw bauxaline®. Although both the rates (5% and 20%) were effective in immobilizing trace elements concentration but the bioavailable fraction of Cu (40%), Cd (55%), and Zn (71.2%), was predominantly immobilized by 20% amendment compared to leaching from control sediment while Mo (11.7%) and As (5.2%) were less immobilized. The addition of gypsum may provide additional sorption sites through precipitation of calcite and the pH of amendment favored the adsorption of cationic trace elements. All the trace elements were found to be within regulatory levels defined for inert waste expect for Mo. The cumulative release of pollutants (see Fig 2 of Article 3) showed that 20% of amendment reduced significantly the total amount of trace elements leaching from sediment. Both solids were found to be effective in reducing toxicity of sediment but stabilization with 20% neutralized bauxaline® significantly

reduced the toxicity of sediment up to 36 ± 18%. The amendment used in this study contains Fe and Al oxides and proper neutralization of this industrial waste can make it an interesting and cost effective immobilizing material for the trace elements in sediments. Further studies should be needed to evaluate the effectiveness of amendment for full scale practical implications as well as supplementary toxicity test should be performed.

3.4 Article 3) Use of neutralized industrial residue to stabilize trace elements (Cu, Cd, Zn, As, Mo, and Cr) in marine dredged sediment from South-East of France

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Use of neutralized industrial residue to stabilize trace elements (Cu, Cd, Zn, As, Mo, and Cr) in marine dredged sediment from South-East of France

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HIGHLIGHTS

- Bauxite residue (bauxaline®) was neutralized with gypsum to lower its pH.
- Neutralized bauxaline® was used as amendment at 5% and 20% for trace elements stabilization in marine dredge sediment.
- 20% neutralized bauxaline® immobilized significantly cationic pollutants.
- Leachates toxicity towards rotifers (*Brachionus plicatilis*) was sufficiently decreased with 20% amendment application.

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ABSTRACT

Management of marine dredged sediments polluted with trace elements is prime issue in the French Mediterranean coast. The polluted sediments possess ecological threats to surrounding environment on land disposal. Therefore, stabilization of contaminants in multi-contaminated marine dredged sediment is a promising technique. Present study aimed to assess the effect of gypsum neutralized bauxaline® (bauxite residue) to decrease the availability of pollutants and inherent toxicity of marine dredged sediment. Bauxaline®, (alumia industry waste) contains high content of iron oxide but its high alkalinity makes it not suitable for the stabilization of all trace elements from multi-contaminated dredged sediments. In this study, neutralized bauxaline® was prepared by mixing bauxaline® with 5% of plaster. Experiments were carried out for 3 months to study the effect of 5% and 20% amendment rate on the availability of Cu, Cd, Zn, As, Mo, and Cr. Trace elements concentration, pH, EC and dissolved organic carbon were measured in all leachates. Toxicity of leachates was assessed against marine rotifers *Brachionus plicatilis*. The Results showed that both treatments have immobilization capacity against different pollutants. Significant stabilization of contaminants (Cu, Cd, Zn) was achieved with 20% application rate whereas As, Mo, and Cr were slightly stabilized. Toxicity results revealed that leachates collected from treated sediment were less toxic than the control sediment. These results suggest that application of neutralized bauxaline® to dredged sediment is an effective approach to manage large quantities of dredged sediments as well as bauxite residue itself.

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1. Introduction

The presence of contaminants in aquatic environment has attracted global attention in the recent years due to their toxicity, abundance and persistence (Sin et al., 2001). Trace elements can be easily adsorbed onto particles, deposited and accumulated in the sediments, making sediments a sink and an ultimate source of contaminants. Contaminants can be released back into water column during natural (tidal movements or storms) and anthropogenic processes (dredging, dredged disposal and fishing) that provoke little variations of pH or redox potential of interstitial water (Calmano et al., 1996; Zoumis et al., 2001; Eggleton and Thomas, 2004). Mediterranean Sea is vulnerable to chemical contamination due to its semi-closed environment with low freshwater inputs. During the past decades, industrial, agricultural and urban waste have been discharged into the Mediterranean Sea

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causing a significant increase of global pollution and a progressive degradation of marine ecosystems (Tessier et al., 2011). Notable concentrations of inorganic (As, Cu, Cd, Zn, Ni and Mo) and organic compounds (PAHs and PCBs) have been reported in Mediterranean sediments (Andral et al., 2004; Mamindy-Pajany et al., 2013). Sediment management in the Mediterranean Sea is closely related to the need of periodic dredging to ensure sufficient depth for navigation. French legislation on marine and estuarine sediment dredging has fixed two levels (N1 and N2) to classify dredged sediments according to metals and PCBs concentrations. According to these quality guidelines, several options for the disposal of dredged sediments exist. Sediments can be dumped back into the sea if the contamination level is below N1. In this case sediment is considered uncontaminated with no ecological effects. Between N1 and N2 levels, sediments are classified as contaminated and offshore disposal is prohibited. Sediments are considered highly polluted when they have contaminants level greater than N2. These sediments are usually disposed on land in controlled landfills; hence their management is a great issue due to potential impacts on surrounding environment (Alzieu, 2005). In addition to sediment quality guidelines, highly polluted sediments must follow the criteria defined by European Council for inert waste management. European Council defined the leaching limit values for chemical compounds (e.g. As, Cd, Cu, Cr, Ni, Zn, Mo) as acceptance criteria for inert waste landfill (European Council, 2002). These values were determined according to the AFNOR protocol for liquid to solid ratio (L/S) of 2 L/Kg and 10 L/Kg of metals measured in the liquid after leaching experiments (AFNOR XP X 31-210, 1998).

The choice of remediation method depends on the contaminant and site characteristics, regulatory requirements, costs and time constrains. Conventionally, ex-situ remediation techniques are applied in case of dredged sediments (Pearl et al., 2006). Dewatering is an essential step for the treatment of dredged sediments. Further treatments have been proposed, including sediment washing, vitrification, electrochemical separation, and thermal treatment. These treatment processes are very expensive considering the huge amount of dredged sediments (Mulligan et al., 2001; Rulkens, 2005). Among dredged sediments treatment processes, solidification/stabilization aims to immobilize contaminants in a solid matrix. This process involves mixing of dewatered sediment with specific bulk material like fly ash, cement, lime and/or other chemicals to limit the leaching of pollutants. However, the successful stabilization of multi-element contaminated sites depends on the combination of critical elements in the sediment and the choice of amendments (Mulligan et al., 2001; Rulkens, 2005; Kumpiene et al., 2008). In this context, the use of low cost materials for stabilization of toxic ions into sediments is a promising area of research and development. Mineral amendments have been largely used for the treatment of metal contaminated sites due to their low cost, efficiency and environment friendliness. Amendments including alumino-silicates (clay, zeolites), and phosphorous minerals (e.g., apatite) were efficient in stabilization of metal contaminants in soils and sediments (Guo et al., 2006; Mamindy-Pajany et al., 2013). However, some limitations have been reported in case of As, Mo, and Cr during field application (Seaman et al., 2001). Recently, nano-hydroxyapatite has also been investigated as amendment for metal contaminated matrices and a significant stabilization of Cd and Pb was obtained (Zhang et al., 2010; He et al., 2013). Iron bearing compounds (e.g. zero-valent-iron, goethite, hematite, and ferrihydrite) have shown satisfactory results in reducing the mobility of As, Cd, Cu, Mo, Ni and Zn in soils and sediments (Kumpiene et al., 2008; Komárek et al., 2013; Mamindy-Pajany et al., 2013). Considering efficiency of iron oxides for contaminants stabilization in sediment matrixes, the use of industrial by-products rich in iron and aluminum oxides has been investigated. Among these interesting by-products, bauxite residues have shown satisfactorily results in case of cationic stabilization in marine sediments (Müller and Pluquet, 1998; Taneez et al., 2015), soils (Lombi et al., 2002; Guo et al., 2006; Garau et al., 2007), and organic pollutants from liquid phases (Liu et al., 2011). Nevertheless, its alkaline nature limits its use especially concerning anionic pollutants. For this reason seawater neutralization and thermal activation of bauxite residue have been applied to provoke synthesis of hydrotalcite in order to enhance the removal efficiency for arsenate, vanadate, and molybdate from aqueous solutions (Palmer et al., 2010). Another possibility to enhance anionic species stabilization is to decrease pH of bauxite residues by gypsum ($CaSO_4 \cdot 2H_2O$) addition. Gypsum addition has shown to decrease pH (due to precipitation of hydroxides and carbonates by calcium), alkalinity and sodicity of bauxite residues and promote growth of grass (Wong and Ho, 1993). Moreover, bauxite residue leachate collected from Ajka, Hungary was neutralized with gypsum and calcite precipitation favored the removal of aluminum and arsenic from solution (Burke et al., 2013).

In our previous work, results have shown that two mineral additives (Bauxaline® and Bauxsol) can effectively limit the leaching of cationic pollutants (Cu, Cd, Zn) from marine sediment but amendment rates appeared to be not sufficient in case of As and Mo (Taneez et al., 2015). To increase the immobilization rate of trace elements especially the anionic species from marine dredged sediment bauxaline® was neutralized with gypsum to lower the initial pH of bauxaline®. In the present study, bauxaline neutralized with gypsum was investigated to evaluate stabilization efficiency of Cu, Cd, Zn, As, and Mo from marine dredged sediment.

