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Heavy metals removal from dredged sediments using electro kinetics

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Abstract. This study focuses on the use of a remediation process to remove particle-bound recalcitrant pollutants (heavy metals) from dredged harbor sediments which must be previously treated before reuse in civil engineering. Electrokinetic (EK) remediation is generally accepted as one of the most suitable technologies for extracting cationic heavy metals from fine grained sediments. Many batch tests were performed to better understand the capacity of various additives to improve sediment decontamination (when applying a constant voltage gradient of 1 V.cm-1), and the combination of enhancing agents (acids + surfactants) were assessed to obtain an efficient removal of heavy metals. We succeeded in proving that mixing citric acid and a nonionic surfactant (Tween 20), additives which are environmentally friendly, was a good association to enhance heavy metals (Cd, Cr, Cu, Pb and Zn) removal.

Key words: Heavy metals, electro kinetics, dredged sediment, remediation, electro-migration

Introduction

Dredging practices constitute a challenge for developing and maintaining harbour and fluvial activities. They also present a contamination risk of coastal waters which can affect the ecosystems. The unsuitability and restriction to marine disposal of dredged sediments leads ultimately the managers to provide a treatment ashore because of the great volume to be treated. Electrokinetic remediation and stabilization is an emerging technology that has received attention as a practical in-situ and ex-situ remediation technique for clay-rich soils. Its use is less advanced on dredged marine sediments, although its use as a mechanism to accelerate dewatering of slurries is well established. Electrokinetic remediation is a controlled application of electrical migration and electroosmosis together with the electrolysis reactions at the electrodes. But since electromigration has generally a higher impact than electroosmosis, EK remediation mainly focuses on charged ions such as heavy metals (Benamar and Baraud, 2011). Indeed, successful laboratory-scale electro remediation has been reported for sediments, sludge or soils contaminated by metals or metalloids (Al-Hamdan and Reddi, 2008; Yan and Chiang, 2008). This technique is one of the developing technologies that offer great promise for the cleanup of soils contaminated with heavy metals. However, the performance of an electrokinetic remediation system depends on the interaction of a complex set of interrelated system variables and parameters (Yvon, 2008). The injection of surfactants in the sediment enhances solubilization and transport (Acar et al., 1995). In our study, electrokinetic experiments were conducted on a model sediment and a dredged sediment under a constant potential gradient (1V.cm-1) with various processing fluids to improve the decontamination of the soil. Results revealed that adding a strong inorganic acid (nitric acid) into the aqueous fluid was more effective than adding a weak acid (citric acid) to remove heavy metals from the sediment, but the complexing citric acid was promising for longer treatments.

Materials and Methods

The experimental set up involves a cell made of Teflon PTFE with 4.9 cm inner diameter and 14.2 cm length (Figure 1). The two electrode compartments were also made of Teflon (4.9 cm diameter, 5 cm length) and were separated from the cell containing the sediment by a porous (0.45 µm) fiber glass filter (Millipore) and a Teflon perforated plate. The filters allow to avoid the migration of colloidal particles toward the electrode compartments. Each rod graphite electrode was also perforated. Gas vents were included in the electrode

