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Alberto Ferraro

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Thèse – Tesi di Dottorato – PhD thesis

Alberto Ferraro

Optimal design and operation of HMs removal from soil by EDDS-enhanced washing

To be defended December 17th, 2015

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Abstract

The subject of the present research work is the optimization of soil-washing processes applied to heavy metal contaminated soils.

The work focuses on the whole cycle of the soil washing technology, including the possible recovery and the proper disposal of the used washing solution.

Both the design and the exploitation of a soil washing treatment are investigated, in order to maximize their efficacy, in terms of cost and process efficiency. At this aim process parameters and reactor configurations are studied in details through lab-scale tests, and the observed kinetics are simulated through mathematical modeling.

Soil samples used for the experimental activity were collected from an agricultural field located in Southern Italy, mainly contaminated by copper.

Among several Aminopolycarboxylate (APC) chelating agents, Ethylenediamine-*N*,*N'*-disuccinic acid (EDDS) was selected, for its recognized biodegradability, widely reported in literature, and its efficiency as extracting agent towards several heavy metals, including Cu that was selected as main model metal in this thesis.

Literature review allowed determining the two most important process parameters to be investigated for washing optimization. The two parameters were identified as EDDS:Cu molar ratio and liquid to soil ratio (L/S). In order to investigate the effect of these parameters on process kinetics and Cu extraction yield, batch washing tests in completely stirred tank reactor configuration (CSTR) were carried out.

EDDS:Cu molar ratio increase was found to be able to enhance process efficiency more than L/S increase. Batch tests clearly displayed a first fast kinetic step at the beginning of the treatment, followed by a second slower kinetic extraction step, which lasted until the end of the treatment. According to this observation, an empirical mathematical model based on two-kinetic terms was formulated. Model parameters were firstly calibrated and then validated using two different sets of experimental data. The derived mathematical model was useful to assess the validity of the two-kinetic steps process hypothesis, and to provide a tool for process efficiency prediction depending on EDDS:Cu molar ratio and treatment time.

Exploitation costs of the process were minimized studying different treatment configurations. In details two Plug-Flow configurations were analyzed and compared to the CSTR one. The two Plug-Flow configurations were simulated using several reactors in series, varying the hydraulic retention

time of the reactors, and fractionating the injection of the washing solution. Achieved results displayed improvements in terms of Cu extraction yield and process kinetics for the tested Plug-Flow conditions compared to the CSTR one, and showed that the use of a Plug-Flow reactor allows to reduce the amount of required washing solution.

Finally, an electrochemical process was tested for the treatment and the recovery of the spent EDDS solution. Batch tests were carried out to optimize electrochemical process parameters (e.g. current density, washing solution pH and conductivity). The recovered solution was also used for a multi-washing test. Results proved the effectiveness of the electrochemical treatment for EDDS solution recovery and its potential application as technique for EDDS-enhanced soil washing costs reduction.

Résumé

Le sujet de ce travail de recherche porte sur l'optimisation des procédés de lavage de sol appliqués au traitement des sols contaminés par des métaux lourds.

Cette étude se concentre sur le cycle complet de ce type de traitement, incluant la possibilité de réutilisation et un traitement adapté de la solution de lavage de sol utilisée.

La conception et l'exploitation d'un procédé de lavage de sol sont étudiées afin d'optimiser son efficacité, en terme de coût et d'efficacité du procédé. Dans ce but, les paramètres et la configuration du réacteur utilisé pour ce procédé sont étudiés en détail à travers des tests à l'échelle du laboratoire, et les cinétiques sont simulées par une modélisation mathématique.

Les échantillons de sol utilisés au cours de cette étude proviennent de terres agricoles du sud de l'Italie, principalement contaminées par du cuivre.

Parmi plusieurs agents chélateurs de la famille des aminopolycarboxylates (APC), il a été choisi d'utiliser l'acide éthylènediamine-N,N'-disuccinique (EDDS) pour sa biodégradabilité reconnue - largement rapportée dans la littérature - et son efficacité importante d'extraction de plusieurs métaux lourds, y compris du cuivre, qui a été choisi comme principal métal modèle au cours de cette thèse.

Le travail bibliographique a permis d'identifier les deux paramètres principaux à étudier pour l'optimisation du procédé de lavage de sol. Ce sont le rapport molaire EDDS:Cu et le rapport liquide-solide (L/S). Des tests réalisés dans un réacteur à agitation continue (RAC) en fonctionnement discontinu ont permis d'étudier l'influence de ces deux paramètres sur le rendement et la cinétique d'extraction du cuivre.

Il a été trouvé que l'augmentation du rapport molaire EDDS:Cu permet une meilleure amélioration de l'efficacité du procédé par rapport à l'augmentation du rapport L/S. Par ailleurs, les tests réalisés en mode discontinu ont clairement mis en évidence une première étape cinétique rapide au début du traitement, suivie d'une seconde étape d'extraction plus lente jusqu'à la fin du traitement. A partir de ces observations, il a été formulé un modèle empirique basé sur deux termes cinétiques. Les paramètres du modèle ont été calibrés puis validés grâce à deux séries de données expérimentales différentes. Ce modèle permet d'abord d'évaluer la validité de l'hypothèse d'un procédé reposant sur deux étapes cinétiques différentes. Cela représente aussi un nouvel outil pour prévoir l'efficacité du procédé en fonction de l'évolution du ratio molaire EDDS:Cu et du temps de traitement.

Les coûts d'exploitation du procédé ont été minimisés en étudiant différentes configurations de traitement. En particulier, deux configurations en réacteur piston ont été analysées et comparées à celle en RAC. Les réacteurs pistons ont été simulés en utilisant plusieurs réacteurs en série et en variant les temps de rétention et le fractionnement de l'injection de la solution de lavage. Comparés à la configuration en RAC, les résultats obtenus en réacteur piston ont montré une amélioration du rendement et de la cinétique du procédé d'extraction du cuivre, ainsi qu'une réduction de la quantité de solution de lavage utilisée.

Pour finir, un procédé électrochimique a été testé pour le traitement et la récupération de la solution d'EDDS utilisée. Des tests en réacteur discontinu ont permis d'optimiser les paramètres de ce procédé électrochimique (densité de courant, pH et conductivité de la solution de lavage de sol). La solution récupérée a ensuite été utilisée pour un test de multi-lavages. Les résultats obtenus ont prouvé l'efficacité du traitement électrochimique pour le recyclage de la solution d'EDDS, et permettent d'envisager l'application de cette technique pour réduire le coût des procédés de lavage de sol utilisant l'EDDS.

Sommario

La ricerca condotta nel corso del triennio di dottorato si pone lo scopo di ottimizzare, dal punto di vista tecnico e gestionale, il processo di "soil washing" applicato alla bonifica di suoli contaminati da metalli pesanti.

L'intero lavoro è stato incentrato sul ciclo completo del suddetto processo, considerando cioè anche le fasi di recupero e/o smaltimento delle soluzioni estraenti esauste.

In particolare nel corso della ricerca si è indagato sulle modalità applicabili per massimizzare l'efficacia e l'efficienza del trattamento di soil washing, attraverso uno studio, a scala banco, dei parametri di processo e delle configurazioni reattoristiche che più facilmente consentissero di raggiungere gli obiettivi prefissati.

Al contempo i risultati sperimentali sono stati impiegati per la calibrazione e la simulazione di modelli matematici in grado di simulare le cinetiche di decontaminazione.

I campioni di suolo - principalmente contaminato da rame (Cu) - impiegati per l'intera attività sperimentale, sono stati prelevati da un'area agricola sita in Sud Italia. Ai fini della rimozione del contaminante, è stato selezionato, come agente estraente, l'acido Etilene diammino-disuccinico (EDDS), appartenente alla categoria degli agenti chelanti Amminopolicarbossilici, per le sue note caratteristiche di biodegradabilità ampiamente riportate in letteratura, e per le elevate efficienze di estrazione di vari metalli pesanti, compreso Cu, rilevate nel corso di studi a varia scala basati sull'utilizzo di questo particolare agente.

L'analisi dello stato dell'arte ha consentito di individuare due principali parametri di processo da investigare per l'ottimizzazione del processo di estrazione: il rapporto molare EDDS:Cu e il rapporto liquido-solido (L/S). Al fine, dunque, di studiare l'effetto dei suddetti parametri sulle cinetiche di processo e sul tasso di estrazione del Cu, sono state condotte prove di lavaggio batch in condizioni di completa miscelazione.

I risultati ottenuti dall'incremento del rapporto molare EDDS:Cu hanno mostrato un miglioramento del processo più marcato rispetto all'incremento del parametro L/S. Inoltre, le prove condotte in modalità batch, hanno chiaramente delineato una cinetica di processo caratterizzata da una prima fase cinetica rapida, seguita da una fase più lenta. In funzione di tali osservazioni è stato possibile formulare un modello matematico empirico fondato su due termini cinetici. La calibrazione e validazione dei parametri del modello sono state effettuate tramite due set distinti di dati

sperimentali. Il modello matematico così ottenuto è stato utile per confermare la validità dell'ipotesi relativa ad un processo basato su due cinetiche, fornendo, inoltre, uno strumento previsionale delle efficienze di processo in funzione del rapporto molare EDDS:Cu e della durata del trattamento.

Lo studio di differenti configurazioni reattoristiche, da impiegare nel processo di lavaggio, è stato condotto al fine di minimizzare i costi operativi del processo stesso; in particolar modo, sono state analizzate due configurazioni con flusso a pistone e confrontate con i risultati ottenuti per la configurazione a completa miscelazione. Le due configurazioni con flusso a pistone sono state simulate, in scala da laboratorio, impiegando vari reattori in serie e facendo variare, in ognuno di essi, i tempi di detenzione e il volume della soluzione di lavaggio impiegata. I risultati ottenuti da tali prove hanno mostrato miglioramenti, in termini di cinetica del processo e tassi di estrazione del Cu, raggiunti con l'impiego delle configurazioni con flusso a pistone, rispetto alla condizione di completa miscelazione. Le configurazioni con flusso a pistone hanno inoltre evidenziato la possibilità di ridurre la quantità di soluzione di lavaggio necessaria al raggiungimento di soddisfacenti livelli di bonifica del suolo contaminato.

La parte finale dell'intera ricerca è stata incentrata sullo studio di un processo elettrochimico per il trattamento e recupero della soluzione esausta di EDDS. Tale indagine è stata condotta mediante test in condizioni batch, ottimizzando i parametri di processo (i.e. densità di corrente, pH e conduttività della soluzione di lavaggio). La soluzione rigenerata è stata, successivamente, impiegata in prove di lavaggio multiplo. I risultati ottenuti hanno comprovato l'efficacia dell'impiego del processo elettrochimico per il recupero della soluzione esausta di EDDS e, la sua potenziale applicazione come tecnica di abbattimento dei costi del processo di soil washing con impiego di EDDS.

Samenvatting

Het onderwerp van deze studie is de optimalisatie van de sanerening van met zware metalen vervuild grondwater.

De hele cyclus van de saneringstechnologie werd onderzocht, inclusief het terugwinnen van metalen en de verwerking van de gebruikte wasoplossing.

Zowel het ontwerp als de exploitatie van de bodemsanering via bodemwassen werden onderzocht om hun effectiviteit, in termen van kosten en procesefficiëntie, te optimaliseren. Daarom zijn testen op lab-schaal uitgevoerd om de procesparameters en reactorconfiguraties in detail te bestuderen, en de waargenomen kinetiek werd gesimuleerd met behulp van wiskundige modellen.

De bodemmonsters gebruikt in de experimenten werden verzameld in een agrarisch gebied in Zuid-Italië, voornamelijk vervuild met koper.

Uit verschillende aminopolycarboxylaat (APC) chelaatvormers, ethyleendiamine-N,N'-dibarnsteenzuur (EDDS) werd geselecteerd als bodemwasvloeistof vanwege zijn biologische afbreekbaarheid, uitgebreid beschreven in de literatuur, en zijn efficiëntie als extractiemiddel van verscheidene zware metalen, inclusief koper dat in dit proefschrift als hoofd modelmetaal werd geselecteerd.

Op basis van literatuuronderzoek zijn de twee belangrijkste procesparameters voor de optimalisatie van de grond saneringstechniek geselecteerd. Deze zijn de EDDS:Cu molverhouding en de vloeistof grond verhouding (L/S). Het effect van deze parameters op de proceskinetiek en koper extractieopbrengst werd zowel in batch saneringtesten als in volledig geroerde tankreactoren (CSTR) onderzocht.

Het onderzoek laat zien dat een stijging van de EDDS: Cu molverhouding de procesefficiency meer verbetert dan de L/S toename. In de batch tests werd een snelle eerste kinetische stap waargenomen aan het begin van de behandeling, gevolgd door een tweede tragere kinetische extractiestap, die duurde tot het einde van de behandeling. Aan de hand van deze observaties werd een empirisch wiskundig model op basis van twee-kinetische termen geformuleerd. The model parameters werden eerst gekalibreerd en vervolgens gevalideerd met behulp van twee verschillende sets van experimentele data. Het afgeleide wiskundig model was nuttig om de geldigheid van de twee-kinetische processtappen hypothetisch te evalueren, en om een tool voor het voorspellen van de procesefficiëntie als functie van de EDDS:Cu molverhouding en behandelingstijd uit te werken.

Verschillende behandelingsconfiguraties werden onderzocht om de exploitatiekosten van de werkwijze te minimaliseren. Twee Plug-Flow configuraties werden in detail geanalyseerd en vergeleken met een CSTR. De twee Plug-Flow configuraties werden gesimuleerd met behulp van verschillende reactoren in serie, variaties van de hydraulische retentietijd van de reactoren, en het fractioneren van de injectie van de wasoplossing. De behaalde resultaten gaven verbeteringen qua Cu extractieopbrengst en proceskinetiek voor de geteste Plug-Flow omstandigheden in vergelijking met een CSTR, en toonden aan dat het gebruik van een Plug-Flow reactor het mogelijk maakt om de hoeveelheid vereiste wasoplossing te verminderen.

Tenslotte werd een elektrochemisch proces getest voor de behandeling en het hergebruik van de EDDS oplossing. Batch proeven werden uitgevoerd om de elektrochemische procesparameters (stroomdichtheid, pH en geleidbaarheid van de wasoplossing) te optimaliseren. De teruggewonnen oplossing werd ook gebruikt voor een multi-wastest. De resultaten toonden de efficiëntie van de elektrochemische behandeling voor de regeneratie van de EDDS oplossing, alsook dat de elektrochemische behandeling de kosten van bodemwastechnieken met EDDS reduceert.

Chapter 1.

Introduction

1.1 Heavy metals contamination in soil

Heavy metals (HMs) can be generally present in soils because of natural phenomena mainly depending on the geology of the parent material that led to the soil formation (McLean and Bledsoe, 1992). Various geologic and anthropogenic activities can cause HMs amount increase in soil matrix up to harmful concentration levels for animals, plants as well as human health (Chibuike and Obiora, 2014; Vaxevanidou et al., 2008). In particular the main anthropogenic activities that can result in HM contamination of soil include industrial and manufacturing processes, use of fertilizers and/or organic manures, irrigation, improper industrial and municipal wastes disposal (Bolan et al., 2014; He et al., 2005).

All mentioned activities can lead HMs to bind with soil constituents. According to the strength of the bindings, HMs can be successively released to other environmental compartments, mainly surface and groundwater, through run-off and/or leakage phenomena. This causes exposure and bodily accumulation for plants, animals and humans through drinking and food uptake (Mulligan et al., 2001), representing a serious hazard.

Depending on the primary source of contamination, HMs can be bound to different soil components. HMs derived by anthropogenic activities are mainly present as dissolved forms in soil solution, bound to exchangeable sites of organic constituent or adsorbed on insoluble organic substances, precipitated as pure or mixed solids (McLean and Bledsoe, 1992). On the contrary, metals retained by primary and/or secondary minerals structure generally derive by natural activities (McLean and Bledsoe, 1992). The different chemical-physical form of associations between HMs and soil can strongly affect the contaminant availability (Maiz et al., 1997). It is in fact reported that geologic derived metals are mainly bound to more stable soil components (e.g. mineral matrixes of the soil) than anthropogenic derived metals that are characterized by an easier leaching from soil (Karczewska, 1996).

Moreover transport and fate of HMs in the environment strongly depend on their chemical form and speciation (Wuana and Okieimen, 2011). These latter also affect HM toxicity (Tchounwou et al., 2012), which can be more or less important for different metals. Examples are given by the higher (25-60 times) toxicity displayed by inorganic As(III) than As(V) (Pena et al., 2005). Higher toxicity and mobility is observed for Cr(VI) compared to Cr(III) (Wuana and Okieimen, 2011). Pb(II) is the more common and reactive Pb species that can form mono and polynuclear oxides and hydroxides (Evanko and Dzombak, 1997). Zn is an essential nutrient for living organisms, but it is reported that its excess can cause negative effect on humans and animals health. On the contrary Cd is a potentially toxic and non-essential element (Zhao et al., 2003).

Further effects on human health are also displayed by Hg, which affect adults nervous system (Zahir et al., 2005), and by some Ni water soluble compounds, which can be carcinogenic depending on their ability to enter into living cells (Cempel and Nikel, 2006).

As far as Cu is concerned, it is generally considered an essential element for human, plants and animals (Wuana and Okieimen, 2011). Nonetheless Cu concentration above certain threshold can be phyto-toxic (Brun et al., 1998) as well as responsible for several disease for human beings (Tchounwou et al., 2008). Furthermore Cu(II) forms inner-sphere complexes with humate components in soil resulting in very stable complexes (Wu et al., 2001).

Because of the mentioned hazards, remediation of HM contaminated soils represents a compelling priority. At the same time it also represents a complex issue, as several preliminary studies and experimental activities have to be carried out, case by case, to succeed in the remediation, and proper investigations are necessary to recommend suitable technologies for the achievement of environmental sustainable levels of contaminations.

1.2 Remediation techniques for heavy metals contaminated soil

Remediation techniques for HM contaminated sites are numerous and differentiated among them. Therefore the selection of the most appropriate one for each specific site can be quite complex (Khan et al., 2004).

Reddy et al. (1999) classified the remediation techniques according to their applicability to the saturated zone or to the vadose one. In the latter case, a further classification is possible, dividing soil remediation techniques in in-situ methods and ex-situ ones (Tables 1.1 and 1.2).

Techniques aimed at immobilizing HMs into the solid matrix are commonly used for both in-situ and ex-situ applications. Examples are given by solidification/stabilization techniques, generally based on the application of different binders, waste products or minerals (e.g. cement, red mud, zeolite) to reduce HM mobility in soils (Finžgar et al., 2006). Another possibility for soil solidification/stabilization is the vitrification technique, carried out through electrodes that are fixed into the soil to generate an high flux of thermal energy responsible for soil liquefaction and successive vitrification as consequence of the cooling down (Jankaite and Vasarevicius, 2005). Use of electrodes is also common for electrokinetic treatment of contaminated soil. In this case contaminants are removed from soil through the action of electromigration, electroosmosis, and electrophoresis transports induced by the presence of an electric field (Probstein and Hicks, 1993). A more environmental friendly and cost effective technique is the phytoremediation, consisting in

the application of green plants to reduce, contain and make harmless both organic and inorganic contaminants (Cunningham and Berti, 1993).

Table 1.1 Comparison of In-situ soil remediation technologies.

Soil remediation technique	Contaminants of applicability	Advantages	Limitations	Reference
Soil vapor extraction	VOCs; SVOCs	Large soil volume treatment with moderate costs	Low soil permeability; high groundwater table	Halmemies et al., 2003; Khan et al., 2004; Yeung and Hsu, 2002
Soil flushing	VOCs; SVOCs; fuels; pesticides; metals; radionuclides	Solubilization and desorption enhancement of contaminants from soil surface	Possible flushing solution leaching to the groundwater; low soil permeability	Alter et al., 2003; Anderson, 1993; Juhasz et al., 2003
Electrokinetics	Metals; organic compounds; radionuclides	Applicable on soils with low permeability; low power consumption	Highly affected by soil chemistry; interference due to the presence of metallic objects, foundations, rocks	Acar and Alshawabkeh, 1993; Acar et al., 1995; Page and Page, 2002; Reddy and Saichek, 2003
Bioremediation	Organic contaminants	Conversion into less toxic and more environmentally acceptable compounds; cost-effective technique	Long treatment time; site specific technique; extensive site monitoring requirement	Chawla et al., 2000; Hicks and Caplan, 1993
Soil heating	Gasoline and diesel	Process uniformity in its vertical and horizontal sweep; almost complete contaminants removal	Possible limitation due to subsurface heterogeneities	Davis, 1997; Stegemeier and Vinegar, 2001

Vitrification	Organic contaminants; metals; radionuclides	Mixed contaminants and multiple areas of applicability	Economic limitations due to high soil permeability and groundwater presence; high energy requirement	Castelo-Grande and Barbosa, 2003; Oma, 1994
Solidification/stabilization	Metals; organic compounds	Effective technology for a wide range of contaminants	Possible interference of contaminated matrix chemical composition, amount of water and ambient temperature on the solidified matrix stability; Suitable for shallow contamination	Evanko and Dzombak, 1997; Jones, 1990; Wuana and Okieimen, 2011
Phytoremediation	Metals; chlorinated solvents, petroleum hydrocarbons, PCBs, PAHs, organophosphate insecticides, explosives, and surfactants; radionuclides	Less secondary waste; applicability on a wide range of contaminants	Suitable for shallow and low concentration levels; long-lasting treatment time; food chain contamination	Khan et al., 2004; Nedunuri et al., 2000

Table 1.2 Comparison of Ex-situ soil remediation technologies.

Soil remediation technique	Contaminants of applicability	Advantages	Limitations	Reference
Soil washing	Organic compound; metal; radionuclide	Volume reduction (physical separation); effective for a broad range of contaminants	High organic matter and humic acid content (physical separation); silty/clay content excess of 30-50% (physical separation); variable efficiency depending on soil/contaminant characteristics and operational conditions (chemical separations)	Dermont et al., 2008; Friend, 1996
Solvent extraction	Organic compounds	High extraction efficiency	Water content in soil	Williamson, 1999; Wu et al., 2013
Chemical dechlorination	Chlorinated organic compounds	Contaminant toxicity decrease	High moisture and clay content	Kowalik et al., 2003; Wood, 1997
Electrokinetics	Metals; organic compounds; radionuclides	Applicable on soils with low permeability; low power consumption	Highly affected by soil/contaminant chemistry	Acar and Alshawabkeh, 1993; Acar et al., 1995; Kim et al., 2002; Pamukcu and Wittle, 1994
Thermal desorption	VOCs	High contaminant removal efficiency; short time required for proper remediation	High soil moisture content; highly abrasive feed; high clay, silt, humic content	Pavel and Gavrilescu, 2008; Sadler, 2001

Incineration	Organic compounds	Effective for a broad range of contaminants; high contaminant removal efficiency	High cost; high clay and rock content	Castelo-Grande and Barbosa, 2003; GAO Report, 1995
Vitrification	Organic compounds; metals; radionuclides	Effective for a broad range of contaminant	High costs; high energy requirement	Friend, 1996; Wuana and Okieimen, 2011
Bioremediation	Organic compounds	Cost effective; permanent elimination of contaminant	Necessity to adjust system conditions; site specific technique	Blackburn and Hafker, 1993; Boopathy, 2000
Solidification/stabilization	Metals; organic compounds	Effective technology for a wide range of contaminants	Volume increase; possible not long-term effectiveness; volatile organic contaminants content	Evanko and Dzombak, 1997; USEPA, 1993

Main mechanisms involved in phytoremediation processes for inorganic contaminants are phytoextraction and phytostabilization. This latter is preferred when contaminant extraction is not achievable (McGrath and Zhao, 2003). Despite the low costs and the reduced environmental impact, the phytoremediation can be properly applied only in the case of shallow contamination and only if the climatic conditions and the metal bioavailability are favorable (Mulligan et al., 2001).

Soil flushing and soil (chemical) washing are widely used for the remediation of HM contaminated soils. In both cases the use of an extracting agents is required. While soil washing is applied ex-situ, soil flushing is applied in-situ, which means that the extracting solutions are infiltrated into the contaminated solid matrix through surface flooding, sprinklers, leaching field etc. (Jankaite and Vasarevicius, 2005). It follows that its efficiency is strongly affected by the permeability and the heterogeneity of the soil (Friend, 1996).

1.2.1 Soil washing application for remediation of heavy metals contaminated soil

Soil washing is an ex-situ process carried out through physical-chemical separation of a wide range of contaminants (organic and inorganic) (Anderson, 1993). Physical separation systems for the remediation of HM contaminated soil are generally applied for particulate forms of contaminants, while chemical extraction is expected for non-detrital metals or ionic forms, adsorbed to the soil (Dermont et al., 2008). Physical separation is aimed at separating coarse soil particles (sand and gravel) from fine ones (clay and silt). This allows to reduce the contaminated soil volume as contaminants are mainly bound to the finest particles (Arwidsson et al., 2010). According to this, it is reported that economically feasible soil washing can be carried out for significant volume reduction achievable for clay and silt content lower than 30-35% (i.e. particles<0.063 mm) (James and Kovalick, 2000).

Chemical extraction treatments are aimed at enhancing contaminants solubility through extracting solutions in which contaminants are dissolved. Several solutions can be used for this purpose such as acid and base solutions, salts and high-concentration chloride solutions, surfactants, reducing or oxidizing agents, chelating agents (Dermont et al., 2008; Van Benschoten et al., 1997).

Of course, various extracting solutions can differently impact on soil properties according to the agent characteristics. Moreover each of them has a specific field of application. For instance, acid solutions highly enhance dissolution occurrence of soil matrix (Neale et al., 1997), while chlorinated salts have a lower effect on soil matrix (Tampouris et al., 2001). Another example is given by the use of surfactants that are more suitable for non-aqueous phase liquids and organic contaminants removal through interfacial tension reduction and solubilization enhancement (Cheah et al., 1998).

Chelating agents are generally very versatile, and represent an efficient alternative to other exctracting agents, especially in case of HM contamination (Peters, 1999). Moreover they can be applied to enhance the efficiency of other remediation techniques such as phytoremediation, soil flushing, and electrokinetic processes (Lestan et al., 2008).

The extraction through chelating agents is carried out by formation of metal-chelant water soluble complexes inactivating metal ions and avoiding further reaction with soil components or different metals (Ali et al., 2014). However many factors have to be considered to select proper chelating agents for chemical-enhanced soil washing and full-scale applications (Arwidsson et al., 2010).

1.2.2 Aminopolycarboxylate chelating agents for enhanced soil washing

Aminopolycarboxylates (APCs) represent a very widely applied chelating agents category for chemical-enhanced soil washing. APCs, as other chelating agents, can form mono, bi or polydentate ligands with HMs. The metal binding is mainly carried out by S, N and O atoms through chemical groups such as –SH, –S-S, $–NH_2$, =NH, –OH, $–OPO_3H$, or >C=O (Flora and Pachauri, 2010).

Main reactions occurring to the APC-metal complexes are represented by metal exchange, APC-metal complex adsorption, mineral dissolution, transport phenomena, degradation and redox reactions (Nowack, 2002). The various phenomena occurring in the contaminated soil-chelating solution system make the outcome of an APCs-enhanced washing not easily predictable. Moreover APCs can display different characteristics that influence their proper applicability in HM contaminated soil remediation. APCs extensively studied in the past, for their assessed efficiency for soil remediation applications, are Nitrilotriacetic acid (NTA) and Ethylenediaminetetraacetic acid (EDTA) (Elliott and Brown, 1989). More recently a strong interest in the scientific community has been focused on the use of biodegradable APCs, such as Ethylenediamine-*N*,*N'*-disuccinic acid (EDDS), in order to reduce negative environmental impact on the treated soil (Begum et al., 2012; Hauser et al., 2005).

1.3 Scope and structure of the thesis

1.3.1 Thesis scope

The present work focuses on the optimization and enhancement of the efficacy of soil washing process applied for the remediation of a HM contaminated soil. The aim was to improve soil washing applicability in its entirety (from contaminated soil collection to treated soil disposal) following an engineering approach. In order to achieve this purpose, the research focused on several aspects, and followed both an experimental approach and a theoretical one.

The entire experimentation was carried out on agricultural soil samples mainly contaminated by Cu, collected in Castel San Giorgio, a small town situated in the south of Italy (Fig. 1.1).

Fig. 1.1 Geographical position of the contaminated soil samples collection area.

Soil washing process was carried out using EDDS, considering its high biodegradability and its recognized ability to remove HMs from contaminated soils. Process performance optimization was initially carried out through experimental activities aimed at investigating extraction efficiency variation with various values of operational parameters (e.g. EDDS:Cu molar ratio and Liquid to soil ratio). Kinetic tendency obtained from the experimental activities was useful to determine a mathematical model able to predict extraction efficiency variation as a function of treatment time and EDDS:Cu molar ratio. Economical process optimization was obtained through further study aimed at investigating and determining more suitable washing configuration conditions to enhance the contaminant extraction yield and lower treatment time and EDDS volume. Finally an electrochemical treatment was tested for the treatment of spent EDDS solution. The scope of this latter part of the study was to verify the possibility of recovering and reusing a spent solution of EDDS in order to reduce the exploitation cost of the washing treatment, and to provide an environmentally safer disposal of the washing solution after the treatment.

1.3.2 Thesis structure

In order to achieve the above reported aims, the entire work was divided in several parts that constitute the various chapters of the present thesis. Fig. 1.2 schemes out chapters and structure of the present work.

Chapter 1 briefly summarizes the characteristics of HMs as soil contaminants, and briefly describes the most frequently used soil remediation technologies, focusing on soil washing.

Brief information is also given on APCs, more deeply investigated in Chapter 2. This latter represents a wide review on the operational parameters affecting the APCs-enhanced washing of contaminated soils. Chapter 2 also reports further details on technologies involved in the physical and chemical soil washing process at pilot and field scale.

Chapter 3 contains the results of a kinetic study on soil washing, carried out in CSTR conditions, varying the EDDS:Cu molar ratio and the liquid to soil ratio. Collected data are used to define, calibrate and validate a mathematical model for process efficiency prediction, which represents an useful tool for decision-making processes.

Chapter 4 reports a comparison between CSTR and two Plug-Flow washing configurations in terms of extraction yield and process kinetics. The same EDDS volume and the same treatment time are applied in all three configurations in order to determine the best washing condition for an efficient and fast soil remediation.

In Chapter 5 further attention is posed on process cost reduction, reporting the experimental results of an electrochemical treatment for the spent EDDS solution recovery and recirculation in a multi-step soil washing.

Finally general discussion and conclusions are reported in Chapter 6 to highlight the results achieved in the present work and suggest possible future perspective, improvements and investigations on APCs-enhanced washing of HMs contaminated soils.

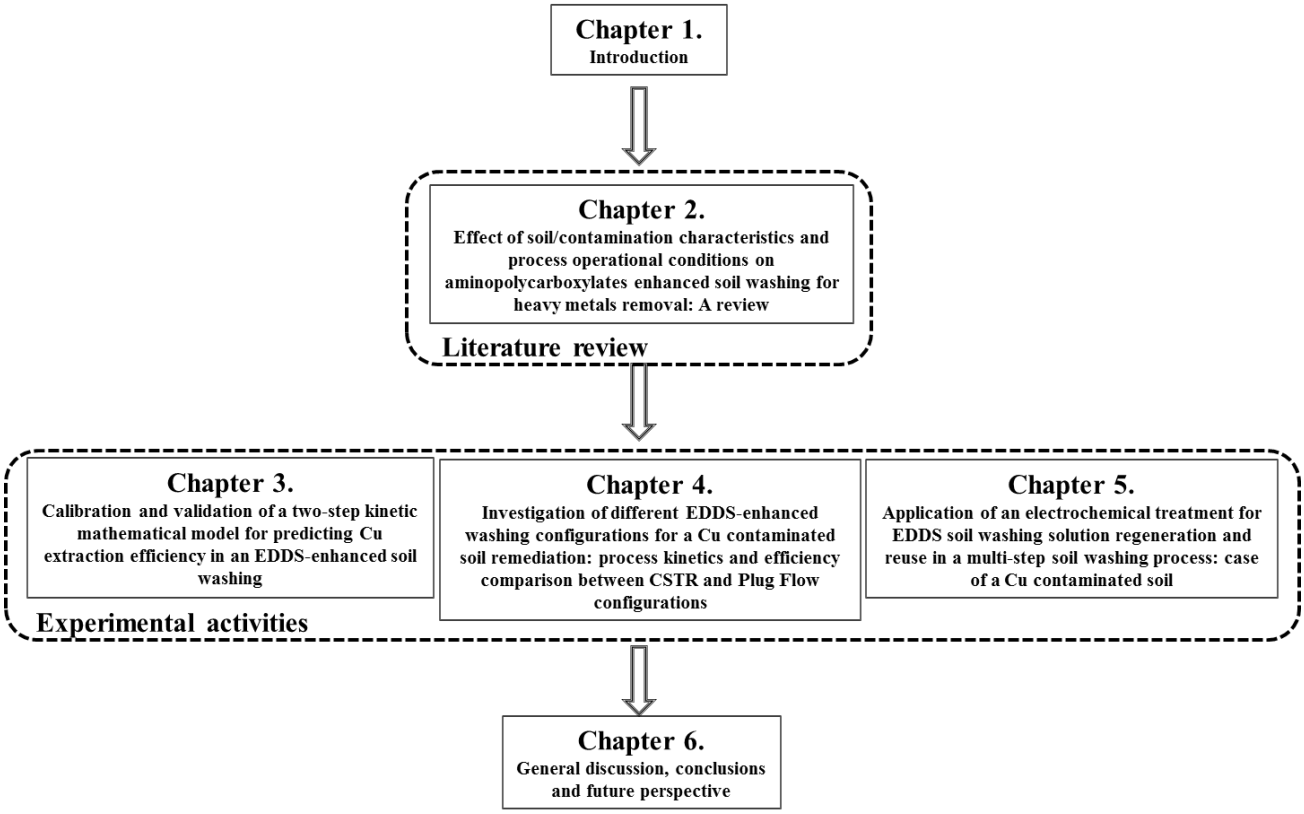

Fig. 1.2 Scheme of chapters subdivision and structure of the thesis.

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Chapter 2.

Effect of soil/contamination characteristics and process operational conditions on aminopolycarboxylates enhanced soil washing for heavy metals removal: A review

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2.1 Introduction

Soil contamination caused by HMs represents a serious threat for human health. Due to their biogeochemical mobilization, HMs can either reach the water bodies used for drinking water supply, or enter the food chain as consequence of plants uptake (Elliott and Shastri, 1999). To prevent such a risk, soil remediation of HMs contaminated sites becomes imperative.

Among many techniques (e.g. dig-and-haul and solidification/stabilization, soil flushing, phytoremediation) adopted for the remediation of HMs contaminated soils, ex-situ washing processes certainly play a primary role, and have been successfully implemented for many years because of their wide applicability and economic feasibility (Chu, 2003; Giannis and Gidarakos, 2005; Griffiths, 1995; Paff et al., 1994; Roy et al., 1994; Saponaro et al., 2002; Semer and Reddy, 1996; Tobia, 1993). Strictly speaking these processes include either a physical separation of the most contaminated soil fractions (physical-washing), or a chemical extraction of the contaminants from the solid matrix (chemical-washing), although in most cases both the physical and the chemical washing coexist (Peters, 1999).

While HMs extraction can be carried out with different chemicals, such as strong acid solutions, diluted acid solutions containing chloride salts, surfactants, reducing and oxidizing agents (Dermont et al., 2008) or chelants, these latter generally show the highest extraction efficiency and are often associated to a less destructive action on soil structure compared to the one caused by strong acids (Dermont et al., 2008).

As previously reported the most frequently used chelants are the APCs. These latter can form very stable and water soluble chelant-HMs complexes leading to the release of the contaminants from soil and avoiding its precipitation (Lestan et al., 2008). As different APCs have different characteristics, not all of them are suitable for full-scale applications of soil washing. NTA is not recommended because it is hazardous for human health (Lim et al., 2004). Diethylene triamine pentaacetic acid (DTPA) is identified as toxic and potential carcinogenetic (Neilson et al., 2003). Only EDTA and EDDS seem to be practically applicable for soil remediation, and therefore most part of the research studies developed in the last 20 years deal with them (Fabbricino et al., 2013).

The aim of the present paper is to review and compare these studies to figure out which parameters mostly affect the development of APCs-enhanced washing of HMs contaminated soils, and to determine the conditions that are able to optimize the amount of used chelants, and to minimize the cost of the process. All the experimental reports presented in this review are aiming at providing fast and wide access to literature knowledge about parameters affecting soil washing performance.

Furthermore, the gathered data can be helpful for proper and effective decision-making process related to the APCs-enhanced washing of HMs contaminated soils.

2.2 Key parameters influencing the process

Chemical washing of HMs contaminated soils is characterized by an extreme variability of the extraction yield because of the competing/synergic effect of many parameters that affect the development of the process. According to several authors (Dermont et al., 2008; Hong et al., 2008; Kim et al., 2003; Lestan et al., 2008; Meers et al., 2008; Nowack et al., 2006; Peters, 1999; USEPA, 1994, 1993; Theo C. M. Yip et al., 2009; Zou et al., 2009)of interest can be gathered into three main categories: i) parameters related to soil physico-chemical characteristics; ii) parameters related to contaminant characteristics; and iii) parameters depending on the process itself (Tsang et al., 2012).

The first group includes the soil properties that affect metal retention and mobility as well as the environmental conditions that may lead to metal leaching (Plant and Raiswell, 1983). These parameters related to soil composition are mainly represented by soil pH, particle size distribution, mineral composition, cation exchange capacity, organic matter content, presence of different inorganic contaminants, redox potential, soil temperature.

The second group of parameters includes metal characteristics (type, speciation / fractionation, concentration), as well as contamination origin (point source emission or continuous input, natural contamination or artificial contamination) and nature of the deposition (soluble or particulate).

Finally the third group includes operative parameters such as: i) washing solution pH, ii) chelant to metals and liquid to soil ratios, iii) chelant characteristics, iv) retention time, v) temperature and vi) sonication.

Apart from the formal classification indicated above none of the mentioned parameters can be considered individually. Their synergic action determines the nature of the bond between the metal and the chelant, which may vary from electrostatic to covalent (Bell, 1977), characterizing a complex more or less stable. Furthermore, the affinity between the target metal and any other cation turns out in a possible competition for the extraction by APCs. The combination of all these factors makes the prediction and the generalization of soil washing processes, in efficiency terms, a difficult task. It is necessary to discern the conditions case-by-case for a better interpretation of the problem. In such regard the analysis of literature data could be considered an useful tool.

2.3 Soil characteristics influence

Not all the soil characteristic parameters have been addressed by research studies available in the scientific literature, which generally focuses on: organic matter and humic acid content, main cations competition, soil particle size distribution, minerals and matrix constituents (Table 2.1).

Fig. 2.1 shows the main metal retention mechanisms on soil and the processes that an APC can face at the liquid-soil interface.

Table 2.1 List of soil parameters main effects on APCs-enhanced soil washing.

