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Effect of EDTA, EDDS, NTA and citric acid on electrokinetic remediation of As, Cd, Cr, Cu, Ni, Pb and Zn contaminated dredged marine sediment

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Abstract In recent years, electrokinetic (EK) remediation method has been widely considered to remove metal pollutants from contaminated dredged sediments. Chelating agents are used as electrolyte solutions to increase metal mobility. This study aims to investigate heavy metal (HM) (As, Cd, Cr, Cu, Ni, Pb and Zn) mobility by assessing the effect of different chelating agents (ethylenediaminetetraacetic acid (EDTA), ethylenediaminedisuccinic acid (EDDS), nitrilotriacetic acid (NTA) or citric acid (CA)) in enhancing EK remediation efficiency. The results show that, for the same concentration (0.1 mol L^{-1}), EDTA is more suitable to enhance removal of Ni (52.8 %), Pb (60.1 %) and Zn (34.9 %). EDDS provides effectiveness to increase Cu removal efficiency (52 %), while EDTA and EDDS have a similar enhancement removal effect on As EK remediation

(30.5~31.3 %). CA is more suitable to enhance Cd removal (40.2 %). Similar Cr removal efficiency was provided by EK remediation tests (35.6~43.5 %). In the migration of metal–chelate complexes being directed towards the anode, metals are accumulated in the middle sections of the sediment matrix for the tests performed with EDTA, NTA and CA. But, low accumulation of metal contamination in the sediment was observed in the test using EDDS.

Keywords Electrokinetic · Remediation · Chelates · Heavy metals · Dredged sediment · Removal

Introduction

Metal contaminants are often observed in dredged marine sediments (Benamar and Baraud 2011), such as arsenic (As) (metalloid), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn). Marine dumping of these contaminated sediments could lead to high environmental impact on the marine ecosystem. Therefore, this operation is strictly limited by the London Convention (1972), Barcelona Convention (1976) and OSPAR Convention (1998) (Rozas and Castellote 2012). In France, two thresholds for heavy metals (HMs) content in dredged marine sediments were defined by observation workgroup on dredging and environment (GEODE) (Agostini et al. 2007). According to this order, contaminated sediments from harbours and inland waterways must be managed and treated on land separately as waste if necessary.

Physicochemical characteristics of dredged sediments are usually different from those of soils. Dredged sediments are heterogeneous arrays that can be characterized by very high levels of organic matter, carbonates, sulphides and chlorides (Peng et al. 2009; Kim et al. 2011). Owing to their high fines

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(smaller than 80 μm) content, sediment particles are subject to complex surface interactions. Organic matter combines with HMs, forming metal–organic complexes which are very stable (Thöming et al. 2000; Mulligan et al. 2001). Also, the carbonates contained in the sediment increase its buffering capacity and impeded the progress of the acidic area from the anode towards the cathode (Ouhadi et al. 2010). All these characteristics directly affect the mobility of HM (Mulligan et al. 2001).

Several technologies have been deeply considered to find an effective soil/sediment remediation method, such as extraction, bioremediation, phytoremediation, thermal treatment, electrokinetic remediation (EK remediation) and integrated remediation technologies (Gan et al. 2009). Among these methods, EK remediation is a kind of cost-effective remediation technology (Acar and Alshawabkeh 1993). This method aims to remove HMs from the matrix of contaminated soil/sediment by applying low current or electrical potential (Acar and Alshawabkeh 1993; Virkutyte et al. 2002; Sawada et al. 2004; Colacicco et al. 2010). The electric potential induces several contaminant transport mechanisms, such as electromigration, electroosmosis, electrophoresis and diffusion. Electromigration refers to the transport of ionic species in the pore fluid, and this is the main mechanism by which the electrical current flows through the sediment (Reddy et al. 2006).

However, similar to most remediation technologies, EK remediation can only extract mobile (dissolved species or sorbed species on colloidal particles suspended in the pore fluid) contaminants from soil matrix. But, extraction of sorbed species on soil particle surfaces and solid species as precipitates requires the enhancement techniques to solubilize and keep them in a mobile chemical state (Yeung and Gu 2011). Moreover, unlike organic contaminants, HMs are not biodegradable and tend to be accumulated in living organisms (Fu and Wang 2011). In recent years, chelating agents have been widely used to increase HMs solubilization for EK remediation (Wong et al. 1997; Amrate et al. 2005; Gidarakos and Giannis 2006; Giannis et al. 2009). Chelating agents are ligands that have the ability to coordinate with central metal atoms or ions at a minimum of two sites to form chelate complexes. Because of the specific molecular structure of chelating agents, they can form several bonds to a single metal ion even from sorbed species and solid species. During EK treatment, metals (M) occur in the form of anionic complexes and could be removed such as M-EDTA^- and M-citrate^- (Yoo et al. 2015).