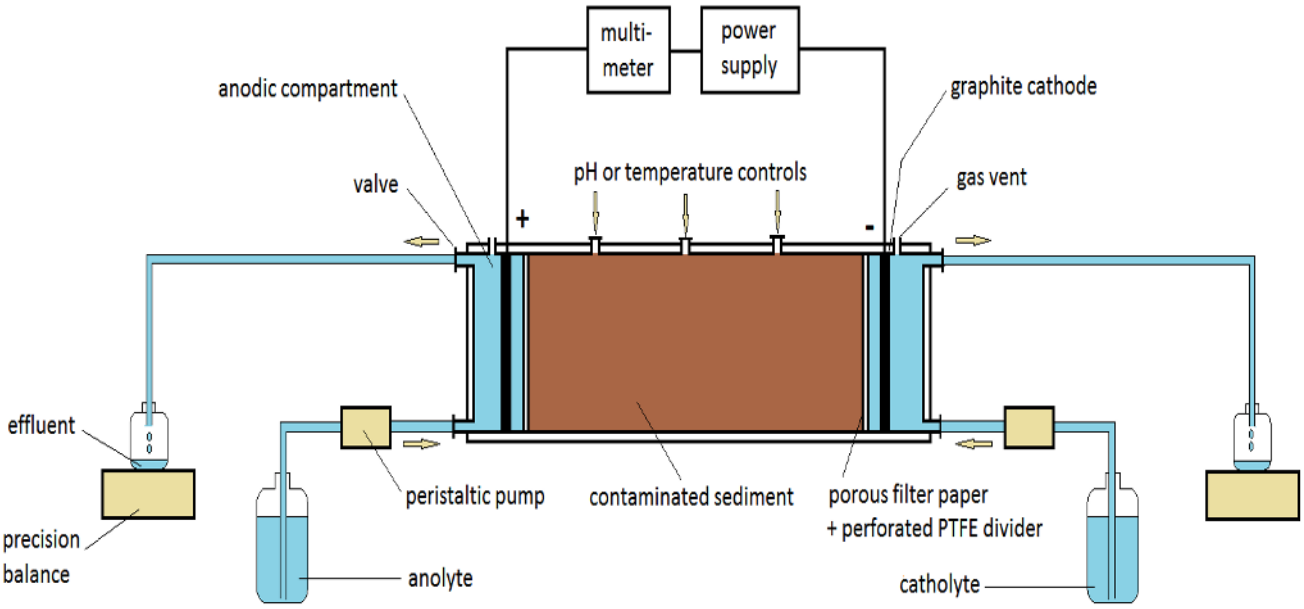

Fig. 1. Drawing schema of electrokinetic experimental set up

Table 1. Test conditions on model sedimenst and removal efficiencies associated

Test no.	fluide	Duration (days)	Cd	Cr	Cu	Pb	Zn
EK1	Deionized water	7	3,4	7,8	14,1	24,9	47,3
EK2	Nitric acid	15	99,8	75,7	85,3	94,1	99,0
EK3	SDS	10	25,9	32,3	33,6	43,6	85,1
EK4	Citric acid	10	94,3	24,6	54,9	61,5	95,2
EK5	Citric acid + SDS	10	49,6	30,2	40,2	9,7	71,2

compartments to allow gases resulting from the electrolysis reactions to escape. Two peristaltic pumps (KNF Stepdos, Germany) are used to fill each electrode compartment with anolyte and catholyte aqueous solutions, with a low flow rate (10 mL.h-1). Two glass flasks collected the anodic and cathodic effluents, whose masses were measured periodically with two precision balances (KERN, Germany): then volumes were deducted, which permitted to calculate the electroosmotic flow (EOF) from the difference between the volume generated by the low hydraulic flow and the volume due to electrokinetics. Three sampling ports were included at approximately 5 cm intervals in the horizontal direction of the sediment chamber, to measure the pH and the electrical conductivity variations during the tests. Two types of sediment were used: a model sediment and a collected sediment. The mixture fabric of kaolinite, silt, and sand was selected as a model sediment to mimic dredged sediments from Le havre (France) harbor (France). Organic matter (OM), obtained from the decomposition of a vegetable material, was also adde to the mixture. The dredged sediment from Tancarville canal (France) whose composition involves sand (5%), silt (75%), clay (5 %).

In order to enhance electrokinetic process, some additives were used. Nitric acid (65%) and hydrochloric acid (37%) were obtained from Panreac (Barcelona, Spain). Sodium chloride (purity 99.5 %), citric acid monohydrate (> 98%) and Tween 20 (>97%) were also purchased from Fisher Scientific.

In order to mimmic the pollution of dredged sediment the model sediment was artificially contaminated by five heavy metals (Cd, Pb, Cu, Cr, Zn). A mixture of five heavy metals was prepared to be introduced in the model sediment containing. Cadmium nitrate tetrahydrate (purity 99.99%), chromium nitrate (99%), copper sulfate (98%), zinc nitrate hydrate (99.99%) and lead nitrate (99.99%) were purchased from Sigma-Aldrich France. They were diluted in 180 mL of deionized water respectively at 0.130 g.L-1, 2.770 g.L-1, 0.452 g.L-1, 3.197 g.L-1 and 0.639 g.L-1, and after they were mixed with 360 g of the dry model sediment. This mixture was shaken for three days after its introduction inside the electrokinetic cell. For each test, approximately 540 g of the moist contaminated model sediment, which initial mass water content was 50%, was fully packed into the testing cell. The cathode and the anode reservoirs were filled with an aqueous solution containing the same additives. A constant voltage gradient (1 V.cm-1) was then applied for 7 to 14 days,