Soil characteristics	Parameters	Main results	Reference
Natural contaminated; Mardin silt loam	Main cations competition	NTA efficiency not affected by Ca and Fe	Linn and Elliott (1988)
Natural contaminated soil (automobile battery recycling facility)	Main cations competition	EDTA and NTA efficiency not affected by Ca and Fe	Elliott and Brown (1989)
Natural contaminated soil	Main cations competition	EDTA efficiency not affected by Ca and Fe	Brown and Elliott (1992)
Natural contaminated soil; high clay and silt content	Main cations competition	EDTA efficiency not affected by Ca and Fe	Peters and Shem (1992)
	Soil particle size distribution	High silt content reduce removal efficiency	
Artificially contaminated silty soil	Organic matter and humic acid content	Extraction efficiency affected in a in a millipond sludge and sand mixture (25% organic content)	Abumaizar and Khan (1996)
Three natural contaminated soils (clay, silt and sand) from eight U.S. Army facilities	Soil particle size distribution	Overall EDTA, DTPA and NTA extraction from a sandy soil higher than a clayey soil	Neale (1996)
Superfund soil	Main cations competition	EDTA, ADA[a] and PDA[b] extraction affected by HMs competition at retention time higher than 2.5 hours	Steele and Pichtel (1998)
Two urban contaminated soils; 69% sand, 24% silt, 7% clay (soil 1); 53% sand, 39% silt, 8% clay (soil 2)	Soil particle size distribution	Higher EDTA extraction for the soil with lower percentage of silt and clay	Tejowulan and Hendershot (1998)
Two real contaminated soils; high Pb contaminated battery recycling soil, high Zn contaminated soil	Minerals and matrix constituents	Higher Zn extraction with oxalate from dilute acid extractable soil fraction than Fe-Mn oxide soil fraction; No significant change for Pb extraction with oxalate	Elliott and Shastri (1999)
Natural contaminated and calcareous soil	Main cations competition	EDTA extraction affected by dissolution of calcite	Papassiopi et al. (1999)
Artificial contaminated goethite	Minerals and matrix constituents	Concurrent Fe extraction with HMs from adsorption goethite and amorphous iron hydroxide and from coprecipitation goethite and	Davranche and Bollinger (2000)

		amorphous iron hydroxide	
Natural contaminated and calcareous soil	Main cations competition	Optimization of the EDTA utilization and reduced dissolution of calcite Na_2Ca EDTA	Theodoratos et al. (2000)
Natural contaminated soils; sandy loam soils; 15% organic matter content	Main cations competition	EDDS extraction affected by Ca and Fe ions in acidic conditions	Vandevivere et al. (2001)
Natural calcareous contaminated soil; contamination by wastes from battery industry	Minerals and matrix constituents	Almost complete Pb extraction from a calcareous soil using EDTA	Wasay et al. (2001)
Four natural contaminated soils (lead smelter, lead mine, rifle range, battery recycling,), one artificially contaminated	Main cations competition	Higher Fe, Ca percentage extracted than Pb using EDTA	Kim et al. (2003)
Artificially contaminated acidic soil	Minerals and matrix constituents	Lower Cr extraction than Pb and Cd for the lower hydrolyzed status and sorption bond strength and larger ionic radius than Cr	Lim et al. (2004)
Three natural contaminated soils; calcaric Regosol (soil 1), non-calcareous Regosol (soil 2), Haplic Luvisol (soil 3)	Main cations competition	Significant Ca and Fe extraction using high concentration of EDTA and EDDS	Tandy et al. (2004)
Artificial contaminated soil; volcanic loamy sand	Main cations competition	Higher dissolution of Ca than Cu at equimolar EDTA:Cu ratio	Di Palma and Ferrantelli (2005)
Natural contaminated soil	Main cations competition	Possible effect on EDTA and EDDS extraction due to Ca and Fe competition	Kirpihtchikova et al. (2006)
Three natural contaminated soil; non-calcareous Regosol (soil 1), calcaric Regosol (soil 2), Haplic Luvisol (soil 3)	Organic matter and humic acid content	High percentage of Fe, Pb, Cd and Cu bound to organic matter in the last part of the test	Tandy et al. (2006)
Natural contaminated forest soil	Minerals and matrix constituents	Interference of Fe-(hydr)oxides on EDTA extraction efficiency	Chrastny et al. (2008)

Four soils; soil organic matter varying between 3.4 and 7.1%; clay varying between 2 and 13%	Main cations competition	EDDS extraction affected by competition between metals for the complexation	Koopmans et al. (2008)
	Minerals and matrix constituents	EDDS extraction affected by Fe-(hydr)oxides	
Pb-paint contaminated soil; high clay content	Organic matter and humic acid content	Decrease of mobilized Pb with increasing soil organic matter for EDTA and EDDS extraction	Sarkar et al. (2008)
	Minerals and matrix constituents	Significant negative correlation is observed between potential mobilized Pb and clay%, carbonate, total calcium and total magnesium	
Goethite, 2-line ferrihydrite, Gibbsite	Main cations competition	EDDS extraction affected by mineral dissolution and the resulting formation of Fe-EDDS and Al-EDDS complexes	Komarek et al. (2009)
Artificially contaminated soil	Main cations competition	High dissolution of Al and Fe by HMs-EDDS complexes; negligible dissolution of Ca and Mn	Tsang et al. (2009)
Artificially contaminated soil	Main cations competition	Decrease of Zn-EDDS and Pb-EDDS and increase of Cu-EDDS with time under EDDS deficiency	Yip et al. (2009a)
Two natural contaminated soils by copper-mine sites	Minerals and matrix constituents	Possible interference on the Cu extraction through EDDS due to the elevated content of Cu-bearing ore minerals	Guo et al. (2010)
Natural contaminated soil; 14.7% sand, 50.2% silt, 35.1% clay	Main cations competition	Possible interference on the Cu extraction through EDTA due to the formation content of Ca- and Fe-EDTA complexes	Voglar and Lestan (2010)
Sandy soil; artificially contaminated	Organic matter and humic acid content	Decreasing extraction of Cu, Zn and Pb with the addition of humic acid	Yip et al. (2010)
	Main cations competition	Lower Al dissolution occurrence with the use of an EDTA/EDDS mixture than EDDS or EDTA used alone; EDDS/EDTA mixture comparable Fe dissolution with the use of an EDDS/EDTA mixture and EDDS and EDTA used alone	

Natural contaminated soil; 64.6% sand, 30% silt, 5.4% clay	Main cations competition	Probable interference in Hg extraction with EDTA for the presence of Ca and Fe	Subirés-Munoz et al. (2011)
Artificial contaminated soil; 1% clay content; dissolved organic matter contamination	Organic matter and humic acid content	Different effects on EDDS extraction (excess and deficiency conditions) induced by different organic compounds (leonardite soil humic acid, Suwannee river fulvic acid, Suwannee river humic acid, Elliott soil humic acid)	Yan and Lo (2011)
Natural contaminated soil; organic-rich soil	Main cations competition	Sufficient concentration of free chelant available to avoid competition effect from the interfering ions at 10:1 chelant/metal ratio fraction	Begum et al. (2012)

[a]**β-alaninediacetic acid**

[b]**Pyridine-2,6-dicarboxylic acid**

2.3.1 Organic matter and humic acid content

Soil organic matter content is considered as one of the main factors affecting the efficiency of washing processes (Abumaizar and Khan, 1996; Yip et al., 2010). This is mainly due to the presence of high molecular weight organic substances that display a high affinity for metals and form water-insoluble metal complexes (Abumaizar and Khan, 1996; Peters, 1999). The affinity between organic substances and metals may entail a link between them (Sparks, 2003; Tipping, 2002), therefore decreasing the extraction efficiency. However the ability for complex formation with natural organic substances is not the same for all the metals and it is highly related to the stability of the newly formed complexes.

Yip et al. (2010) stated that humic acid can inhibit metal extraction because of the direct adsorption of metal-humate complexes on the soil mineral surface and because of the competition between the used APCs and the sorbed humic acid that can bind heavy metals through its acidic functional groups (Fig. 2.1). This latter phenomenon is due to the deprotonation of acid functional groups of humic acid that bind with heavy metals (Dermont et al., 2008). The Authors showed that Pb extraction by EDDS could be greatly suppressed due to high affinity of this metal towards natural organic matter, even in presence of low concentrations of humic acid. The effect is particularly pronounced because of the low stability of Pb-EDDS complexes, and the occurrence of metal exchange processes that liberate Pb for binding with humic acid (Yip et al., 2010). The concentration of EDDS in the washing solution does not seem to be a factor that can be opposed to

the affinity of Pb with organic matter. Sarkar et al. (2008) noticed a negative correlation between Pb extraction and organic matter content, for soil pH in the range of 5.5-6.1, even under EDDS excess conditions.

The competition between dissolved organic matter and EDDS affects also the removal of Cu, as reported by Tandy et al. (2006) and by Yan and Lo (2011). Tandy et al. (2006) noticed a dominance of Ni-EDDS instead of Cu-EDDS at low concentration of EDDS, due to the strong copper-binding by dissolved organic matter. The origin of natural organic matter induces different effects on the metal extraction yield (Yan and Lo, 2011). High concentration of dissolved leonardite soil humic acid involves an enhancement of Cu, Zn and Pb extraction by EDDS, maybe due to the metals-humate complexes formation and the increase of mineral dissolution. In contrast, low concentration of dissolved leonardite determines a reduction of Zn and Pb extraction efficiency most likely because of the adsorption of Zn-humate and Pb-humate onto soil particles. A comparison between dissolved river humic acid and fulvic acid showed a higher affinity of metals for this latter, maybe due to the presence of more carboxyl groups (Yan and Lo, 2011). Finally the presence of Elliot soil humic acid, provided in this case by the International Humic Substance Society (IHSS), is responsible for a relevant decrease in the efficiency of the washing process due to the increase of chelant adsorption onto soil particles (Yan and Lo, 2011).

2.3.2 Main cations competition

The mobilization through dissolution of metal ions contained in the solid matrix coexisting with the targeted pollutants may result in a decrease of the extraction efficiency by APCs (Dermont et al., 2008; Steele and Pichtel, 1998) (Fig. 2.1). The dissolution of soil (oxy)hydroxides (e.g. Fe- and Al-) can be due to the formed soluble metal-chelant complexes together with the free chelant (Komárek et al., 2009).

Then, the consequent release of cations, is responsible for the formation of soluble metal-chelant complexes which reduce the amount of the ligands available for the targeted metals (Kim et al., 2003; Koopmans et al., 2008; Subirés-Muñoz et al., 2011; Voglar and Lestan, 2010). The effect is particularly important for chelant to metal molar ratio lower than 1 (Begum et al., 2012): this reflects the necessity of APCs excess amount to ensure the adequate removal of contaminants (Lestan et al., 2008; Tandy et al., 2004).

Despite the dissolution of Mn and Ca in the presence of EDDS is negligible compared to Al and Fe dissolution (Tsang et al., 2009), it is reported a negative effect, in acidic conditions, due to Ca ions

presence, besides Fe ions, on EDDS performances (Vandevivere et al., 2001). The same effect is not observed for NTA (Elliott and Brown, 1989; Linn and Elliott, 1988) and for EDTA (Brown and Elliott, 1992; Elliott and Brown, 1989), even if $CaCO_3$ is strongly dissolved in EDTA solution for pH ranging between 4 and 5, and calcium concentration reaches very high values compared to the targeted heavy metal (Di Palma and Ferrantelli, 2005). Despite the lower degree of heavy metal complexation with EDTA (Papassiopi et al., 1999; Theodoratos et al., 2000), the lack of Ca interference can be also due to the less stable complexes that Ca forms with EDTA compared to other metals, such as Pb, Zn or Fe (Papassiopi et al., 1999).

At low chelant concentration the effect of competitive cation can also occur as consequence of exchange processes (Tsang et al., 2009; Yip et al., 2009a). A large portion of extracted metals can be dissociated from the used APCs due to metal exchange processes if the chelant is not present in large amount. The effect is instead irrelevant at high ligand/soil ratios (Kirpichtchikova et al., 2006). In order to achieve less competition for a particular chelant, and in turn, less metal exchange and metal re-adsorption chelants mixture can be involved. This is corroborated by a higher HMs extraction by EDTA and EDDS mixture compared with the individual chelant application (Yip et al., 2010).

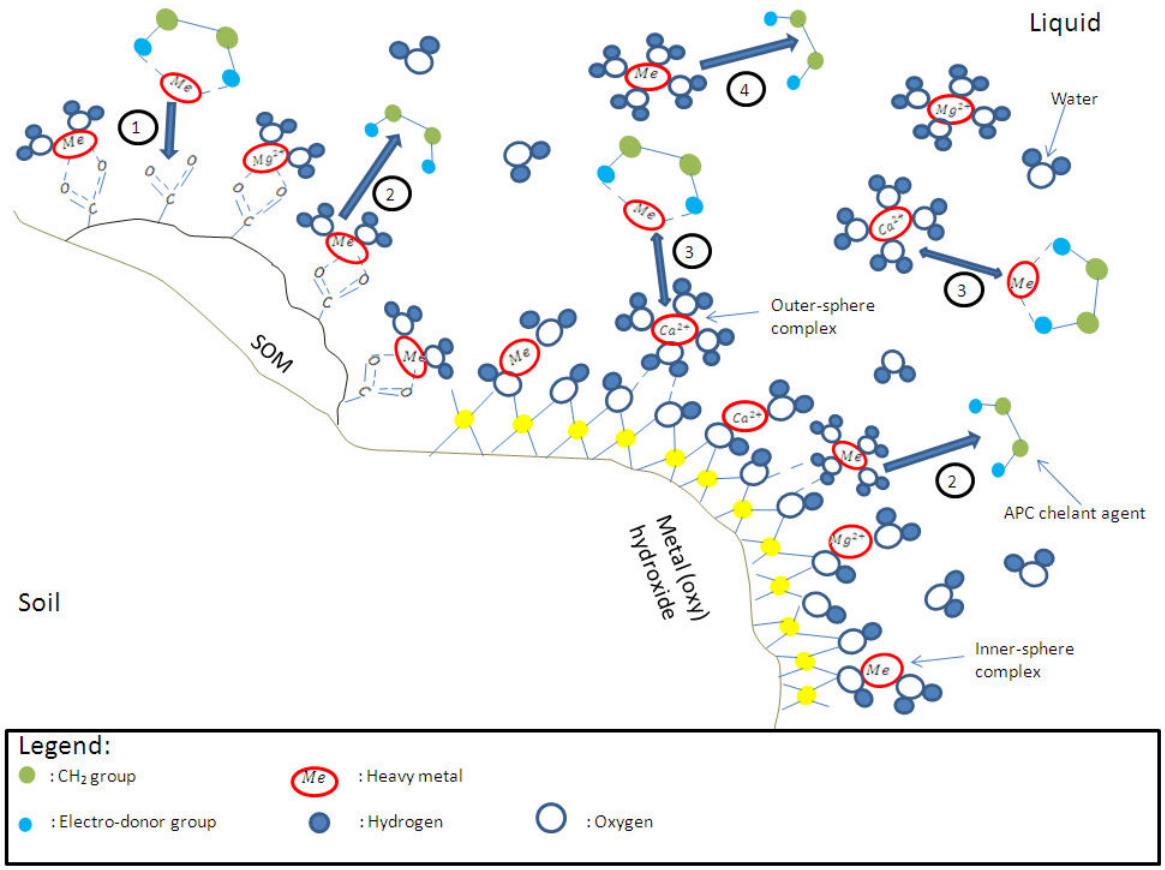

Fig. 2.1 Metals retention mechanism and processes faced by APCs on soil: 1) APC-metal complex sorption by soil organic matter's functional groups; 2) APC chelation of metal linked to organic matter/surface metal(oxy)hydroxide; 3) Ion exchange due to the main cations competition; 4) Soluble metal complexation by APC.

2.3.3 Soil particle size distribution

Although not well detailed by available research studies, it can be generally stated that the particle size distribution of the treated soil can influence the performance of soil washing processes, as the process is not efficient in presence of silt and clays (Dermont et al., 2008; USEPA, 1993). In fact, Tejowulan and Hendershot (1998) observed that, considering HMs extraction from two urban soils, removal efficiency is lower for the soil with higher silt and clay content. Peters and Shem (1992) reported that a maximum of 64.2% and 19.1% of metal is washed, respectively, from soil with high clay and high silt content, while removal of metal as Pb by several APCs is more effective from a sandy soil (Neale, 1996).

2.3.4 Minerals and matrix constituents

The interaction between HMs and solid matrix constituents such as metal oxides can influence the targeted metal mobility due to the development of cation exchange processes (Peters, 1999) or to

the embedment of the HMs in the mineral lattices or discrete particle forms (Dermont et al., 2008). This makes clear that differences in extraction efficiencies are due to the various modes of metal retention in soils (Elliott and Shastri, 1999). In order to achieve a good rate of metal removal, it is impossible not to consider factors such as the sorption bond strength, and the ionic radius, which determines the grade of diffusion of heavy metals into structural lattice of soil particles (Lim et al., 2004).

Potential mobilized Pb showed a significant negative correlation with percentage of clay and carbonate (Sarkar et al., 2008) and with its amount associated with the Fe and Mn-oxide (Elliott and Shastri, 1999). The influence of Fe-(hydr)oxides on the EDTA/EDDS extraction efficiency of various HMs (i.e. Pb, Cu, Ni, Zn, Cd) is also reported (Chrastný et al., 2008; Davranche and Bollinger, 2000; Koopmans et al., 2008).

Wasay et al. (2001) stated that EDTA complexing process may be efficient in treating calcareous soils. Tests carried out by Guo et al. (2010) showed that the extraction efficiency of Cu increases slightly by increasing the EDDS:Cu molar ratio over 1; despite the relatively low extraction efficiency is probably due to the elevated content of Cu mainly associated with the reducible and oxidisable fraction in the mine soil used for the research.

HMs metal binding with soil host phase and minerals also determine the metal fractionation, which greatly accounts for soil washing performances, as better specified later on.

2.4 HMs characteristics

Table 2.2 lists the studies related to the effect of contaminant characteristics on the process performances, which mainly concern metal speciation, metal fractionation inside the soil matrix and the typology of contamination (i.e. natural vs. artificial soil contamination).

Table 2.2 List of HMs parameters main effects on APCs-enhanced soil washing.

Heavy metal	Parameter	Main results	Reference
Pb	HMs speciation and fractionation	Lower dissolution of Fe oxides affected by its high amount in the oxide occluded and residual fractions compared to Pb mainly inside soluble and weakly sorbed fractions	Elliott et al. (1989)
Pb	Contamination typology	Independency of Pb extraction efficiency from EDTA molarity for most of the artificially contaminated soils	Cline and Reed (1995)
Pb	Contamination typology	Less HM amount expected in labile forms with the increase of the age of contamination	Van Benschoten et al. (1997)
Cd, Cr, Pb, Zn	HMs speciation and fractionation	Slow extraction resulting from an initial faster release for the weakly bound HMs	Abumaizar and Smith (1999)
Zn, Pb, Cd	HMs speciation and fractionation	HMs extraction affected by their modes of retention inside the soil	Elliott and Shastri (1999)
Cu, Zn, Pb	HMs speciation and fractionation	Extracted amount of HMs influenced by the sum of exchangeable, carbonate and reducible fractions	Peters (1999)
Pb, Ni, Zn	HMs speciation and fractionation	HMs extraction affected by their modes of retention inside the soil	Barona et al. (2001)
Zn, Pb, Cu, Cd	HMs speciation and fractionation	Cu and Zn extraction kinetics affected by their fractionation inside the soil; no consistent pattern in the different fractions yielded by Pb fractionation	Vandevivere et al. (2001)
Pb	Contamination typology	Higher Pb extraction from an artificially contaminated soil than 4 naturally contaminated soils for an ample range of EDTA-Pb stoichiometric ratio values	Kim et al. (2003)
Cu, Zn, Cd (soil 1 and 2); Zn, Pb, Cd (soil 3)	HMs speciation and fractionation	HMs higher availability for the extraction affected by their speciation inside the soil	Tandy et al. (2004)
Cu	Contamination typology	Decrease of exchangeable Cu with increasing incubation time	Arias-Estevez et al. (2007)
Pb, Zn, Cd, Cu	Contamination typology	HMs speciation affected by the incubation time; mainly HMs content decrease in the more labile fractions with the increase of incubation time	Jalali and Khanlari (2008)
Cd, Cu, Pb	HMs speciation and fractionation	High correlation between Cu in the sum of non-residual fractions with EDTA extraction	Komarek et al. (2008)

		and EDDS extraction	
	Contamination typology	Higher potential availability of anthropogenic Cu than older or background Cu	
Cu, Pb, Zn	HMs speciation and fractionation	Higher extraction of Cu and Pb than Zn that is mainly bound to the organic matter and sulfides soil fraction	Cesaro and Esposito (2009)
Cu, Zn, Pb	HMs speciation and fractionation	Considerable HMs amounts extracted from exchangeable and carbonate fractions, minor amounts extracted from organic matter and residual fractions, and also from the oxide fraction over long treatment periods	Yip et al. (2009a)
As, Pb, Cu, Cd, Zn	HMs speciation and fractionation	Consequent oxide dissolution for the extraction of oxide bound HMs through EDTA use	Qiu et al. (2010)
As, Cd, Ni, Pb, Zn	HMs speciation and fractionation	Feasible metals extraction through EDDS from Mn-oxides, organic complexes and labile exchangeable fractions; no appreciable metals extraction through EDDS from Fe-oxides or silicates	Wen and Marshall (2011)
Cu	HMs speciation and fractionation	Ineffectiveness of EDDS multi-washing test after two washing steps for the Cu content decrease in the non-detrital soil fractions	Ferraro et al. (2015)

2.4.1 HMs speciation and fractionation inside the soil

As previously mentioned, metal retention mechanisms within soils have a dramatic influence on the release of metals from contaminated soils (Barona et al., 2001; Elliott and Shastri, 1999). This retention is function of metal speciation or chemical form, which plays a vital role on leachability and bioavailability of metals (Tandy et al., 2004; van Hullebusch et al., 2005a).

Besides the speciation of HMs, their fractionation inside the soil is, as well, an essential parameter affecting the HMs mobility and, also, the efficacy of specific APCs toward different metals (Elliott et al., 1989).

In order to determine the different soil fractions involved in the HMs retention, the sequential extraction method has been investigated and utilized, through different modified versions, by several authors (Benitez and Dubois, 1999; Doelsch et al., 2008, 2006; Maiz et al., 2000, 1997; Qiang et al., 1994; Rauret et al., 1999, 1989; Ryan et al., 2008; Shan and Chen, 1993; Tessier et al., 1979; Ure et al., 1993; van Hullebusch et al., 2005b).

The aim of this experimental technique is to evaluate the amount of HMs that can be present inside the non-detrital (i.e. exchangeable, carbonate bound and reducible fractions) and detrital (i.e. oxidisable and residual fractions) parts of the soil.

As reported by different Authors in this section, HMs retained in the non-detrital fractions can be more easily removed than the ones inside the detrital fractions. It is the sum of exchangeable, carbonate and reducible fractions that approximates the portions of metal that can be dislodged by complexometric washing procedures (Peters, 1999).

In soils with a larger portion of metals associated with exchangeable and carbonate fractions it has been observed a faster and greater efficiency of the extraction process by APCs (Yip et al., 2009a) while lower extraction occurred for organic matter and sulfides bound metals (Cesaro and Esposito, 2009). In fact, the weakly bound metals can be released with a rapid initial rate into the washing solution followed by a slower release of metals with stronger bond to the soil (Abumaizar and Smith, 1999). For instance, it is reported the ineffectiveness of EDDS multi-washing after two washing steps for metal content decrease in more accessible soil fractions (e.g. exchangeable and reducible fractions) (Ferraro et al., 2015).

The extraction process can be effectively conducted for metal associated with non-detrital soil components and organically bound metals (Pickering, 1986) or generally with the sum of non-

residual fractions (Komárek et al., 2008). It follows that the association of metals to the residual fraction affects the efficiency of the washing treatment (Dermont et al., 2008).

The efficiency can be also affected by the presence of hydrous oxides that tightly bond the metal ions resulting in a not easy detachment. This result can be observed for both EDTA (Elliott and Shastri, 1999; Qiu et al., 2010), and EDDS (Wen and Marshall, 2011). To extract metals occluded within the hydrous oxides, an overdose of APCS is therefore usually required (Vandevivere et al., 2001).

2.4.2 Contamination typology (naturally and artificially contaminated soils)

Generally APCs-enhanced washing efficiency can highly vary according to the soil contamination typology. For instance, it is reported a significant enhancement of HMs extraction efficiencies when chelating agents are applied to artificially contaminated soils compared to soils with field contamination (Kim et al., 2003). Furthermore, it is also observed metals extraction yield independency from soil type and washing solution concentration (such as EDTA solution) for various kind of spiked soils (Cline and Reed, 1995).

The difference in the efficiency lies mainly on the different extraction time required: acceptable extraction threshold from a real polluted soil is achieved only after several hours or days of contact time, depending on the particular metal to be extracted, while the extraction in an artificially polluted soil is faster (Vandevivere et al., 2001). The reason for these differences is due to the age of contamination (Zhang et al., 2008). It is reported that metals often show high binding strength with soil solid phase of aged contaminated sites (Finzgar and Lestan, 2007; Pichtel et al., 2001; Zhang et al., 2008; Zou et al., 2009). This can be mainly ascribable to the formation of more stable surface complexes or solids as the contaminated soil age increases (Reed et al., 1996). In recently contaminated soils, as well as in artificially contaminated laboratory soils, metals are more labile and accessible than in soils that are historically contaminated (Jalali and Khanlari, 2008; Peters, 1999; Tandy et al., 2004). As immediate consequence, the removal efficiencies are likely to be greater in artificially contaminated soils than in soils that have been weathered for long periods of time in situ (Pichtel and Pichtel, 1997). Examples of the role that aging plays on metals binding is reported for both industrial sites (Van Benschoten et al., 1997) and vineyard soils (Arias-Estevez et al., 2007; Komárek et al., 2008).

2.5 Process parameters

While soil properties and contaminant-related parameters are fixed and unchangeable (Zou et al., 2009), process parameters can be varied to optimize the efficiency and the cost of the treatment and are therefore peculiarly important for full-scale application of the process. A list of studies focusing on process parameters is reported in Table 2.3.

Table 2.3 List of process parameters main effects on APCs-enhanced soil washing.

Agent involved	Parameter	Main results	Reference
NTA	Chelant/metal ratio	Extraction efficiency increase for Cu and for Zn increasing NTA solution molarity (range from 10^{-5} to 10^{-3} M)	Linn and Elliott (1988)
EDTA, NTA	Chelant/metal ratio	Extraction efficiency increase for Pb increasing NTA and EDTA solution molarity (range from 0.01 to 0.08M for NTA; range from 0.02 to 0.08M for EDTA)	Elliott and Brown (1989)
	Washing solution pH	Pb extraction through NTA generally higher at acidic pH; Similar Pb extraction for almost all pH values through EDTA	
	Washing solution pH	Soluble Fe(III) increase with decreasing pH; Pb extraction nearly invariant with pH	
EDTA, NTA	Chelant/metal ratio	Greater Pb release at higher chelant concentrations	Elliott et al. (1989)
	Chelant characteristics	Specific APC efficiency toward different metals not ranked by the order of magnitude of stability constants	
EDTA, sodium hypochlorite	Washing solution pH	Cr(VI) higher adsorption at low pH; Cr(III) precipitation above pH 5.5	Hsieh et al. (1989)
	Multi-step washing	Amount of removed Cr proportional to the number of washings performed	
EDTA, NTA	Washing solution pH	pH-dependence for Pb removal using NTA; Similar Pb extraction for almost all pH values through EDTA	Peters and Shem (1992)
	Chelant/metal ratio	Little effect for Pb extraction through EDTA over a high range of molarity (range from 0.01 to 0.10 M)	

HCl, HNO_3, EDTA, acetic acid, $CaCl_2$	Chelant/metal ratio	Pb removal not affected by the chelant concentration	Cline et al. (1993)
EDTA, citric acid	Washing solution pH	Higher HMs removal at acidic pH than alkaline pH	Peters et al. (1993)
HCl, EDTA, Acetic acid, $CaCl_2$	Chelant/metal ratio	Not significant differences for Pb extraction with increasing EDTA solution molarity (0.01 and 0.1 M)	Cline and Reed (1995)
PDA, EDTA	Washing solution pH	HMs recovery decrease under alkaline condition	Macaulaey and Hong (1995)
EDTA, citric acid	Washing solution pH	Decrease of HMs extraction with increasing washing solution pH	Peters (1995)
NTA, EDTA, EGTA[a], DCyTA[b]	Washing solution pH	Cd dissolution through NTA and EDTA affected by washing solution pH; Complete Cd through DCyTA and EGTA over the entire washing solution pH range	Hong and Pintauro (1996a)
HNO_3, HCl, fluorosilicic acid, citric acid, EDTA, DTPA, NTA	Washing solution pH	EDTA, DTPA and NTA typical pH extraction system at approximately 9.5, 9.5 and 8.5 respectively	Neale et al. (1997)
EDTA, NTA, SDS[c], HCl	Chelant/metal ratio	Cr and Pb maximum recovery at greater than 1:1 chelant:metal ratios	Pichtel and Pichtel (1997)
EDTA	Washing solution pH	Pb reduction in soil by lowering pH	Van Benschoten et al. (1997)
	Liquid/soil ratio	Slight Pb removal improvement when increasing L/S ratio from 5 and 20	
	Temperature	Slight Pb removal improvement when increasing temperature from 25 and 50°C	
EDTA	Washing solution pH	HMs extraction not affected by the washing solution pH	Ghestem and Bermond (1998)
EDTA, ADA, PDA, HCl	Chelant/metal ratio	HMs extraction increase with increasing APC's solution molarity (range from 0.0225 to 0.075 M)	Steele and Pichtel (1998)
EDTA, sodium metabisulfite, EDTA + sodium metabisulfite	Chelant/metal ratio	Pb extraction increase with increasing EDTA solution molarity; slight increase of Zn, Cd and Cr extraction increasing EDTA solution molarity (0.01 and 0.1 M)	Abumaizar and Smith (1999)
	Liquid/soil ratio	HMs extraction increase with increasing soil to solution ratio from 1:5 to 1:12.5; HMs extraction decrease with increasing soil to	

		solution ratio from 1:12.5 to 1:25	
	Retention time	Rapid initial release rate of all metals and slow on-going release of metals	
Oxalate, EDTA	Washing solution pH	Decreasing removal efficiency for Cd and Zn for both oxalate and EDTA with increasing pH	Elliott and Shastri (1999)
EDTA	Multi-step washing	Better extraction performance achieved with more washing cycles	Hong et al. (1999)
EDTA	Washing solution pH	Pb removal efficiency decrease through fresh EDTA and Fe-precipitated EDTA solutions with increasing pH; Pb removal efficiency increase through Fe-EDTA solutions with increasing pH	Kim and Ong (1999)
EDTA	Chelant/metal ratio	Removal efficiency increase for Pb, Zn, Cd increasing EDTA solution molarity (range from 0.025 to 0.25 M)	Papassiopi et al. (1999)
EDTA, NTA, oxalate, citrate, citranox, gluconate H_3PO_4, ammonium acetate, pH-Adjusted H_2O	Washing solution pH	Decreasing of removal efficiency with increasing pH	Peters (1999)
	Sonication	Ineffectiveness of sonication in the enhancement of heavy metal extraction efficiencies associated with chelant extraction	
EDTA	Retention time	>70% of EDTA-extracted trace metals in the first 30 min	Bermond and Ghestem (2001)
EDDS, EDTA, NTA, $CaCl_2$	Washing solution pH	Maximum metals extraction at pH 9 and efficiency decrease below pH 7 using EDDS	Vandevivere et al. (2001)
	Chelant/metal ratio	Increasing extraction for all metals with increasing EDDS:HMs molar ratio	
	Chelant characteristics	Higher extraction for EDTA than EDDS and NTA after 2 hrs; Higher or equal extraction for EDDS than EDTA and NTA after 3 days	
	Retention time	Maximum extraction achieved after 3 days for Zn, about 2 days for Pb, after 6 days for Cu	
	Temperature	Zn, Pb and Cd extraction affected by temperature increase except for Cu	
	Sonication	Heavy metals (especially Zn) extraction affected by sonication	
	Agitation	Heavy metals extraction affected by the modality agitation; greatest extraction obtained with mix by Teflon-coated four-blade procelle at 500 rpm during daily 45-	

		min periods	
D-gluconic acid, D-glucaric acid	Washing solution pH	Low extraction efficiency at neutral condition; sharp increase of extraction between pH 12 and 13	Fischer and Bipp (2002)
EDTA, EDDS, NTA	Washing solution pH	Higher extraction efficiency, for almost all metals, at pH 4 than pH 7 using EDTA and; decreasing extraction efficiency, for almost all metals, increasing pH from 3 to 8 using NTA	Ritschel (2003)
$CaCl_2$, $NaNO_3$, acetic acid, EDTA, DTPA	Washing solution pH	Increasing extractability for element with an intermediate mobility (Cu, Ni) and fixed elements (Pb, Cr) increasing acidity (effect minimized for HMs extraction on acidic soils)	Sahuquillo et al. (2003)
EDTA, NTA, DTPA	Washing solution pH	Possible readsorption of Pb and Cd on the soil solids at low pH and high chelant (EDTA) concentration	Lim et al. (2004)
	Chelant/metal ratio	No enhancement for Pb and Cd using EDTA and DTPA and marginally enhancement using NTA beyond some value of chelant/metal ratio (range from 0.001 to 0.01 M)	
	Retention time	Very rapid release of Pb and Cd within 15 min and no further enhancement after this time; Insignificant extraction for Cr within a short extraction time and steadily increase with increasing time remaining insignificant at the of 240 min extraction	
EDTA, EDDS, IDSA[d], MGDA[e], NTA	Washing solution pH	Higher removal for Cu, Zn and Pb with lower pH except for Pb extraction using EDDS where higher removal occurred at pH ≃ 8 (chelant:metal ratio = 1) and pH ≃ 5.5 (chelant:metal ratio=10)	Tandy et al. (2004)
	Chelant/metal ratio	Less pronounced pH dependence and differences between compounds at chelant:metal ratio = 10 than chelant:metal ratio = 1	
	Chelant characteristics	Different rate of extraction efficiencies for various HMs using several APCs	
Citrate, EDTA, EDDS	Chelant/metal ratio	No significance for complexation with competing ligands, desorption and cation exchange at high ligand:solids concentration ratio	Kirpihtchikova et al. (2006)
EDTA	Washing solution pH	Less pH dependence in the pH from 6 to 9 for Pb removal; More pH sensitive removal	Zhang and Lo (2006)

		for Zn with highest removal at pH 9	
	Chelant/metal ratio	Increase of Zn and Pb removal with increasing EDTA:HM ratio (range from 1 to 2)	
	Chelant characteristics	EDTA-Pb complex favourite on EDTA-Zn complex at EDTA stoichiometrically insufficient condition; Same removal for Pb and Zn at EDTA stoichiometrically excess condition	
	Retention time	High Pb and Zn removal in the first 2 hrs; No substantial increase in removal efficiency after 2 hrs	
EDTA, Citrate	Sonication	Different effects of sonication on HMs removal efficiency for EDTA and citrate extraction	Hwang et al. (2007)
EDTA, citric acid, histidine	Chelant/metal ratio	Cr and Ni extraction increase with increasing chelating agent concentration (range from 0.001 to 0.2 M for EDTA)	Jean et al. (2007)
EDTA	Washing solution pH	Decrease of Pb extraction using EDTA the pH range from 7 to 9	Hong et al. (2008)
	Sonication	Pb extraction increase with increasing pressure and number of pressure cycles	
	Multi-step washing	High Pb extraction with 3 consecutive washings	
	Agitation	Faster Pb removal using pressure-assisted extraction (agitation via gas and liquid motion) than without pressure cycles and under the same EDTA concentration conditions	
EDTA, EDDS	Chelant/metal ratio	Increase of the mobilized Pb over the study period increasing the rate of chelant addition (range from 5 to 15 mM/kg)	Sarkar et al. (2008)
	Chelant characteristics	EDTA stronger influence on solubilizing soil-bound Pb and maintaining high available Pb concentration over the experimental period than EDDS	
EDTA, SDS	Chelant/metal ratio	More noticeable influence of marine diesel fuel at lower EDTA concentration	Zhang et al. (2008)
EDDS	Chelant/metal ratio	Higher dissociation of extracted from EDDS complexes for metal exchange when EDDS is insufficient	Tsang et al. (2009)
EDDS	Chelant/metal ratio	Higher surface adsorbed concentration of EDDS and enhancement of mineral	Yip et al. (2009a)

		dissolution for high EDDS concentration	
	Chelant characteristics	Less influence of metal-EDDS stability constant than metals distribution for EDDS excess conditions	
EDTA	Washing solution pH	Decreasing removal efficiencies for As, Cd, Cu, Pb and Zn with increasing pH up to 10; Weak pH dependency of Pb removal in the range between 5 and 9; Removal efficiency increase for As and Cd with increasing pH over 10	Zou et al. (2009)
	Chelant/metal ratio	Heavy metals removal efficiency increase with increasing EDTA molarity; constant Pb and Zn removal above 0.02 EDTA solution molarity (range from 0.005 to 0.1 M)	
	Liquid/soil ratio	Steady increase for Cd, Cu and Pb removal increasing Liquid/soil ratio from 5 to 40 and no further removal increase with higher ratio	
	Temperature	Higher heavy metals removal at 75°C than 35°C	
	Sonication	Heavy metals extraction improvement after ultrasound involvement	
EDDS	Washing solution pH	High Cu extraction at pH 3 using EDDS; No significant effect on Cu extraction at pH 7 and 9	Guo et al. (2010)
	Chelant/metal ratio	Steady increase of Cu extraction with further increase of EDDS:Cu molar ratio (range from 1 to 8)	
EDTA, oxalate	Chelant/metal ratio	High percentage of chelant bound with major elements with molarities of major elements ten times or higher than trace element molarities conditions	Qiu et al. (2010)
	Chelant characteristics	Higher stability constant of complex for Na_2EDTA and metals than the corresponding complex for oxalate and metals	
EDTA	Washing solution pH	Degree of EDTA protonation and complexation with metals influenced by washing solution pH	Voglar and Lestan (2010)
	Chelant/metal ratio	Increasing Cu removal with EDTA concentration increase; Considerably decrease of removal efficiency at higher EDTA concentrations (range from 10 to 60 mmol/kg)	

EDTA, DTPA, NTA, GLDA, HEDTA[f], EDG[g], MGDA (tested in acidic aqueous solution)	Washing solution pH	Soluble presence of GLDA even at very acidic pH and in high concentrations	De Wolf et al. (2010)
EDTA, EDDS	Chelant/metal ratio	Heavy metals extraction slowing down or decrease for long treatment periods under EDDS deficiency conditions	Yip et al. (2010)
EDDS	Chelant characteristics	Initial extraction without selective heavy metals removal; selective extraction in the latter part of the kinetics according to the stability constants of the respective metal-EDDS complexes (under EDDS deficiency)	Yan and Lo (2011)
EDTA, Citric acid	Washing solution pH	Higher effectiveness of EDTA and Citric acid at pH 3 and 4 than 5, 6 and 7 especially for Cu extraction	Qi et al. (2011)
	Chelant/metal ratio	Increasing of Pb, Ni, Cu, Zn and Cd extraction with increasing chelant/metal molar ratio (range from 2 to 10)	
	Chelant characteristics	Higher extraction with EDTA and Citric acid for Cu, Pb and Zn than Ni and Cd for larger stability constants of their complexes	
	Sonication	Heavy metals extraction sharp increase with a little decline by less than 5% for one hour being not sufficient to achieve equilibrium	
NaCl, EDTA, HNO_3, KI, $Na_2S_2O_3$	Chelant/metal ratio	Low Hg extraction at lower EDTA concentration due to the competition for EDTA with cations in high concentrations (such as Ca and Fe) (range from 0.01 to 1M)	Subirés-Munoz et al. (2011)
EDDS + Brij98 (nonionic surfactants)	Sonication	Percentage of mobilized elements increase between 5 and 30 min of ultra-sonication; No significant increase for metal recovery increasing sonication time from 20 to 30 min	Wen and Marshall (2011)
EDTA, EDDS, IDSA, MGDA, GLDA, HIDS[h]	Washing solution pH	Removal efficiency decrease with increasing of washing solution pH for almost all heavy metals through different APCs extraction	Begum et al. (2012)
	Chelant/metal ratio	Higher competition of Ca and Mg with the targeted pollutants for lower chelant:metal ratio lower than 1	
	Chelant characteristics	Higher stability in solution between chelants (EDTA, EDDS, IDSA, MGDA, GLDA and HIDS) and Cu; Lower stability in solution	

		between chelants (EDTA, EDDS, IDSA, MGDA, GLDA and HIDS) and Cd; No uniform pattern for Zn, Pb and Ni	
EDTA	Washing solution pH	Lower Fe extraction with EDTA at alkaline pH than neutral pH	Voglar and Lestan (2014)

[a]Ethylene glycol-(-aminoethylether)-N, N, N', N'-tetraacetic acid

[b] 1,2-diaminocyclohexane N, N, N', N'-tetraacetic acid

[c]Sodium dodecyl sulfate

[d]Iminodisuccinic acid

[e]Methylglycine diacetic acid

[f]Hydroxyethyl ethylenediamine triacetic acid

[g]Ethanoldiglycine

[h]3-hydroxy-2, 2′-iminodisuccinic acid

2.5.1 Washing solution pH

The pH plays a significant role in the extractability of HMs from soils by APCs (Atanassova and Okazaki, 1997). Although the acid-base characteristics of hydroxyl and carboxylic surface functional groups of the soil contribute to the formation of a characteristic surface charge that plays an important role in metal retention (Abumaizar and Smith, 1999), the natural pH of soil is usually modified during the washing process. Therefore pH is listed among the main operative parameters affecting soil washing efficiency. In particular pH value is expected to affect the APCs capability of metal extraction by controlling the aqueous metal species concentration, the solubility of the chelants, the sorption/desorption processes, the ion-exchange behavior of metal ions and the re-adsorption mechanism of the newly formed metal-chelant complexes (Güçlü and Apak, 2000; Kim and Ong, 1999; Lim et al., 2004; Nowack and Sigg, 1996; Qi et al., 2011; Stumm and Morgan, 1996; Zou et al., 2009). Furthermore the stability constants of the metal-chelant complexes are pH dependent (Lestan et al., 2008). Peters (1999) reports that solution pH can influence the acid-base equilibrium reactions of the surface groups. This affects the soil retention of metals by adsorption and complexation with metal ions and also metal-chelant complexes at different degrees depending on the pH of the zero point of charge (pH_{pzc}) of the soil. It has been observed that APCs are more effective in extracting heavy metals for pH values higher than pH_{pzc} (Lim et al., 2004).

Generally the removal of metals is higher in acidic conditions (Elliott and Shastri, 1999; Peters, 1995; Peters et al., 1993; Van Benschoten et al., 1997) than in alkaline conditions (Elliott and Brown, 1989; Elliott et al., 1989; Macauley and Hong, 1995), while in alkaline condition can be observed a rather higher removal than in neutral condition, or somewhat comparable for some

metals, including Cu (Begum et al., 2012). The effect is less important for mobile metals than for those fixed or having an intermediate mobility (Sahuquillo et al., 2003). The involvement of very low pH affects negatively the extraction of HMs. EDTA shows lower efficiencies at pH 1 (Van Benschoten et al., 1997), due to the competition for binding sites between the hydrogen and the metal ions, which causes a net decrease in metal solubilization (Neale et al., 1997).

The best removal observed at acidic pH can be due to the dissolution of the organic matrix inside the soil, which results in a pronounced metal release from the oxidizable fraction that strongly links with metals. Moreover HMs hydrolysis is favored over APCs complexation at low pH values (Elliott et al., 1989; Peters, 1999). Other phenomena also contribute to this effect, including the protonation of APCs species that depends on the pH of the washing solution (Voglar and Lestan, 2010). Finally in alkaline conditions the formation of soluble compounds of APCs is favored (Fischer and Bipp, 2002).

At pH<5, carbonates are completely soluble and carbonate-bound metals become easily accessible to the chelant so that the removal is favored, although high levels of reactive iron cause a best chelant washing of solids under alkaline conditions able to keep Fe(III) insoluble (Vandevivere et al., 2001). In fact, lower iron extraction occurs at alkaline pH compared to neutral pH (Voglar and Lestan, 2014).