Chelating agents may be classified into two categories: aminopolycarboxylic acids (APCAs) and low-molecular-weight organic acids (LMWOA). Ethylenediaminetetraacetic acid (EDTA), a kind of synthetic APCA, has been widely used in environmental and medical fields. For example, EDTA has been promoted to the removal of lead (Pb) from human body (Wong et al. 1997). However, EDTA and metal–EDTA complexes present low biodegradation and high environmental

persistence and could dramatically increase risks of leaching (Egli 2001; Meers et al. 2005). Similar to the metal-chelating capacity of EDTA, biodegradable APCA, ethylenediaminedisuccinic acid (EDDS) and nitrilotriacetic acid (NTA) have become tested in soil remediation technologies in recent years (Luo et al. 2005; Lozano et al. 2011; Cao et al. 2013). The observed half-life of EDDS is varied between 2.5 and 4.6 days (Meers et al. 2005) and ranged from 5 to 7 days for NTA (Lan et al. 2013). LMWOA is another kind of chelating agents, such as citric acid (CA), oxalic acid, etc. Because of the particular importance of its complex properties, it played a significant role in HMs solubility (Evangelou et al. 2007). On the other hand, the migration of OH^- ions generated by electrolysis reaction from the cathode may lead to precipitate HMs and reduce their mobility during EK remediation (Lee and Yang 2000; Zhou et al. 2005). Numerous studies illustrate that pH controlled by organic acid neutralization in the cathode could enhance the metal removal efficiency (Giannis and Gidarakos 2005; Gidarakos and Giannis 2006). The comparison of the conditional stability constant values of some complexes of metals with EDTA and EDDS shows that these constants pass for all metal complexes through maximum as a function of pH value (Treichel et al. 2011). The pH of the solutions has an obvious effect on the sorption of Cu(II), Zn(II), Cd(II) and Pb(II) complexes with the used complexing agents (Kołodźńska 2013). In the case of the anion exchange process, pH value should be maintained above 4.0 in order to enable the anionic complex sorption. The combined application of EDTA and CA in phytoremediation (Chigbo and Batty 2013) showed that in Cr-contaminated soil, the increase of Cr removal from the soil could reach 54 %.

In previous studies of EK remediation performed on both a spiked model sediment (Ammami et al. 2014) and a dredged sediment (Ammami et al. 2015), CA, when used as electrolyte, was found to be an enhancing chelating agent for the removal of many metals and PAHs. Owing to its biodegradability, CA is considered as an interesting chelating agent in the case of in situ remediation. In order to investigate the metal removal efficiency of other chelating agents, a set of EK remediation tests, enhanced by different chelating agents, are performed. This paper aims to evaluate and compare the enhancement effect of CA, EDTA, EDDS and NTA in EK removal of HMs (As, Cd, Cr, Cu, Ni, Pb and Zn) from dredged contaminated sediment.

Materials and methods

Sediment sampling

Sediment samples are collected from storage site (Tancarville, Haute-Normandie, France) using shovel and stored in an airtight plastic barrel at a temperature of 4 °C. Particle size

distribution of the material (provided by laser particle size analyzer Multisizer 2000-Malvern), pH and electrical conductivity (EC) were measured according to NF ISO 10390 and NF ISO 11265 standards, respectively. Moisture content was obtained in accordance with NF P 94-050 standard, while organic matter and carbonate content were measured in accordance with NF EN 12879 and NF EN ISO 10693 standards, respectively. The hydraulic conductivity was obtained according to NF X30-442. Initial metal concentrations in sediment were also measured following the analytical process, which is described later. The obtained values of these physicochemical parameters are listed in Table 1.

EK tests

The experimental EK remediation setup, described in previous papers (Ammami et al. 2014; 2015), is shown in Fig. 1. The main device, made of Teflon polytetrafluoroethylene (PTFE) material, includes a sediment chamber (cylinder of 4.9-cm diameter and 14-cm length) and two electrode compartments. These three elements are assembled with four clamping rods and sealed by two O-rings. The dredged sediment sample was packed into the chamber by compacting 380 g of wet dredged sediment in a manner to obtain a homogeneous specimen. Graphite electrode plates were placed in each electrode compartment, separated from the sediment by porous (0.45 μm) fiberglass filter paper (Millipore) and a perforated grid made of Teflon. Two pumps (from KNF) filled the electrode reservoirs with aqueous processing fluids (10 mL h⁻¹). A voltage gradient was applied continuously, and the electrical current was periodically measured. During tests,

effluents were collected by two overflow holes from both electrodes and then stored in glass flasks. Different processing electrolytes (EDTA-Na provided by VWR (France), EDDS-Na and NTA-Na provided by Sigma-Aldrich (France), and CA) were prepared at a concentration of 0.1 mol L⁻¹ and used to feed both electrode compartments. The tests were performed under an electrical field of 1.0 V cm⁻¹ for a duration of 21 days. As a control test, distilled water (DW) was previously used as electrolyte. During the test, the volume of outlet effluent was monitored and the cumulative electroosmotic flow (EOF) was calculated as the difference between the input and output volumes of electrolyte in the electrode compartment. At the end of each test, the sediment was extracted and cut into four slices (S1 to S4, from anode to cathode) which were air-dried and submitted to physicochemical analysis (metal concentration, pH and EC).