2. Materials and methods

2.1. Materials

The sediment was collected from French Navy harbor area of Toulon (South-East of France) during a dredging campaign by port authorities using a Shipek grab. Toulon bay is a semi-closed Mediterranean area particularly subjected to various anthropogenic activities such as marina, industrial and Navy. Toulon Bay sediments accumulate contaminants as a consequence of high nautical activities and the limited water exchange. Sediments in this area are considered heavily polluted. The sediment sample after dredging was composted in a terrestrial disposal site for four months under natural sun light. During that period the sediment sample was mechanically turned over and humidification took place once a week. The composting process has promoted microbial activity, decreased organic pollutants concentration and sediment salt content. For pilot scale experiment, sub samples of sediment were collected and brought back to laboratory. Bauxaline® (bauxite residue) was provided by ALTEO plant (Gardanne, Bouches-du-Rhône, France) that supplies alumina specialties since 1893. Bauxaline® was neutralized with 5% of plaster (net content of gypsum is 5.88%) by INERIS. This mixture was hydrated and equilibrated for 7 days with Milli-Q water and then the slurry was air-dried. The final product was then supplied to the laboratory. Mineralogical data of neutralized bauxaline® was provided by ALTEO and INERIS.

The pH and electrical conductivity (EC) values of sediment and neutralized bauxaline® were measured in suspension of (100 g/L) using pH (Consort bvba, Belgium) and electrical conductivity meter (Crison, Barcelona, Spain) respectively. ISO standard BET method was used to determine the specific surface area (ISO 9277, 2010 (E)). Hexamminecobalt trichloride solution was used to determine the cation exchange capacities (CEC) of solids (ISO 23470, 2007). Total organic carbon (TOC) in sediment was measured with sulfochromic

oxidation according to AFNOR protocol (AFNOR NF ISO 14235, 1998). Dissolved organic carbon (DOC) was measured in leachates using total organic carbon analyzer (TOC-V_{CPH} Shimadzu Corporation, Kyoto, Japan). Sediment and Neutralized bauxaline samples were digested using (DigiPREP HT, SCP Science, Quebec, Canada) according to US EPA method 3050B. Total and leachates content of inorganic pollutants (As, Cd, Cu, Mo, Cr, and Zn) from pilot experiment were analyzed by ICP-OES (Optima 2000, Perkin Elmer Corporation, Massachusetts, USA).

2.2. Pilot experiment

In the present study, bauxaline® (bauxite residue) was mixed with plaster: bauxaline® (95% dry mass) and plaster (5% dry mass, equivalent to 5.93% gypsum). The net content of gypsum was then 5.88% (= 5.93/(95 + 5.93)). Addition of gypsum was expected to decrease the pH of bauxaline® and consequently to improve the rate of trace elements (especially anionic species) in marine dredged sediments. Neutralized bauxaline® was applied at two rates (i.e., 5% and 20%). The concentration of trace metals leached from the untreated sediment and treated sediment were monitored for 3 months in pilot experiment. Stabilization process can minimize the bioavailability of trace elements. Therefore, toxicity of the leachates was tested against marine rotifers. pH, electrical conductivity and dissolved carbon content were monitored in the leachates.

The pilot experiment was conducted in Nice, (France) from May 2014 to July 2014 to investigate the capacity of bauxite residue to stabilize trace elements in polluted sediments. In the experiment, three boxes of equal size (40 × 40 × 20 cm) each containing 6 kg of sediment were used. Neutralized bauxaline® was added to sediment at the rate of 5% and 20% as amendment. A square plastic mesh was fixed at the bottom of each box for the collection of leachates. A geotextile cover was placed in the inner surface of each box to prevent the loss of fine particles. Three treatments were prepared: (1) untreated sediment (as control), (2) Sediment + 5% Neutralized bauxaline®, (3) Sediment + 20% Neutralized bauxaline®. Two liters of tap water was used to pre-treat the sediment in following steps. 1) 1 L of tap water was sprinkled onto the top of each box homogeneously; 2) sediment samples were thoroughly aerated using garden shovel, and 3) 1 L of tap water was poured again onto materials. The leachates were then allowed to drain for 1 h and collected in plastic containers placed under each box. In the first and second week, leachates were collected 3 and 2 times respectively. Afterwards, this draining and mixing was repeated weekly during 3 months of experimental period. Leachates were filtered through (0.45 μm membrane filter) and trace elements concentrations were measured after acidification at 1% with HNO_3 (69%).

2.3. Rotifers toxicity

Toxicity test is considered to be one of the important tools and current regulations imply toxicity test to assess the potential impacts of sediment disposal after dredging. We chose *Brachionus plicatilis* as test organisms because these marine rotifers are able to tolerate wide range of salinity e.g., (5-35 PSU). Since the successive leaching with tap water during stabilization experiments decreased the salinity, *B. plicatilis* appeared to be the most suitable organism to be tested according to our experimental protocol. All the leachates collected during 3 months experiment were subjected to toxicity test with *B. plicatilis*. Commercially available Rotoxkits M were purchased from microbiotest Inc., Belgium. Rotoxkit M is based on 24 h–48 h mortality bioassay and sensitivity to particular chemicals or mixtures increased substantially with exposure time of 48 h. Hatching of rotifer cysts were made in standard seawater of reduced salinity (20 PSU) at 25 °C under continuous illumination of 3000–4000 lux for 28 h. Within 2 h of hatching the neonates were transferred to multi-well test plate containing leachate samples. After transferring 5 rotifers into each well the plates were covered with paraffin film and incubated at 25 °C in darkness. The number of dead rotifers in each well was counted after 24 h and 48 h incubation. Hence, mortality after 24 h and 48 h can be estimated. Rotifers are considered dead if they do not exhibit any internal or external movement in 5 s observation. For the rotifers test to be valid, control mortality in standard seawater (35 PSU) must not exceed 10%. For this test, potassium dichromate was used as reference toxicant.

3. Results and discussion

3.1. Sample characteristics

The main properties of neutralized bauxaline® are presented in Table 1. Neutralized bauxaline® has pH equal to 9.02. Gypsum addition decreased the initial pH of bauxaline® previously reported (Taneez et al., 2015), EC of neutralized bauxaline® remained high (3.69 mS/cm). Cation exchange capacity (CEC) and specific surface areas of neutralized bauxaline® are 40.15 meq/kg, and 19 m^2/g respectively. Neutralized bauxaline® contain Cr at level superior to N2 level while others elements are within permissible N1 limit. The major mineralogical phases of both solids are iron and aluminium oxides making these solids interesting material for adsorption of pollutants.

The main physicochemical characteristics of sediment and French sediment quality guideline (N1 and N2 level) for trace metals (As, Cd, Cu, Ni, Zn and Cr) are reported in Table 1. pH of sediment is alkaline near to sea water pH and has high EC value due to the presence of salts. CEC and specific surface area of sediment are 105.3 meq/kg and 3.5 m^2/g, respectively. Total organic carbon in solid phase of sediment is 55.91 g/kg. Concerning the quality of sediment, total concentrations of trace elements measured in whole sediment were compared with N1 and N2 levels. Sediment is found to be contaminated with As, Cu, Cd, and Zn as the concentration of these elements is greater than N2 permissible level. Ni and Cr concentrations are lower than N1 regulatory limit in the sediment. GEODRISK software ranked sediment risk score greater than 2 according to its level of contamination (Alzieu and Quiniou, 2001). This kind of sediment is considered as waste and cannot be dumped back into the sea. According to the French legislation the contaminants in such sediment must be stabilized before landfill and thereafter evaluated again on the basis of European Council criteria for inert waste management. Table 2 presents the composition of neutralized bauxaline®. The mineral amendment is composed of Fe, Al, and Ti oxides.

3.2. Stabilization of trace elements

During pilot experiment, addition of alkaline amendment did not notably change the pH of the sediment that remained constant around 8.2 ± 0.1 due to inherent buffering capacity of sediment (Prokop et al., 2003). However, a decrease of the electrical conductivity of sediment was observed from 44 ± 2 mS/cm to 13 ± 5 mS/cm in the first 20 days. Then it stabilized around 12 ± 4 (mS/cm) until the end of experiment. Continuous humidification of sediment with tap water allowed to decrease the salinity and made it suitable for landfill. Leached trace elements (Cu, Cd, Zn, As, Cr, and Mo) concentrations per kg of sediment were depicted in Fig. 1 during the experiment. An increased rate of trace elements occurred during the first 20 days due to rapid decrease in salinity.

Table 1
Physicochemical characteristics of sediment and neutralized bauxaline®.