If low pH prevents from the competition between Ca or Mg cations and APCs (Elliott et al., 1989; Hong et al., 2008), it is also stated that low pH value can favors metal-APCs readsorption by soil solids (Lim et al., 2004), so extractions at pH 7 are considered to represent an optimal compromise between trace metal complexation and macro-element complexation (Ritschel, 2003).

It is interesting to notice that pH influence is not univocal, confirming that extraction efficiency is highly variable depending on the interaction between different parameters. For example Pb removal efficiency is less pH dependent, in the pH range 6-9 (Peters and Shem, 1992; Zhang and Lo, 2006), than Zn removal efficiency (Zhang and Lo, 2006). Cu extraction by EDDS does not seem to be dependent on pH values, most likely because Cu-EDDS complexes are stable in a wide range of pH (Guo et al., 2010; Tandy et al., 2004). A similar effect can be noted in presence of EDTA, whenever dosed in large excess respect to the stoichiometric requirements (Ghestem and Bermond, 1998). Cr(VI) has a higher adsorption at low pH and Cr(III) precipitates above pH 5.5 (Hsieh et al., 1989). As and Cd, usually present in anionic forms, are favorably desorbed at high pH because most of soil colloids have net negative charges (Hong and Pintauro, 1996a; Zou et al., 2009). In the acidic conditions generated by Glutamic acid-N,N-diacetic acid (GLDA) due to the aqueous acid in the

soluble state, which remains in solution over a wide range of concentration than the other chelants, the efficiency of extraction is higher (De Wolf et al., 2010).

Therefore, the optimal pH value has to be assessed case by case, considering several chemical phenomena that can affect the extraction.

2.5.2 Chelant/metal and liquid/soil ratio

APCs concentration during the soil washing determines the chelant/metal ratio that generally has to be above 1 to give a satisfactory extraction (Elliott and Brown, 1989; Jean et al., 2007; Tandy et al., 2004) or even in several-fold excess (Linn and Elliott, 1988). This is mainly due to the possible competition of different compounds for the available chelant complexing sites, that is particularly important for chelant:metal ratio equal to one, as already observed (Begum et al., 2012; Kirpichtchikova et al., 2006; Qiu et al., 2010). An overdose of APCs is also required whenever the metal is occluded within the mass of iron oxyhydroxides (Vandevivere et al., 2001). Increasing the rate of chelant addition generally increases metal mobilization (Abumaizar and Smith, 1999; Elliott et al., 1989; Sarkar et al., 2008).

EDTA, when present in excess, results to be a powerful extractant of trace metals (Pichtel and Pichtel, 1997; Voglar and Lestan, 2010; Wen and Marshall, 2011), characterized by a metal removal linearly increasing with chelant concentration (Papassiopi et al., 1999; Zhang and Lo, 2006).

Low concentration or chelant deficiency can cause a lower extraction, due to the already mentioned competition of the other metals such as Ca and Fe with the chelating agent (Subirés-Muñoz et al., 2011) and the dissociation from chelant with a re-adsorption of extracted HM due to the metal exchange with other contaminants on the soil surface (Lo et al., 2011a, 2011b; Tsang et al., 2009; Yip et al., 2010, 2009a). Moreover, the low chelant concentration makes more noticeable the detrimental effect on HMs extraction of other contaminants, usually organic, that can be present in the soil (Zhang et al., 2008).

For some HMs, including Pb (Cline and Reed, 1995; Cline et al., 1993; Peters and Shem, 1992; Qi et al., 2011), the extraction does not enhance or marginally enhance with increasing dosage of EDTA, DTPA and NTA as consequence of re-adsorption phenomena of complexes onto the soil (Lim et al., 2004). Further reasons can be either the high content of metal-bearing ore minerals

present in the soil (Guo et al., 2010) or the use of dosages above the soil requirements (Elliott and Brown, 1989; Steele and Pichtel, 1998; Zou et al., 2009).

Metal extraction is generally independent on chelant concentration during the first hour of extraction, while the removal is significantly affected by concentration as reaction time increases (Steele and Pichtel, 1998). Such a result can be explained considering the release of weakly-bound metals that occurs at the beginning of the process while, as the time increases, the necessity of high chelant concentration to hinder oxyhydroxides occluding metals and main cations competition, becomes predominant.

Mixed effects on different metals can be observed due to the variation of the liquid to soil ratio (Tandy et al., 2004; Vandevivere et al., 2001; Yan et al., 2010; Zou et al., 2009). Decreasing the liquid to soil ratio (L/S ratio), results in the decrease of the extraction efficiency for cadmium, chromium, zinc and lead (Abumaizar and Smith, 1999). Especially for Pb extraction, it has been observed a low effect with L/S variation (Van Benschoten et al., 1997) or an independence with the same parameter at the same chelant/metal molar ratio (Tsang et al., 2012).

Besides lead, a steadily increase is also reported for L/S ratio ranging from 5 to 40, although no further improvement is obtained when the ratio becomes higher for many metals such as copper, zinc, cadmium and arsenic (Zou et al., 2009). On the other hand, Tsang et al. (2012) reported a copper extraction decrease with increasing L/S ratio, contrasting with the zinc extraction increase maybe due to a change in the concentration of counter ions in solution or organic matter dissolution.

2.5.3 Chelant characteristics

The main parameter that characterizes a chelant is the stability of the metal-chelant complexes in solution that is considered the key issue for the applicability of APCs-enhanced washing of HMs contaminated soils (Begum et al., 2012; Vandevivere et al., 2001). The evaluation of stability constant for metal-ligand complexes can be carried out through two different categories of methods that can be based on direct determination or on a separation step involvement (Xing and Beauchemin, 2009). Direct evaluation methods were carried out by several authors through potentiometric, polarographic and spectrophotometric methods (Ernst et al., 1975; Ghomi and Mazinani, 2013; Luther et al., 1996; Matusinović and Filipović, 1981; Shtacher, 1966; Tella and Obaleye, 2010). Methods involving separation step instead were generally carried out through techniques such as ultrafiltration and ion exchange chromatography coupled with equipment for elements detection (e.g. atomic spectrometry, inductively coupled plasma mass spectrometry)

(Nifant'eva et al., 1999; Pitluck et al., 1987; Wacker and Seubert, 2014; Xing and Beauchemin, 2009).

Table 2.4 lists the values of different stability constants of metal-chelant complexes reported in literature by several Authors.

The order of magnitude of stability constants can be used to rank different APCs according to their general efficacy but not to rank the efficacies of a specific APC toward different metals because this latter is also influenced by the metal speciation in a given matrix (Elliott et al., 1989).

Moreover, stability constants can have limited significance for predicting the speciation in systems with various cations where the amount of captured ligands by metal ion depends on the product of the stability constant multiplied the free metal ion concentration (Nowack, 2002). Some experiences report the higher extraction of Cu, Pb and Zn with EDTA compared to Ni and Cd mainly because of the larger stability constants of their complexes (Qi et al., 2011). However EDTA shows, for all metals, higher stability constant than other ligands (Qiu et al., 2010). Compared to EDDS, EDTA-Ca^{2-} interacts faster with negatively charged solid particles than EDDS-H^{3-} and this fact speed up metal extraction (Vandevivere et al., 2001). Generally it is observed a better Cu removal by EDDS than EDTA and a better Pb removal by EDTA than EDDS (Tandy et al., 2004). EDTA has a relatively stronger influence on solubilizing soil-bound Pb and maintaining a high available Pb concentration (two to six time higher) over the experimental period than EDDS (Sarkar et al., 2008).

Stability constant of metal-chelant acquires more or less importance according to chelant concentration and type. In case of EDTA deficiency condition it is possible to observe selective HMs extraction due to the stability-constant of the complex, while this does not happen with EDTA concentration higher than the stoichiometric requirement (Zhang and Lo, 2006). In case of EDDS dosed in defect respect to the stoichiometric requirements, HMs removal turns out to be more related to the stability constants of the complexes than to metal distribution in the latter part of extraction process (Yan and Lo, 2011). The opposite is found when EDDS is dosed in excess (Yip et al., 2009a). Besides the nature of ligand, other parameters affecting stability constant values are represented by type of solvent, temperature and ionic strength (Durrani, 2011; Janrao et al., 2014; Zaid et al., 2013). This further suggests the high dependence of metal-ligand complexes stability constant with experimental conditions involved for its determination.

Table 2.4 Stability constants of Metal-APCs chelant complexes.

HMs	APCs	Stability constants (log K)	Ionic strenght (M)	Temperature (°C)	References
Cd	NTA	6.4	0.1	25	Linn and Elliot (1988)
		9.5-10.1	Not reported	Not reported	Hong and Pintauro (1996b); Vandevivere et al. (2001)
	EDTA	16.5	0 (Qiu et al., 2010)	18 (Qiu et al., 2010)	Hong and Pintauro (1996b); Ghestem and Bermond (1998); Tejowulan and Hendershot (1998); Elliott and Shastri (1999); Vandevivere et al. (2001); Zou et al. (2009); Qiu et al. (2010); Begum et al. (2012); Voglar and Lestan (2014)
			0.1 (Begum et al., 2012; Voglar and Lestan, 2014)	25 (Elliott and Shastri, 1999; Begum et al., 2012; Voglar and Lestan, 2014)	
			1 (Elliott and Shastri, 1999)		
	EGTA	16.7	Not reported	Not reported	Hong and Pintauro (1996b)
	DCyTA	19.2	Not reported	Not reported	Hong and Pintauro (1996b)
	EDDS	10.8	Not reported	Not reported	Vandevivere et al. (2001)
		10.9	0.1	20	Begum et al. (2012)
		12.70	0 (Tandy et al., 2006; Koopmans et al., 2008)	Not reported	Tandy et al. (2006); Koopmans et al. (2008)
	IDSA	8.33	0.1	25	Begum et al. (2012)
	MGDA	10.61	0.1	20	Begum et al. (2012)
	GLDA	10.31	0.1	25	Begum et al. (2012)

	HIDS	7.58	0.1	25	Begum et al. (2012)
	Gluconate	1.15 (weak acid/neutral pH)	Not reported	Not reported	Fischer and Bipp (2002)
		15.6 (strongly alkaline pH)	Not reported	Not reported	Fischer and Bipp (2002)
Cr(III)	NTA	-	0.1	25	Linn and Elliot (1988)
	EDTA	23.4	0.1	25	Jean et al. (2007)
Cu	NTA	12.7-12.94	0.01 (Ritschel, 2003) 0.1 (Linn and Elliott, 1988; Tandy et al., 2004)	25 (Linn and Elliott, 1988; Ritschel, 2003; Tandy et al., 2004)	Linn and Elliot (1988); Hong and Pintauro (1996b); Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004)
	EDTA	18.78-18.8	0 (Qiu et al., 2010) 0.1 (Tandy et al., 2004; Kirpichtchikova et al., 2006; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Begum et al., 2012) 0.01 (Ritschel, 2003)	18 (Qiu et al., 2010) 20/25 (Kirpichtchikova et al., 2006) 25 (Ritschel, 2003; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Begum et al., 2012)	Hong and Pintauro (1996b); Ghestem and Bermond (1998); Tejowulan and Hendershot (1998); Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004); Di Palma and Ferrantelli (2005); Kirpichtchikova et al. (2006); Udovic and Letsan (2007); Zou et al. (2009); Voglar and Lestan (2010); Qiu et al. (2010); Yip et al. (2010); Qi et al. (2011); Wen and Marshall (2011); Begum et al. (2012)

	17.8	Not reported	Not reported	Sahuquillo et al. (2003)
EGTA	17.8	Not reported	Not reported	Hong and Pintauro (1996b)
DCyTA	21.3	Not reported	Not reported	Hong and Pintauro (1996b)
	17	Not reported	Not reported	Xiaofeng et al. (2006)
EDDS	18.4-18.5	0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004; Kirpichtchikova et al., 2006; Udovic and Lestan, 2007; Arwidsson et al., 2010; Begum et al., 2012)	25 (Ritschel, 2003; Udovic and Lestan, 2007; Begum et al., 2012) 20/25 (Kirpichtchikova et al., 2006)	Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004); Kirpichtchikova et al. (2006); Udovic and Lestan (2007); Arwidsson et al. (2010); Yip et al. (2010); Wen and Marshall (2011); Yan and Lo (2011); Begum et al. (2012)
	≃19	Not reported	Not reported	Guo et al. (2010)
	20.46	0 (Tandy et al., 2006; Koopmans et al., 2008)	Not reported	Tandy et al. (2006); Koopmans et al. (2008)
IDSA	12.7	0.1 (Tandy et al., 2004; Begum et al., 2012)	25 (Begum et al., 2012)	Tandy et al. (2004); Begum et al. (2012)
MGDA	13.88	0.1 (Tandy et al., 2004; Arwidsson et al., 2010; Begum et al., 2012)	20 (Begum et al., 2012)	Tandy et al. (2004); Arwidsson et al. (2010); Begum et al. (2012)
GLDA	13.03	0.1	25	Begum et al. (2012)
HIDS	12.58	0.1	25	Begum et al. (2012)
Gluconate	2.15 (weak acidic/neutral pH)	Not reported	Not reported	Fischer and Bipp (2002)

		18.3 (strongly alkaline pH)	Not reported	Not reported	Fischer and Bipp (2002)
	NTA	11.5	0.1	25	Linn and Elliot (1988)
	EDTA	18.4	0.1	25	Begum et al. (2012)
		20.1	0.1	25	Jean et al. (2007)
		16.8	Not reported	Not reported	Xiaofeng et al. (2006)
Ni	EDDS	18.36-18.50	0 (Tandy et al., 2006; Koopmans et al., 2008) 0.1 (Begum et al., 2012)	25 (Begum et al., 2012)	Tandy et al. (2006); Koopmans et al. (2008); Begum et al. (2012)
	IDSA	11.68	0.1	25	Begum et al. (2012)
	MGDA	11.99	0.1	20	Begum et al. (2012)
	GLDA	12.74	0.1	25	Begum et al. (2012)
	HIDS	11.3	0.1	25	Begum et al. (2012)
	Gluconate	1.82 (weak acidic/neutral pH)	Not reported	Not reported	Fischer and Bipp (2002)
Pb	NTA	11.3-11.8	0.01 (Ritschel, 2003) 0.1 (Linn and Elliott, 1988; Tandy et al., 2004)	25 (Linn and Elliott, 1988; Ritschel, 2003)	Linn and Elliot (1988); Elliott and Brown (1989); Hong and Pintauro (1996b); Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004)
	EDTA	17.7-18.8	0 (Vaxevanidou et al., 2008; Qiu et al., 2010) 0.01 (Ritschel, 2003)	18 (Qiu et al., 2010) 20/25 (Kirpichtchikova	Elliott and Brown (1989); Hong and Pintauro (1996b); Ghestem and Bermond (1998); Tejowulan and Hendershot (1998);

			et al., 2006)	Elliott and Shastri (1999); Papassiopi et al. (1999); Theodoratos et al. (2000); Vandevivere et al. (2001); Ritschel (2003); Sahuquillo et al. (2003); Tandy et al. (2004); Kirpichtchikova et al. (2006); Finzgar and Lestan (2007); Chrastny et al. (2008); Sarkar et al. (2008); Vaxevanidou et al. (2008); Zou et al. (2009); Qiu et al. (2010); Yip et al. (2010); Qi et al. (2011); Begum et al. (2012); Voglar and Lestan (2014)
		0.1 (Tandy et al., 2004; Kirpichtchikova et al., 2006; Finzgar and Lestan, 2007; Begum et al., 2012; Voglar and Lestan, 2014) 1 (Elliott and Shastri, 1999)	25 (Elliott and Shastri, 1999; Ritschel, 2003; Finzgar and Lestan, 2007; Vaxevanidou et al., 2008; Begum et al. 2012; Voglar and Lestan, 2014)	
EGTA	14.6	Not reported	Not reported	Hong and Pintauro (1996b)
DCyTA	19.7	Not reported	Not reported	Hong and Pintauro (1996b)
EDDS	12.7-14.46	0 (Tandy et al., 2006; Koopmans et al., 2008) 0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004; Kirpichtchikova et al., 2006; Arwidsson et al., 2010; Begum et	20 (Begum et al., 2012) 20/25 (Kirpichtchikova et al., 2006) 25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004); Kirpichtchikova et al. (2006); Tandy et al. (2006); Koopmans et al. (2008); Sarkar et al. (2008); Yip et al. (2009a); Arwidsson et al. (2010); Yip et al. (2010); Yan and Lo (2011); Begum et al. (2012)

			al., 2012)		
	IDSA	9.75	0.1 (Tandy et al., 2004; Begum et al., 2012)	25 (Begum et al., 2012)	Tandy et al. (2004); Begum et al. (2012)
	MGDA	12.1	0.1 (Tandy et al., 2004; Arwidsson et al., 2010; Begum et al., 2012)	20 (Begum et al., 2012)	Tandy et al. (2004); Arwidsson et al. (2010); Begum et al. (2012)
	GLDA	11.6	0.1	25	Begum et al. (2012)
	HIDS	10.21	0.1	25	Begum et al. (2012)
	Gluconate	2.13 (weak acidic/neutral pH)	Not reported	Not reported	Fischer and Bipp (2002)
		16.7 (strongly alkaline pH)	Not reported	Not reported	Fischer and Bipp (2002)
	NTA	10.5-10.7	0.01 (Ritschel, 2003)	25 (Linn and Elliot, 1988; Ritschel, 2003)	Linn and Elliot (1988); Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004)
			0.1 (Linn and Elliot, 1988; Tandy et al., 2004)		
Zn		17.5	1 (Elliott and Shastri, 1999)	25 (Elliott and Shastri, 1999)	Hong and Pintauro (1996b); Tejowulan and Hendershot (1998); Elliott and Shastri (1999)
	EDTA		0 (Qiu et al., 2010)	18 (Qiu et al., 2010)	Ghestem and Bermond (1998); Papassiopi et al. (1999); Theodoratos et al. (2000); Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004); Kirpichtchikova et
		16.44-16.5	0.01 (Ritschel, 2003)	20/25 (Kirpichtchikova et al., 2006)	
			0.1 (Tandy et al., 2004; Kirpichtchikova et	25 (Ritschel, 2003; Finzgar and	

		al., 2006; Finzgar and Lestan, 2007; Begum et al., 2012; Voglar and Lestan, 2014)	Lestan, 2007; Begum et al., 2012; Voglar and Lestan, 2014)	al. (2006); Finzgar and Lestan (2007); Zou et al. (2009); Qiu et al. (2010); Yip et al. (2010); Qi et al. (2011); Begum et al. (2012); Voglar and Lestan (2014)
	16.36	0.1	25	Davis and Singh (1995)
	18.0	0 (Vaxevanidou et al., 2008)	25 (Vaxevanidou et al., 2008)	Vaxevanidou et al. (2008)
EDDS	13.4-15.34	0 (Tandy et al., 2006; Koopmans et al., 2008) 0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004; Kirpichtchikova et al., 2006; Arwidsson et al., 2010; Begum et al., 2012)	20 (Begum et al., 2012) 20/25 (Kirpichtchikova et al., 2006) 25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004); Kirpichtchikova et al. (2006); Tandy et al. (2006); Koopmans et al. (2008); Arwidsson et al. (2010); Yip et al. (2010); Yan and Lo (2011); Begum et al. (2012)
IDSA	9.88	0.1	25	Tandy et al. (2004); Begum et al. (2012);
MGDA	10.98	0.1 (Tandy et al., 2004; Arwidsson et al., 2010; Begum et al., 2012)	25 (Begum et al., 2012)	Tandy et al. (2004); Arwidsson et al. (2010); Begum et al. (2012)
GLDA	11.52	0.1	25	Begum et al. (2012)
HIDS	9.76	0.1	25	Begum et al. (2012)

	Gluconate	1.70	Not reported	Not reported	Fischer and Bipp (2002)
	DTPA	18.29	0.1	25	Davis and Singh (1995)
Fe(II)	EDTA	14.3	0.1 (Finzgar and Lestan, 2007; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Voglar and Lestan, 2014)	25 (Finzgar and Lestan, 2007; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Voglar and Lestan, 2014)	Finzgar and Lestan (2007); Udovic and Lestan (2007); Voglar and Lestan (2010); Voglar and Lestan (2014)
		16.0	0.1	25	Vaxevanidou et al. (2008)
	NTA	15.9	0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004)	25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004)
Fe(III)	EDTA	27.2-27.7	0 (Vaxevanidou et al., 2008)	25 (Vaxevanidou et al., 2008)	Nowack (2002); Vaxevanidou et al. (2008)
		26.5	1 (Elliott and Shastri, 1999)	25 (Elliott and Shastri, 1999)	Elliott et al. (1989); Van Benschoten et al. (1997); Elliott and Shastri (1999)
		25.1- 25.5	0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004; Kirpichtchikova et al., 2006; Finzgar and Lestan, 2007; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Voglar and	20/25 (Kirpichtchikova et al., 2006) 25 (Ritschel, 2003; Finzgar and Lestan, 2007; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Voglar and Lestan, 2014)	Ghestem and Bermond (1998); Vandevivere et al. (2001); Ritschel (2003); Sahuquillo et al. (2003); Tandy et al. (2004); Kirpichtchikova et al. (2006); Finzgar and Lestan (2007); Udovic and Lestan (2007); Chrastny et al. (2008); Voglar and Lestan (2010);

			Lestan, 2014)		Yip et al. (2010); Voglar and Lestan (2014)
	EDDS	22.0	0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004; Kirpichtchikova et al., 2006)	20/25 (Kirpichtchikova et al., 2006) 25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004); Kirpichtchikova et al. (2006); Xiaofeng et al. (2006); Yip et al. (2010); Yan and Lo (2011)
		23.68	0 (Tandy et al., 2006; Koopmans et al., 2008)	Not reported	Tandy et al. (2006); Koopmans et al. (2008)
	IDSA	15.2	0.1	Not reported	Tandy et al. (2004)
	MGDA	16.5	0.1	Not reported	Tandy et al. (2004)
	NTA	6.4	0.01 (Ritschel, 2003) 0.1 (Linn and Elliott, 1988; Tandy et al., 2004)	25 (Linn and Elliott, 1988; Ritschel, 2003)	Linn and Elliot (1988); Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004)
		8.2	Not reported	Not reported	Hong and Pintauro (1996b)
Ca			0 (Qiu et al., 2010)	18 (Qiu et al., 2010)	
	EDTA	10.6-10.7	0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Voglar and	25 (Ritschel, 2003; Udovic and Lestan, 2007; Voglar and Lestan, 2010; Voglar and Lestan, 2014)	Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004); Udovic and Lestan (2007); Qiu et al. (2010); Voglar and Lestan (2010); Voglar and Lestan (2014)

			Lestan, 2014)		
		10.81	0.1	20/25	Kirpichtchikova et al. (2006)
		10.59	Not reported	Not reported	Di Palma and Ferrantelli (2005)
		11.4	Not reported	Not reported	Guclu and Apak (2000)
		12.20-12.44	0 (Vaxevanidou et al., 2008)	25 (Vaxevanidou et al., 2008)	Papassiopi et al. (1999); Theodoratos et al. (2000); Chrastny et al. (2008); Vaxevanidou et al. (2008)
	EGTA	10.9	Not reported	Not reported	Hong and Pintauro (1996b)
	DCyTA	12.3	Not reported	Not reported	Hong and Pintauro (1996b)
	EDDS	4.2-4.58	0.01 (Ritschel, 2003) 0.1 (Tandy et al., 2004)	25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003); Tandy et al. (2004)
		4.7-4.72	0.1 (Kirpichtchikova et al., 2006)	20/25 (Kirpichtchikova et al., 2006)	Kirpichtchikova et al. (2006); Xiaofeng et al. (2006)
		6.34	0 (Tandy et al., 2006; Koopmans et al., 2008)	Not reported	Tandy et al. (2006); Koopmans et al. (2008)
	IDSA	4.3	0.1	Not reported	Tandy et al. (2004)
	MGDA	6.97	0.1	Not reported	Tandy et al. (2004)
Mg	NTA	5.4-5.5	0.01 (Ritschel, 2003)	25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003)
	EDTA	10.60	Not reported	Not reported	Papassiopi et al. (1999)

		8.7-8.83	0.01 (Ritschel, 2003)	25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003)
	EDDS	5.8	0.01 (Ritschel, 2003)	25 (Ritschel, 2003)	Vandevivere et al. (2001); Ritschel (2003); Xiaofeng et al. (2006)
		7.77	0 (Tandy et al., 2006)	Not reported	Tandy et al. (2006)
	NTA	7.4	0.01	25	Ritschel (2003)
Mn	EDTA	13.6-13.87	0.01 (Ritschel, 2003) 0.1 (Voglar and Lestan, 2014)	25 (Ritschel, 2003; Voglar and Lestan, 2014)	Papassiopi et al. (1999); Ritschel (2003); Voglar and Lestan (2014)
	EDDS	10.77	0 (Tandy et al., 2006; Koopmans et al., 2008)	Not reported	Tandy et al. (2006); Koopmans et al. (2008)
		8.95-9.0	0.01 (Ritschel, 2003)	20 (Ritschel, 2003)	Ritschel (2003); Xiaofeng et al. (2006)
	EDTA	18.90	Not reported	Not reported	Papassiopi et al. (1999)
		19.1	Not reported	Not reported	Yip et al. (2010)
Al	EDDS	12.9	0.1 (Koopmans et al., 2008)	Not reported	Koopmans et al. (2008); Komarek et al. (2009); Yip et al. (2010); Yan and Lo (2011)
	NTA	12.7	Not reported	Not reported	Vandevivere et al. (2001)
Hg	EDTA	21.8	Not reported	Not reported	Vandevivere et al. (2001)
	EDDS	17.5	Not reported	Not reported	Vandevivere et al. (2001)
Co(II)	EDTA	18.2	Not reported	Not reported	Nowack (2002)

Co(III)	EDTA	39.8	Not reported	Not reported	Nowack (2002)

2.5.4 Retention time

Contact time is of course one of the process parameters that mostly affects the effectiveness of the extraction process (Vandevivere et al., 2001) and it is generally involved in several mathematical models for simulation of HMs kinetic release in APCs-enhanced washing process.

For instance, time-dependent change in EDDS extraction efficiency was correlated to the HMs concentration variation in soil fractions (Yip et al., 2009b). The Authors suggested an empirical equation with the following form integrated as function of time:

$$E_{metal}(t) = \frac{C_0 - [C_1 + C_2 + C_3]}{C_0}(100\%) \qquad (2.1)$$

E_{metal} was the EDDS extraction efficiency, t (h) was the time, C_0 (mmol kg^{-1}) was the total metal concentration and C_1, C_2 and C_3 (mmol kg^{-1}) were representing the metal concentration bound to exchangeable + carbonate, oxide, and organic matter + residual fractions respectively. In Eq. (2.1) the generic C_i term was expressed as a function of fast and slow extraction and its final form was described as follows:

$$C_i(t) = f_i C_{i0} e^{-k't} + (1 - f_i) C_{i0} e^{-k''t} \qquad (2.2)$$

f_i was a dimensionless term for the proportion of fast extraction of the corresponding fractions, C_{i0} (mmol kg^{-1}) was the initial concentrations of the corresponding fractions while k' and k'' (h^{-1}) were the apparent first-order rate constants of the fast and slow extraction respectively.

Similarly Bermond et al. (1998) suggested a first-order reaction model based on two terms related to labile and non-labile metals:

$$Q = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} \qquad (2.3)$$

Q was the metals amount extracted at time t, C_1 and C_2 were in this case metals amount in labile and non-labile forms respectively, while k_1 and k_2 were their associated kinetic constant.

Further work focused on the comparison of three mathematical models for experimental kinetic data analysis (Yu and Klarup, 1994). The three models involved in the work of Yu and Klarup (1994) were multiple first-order (or pseudo-first-order) reactions model, diffusion model and two constant model (Eqs. 2.4-2.6) which their analytical solutions were expressed respectively as follows:

$$C = C_0\alpha(1 - e^{-k_1 t}) + C_0(1 - \alpha)(1 - e^{-k_2 t}) \quad (2.4)$$

$$\frac{C_t}{C_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{\frac{-Dn^2\pi^2 t}{a^2}} \quad (2.5)$$

$$C = At^B \quad (2.6)$$

Similarly to Eq. (2.2), terms in Eq. (2.4) were defined as follows: C_0 was total sorbate amount that can be released at equilibrium, t was the time, α was the fraction of sorbate amount that can be released in the fast reaction (indicated with 1) and the general k_i was the first order rate coefficient for each reactive site i. In Eq. (2.5) C_t was the concentration in the solution at time t, C_∞ was the concentration at equilibrium condition, *a* was the particle radius, D was the diffusion coefficient. Finally, in Eq. (2.6) C was the concentration of desorbed metal in solution, t the time, A and B were constants. It can be observed that kinetic models are mainly based on two-step kinetic extraction characterized by a faster HMs release occurring at the beginning of the washing process followed by a slower extraction efficiency.

The release can be so rapid to reach the equilibrium within 15 min (Abumaizar and Smith, 1999; Bermond and Ghestem, 2001; Lim et al., 2004; Steele and Pichtel, 1998). In most cases the HMs removal process achieves up to 90% of the total extraction efficiency in the first hours (Zhang and Lo, 2006), although this result is extremely variable as function of the percentage of the metal weakly bound to the soil (Abumaizar and Smith, 1999). Successively the extraction is influenced by the amount of HMs linked with the detrital fraction characterized by strongest bonds with contaminants. In this phase the extraction increases very slowly, and no sensible improvement can be observed increasing the reaction time from 24 to 144 hours (Kirpichtchikova et al., 2006).

2.5.5 Temperature

Compared to other process parameters the temperature hardly affects that much the efficiencies of the soil washing process. Slight removal improvement can be observed by increasing the temperature in a wide range, from 8 to 48°C (Vandevivere et al., 2001). Higher efficiencies can be achieved only at very high temperature values, around 75°C (Zou et al., 2009), mainly because of the release of the Fe oxide bound metal (Van Benschoten et al., 1997).

2.5.6 Sonication

The involvement of ultra-sonication can be exploited to enhance the performance of soil washing (Zou et al., 2009). It has been stated that this performance enhancement can be due to the acceleration of the surface cleaning of soil particle and improving the leaching of metal (Mason, 2007; Sandoval-Gonzalez et al., 2007) and the particle fracture under repeated compression and decompression cycles as well (Hong et al., 2008). Ultrasound can affect the process with a sharp acceleration of heavy metals extraction kinetics (Qi et al., 2011). The pressure-assisted extraction can reach efficiency comparable to process without pressure cycles or involving oscillation in less time (10-15 min) (Hong et al., 2008; Qi et al., 2011). In some case the efficiency increases, depending on sonication time, reaching a maximum in a very short time (12 min) (Hwang et al., 2007), thereafter a further increase in sonication time, for example from 20 to 30 min, only slightly enhances the HMs removal (Wen and Marshall, 2011).

Pressure and number of pressure cycles is reported to influence the metal extraction (Hong et al., 2008). In fact at 150 psi, the extracted amount increases rapidly with cycles at low number of cycles (e.g., 10-20) but diminishes at higher number of cycles (e.g., 40-60). With the same number of pressure cycles, metal extraction increases with increasing pressure and becomes stable around 150 psi whereas results at 200 psi and beyond have not show any significant improvement over those at 150 psi (Hong et al., 2008). The achievement of boiling point with short daily sonication improves the metal extraction as well (Vandevivere et al., 2001).

On the other hand, it is also reported that sonication has been ineffective in enhancing the heavy metal extraction efficiency (Peters, 1999), likely due to the readsorption of metals onto the soil during the solid/liquid separation phase for the analysis.

2.5.7 Multi-step washing and agitation

Multi-step washing (MSW) can improve the extraction efficiency. Contaminant amount washed out from the soil is proportional to the number of washing steps performed and to the amount of extracting agents used (Hong et al., 1999; Hsieh et al., 1989).

An increased HMs extraction with successive 1 hour washings compared to a 5 hours single step washing has been observed (Steele and Pichtel, 1998). Moreover if compared to a single washing process, MSW allows to reduce the concentration of used APCs (Hong et al., 2008).

Experiments carried out without sufficient agitation show hampered extraction even after prolonged exposure to high chelating agent concentration (Hong et al., 2008). As observed by Vandevivere et al. (2001), greatest extraction was obtained when the soil slurry was intensively mixed with a Teflon-coated four-blade propeller at 500 rpm during daily 45 min periods, while the conventional rotary shaking at 140 rpm increased the extraction of all metals by 10 percentile points.

2.6 Pilot/full scale soil washing systems and affecting parameters

Soil washing systems involved in pilot and full scale application for semi-batch and continuous washing can be mainly divided in two groups i) physical and ii) chemical technologies (Dermont et al., 2008). In the next subsections physical and chemical methodologies in pilot and full scale soil washing are reported as well as main parameters affecting these techniques.

2.6.1 Pilot/full scale physical systems for soil washing

The involvement of physical techniques is mainly focused on the separation of generally cleaner higher size particles (gravels and sands) from the more polluted finest particles (silt and clay) (Mulligan et al., 2001). As a consequence HMs can be concentrated in smaller amount of soil (Dermont et al., 2008) and this can lead to operational costs decrease.

Among several techniques involved in physical separation the ones widely applied are based on hydrodynamic classification and gravity concentration. Hydrodynamic classification can be generally carried out through various technologies such as hydrocyclones, screw and fluidized bed classifiers (Anderson et al., 1999; Hempei and Thoeming, 1999; Van Benschoten et al., 1997; Wang, 2004). Hydrocyclone technology allows particle settlement to the apparatus circumference through centrifugal forces while drag forces affect soil particles due to radial flow to the central part of the hydrocyclone (Werther et al., 2001). Differently soil particle separation in screw classifier is based on the Stokes Law and settlement velocity is depending on the diameter of particles (Anderson et al., 1999). Finally fluidized beds are generally involved as elutriation systems for particle separations (Dermont et al., 2008). It is reported that hydrocyclone system can properly separate particles size higher than 5-150 μm while particles size higher than 50 μm represents a suitable range for elutriation systems (USEPA, 1995). Finally particle greater than 250 μm can be generally separated by screw classifier (Anderson et al., 1999).

Gravity systems lead to soil particles separation based on particle characteristics (i.e. density, shape, size, weight) and jig, spiral concentrators and shaking tables are equipments mainly involved

(USEPA, 1995). Among these characteristics particle density turns out to be the more significant as high density difference between contaminant and soil particles is fundamental for an effective separation (Mann, 1999). Suitable particle sizes are reported for gravity separation systems: higher than 150 μm for jigs, 75–3000 μm for spiral concentrators and shaking tables (USEPA, 1995).

Attrition scrubbing systems can be generally involved to improve the physical separation process (Marino et al., 1997). This is achieved by abrasion of particles that allows removal of adhered fine particles from the coarse sand ones (Anderson et al., 1999).

Further physical treatment can be made through flotation systems for particle sizes ranging from 5 to 500 μm (USEPA, 1995). This system bases its operation on air bubbles introduction in the suspension and effective separation performance can be achieved for high hydrophobicity of the particle surfaces (Vanthuyne et al., 2003). Then it can be required involvement of suitable surfactant to increase particles hydrophobic properties (Mann, 1999).

Magnetic techniques can be also involved in physical separation treatment of contaminated soils and they are based on magnetic susceptibility characteristics of metals and common soil minerals (Rikers et al., 1998). Drums, belts and grates are conventionally devices involved in magnetic separations (Oberteuffer, 1974). However general classifications of magnetic devices can be made according to various criteria i) medium carrying the ore (i.e. dry and wet), ii) system requirements (i.e. iron removal, valuable magnetic constituents removal, deleterious magnetic impurities removal, etc.), iii) way of magnetic field generation (i.e. permanent magnets, electromagnets with iron yoke, resistive solenoids, superconducting magnets), iv) magnitude and gradient of the magnetic field (i.e. low-intensity, high intensity and high gradient magnetic separators) (Svoboda, 2004).

Further group of separation techniques is represented by electrostatic separation processes based on particles electrical conductivity although they are poorly reported in literature due to their rare and limited application (Dermont et al., 2008).

2.6.2 Pilot/full scale chemical systems for soil washing

Chemical soil washing for ex-situ treatment can be divided in two main categories that are represented by i) heap and vat leaching, ii) agitated leaching (Gupta and Mukherjee, 1990).

Heap leaching is generally a simple technique where excavated soil is mounded on a treatment area (Finzgar and Lestan, 2006) making it an economical option for large scale applications (Finzgar and

Lestan, 2007). This configuration can be carried out through continuous extracting agent flow through the soil maximizing the metal contaminants removal (Tampouris et al., 2001).

In vat leaching configuration the contaminated soil is excavated and placed in an agitated vessel (Hanson et al., 1992). Soil washing in this case can be carried out through a countercurrent extracting agent flow as an upward or downward percolation according to the flow direction (Gupta and Mukherjee, 1990). More commonly vat leaching is applied for continuous washing involving an extracting solution flowing through a series of vessels (Gupta and Mukherjee, 1990).

Finally agitated leaching is considered a highly aggressive extraction method (Bricka et al., 1999) where contaminated soil and extracting agent are mixed for a certain treatment time (Oldshue, 1983). This technique is generally preferred to heap or vat leaching when solids mean porosity prevents the extraction solution flow through contaminated soil interstices (Gupta and Mukherjee, 1990). In this configuration metals solubilization continues until equilibrium condition achievement after which no more extraction can be observed (Bricka et al., 1999).

2.6.3 Parameters affecting pilot/full scale soil washing systems

Effects of the various parameters listed in the present work can be generally addressed to the performance variation of pilot/field scale chemical systems previously reported. Additional consideration can be made for soil porosity and flow rate of the extraction solution in heap and vat leaching systems. In fact these two parameters could affect proper contaminated soil/washing solution contact condition and suitable treatment time for proper remediation yield achievement.

Parameters mainly affecting pilot/field scale physical systems are represented by soil characteristics as well as contamination typology.

For instance, physical separation techniques can achieve higher efficiency for metal-bearing particles than sorbed metal and metal contamination extended to all soil particle size fractions (Dermont et al., 2008). Different separation efficiency can be displayed also if contamination is occurring in mineral phases (Xu et al., 2014). According to this also soil mineralogy determination can be fundamental to predict physical techniques efficiency (Mercier et al., 2001) as HMs can be retained with different binding strength depending by soil mineral composition.

According to the operational way of the physical techniques reported it can be assumed that soil particles characteristics (i.e. soil matrix heterogeneity, density differences between soil matrix and

metal contaminants, magnetic properties, and hydrophobic properties) can generally affect the various separation technologies at various extent (Williford and Bricka, 2000).

However it is reported that particle size distribution can mainly influence physical separation techniques performance because these latter can properly works on specific particle size range. Then involvement of single technique can be often insufficient for achievement of proper soil clean-up goal as soil is generally characterized by wide range of particle size (USEPA, 1995).

2.7 Conclusions

Despite the asserted good removal efficiencies which can be generally obtained, different operational conditions can influence the washing method and can even make ineffective the chelant extraction properties. Indeed, the involvement of several parameters makes the results of soil washing process different case by case and strictly depending on the different soil properties. Therefore the knowledge of literature experiences can help to make previsions about the final removal efficiency, identifying the most suitable conditions for the APCs-enhanced washing of any specific soil contaminated by HMs.

According to the experimental studies reviewed in this paper it is possible to conclude that:

- None of the parameters influencing the process should be considered individually as all of them are mutually correlated;
- The characterization of the solid matrix and contamination is essential in order to identify case by case the most suitable operational conditions for the remediation process;
- A decision-making path, subsequent to the identification of the case of study, is necessary to determine and select proper washing conditions. Fig. 2.2 shows an example of decision tree that represents a possible way to fulfill a cost-effective and environmental sustainable process for specific soil and contamination characteristics.

Finally, sustainability and efficacy of properly optimized APCs-enhanced washing can be displayed through a) lower deterioration of soil characteristics after treatment, b) involvement of reduced amount of chelating agents, c) decrease of process costs and d) lower treatment time required to achieve sustainable contamination levels. These improvements can enhance soil washing performance in order to further increase its competitiveness among various techniques involved for contaminated soil remediation.