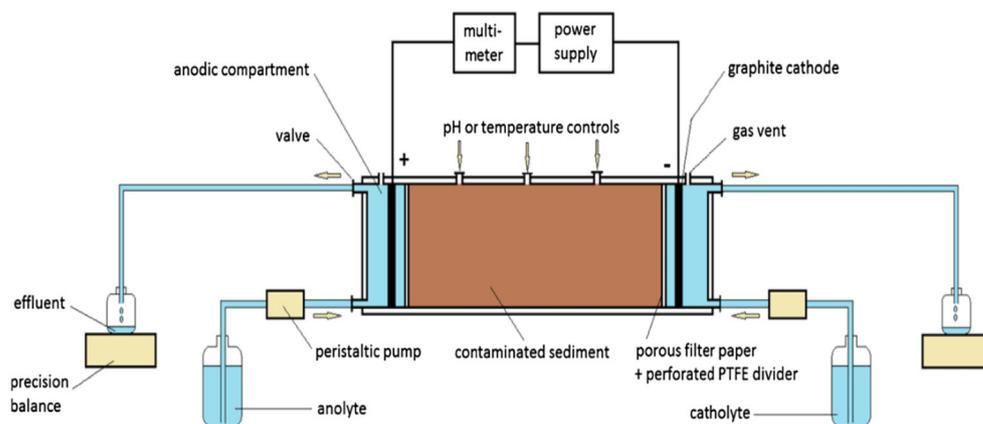
Analytical methods

The metal extraction method used a device of acid digestion process (Discover SP-D, CEM Corporation, Matthews, USA). About 0.5 g of dry sediment sample was digested in 35-mL pressurized vessel using 8 mL of a mixture of nitric acid and hydrochloric acid in the proportion 3:1 (v/v). The vessel was subjected to microwave irradiation at a temperature of 200 °C for 4 min of ramping time and 4 min of holding time. The mineralized solutes were completed to 25 mL with deionized water and filtered by a PTFE filter (0.45 μm). The metal (As, Cd, Cr, Cu, Ni, Pb and Zn) concentrations were measured in triplicate using ICP-AES (ICAP6300, Thermo Fisher Scientific, Waltham, USA).

Table 1 Characteristic of the sediment sample

	Parameter	Values	Method
Sediment sample	Clay	6.3 %	Particle size analyzer Multisizer 2000, Malvern
	Silt	86.2 %	
	Sand	7.5 %	
	Organic matter	11.59 %	At 450 °C for 6 h
	Carbonate	30.5 %	Bernard calcimeter
	Hydraulic conductivity	1.0 10 ⁻⁷ m s ⁻¹	Falling-head method
	pH (1:10 water) EC (1:10 water)	8.4 ± 0.2 1.57 ms cm ⁻¹	(1:10) Sediment-water
Initial metal contaminant concentration (mg kg ⁻¹)	As	14.95	ICP-AES
	Cd	4.6	
	Cr	136.34	
	Cu	63.97	
	Ni	38.97	
	Pb	63.93	
	Zn	222.8	

Fig. 1 A schematic diagram of the experimental setup



Results and discussion

Electric current change and cumulative EOF

The measured electric current for the EK tests is plotted as a function of time for different EK test conditions in Fig. 2. The general trend of electrical current shows an instantaneous increase, reaching rapidly a maximum measured value at the beginning of the test, before decreasing down, and then stabilizing at a residual low value, as also reported by Colacicco et al. (2010) and Ammami et al. (2015). The initial high values are due to the large amount of ions in the solution and the solubilization of salt precipitates, which leads to the fast increase of the EC. However, over time, the ions are depleted as they move by electromigration, and then, the current intensity decreases before reaching quite stable values. The highest electric current value was measured for EDTA test, while the lowest value was obtained with deionized water (DW) test. The electric current was higher in the order EDTA > EDDS > NTA > CA > DW. When using EDTA, EDDS and NTA as electrolyte additives, the electric current change can be explained by the available high ionic strength that promotes high values of electric current at the beginning of the EK treatment. Chelating agents help to solubilise various inorganic species contained in the sediment, leading to the rise of electric current and also conductivity. For the processing fluid introducing CA (non-reactive ions), the value of electrical current was slightly higher than that obtained with DW.