	Sediment	Neutralized bauxaline®	N1	N2
pH	8.2 ± 0.02	9.02 ± 0.03		
EC (mS/cm)	7.45 ± 0.01	3.69 ± 0.01		
CEC (meq/kg)	105.3 ± 0.8	40.15 ± 0.30		
Total organic carbon (g/kg)	57.83 ± 2.72	8.203 ± 0.009		
Specific surface area (m^2/g)	3.5	19.0		
Fine particles (a < 63 μm, b < 80 μm, c > 63–2000) (%)	21.8[a], 61.7[c]	90[b]		
As (mg/kg)	201.4	<2.5	25	50
Cd (mg/kg)	4.8	<2.5	1.2	2.4
Cu (mg/kg)	1880.9	9.0	45	90
Mo (mg/kg)	7.4	<2.5	–	–
Ni (mg/kg)	21	6.2	37	74
Zn (mg/kg)	3068.5	3.7	276	552
Cr (mg/kg)	43	1977.9	90	180

Table 2
Composition of neutralized bauxaline®.

Mineralogical major phases (XRD) of neutralized bauxaline®
Hematite 42 (%), Goethite 27 (%), Cancrinite $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$ 11 (%), Calcite 6 (%),
Rutile 4 (%), Katoite $Ca_{2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}$ 4 (%), Gibbsite 2 (%), Quartz 2 (%),
Portlandite 1 (%), Boehmite 1 (%), Anatase (traces)

During this time period, ecological risk is higher when the sediment is treated on land due to labile fraction of elements. This has already been observed in a previous study in which an increasing rate of Cd and Zn mobilization was observed during land disposal of contaminated sediment (Prokop et al., 2003). This higher mobilization can be due to oxidation of sulphides (CdS and ZnS) that are mobilized during oxic disposal (Panfili et al., 2005). Nevertheless, treated sediment with neutralized bauxaline® altered the rate of trace elements mobilization compared to control. Application of 5% neutralized bauxaline® has decreased the bioavailable fraction of trace elements at following rates: Cu (26.5%), Cd (24%), Zn (35%), As (9.6%), and Mo (2.2%). Whereas with 20% neutralized bauxaline® Cu (40%), Cd (55%), and Zn (71.2%), were predominantly stabilized compared to leaching from control sediment while Mo (11.7%) and As (5.2%) were less immobilized. Mixing sediment with high rate of mineral additive (20%) stabilizes promisingly cationic pollutants (Cu, Cd, Zn) compared to control sediment. The stable pH of sediment around 8.2 enhanced the sorption of cationic pollutants. In our previous work the stabilization rates with 5% of bauxaline® were 9% (Cu), 35% (Cd), 26% (Zn), 10% (Ni), 5.6% (Mo). The rate of Cu (26.5%) removal was higher in case of 5% neutralized bauxaline® meaning that Cu had a greater affinity for bauxite reside due to the presence of $CaCO_3$ that favored the formation of atacamite (Ma et al., 2009), while Zn and Cd were stabilized at rate of 35% and 24%, respectively. During gypsum neutralization Ca^{2+} is removed from the leachate by calcite precipitation. Rapid dissolution of atmospheric CO_2 provides carbonate ion at alkaline pH to support this reaction and full conversion of gypsum to calcite was observed. The carbonate precipitate may also provide additional sorption sites for the removal of trace elements (Burke et al., 2013). Hence, gypsum addition favored the pH of amendment due to which increased rates of cationic elements were observed.

Low immobilization rates were observed for anionic species (As, and Mo) in sediment with 5% and 20% neutralized bauxaline®. This can be attributed to the alkaline pH ≈ 9 and negatively charged surface of the amendment as well as complex matrix of sediment. However, compared with 5% of neutralized bauxaline®, the stabilization rate for Mo increased from 2.2 to 11.7% when 20% of neutralized bauxaline® was added. On the other hand the stabilization rate of As did not change whatever the amount of neutralized bauxaline®. As and Mo being anionic species, adsorption is expected to be maximum at low pH values (Goldberg et al., 1996; Zhang et al., 2008). Considering the pH of the solid after neutralized bauxaline® addition (8.2) it can be concluded that gypsum addition did not allowed a sufficient decrease of pH to improve anionic species stabilization.

The presence of Cr in the leachates is due to the amount of neutralized bauxaline® added to the sediment. Indeed, sediment did not contain initial amount of Cr but the high rate of Cr released from sediment amended with 20% of neutralized bauxaline® is due to the amount of Cr found in bauxaline® and thus neutralized bauxaline®. XPS analyses (data not presented) showed that Cr in raw bauxaline® is present in the form of Cr (III) which is a less toxic form than Cr (VI).

Leaching rates were calculated for all elements taking into account their total concentrations present in the dredged sediment (Table 1) using the formula:

$$\left(\text{rate of mobilization}(\%) = \frac{\text{leached concentration of element during3 months}}{\text{total conecentaion of element present in sediment}} \times 100\right)$$

The rates were found to be in the following order Cu (0.12%), Cd (0.63%), As (0.089%), Zn (0.054%) and Cr (0.15%). Leachability of all the elements remained lower than 1% except for Mo (12.86%). This has already been reported previously (Salomons, 1998). Hence, the bioavailable fraction of trace elements remained low compared to their total concentrations in dredged sediment. The rates of trace elements mobilization were also calculated for stabilized sediment with 5% and 20% of neutralized bauxaline®. With 5% amendment the mobilization rates for Cu (0.088%), Cd (0.47%), As (0.08%), Zn

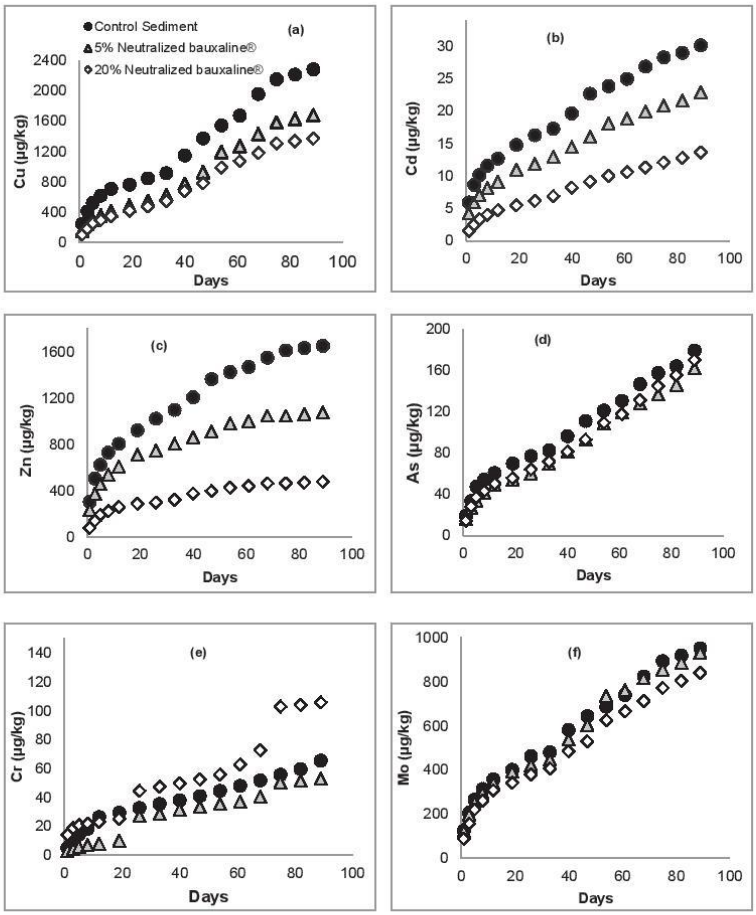

Fig. 1. Quantities of trace elements Cu (a), Cd (b), Zn (c), As (d), Cr (e) Mo (f) released from control and stabilized sediments during pilot experiment.

(0.035%) and Cr (0.0026%) were lower than 1% except for Mo (12.58%). 20% neutralized bauxaline® reduced mobilization of Cu (0.072%), Cd (0.28%), As (0.084%), Zn (0.015%) and Cr (0.005%) except for Mo (11.35%) which is superior to 1%. The increased rate of Mo during stabilization experiment can be due air drying as mentioned in a study conducted on accumulation and release of trace elements (As, V and Mo) from sediment in constructed wetland. Most of molybdenum is transformed into water soluble form during air drying process and its leaching was increased (Fox and Doner, 2002). Fig. 2 represents the total amounts of pollutants released over the period of 3 months and it is clearly depicted that treatment of sediment with neutralized bauxaline® has reduced the total availability of pollutants.

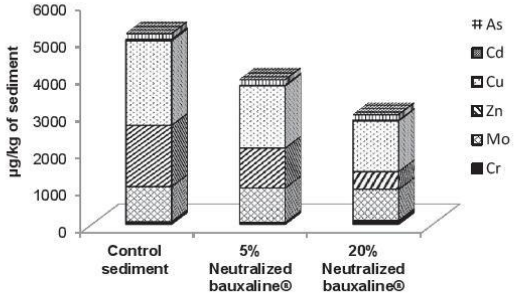

Fig. 2. Total amounts of pollutants released during pilot experiment.