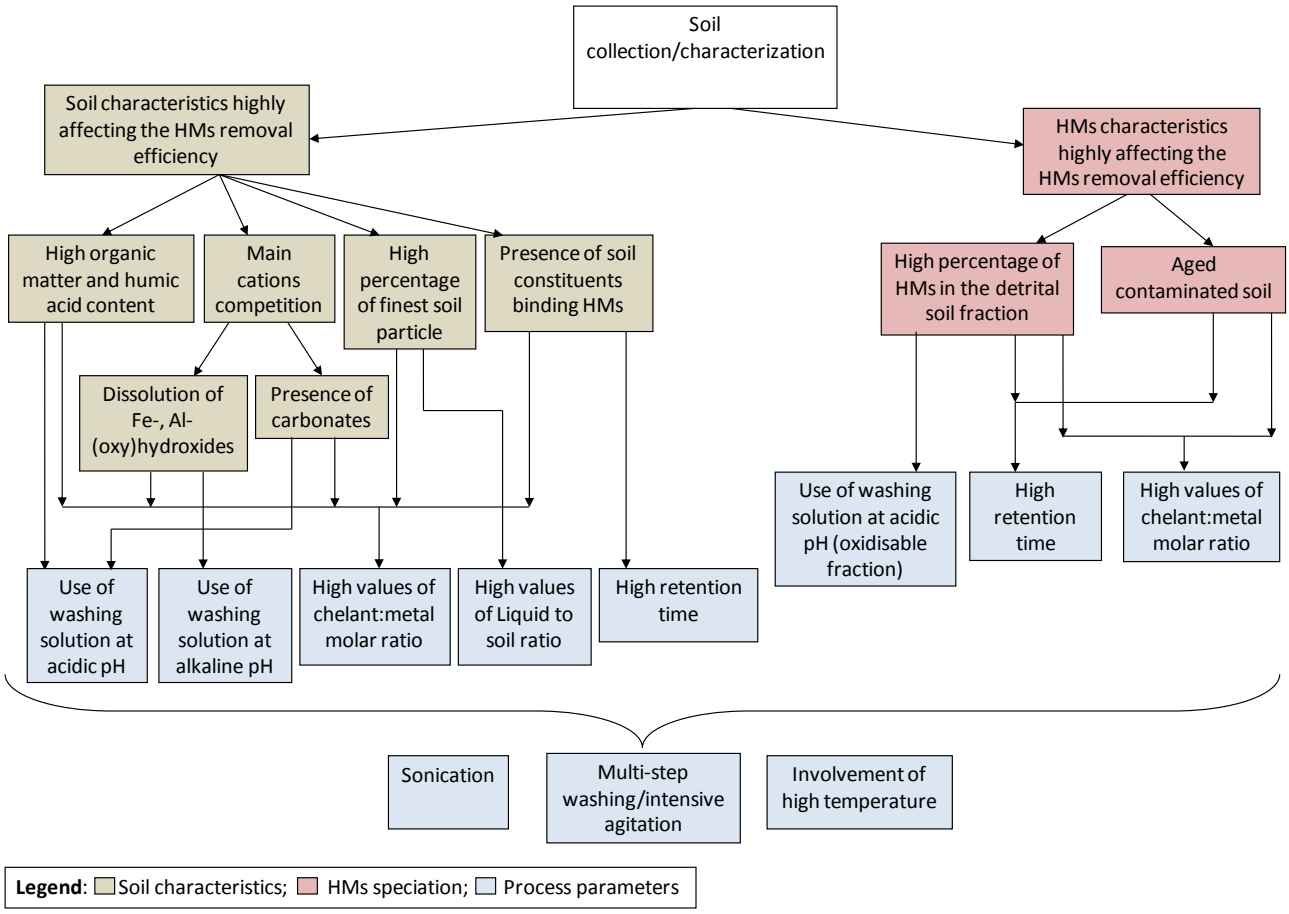

Fig. 2.2 Decision tree for an APCs-enhanced washing.

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Chapter 3

Calibration and validation of a two-step kinetic mathematical model for predicting Cu extraction efficiency in an EDDS-enhanced soil washing

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3.1 Introduction

In chapter 2 it was reported that multiple parameters contribute to the efficiency of soil washing process aiming at HMs extraction. Furthermore it was shown that these parameters can be mainly grouped into: i) soil characteristics (e.g., particle size), ii) metal chemistry (e.g., crystallinity, exchangeability, water solubility, metal speciation), and iii) extractant chemistry and processing condition (Peters, 1999).

Among these, only the latter can be varied by the operator to optimize the efficiency and minimize the cost of the treatment. The conditions that can be controlled include the HM-to-extracting solution molar ratio, liquid-to-soil (L/S) ratio, extracting solution pH and chemistry, retention time, temperature, agitation, and washing configurations. Of these factors, the molar ratio between the HMs and the extracting solution (mainly chelant agents) and the liquid-to-soil ratio have been investigated the most. Generally, it has been shown that an increase in the chelant addition enhances the mobilization of metals (Elliott et al., 1989; Sarkar et al., 2008). A decrease in the HM extraction has also been observed for decreasing values of the L/S ratio (Abumaizar and Smith, 1999). Despite these general results, soils can be highly variable and it is necessary to consider their solid matrix and contamination properties for proper decision-making practices about the remediation process.

For this purpose, mathematical models able to simulate the process can contribute to predict the process performances and support decision making for process optimization. Similar examples in the literature include studies on a soil flushing process aimed at modeling the transport of ethylenediaminetetraacetic acid (EDTA)-HMs chelates (Friedly et al., 2002; Kedziorek et al., 1998; Samani et al., 1998; Tsang et al., 2007). Another report described an empirical equation for the time-dependent change in the ethylenediamine-N,N'-disuccinic acid (EDDS) extraction efficiency correlated to a change in metals concentrations in different soil fractions (Yip et al., 2009).

The present work focuses on the kinetics of a soil washing process applied to Cu-contaminated soil using EDDS. This ligand was selected among several aminopolycarboxylate chelating agents for its reported biodegradability (Fabbricino et al., 2013; Hseu et al., 2013; Jones and Williams, 2001; Lingua et al., 2014) and high Cu extraction capacity (Begum et al., 2012; Yip et al., 2010). Several long kinetic batch soil washing tests were conducted at five different values of the EDDS-Cu (M) molar ratio and L/S ratio in order to determine the Cu extraction kinetic trends under different operational conditions.

The resulting data were used to define a mathematical model to describe the kinetic correlation between the Cu mobilization efficiency and the studied operational parameters. This model was

calibrated and later validated with two different sets of data to assess its suitability. The resulting model has potential for prediction of soil washing performance and as a tool to determine optimal operational conditions.

3.2 Materials and methods

3.2.1 Soil metal content characterization

Contaminated soil samples used in the present work were collected from an area located in Castel San Giorgio (Italy) formerly devoted to agricultural activities.

Soil matrix mineralization was conducted through microwave-assisted acid digestion (USEPA, 1995) using a Milestone START D microwave oven. Acid solutions from mineralization tests were then filtered through 0.45 μm fiberglass filters, diluted and stored at 4°C prior analysis. This treatment aimed at determining the total Cu content as well as the amount of main competitor cations (i.e. Ca, Mg, Fe, Mn).

Characterization in terms of Cu fractionation was performed through a modified BCR (Community Bureau of Reference) three-step sequential extraction (Pueyo et al., 2008) to determine its concentration in the non-detrital (exchangeable and reducible) and detrital (oxidizable and residual) fraction of the soil.

3.2.2 Prior preparation of glassware, soil samples, and EDDS washing solutions

Prior to batch mode soil washing treatment, the collected soil samples were sieved at 2 mm to focus the entire study on the treatment of the finest fraction of the soil.

To remove the field moisture, the samples were dehydrated by maintaining them under a vacuum condition until the soil samples reached a constant weight. Hygroscopic salts (e.g., anhydrous silica and calcium chloride) were added to the vacuum drier chamber separately to the soil samples in order to enhance the moisture content removal. Fresh EDDS (Sigma Aldrich, 35% concentrated) was used to prepare the washing solutions. The latter were made by adding the appropriate EDDS volume to deionized (DI) water in order to achieve the selected M ratio for the batch soil washing experiments.

Glassware was kept overnight in a 2% HCl acid bath and then washed with DI water before each experimental test.

3.2.3 Batch soil washing kinetic tests

Batch soil washing tests were performed in a 500 ml glass beaker reactor that was properly closed on the top by Parafilm® layer to avoid evaporation of the washing solution during the treatment time. Moreover, the same tests were carried out in dark conditions to prevent the occurrence of photo-degradation phenomenon of EDDS washing solution during the soil treatment. Continuous flow stirred-tank reactor (CSTR) conditions were simulated through an accurate mix using ISCO jar test equipment at 150 rpm. In order to obtain long-duration kinetic trends, all tests were conducted over a retention time of 96 hrs. Sample volumes of 10 ml were collected during the experiment using a 50 ml plastic syringe at 1, 3, 6, 18, 24, 48, and 96 hrs. The samples were centrifuged at 4600 rpm for 20 min in an IEC CENTRA GP8R centrifuge to separate the washed soil from the spent washing solution. Then, the solid phase was discharged while the liquid phase was filtered using 0.45 μm fiberglass filters. The filtered solutions were stored at 4 °C until analysis. The pH of the washing solution was measured at each sampling time to check its evolution using a pH meter (Orion 420A$^+$, Thermo). Initial soil pH was also determined in a mixture with a soil:distilled H_2O ratio=1:2 (w/v). Tests were conducted at five different values of the M ratio and L/S ratio in order to define the kinetic trend of Cu removal from soil based on variations in these two operational parameters.

At L/S=10, the molar ratios tested were 1:1, 10:1, 20:1, 30:1, and 50:1. At M=10, the L/S ratios tested were 5, 15, 25, 35, and 45. All tests were performed in triplicate and an analysis aiming at HM detection was conducted through atomic adsorption spectrometry (AAS) using a Varian Model 55B SpectrAA (F-AAS) equipped with a flame (acetylene/air) and a deuterium lamp for background correction.

3.2.4 Mathematical model

A mathematical model was developed to investigate the dependence of the Cu extraction efficiency on the treatment time while varying the M ratio. This model was calibrated and then validated with

two different experimental data sets in order to prove its suitability for the prediction of EDDS-enhanced washing efficiency for Cu-contaminated soil.

3.2.4.1 Mathematical model calibration

A mathematical model calibration was performed in order to determine the values of the model parameters and to investigate their dependence on the experimental time. To accomplish this, a fitting was conducted using four sets of experimental data (M=1, 10, 30, and 50 at L/S=10). The same set of data was used to calibrate a mono-step and a two-step kinetic model for comparison and to assess the best suitability for soil washing efficiency prediction.

The determination of the model parameters was made by minimizing the normalized root mean square error (NRMSE), as shown below:

$$NRMSE = \frac{\sqrt{\frac{\sum_{i=1}^{K}\left(y_i - y_i'\right)^2}{K}}}{y_M} \tag{3.1}$$

K represents the number of observed values, y_i are the simulated values for each i, y_i' are the observed values, and y_M is the average of the observed values. The NRMSE represents a standardized alternative to the root mean square error index (RMSE) used to assess the agreement between model prediction and experimental data around the mean value of the observed data (Janssen and Heuberger, 1995). In the present work NRMSE was involved instead of RMSE in order to obtain index values not depending on the experimental data magnitude. Suitable agreement between experimental and predicted values is achieved for NRMSE values approaching 0.

The model parameter values obtained at different M values were then used to investigate the model dependence on the M ratio itself and the mathematical expressions of the model parameters. The latter were also calibrated minimizing the NRMSE between the experimental and predicted values. The minimizing procedure was performed using the “fminsearch” algorithm in Matlab®.

3.2.4.2 Mathematical model validation

A validation of the calibrated mathematical model was conducted in order to evaluate its suitability for predicting the process efficiency under experimental conditions that differ from those in the calibration phase. A different experimental set of four soil washing experiments was involved, with a L/S value of 10 and M values of 5, 15, 25, and 40.

The comparison between the experimental data and mathematical model was made using the NRMSE and two more indexes that are extensively used for model calibration and validation in various experimental fields (Esposito et al., 2011; Frunzo et al., 2012). These two indexes are the modeling efficiency (ME), the index of agreement (IoA). The involvement of two different indexes for model validation was made to further assess the suitability of the model calibrated through NRMSE minimization. The ME and IoA indexes are defined as follows:

$$ME = 1 - \frac{\sum_{i=1}^{K}(y_i - y_i')^2}{\sum_{i=1}^{K}(y_i' - y_M)^2} \tag{3.2}$$

$$IoA = 1 - \frac{\sum_{i=1}^{K}(y_i - y_i')^2}{\sum_{i=1}^{K}(|y_i' - y_M| + |y_i - y_M|)^2} \tag{3.3}$$

where K, y_i, y_i', and y_M have the same meaning as in Eq. (3.1).

According to the above definitions for the two indexes, the best validation result is obtained for ME and IoA values close to 1. The mathematical model was then validated by determining the previously reported index values (Eqs. 3.1–3.3).

3.3 Results and discussion

3.3.1 Batch soil washing kinetic tests

Soil acid digestion tests show total concentrations of 167.46 mg/kg for Cu, 33178.55 mg/kg for Fe, 56138.10 mg/kg for Ca, 483.44 mg/kg for Mg and 459.15 mg/kg for Mn. Therefore it was possible to observe the presence of high amounts of competitor cations extensively involved in competition phenomena for chelation with EDDS. Results from BCR three-step sequential extraction tests show a Cu fractionation of 2.2% for the exchangeable fraction, 15.8% for the reducible fraction, 50.7% for the oxidizable fraction and 31.3% for the residual fraction. Initial pH values of the involved EDDS washing solutions were in a range of 9.3±0.4 while soil pH displayed a value of 7.81. However all washing solutions reached pH values close to the soil pH within few minutes of treatment and remained constant throughout the tests. This latter result was probably ascribable to the soil buffering capacity and also suggested no process condition variations and significant soil properties alteration occurrence during the soil washing treatment.

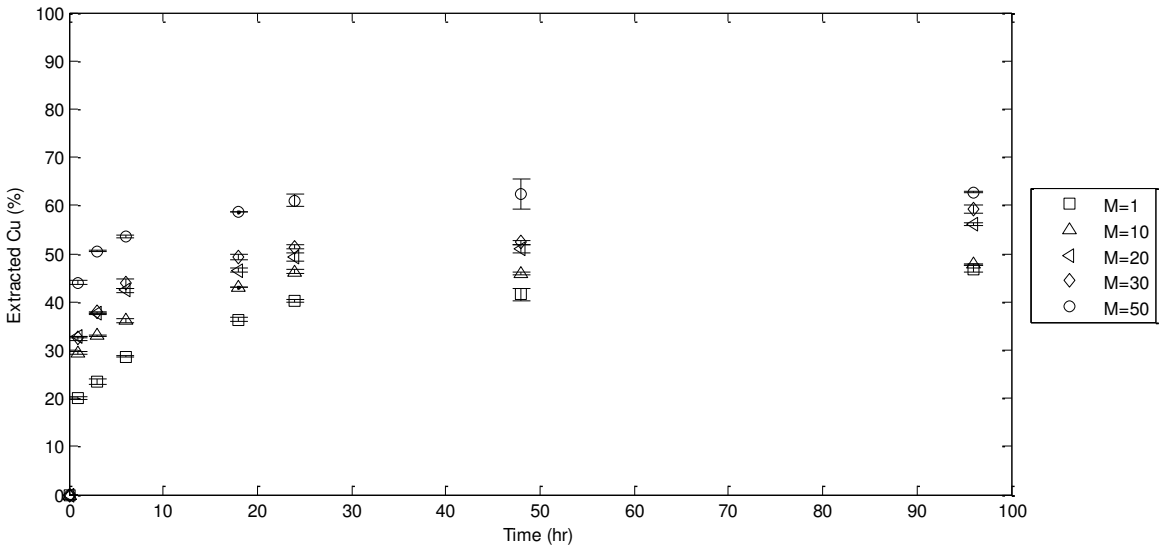
Fig. 3.1a shows the percentage of Cu that is extracted as the M ratio changes from 1 to 50. Cu extraction yield increases with increasing EDDS molar concentration. This result can be due to the competition between the chelating agent and the different competitor cations (e.g. Ca, Mg, Mn, etc.) occurring mainly at a low HMs:chelant molar ratio (Kirpichtchikova et al., 2006; Qiu et al., 2010).

In the present work, the extraction percentage for Ca, Mg, Mn and Fe at different M ratio is reported in Figs. 3.1a, b, c and d of Appendix A respectively. Results show that increasing extraction of the above mentioned elements is occurring by increasing EDDS moles as also observed for Cu extraction. Nonetheless, high values of EDDS moles in the system allow to achieve significant Cu extraction yield highlighting the main cation competition effect decrease. This result is further assessed by considering the final Cu extraction yield (shown in Fig. 3.1a) that displays values around 47% for tests at M=1 and 10 while a slight increase occurs (up to 53%-56%) for M=20 and 30. The highest efficiency is achieved with a molar ratio of 50, with final Cu extraction yield of 60%.

Considering the Cu extraction percentage, all results show a kinetic trend that has two distinct parts. First, a fast extraction kinetic trend occurs in the initial part of the experiments (mainly from 1 to 3 hr), and it is more noticeable with shorter retention times as the M ratio increases (from 1 to 50). In the second washing step, the extraction kinetic appears to slow down until it reaches a horizontal plateau after 24 hr. The M increase can influence the initial fast kinetic step, with a higher

cumulative extracted Cu percentage than the one achieved during the slow kinetic step. Despite this result, the Cu extraction continues until almost 24 hr before reaching a plateau for all tested M values. The latter behavior can be due to the Cu extraction being more affected by the chelant concentration as the retention time increases (Steele and Pichtel, 1998). In this phase the HMs retained by the soil detrital fraction and the cation competition for chelation become predominant as the EDDS tends to form complexes with main cation competitors (Ferraro et al., 2015). Then the high presence of the chelant agent can represent a source for further extraction until the beginning of the horizontal plateau.

a



b

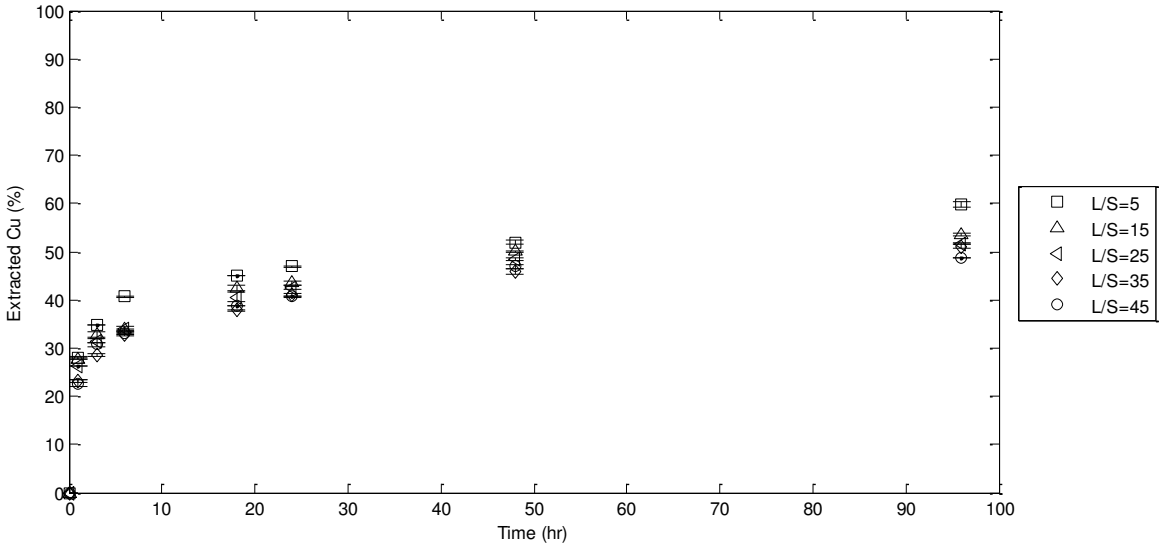


Fig. 3.1 Extracted Cu percentage at (a) M values of 1, 10, 20, 30, and 50, L/S=10 and (b) L/S ratio of 5, 15, 25, 35, and 45, M=10.

Similar kinetic extraction trends were observed for experiments conducted at a different L/S ratio (Fig. 3.1b). In this case, a fast kinetic extraction occurs until a retention time of 3 hr for all tests, while a still slower kinetic characterizes the process up to 24 hr. This is then followed by a horizontal plateau. The increase in the L/S ratio does not seem to accelerate the fast extraction step; instead, a slight decrease in terms of final Cu extraction efficiency is observed, with a final value around 48.8% for the highest L/S ratio=45. A high Cu removal decrease is observed from L/S=5 to 15, while no significant differences are observed for higher L/S ratios.

Generally, the slight effect of the L/S variation on various HM removal efficiencies has been reported for a wide range of L/S ratios (Van Benschoten et al., 1997; Zou et al., 2009); furthermore, no effects have been reported in tests with different L/S ratios while keeping the same HMs:chelant molar ratio (Tsang et al., 2012). Other investigations into Cu removal show an extraction yield decrease with increasing values of the L/S ratio, which mainly can be due to a change in the concentration of counter ions in solution or organic matter dissolution (Tsang et al., 2012).

However, the effect of L/S ratio values on soil washing efficiency can be different according to the experimental conditions selected in order to increase/decrease the ratio itself. For instance, while keeping a constant chelant concentration in solution while the L/S ratio increases, the chelant dose increases in respect to the soil amount, resulting in a consequent extraction efficiency enhancement (Mohanty and Mahindrakar, 2011). In the present work, EDDS:Cu molar ratio was kept constant for each test and L/S ratio was increased by reducing the amount of soil to treat in order to avoid a reactor volume change. This entails a lower amount of initial Cu moles to be treated and a lower EDDS dose to maintain a constant EDDS:Cu molar ratio among the different experiments. As previously observed, low EDDS mole concentration can lead to the preponderance of the chelation competition phenomenon between Cu and other competitor cations resulting in a lower Cu extraction with increasing L/S values. This latter was also assessed by extraction percentage of Ca, Mg, Mn and Fe with different L/S ratio (Figs. 3.2a, b, c and d of Appendix A). Results displayed final extraction yield increase with increasing L/S ratio values for Ca, Mg and Fe (Figs 3.2a, b and d of Appendix A) while highest final Mn extraction yield was achieved at L/S ratio=5 (Fig. 3.2c of Appendix A). However extraction percentage increase was significantly noticeable for Ca (Fig. 3.2a of Appendix A) while slight extraction increase was occurring for Mg and Fe by increasing L/S values (Figs. 3.2b and d of Appendix A). Competition phenomenon occurrence was further confirmed from data obtained with the lowest value of M (Fig. 3.1a).

3.3.2 Mathematical model prediction of soil washing process efficiency

3.3.2.1 Mathematical model

Experimental results show that the Cu removal efficiency is more affected by M than the L/S ratio. One could therefore consider that the L/S contribution is negligible on the soil washing efficiency variation, and deem the M ratio as the predominant parameter to include in a mathematical model.

According to data observed in Fig. 3.1a, a typical first-order reaction occurred and should be included in a soil washing removal efficiency prediction. Its general solution is expressed as follows:

$$C = a * (1 - e^{-b*t}) \tag{3.4}$$

where C is the extracted Cu percentage and t is the reaction time. From Eq. (3.4), it is possible to determine parameters a and b as follows:

$$For\ t \rightarrow \infty \qquad a = C$$

$$For\ C \rightarrow \frac{a}{2}; t \rightarrow t_{1/2} \qquad b = \frac{\log(\frac{2}{a})}{t_{1/2}}$$

Considering $t_{1/2}$ as the half-lifetime of the general reaction, it is possible to assume that a represents the maximum extracted Cu percentage while b is the reaction rate.

Eq. (3.4) was then written with two terms expressing the fast and slow kinetic steps, respectively:

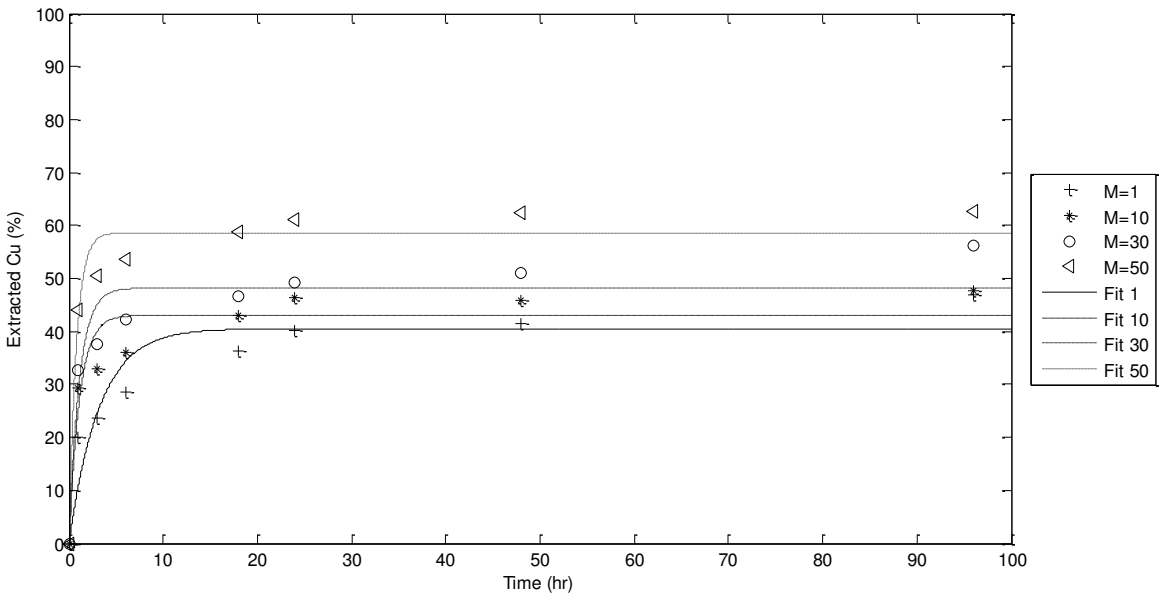
$$C = a * (1 - e^{-b*t}) + c * (1 - e^{-d*t}) \tag{3.5}$$

In this case, *C* represents the extracted Cu percentage during the soil washing process, and *t* is the treatment time. As with Eq. (3.4), *a* and *c* represent the maximum extracted Cu percentage during the fast and slow kinetic steps, respectively, and *b* and *d* are the reaction rates of the fast and slow kinetic steps, respectively. The above discussed and defined mathematical model represents a new approach for predicting soil washing extraction efficiency variation as a function of chelant:HMs molar ratio and contact time. Moreover, the mathematical correlations between extraction efficiency and process parameters can represent an important process optimizing tool due to its versatility. This latter characteristic derives from the possibility to concurrently apply the model for both extraction efficiency assessment with established values of process parameters or their optimization according to selected process efficiency.

3.3.2.2 Mathematical model calibration

The results for model calibration using Eqs. (3.4) and (3.5) are reported in Figs. 3.2a and 3.2b.

a



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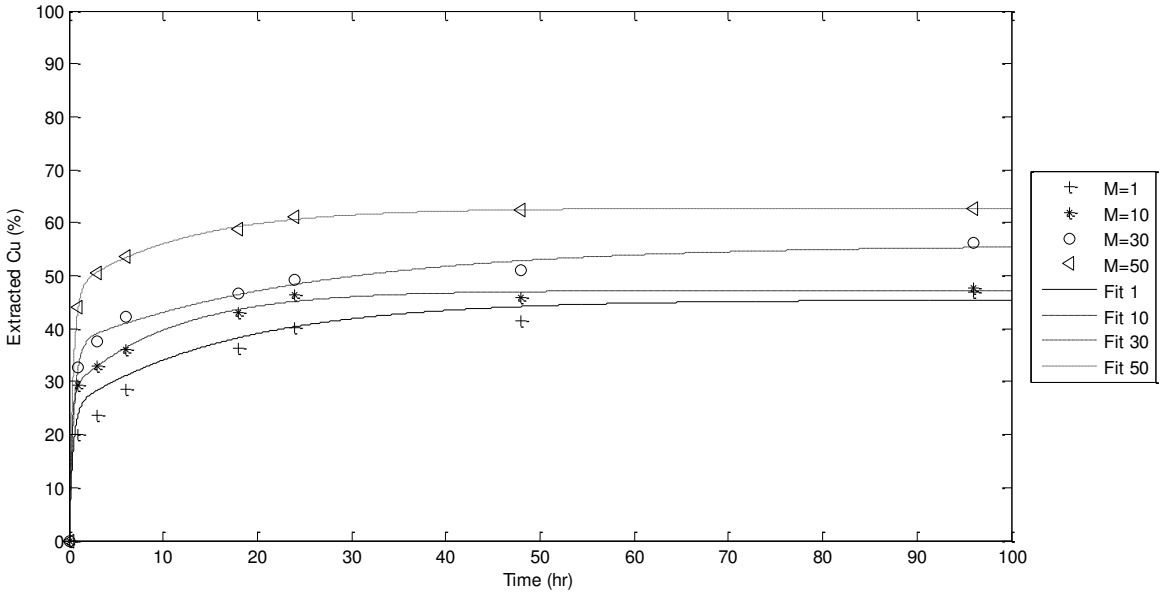

Fig. 3.2 Curve fit for tests at M=1 (Fit 1), M=10 (Fit 10), M=30 (Fit 30) and M=50 (Fit 50) (a) using Eq. (3.4), (b) using Eq. (3.5).

A comparison of the results from Figs. 3.2a and 3.2b shows that the best fit was achieved when the Cu extraction percentage with time was predicted by Eq. (3.5) instead of Eq. (3.4). Further confirmation of the higher prediction suitability of the two-step model over the mono-step model is obtained by comparing their minimized NRMSE from the equation coefficients calibration (Table 3.1).

Table 3.1 Minimized NRMSE obtained from calibration of Eq. (3.4) and Eq. (3.5) coefficients.

	Mono-step kinetic equation coefficient			Two-step kinetic equation coefficient				
Test	a	B	NRMSE	A	b	c	d	NRMSE
M=1	40.55	0.31	0.1569	25.09	2.41	20.36	0.06	0.0382
M=10	43.03	0.89	0.1239	28.27	3.91	18.94	0.09	0.0178
M=30	48.17	0.91	0.1202	37.08	1.99	18.70	0.04	0.0272
M=50	58.60	1.29	0.0762	47.26	2.36	15.47	0.08	0.0052

Table 3.1 shows lower minimized NRMSE values for Eq. (3.5) than for Eq. (3.4) calibration. This result indicates the higher suitability of a two-step kinetic model for predicting the soil washing extraction efficiency for Cu removal. Furthermore, it is worth noticing that the *b* and *d* coefficients

do not display a specific trend, but similar values are obtained for all the investigated tests at different M ratios. Then, according to the *b* and *d* definitions, this suggests that the reaction rates for both the fast and slow kinetic step does not depend on the M ratio but mostly change with the half-lifetime. Therefore, constant *b* and *d* values were assumed for the Eq. (3.5) calibration, with values equal to the average of their results from Table 3.1 (*b*=2.67, *d*=0.07). In contrast, an increasing tendency is observed for *a* while a decreasing tendency is observed for *c* as the M values increase (Fig. 3.3).

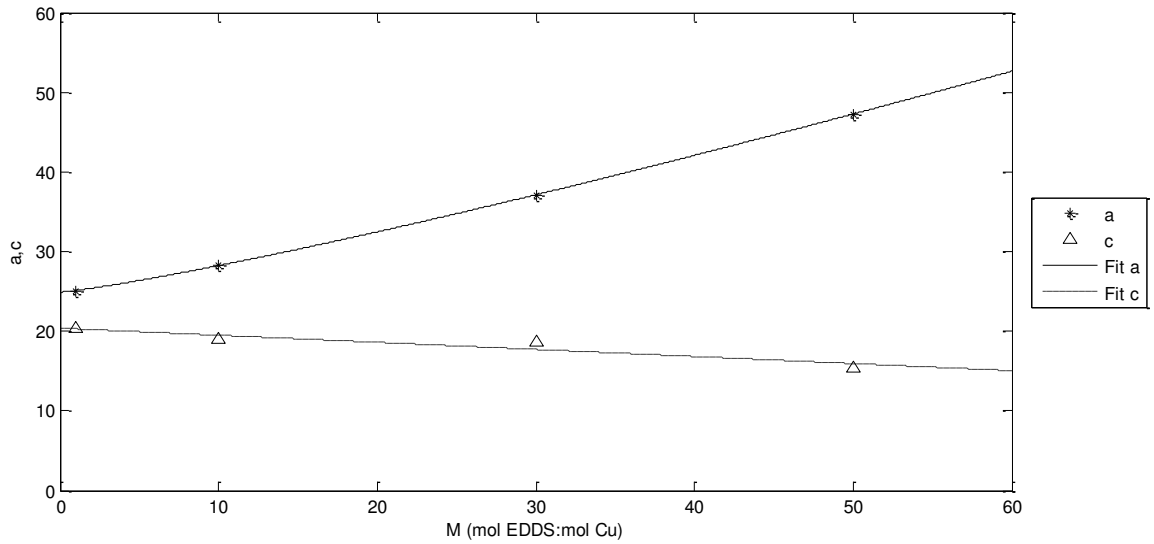

Fig. 3.3 The dependence of the a and c coefficients on the M ratio.

The observed decrease in *c* is not related to the lower maximum Cu extraction occurring at a higher EDDS:Cu ratio. Instead, it is attributed to the increase of the cumulative extracted Cu percentage during the fast kinetic step as observed from experimental data (Fig. 3.1a) and the resulting decrease of the cumulative extraction during the slow kinetic step. As a consequence, the maximum Cu extraction slows down in the last kinetic step at higher M values that is consistent with the experimental curves and their translation along the y-axis as the M ratio increases (Fig. 3.1a).

Based on the data observed in Fig. 3.3, a generic power function equation (Eq. 3.6) was used to describe the dependence of the *a* coefficient on M, while a linear equation was used to define the dependence of the *c* coefficient on M (Eq. 3.7). The rates *b* and *d* were assumed to be constants and their values were set to the average of their calibrated values at different M values. Equations (3.6) and (3.7) are expressed as follows:

$$a = e_1 * M^{e_2} + e_3 \tag{3.6}$$

$$c = e_4 * M + e_5 \tag{3.7}$$

Fig. 3.3 also shows the results for the calibration of the *a* and *c* values using Eqs. (3.6) and (3.7). The calibration results from Eq. (3.6) were e_1=0.22, e_2=1.18, and e_3=24.89 with a minimized NRMSE=0.00087. From Eq. (3.7), the calibration values were e_4=-0.09 and e_5=20.39, obtained with a minimized NRMSE=0.0333. The low obtained NRMSE values assess the suitability of applying Eqs. (3.6) and (3.7) to the prediction of the *a* and *c* tendency as the M ratio changes.

Then, according to the e_1, e_2, e_3, e_4, and e_5 values, the calibrated Eqs. (3.6) and (3.7) were expressed as follows:

$$a = 0.22 * M^{1.18} + 24.89 \tag{3.8}$$

$$c = -0.09 * M + 20.39 \tag{3.9}$$

Substituting Eqs. (3.8) and (3.9) and the constant values of *b* and *d* into Eq. (3.5), the following prediction mathematical equation is obtained:

$$C = (0.22 * M^{1.18} + 24.89) * \left(1 - e^{-(2.67*t)}\right) + (-0.09 * M + 20.39) * \left(1 - e^{-(0.07*t)}\right)$$

$$t: [0\,; +\infty[\quad and \quad M: [1\,; +\infty[\tag{3.10}$$

Equation (3.10) represents the final mathematical model for the extracted Cu percentage prediction, depending on the reaction time and the M ratio, with the coefficient calibration based on the

investigated soil. It is assumed that the model prediction is valid for reaction times ranging from 0 to +∞ and for M ratio higher than stoichiometric value.

3.3.2.3 Mathematical model validation

Fig. 3.4 shows the experimental data for the extracted Cu percentage obtained in tests at M ratios ranging from 5 to 40. Fast and slow process kinetics can be distinguished, and washing improvement in terms of the extracted Cu is observed with increasing M values (as in Fig. 3.1a).

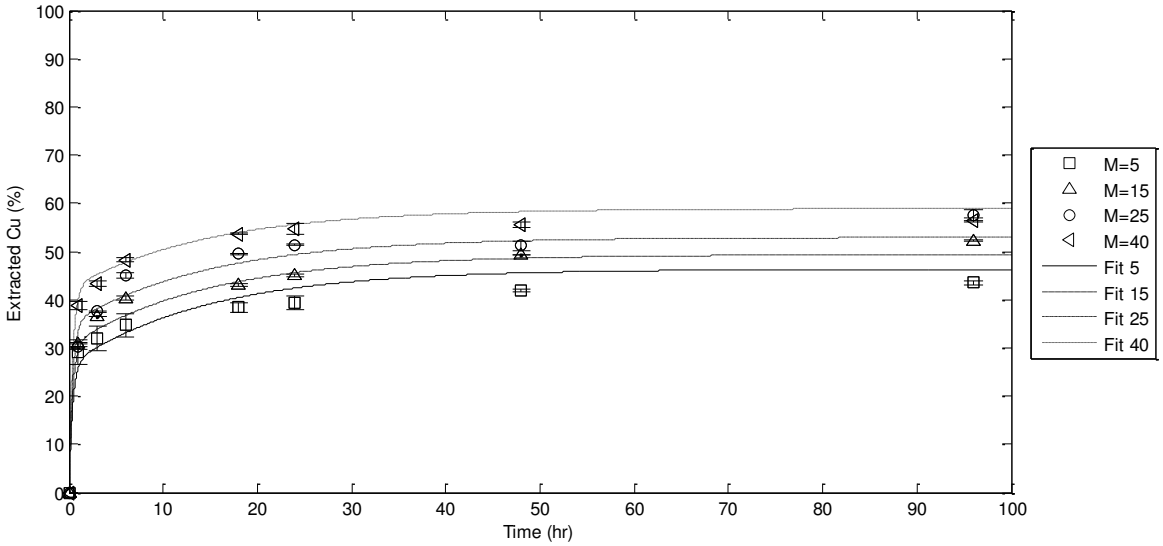

Fig. 3.4 Extracted Cu percentage at M values of 5, 15, 25, and 40 and L/S=10 and data fitting for tests at M=5 (Fit 5), M=15 (Fit 15), M=25 (Fit 25), and M=40 (Fit 40) using Eq. (3.10).

The graphical fitting using Eq. (3.10) with experimental data is also reported in Fig. 3.4. The quantitatively evaluated values of the NRMSE, IoA, and ME indexes for each fitting are reported in Table 3.2.

Table 3.2 NRMSE, IoA, and ME values from the Eq. (10) validation on data with M = 5, 15, 25, and 40.

Test	NRMSE	IoA	ME
M=5	0.0787	0.9979	0.9620
M=15	0.0537	0.9990	0.9833
M=25	0.0676	0.9985	0.9750
M=40	0.0355	0.9995	0.9922

The results in Table 3.2 show that all the NRMSE values are very close to 0 assessing the good validity of the model. Furthermore, a more direct evaluation of the agreement between the experimental and predicted data is given by the IoA determination, and the results in the present work show values higher than 0.99 for all investigated M ratios. Furthermore, the ME values are higher than 0.96 for all experimental tests, which suggest good agreement between the individual observed data points and the predicted data.

These results indicate that the prediction agreement of Eq. (3.10) with experimental data is valid for the Cu extraction efficiency. Good values of the indexes obtained in the validation tests with all involved M ratios also demonstrate the model efficacy under various operational conditions. However soil washing extraction performance can be affected by further parameters besides process conditions. Soil properties (i.e. organic matter and humic acid content, main cation competition, soil particle size distribution, soil mineralogy, soil pH) and HMs characteristics (i.e. HMs speciation/fractionation, age of contamination) strongly determine the rate and extent of contaminant extraction from soil due to both their individual and synergic actions (Ferraro et al., 2016). For instance, chemical speciation affects transport and fate of HMs in the environment (Wuana and Okieimen, 2011) while HMs fractionation in soil is strictly related to the kinetic of the contaminant extraction (Abumaizar and Smith, 1999). Further example is given by soil pH affecting HMs retention due to acid-base characteristics of soil hydroxyl and carboxylic surface functional groups that contribute to the surface charge formation (Abumaizar and Smith, 1999). According to this, it is clear that maximum extracted HMs percentage and reaction rates of the fast and slow kinetic steps in the suggested model can display values strictly related and variable according to the study case. Then, mathematical equation recalibration procedure needs to be carried out case by case in order to determine proper model coefficients values before to proceed with process efficiency prediction. Moreover, further model improvement can be achieved in calibration phase by considering more experimental data points during kinetic tests. This latter consideration can be

especially referred to the fast kinetic step in order to determine a more accurate value of its reaction rate represented by coefficient "*b*".

Finally, possible biodegradation phenomenon of EDDS washing solution could be a further point of interest for the suggested mathematical model. For this purpose, coupling the two-step kinetic model with mathematical equations for organic substance biodegradation (such as Michaelis-Menten kinetics) could be a suitable way to properly describe kinetic and rate of EDDS concentration decrease during soil washing treatment.

3.4 Conclusions

A two-step kinetic model for the prediction of Cu removal efficiency at various treatment times and EDDS:Cu ratios is proposed. The experimental and model results indicate the following considerations:

- Stronger dependence of the Cu leaching occurred with the M ratio than with the L/S ratio. An increase in the initial fast kinetic step was observed as the M ratio increases mainly due to the higher quantity of free chelant in solution. In contrast, no varying kinetic behavior was observed with different L/S ratios.
- Batch soil washing tests showed the two-step kinetic tendency of the Cu extraction as the reaction time increases with an initial fast kinetic extraction followed by a slow kinetic extraction that proceeds until a plateau is reached. NRMSE values assessed the better suitability of the two kinetic model than the mono-step kinetic model in predicting the Cu extraction efficiency.
- The reaction rates of the fast and slow kinetic reaction (*b* and *d*) are mainly dependent on the treatment time (in particular the half-lifetime), while there is no relation to the M ratio. In contrast, *a* coefficient displayed an increasing tendency with increasing M ratio, while a decreasing tendency was observed for *c*. This result is consistent with the growth of the cumulative extracted Cu percentage during the fast kinetic step with increasing M ratio as observed from the batch tests.
- Besides the very low NRMSE values achieved, index values above 0.99 for IoA and above 0.96 for ME were obtained for all validation tests, indicating the validity of the two-step kinetic model.

The suggested model represents a useful tool for the prediction of soil washing efficiency at various process conditions related to the chelant-metal ratio and treatment time although the coefficients recalibration would be necessary for different study cases. Nonetheless the present model application can provide proper process simulation reducing the number of tests needed for soil washing set-up and optimization under different conditions. Further model improvement could be achieved taking into account contaminant fractionation in the soil and operational parameters accounting for the reaction volume for reactor design purposes.

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Chapter 4.

Investigation of different EDDS-enhanced washing configurations for remediation of a Cu contaminated soil: process kinetics and efficiency comparison between CSTR and Plug Flow configurations

This chapter will be submitted for publication in Environmental Pollution as:

"Ferraro, A., Fabbricino, M., van Hullebusch, E.D., Esposito, G., 2016. Investigation of different EDDS-enhanced washing configurations for remediation of a Cu contaminated soil: process kinetics and efficiency comparison between CSTR and Plug Flow configurations. Environ. Pollut."