The calculated cumulative EOF in the cathode compartment for each test is shown in Fig. 3. The maximum cumulative EOF (1607 mL) was obtained for the control test (DW test). The lower cumulative EOF observed in other tests may be due to high viscosity of chelating agents and/or the variation of zeta potential during the test (Acar and Alshawabkeh 1993). Moreover, it is known that the zeta potential is affected by the matrix type, the pH and the ion concentration of the pore solution (Kaya and Yukselen 2005a). These factors are able to affect the EOF direction (inversed from cathode to

anode). Chelating agents used in these tests do not only enhance the removal efficiency by forming chelates/complexes and increasing the solubility of HMs, but also change the pore fluid chemistry and therefore have direct influence on the zeta potential of soil particle surfaces (Popov et al. 2007; Gu et al. 2009b). The result obtained with EDDS test, which shows a drastic decrease of cumulative EOF after 168 h of treatment, could be explained by the reversed EOF. Slight inversion of EOF was also obtained for the tests performed with EDTA and NTA. This behaviour of EOF inversion was observed in previous studies (Zhou et al. 2004; Kaya and Yukselen 2005b; Baek et al. 2009; Ammami et al. 2015).

Sediment parameters after EK remediation treatments

Figure 4a shows pH values that were measured in the different sections of the sediment after each EK treatment. It indicates that the sediment underwent an overall, but low acidification process compared to the initial pH value, and this tendency was more pronounced near the anode. Using CA as a processing fluid aims to maintain an acidic pH along the sediment specimen, but the carbonates in the natural sediment increased its buffering capacity and impeded the progress of the acidic front from the anode towards the cathode (Ouhadi et al. 2010). As can be seen, a treatment with NTA led to an important acidification of the sediment, reaching pH values of 3.2 and 7.2 near the anode and the cathode, respectively. Ultimately, using EDDS as electrolyte leads to significant increase in pH value throughout the sediment matrix, leading to alkaline pH of 8.3 and 10.1 near the anode and cathode, respectively. This behaviour can be related to the neutralization of H^+ ions generated at the anode during the electrolysis reaction, leading to initial pH value close to 9.0 in the EDDS solution, and to reversed EOF obtained with this alkaline process fluid (Fig. 3) which transports OH^- ions towards the anode.

As regards the sediment electrical conductivity (EC) at the end of each test (Fig. 4b), the general trend is that EC is increased during EK remediation near the anode where pH is more acid and is decreased near the cathode because of

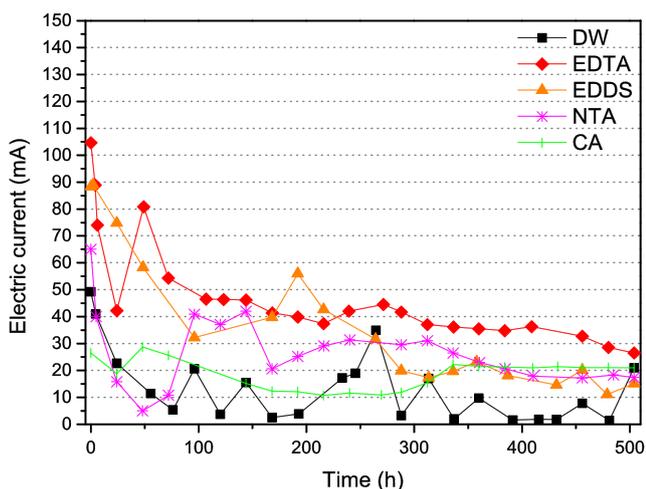


Fig. 2 Electric current variation

the global chemical precipitation and, consequently, the strong depletion of mobile ionic species near the cathode. The relatively elevated EC values in sections near the anode are a result of the solubilization of mineral precipitates due to the decrease of pH in these particular sections and/or the presence of high amounts of ionic species migrated from cathode area. In the case of EDTA and EDDS tests, the EC of the sediment was maintained in lower levels than its initial value. This behaviour is a result of ion precipitation due to high pH, which leads to a lower EC.

Metal removals

In order to investigate the movement of metals within the specimen towards the electrode compartments, the measured concentrations in different sections and the initial concentration value are used to quantify the distribution of metal normalized concentration (Fig. 5) and the removal efficiency (Fig. 6). The chelate agents EDTA, EDDS and NTA are anionic complexes, which migrate from the cathode to the anode