Dissolved organic carbon was determined in all the leachates collected during stabilization experiment. At the first day, the concentration of DOC was 177 mg/L, 126 mg/L and 128 mg/L in the control sediment, sediment stabilized with 5% and 20% of neutralized bauxaline®, respectively. The amounts of DOC gradually decreased till 20 days. At the end of the experiment, DOC values were 102 mg/L (control sediment), 144 mg/L (5% neutralize bauxaline®) and 122 mg/L (20% neutralized bauxaline®). Trace elements in sediments are bound to mineral and organic fractions with different strengths. Organic matter plays a crucial role in the

Table 3
Comparison of regulatory levels defined for inert waste with trace element measured in leachates at liquid to solid ratio of 2 L/kg.

	Regulatory levels (μg/kg)	Control sediment (μg/kg)	5% Neutralized bauxaline® (μg/kg)	20% Neutralized bauxaline® (μg/kg)
As	100	69.7	54.2	55.5
Cd	30	14.8	10.9	5.4
Cu	900	762.8	486	417
Zn	2000	921.1	707.8	286.5
Mo	300	401	392	341
Cr	200	29.4	10	25

bioavailability of trace elements. Trace elements bound to organic fraction are considered relatively stable and can remain in the sediment for longer period. However, due to organic matter degradation with time it is important to monitor the release of trace elements. During organic matter degradation pH changes which leads to an increased leaching of contaminants (Peng et al., 2009).

After stabilization of pollutants the studied sediment was evaluated on the basis of European Council permissible limits for dumping of inert waste on land. These values correspond to metal percolation from inert waste at different liquid to solid ratios. In Table 3 comparisons of leached trace elements during stabilization experiment with regulatory levels is presented for liquid to solid ratio 2 L/kg. This ratio was achieved in the first 20 days of successive leaching with tap water in pilot study. All the trace metal concentrations were under regulatory levels in case of inert waste in control sediment except for Mo. Addition of neutralized bauxaline® further stabilized the pollutants in sediment. Stabilization with 20% amendment is more efficient than with 5%. Neutralized bauxaline® can be used to as a stabilizing agent to manage the huge quantities of dredged sediment.

3.3. Toxicity of sediment

Toxicities of sediment and sediment treated with 5% and 20% of neutralized bauxaline® were tested by incubating rotifers (*B. plicatilis*) with leachates samples collected during pilot study. Rotifer mortality was recorded after 24 h and 48 h of incubation. Standard seawater (35 PSU) is used as control and rates of mortality were compared (Table 4). Results showed that there was no toxic effect after contact time of 24 h and 48 h in standard seawater. After 24 h of contact, no mortality was observed in all the leachates. After 48 h of contact, rate of mortality was 72 ± 19% in the control sediment, and reached up to 49 ± 25% and 36 ± 18% in the 5% neutralized bauxaline® sediment and the 20% neutralized bauxaline® sediment, respectively. Both treatments were found to be effective in reducing toxicity of sediment but stabilization with 20% neutralized bauxaline® significantly reduced the toxicity of sediment up to 50%. The results were in agreement with the previous studies that Fe bearing mineral additives such as hematite decreased the toxicity of sediment against several bioassays (Mamindy-Pajany et al., 2010).

The results of the study show that the use of neutralized bauxaline® to stabilize trace elements in marine dredged sediments is a cost effective approach. It can efficiently stabilize cationic pollutants in marine dredged sediments and decrease inherent toxicity of sediment by limiting the leaching of pollutants. Addition of neutralized bauxaline® to contaminated dredged sediment can be helpful especially when large quantities of dredged sediments have to be managed. This study can provide a better insight for the different uses of industrial by-products rich in Fe and Al oxides.

Table 4
Average rotifers toxicity.

Mortality (%)	Standard Seawater	Control Sediment	5% Neutralized bauxaline®	20% Neutralized bauxaline®
After 24 h	0 ± 0	0 ± 0	0 ± 0	0 ± 0
After 48 h	0 ± 0	72 ± 19	49 ± 25	36 ± 18

4. Conclusions

Dredged marine sediments and industrial residues (such as bauxite) are important issues to be managed considering the large amounts dredged or produced yearly worldwide. In this work, marine dredged sediment was amended with 5% and 20% of neutralized bauxaline®. Addition of neutralized bauxaline® had no impact on the pH value but decreased the EC and the soluble and extractable metal concentrations from the sediment compared to the control. Neutralization of bauxaline® with gypsum significantly decreased the leachability of cationic pollutants from the sediment. The stabilization rates were as follows Zn > Cd > Cu. The bioavailable fraction of Cu, Zn and Cd was reduced more efficiently with 20% amendment. Nearly 72% of Zn, 55% of Cd, and 40% of Cu were stabilized. For anionic pollutants such as As, and Mo, the rate of stabilization were not so efficient and did not exceeded 10%. Gypsum addition in bauxaline® decreased the pH from 10.60 to 9.0 but when neutralized bauxaline® was added to marine sediment no effect on the pH was observed. Consequently, stabilization of anionic species (As, Mo) was not significantly improved. Toxicity of the sediment towards the marine rotifer *B. plicatilis* was significantly reduced after addition of 20% neutralized bauxaline® compared to the control.

The bauxite residue investigated in this study contains Fe bearing minerals and proper neutralization and application rate can make this industrial residue an emerging low cost material for treatment of sediment polluted with cationic species. Sediment stabilization can consume large volume of bauxite residues as amendment in an eco-environmental friendly way. Therefore, its use for field study (more than 3 months) should be investigated for full scale practical implementation and further investigations have to be performed to significantly enhance the stabilization of anionic species in marine sediments.

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Reduced sediments commonly become oxidized when they are exposed to air by dredging and disposal on land. Oxidative processes are known to increase contaminant availability(Lions et al., 2010). In order to reduce the danger of pollution to surrounding environment, it has been shown in this work that stabilization with iron based mineral can be effective technique to limit the contaminants leaching. The above two articles reported the feasibility of stabilization process in marine sediments using alumina industry by-product (bauxite residue). The application of bauxite residues (bauxaline®, bauxsol(5%) and neutralized bauxaline® (5 and 10%) to multi-contaminated sediment at various rates presents merits of techniques and highlights certain limitations. The EC of leachates was reduced successively throughout the experiment due to the decrease in salt content from the sediment. The pH of the mixture remained stable at 8.2 due to buffering effect of sediment components. The behavior of raw bauxaline® was quite similar to 5% bauxsol and neutralized bauxaline® towards stabilization of cationic elements (Cu, Cd, Zn). The rate of Cu retention increased from 9% to 27% using 5% bauxsol and neutralized bauxaline® due to the neutralization treatment (brine or seawater and gypsum) that reduced the pH of bauxaline® causing hydroxide, carbonate or hydroxycarbonate minerals to be precipitated which in turns enhanced the sorption of Cu onto these mineral phases. Significant reduction in leaching rates of Cu, Cd and Zn was observed when neutralized bauxaline® was mixed with marine sediment at higher rate (20%). A high quantity of solid increased sorption sites for contaminants, as well as sediment mixture pH was favorable for the retention of cationic elements and significantly lessened sediment toxicity. However, some limitations was recorded in case of anionic trace elements (As, and Mo). Though, addition of 20% neutralized bauxaline® stabilized As but the rate of immobilization did not exceeded 5.2%which is attributed to the pH, effect of competing ions, drying and humidification cycles. In order to compare the rate of trace elements stabilization other two amendments (bauxaline®, and bauxsol) were also evaluated at higher rate (20%) in the 2nd pilot experiment and the results are presented in the following section.

3.5 Stabilization of marine dredged sediments with 20% Bauxaline®, and Bauxsol

3.5.1 Monitoring of trace elements concentration in pilot experiment

Addition of 20% bauxaline® and bauxsol to the sediment had no effect on pH that remained constant around 8.2 ± 0.1 until the end of experiments (fig. 6) due to the inherent sediment buffering capacity, related to their high carbonate content, as previously reported (Prokop et al., 2003; Mamindy-Pajany et al., 2013; Taneez et al., 2015). During the first week of treatment the Electrical conductivity (EC) values were near to seawater i.e. (45± 2 mS/cm). Rapid decrease in EC was observed due to successive leaching and during first 20 days it reached up to 14±4 mS/cm, afterwards, the EC was stable around 13± 5mS/cm. The presence of amendments (bauxaline® and bauxsol) did not appear to influence the pH and EC values recommending that the sediment properties play a crucial role on the binding capacities of mineral amendments towards trace elements.