4.1 Introduction

Studies reported in Chapter 2 displayed various advantages due to APCs involvement. These latter extractants in fact are characterized by many advantages such as high metal extraction efficiency, high metal complexes stability and solubility, low chelating agent adsorption phenomena on the soil (Fischer et al., 1998). Furthermore, the involvement of biodegradable chelating agents such as EDDS in the soil washing entailed the implementation of more environmental friendly and safety remediation process (Hauser et al., 2005; Tandy et al., 2006).

Nonetheless, soil washing process can prove to be an expensive remediation technique when high contaminated soil amount needs to be treated. Further reasons can be ascribed to the high cost of extracting agents as well as the required treatment of spent washing solution for its safe disposal (Lim et al., 2005). For this purposes, physical separation techniques are often involved in pilot and full-scale soil washing unit to concentrate metal contaminants in smaller soil volume (Dermont et al., 2008). Whereas different recovery techniques were investigated to reuse the spent extracting solution in further washing steps (Ager and Marshall, 2003; Allen and Chen, 1993; Di Palma et al., 2005, 2003; Pociecha and Lestan, 2010; Voglar and Lestan, 2010; Zeng et al., 2005). These latter will be better detailed in Chapter 5.

Besides these different techniques aimed at lowering soil washing procedures costs, proper washing configuration could represent a further parameter to consider for process efficiency/cheapness optimization. Then additional tests are needed to simulate various conditions for contaminated soils washing.

The aim of this study is to investigate at lab-scale different EDDS-enhanced washing configurations on an agricultural Cu contaminated soil in order to establish proper washing conditions for efficient Cu extraction. Besides the commonly applied CSTR configuration, two different Plug-flow configurations were studied: i) Recirculated Flow (RF) and ii) Concurrent Flow (CF) configurations. CSTR configuration tests allowed to determine suitable process parameters (e.g. EDDS volume, liquid to soil ratio, treatment time) in order to achieve high Cu extraction efficiency. These suitable process conditions were involved in PF and CF configuration tests fractionating the optimal EDDS volume and reaction time in different ways for consecutive washing steps. The outcomes from the tests were used to assess the best combination of EDDS/treatment time fractionation and washing configuration in order to improve the soil washing process in terms of Cu extraction efficiency minimizing the amount of EDDS and operational time.

4.2 Materials and methods

4.2.1 Soil physical-chemical characteristics

The experimental activities were carried out on a Cu contaminated agricultural soil collected in Castel San Giorgio in the South of Italy. Soil pH and electrical conductivity (EC) were determined using a pH meter (Orion 420A$^+$, Thermo) and an EC meter (XS Cond 6), respectively, in a mixture with a soil:distilled H_2O ratio=1:2 (w/v). ASTM methodologies were used to evaluate the soil particle size distribution (ASTM D 422-63, 2007) and initial field moisture and volatile solids (ASTM D 2974-00, 2000). Soil samples were heated at 105 °C for the initial field moisture content and at 550 °C in a muffle furnace for the volatile solids determination.

The chemical properties were determined in terms of cation exchange capacity (CEC) and HMs content. The ammonium acetate method was used to evaluate CEC (Chapman, 1965). Soil mineralization was conducted through microwave-assisted acid digestion (USEPA, 1995) using a Milestone START D microwave oven.

Characterization in terms of soil fractionation was performed through a modified BCR three-step sequential extraction (Pueyo et al., 2008) to determine the Cu concentration in the non-detrital (exchangeable and reducible) and detrital (oxidizable and residual) fraction of the soil. Table 4.1 of Appendix A shows the values of the above cited soil properties.

4.2.2 EDDS solution, glassware preparation and analytical methods

EDDS complexing agent (35% concentrated) for washing solution preparation was provided by Sigma Aldrich. Proper volume of EDDS was mixed with DI water for each experimental set according to the EDDS:Cu molar ratio established for the specific test.

All the glassware involved for solution preparation and soil washing process reactor was stored in 2% HCl bath overnight and rinsed with DI water prior use. All the samples collected from soil mineralization and soil washing tests were analyzed through atomic adsorption spectrometry (AAS) using a Varian Model 55B SpectrAA (F-AAS) equipped with a flame (acetylene/air) and a deuterium lamp for background correction to determine the amount of extracted Cu.

The reported data were averaged from triplicate performed experiment results in order to assess better validity of the values and corresponding standard deviations were showed as error bars.

4.2.3 Lab-scale soil washing tests

Prior each soil washing test, the contaminated soil samples were sieved at 2 mm in order to focus the investigation on the finest particle size. Furthermore, initial soil moisture was removed dehydrating the soil samples maintaining them under vacuum condition in the presence of anhydrous silica and calcium chloride until the soil constant weight was reached.

Soil washing tests were performed in 500 ml glass beaker reactors and total washing solution volume of 400 ml. Proper mix of soil and EDDS solution was obtained through a ISCO jar test equipment at 150 rpm. The reactors were closed by Parafilm® layer on the top in order to avoid the EDDS solution evaporation and alteration of the selected L/S ratio during the treatment time. EDDS washing solution pH was monitored all along the tests displaying values of 8±0.20 that represented the natural pH of the investigated soil.

All the collected samples were centrifuged using an IEC CENTRA GP8R centrifuge at 4600 rpm for 20 min to separate the treated soil from the liquid phase. The latter was then filtered through 0.45 μm fiberglass filters to remove residual soil particle and stored at 4°C until analysis.

4.2.3.1 CSTR washing configuration

CSTR conditions were simulated through single washing step tests with long treatment time of 96 hr in order to reach Cu extraction plateau. Different values of EDDS:HMs molar ratio and L/S ratio were investigated to optimize the operational parameters. Experiments with different molar ratio were performed at EDDS:(Cu+Cd+Pb+Co+Ni+Zn) molar ratio (EDDS:M ratio) equal to 1, 10, 20, 30 and L/S ratio fixed at 15 (v/w). Sum of various HMs was considered for the molar ratio in order to have available EDDS moles for Cu extraction and avoid competition phenomena of these contaminants for EDDS chelation. Ca, Fe, Mg and Mn elements were not considered in the EDDS:M ratio determination due to their significant concentration in the investigated soils, i.e. their involvement in the EDDS:M ratio calculation would entail high EDDS amount to achieve selected values of the molar ratio. Then, calculation was delimited to the soil contaminants. In particular, the present study focused on the Cu extraction as main contaminant in the investigated soil. Regarding tests with different L/S ratio the investigated values were 15, 25, 35 and 45 with EDDS:M ratio fixed at 10. Fig. 4.1a reports a scheme of CSTR configuration.

4.2.3.2 Plug-flow washing configurations

The Plug-flow configurations were simulated by performing multi-washing steps. EDDS:M ratio=10 and L/S ratio=25 were selected from the CSTR tests according to the significant extracted Cu percentage and to lower EDDS and soil amount to involve. EDDS molarity of 3.14 mM was corresponding to the EDDS:M ratio=10 with a total EDDS volume of 1.02 ml in 400 ml of washing solution to achieve the reported molarity value. Total treatment time was selected equal to 24 hr that was representing the final value before the Cu extraction plateau occurrence. RF and CF configurations were then performed fractionating the total treatment time and total EDDS volume in 8 washing steps. Furthermore, volume solution of 50 ml was considered for each step starting from initial 400 ml involved for the CSTR configuration tests.

RF configuration tests were carried out washing the same soil with fresh EDDS solution in each step and 4 different washing conditions were simulated: **A1)** constant EDDS volume (0.128 ml) and treatment time (3 hr) for each washing step, **A2)** increasing EDDS volume (0.040, 0.065, 0.090, 0.115, 0.140, 0.165, 0.190 and 0.215 ml) and constant treatment time (3 hr) for each washing step, **A3)** decreasing EDDS volume (0.215, 0.190, 0.165, 0.140, 0.115, 0.090, 0.065 and 0.040 ml) and constant treatment time (3 hr) for each washing step, **A4)** constant EDDS volume (0.128 ml) and increasing treatment time (0.5, 1, 1.5, 2, 2.5, 3.5, 5 and 8 hr) for each washing step. A1, A2 and A3 washing conditions were selected in order to study all possible EDDS volume fractionation modalities. The aim was to investigate the washing efficiency enhancement expecting significant Cu extraction yield in the initial washing steps for A1 and A3 tests. On the contrary, longer process kinetics and Cu extraction yield enhancement were expected in the final washing steps for A2 test. Finally, A4 washing condition was selected decreasing initial steps treatment time and increasing final steps treatment time. In this case the aim was to extract Cu present in non-detrital soil fractions with very fast washing steps and to enhance extraction of less labile Cu forms with final longer washing steps. Table 4.1 summarizes the experimental set-up of the above reported washing conditions while Fig. 4.1b reports a scheme of A1, A2, A3 and A4 configurations.

Table 4.1 RF configurations experimental set-up.

Washing conditions	EDDS volume	Treatment time	Washing step
A1	Constant	Constant	8
A2	Increasing	Constant	8
A3	Decreasing	Constant	8
A4	Constant	Increasing	8

CF configuration was carried out involving 8 different soils (S1, S2, S3, S4, S5, S6, S7 and S8) and 2 fresh EDDS solution. The first EDDS solution performed the 8 steps washing process from S1 to S8 (Co-current washing) while the second EDDS solution performed the 8 steps washing process from S8 to S1 (Counter-current washing) (Fig. 4.1c). The EDDS volume was equally divided between the washing solutions (0.510 ml) and constant treatment time (3 hr) was used for each washing step. In order to compare the cumulative extracted Cu with previous washing configurations on the same initial amount of treated soil, the latter was equally fractionated in the 8 washing steps. Treatment time was selected equal to 1.5 hr for each washing step in order to have a total time of 24 hr.

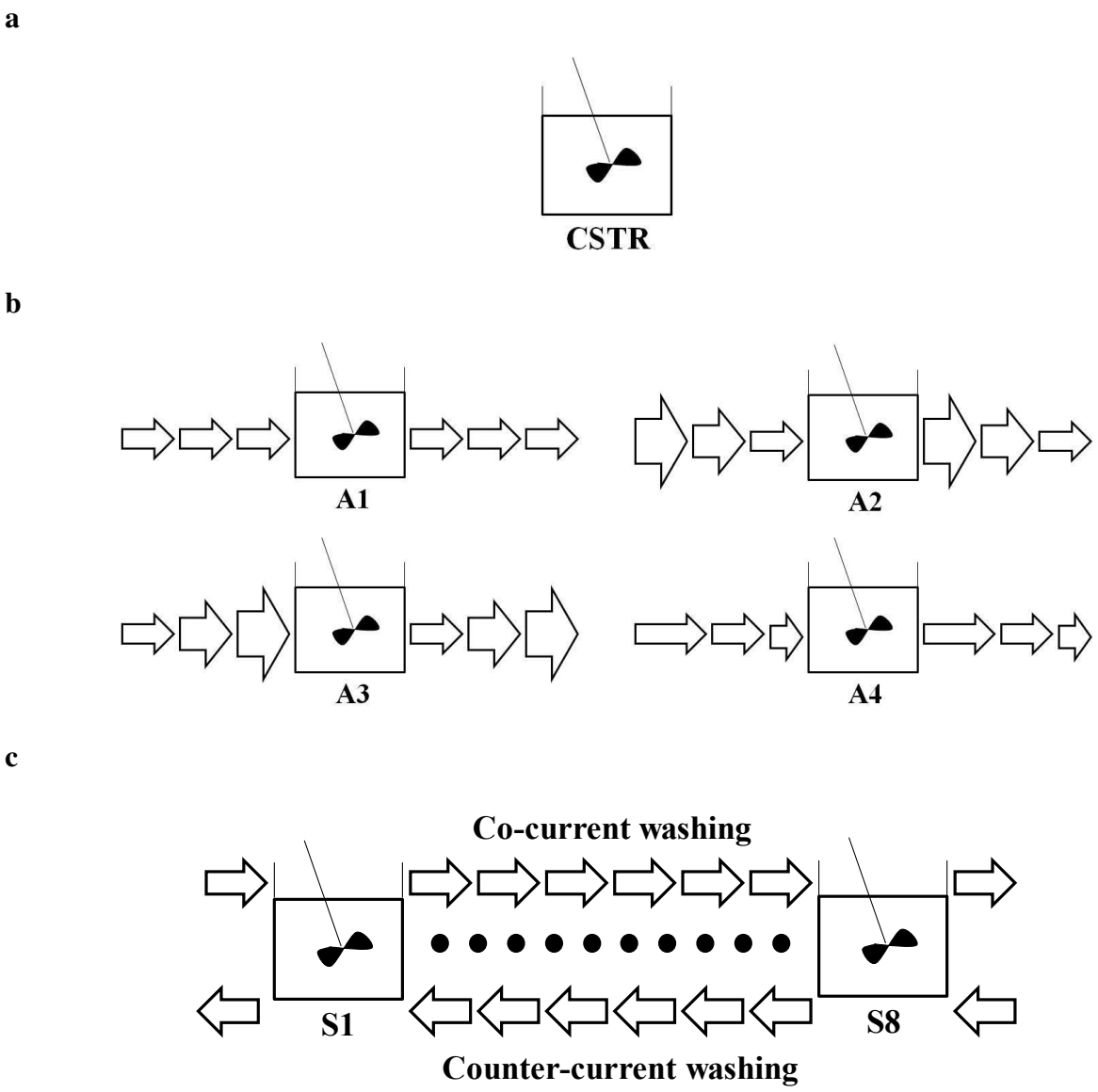


Fig. 4.1 Graphic scheme of (a) CSTR washing configuration; (b) A1, A2, A3 and A4 tests of the RF configuration; (c) Co-current and Counter-current washings of the CF configuration. Arrows size is related to the EDDS volume and arrows length is related to the treatment time.

4.3 Results and discussion

4.3.1 CSTR washing configuration

Fig. 4.2a shows the cumulative extracted Cu percentage after each sampling time with various molar ratio. Two main extraction kinetic paths can be distinguished as the reaction time increases. A Cu fast extraction occurred in the early hours of treatment followed by an extraction rate declining up to a final plateau. Besides the effect of treatment time that highly affects the effectiveness of the extraction process (Vandevivere et al., 2001) it is also reported that heavy

metals speciation into the soil can affect the contaminant mobility and solubilization by chelating agents used (Elliott et al., 1989).

Generally the sum of non-detrital fractions (e.g. exchangeable, carbonate and reducible fractions) determines the metal amount that can be extracted by soil washing process enhanced by chelating agents (Peters, 1999). Then weakly bound metals undergo to an initial faster extraction rate that is followed by a slower release of the metals strongly bound to the soil (Abumaizar and Smith, 1999).

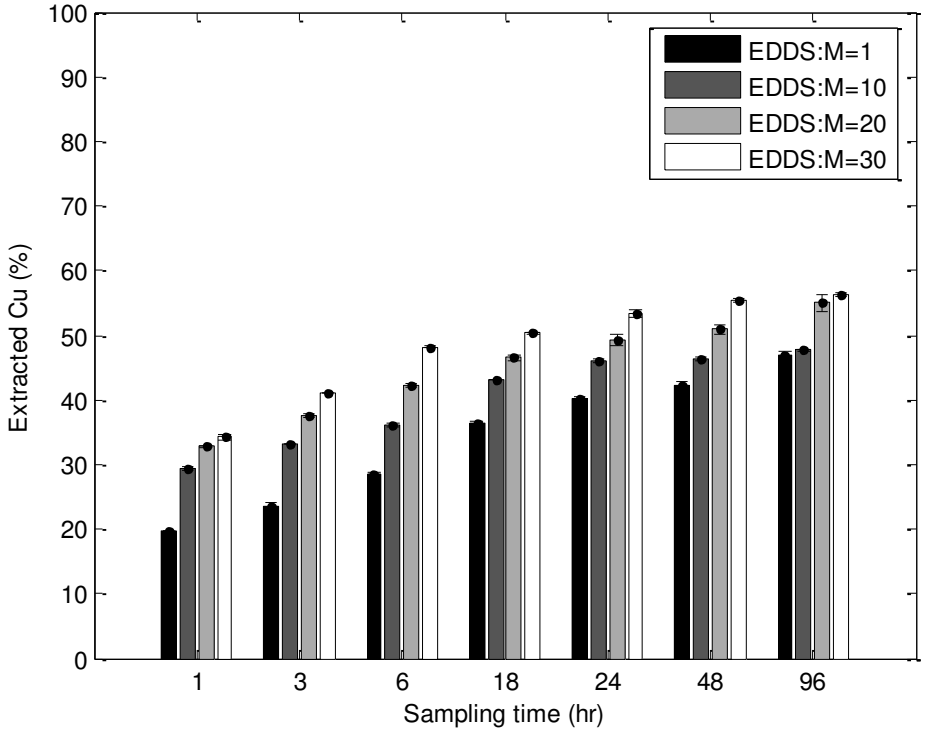
As observed in a previous work, sequential extraction results showed for the studied soil that only 2.2% and 15.8% of Cu was present in the exchangeable fraction and reducible fraction, respectively, while 50.7% for the oxidizable fraction and 31.3% for the residual fraction (Ferraro et al., 2015). According to this, only the test with EDDS:M ratio equal to 1 showed an extracted Cu percentage in the early treatment hours as expected from the weakly bound Cu percentage.

In contrast, the increase of EDDS:M ratio displayed a higher extraction efficiency than expected since the beginning of the treatment. This latter result could be mainly ascribable to metals mobility enhancement due to the higher concentration of chelating agents (Abumaizar and Smith, 1999; Elliott et al., 1989; Sarkar et al., 2008).

A further factor decreasing the metals extraction efficiency can be the release of cations (e.g. Ca and Fe) coexisting with the pollutants from the soil due to the soil matrix constituents dissolution (Steele and Pichtel, 1998). As a consequence, competition phenomena for the chelant complex formation can occur between main cation competitor and HMs reducing the amount of free ligand available to chelate the soil pollutants (Kim et al., 2003; Koopmans et al., 2008; Subirés-Muñoz et al., 2011).

Competition phenomena effects can be more noticeable at low values of chelant:HMs molar ratio and especially lower than 1 (Begum et al., 2012). Then high chelant moles excess is required in order to increase HMs extraction from soil (Lestan et al., 2008; Tandy et al., 2004).

a



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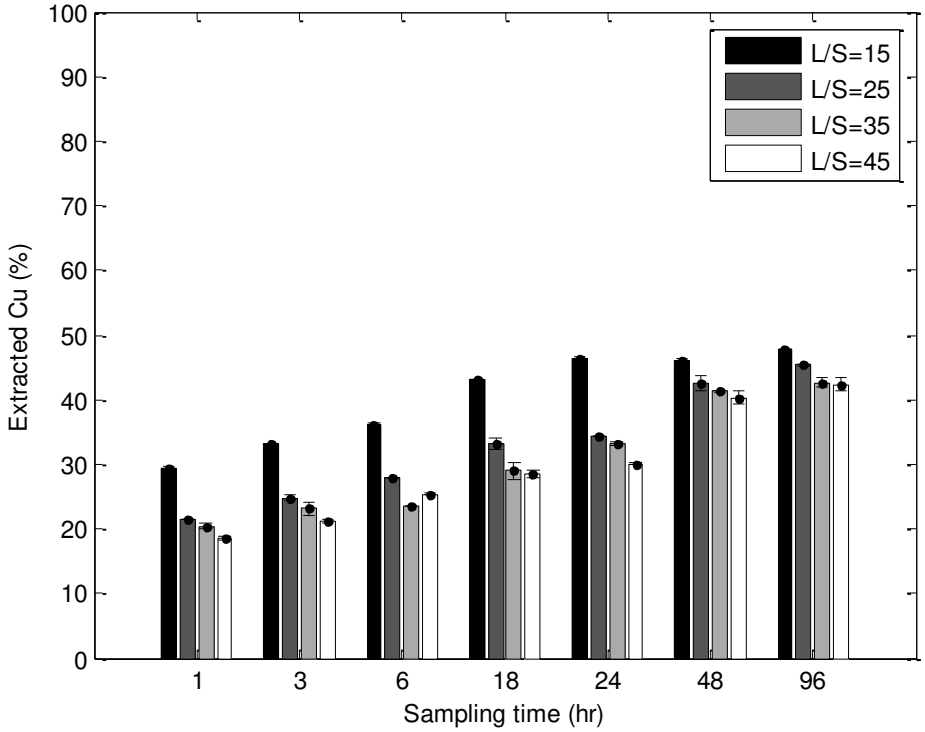


Fig. 4.2 Cu extraction efficiency at (a) EDDS:M ratio ranging from 1 to 30 and L/S ratio equal to 15; (b) L/S ratio ranging from 15 to 45 and EDDS:M ratio equal to 10.

Fig. 4.2b reports the Cu extraction efficiency at L/S ratio values ranging from 15 to 45. In contrast to the results observed by varying the EDDS:M ratio, it was possible to notice that extracted Cu percentage was decreasing with increasing L/S ratio values. It is reported that L/S ratio increase can generally entail positive effect on the soil washing process efficiency (Zou et al., 2009). This result is ascribable to the increase of chelant:HMs molar ratio with increasing L/S ratio when chelant molarity in solution is kept constant (Zou et al., 2009).

Besides the soil washing process improvement achievable at high L/S values, it was also observed that slight effect in terms of extraction efficiency was occurring varying the same parameter or mainly no effect with constant value of chelant:HMs molar ratio (Tsang et al., 2012; Van Benschoten et al., 1997). In the present case of study the increase of L/S ratio was achieved through soil amount decrease with constant values of EDDS:M ratio and liquid phase volume. As a consequence decreasing moles of HMs and EDDS were obtained for L/S ranging from 15 to 45. This likely led to higher chelation competition occurrence at the lowest EDDS mole values as already observed from results with different EDDS:M ratio (Fig. 4.2a).

However, Fig. 4.2b displays similar Cu extraction percentages among all tests occurring after 24 hr of treatment time. These latter results suggested that increasing L/S ratio values were mainly delaying the washing process resulting in necessary longer treatment time for suitable extraction efficiency achievement.

4.3.2 Plug-flow washing configurations

4.3.2.1 Recirculated Flow washing configuration

Results obtained from the 4 experimental set-up of the RF washing configuration are reported in Fig. 4.3.

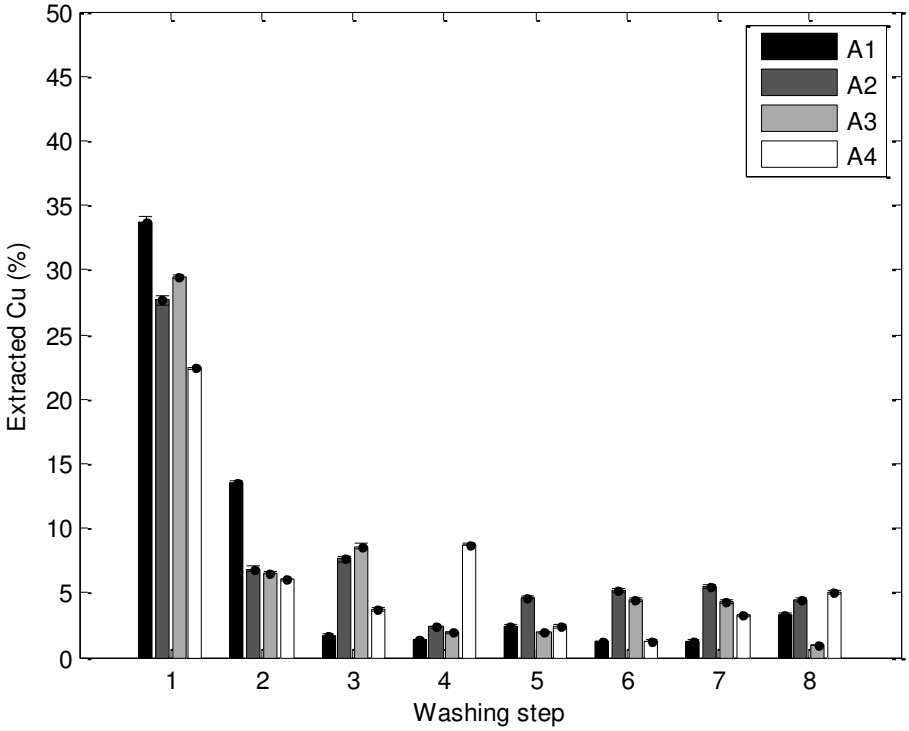


Fig. 4.3 Extracted Cu percentage related to each washing step in the four experimental set-up of the Recirculated Flow washing configuration.

A comparison among the four experimental set-up displayed main differences in terms of extracted Cu percentage after the first washing step while similar values were showed in the following ones.

In the steps 1 and 2, A1 test showed higher efficiency than A2, A3 and A4 tests. Following washing steps did not display significant Cu extraction percentage for A1 test. In contrast, the A2, A3 and A4 tests showed long-lasting Cu extraction percentage throughout the washing steps despite low values of extracted Cu were achieved.

The different behavior revealed from the four tests can be ascribable to the different operational conditions involved in terms of EDDS volume for A1, A2 and A3 tests and treatment time for A4 test. Further reason can be due to the differences in terms of EDDS:M ratio variation trend that can be observed among the different tests step by step (Table 4.2).

Table 4.2 EDDS:M ratio variation at each washing step for A1, A2, A3 and A4 tests.

EDDS:M molar ratio (mol/mol)								
Test	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8
A1	9.99	11.27	11.65	11.71	11.74	11.80	11.83	11.74
A2	3.13	5.62	7.93	10.34	12.05	14.34	16.71	19.14
A3	16.85	15.82	13.94	12.05	9.94	7.81	5.70	3.54
A4	9.99	10.46	10.59	10.68	10.88	10.94	10.97	11.05

In the test A1 it can be observed a sharp increase of EDDS:M ratio in the washing step 1 and 2 followed by a plateau from the third to the last step. This tendency is consistent with the Cu extraction results in Fig. 4.3 where a high efficiency drop was occurring after the second washing step. Also, the EDDS:M ratio variation reported in Table 4.2 suggested that the washing condition involved in the A1 test entail a very fast kinetic in the first treatment hours. This latter result makes the A1 conditions suitable for rapid treatment on soil characterized by contamination mainly bound to non-detrital fractions. For the A2 tests a linear increasing tendency for the molar ratio was observed allowing the lower but constant Cu extraction after the second washing step. In contrast, slower kinetics were observed compared to A1 test results due to the initial low volume of EDDS involved.

Lower Cu extracted percentages in steps 1 and 2 than the ones achieved in A1 test were also observed for A3 test. In contrast, data showed higher Cu extraction for A3 test than A1 in steps from 3 to 7. Nonetheless, it was also observed a process kinetic decrease concurrently to the EDDS:M ratio lowering step by step.

Compared to the Cu extraction yield displayed from the A1 configuration, the ones observed for A2 and A3 suggested that these configurations are well suited for soil remediation cases where several washing steps are needed. This was indicated by the extraction efficiency enhancement of the washing steps from 3 to 8 and especially in the A2 configuration where increasing EDDS:M ratio was obtained.

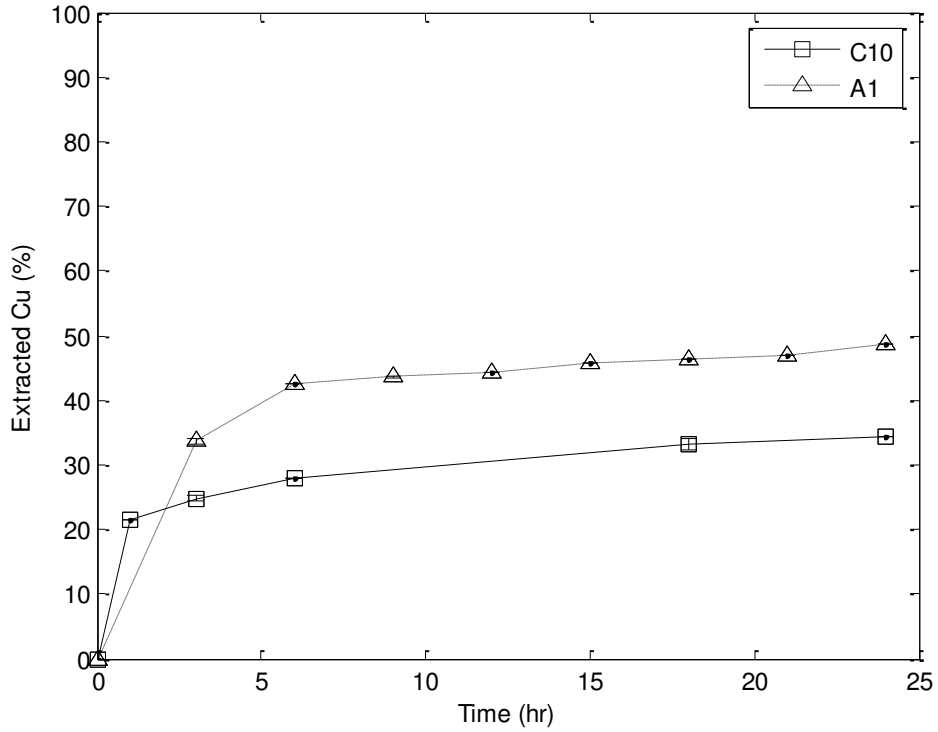
A4 test was carried through increasing soil treatment time in each washing steps. In this case, results did not display significant improvement in terms of Cu extraction efficiency for each washing step. Treatment time decrease during the initial washing steps did not allow to achieve high Cu extraction percentage. Furthermore, it was not observed extraction enhancement for step 7 and 8 corresponding to a treatment time of 5 and 8 hr respectively. Despite the long treatment time, this

result could be ascribable to the lower residual Cu concentration in the soil non-detrital fractions after 6 washing steps.

Nonetheless, comparable Cu extraction with A2 and A3 configurations in 6 hr were achieved with a total treatment time of 5 hr that was corresponding to the washing carried out until step 4.

A further comparison can be made between CSTR and RF configurations. Figs. 4.4a, 4.4b and 4.4c show the Cu cumulative extraction for the tests A1, A2, A3, A4 and the tests carried out at EDDS:M ratio equal to 10 and L/S=25 in the CSTR condition (C10).

a



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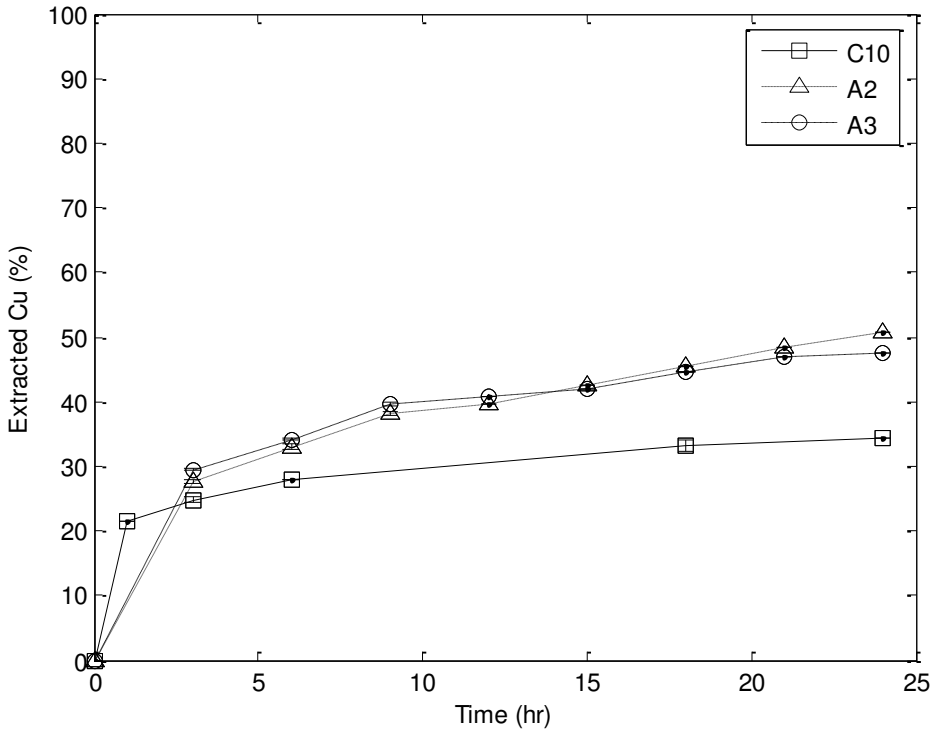

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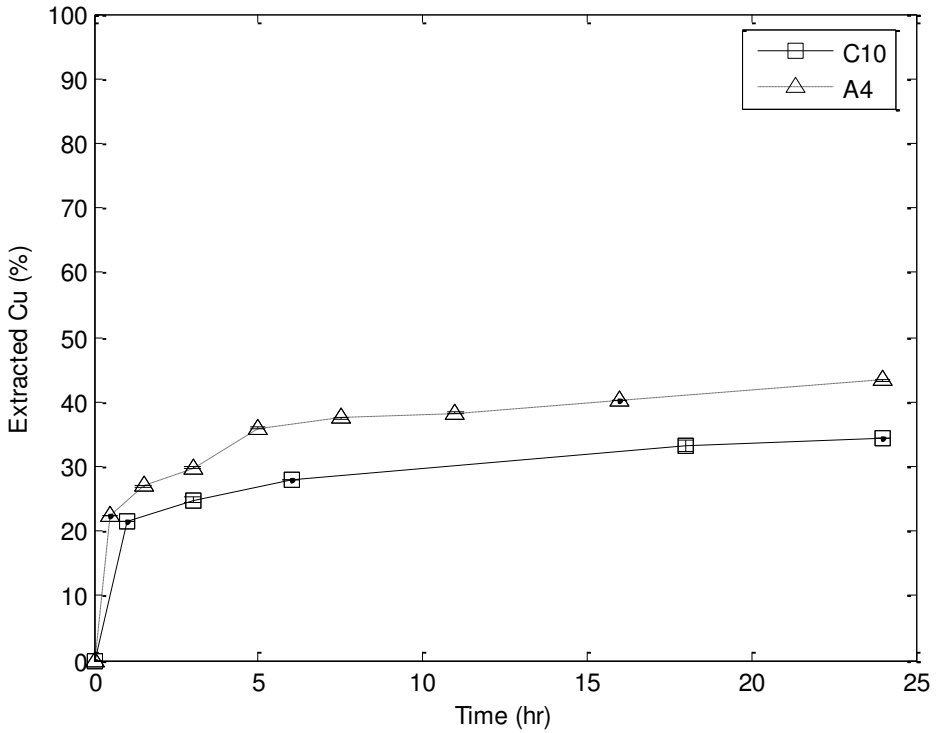


Fig. 4.4 Comparison of the cumulative extracted Cu for the tests (a) C10 and A1; (b) C10, A2 and A3; (c) C10 and A4.

Results showed that A1 conditions allowed to achieve fast Cu extraction enhancement after 3 hr of total treatment time compared to extracted Cu observed in test C10 (Fig. 4.4a). In contrast, A2 and A3 tests show significantly higher Cu cumulative extraction than C10 test after 9 hr following similar extraction tendency (Fig. 4.4b). These results were consistent with the slow kinetic of A2 and A3 tests reported in terms of Cu extraction efficiency (Fig. 4.3).

Furthermore results observed for A1, A2 and A3 experimental conditions were consistent with previous studies reporting that multi-step washing configuration can improve the HMs extraction efficiency of the soil washing process. It is reported in fact that multi-step washing configuration allowed to involve lower chelating agent dose than the one used for the single step washing (Finzgar and Lestan, 2007; Hong et al., 2008; Mohanty and Mahindrakar, 2011). Further improvement deriving from a shorter treatment time needed to achieve comparable HMs extraction results with a single washing step was also reported (Theodoratos et al., 2000). This was confirmed by results related to the comparison between C10 and A4 tests (Fig. 4.4c). It was in fact possible to observe that extracted Cu after 0.5 hr in test A4 was slightly higher than Cu extraction after 1 hr in test C10. Then cumulative extracted Cu from A4 test lingered higher than C10 values all along the test. Nonetheless, overall extracted Cu achieved in A4 was considerably lower than the extraction observed in tests A1, A2 and A3 despite the longer treatment time involved in the A4 step 7 and 8. This latter result further demonstrated the higher effect of the volume fraction than the treatment time on the soil washing process efficiency. Moreover a comparison in terms of process kinetics was carried out among C10, A1, A2, A3 and A4 tests. A first order kinetic was used to describe the Cu extraction process. The first order equation used for the specific case is the following:

$$\frac{d[Cu]}{dt} = -k \cdot t \qquad (4.1)$$

In Eq. (1), the terms [Cu] represents the Cu concentration (mg kg^{-1}), t is the treatment time (hr) and k is the first order kinetic constant (hr^{-1}). The integrated law of Eq. (4.1) can be expressed as follows:

$$[Cu] = [Cu]_0 \cdot e^{-k \cdot t} \qquad (4.2)$$

where $[Cu]_0$ is the initial Cu concentration in the soil. Finally, Eq. (4.2) can be modified in a linear form in order to determine k:

$$\ln[Cu] = \ln[Cu]_0 - k \cdot t \qquad (4.3)$$

Figs. 4.1 and 4.2a, b, c and d of Appendix A show the plot of ln[Cu] decrease in the soil vs. t for tests C10, A1, A2, A3 and A4 respectively. In the same Figs. the Eq. (4.3) term values determined for each test are also reported. It is possible to notice that experimental data follow an exponential tendency that can be approximately divided in two kinetic steps for C10, A1, A2 and A3 tests (Figs. 4.1 and 4.2a,b,c of Appendix A) and three kinetic steps for A4 test (Fig. 4.2d of Appendix A). The two kinetic steps were distinguished with $\ln[Cu]_1$ and $\ln[Cu]_2$ for the first and second kinetic step, respectively, while k_1 and k_2 represented their related kinetic constants. For the third kinetic step was used $\ln[Cu]_3$ and k_3 was its related kinetic constant.

In particular, results from C10, A1, A2 and A3 tests showed an initial faster kinetic step followed by a slower one until end of the washing process. Initial fast kinetic step was occurring up to 1 hr of treatment for C10 and 3 hrs of treatments for A1, A2 and A3 configurations. This assumption was strengthen by Cu cumulative extraction observed in Figs. 4.4a and 4.4b reporting a 62.3% of the total Cu extraction occurring after 1 hr for C10 and 69.1, 54.1 and 62.1% of the total Cu extraction occurring after 3 hrs for A1, A2 and A3, respectively.

Similarly for test A4, first kinetic step was limited to the initial treatment time corresponding to 0.5 hr, after which 51.6% of the total Cu cumulative extraction was observed (Fig. 4.4c). Furthermore, A4 test showed a second kinetic step occurring between 1.5 to 5 hrs of treatment where 31.4% of total Cu extraction was achieved. On the contrary only 17% of total Cu extraction was observed for last part of the washing corresponding to a third slowest kinetic step.

According to the cumulative extracted Cu percentages, it can be observed that initial faster kinetics are obtained for C10, A1 and A4 configurations (Figs. 4.4a and 4.4c). In particular, C10 displayed an initial faster kinetic than A1 configuration due to similar extracted Cu percentage achieved in less treatment time (1 hr). On the contrary similar initial kinetic was observed comparing C10 and A4 configurations. However, comparable kinetics were observed for C10 and A1 second steps and A4 third step ($k_2 = 0.0064\ hr^{-1}$ for C10 and A1, $k_3 = 0.0062\ hr^{-1}$ for A4).

Higher kinetic constant values ($k_2 = 0.0163\ hr^{-1}$ for A2 and $k_2 = 0.0117\ hr^{-1}$ for A3) were obtained for A2 and A3 tests in the second kinetic step compared to C10 and A1 configurations suggesting best suitability of A2 and A3 treatments for long-lasting washings.

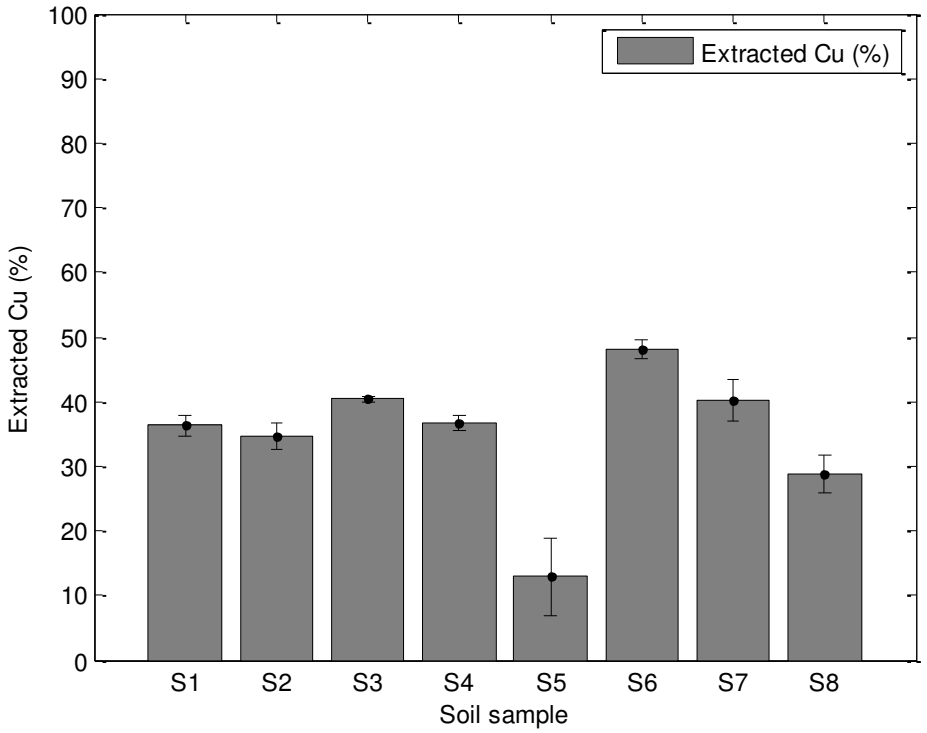
Finally, comparison of k_2 values among A2, A3 and A4 tests displayed higher values of k_2 for A4 than A2 and A3 configurations ($k_2 = 0.0163\ hr^{-1}$ for A2, $k_2 = 0.0117\ hr^{-1}$ for A3 and $k_2 = 0.0379\ hr^{-1}$ for A4). This latter result was in accordance to the comparable extracted Cu percentage achieved in lower treatment time with A4 test (5 hrs) than A2 and A3 tests (6 hrs).