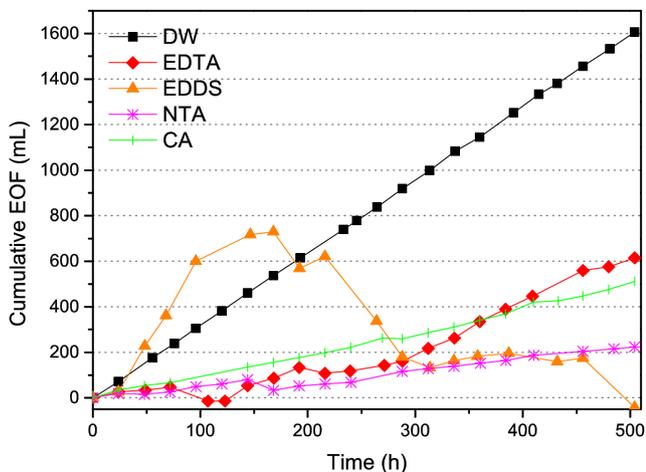


Fig. 3 Variation of cumulative EOF with time

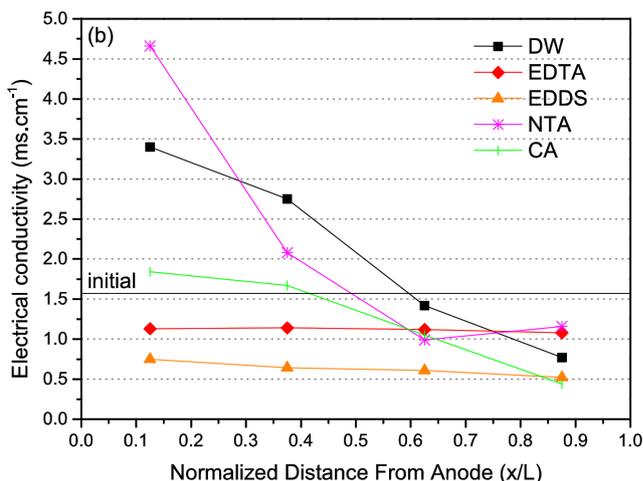
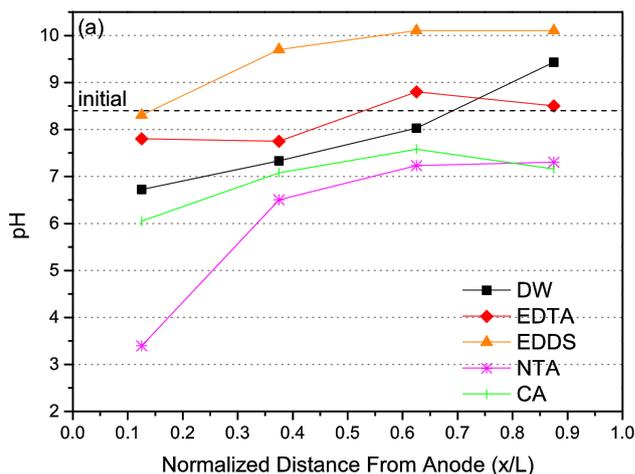
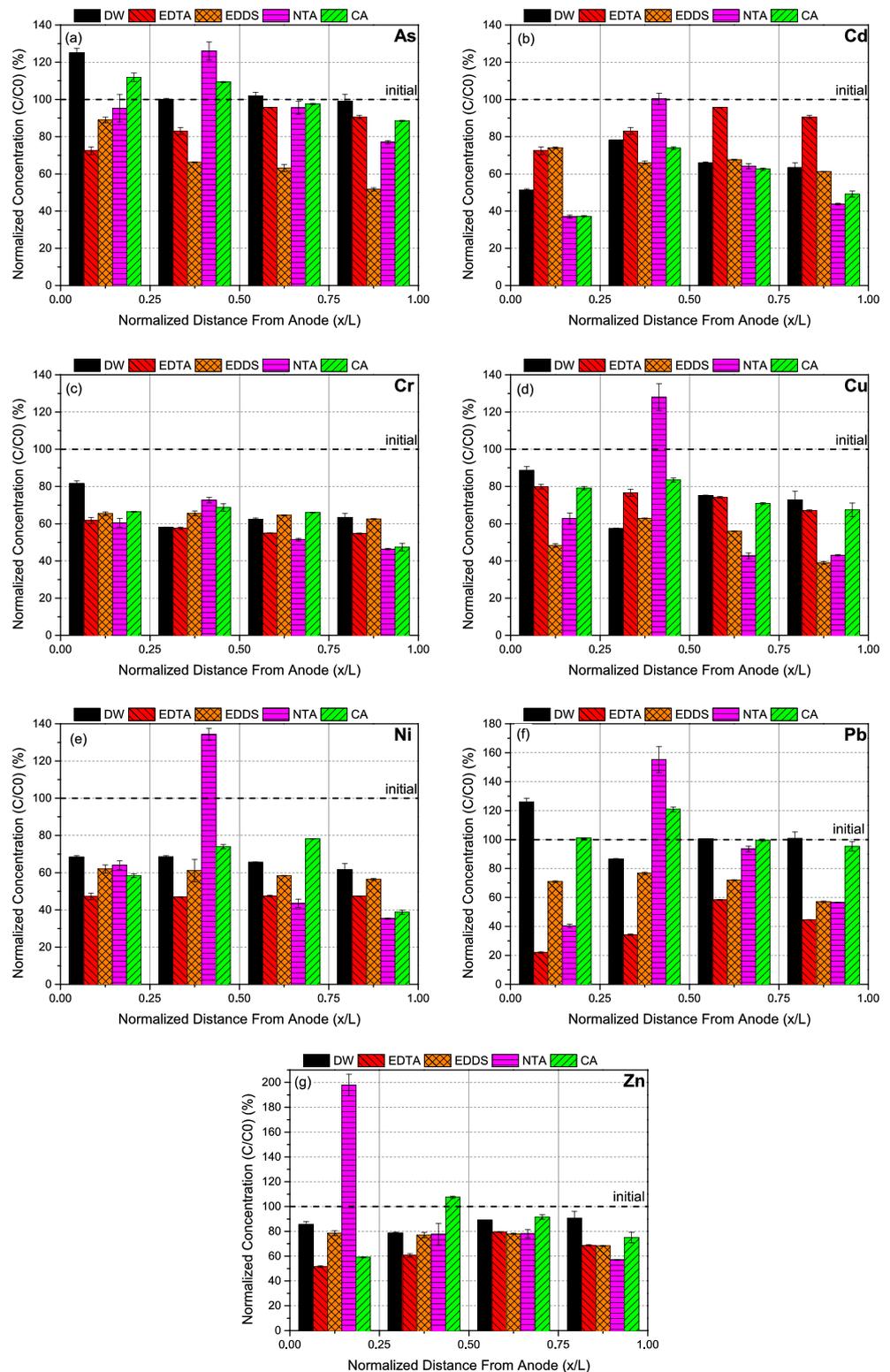