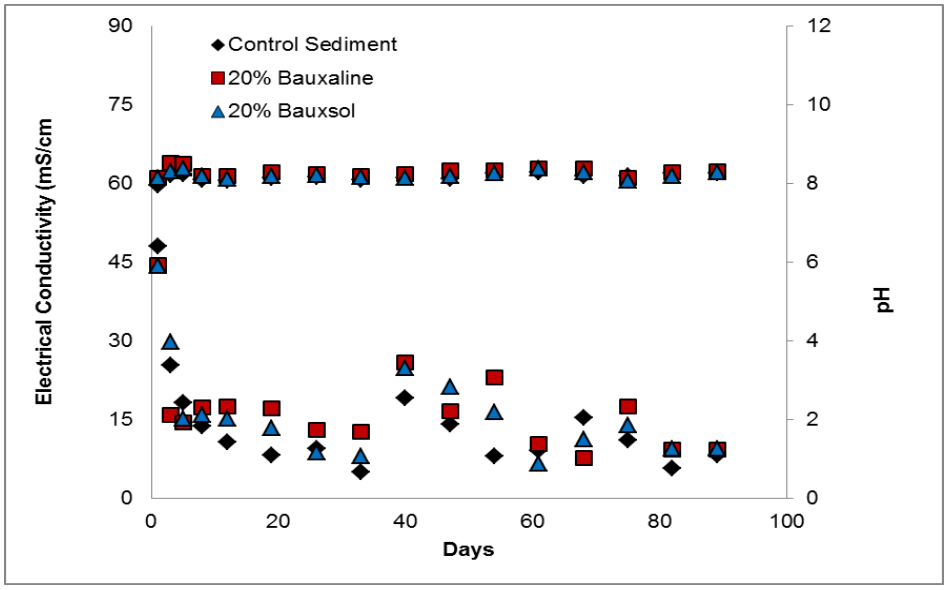

Fig. 6 Electrical conductivity and pH values in leachates from control and stabilized sediment samples as a function of time.

The cumulative amounts of trace element released per kg of sediment as a function of time are shown in Fig. 7. Leached amount of trace elements was higher during first 20 days in case of all samples indicating that the ecological risk mainly occurred at short term after the sediment deposit. A comparable pattern was also observed in a field study on terrestrial deposit of fluvial dredged sediment submitted to atmospheric conditions (Isaure et al., 2002; Piou et al., 2009). Mineral amendments (20% bauxaline® and bauxsol) changed the mobility of trace elements from sediment (Fig 7). The sediment sample treated with 20% bauxaline® reduced the mobility of trace elements compared to control in the following rates: Cu(52%), Cd(61.4%), Zn(83%), As(11%) and 20% bauxsol limit the water soluble fraction of elements as: Cu(58.2%), Cd(58%), Zn(80%), As(17.8%). The amendments have remarkable effect on limiting the leaching of cationic trace elements. Among the cationic pollutants Zn was greatly stabilized i.e., approx 80-83% in case of both amendment's. The amendments seem to be ineffective in case of anionic trace elements such as arsenic was immobilized only up to 11-17.8% by both amendments while Mo stabilization was insufficient. As and Mo have low affinity towards organic matter and dissolved organic matter can compete with As for sorption sites and displace both As(V) and As(III) from iron oxides (Redman et al., 2002). Additional leaching of Cr was observed in leachates after amendments application because of the initial Cr concentration present in both amendments.

Organic matter is heterogeneously complex component of sediment and its solubility determines the bioavailability of trace elements (Fernandes et al., 2011). Dissolved organic carbon (DOC) concentrations in leachates measured at the beginning of experiment in control and treated sediment (20% bauxaline® and bauxsol) samples were 177 mg/L, 146 mg/L, and 139 mg/L respectively. The degradation of organic matter was slow and less than 0.03% of organic matter dissolved compared to the total organic content present in the sediments. After 3 months (end of experiments), DOC values were measured near to 100 mg/L, 102 mg/L, and 97 mg/L in case of control sediment, and amended sediment with 20% bauxaline® and bauxsol. By the same way than electrical conductivity values, DOC concentrations decreased all along the experiments. This confirms that successive and regular leaching provoked dissolution of organic matter either linked to the most labile

mineral phases of the sediment or present as a free organic phase. Organic matter is also suspected to bind trace elements that can be mobilized through the dissolution process of organic matter.

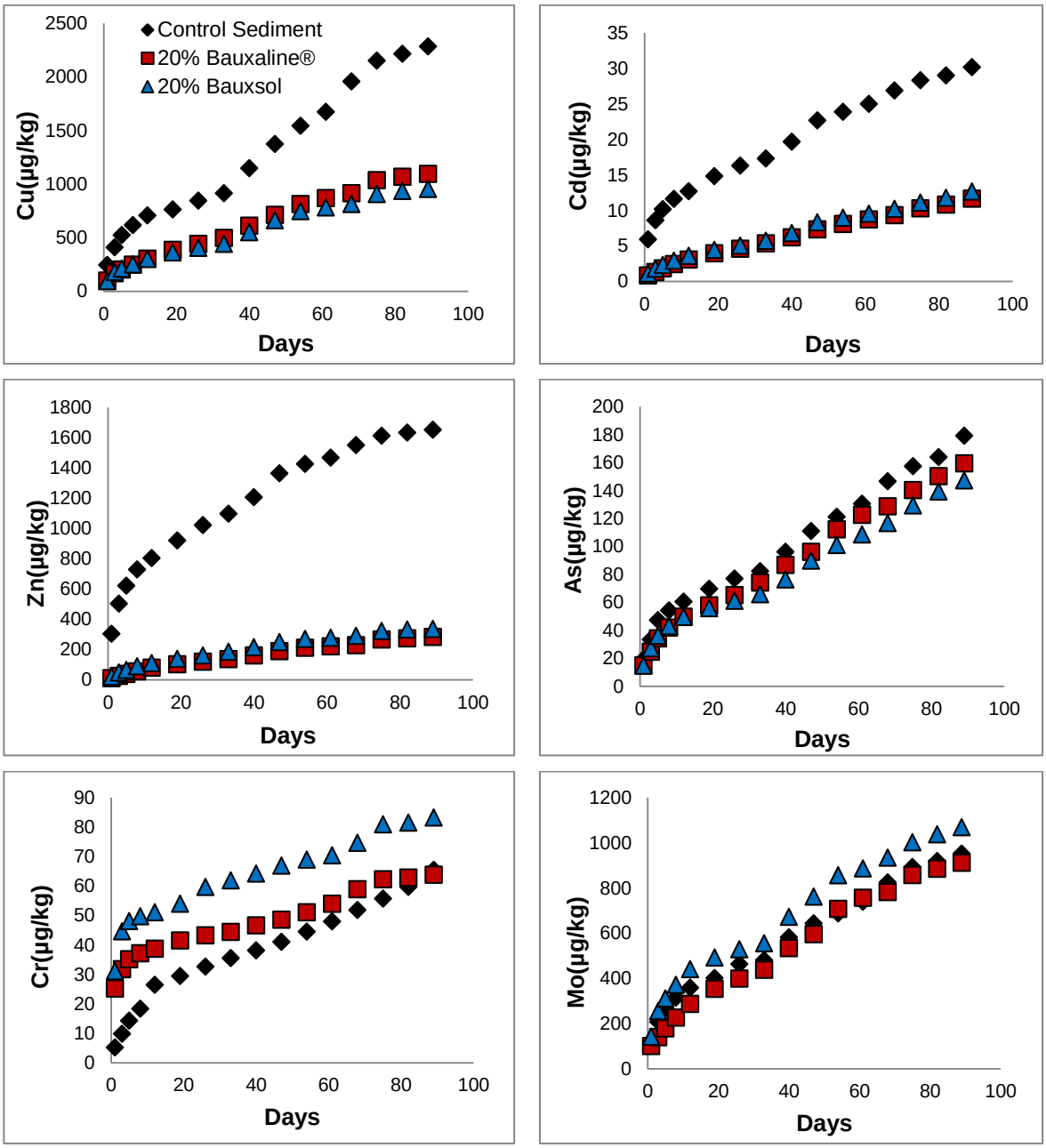

Fig. 7 Cumulative amounts of trace elements released in leachates from control and stabilized sediment samples as a function of time.

European Council defined permissible limit for the contaminants under inert waste classification and leaching of trace elements from control and stabilized sediment was then compared with these regulatory levels. These permissible levels correspond to percolation of trace elements from inert waste at different liquid to solid ratios. In table 10 the amounts of trace elements in leachates were compared with regulatory levels for liquid to solid ratio 2L/kg. This ratio was achieved in first 20 days of stabilization experiments with successive leaching. Addition of bauxaline® and bauxsol limit the percolation of trace elements and all the trace elements were under regulatory levels except for Mo.

Table 10. Comparison of leached trace elements with regulatory levels at liquidtosolidratio2L/kg for inert waste

	Regulatory levels	**Control sediment**	**20% Bauxaline®**	**20% Bauxsol**
	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)
As	100	69.7	57.8	56
Cd	30	14.8	4.0	4.4
Cu	900	762.8	384.8	361
Zn	2000	921.1	103.2	137.4
Mo	300	401	353.5	492.4
Cr	200	29.4	41.5	53.9

Leaching rate of trace elements (calculated over total concentrations) in the control sediments sample during the experimentation period (i.e. 3 months) was: Cu (0.121%), Cd (0.63%), As (0.089%), Zn (0.054%), Cr (0.15%) and Mo (12.86%). After the addition of amendments (i) 20% bauxaline® the rate was: Cu (0.057%), Cd (0.21%), As (0.079%), Zn (0.009%), Cr (0.003%) and Mo (12.32%). (ii) 20% bauxsol mobilization the rate was: Cu (0.05%), Cd (0.23%), As (0.073%), Zn (0.01%), Cr (0.005%) and Mo (14.43%). Leaching rates remained inferior to 1% (except for Mo) compared to their total concentration present in the sediment sample meaning that less than 1% of contaminants are available, while 99% are stored in the sediment (Salomons, 1998). The possibly high leaching of Mo was not in agreement with its total concentration present in the sediment since Mo was a less

concentrated contaminant. Under outdoor condition Mo was more solubilized due to repeated humidification. A similar trend was reported in a study that Mo transform into water soluble for after air drying (Fox and Doner, 2002), and pre-treatment of sediment could lead potentially large amounts of Mo in leaching waters. A comparison of amendments are represented in Fig 8 (a), and (b) clearly indicate that the higher rate of amendments (20%) decreased significantly the leaching of total amounts of trace elements compared to control while 5% amendment rate was not sufficiently enough to reduce the total amount of contaminants. The behavior of both solids (bauxaline® and bauxsol) was quite similar towards most of the trace elements. The rate of immobilization according to solids was: Bauxaline® ≈ Bauxsol > Neutralized bauxaline®.