4.3.2.2 Concurrent Flow washing configuration

Figs. 4.5a and 4.5b display results related to the CF washing configuration in terms of Cu extraction efficiency related to each step. Washing step from S1 to S8 sample showed an almost similar Cu extraction yield for each test (Fig. 4.5a). The highest extraction kinetic drop is observed for the S5 sample. Similar results were observed in a previous study where an electrochemically recovered EDDS solution was involved in a multi-step soil washing (Ferraro et al., 2015). Besides the possible occurrence of the regenerated EDDS solution degradation, competition phenomena between cation competitors and Cu for EDDS chelation was a further reason for process kinetic slow-down after 5 washing steps (Ferraro et al., 2015).

The kinetic extraction was then followed by a sharp increase on the S6 sample and a slighter decrease in the following steps. The higher Cu extraction achieved for S6, S7 and S8 samples than S5 can be reasonable considering that competition phenomena can occur at various extent according to different process conditions. It was in fact reported that high influence on EDDS-enhanced washing performances were displayed by cation competitors (i.e. Ca and Fe) especially in acidic conditions (Vandevivere et al., 2001). Slight alkaline pH observed in the present study could be a possible reason for delimited competition phenomena observed in the tests. Further reason could derive from the less stable complexes that cation competitors, such as Ca, form with chelating agent comparing to contaminant HMs (Papassiopi et al., 1999).

a



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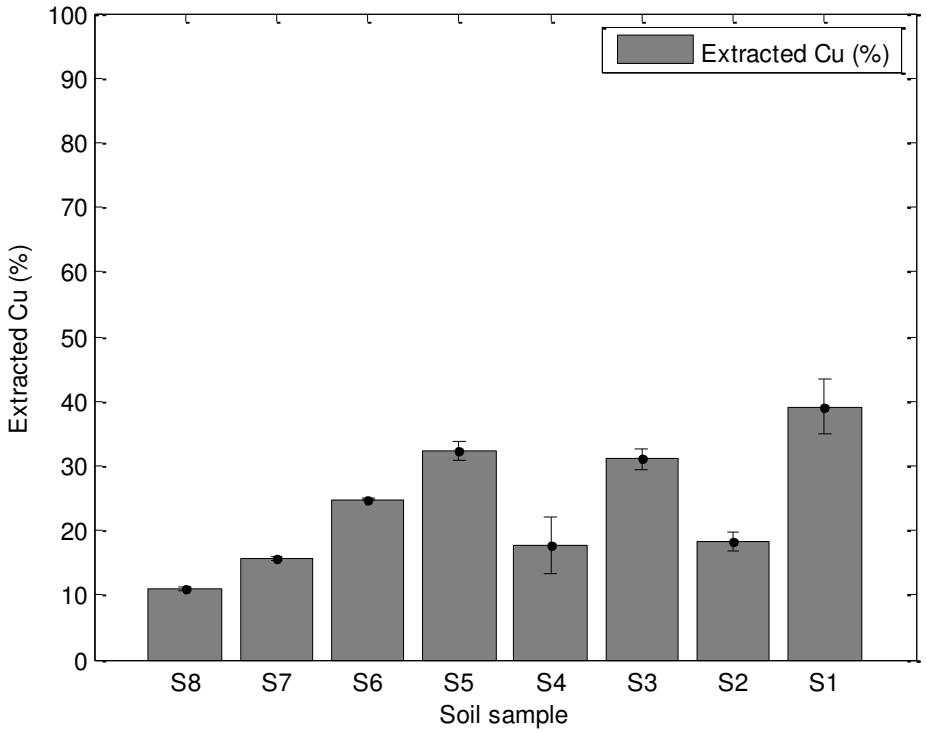

Fig. 4.5 Extracted Cu percentage in the Concurrent Flow washing configuration for (a) the Co-current washing; (b) the Counter-current washing.

From Fig. 4.5b it was possible to observe that fresh EDDS solution involvement for further soil treatment did not initially display significant Cu extraction while higher values are achieved in following steps. Moreover, generally lower extractions were observed for all the steps in the Counter-current washing compared to Co-current washing. This was ascribable to the possible Cu reduction in the non-detrital soil fractions during Co-current washing while high Cu amount in the detrital fractions was left during the Counter-current washing. As a consequence, lower Cu extraction extent was achieved during the Counter-current washing due to the presence of strongly bound Cu.

More clear kinetics were observed from results displayed in Fig. 4.5b. Cu extraction yield is characterized by a main increasing tendency step by step besides two decreases for S4 and S2 samples. These discrepancies could be ascribable to circumscribed competition phenomena occurrence as previously observed for the Co-current washing (Fig. 4.5a).

An overall comparison in terms of cumulative extracted Cu percentage between test C10 of CSTR configuration and Co-current and Counter-current washings of the CF configuration is reported in Fig. 4.6.

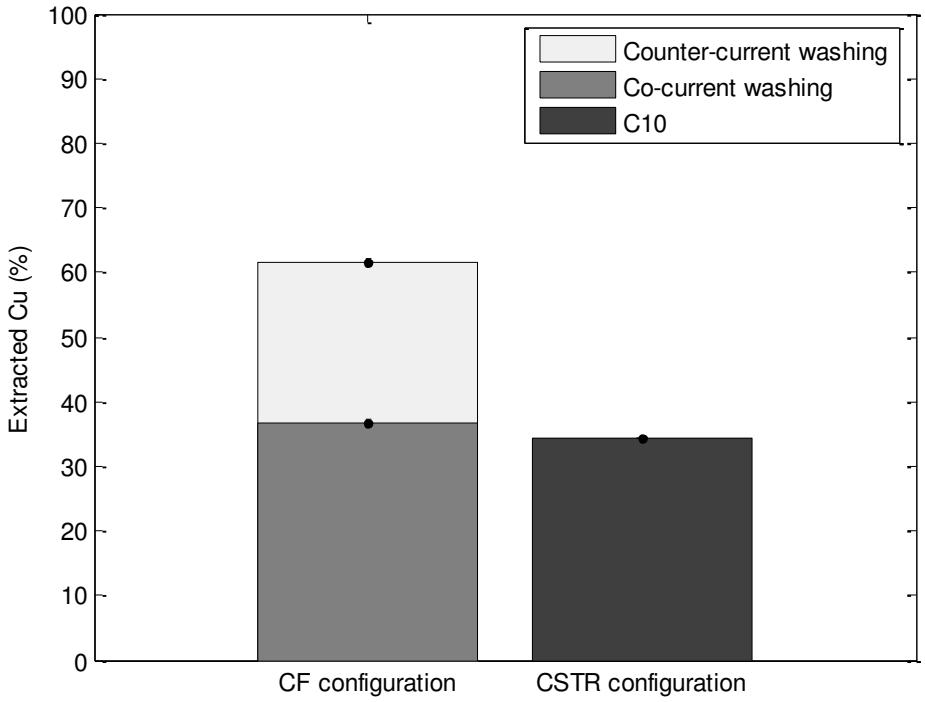

Fig. 4.6 Comparison of overall Cu cumulative extraction after 24 hr between CF configuration (Co-current and Counter-current washing tests) and CSTR configuration (C10 test).

Results showed a Cu extraction yield increase of about 27% after a total treatment time of 24 hr. Higher cumulative extracted Cu of 36.8% was achieved during the Co-current washing after 12 hr of treatment while only 24.7% of cumulative Cu was extracted during the Counter-current washing test.

Cumulative extracted Cu percentage in the Co-current washing after 12 hr was higher than value achieved after a treatment of 24 hr in C10 test (34.4%) whereas comparable cumulative extracted Cu was achieved in tests A1, A2, A3 and A4 for shorter treatment time (Figs. 4.5a, 4.5b and 4.5c). This suggested that CF configuration enhanced process kinetics in terms of Cu extraction only compared to the CSTR configuration.

Nonetheless, overall process efficiency improvement was observed comparing CF with both the CSTR and RF configuration results (Figs. 4.5a, 4.5b, 4.5c and 4.6). This general process enhancement in the CF configuration could be mainly ascribable to the fractionation of total amount of soil to treat in the 8 washing steps involving a fixed amount of EDDS volume in the washing solution. This led to the substantial increase of the L/S ratio avoiding main cation competitors effect due to the concurrent lowering of both HMs and EDDS moles as previously observed for CSTR tests (Fig 4.2b).

4.4 Practical implications for full-scale soil washing

The various washing conditions investigated in the present study can represent a valuable alternative to CSTR configuration for soil washing full-scale application. Data reported in terms of Cu extraction yield and process kinetics displayed process efficiency enhancement for all the suggested configurations. Process improvements were reached in terms of treatment time and involved EDDS volume required for environmentally feasible standards achievement after treatment. These results can further lead to various benefits for the operator/company according to economic/operational criteria decided for the soil washing technique.

EDDS volume lowering involves also a lower amount of EDDS per kg of soil required for proper efficient washing treatment. This leads to two main beneficial effects for soil washing.

A first one is represented by process costs decrease especially for full-scale applications where high amount of soil is generally involved in the treatment. Then economic return by decreasing EDDS amount per soil kg could be significant.

A second aspect is related to the achievement of a washing process less affecting soil characteristics. This latter advantage also could derive by reducing EDDS amount per soil kg and thus the total amount of chemical agent to be used. This could lead to avoid significant soil characteristics alteration and ensure environmentally safer soil disposal after treatment.

Additional advantages derive from the treatment time lowering, which can result either in the decrease of the full-scale reactor size and thus the plant costs or in the increase of the flow rate of soil that can be treated. In this latter case, main benefit can be represented by the involvement of a faster process and the decrease of overall time required for a contaminated area remediation. This can lead to a fleeting treated soil disposal in the original place of collection and rapid remediation of previously contaminated area.

4.5 Conclusions

In the present study an investigation about kinetics and extraction yield of various soil washing configurations was carried out leading to the following results:

- CSTR tests showed a higher influence of EDDS:HMs molar ratio compared to L/S ratio on Cu extraction in terms of process kinetics and efficiency. Increasing EDDS:HMs molar ratio values led to a well-defined process improvement as well as higher extraction percentage achieved in the initial treatment hours. In contrast, higher L/S ratio values did not show process enhancement and longer treatment time was necessary to achieve significant Cu extraction results.
- Different fractionations of EDDS volume and treatment time in the RF configuration displayed an overall process improvement compared the CSTR configuration. Furthermore, RF washing conditions showed different suitability according to various study cases. In fact the high fast kinetic extraction observed in A1 test suggested a better suitability of this condition for contamination mainly present in exchangeable and reducible soil fractions. Whereas A2 and A3 conditions showed best applicability for higher contamination where longer treatment times are needed. A4 test generally showed lower extracted Cu percentage than A1, A2 and A3 tests despite extraction kinetic increase was achieved in the initial treatment hours.
- Co-current washing results in CF configuration showed more constant process kinetic and higher Cu extraction yield than Counter-current washing. CF configuration led to a process kinetic enhancement only compared to the CSTR configuration. On the contrary, CF

configuration showed higher Cu extraction yield than CSTR and RF configurations after an overall treatment time of 24 hr.

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Chapter 5.

Application of an electrochemical treatment for EDDS soil washing solution regeneration and reuse in a multi-step soil washing process: case of a Cu contaminated soil

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5.1 Introduction

In the previous Chapters, several benefits in terms of soil washing process performances enhancement were reported. Nonetheless, full-scale applications of organic chelating agents are still limited because of the leaching agent cost as well as the discharge cost of the exhausted solution (Lim et al., 2005). This led several authors to investigate treatment processes aiming at regenerating washing solutions. For instance, alternative techniques followed by precipitation have been proposed for treatment and reuse of Pb contaminated washing solutions (Ager and Marshall, 2003; Hong et al., 1999; Kim and Ong, 1999; Zeng et al., 2005). Evaporation followed by acidification (Di Palma et al., 2005, 2003a) and reversal osmosis (Di Palma et al., 2003b) have been applied as well. Electrochemical processes have been investigated using different configurations like two chamber cell separated by a cation-selective membrane (Allen and Chen, 1993) or through a single chamber electrolytic cell and a sacrificial Al anode in alkaline conditions (Pociecha and Lestan, 2010; Voglar and Lestan, 2010). In all the previous cases the processes were tested on EDTA solutions. Only in a few cases the treatment of EDDS solutions has been addressed (Satyro et al., 2014). However EDDS is replacing EDTA in many cases (Kos and Lestan, 2003; Tandy et al., 2004; Zhang et al., 2008), because of its high biodegradability (Fabbricino et al., 2013).

The present paper aims at investigating the applicability of an electrochemical process for the recovery of metals from contaminated soils and the reuse of an EDDS spent washing solution by optimizing the process parameters (e.g. current density, pH and, conductivity of the washing solution). The investigated metal was Cu as main contaminant in the studied soil while Ca, Mg, Fe and Mn were investigated as main competitor elements in the chelation process. The efficiency of the process was evaluated by the amount of metal removed from the soil washing solution to better understand the mechanism of its regeneration. TCLP (Toxicity Characteristic Leaching Procedure) analysis was applied on the sludge produced by the electrochemical treatment in order to determine its potential toxicity prior further disposal in landfill. The regenerated soil washing solution was used in a multi-step washing treatment alternating soil washing and the electrochemical recovery of the exhausted washing solution. These tests were carried out to verify the residual chelating capability and durability of the regenerated soil washing solution in a closed-loop and waterfall washing configuration. The results were used for the determination of three indices to assess the decrease of the regenerated washing solution in terms of efficacy and potential extraction power.

5.2Material and methods

5.2.1 Soil, reagents and analytical methods

The investigated soil was sampled in Castel San Giorgio (Italy). Soil samples were air-dried, and sieved at 2 mm. The soil finest fraction was acid digested to determine its metal content using Aqua regia (European Standard EN 16174, 2012). An accelerated BCR sequential extraction (Pérez-Cid et al., 1998) using a sonicator (Branson Sonifier 250) was implemented in order to determine major and trace elements fractionation. Soil characteristics are summarized in Tables 4.1, 4.2 and 4.3 of the Appendix A.

$CaCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$ and, $MnCl_2 \cdot 4H_2O$ salts supplied by Sigma Aldrich were used to prepare synthetic washing solution (SWS) with proper amount of the investigated elements. Selected volume of EDDS 35% concentrated was used as chelating agent in the SWS. Dilutions were performed using ultrapure water. Before use, glassware were soaked overnight in a 2% HCl solution. Element analysis was performed using an Inductively Coupled Plasma (ICP) spectrometer Perkin Elmer Optima 8300 at proper wavelengths for each element (Ca, 315.887 nm; Cu, 324.752 nm; Fe, 238.204 nm; Mg, 285.213 nm and Mn, 257.610 nm). All experiments were carried out in triplicate and average values with related standard deviations were reported.

5.2.2 Electrochemical batch tests

Experimental set up involved for the electrochemical batch treatment is shown in Fig. 5.1.

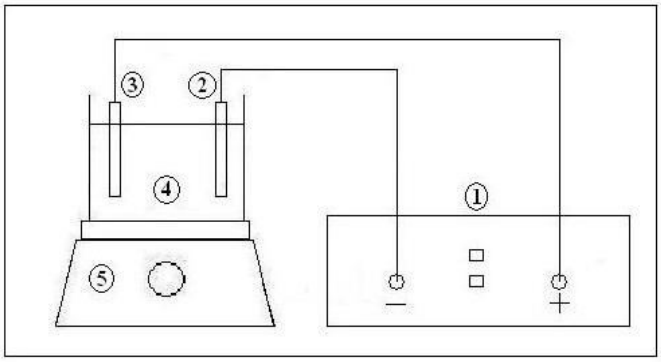


Fig. 5.1 Experimental set up for the electrochemical batch treatment: (1) Power supplier; (2) Fe-cathode; (3) Fe-anode; (4) Reaction volume; (5) Magnetic stirrer.

The tests were carried out at laboratory scale on 400 ml of SWS. The SWS was prepared by dissolving the above reported chlorinated salts of Ca, Cu, Fe, Mg, and, Mn in a 3.14 mM EDDS solution to achieve the following concentrations: Ca 45 $mg \cdot l^{-1}$, Cu 4 $mg \cdot l^{-1}$, Fe 18 $mg \cdot l^{-1}$, Mg 18 $mg \cdot l^{-1}$, Mn 2 $mg \cdot l^{-1}$. These values were chosen as they were the concentrations detected in the EDDS extraction solution after a 3 hours batch soil washing test on the investigated soil.

An electrochemical confirmative test (ECT) was also performed on a real exhausted washing solution from the investigated soil having the following concentration of the same elements: Ca 28.33 $mg \cdot l^{-1}$, Cu 2.18 $mg \cdot l^{-1}$, Fe 4.4 $mg \cdot l^{-1}$, Mg 18.53 $mg \cdot l^{-1}$ and trace concentration of Mn. The ECT was carried out setting the operational parameters with the optimal values selected during the batch electrochemical tests (5 $mA \cdot cm^{-2}$, pH = 8, conductivity 8 $mS \cdot cm^{-1}$).

The experimental set-up was constituted by a 500 ml electrochemical chamber set with a couple of identical Fe/Fe electrodes having a total surface of 100 cm^2, connected to a power supply (Hameg Triple Power Supply HM 8040). Treatment time was fixed at 2 hours in order to study the process kinetics on a quite long experimental time. Samples were taken at 5, 10, 15, 30, 60, 90 and 120 min. Tests were performed at different current density values (from 0.5 to 8 $mA \cdot cm^{-2}$), varying the pH and the conductivity of the washing solution from 4 to 12 and from 2 to 10 $mS \cdot cm^{-1}$, respectively. The electrochemical reactor was operated at constant current that was guaranteed by fixing the selected values through the power supply. The values for pH and conductivity were selected in order to have a wide experimental range while current density lowest values were considered to test the process efficiency in low power energy consumption conditions. Selected amount of HCl 0.1 M and NaCl 0.1 M were added to the SWS in order to obtain the established values of pH and conductivity. pH was monitored all along the electrochemical tests and continuously adjusted to the fixed values using a HCl 0.1 M solution. Electrodes were washed with HCl 0.1 M and scratched for cleaning after each electrochemical test.

5.2.3 TCLP, XRD and sludge analysis

Sludge analysis was conducted on the sludge produced during the ECT. After the 2 hours treatment, the solution was subjected to vacuum filtration using a 0.2 µm fiber-glass filter and dried at 105 °C. On the resulting solid phase both mineralization and TCLP tests were carried out. Mineralization experiments were performed with Aqua regia (European Standard EN 16174, 2012) using a Labtech Digiblock ED16S heater for 120 min. Extracted solutions were then filtered through vacuum

filtration with 0.2 μm fiber-glass filters and diluted to 100 ml with ultrapure water prior to elemental analysis.

TCLP procedure was carried out on the same sludge through two extraction fluids at pH=4.93±0.05 and pH=2.88±0.05 (USEPA, 1992). The mixing between extractant solutions and sludge was conducted according to standard methods (USEPA, 1992), through a Grant-Bio PTR 35 Multi-Rotator for 20 hours. After the mixing, the extraction solutions and the treated sludge were separated trough filtration with 0.2 μm fiber-glass filters. Solution samples were stored at 4°C until analysis.

X-ray diffraction (XRD) analyses were performed to characterize the mineral phases of the sludge produced from the ECT. Sludge samples were air dried and crushed to powder prior to be analyzed. XRD analysis was performed on a Bruker D8 Advance diffractometer equipped with an energy dispersion Sol-X detector with copper radiation (CuKα, λ = 0.15406 nm). The acquisition was recorded between 10° and 80°, with a 0.02° scan step and 1 s step time.

5.2.4 Multi-step soil washing tests

Soil washing tests were performed in 500 ml glass bottles in a rotoshaker Gerhardt Laboshake RS12 for accurate stirring.

Fresh EDDS solution 3.14 mM was used for the initial soil washing step while regenerated EDDS solutions were used for the following steps. After a 3 hours soil washing step, the washing solution was recovered by centrifugation using a laboratory centrifuge SIGMA 2-16P at 3000 rpm for 20 min. The regenerated solution was obtained through 2 hours electrochemical treatment of the EDDS 3.14 mM exhausted solution applying the working parameters optimized during the above described electrochemical batch tests.

The washing procedure was performed in two different configurations, indicated as closed-loop configuration and waterfall washing configuration (Figs. 5.2a and 5.2b). For both configurations, an initial EDDS:Cu ratio equal to 10:1 and a liquid to soil ratio equal to 25 were adopted. In the closed-loop set-up, the same EDDS washing solution was used, separated from the soil, regenerated, and recirculated on the same soil after the electrochemical treatment, for a total of 5 times (Fig 5.2a). In the waterfall washing configuration, the same EDDS washing solution was regenerated and reused on untreated soil samples up to 5 times (Fig 5.2b). As a comparison the

closed-loop set-up was implemented by using a fresh solution for each of the 5 washing steps (Reference test).

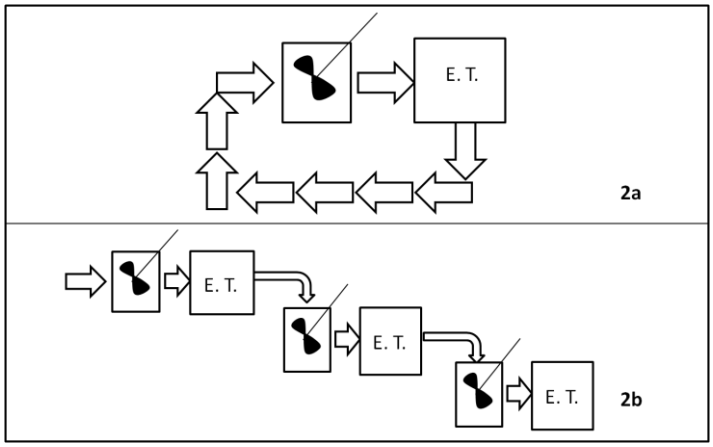


Fig. 5.2 Soil washing and electrochemical treatment (E.T.) tests in the (a) Closed-loop washing configuration and in the (b) Waterfall washing configuration.

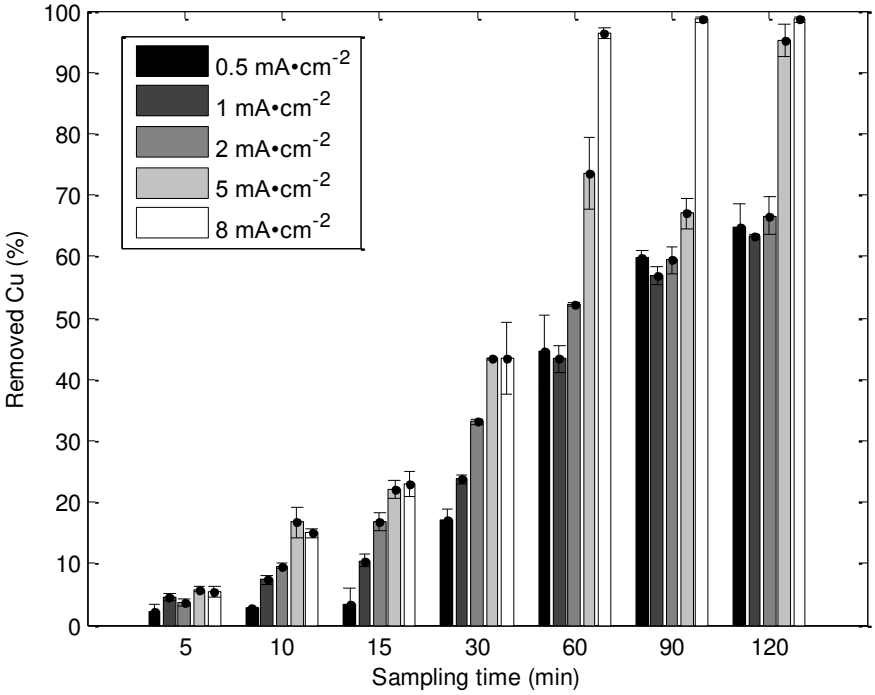
5.3 Results and discussion

5.3.1 Electrochemical batch tests

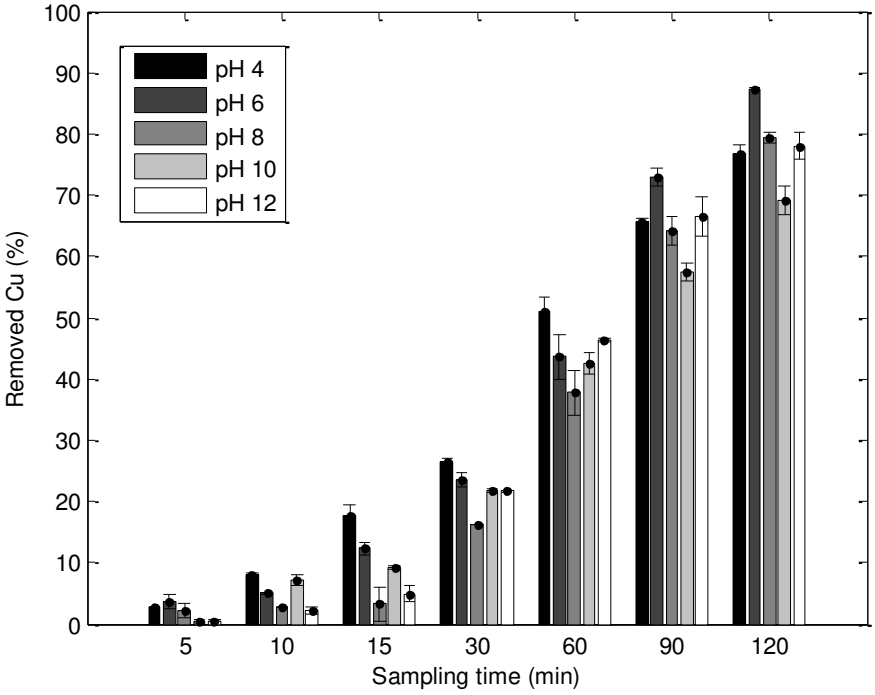
5.3.1.1 Ca, Cu, Mg and Mn removal efficiency from SWS and real soil washing solutions

The Cu removal yield at different current density (Fig. 5.3a), pH (Fig. 5.3b) and conductivity (Fig. 5.3c) is reported. Similar experimental tendencies were obtained for Mg, and Mn removal (data not shown). For all the tested conditions process kinetics were characterized by a two-phases trend. Initial Cu removal increasing tendency was observed followed by a stable removal phase (Fig. 5.3a). Both the slope of the linear phase as well as the occurrence of the plateau were function of the current density (*d*), and increased with *d* (Fig. 5.3a): as a result the plateau was not reached in the 2 hours reaction time if *d* was lower than 1 $mA \cdot cm^{-2}$ (Fig. 5.3a). The increase of metal removal in the exhausted solution with increasing values of *d* was likely due to the formation of a larger amount of coagulants that was effectively favored by the current flow passing through the electrodes (Escobar et al., 2006). A sufficiently high value of *d* must therefore be maintained in the electrochemical cell to obtain the required regeneration efficiency.

a


0.5 mA•cm-2
1 mA•cm-2
2 mA•cm-2
5 mA•cm-2
8 mA•cm-2
Removed Cu (%)
Sampling time (min)
0
10
20
30
40
50
60
70
80
90
100
5
10
15
30
60
90
120

b


pH 4
pH 6
pH 8
pH 10
pH 12
Removed Cu (%)
Sampling time (min)
0
10
20
30
40
50
60
70
80
90
100
5
10
15
30
60
90
120

c

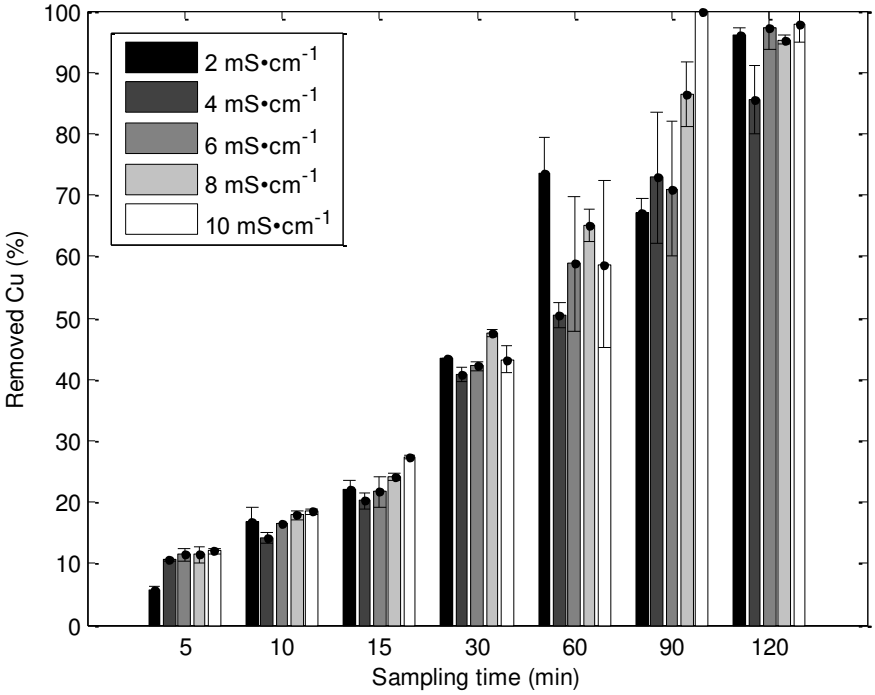


Fig. 5.3 Removed Cu at (a) current density ranging from 0.5 to 8 mA•cm^{-2}, pH = 8 and conductivity = 2 mS•cm^{-1}; (b) pH ranging from 4 to 12, current density = 0.5 mA•cm^{-2} and conductivity = 2 mS•cm^{-1}; (c) conductivity ranging from 2 to 10 mS•cm^{-1}, pH = 8 and current density = 5 mA·cm^{-2}.

Almost no effect of the pH (Fig. 5.3b) and conductivity (Fig. 5.3c) of the solution on the kinetic trend and the overall removal efficiency was observed. Both results were consistent with previous observations (Akbal and Camcı, 2011) although in that case higher extraction percentages were achieved even for a retention time lower than 2 hours, probably because of the presence of non chelated soluble Cu species, and the higher values of *d* (from 2.5 to 10 mA·cm^{-2}).

Fig. 5.1 of the Appendix A shows the maximum removal rates of Cu, Mg and Mn obtained during the tests carried out at the highest values of *d*, conductivity and pH (Tests A, B and C). These data showed that Cu removal yield was almost 50-55% higher than Mg removal, and 22-31% higher than Mn removal for Test A and B, while Cu removal yield was 70% higher than Mg removal in Test C. Ca concentration has lingered almost unvaried for all the tests suggesting a quite low Ca removal during the treatment (data not shown). The higher Cu removal yield compared to Ca, Mg and Mn was reasonable considering the standard potentials of the mentioned metals, equal to 0.340V for Cu^{2+}/Cu, -1.18V for Mn^{2+}/Mn, -2.356V for Mg^{2+}/Mg and -2.84 ± 0.01V for Ca^{2+}/Ca

(Bertocci and Wagman, 1985; Hunter and Kozawa, 1985; Perrault, 1985; Toshima, 1985). Higher potential corresponds to an easier removal of Cu compared to the other investigated cations.

It has to be specified that Fig. 5.1 of the Appendix A does not display the results obtained for Mn removal at pH 12. This latter became extremely high even after few minutes of reaction time because of the precipitation of Mn in its hydroxide form which can occurs at pH > 10 (Spellman, 2008).

Results of the ECT showed a final concentration in solution of Cu 0.14 $mg \cdot l^{-1}$, Mg 10.16 $mg \cdot l^{-1}$, Ca 21.07 $mg \cdot l^{-1}$, Fe 151.43 $mg \cdot l^{-1}$. The removal for all the investigated elements was characterized by a kinetic trend similar to the one obtained for the SWS for all detected species. Once more the Cu removal was higher than Mg and Ca removal.

5.3.1.2 Iron removal efficiency

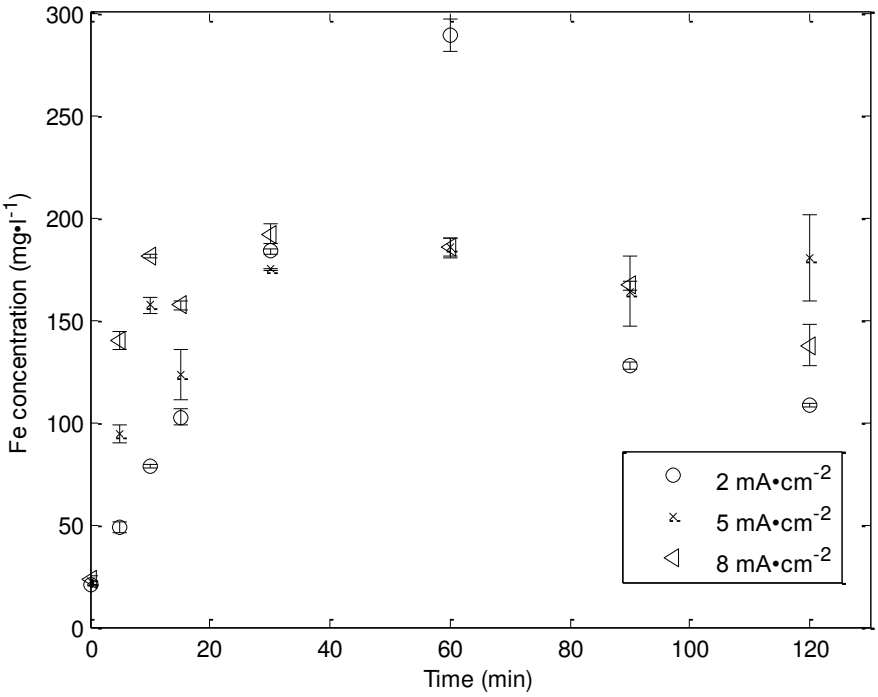
A different behavior was observed in the case of Fe removal. Fe precipitation was partially compensated by Fe dissolution resulting from the electrochemical oxidation of the anode and the resulting release of Fe ions (Arroyo et al., 2009). As a consequence, Fe removal followed a non-monotonic kinetic trend. Fe concentration in the exhausted washing solution rapidly increased during the first 30-40 minutes of the treatment for all tested conditions (Figs. 5.4a and 5.4b) due to the anode dissolution.

In alkaline pH conditions, the Fe dissolved from anode rapidly hydrolyzes to ferric hydroxide and polymeric Fe and formation of rust (dehydrated hydroxides) occurs as well (i.e. hematite, maghemite, goethite, etc.) (Moreno et al., 2007). The produced Fe hydroxide can further react with metal ions in solution and remove them through precipitation as flocs (Parga et al., 2014).

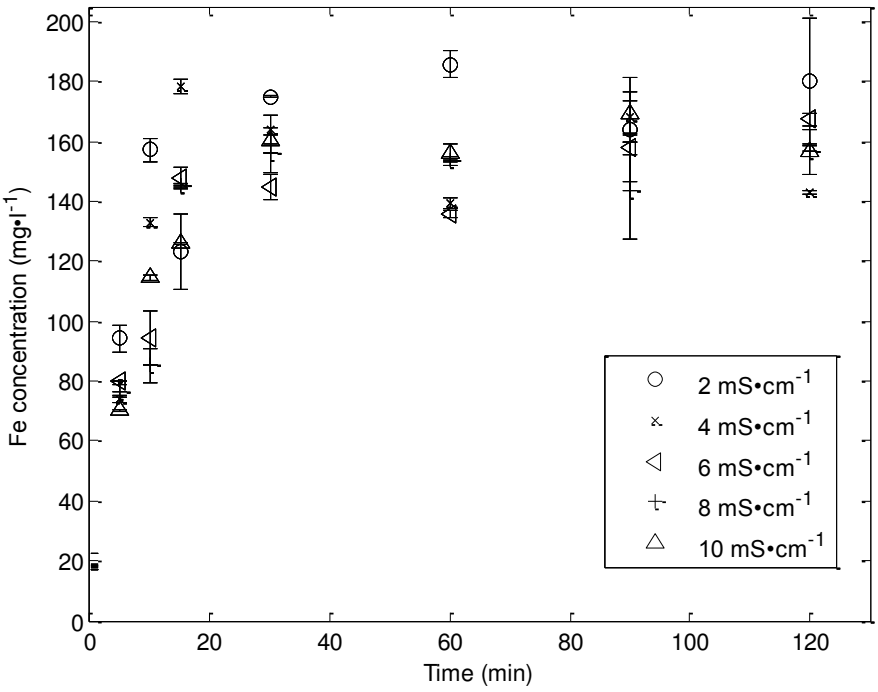
Removals observed for the investigated elements at these *d* values can strengthen the possible occurrence of flocculation with produced Fe hydroxide.

In some tests the increase of Fe in solution was then followed by an iron concentration decrease as a main consequence of Fe precipitation due to its supersaturation in the solution. This latter observation can be further strengthened by the higher extent of Fe concentration decrease compared to other elements, which suggests a stronger occurrence of Fe precipitation due to its supersaturation than the concurrent precipitation of other elements with Fe-flocs. This can be ascribed to the slower rate of Fe-element floc precipitation compared to the Fe dissolution from anode.

a


Fe concentration (mg•l-1)
Time (min)
2 mA•cm-2
5 mA•cm-2
8 mA•cm-2

b


Fe concentration (mg•l-1)
Time (min)
2 mS•cm-1
4 mS•cm-1
6 mS•cm-1
8 mS•cm-1
10 mS•cm-1

c

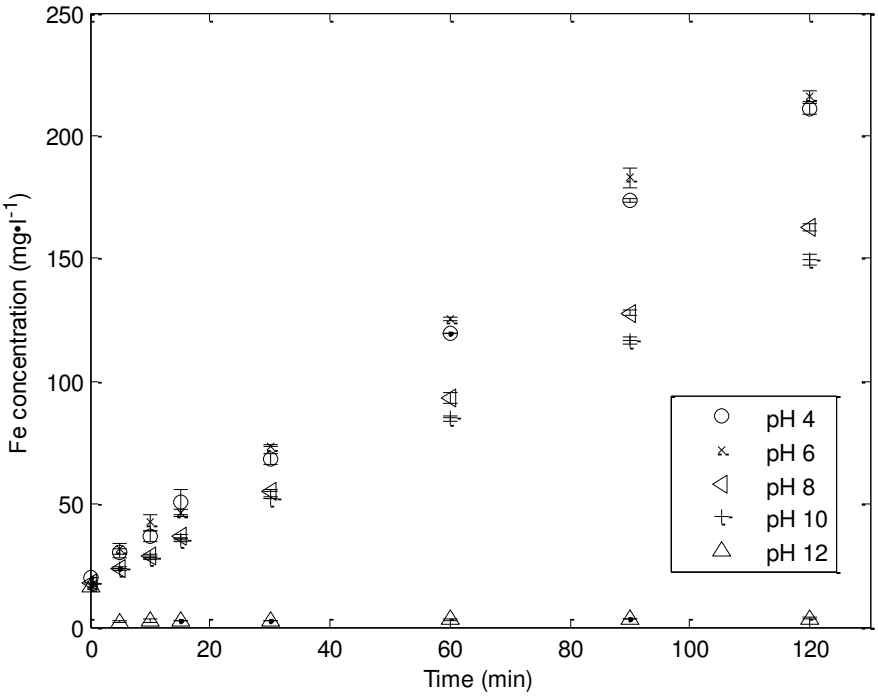


Fig. 5.4 Fe concentration in solution at (a) current density ranging from 2 to 8 mA•cm^{-2}, pH = 8 and conductivity = 2 mS•cm^{-1}; (b) conductivity ranging from 2 to 10 mS•cm^{-1}, pH = 8 and current density = 5 mA•cm^{-2}; (c) pH ranging from 4 to 12, current density = 0.5 mA·cm^{-2} and conductivity = 2 mS·cm^{-1}.

While no substantial effect of d (Fig. 5.4a) and conductivity (Fig. 5.4b) was observed, pH variation played an important role in determining the amount of Fe in the solution (Fig. 5.4c). The highest final value (215.9 mg·l^{-1}) was obtained at pH 6, and was almost 60 times higher than the final value obtained at pH 12 (3.6 mg·l^{-1}). The decrease of dissolved Fe concentration was mainly observed at alkaline pH. It is in fact reported that minimum solubility of Fe hydroxide is in the pH range of 7-8 (Parga et al., 2014). Furthermore rapid polymerization of aqueous Fe hydroxide forming its solid form occurs at higher extent in alkaline conditions (Henry et al., 1992; Livage et al., 1988).

5.3.2 Sludge characterization

Data about Cu and main competitor cations detection in the sludge produced during the ECT are summarized in Table 5.1.

Table 5.1 Amount of metals leached after acid digestion and TCLP tests.

Test	Cu ($g \cdot kg^{-1}$)	Mg ($g \cdot kg^{-1}$)	Ca ($g \cdot kg^{-1}$)	Mn ($g \cdot kg^{-1}$)	Fe ($g \cdot kg^{-1}$)
Total digestion	0.4±0.1	2.60±0.28	2.80±0.16	Below detection limit	535.60±4.46
TCLP (pH = 2.88)	0.033±0.010	0.60±0.01	0.50±0.11	Below detection limit	1.04±0.10
TCLP (pH = 4.93)	0.025±0.002	0.90±0.05	0.20±0.001	Below detection limit	1.02±0.04

Based on final and initial metals concentration in the ECT and the reaction volume (400 ml) it was possible to evaluate the total mass of removed elements. These values were 2.9 mg for Ca, 0.8 mg for Cu, 3.3 mg for Mg while final mass of Fe in solution was 60.6 mg as it increased during the test. From the concentrations measured in the acid digested solutions it was possible to determine a total mass contained in the sludge equal to 1.3 mg for Ca, 0.2 mg for Cu, 234.1 mg for Fe and 1.2 mg for Mg. This calculation was carried out considering a total acid digested solution volume of 100 ml.