Fig. 4 Distribution of pH (a) and electrical conductivity (b) within sediment after treatment

through the matrix, and help to the desorption of metals and the formation of anionic complexes (Giannis et al. 2009; Suzuki et al. 2014; Zhang et al. 2014; Yoo et al. 2015).

In the case of EDTA test, the results indicate that the great part of Pb and Ni is extracted from the sediment, Pb being the most mobile metal and Cd is the least mobile. By the end of the experiment, about 60 % of Pb had been removed from sediment. Using EDTA as chelating agent, the best recoveries are obtained in the order Pb > Ni > Cr > Zn > As > Cu > Cd. For example, it is also known that Pb-EDTA²⁻ is the dominant form under neutral and alkaline sediment pH. Therefore, negatively charged Pb-EDTA complexes were transported towards the anode by electromigration (Yoo et al. 2015). Thereby, EDTA can be considered as a relative more effective processing fluid which operates for metal removal in this research. Figure 6 shows that removal efficiency with EDTA obtained for five HMs: Zn, Pb, Ni, Cr and As reaches consistent values. The stability constants of M-EDTA complexes are much higher than those of other complexes. Moreover, as a kind of chelating agent, EDTA could be attached to a metal

Fig. 5 Distribution of metals within sediment after EK treatments [a As, b Cd, c Cr, d Cu, e Ni, f Pb and g Zn]



ion up to six sites and makes metals desorb from the surface of matrix particle and increases the rate migration of metal ions in the material (Zhang et al. 2014). The pH of the system and the environment can affect the stability and effectiveness of

the chelating system. EDTA dissolves better in more alkaline solutions (Chang et al. 2007).

As regard to EDDS enhancement, the stability constant values for Ca, Mg and Fe are always considerably lower,

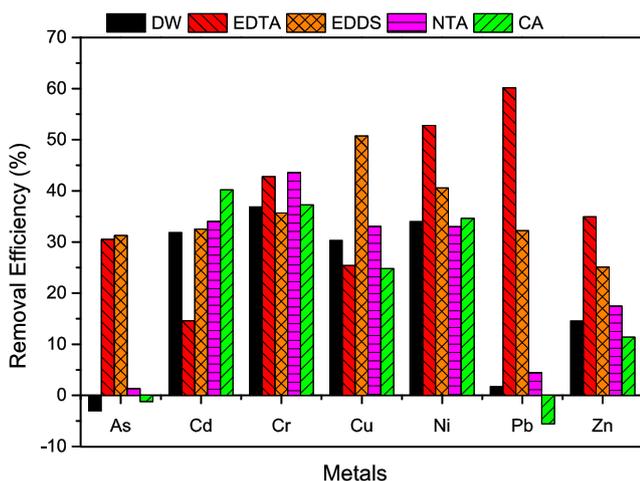


Fig. 6 Metal removal efficiency after each test

while they are remarkably higher for EDTA and the other chelating agents. This leads to the reduction of the competition between major cations and HMs for complex formation in the case of EDDS and shows good extraction efficiencies for Cd, Cu, Pb and Zn (Poletini et al. 2006). In the test using EDDS as chelating agent, the results (Fig. 6) indicate that the best removed metal is Cu (about 51 %) and Zn is the least recovered metal (about 26 %). By the end of the experiment, the best recoveries were obtained in the order Cu > Ni > Cr > Cd ≈ Pb > As > Zn. In this case, concentration profiles (Fig. 5) show rather homogeneous distribution and low accumulation of residual HMs within the specimen after EK remediation.