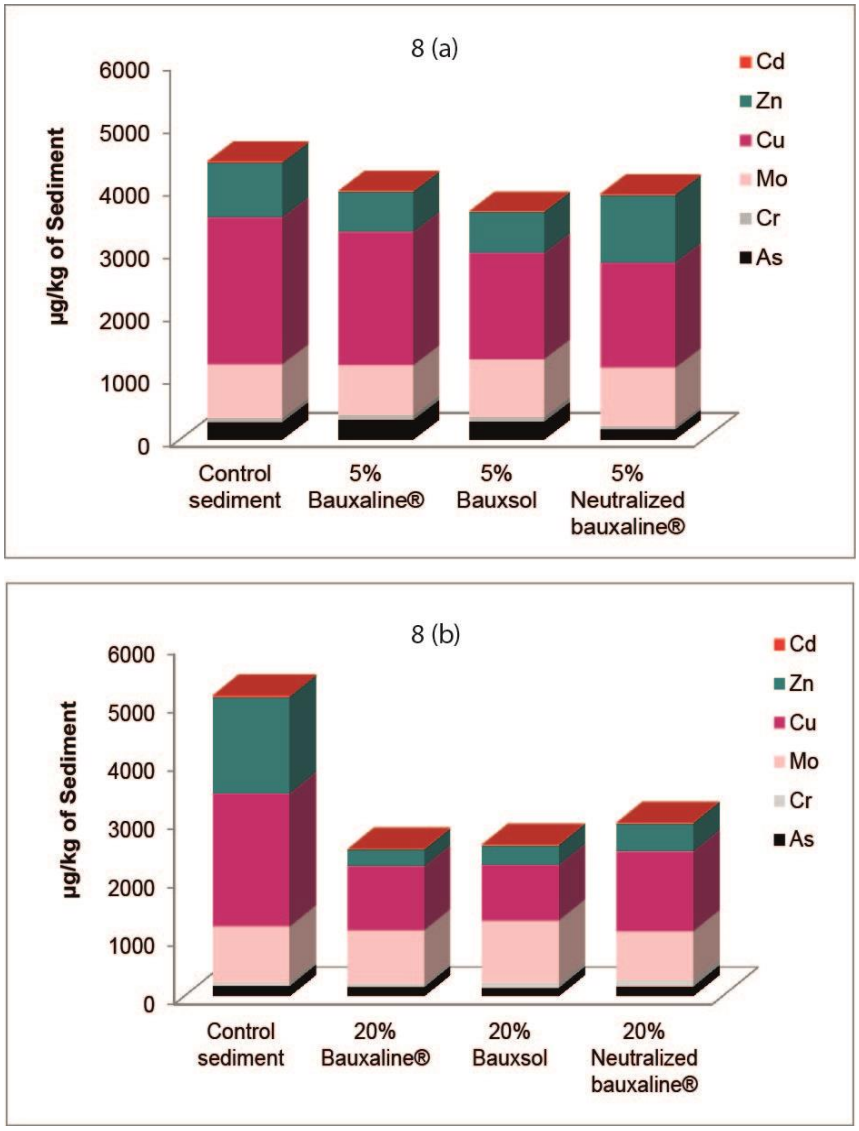

Fig 8. Total amount of contaminants release from control and stabilized sediment samples (a) amendments applied at 5% rate (b) amendments applied at 20% rate

3.5.2 Leachates toxicity

Leachates collected during pilot experiment from control and stabilized sediments with 20% bauxaline® and bauxsol were tested for toxicity. The test organism *Brachionus plicatilis*was incubated with all the leachates collected during 3 months because of the survival capacity of this organism in wide salinity range. Table 11 shows the results of mortality noted after 24 h and 48 h of incubation. The mortality rates were compared with

standard seawater used as control in this test. The results revealed that there was no mortality after 24 h and 48 h of contact time in standard seawater. The mortality in control sediment, treated sediment with 20% bauxaline® and bauxsol was 72 ± 19%,22 ± 17%, and 28± 205, respectively after48 h of contact. The reduction in toxicity with increased amendment application was in agreement with the previous study in which addition of 20% neutralized bauxaline® significantly reduced the toxicity of marine sediment. Bauxite residues contain high content of iron oxides and trace elements binding with the mineral phases reduced the availability and consequently the toxicity of sediments.

Table 11. Average toxicity of leachates towards *B.plicatilis*

Mortality (%)	Standard seawater	Control sediment	20% Bauxaline®	20% Bauxsol
After 24 h	0±0	0±0	0±0	0±0
After 48 h	0±0	72±19	22±17	28±20

3.6 Conclusion

Sediment functions as sink as well as ultimate source of contaminants (Förstner, 1989; Eggleton and Thomas, 2004). Deposits of contaminated sediments, which can now be found in many of the world's coastal regions, have become the subject of environmental concern because the contaminants they contain may be released to the water column and enter the tissue of living organisms. Several studies highlighted the efficiency of stabilization process with bauxite residue in contaminated soils (Lombi et al., 2002b; Friesl et al., 2003; Kumpiene et al., 2008; Lee et al., 2009; Lee et al., 2011). Present study investigated the utilization of industrial by-product (bauxite residue) as stabilizing agent of contaminated sediments in landfill storage context. Primarily, we examined adsorption potential of bauxite residues in aqueous medium using synthetic solutions of inorganic contaminants (As, and Cd) in batch type test. The results supported the fact that the iron and aluminium based minerals have great affinity to adsorb As and Cd and optimum removal can be achieved in the neutral pH range. However, at high pH (9.74) the adsorption of As decreased due to negatively charged surface of adsorbent and desorption of As could occur. Cd precipitation along with surface adsorption would likely to occur under high pH and adsorbate concentrations. The results of preliminary test indicated that

these amendments can be used as stabilizing in marine dredged sediments. Then the stabilization of trace elements in the solid matrix (sediment) by the addition of bauxite residues (bauxaline®, bauxsol and neutralized bauxaline®) at 5% and 20 % rate was carried out in two pilot experiments. The results of first pilot study revealed that amendments (5%) were effective only for the stabilization of Cu, Cd, and Zn while As, Mo, and Cr were mobile. The toxicity results indicated that the amendments were also less effective in decreasing the toxicity of sediment. The mortality rate of marine rotifers was high (88%). In 2nd pilot experiment, we observed that sediment stabilized with 5% neutralized bauxaline® has similar rate of trace elements stabilization which was obtained in case of 1st pilot study for bauxsol. The amendment was found to be effective in decreasing the toxicity of sediment compared to control sediment. In 2nd pilot experiment, we also used high rates of bauxite residues (i.e. 20%) and water soluble fraction of cationic trace elements (Cu, Cd, and Zn) was found to be significantly decreased in leachates. Bauxaline® and bauxsol can limit leaching of Zn nearly 80-83% in the sediment and the retention of Cd and Cu was 58-61%, and 52-58%, respectively. A little difference in retention capacity of neutralized bauxaline® for Cu, Cd, and Zn was observed and the adsorption of these elements in sediment matrix was less compared to bauxaline® and bauxsol. In case of As, bauxsol exhibited greater immobilization potential (17.8%) compared to bauxaline (11%), and neutralized bauxaline® (5.2%), while Mo immobilization remained low in all treatments. Increased leaching of Cr was observed when high quantities of additives were used due to initial concentration of Cr(III) present in bauxaline®. The stabilization of trace elements in multi-contaminated sediment is mainly governed by pH, clay, organic and iron hydroxide contents of sediment. We observed high retention rates of Cu, Cd and Zn in the presence of high amendments because the pH of the sediment was favorable for the retention of these contaminants while anionic pollutants were less retained due to unfavorable pH as well as competition with other ions diminishing their adsorption on mineral phases. By the addition of 20% amendments a substantial decrease in the toxicity of sediments towards marine rotifers was obtained. The mortality rate of rotifers was decreased to 22-28% when bauxaline® and bauxsol were applied compared to control sediment which has mortality rate up to 72. Because of the similar behavior of bauxaline® and bauxsol the reduction in toxicity of

sediment was mostly the same. The toxicity of 20% neutralized bauxaline® was reduced up to 36. The results were in agreement with the previous studies showing that Fe bearing mineral additives such as hematite decreased the toxicity of sediment against several bioassays (Mamindy-Pajany et al., 2010).