A comparison among Ca, Cu and Mg mass balances from the ECT and the sludge total digestion shows a lower element mass in the sludge than that removed during the treatment. This could be attributed to a possible electro-deposition of the elements on the cathode resulting in an incomplete coagulation of the removed elements with Fe-hydroxides. Furthermore it is worth noticing that the Fe mass detected from the sludge total digestion is much higher than the final concentration in the treated solution of the ECT. This indicates a larger amount of Fe in non-soluble form involved in flocculation and precipitation phenomena with the subsequent formation of the sludge.

A comparison between total digestion and TCLP results showed a low mobilization of the studied elements from the sludge (Ca, 9-19%; Cu, 6-9%; Mg, 25-33% and Fe, 0.19%). Despite these results reveal no considerable leaching phenomena it is to specify that regulation does not provide normative limits for the considered elements (USEPA, 2012). This suggests that no toxicity characteristics subsist for the investigated sludge.

Fig. 5.5 shows results of XRD analysis on the sludge collected from the ECT test. It can be noticed that sludge mineral composition is mainly composed by lepodicrocite, maghemite and goethite that are all identified electro-coagulation process by-products (Roy et al., 2014). Such result is consistent with data from sludge total mineralization that showed Fe as main contained element.

The presence of Fe-oxyhydroxide minerals in the sludge can further strengthen the possibility of Cu removal from solution through interaction with Fe-oxyhydroxide.

It is in fact generally reported that interactions between hydrous oxides and metals can include adsorption, surface precipitation and coprecipitation phenomena (Karthikeyan et al., 1999). For instance, Cu adsorption on Fe-oxyhydroxide surface can occur due to electrostatic attractions when the Fe mineral species show magnetic characteristics (such as lepidocrocite and magnetite) (Parga et al., 2013).

Furthermore studies were carried out showing adsorption of Cu onto goethite and lepidocrocite surfaces with the formation of inner-sphere complexes in pH ranging from 2 to 7. Higher Cu adsorption was occurring at higher pH (Peacock and Sherman, 2004) that can be expected since increase of metal cation sorption was observed with increasing pH values (Violante et al., 2010). Cu adsorption is reported through maghemite nanoparticles as well and mainly at pH above 6.5 (Hu et al., 2006). In this case electrostatic attractions between Cu and maghemite were enhanced for pH higher than the zero point of charge pH (pH_{zpc}= 6.3 for maghemite) that causes negative charges formation on the adsorbent surface. In contrast Cu adsorption due to Cu^{2+} and H^{+} ion exchange was mainly occurring onto maghemite surface for pH lower than pH_{zpc} (Hu et al., 2006). In the present work no preferential Cu removal is observed for both electrostatic attraction and Cu^{2+}/H^{+} ion exchange mechanisms since the overall Cu removal shows almost no differences for the whole investigated pH range (Fig. 5.3b).

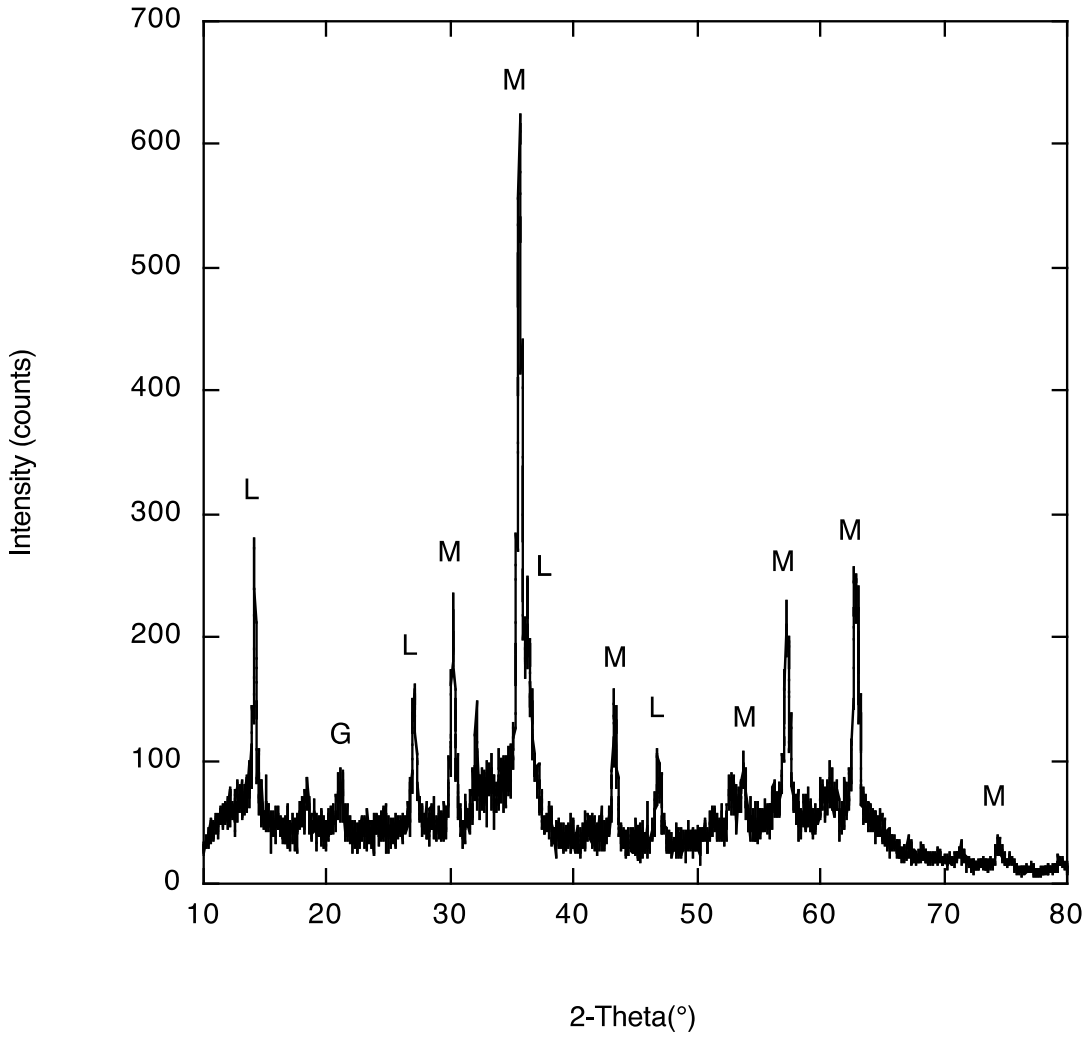
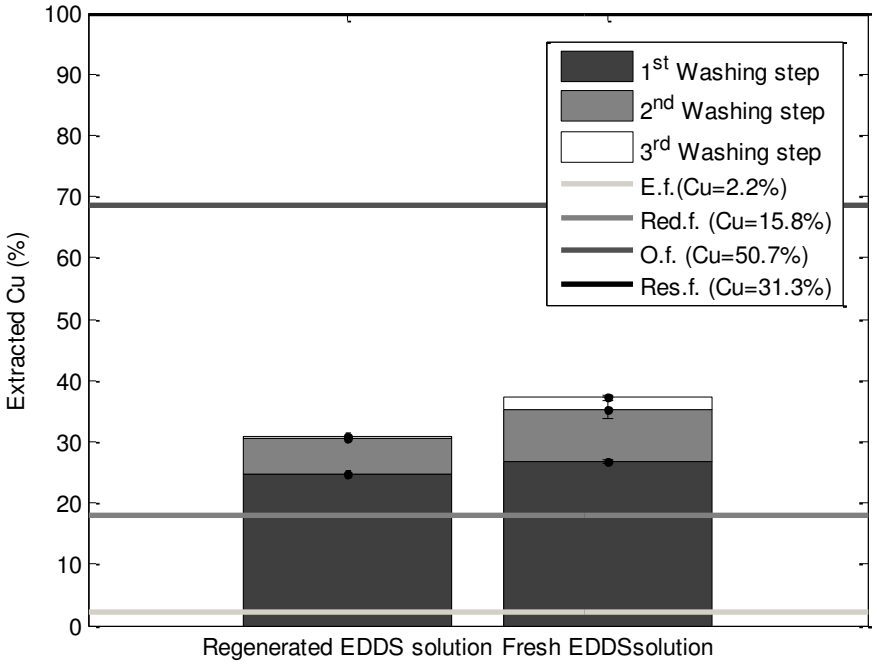


Fig. 5.5 XRD spectrum of sludge from ECT (L : Lepidocrocite; G : Goethite; M: Maghemite).

5.3.3 Multi-step soil washing tests

Fig. 5.6a reports the extraction efficiencies of the closed-loop configuration together with the extraction efficiency of the Reference test in terms of Cu removal. Only results of the first three steps are reported because in both tests no extraction was obtained in the fourth and fifth extraction step. They are compared to the soil Cu content resulting from the sequential extraction analysis (exchangeable fraction = 2.2%, reducible fraction = 15.8%, oxidisable fraction = 50.7%, residual fraction = 31.3%). Lines in Figs. 5.6a and 5.6b represent the Cu cumulative percentage in the various soil fractions.

a



b

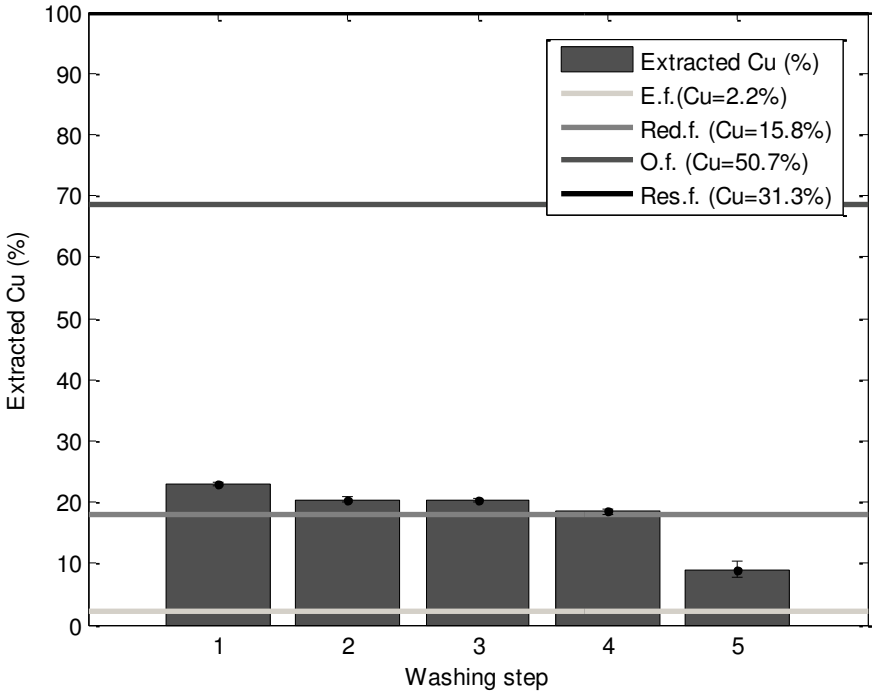


Fig. 5.6 Percentage of extracted Cu in the (a) Closed-loop configuration and a Multi-washing involving fresh EDDS solution at each step and (b) Waterfall configuration step by step with lines representing the Cu cumulative percentage in the various soil fractions: Exchangeable fraction (E.f.), Reducible fraction (Red.f.), Oxidisable fraction (O.f.), Residual fraction (Res.f.).

According to the available results it was possible to evaluate an Efficiency Removal Decrease index (ERD index) expressed as follows:

$$ERD\ index = \frac{\sum_{i=1}^{n}\left(\frac{R_{i+1}}{R_i}\right)}{\sum_{i=1}^{n}\left(\frac{R'_{i+1}}{R'_i}\right)} \quad (5.1)$$

R is defined as the removal efficiency obtained in the generic washing step i using the regenerate EDDS solution, while R' is the removal efficiency obtained in the same washing step of the Reference test, using only fresh EDDS. The ERD index aims at defining the overall reduction in terms of extraction efficiency of the regenerated washing solution compared to the extraction efficiency of the fresh one. From the obtained results the ERD index turns out to be 0.733 if it is calculated considering the 1st and 2nd washing step while it decreases to 0.508 when considering the 2nd and 3rd washing step. This result suggests that the difference in terms of removal efficiency among the steps of two washing configurations remained almost constant as long as the removal process occurred.

The high decrease after the first washing step and then the ineffectiveness in Cu removal after the second step could be due to the lowering of Cu content in the more accessible soil fractions (e.g. exchangeable and reducible fractions) occurring during the first two steps (Fig. 5.6a). A second reason can be the tendency of EDDS to chelate the major cation competitors, which are present in high concentrations.

In Table 5.2 the percentages of extraction of Ca, Mg and Mn in the closed-loop test are reported.

Table 5.2 Ca, Mg and Mn removal in the Closed-loop washing configuration (pH = 8, current density = 5 mA•cm^{-2}, conductivity = 8 mS•cm^{-1}).

Washing step	Extracted Ca (%)	Extracted Mg (%)	Extracted Mn (%)
I	1.15	2.99	Below detection limit
II	0.13	0.16	13.44
III	0.44	0.07	2.78
IV	0.78	0.14	Below detection limit
V	2.77	0.12	0.98

Data were extremely variable from one step to another, and showed no clear tendency. Despite the low removal percentages for these elements, the values corresponded to a high amount of elements in terms of mg·kg^{-1} according to their initial concentration in the contaminated soil. This can further validate their favored extraction by EDDS over Cu removal.

The maximum removal efficiencies achieved during the electrochemical treatment of the spent washing solution were almost 17% for Ca, 100% for Cu and Mn, 80% for Mg (data not shown). These results were comparable to the removal efficiencies achieved in the SWS batch treatments.

Fe was exhibiting a different behavior as its concentration in solution in terms of mg·l^{-1} after each electrochemical step was 105.2, 68.1, 25.9, 47.4 and 7.5. Comparing these data to leached Fe concentrations from the first to the last soil washing step (1.1, 117.2, 67.6, 24.5 and 3.8 mg·l^{-1}), it appears that concentrations achieved during electrochemical treatment were higher than the ones obtained in the following washing steps. In the only case of the second and third washing step Fe amount from soil washing was higher than the one resulting after the electrochemical treatment and it was possible to define effective removal efficiencies. For the other washing steps it can be assumed that Fe precipitation during the soil treatment was occurring. This can be stated for the lower Fe concentration outgoing from the soil washing compared to the incoming Fe concentration from the previous electrochemical test. Fe amount in the washing solution after soil washing increased until the second washing step then it kept decreasing in the following steps. Fe overproduction from the electrochemical treatment decreased as well. Results concerning Cu extraction during the waterfall washing configuration are summarized in Fig. 5.6b.

The removal efficiency of the washing solution decreased step by step. Considering that each washing step was carried out on untreated soils, and therefore the amount of Cu content was always the same, and Cu was always present in the more easily accessible soil fractions, the extraction yield decrease could be due to the partial degradation of EDDS after the electrochemical treatment. Further reason could be the chelant-metal complex adsorption to the hydroxyl groups that can be present on the Fe oxide surface although this phenomena is mainly stated for EDTA adsorption onto Fe oxide (Nowack and Sigg, 1996; Nowack et al., 1996). Data on EDDS-metal complex adsorption are also reported with higher adsorption rate at pH 5.5 than 8 (Tsang et al., 2009). It is noteworthy to underline that at increasing pH chelant-metal complex can adsorb through metal bonds (type A ternary surface complexes) while chelant bonds (type B ternary surface complexes) prevail at decreasing pH (Nowack, 2002).

Results reported in Fig. 5.6b were used for the determination of a second index: Loss in Potential Extraction. This latter can be expressed in two different ways as Loss in Potential Extraction Absolute index (LPEA index) and Loss in Potential Extraction Relative index (LPER index). They are defined as follows:

$$LPEA\ index = \frac{R_0 - R''_{i+1}}{R_0} \tag{5.2}$$

$$LPER\ index = \frac{R''_i - R''_{i+1}}{R''_i} \tag{5.3}$$

R_0 represents the removal efficiency achieved in the first washing step, while R'' represents the removal efficiency obtained in the generic washing step i.

LPEA index indicates the decrease of the extraction potential of the washing solution after each electrochemical treatment. It is therefore an indirect index of the EDDS biodegradation during the electrochemical process. On the other hand, LPER index can be useful to better specify the tendency of potential extraction decrease as it represents the efficiency drop step by step.

Data showed that from the second to the fifth washing step LPEA index increased from 0.106 to 0.604 suggesting a high drop in terms of chelating capacity of the solution.

LPER index is characterized by a non-monotonic trend. It decreased from 0.106 to 0.005 going from step 2 to step 3, and then increased to 0.089 after step 4, and to 0.512 after step 5. According

to these data it was possible to notice that the highest efficiency drop occurred in the fifth step after a lag phase from the 2nd to the 4th step.

Similarly to the closed-loop configuration the extraction percentages of Mg, Ca and Mn were very low, while slightly lesser removal yields were achieved during the electrochemical tests. Even for soluble Fe in the washing solution results showed a maximum at the 2nd washing step as already observed for the closed-loop configuration. Fe concentration started to decrease in the following washing steps. In the same way the Fe overproduction occurring in the electrochemical tests decreased until the 4th electrochemical treatment step (data not shown).

5.4 Conclusions

- Results from this work showed the feasibility of electrochemical treatment for recovery of spent biodegradable washing solutions and their reuse in soil washing. This represents a possibility for a more economically sustainable soil remediation.
- Batch experiments on synthetic solutions and confirmative test with a real EDDS solution showed that elements removal yield was strongly depending on *d* variation. Generally, the process kinetics showed an initial linear phase followed by a plateau that was more noticeable at high *d* values (5-8 mA·cm^{-2}).
- Acid digestion on the sludge showed that Fe is the main component while negligible leaching from sludge after TCLP tests occurred for all the investigated elements. Sludge mineral phases identification by XRD showed the presence of lepodicrocite, maghemite and goethite. Such Fe-oxide minerals are involved in Cu adsorption and co-precipitation.
- Results from the closed-loop configuration showed Cu extraction until the second washing step. Nonetheless the loss in terms of metal extraction efficiency between the regenerated and fresh washing solution was constant step by step as suggested by the ERD index values.
- Waterfall configuration data showed that the electrochemical treatment can be sustainable for the remediation of an EDDS solution avoiding high degradation process of the chelant itself. In fact LPEA and LPER indexes showed a high chelating capability drop after the fourth washing step.

- Adequate electrochemical process set up for application on higher operational scale can be of interest for further investigations along with kinetic mathematical modeling for plant design and management.

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Chapter 6.

General discussion, conclusions and future perspective

6.1 General discussion

6.1.1 Main parameters affecting the soil washing process

Soil matrix represents a heterogeneous mean that can be composed by variable mineralogy, organic matter content, particle size distribution. According to this, deep investigations are necessary when soil remediation technologies need to be applied on contaminated soils.

In Chapter 2 it was indicated that soil and HMs characteristics are strictly related and highly affect the efficiency of soil washing process. High presence of organic matter and humic acid generally reduce the mobility of HMs into the soil (Abumaizar and Khan, 1996). Nonetheless the stability of the formed complex can be variable according to HMs involved and its quantitative determination can be carried out taking into account the various physical-chemical characteristics of the polymer molecule active sites (Reuter and Perdue, 1977).

Soil minerals constituents and organic matter content can influence the fractionation of HMs in soil. Despite the lower extraction observed for Fe- and Mn-oxide bound metals (Elliott and Shastri, 1999) it is also reported that higher effect on soil washing efficiency is detected for HMs bound to organic matter (Cesaro and Esposito, 2009).

This behavior was also assessed by results displayed in Figs. 3.1a, 4.2a, 4.5b and 5.6a of Chapters 3, 4 and 5 for both CSTR and multi-step washing configurations. These graphs showed that the kinetics of the extraction process decrease with increasing treatment time/number of washing steps due to the higher binding strength displayed between detrital soil fractions and HMs.

Particle size distribution also affects the HMs retention in soils, since finest soil particles stronger retain HMs (Tejowulan and Hendershot, 1998). According to this, high presence of silt and clay could make soil washing economically prohibitive due to the low volume reduction achievable for the soil treatment (James and Kovalick, 2000). However, high particle size distribution variability could increase process costs because of the requirement of copious equipment suitable for each particle size range separation.

Soil and HMs parameters strongly influence the selection and the determination of proper operational parameters. This is indicated, for example, by the results reported in the present work showing that higher EDDS:Cu molar ratio was needed in order to enhance the Cu extraction yield (Figs. 3.1a and 4.2a). These result are confirmed by literature data, since high values of APCs:HMs molar ratio are required to reduce the effect of main cations competition and increase metal

mobilization by enhancing strongly bound metals release (Begum et al., 2012; Sarkar et al., 2008; Vandevivere et al., 2001).

Among various process parameters that can be varied to improve soil washing efficiency, APCs:HMs molar ratio and L/S ratio have been generally the most frequently investigated. This can be mainly ascribable to the reduced impact on soil characteristics obtained by varying these two parameters.

On the contrary, parameters such as washing solution pH, sonication systems and temperature can have strong effect on soil properties. Acidic pH conditions are generally most effective for HMs extraction (Van Benschoten et al., 1997). Nonetheless, low pH values cause organic matrix dissolution as well as carbonates in soils (Vandevivere et al., 2001).

Similarly, soil washing process enhancement can be achieved by sonication systems due to soil particle fracture for the repeated compression and decompression cycles (Hong et al., 2008). Finally significant HMs extraction were noticed at high values of temperature (Zou et al., 2009). This latter result can be ascribable to the HMs mobility enhancement. However concurrent soil properties alteration, such as alteration of mineralogical composition, could also occurs at very high temperature (Zihms et al., 2013).

Despite the wider investigations carried out for APCs:HMs molar ratio and L/S ratio, this latter did not show significant effect on the extraction efficiency of the washing process (Tsang et al., 2012; Van Benschoten et al., 1997). Results from Figs. 3.1b and 4.2b further confirmed the ineffectiveness on the Cu extraction yield of increasing L/S ratio values. In the present work this latter result was mainly due to the smaller amount of the treated soil used to increase L/S ratio values, in order to avoid a variation of the reactor volume. As a consequence, less moles of EDDS were needed in order to keep the EDDS:Cu molar ratio constant, leading to a higher main cation competition effect as observed from Fig. 3.1a.

Accordingly with literature review and batch experimental washing tests data, EDDS:Cu molar ratio was selected and deeply investigated as the main parameter for soil washing efficiency optimization and contaminant kinetic extraction determination. These further studies were useful to develop a mathematical model for process performances prediction and carry out investigations on suitable washing configurations presented in the next subsection.

6.1.2 Soil washing process kinetics and extraction yield

Data obtained from soil washing experiments in CSTR configuration showed that process kinetic was characterized by two phases (Fig. 3.1a): an initial fast kinetic step and a subsequent slower kinetic step. Further validation of the two-kinetic step behavior was assessed by the better model calibration results achieved by fitting experimental data with two-kinetic step equation (Eq. 3.5) than by fitting experimental data with mono-kinetic step equation (Eq. 3.4) (Figs. 3.2a and 3.2b). Moreover, good values of NRMSE, ME and IoA indexes achieved in the two-kinetic step equation also demonstrated its suitability for process efficiency prediction (Fig. 3.4 and Table 3.2). Further confirmations were reported by various literature works (Kirpichtchikova et al., 2006; Lim et al., 2004; Zhang and Lo, 2006).

The occurrence of initial fast kinetic extraction and following slow extraction can be mainly ascribed to the contaminant fractionation in the soil matrix. Many mathematical models in fact described HMs extraction as a function of metal concentration in labile and non-labile soil fractions besides treatment time (Bermond et al., 1998; Yip et al., 2009; Yu and Klarup, 1994). According to this, high extraction percentage of HMs can be achieved in few hours of treatment followed by a process slowing down as the labile HM forms amount decreases.

Besides treatment time, EDDS:Cu molar ratio variation displayed higher influence on soil washing efficiency. Main effect observed on the overall process performance by increasing EDDS:Cu molar ratio was obtained in the fast kinetic extraction. In this step in fact a higher cumulative Cu amount is observed as the EDDS:Cu molar ratio increases (Figs. 3.1a and 4.2a). This result is mainly due to the reported efficacy of high APCs:HMs molar ration in lowering the main cation competition effect on chelation with APCs (Subirés-Muñoz et al., 2011).

However, further confirmation about Cu cumulative extraction enhancement in the fast kinetic step was given by the calibration procedure of the mathematical model (Fig. 3.3). Results in Fig. 3.3 displayed positive exponential tendency with increasing EDDS:Cu ratio for maximum Cu extraction achievable in the fast kinetic step while negative linear correlation was found between maximum Cu extraction in the slow kinetic step and EDDS:Cu molar ratio.

More in details, kinetic of soil washing in CSTR configuration could be divided in three kinetic steps. From results in Fig. 4.1 of Appendix A it was observed a fast kinetic extraction until 1hr of treatment, followed by a slow kinetic step until the end of the treatment. According to this, approximation to the two-kinetic step model resulted a proper and generally applicable solution

although sharp distinction between first and second kinetic step could not be observable for each case.

Interesting kinetic results were observed when varying the washing configuration. Fast kinetic step enhancement was achieved for RF washing configuration mainly when fractionating the treatment time (Fig. 4.2d of Appendix A). Despite the higher kinetic constant of the fast kinetic step observed for A4 test, it is worth noticing that this value is achieved on a very short time (0.5 hr).

However further kinetic enhancements were also reported for the second kinetic step of A1 and A4 with similar kinetic constant values of C10 test (Figs. 4.2a and 4.2d of Appendix A) while A2 and A3 configurations improve the process kinetics mainly in the final slow extraction step (Figs. 4.2b and 4.2c of Appendix A). Besides the process kinetic improvement, extraction yield enhancement was also observed when fractionating EDDS volume and treatment time in RF washing configurations (Figs. 4.4a-4.4c, Chapter 4). Also in this case extraction yield enhancement was strictly related with process kinetic of each test. For instance, A1 and A4 configurations allowed to reach significantly higher Cu extraction percentage than C10 configuration after few hours of treatment although higher final cumulative extracted Cu was observed in A1 test (Figs 4.4a and 4.4c, Chapter 4). On the contrary, more noticeable Cu extraction improvements compared to C10 configuration were observed after 9 hr treatment for A2 and A3 configurations further confirming their higher kinetics in the second part of the treatment (Figs. 4.4b, Chapter 4). This also entailed the achievement of significant extracted Cu percentage in the last hours of washing process almost comparable with results in A1 test and better than performances in A4 test.

Generally, a higher Cu extraction efficiency was observed by using CF washing configurations especially if compared to the CSTR washing configuration (Figs. 4.5a, 4.5b and 4.6, Chapter 4). A better extraction was noticed in the Co-current washing (36.8%) compared to the Counter-current washing (24.7%) probably ascribable to the HMs decrease in more easily extractable forms after the first treatment. Nonetheless overall extracted Cu for A1, A2, A3 and A4 were comparable with values obtained from CF configuration.

Improvements achieved in terms of treatment time and extraction efficiency using multi step washing (RF and CF washing conditions) for HMs contaminated soil remediation were consistent with literature works reported in Chapter 2 (Hong et al., 2008; Hsieh et al., 1989; Steele and Pichtel, 1998).

6.1.3 Electrochemical treatment for spent EDDS solution recovery

In Chapter 5 experimental activities about batch electrochemical treatment through iron electrodes used for the recovery and reuse of EDDS spent solution were reported. Results displayed that process efficiency in terms of Cu removal was affected more by current density optimization than by conductivity and pH of washing solution (Figs. 5.3a, 5.3b and 5.3c).

A higher removal efficiency was obtained for Cu compared to Mg, Mn and Ca (Cu>Mn>Mg>Ca). This was mainly ascribable to their reported standard potentials values, decreasing from Cu to Ca (Bertocci and Wagman, 1985; Hunter and Kozawa, 1985; Perrault, 1985; Toshima, 1985). This tendency was confirmed by the electrochemical treatment of both synthetic and real EDDS washing solutions.

Fe dissolution from anode during the electrochemical treatment could possibly lead to both positive and adverse consequences on the removal process efficiency. Firstly, high Fe dissolution was needed in order to form Fe-hydroxide flocs useful for the co-precipitation and removal of investigated elements. The occurrence of this phenomenon was assessed by the analysis on the acid digested solution of the electrochemically-produced sludge as well as by the XRD analysis (Table 5.1 and Fig. 5.5). The analysis of acid digested solution allowed to detect Cu, Mg, Mn and Ca presence into the sludge confirming their co-precipitation with Fe-flocs. Furthermore, it was highlighted that the amount of investigated elements in the sludge was lower than their overall amount removed from washing solution suggesting concurrent occurrence of electro-deposition phenomena onto the cathode besides electro-coagulation process. XRD analysis better detailed sludge mineralogy displaying presence of lepidocrocite, goethite and maghemite that can generally adsorb HMs such as Cu through ion exchange or electrostatic attractions depending on pH (Hu et al., 2006; Parga et al., 2013; Peacock and Sherman, 2004). On the contrary, excessive Fe dissolution could represent source of interference for EDDS chelation with contaminant elements in further washing steps. However, the obtained results showed that Fe dissolution was partially balanced by Fe concentration decrease due to co-precipitation phenomena with investigated elements and its supersaturation in solution. Furthermore, no significant effect on the following washing steps was assessed in results from Closed-loop and Waterfall washing configurations where both extracted Fe from soil and overproduce Fe amount from electrochemical treatment decreased step by step. TCLP analysis on the electrochemically-produced sludge also displayed low leaching percentage of investigated elements proving sludge suitability for environmental safe disposal (Table 5.1).

Cu extraction efficiency of the spent EDDS solution was reported for further washing steps in the Closed-loop and Waterfall washing configuration tests (Figs. 5.6a and 5.6b). In the Closed-loop

configuration, electrochemically recovered EDDS solution showed efficacy in Cu extraction and comparable results with a fresh EDDS solution involvement up to a second soil washing step. Similar result is also obtained by comparing data from Closed-loop configuration with A2 and A3 tests of RF configuration (Fig. 4.4b). Once more, comparable cumulative extracted Cu percentages were observed after two washing steps (6 hr) between reused EDDS solution and fresh EDDS solution at increasing and decreasing EDDS volume (A2 and A3 respectively). The overall extraction efficiency of the reused EDDS solution compared to the fresh one was quantitatively determine by the ERD index. The ERD index values suggested that constant efficiency differences between the two solutions occur step by step highlighting no significant efficacy gap as long as Cu extraction occurs.

Finally Waterfall configuration results allowed determining LPEA and LPER indexes useful to evaluate general and step specific loss in potential extraction efficiency of the regenerated EDDS solution. Specifically, LPEA index quantified a high efficiency drop after five washing steps that was mainly occurring in the fifth washing step as suggested by LPER values (LPER = 0.512, after the fifth step). Comparison between data from Waterfall configuration and CF configuration during the Co-current washing displayed similar tendency in terms of extracted Cu after five washing steps (Figs. 5.6b and 4.5a). Main efficiency drop was observed after four washing steps for both configurations although the reasons could be different. For CF configuration, Cu extraction efficiency drop was then followed by a further extraction increase in the following steps. This suggested that extraction drop delimited to the fourth step could mainly occur due to the competition phenomena followed by ion exchange in the following steps.

In the case of Waterfall configuration, further reason for efficiency drop could be related to the partial EDDS solution biodegradation after electrochemical treatment or co-precipitation of EDDS complexes with Fe-hydroxide flocs. However extracted Cu percentage achieved in the four steps of CF configuration are always higher than Waterfall configuration suggesting better performance of the fresh EDDS solution.

Indirect evaluation of EDDS solution biodegradability after each electrochemical step given by LPEA and LPER indexes values showed that the regenerated EDDS solution preserved its chelating capability for several washing steps. This confirmed the electrochemical treatment suitability for the EDDS solution recovery avoiding excessive deterioration of regenerated washing solution.

6.2 Conclusions and future perspective

The entire study carried out in the present work focused on the various steps that represent the soil washing process from soil collection and characterization, to washing solution and treated soil disposal. Literature review studies highlighted complexity in determining the suitable conditions for proper HMs contaminated soil remediation. This is mainly due to the extreme variability and copious quantity of parameters that have to be taken into account when designing a soil washing treatment. Further complication derives from the not easily predictable effects on process performance due to the synergic actions of soil and HMs characteristics with process parameters.

Then, efforts are necessary for deeply determining all the characteristics of the study case before application of soil washing. However, only process parameters can be varied by the operators, and therefore the identification of the main parameters affecting process efficiency is fundamental. In the present work EDDS:Cu molar ratio showed high effect on the Cu extraction yield as well as on the kinetics of the washing process.

EDDS volume and treatment time involved in the soil treatment display a crucial role for both contaminant extraction efficiency and washing cheapness. As a consequence, proper process optimization is required to enhance soil washing efficacy/economical competitiveness among several soil remediation techniques.

First step for process optimization was to determine a mathematical tool for washing performance prediction. Two-kinetic step equation was identified as suitable model to describe extraction efficiency evolution at varying EDDS:Cu molar ratio and treatment time.

Further improvements were achieved by enhancing soil washing performance through investigation on various washing configurations. Higher extracted Cu percentage obtained with lower EDDS volume and treatment time was an important result from experimental activities carried out through Plug Flow washing configurations. Besides this, various studied configurations displayed better suitability for different cases of soil contamination. These results together with the defined two-kinetic step mathematical model provided interesting options to consider in a preliminary decision-making process referred to a HMs contaminated soil remediation problem.

Treatment of EDDS solution after soil washing treatment represents an important step regarding economical/environmental safety aspect of the process. Electrochemical treatment showed a very good efficiency, and resulted in a useful option for the reuse of the solution in further soil washing steps.

Investigations reported in the present work represent a contribution on soil washing process enhancement. However, further aspects about this topic need to be studied. Outcomes achieved in this work can be applied in future investigations related to higher experimental-scale (pilot and full-scale applications). Additional kinetic study can be carried out to improve and link mathematical model to soil/HMs characteristics as well as structural aspects of soil washing reactors. This could provide enhanced tool not only able to predict process performance but also to determine optimal conditions for reactor design purposes.

Moreover, pilot-scale studies are highly recommended for future activities. This could be a fundamental step in order to assess the real suitability of the results achieved to higher scales. Moreover, pilot-scale tests should be combined with a cost-benefit analysis taking into account the reactor volume, the amount of soil and washing solution and the energy consumption in order to obtain a feasibility assessment for the specific case study. Finally, toxicity studies on the treated soil represent a crucial future investigation from the environmental safety point of view. The latter can be useful in order to assess the time required for the washing solution biodegradation according to the HM, which is forming the chemical complex. Benefits out coming from these studies would be the prevention of possible contamination due to the persistence of chelant-HMs in disposed soil. As a consequence, it would be possible to properly select safe chelating agents aiming at a future reuse and revaluation of the treated and disposed soil.

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Appendix A

Table 4.1 Physical properties of the soil.

Initial field moisture[a] (%)	Volatile solids[a] ($g \cdot kg^{-1}$)	Electrical conductivity[b] ($\mu S \cdot cm^{-1}$)	Soil pH[b]	Cation Exchange Capacity[c] (meq/100g of soil)
20	75.64	430.67	7.81	29.56

[a] ASTM D 2974-00, 2000. Standard test methods for moisture, ash and organic matter of peat and other organic soils.

[b] soil:ultra pure H_2O ratio = 1:2

[c] Chapman, H.D., 1965. Cation-exchange capacity, in: Norman, A.G. (Ed.), Method Of Soil Analysis. Part2. Chemical And Microbiological Properties. pp. 891–901.

Table 4.2 Particle size distribution of the soil.

Clay[d] (%)	Silt[d] (%)	Sand[d] (%)	Gravel[d] (%)
20	75.64	430.67	7.81

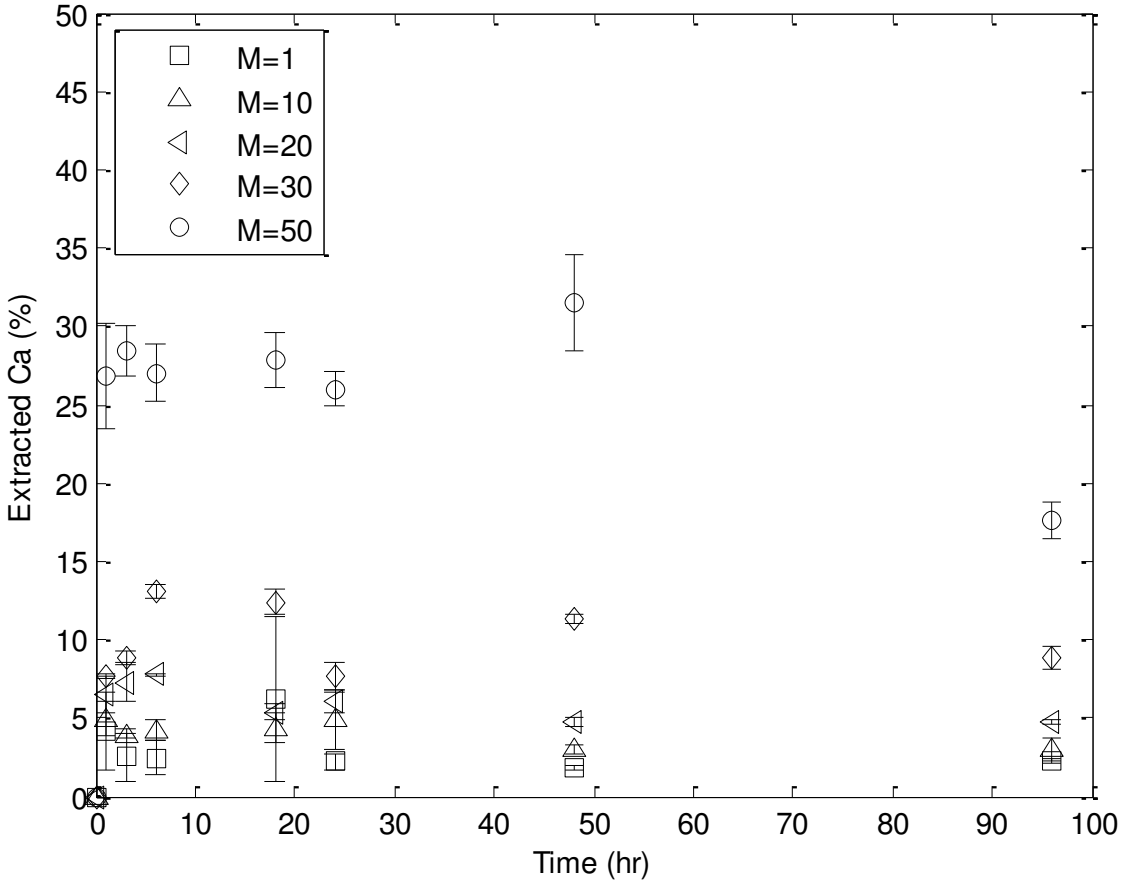
[d] ASTM D 422-63, 2007. Test Method for Particle-size Analysis of Soils.

Table 4.3 Investigated elements total concentration in the soil.

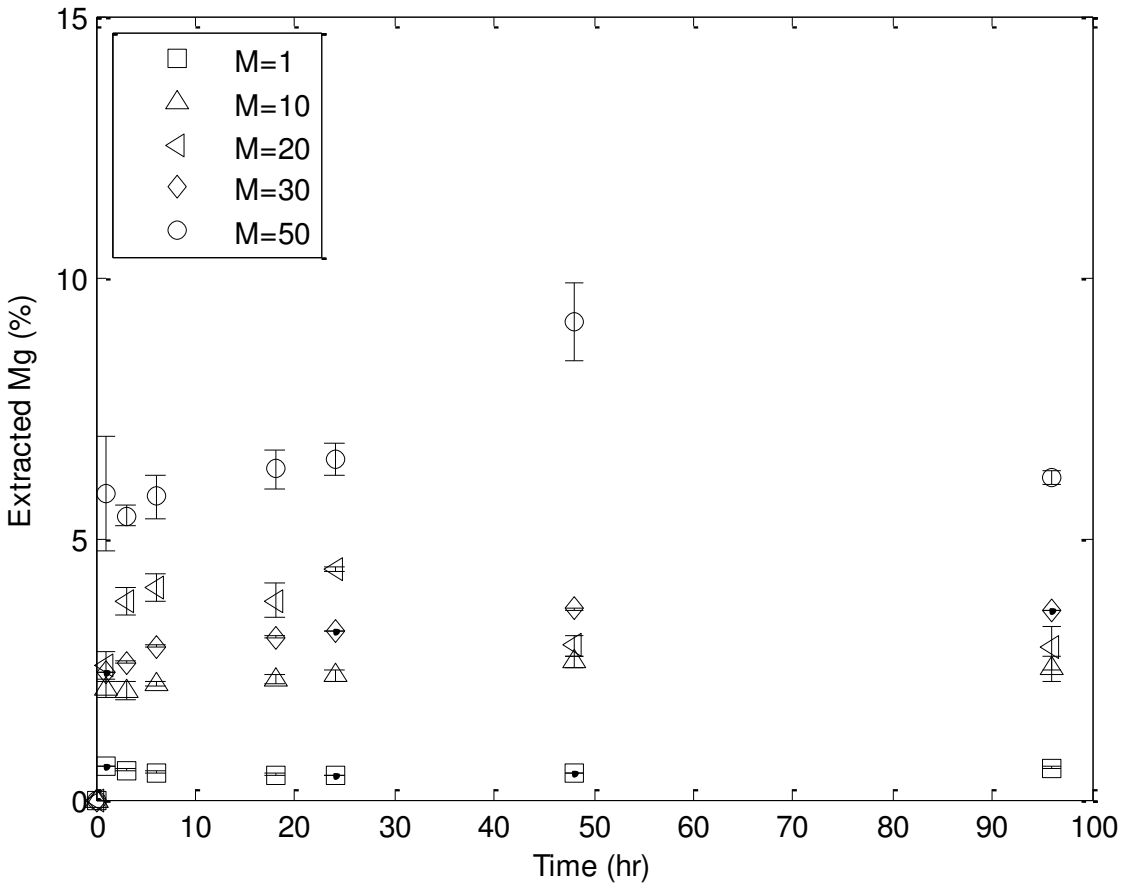
Total Cu[e] ($mg \cdot kg^{-1}$)	Total Cd[e] ($mg \cdot kg^{-1}$)	Total Pb[e] ($mg \cdot kg^{-1}$)	Total Co[e] ($mg \cdot kg^{-1}$)	Total Ni[e] ($mg \cdot kg^{-1}$)	Total Zn[e] ($mg \cdot kg^{-1}$)	Total Fe[e] ($mg \cdot kg^{-1}$)	Total Ca[e] ($mg \cdot kg^{-1}$)	Total Mg[e] ($mg \cdot kg^{-1}$)	Total Mn[e] ($mg \cdot kg^{-1}$)
167.5	0.743	74.81	7.73	61.88	125.89	33178.6	56138.1	483.4	459.2

[e] European Standard EN 16174, 2012. Digestion soil, sludge, biowaste and waste for the extraction of aqua regia soluble elements – Horizontal Draft Standard. www.ecn.nl/library/horizontal.