When using NTA, the metals As, Cd, Cu, Ni and Pb accumulated up in the middle of the cell forming focusing band (from 0.25 to 0.5 of normalized distance from the anode). However, Zn accumulated near the anodic area (from the anode to 0.25 of normalized distance from the anode). Due to the low pH close to the anode, all metals except Cr are positively charged ions (cations) and migrated towards the cathode. NTA enhanced the formation of M-NTA⁻ complexes, which migrated towards the anode. These opposite directions lead metals to accumulate in the middle area of the specimen. At the end of the experiment using NTA, it was removed 43 % of Cr, 38 % of Cd and 34 % of Cu from the sediment. Ni seems to follow the same trend as Cu (see Fig. 6). As and Pb remained immobilized in the sediment and apparently did not form high amounts of soluble complexes with NTA. When NTA is used as chelating agent, the order of extraction efficiency is Cr > Cd > Cu ≈ Ni > Zn > Pb ≈ As.

In our test, when using CA as an additive, metal removal efficiencies were better in the order Cd > Cr > Ni > Cu > Zn > As > Pb. The results show a trend such as As, Pb and Zn accumulated up in the middle of the cell (from the 0.25 to 0.5 of the normalized distance from the anode range) (Fig. 5).

Arsenic (As) can occur in the environment in several oxidation states but usually found as trivalent arsenate

[As(III)] or pentavalent arsenate [As(V)], and the As speciation is usually negatively charged or non-charged (Smedley and Kinniburgh 2002), and so, during EK remediation, electromigration of As will occur towards the anode. Moreover, it is known that As has a high binding affinity which may be due to the co-precipitation in ions Fe(III) and Al(III) with As(III) and As(V) to form a precipitation of iron hydroxide and hardly to be removed (Belzile and Tessier 1990; Gerth et al. 1993; Tokunaga and Hakuta 2002; Poletini et al. 2006; Rahman et al. 2008). The efficiency of EK process in removing As from matrix is influenced by a number of factors such as the pH, the chemical forms of As species and the electroosmosis affected by the zeta potential and the electric field intensity (Kim et al. 2005). Others spiked test inferred that the releasing of to aqueous phase cannot be enhanced in low-pH environment (Yuan and Chiang 2008). As a result of high pH value in the sediment after EDTA and EDDS tests, As was more effectively removed from the sediment matrix. On the other hand, using chelating agents as an enhanced technology could increase the availability of desorption or mobilization of As species from ion plaque due to the complexation of irons (Azizur Rahman et al. 2011; Abbas and Abdelhafez 2013). The high pH and chelating agent enhancement of As removal were also reported in the other researches (Kim et al. 2005; Yuan and Chiang 2008).

Desorption of Cd(II) from the matrix without chelating enhancement is pH dependent and can be desorbed from soil particle surface by DW when the soil pH blows to 7 (Gu et al. 2009a). Means that released Cd ions could be reabsorbed by the particle surface when the soil pH increased. In the DW test, Cd is accumulated in the section S2 (from 0.25 to 0.5 of normalized distance from the anode). The results of EDTA and EDDS tests do not illustrate their chelate enhancement on this metal, comparing with DW test owing to the pH low value involved in this test. This result may be due to the relatively large size and low mobility of EDTA and the opposed direction of the complex migration to EOF (Reddy et al. 2004). Using NTA or CA could slightly increase Cd removal efficiency. As a result of acidification at anode, Cd normalized concentrations near anode in these tests were relatively low. So, Cd cations migrate towards cathode and tend to precipitate and accumulate in the middle part of the matrix (S2) with the increasing pH value.

Ni exists as Ni(II) cation form when pH is less than about 6.0 and precipitates as Ni(OH)₂ when pH becomes greater than around 8.0 (Reddy et al. 2004). So, Ni removal presents quite similar removal efficiency (33–35 %) for DW, NTA and CA tests (Fig. 6). However, the removal efficiency of Ni was increased (reaching 40.5 and 52.7 %) after the EK treatment enhanced by EDDS and EDTA, respectively. The enhancement involved by EDTA compared with DW and CA has been also reported by Iannelli et al. (2015).

Pb(II) had been demonstrated to be difficult to be removed from sediments when using DW and CA treatments (Suzuki

Table 2 Electric energy consumption of EK remediation

	DW	EDTA	EDDS	NTA	CA
Total consumption (Wh)	345.48	2711.49	2120.22	1527.14	727.79
Removing 1 % As (kWh T ⁻¹)	–	88.97	67.84	1168.23	–
Removing 1 % Cd (kWh T ⁻¹)	10.85	186.19	65.20	44.93	18.11
Removing 1 % Cr (kWh T ⁻¹)	9.38	63.43	59.52	35.08	19.55
Removing 1 % Cu (kWh T ⁻¹)	11.41	106.72	41.82	46.24	29.38
Removing 1 % Ni (kWh T ⁻¹)	10.16	51.38	52.29	46.28	21.01
Removing 1 % Pb (kWh T ⁻¹)	197.42	45.10	65.87	344.26	–
Removing 1 % Zn (kWh T ⁻¹)	23.68	77.73	84.55	87.71	63.81

et al. 2013; Zhang et al. 2014; Ammami et al. 2015). On the other hand, NTA is less effective for releasing Pb from matrix than EDTA when used at low concentration (0.1 mol L⁻¹) and in a low-pH environment (pH <8.5) (Elliott and Brown 1989). However, Pb removal efficiency for the EDTA test is two times higher than Pb removal efficiency with EDDS, because EDTA has a great affinity for Fe(III), and most Pb was fractionated on Fe–Mn oxides (Kim et al. 2003; Yoo et al. 2013). Some authors reported that M-EDTA complexation depends on the fractionation of metals in sediments and might be limited to metals bound to easily extractable fractions (Yoo et al. 2013).