The conclusion drawn on the basis of this study is that bauxite residues can be efficient adsorbent to trap contaminants from aqueous and solid media. With regard to the properties of bauxite residue, neutralization is important to prevent classification as hazardous material or waste, minimize impacts on environment, and for its better utilization in environmental remediation as well for construction material. Bauxite residue can serve as a low cost and environmental friendly additive for the stabilization of trace elements in marine dredged sedimentsby adjusting the pH of the bauxite residue and taking care of other sediment parameters such as pH, organic matter and clay content. Nevertheless, care should be taken in homogenizing sediment sample as well as factor of competing ions could not be excluded. Field study should be conducted to investigate the long term effectiveness of stabilization process and degradation of organic matter should be closely monitored. Toxicity of sediment must be evaluated using battery of assays. Bauxite residue could be tested in combination with other minerals with low pH. Inshore treatment of fresh sediment as compared to composted sediment with bauxaline® could be better choice for the stabilization of pollutants due to precipitation of hydrotalcite and other Mg, Ca, and Al hydroxides and carbonate minerals. Combined neutralization treatments of bauxite residue could also be applied to enhance the efficacy of contaminants retention in solid phase. Each contaminated sediment sample requires specific consideration to find an appropriate amendment and application rate.

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General conclusion and perspectives

Marine sediments accumulate many chemicals including trace elements and organic substances. The Mediterranean port sediments cannot be discharged at sea due to their level of contamination and must be treated on land. During the land disposal of contaminated materials, pollutants may be transferred to the surrounding ecosystems, surface water or groundwater. Therefore, contaminated sediments must be treated before storage in order to limit the impact of the deposit on the receiving environment. The sediment used in this study was found to be contaminated by arsenic, copper, cadmium and zinc and the level of these contaminants were well above GÉODE N2 threshold value (recommended in the inter-ministerial order dated 14th June 2000).

This thesis work aimed to study the feasibility of stabilization treatment by mixing bauxite residues (bauxaline®, bauxsol and neutralized bauxaline®) with composted dredged marine sediment. The effectiveness of stabilization treatment was evaluated by monitoring the leached trace elements concentration and toxicity of sediment leachates. In order to achieve this aim, we investigated adsorption of inorganic pollutants (As, Cd) on bauxaline®, and bauxsol prior to stabilization experiments. Adsorption experiments were carried out according to various physico-chemical conditions (pH, and adsorbate concentration) in order to test effectiveness of additives. Both bauxite residues (bauxaline® and bauxsol) showed good adsorption percentages due to the constituents of bauxite residues (presence of Fe, Al and Ti oxides) and favorable removal was obtained at neutral pH (7-8). The adsorption data was modeled and proposed mechanism of retention was surface complexation on iron and aluminum oxides surface sites with surface precipitation.

The trace element concentrations (Cd, Cu,Zn, Ni, As, Cr and Mo) in composted dredged marine sediment indicated that the study matrix is highly contaminated and the level of contamination for Cu, Cd, Zn and As was higher than permissible level N2. Chemical stabilization of trace elements (Cd, Cu,Zn, Ni, As, Cr and Mo) in composted marine dredged sediment has been conducted in pilot device considering 5% and 20% amendment rates of bauxaline®, bauxsol and neutralized bauxaline®, as stabilization agents. Outdoor experiments (under real conditions) were conducted for three months. Initially, two amendments bauxaline® and bauxsol were applied at 5% rate and this treatment was efficient in reducing cationic elements concentrations in leachates. However, the

amendment rate was insufficient to immobilize anionic trace elements. The EC of stabilized sediment was decreased due to successive leaching while pH remains constant around 8.2 due to buffering capacity of sediment. Afterwards, the amendments (bauxaline®, bauxsol and gypsum neutralized bauxaline®) were mixed with composted sediment at higher rate (20%) and results showed that the additives can significantly reduce cationic trace element concentrations in the leachates. Bauxaline® and bauxsol decreased cationic trace elements concentration by 52 to 80%, and neutralized bauxaline® by 40 to 71%. The effectiveness of iron-based amendments in case of cationic pollutants is explained by the neutral pH (7-8) of the sediment that maintains favorable conditions for their retention. However, certain limitations were observed in case of anionic elements (As, Mo) as the immobilization rate was not significantly high. Stabilization rate for As reached only up to 17.8% by 20% bauxsol, and 11% by 20% bauxaline® while in case of neutralized bauxaline® it was not greater than 6%. These amendments make possible to significantly improve the quality of percolating water by reducing the amount of cationic pollutants in the leachates. The concentrations of all trace elements leached from stabilized sediment were significantly lowered and met the quality criteria defined for inert waste at 2 L/kg for all elements except Mo.

Assessment of sediment leachates toxicity using marine rotifers as test organism has shown 85-87% mortality rate by 5% mineral additives (bauxaline® and bauxsol) meaning that the additives at this rate were not sufficient enough to decrease the toxicity of sediment. Leachates of sediment stabilized by 20% of bauxaline®, bauxsol and gypsum neutralized bauxaline® were less toxic than control sediment. The mortality rate was reduced up to 30-40 % due to the decrease of trace elements concentration in percolating water. The results obtained for the stabilization of trace elements (Cd, Cu, Zn, Ni, As, Cr and Mo) under outdoor natural environment has shown that the addition of iron based mineral amendments to the sediment can effectively modify contaminants mobility. The effectiveness of treatment is also closely related to the physico-chemical characteristics of the sediments (organic matter content, pH etc.).

Based on the results of this thesis, the stabilization by addition of mineral amendments is a promising approach in the field of contaminated dredged marine sediments management. This technique improves the chemical and ecotoxicological quality of leachates from

contaminated sediments. This study demonstrates the feasibility of stabilization treatment of multi-contaminated marine sediments and provides valuable information on the potential mobility of trace elements. The results clearly show a decrease in trace elements concentration in sediment elutriates treated by 20% of three amendments accompanied by a lowering of toxicity of elutriates.

Though, the study revealed possible usage of industrial by-product (bauxite residue) as amendment in marine sediments, there are some perspectives to be considered for this work.

(i) It would be interesting to investigate the long term effectiveness of stabilization process in field experiments using large volume of sediment.

(ii) In order to provide additional information, effect of temperature, organic matter degradation, moisture and humidification and drying cycles should be studied.

(iii) In situ capping experiment using bauxite residue could be tested to treat contaminated sediment sites (especially by cationic pollutants).

(iv) To increase the effectiveness of stabilization process, bauxite residue can be neutralized prior to utilization. The selection of neutralization treatment depends on the type of pollutant to be addressed in sediments. Seawater or acid neutralization combined with other treatments can be used to enhance the adsorption of anionic trace elements. The cost of neutralization is associated with the type of neutralization process used, for example acid neutralization of bauxite residue is quite expensive since large volumes of reagents are required to fully neutralize it.

(v) Use of additives in combination with other industrial by-products composed of iron (slag) or composite minerals could be tested as stabilizing agents to improve the efficiency of treatment of sediments, especially for anionic contaminants.

Conclusion générale et perspectives

Les sédiments marins accumulent de nombreux produits chimiques, y compris des éléments traces et des substances organiques. Les sédiments portuaires méditerranéens pollués ne peuvent pas être rejetés en mer en raison de leur niveau de contamination et doivent être traités sur terre.Au cours du dépôt des sédiments contaminés sur terre, les polluants peuvent être transférés dans les écosystèmes environnants, les eaux de surface ainsi que dans les eaux souterraines.Par conséquent, les sédiments contaminés doivent être traités avant l'étape de stockage à terre afin de limiter l'impact du dépôt sur le milieu récepteur.Le sédiment utilisé dans cette étude est contaminé par l'arsenic, le cuivre, le cadmium et le zinc et le niveau de ces contaminants est bien au-dessus des valeurs seuils GÉODE N2 (recommandé dans l'arrêté interministériel en date du 14 Juin 2000).

Ce travail de thèse a pour but d'étudier la faisabilité d'un traitement de stabilisation en mélangeant les résidus de bauxite (de Bauxaline®, Bauxsol et Bauxaline® neutralisée) avec un sédiment marin dragué. L'efficacité du traitement de stabilisation a été évaluée en mesurant l'évolution des concentrations en éléments traces présents dans les lixiviats de sédiments ainsi que leur toxicité. Tout d'abord, nous avons étudié l'adsorption des polluants inorganiques (As, Cd) sur la Bauxaline® et le Bauxsol en batch afin d'évaluer l'efficacité de rétention de ces deux matériaux vis-à-vis de l'arsenic et du cadmium en fonction du pH, et de la concentration en adsorbat. Les deux résidus de bauxite (Bauxaline® et Bauxsol) ont montré de bons pourcentages d'adsorption en raison de la présence de certains constituants (oxydes de fer, d'aluminium et oxydes de titane) et nous ont permis d'obtenir un taux de rétention important à pH neutre (7-8). Les données d'adsorption ont été modélisées à l'aide d'un modèle basé sur la théorie de complexation de surface et une bonne corrélation a été obtenue entre les résultats expérimentaux et le modèle lorsque seuls les sites de surfaces d'oxyde de fer et d'aluminium sont considérés.