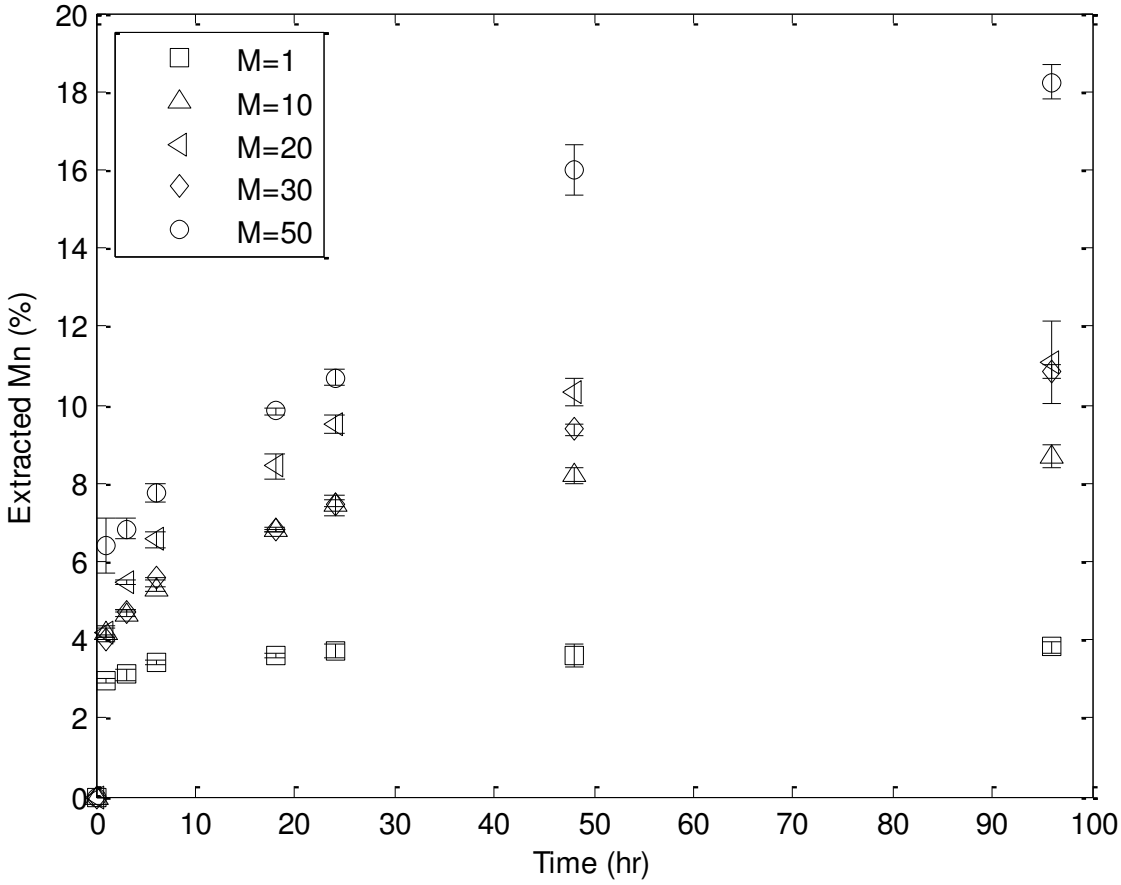
a


M=1
M=10
M=20
M=30
M=50
Extracted Ca (%)
Time (hr)
0
5
10
15
20
25
30
35
40
45
50
0
10
20
30
40
50
60
70
80
90
100

b


M=1
M=10
M=20
M=30
M=50
Extracted Mg (%)
Time (hr)
0
5
10
15
0
10
20
30
40
50
60
70
80
90
100

c


M=1
M=10
M=20
M=30
M=50
Extracted Mn (%)
Time (hr)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80
90
100

d

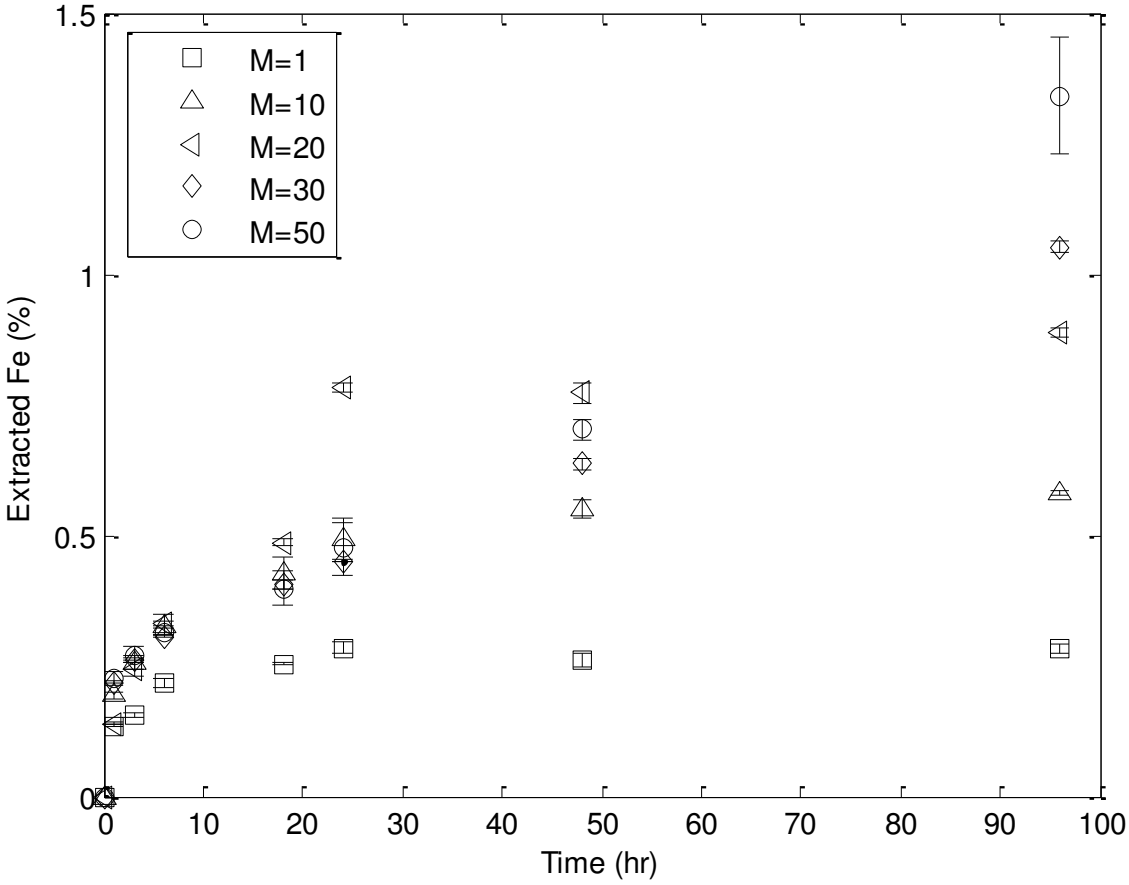
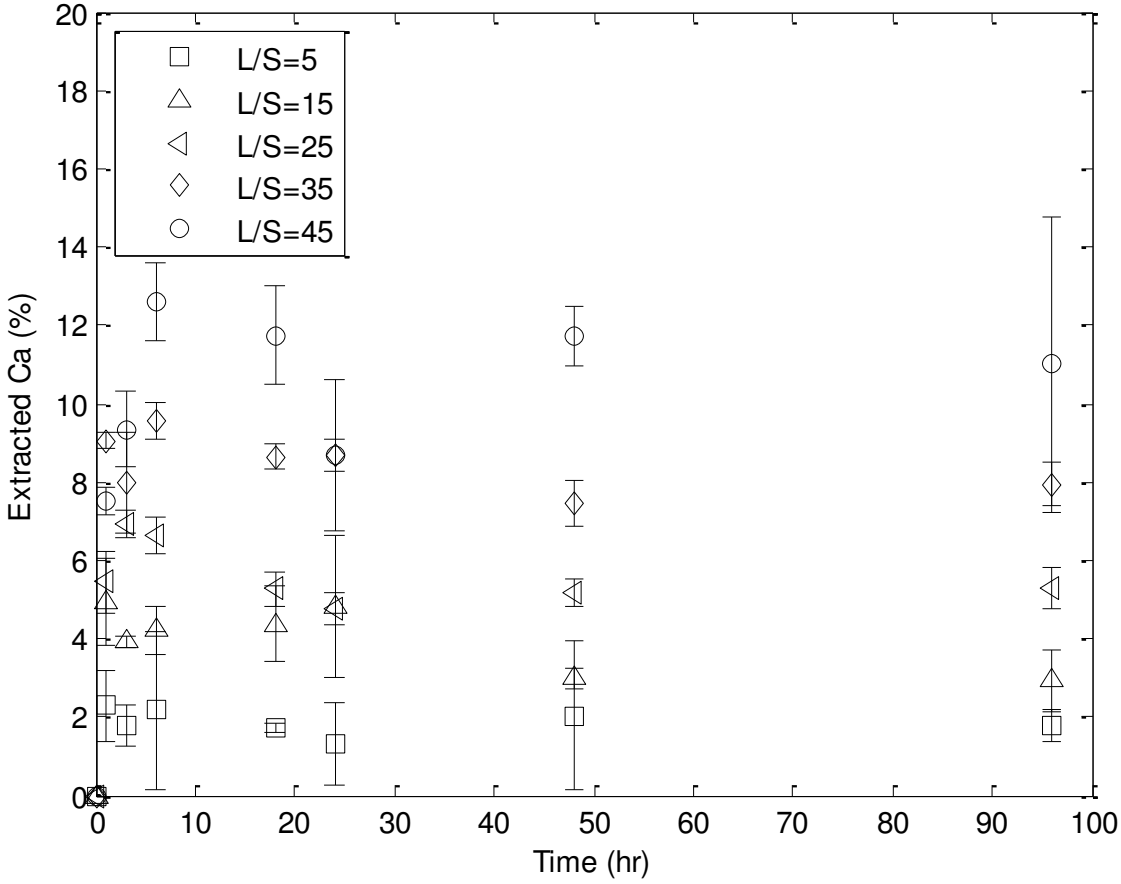
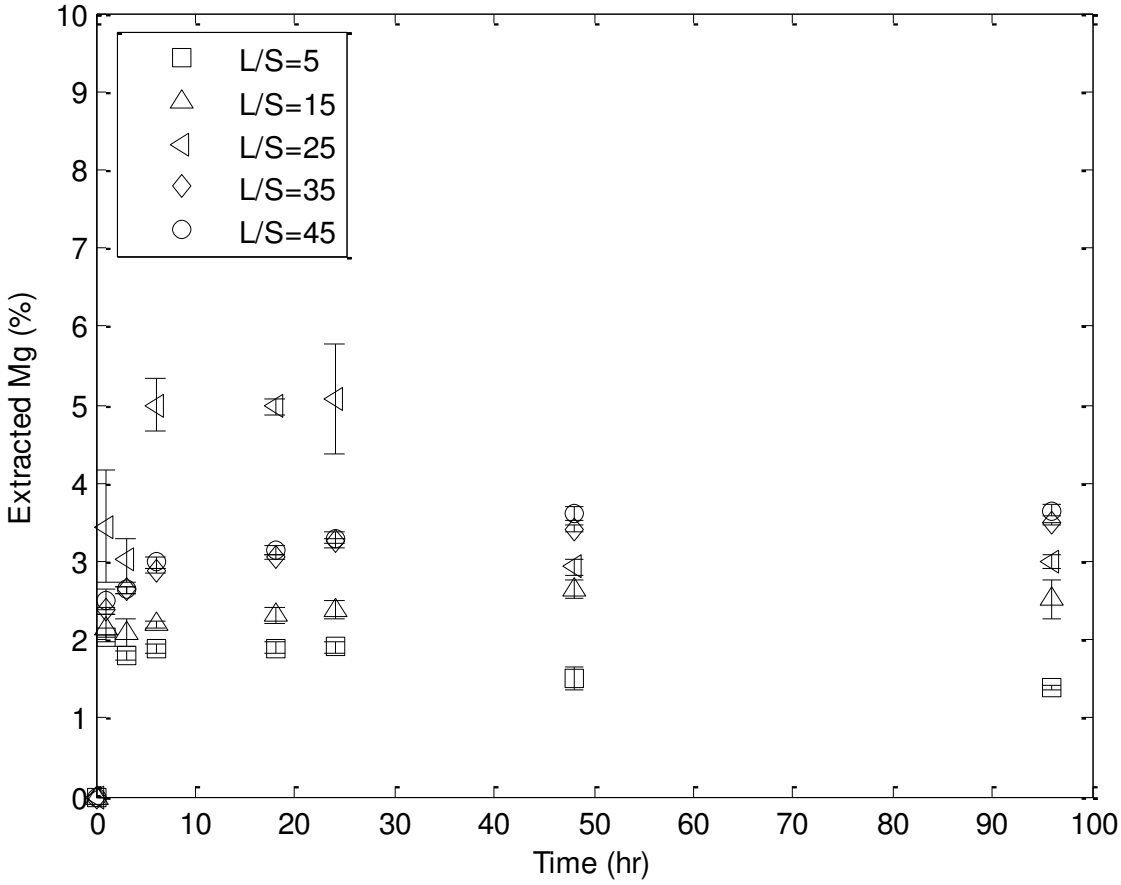


Fig. 3.1 Extracted percentage of (a) Ca, (b) Mg, (c) Mn and (d) Fe at M values of 1, 10, 20, 30, and 50, L/S=10.

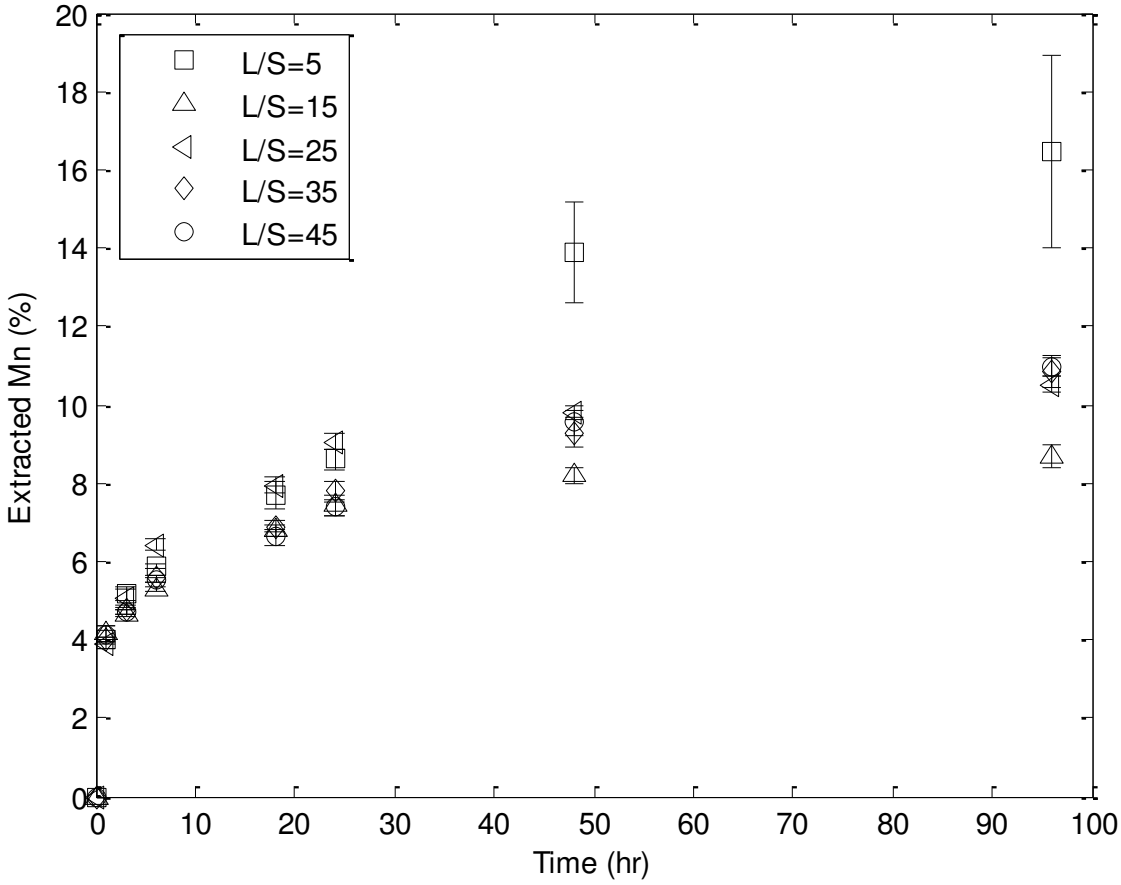
a


L/S=5
L/S=15
L/S=25
L/S=35
L/S=45
Extracted Ca (%)
Time (hr)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80
90
100

b


L/S=5
L/S=15
L/S=25
L/S=35
L/S=45
Extracted Mg (%)
Time (hr)
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100

c


L/S=5
L/S=15
L/S=25
L/S=35
L/S=45
Extracted Mn (%)
Time (hr)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80
90
100

d

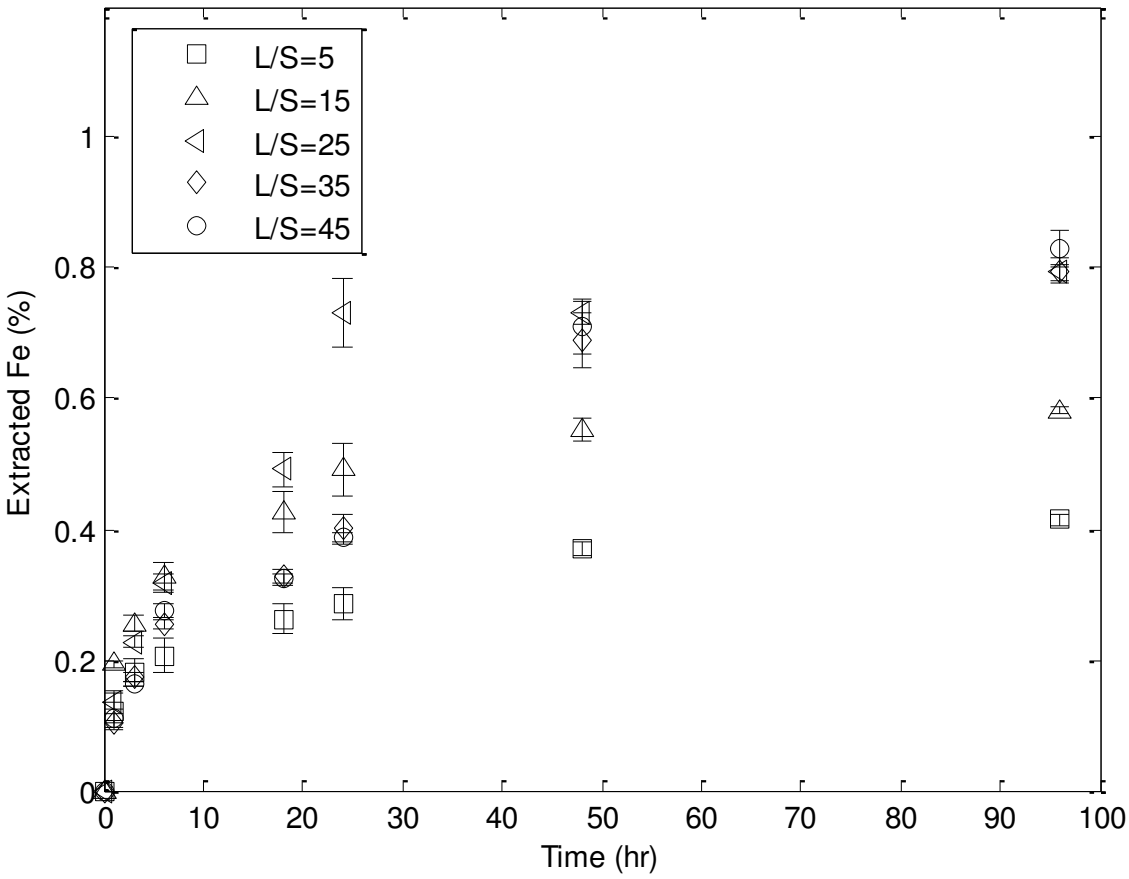


Fig. 3.2 Extracted percentage of (a) Ca, (b) Mg, (c) Mn and (d) Fe at L/S ratio of 5, 15, 25, 35, and 45, M=10.

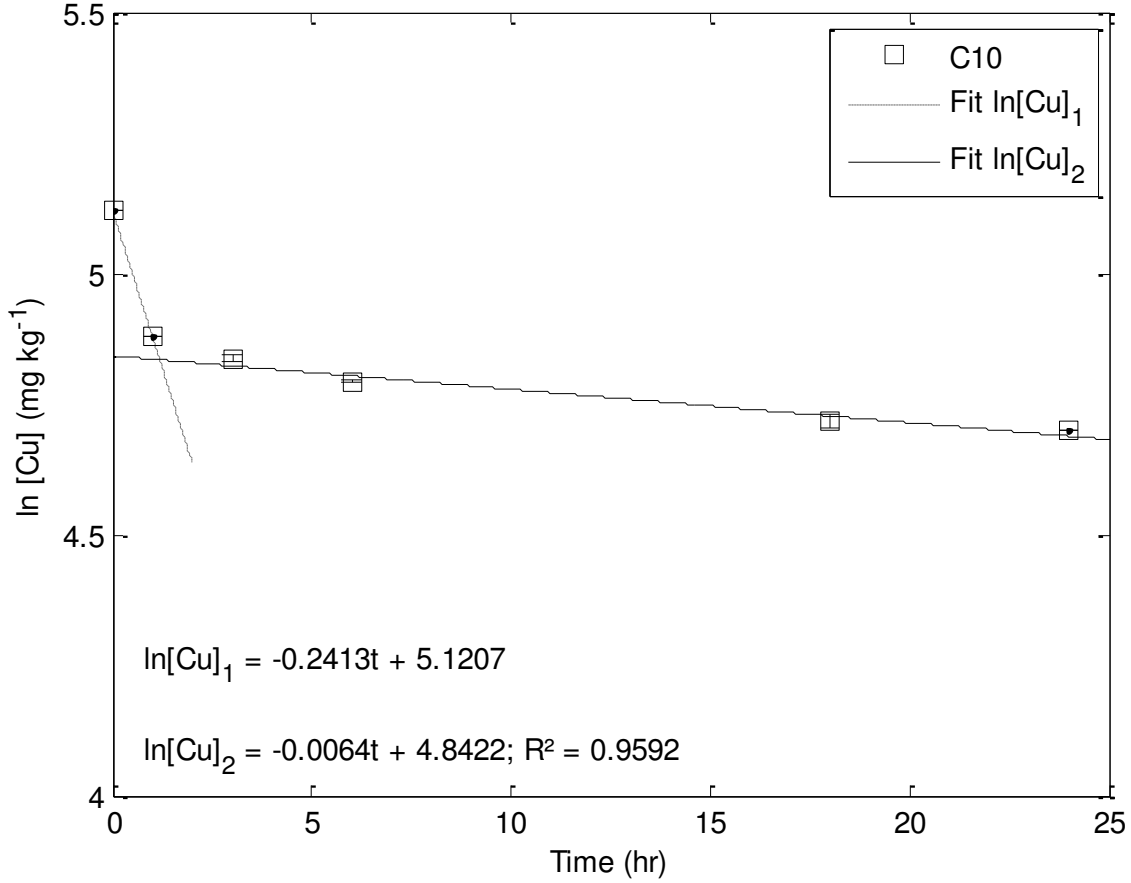
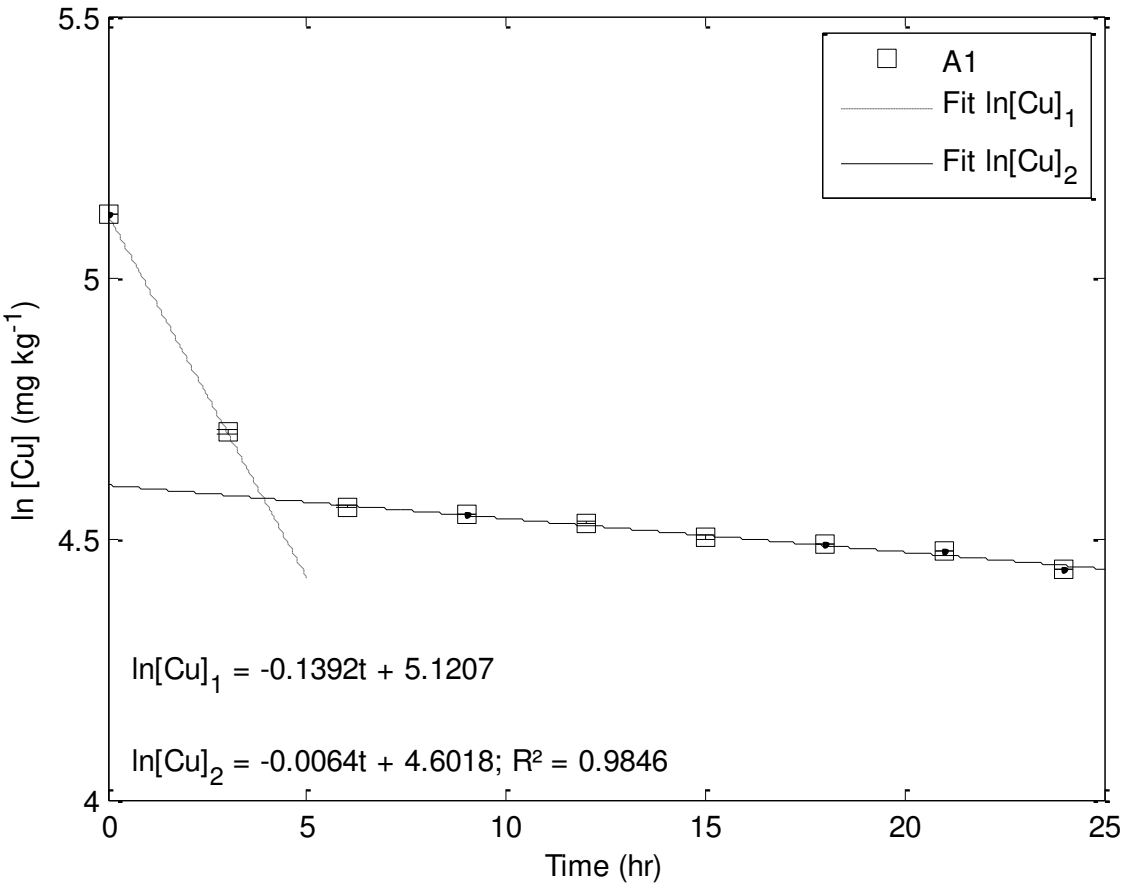
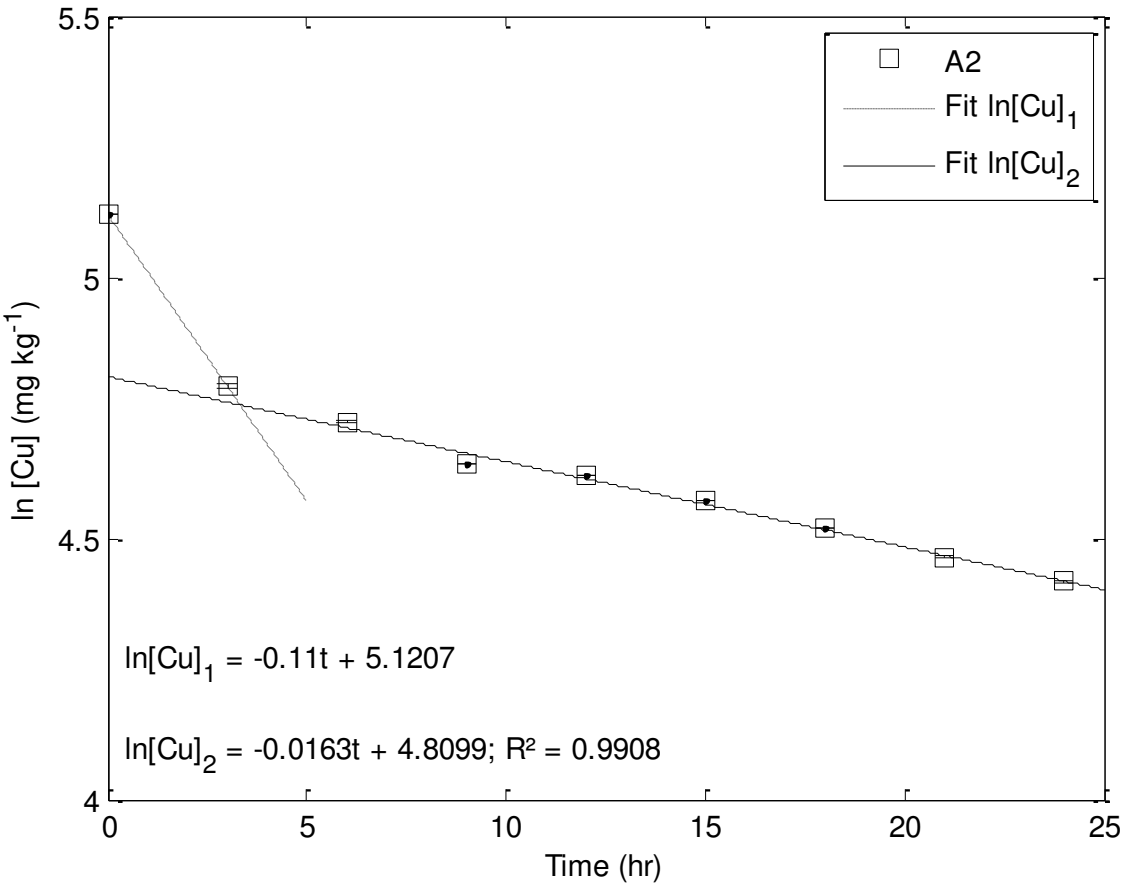


Fig. 4.1 Cu concentration decrease in soil and first order kinetic equation fitting with two kinetic steps (Fit ln[Cu]1 and Fit ln[Cu]2) for C10 test.

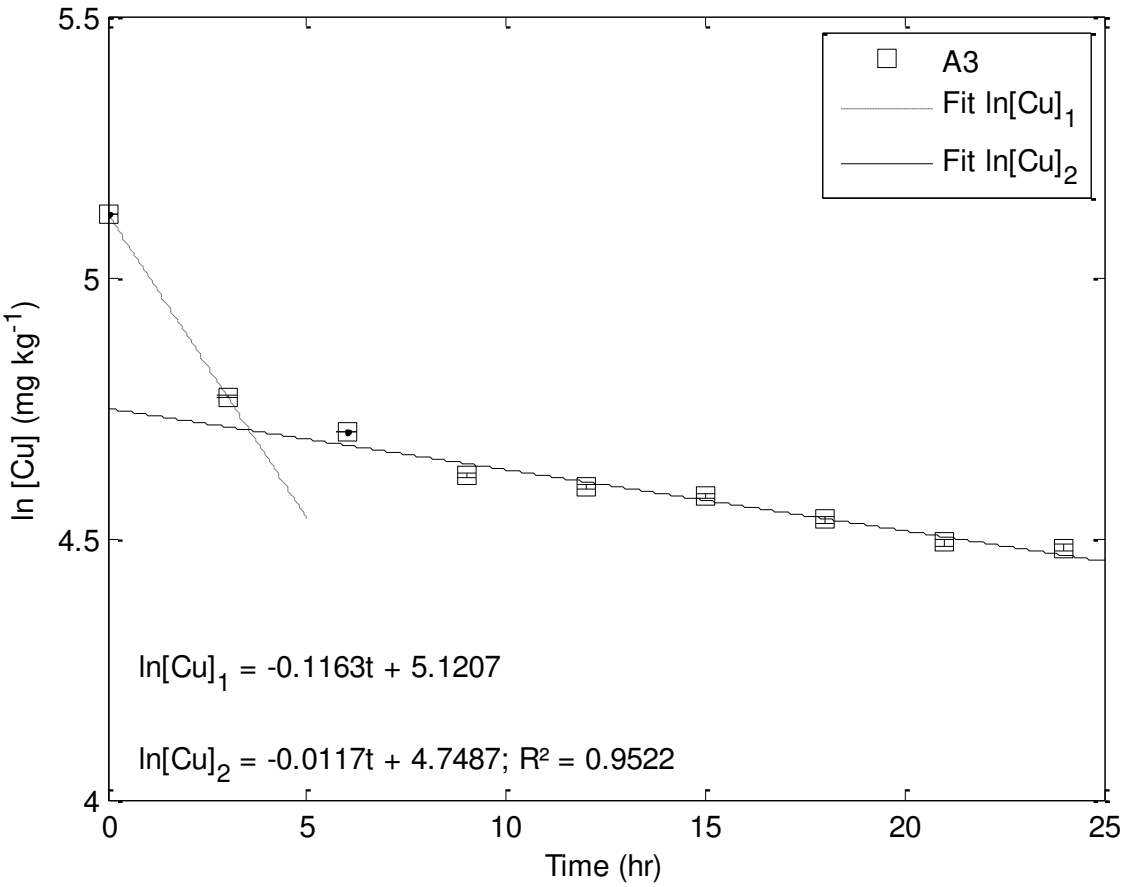
a


5.5
5
4.5
4
0
5
10
15
20
25
Time (hr)
ln [Cu] (mg kg-1)
A1
Fit ln[Cu]1
Fit ln[Cu]2
ln[Cu]1 = -0.1392t + 5.1207
ln[Cu]2 = -0.0064t + 4.6018; R² = 0.9846

b


5.5
5
4.5
4
0
5
10
15
20
25
Time (hr)
ln [Cu] (mg kg-1)
A2
Fit ln[Cu]1
Fit ln[Cu]2
ln[Cu]1 = -0.11t + 5.1207
ln[Cu]2 = -0.0163t + 4.8099; R² = 0.9908

c


5.5
5
4.5
4
0
5
10
15
20
25
Time (hr)
ln [Cu] (mg kg-1)
A3
Fit ln[Cu]1
Fit ln[Cu]2
ln[Cu]1 = -0.1163t + 5.1207
ln[Cu]2 = -0.0117t + 4.7487; R² = 0.9522

d

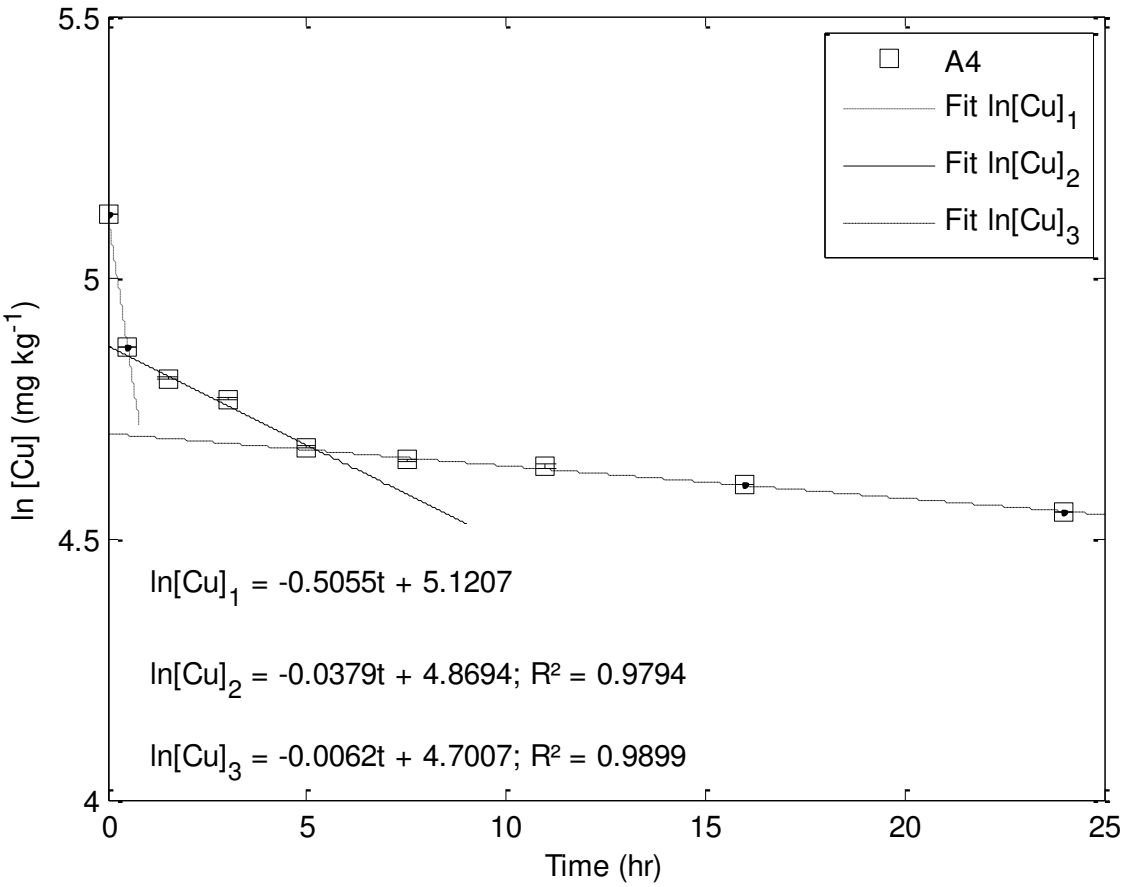


Fig. 4.2 Cu concentration decrease in soil and first order kinetic equation fitting with two kinetic steps (Fit $\ln[Cu]_1$ and Fit $\ln[Cu]_2$) for (a) A1 test, (b) A2 test, (c) A3 test, and three kinetic steps (Fit $\ln[Cu]_1$, Fit $\ln[Cu]_2$ and Fit $\ln[Cu]_3$) for (d) A4 test.

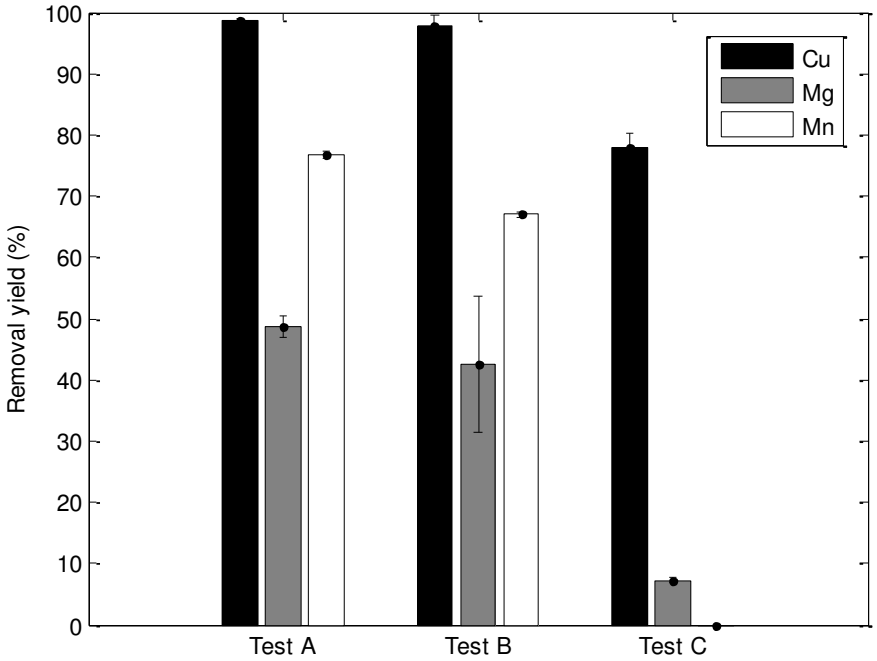


Fig. 5.1 Maximum removal yield achieved for Cu, Mg and Mn in Test A (8 mA·cm^{-2}, 2 mS·cm^{-1}, pH = 8), Test B (5 mA·cm^{-2}, 10 mS·cm^{-1}, pH = 8) and Test C (0.5 mA·cm^{-2}, 2 mS·cm^{-1}, pH = 12).