For the marine sediment, the enhancement of Cu removal by EDTA and CA chelates was low, even lower than that obtained in DW test (see Fig. 6). Similar results have been obtained by Iannelli et al. (2015) and Ammami et al. (2015). However, the enhancement of EDDS was more reflected in Cu removal (52 % removed), this value being two times higher than that obtained in EDTA test (see Fig. 6). The comparatively low extraction efficiency of EDTA for Cu resulted from competition between HMs and co-extracted Ca (Tandy et al. 2004; Luo et al. 2005). Also, citrate was not effective for the extraction of metals from sediments because of relatively high pH and high content of Fe (Yoo et al. 2013). As regard to EDDS enhancement, the stability constant values for Ca, Mg and Fe are always considerably lower, while they are remarkably higher for EDTA and the other chelating agents. This leads to the reduction of the competition between major cations and HMs for complex formation.

Figure 6 shows that Zn(II) has a significant removal efficiency overall the enhancing chelating tests. The removal efficiency in DW and CA tests is relatively low (respectively, 14.6 and 11.5 %). These results can be laid to the fact that Zn tends to precipitate as a hydroxide at pH >7 (Ammami et al. 2015). However, using chelate agents increases the removal efficiency of this metal as the order EDTA > NTA > EDDS. The sorption capacity of metals is influenced by many factors, including the properties of metal ions and experimental conditions, and one of the most important parameters is pH.

From another point of view, the efficiency of chelating agent in the extraction of metals is generally rated with the

stability constants of the metal–chelate complexes, where higher constants indicate greater stability (Yoo et al. 2013). This is not the alone criteria because metal removal is also influenced by the metal speciation in a given matrix, the ratio of chelating agent to toxic metals and the pH (Giannis et al. 2009).

Electric energy consumption

The electric energy consumption is an important factor to evaluate the cost-effectiveness of the enhancement by using chelating agent as electrolyte solution. Table 2 shows the total electric energy consumptions and the electrical energy required to remove 1 % of each metal from the sediment for all tests. Meanwhile, As (for the DW and CA tests) and Pb (for the test CA) were not calculated because of their negative removal values. Moreover, the energy ratio obtained for As with NTA additive is over the range values obtained for overall metals because of no significant removal (close to zero). According to the obtained results, the order of total energy consumption is as follows: EDTA > EDDS > NTA > CA > DW. EDTA shows its more cost-effectiveness in removing Pb while EDDS is more efficient for removing As. For the other metals, DW shows more cost-effectiveness.

Conclusion

Through this experimental study, EK remediation was shown to be an effective process to remove HMs contaminants from dredged marine sediments when using chelating agents as electrolyte solution. The results indicate that pH of aqueous solutions has an obvious effect on the sorption of many metal complexes with used complexing agents. However, without enhancement, EK remediation has showed its shortcomings in removing several kinds of metals such as As (metalloid) and Pb. Among all the additives tested for metal removal, EDTA showed a good removal efficiency for overall tested HMs. But, EDDS, which is environmentally friendly, was also very interesting. When assessing the comparison of the effect of different chelating agents (EDTA, EDDS, NTA and CA) on

the HMs removal efficiency and their cost-effectiveness, the following conclusions can be drawn:

1. The physicochemical parameters of sediment (pH and electric conductivity) can be modified as the result of EK remediation with/without chelate enhancement.
2. EDTA is an effective chelating agent for removing Ni, Pb and Zn, while EDDS (biodegradable) shows its enhancement effect on removing Cu. EDTA and EDDS had a similar efficiency in removing arsenic, but CA as a kind of organic acid is quite effective in Cd removal.
3. Reversed electroosmotic flow (EOF) heading towards anode was observed during the EDDS test. This behaviour may be helpful to reduce the accumulation of HMs in the middle part of the sediment matrix as caused by other chelating agents (EDTA, NTA and CA).
4. This study confirmed that the metal removal efficiency was not only related to the stability constants of metal–chelate complexes but also depended on the type of chelating agent used, the pH of the aqueous solution and the metal speciation, as reported in previous studies.

To go further, the relationship among the accumulation of different metal distributions within the sediment, pH and EOF and the influence of different concentrations of chelating agents should be investigated deeply.

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