Les concentrations en Cd, Cu, Zn, Ni, As, Cr et Mo dans la matrice sédimentaire étudiée (sédiment marin composté) ont révélé que le sédiment étudié etait fortement contaminé et le niveau de contamination pour le Cu, Cd, Zn et As était plus élevé que le niveau admissible N2. La stabilisation chimique des éléments traces (Cd, Cu, Zn, Ni, As, Cr et Mo) dans le sédiment marin dragué a été menée dans un dispositif pilote en considérant des taux de 5% et 20% de Bauxaline®, de Bauxsol et de Bauxaline® neutralisée, comme agents de stabilisation. Des expériences en plein air (en conditions réelles) ont été menées

durant trois mois. L'application d'un taux de 5% en masse de Bauxaline®, l Bauxsol et de Bauxaline® neutralisée a permis de réduire efficacement la concentration en éléments cationiques dans les lixiviats. Cependant ce taux s'est révélé insuffisant pour l'immobilisation des éléments traces anioniques.. Sur la base de ce résultat, un taux de Bauxaline®, Bauxsol et de Bauxaline® neutralisée de 20% a été considéré. Les résultats obtenus ont montré que les additifs permettent de réduire significativement les concentrations en éléments traces cationiques dans les lixiviats à des niveaux d'efficacité variables. La Bauxaline® et le Bauxsol ont permis de diminuer le taux d'éléments traces cationiques de 52 à 80%, la Bauxaline® neutralisée quant à elle, a permis d'obtenir une diminution de 40 à 71%. L'efficacité des additifs à base de fer dans le cas des polluants cationiques est expliquée par le pH neutre (7-8) du sédiment qui maintient des conditions favorables à leur rétention. Cependant, certaines limites ont été observées dans le cas d'éléments anioniques (As, Mo) pour lesquels de faibles taux d'immobilisation ont été obtenus. Le taux de stabilisation obtenu pour As n'atteint que 17,8% pour 20% de Bauxsol ajouté, 11% pour 20% de Bauxaline® ajoutée tandis que dans le cas de la Bauxaline® neutralisée, le taux de stabilisation obtenu n'a pas dépassé les 6%. Ces modifications permettent d'améliorer considérablement la qualité de l'eau de percolation en réduisant la quantité de polluants cationiques dans les lixiviats. Les concentrations en éléments traces lessivés à partir des sédiments stabilisés ont été considérablement abaissées et répondaient alors aux critères de qualité définis pour les déchets inertes à 2 L / kg pour tous les éléments à l'exception du Mo. L'évaluation de la toxicité des lixiviats de sédiments vis à vis des rotifères marins a montré un taux de mortalité 85-87% lorsque un taux de 5% d'additifs minéraux était appliqué, ce qui confirme que les additifs à ce taux ne sont pas suffisants pour diminuer la toxicité des sédiments. Les lixiviats de sédiments stabilisés par 20% d'additifs étaient moins toxiques que le sédiment de référence. Le taux de mortalité a été réduit jusqu'à 30-40% en raison de la diminution de la concentration en éléments traces dans l'eau de percolation. Les résultats obtenus pour la stabilisation des éléments traces (Cd, Cu, Zn, Ni, As, Cr et Mo) dans un environnement naturel extérieur ont montré que l'ajout d'additifs minéraux à base de fer peut modifier efficacement la mobilité des contaminants dans le sédiment. L'efficacité du traitement est aussi étroitement liée aux caractéristiques physico-chimiques des sédiments (teneur en matière organique, pH, etc.).

Sur la base des résultats de cette thèse, la stabilisation par addition de minéraux est une approche prometteuse dans le domaine de la gestion des sédiments marins contaminés issus du dragage. Cette technique améliore la qualité chimique et écotoxicologique des lixiviats de sédiments contaminés. Cette étude démontre la faisabilité du traitement de stabilisation des sédiments marins contaminés. Les résultats obtenus démontrent clairement la diminution des concentrations en éléments traces dans les lixiviats de sédiments traités avec 20% des trois additifs considérés ainsi qu'une diminution de la toxicité. Bien que ce travail démontre la possibilité d'utiliser des sous-produits de l'industrie (résidus de bauxite) comme additif dans les sédiments marins, certaines perspectives restent à prendre en considération à la suite de ce travail.

(i) Il serait intéressant d'étudier l'efficacité à long terme du processus de stabilisation dans des expériences de terrain en utilisant un grand volume de sédiments.

(ii) Afin de fournir des informations supplémentaires, l'effet de la température, la dégradation de la matière organique, l'humidité et les cycles d'humidification et de séchage doivent être étudiées.

(iii) Des expériences de capping en utilisant les résidus de bauxite pourraient être testés pour traiter les sites de sédiments contaminés (en particulier par des polluants cationiques).

(iv) Pour accroître l'efficacité des processus de stabilisation, les résidus de bauxite peuvent être neutralisés avant l'utilisation. La sélection du traitement de neutralisation dépend du type de polluant à traiter dans les sédiments. L'eau de mer ou la neutralisation par l'acide combiné avec d'autres traitements peuvent être utilisés pour améliorer l'adsorption des éléments traces anioniques. Le coût de neutralisation dépend du type de procédé de neutralisation utilisé, par exemple la neutralisation de résidus de bauxite par l'utilisation d'acide est très coûteuse car de grandes quantités de réactifs sont nécessaires.

(v) L'utilisation d'additifs combinés avec d'autres sous-produits industriels composés de fer (laitier) ou des minéraux composites comme agents stabilisants pourrait être testée pour améliorer l'efficacité du traitement des sédiments, en particulier pour les contaminants anioniques.

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Abstract

Management of polluted marine dredged sediments is an important issue in the Mediterranean region. In this work, we aimed to study the feasibility of stabilization treatment by mixing bauxite residues (Bauxaline®, Bauxsol and Neutralized bauxaline®) with composted dredged marine sediment. The efficiency of treatment process was evaluated by monitoring the leached trace elements concentration and toxicity of sediment leachates. Preliminary sorption tests in aqueous medium indicate that good removal of As and Cd can be achieved in neutral pH. For stabilization of trace elements, adsorption results allowed to use bauxite residues (rich in Fe and Al oxides) as stabilizing agent in contaminated marine sediments. The stabilization of composted dredged marine sediment carried out in outdoor experiments by 5% and 20% of amendments confirmed that the treatment is efficient when high rate of amendments were used. The concentration of cationic trace elements decreased up to 52-83% by 20% bauxaline® and bauxsol, while 20% neutralized bauxaline® reduced up to 40-71%. The amendments were found to be less effective in case of anionic elements (As, Mo), and stabilization rate for As reached only up to 17.8% by 20% bauxsol. The labile fraction was significantly lowered and met the quality criteria defined for inert waste at 2 L/kg for all elements except Mo. Significant reduction in toxicity of sediment leachates towards marine rotifer was achieved by 20% of amendments treatment. Thus, the amendment of polluted marine sediments by bauxite residue would improve the chemical and toxicological quality of leachates and would also provide a way of promoting this type of industrial by-product.
Keywords: Dredged marine sediments; stabilization, bauxite residues, neutralization, trace elements, toxicity, rotifers

Résumé

La gestion des sédiments marins pollués dragués est une problématique dans la Méditerranée. Dans ce travail, nous avons cherché à étudier la faisabilité d'un traitement de stabilisation en mélangeant les résidus de bauxite (Bauxaline®, Bauxsol et Bauxaline® neutralisé) avec les sédiments marins de dragage pollués. L'efficacité de cette méthode de traitement a été évaluée en mesurant la concentration en éléments traces lixiviés et la toxicité des lixiviats des sédiments. Les essais préliminaires de sorption en milieu aqueux indiquent une bonne adsorption de As et Cd par les résidus de bauxite à pH neutre. Ainsi, ces résidus de bauxite (riche en oxyde de Fe et Al) ont été envisagés pour la stabilisation des éléments traces dans un sédiment marin contaminé. Une série d'expérimentation pilote a été menée, en considérant deux pourcentages d'amendement: 5% et 20%. Les résultats ont montré que la stabilisation des éléments chimiques était plus efficace lorsqu'un amendement de 20% était appliqué. L'amendement du sédiment marin avec 20% de Bauxaline® ou de Bauxsol a permis une diminution de la concentration des éléments traces cationiques lixiviés de 52 à 3%, alors que la Bauxaline® neutralisée appliquée à 20% a permis une diminution de 40 à 71%. Quel que soit l'amendement, une faible efficacité de la stabilisation a été observée pour les éléments anioniques (As, Mo). L'application d'amendements de résidus de bauxite a permis une réduction significative de la fraction labile de l'ensemble des éléments chimiques puisqu'elle satisfait aux critères de qualité définis pour les déchets inertes à 2 L / kg, excepté pour le Mo. Après un amendement de 20%, la toxicité des lixiviats a été significativement réduite. Ainsi, l'amendement de sédiments marins pollués par résidus de bauxite permettrait d'améliorer la qualité chimique et toxicologique des lixiviats et permettrait également de proposer une voie de valorisation de ce type de co-produit industriel.
Mots-clés: sédiments marins dragués, stabilisation, résidus de bauxite, neutralisation, éléments traces, toxicité, rotifères