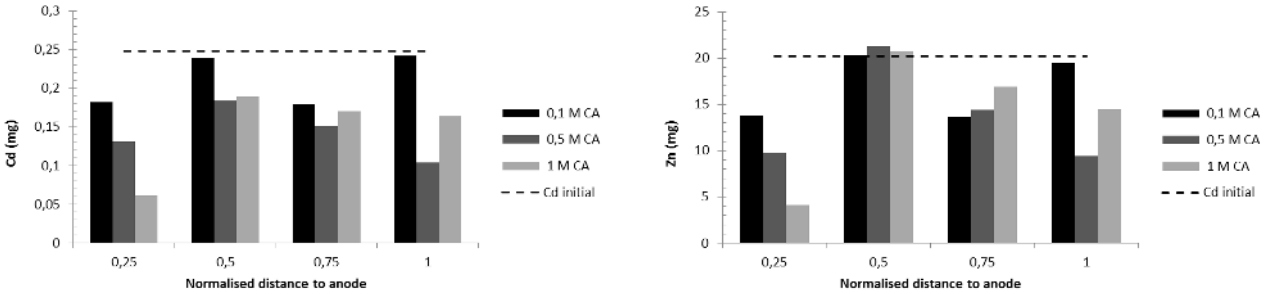

Fig. 2. Cd and Zn in the sediment after tests for different electrolyte (CA+TW20) concentrations

and electrical current was periodically measured during test. Every 24 h, cathodic and anodic effluents were taken so that the metals concentrations could be measured. At the end of a selected test duration, the model sediment was extracted from the cell and was sliced into 4 equal layers from which residual amounts of metals could be extracted and analyzed to obtain concentration profiles from the anode toward the cathode and to gain insights into the transport characteristics of contaminants in the sediment. Moreover, electrical conductivity, pH and redox potentials were measured in the four sediment layers. Sediment samples were freeze-dried as defined in the standard ISO 16720:2005 then ground and sieved at 200µm. For extraction, 0.5 g duplicate subsamples were weighed into digestion tubes (ISO 12914). Digestion samples was performed in 8 mL aqua regia and 2 mL MilliQ water in closed PTFE vessels using a microwave accelerated reaction system by 3 stages set and 70% power alternating 2 stages cooling. Mineralized solutes were transferred into 100 mL volumetric flasks and completed with MilliQ water. After shaking, the sample was centrifuged (7 min, 9000 rpm) and the supernatant was analysed. Heavy metals were also quantified in the aqueous cathodic and anodic effluents which were filtered with a Phenex Teflon PTFE filter (0.45 µm) before analysis. The heavy metal concentrations were analysed using an ETAAS (Spectra A220Z – GTA-110Z, Varian Corporation, Palo Alto, USA).

Results and Discussion

Five tests under various processing fluids were performed on model sediment (Table 1). Results show that salinity changes the distribution of metals after completion of the experiment. Salinity generally increases the mobility of metals and consequently their removal. Effectively, we can see on Table 1 that the removal of metals in EK2 treatment was better than EK1 treatment. When adding high contents of NaCl in the pore fluid, the best recoveries were obtained in the order Pb>Cu>Zn>Cr>Cd. It was already stated that an increase of salinity though addition of NaCl promoted a higher release of Pb than of Cu and Zn from soils (Acosta et al., 2011). The higher electrical current and sediment conductivity were responsible for a rapid migration of solubilized metals at the first stage of the treatment with NaCl, but metals were however rapidly stopped (24 to 48 h) by the formation of the alkaline front near the cathode. Enhanced electromigration methods are used to avoid the precipitation of metals, by neutralizing for instance part of the hydroxides generated at the cathode. Thus using nitric acid as an additive led to important metals recoveries from the sediment, from 77 to 99.9%.

After the completion of experiments, the sediment samples were sectioned into four equal layers and the metal concentrations were determined for each of these sections in triplicate in order to understand their migration behavior. Figure 2 shows the residual distribution of Cd and Zn respectively in Tancarville sediment treated with citric acid and Tween processing fluids. Increasing acid concentration of processing fluid leads to great removal of heavy metals. The distribution of metal concentration along the sample indicates that the cathode side is more concerned by electrokinetic remediation. A general trend which could be observed is that Zn was the easier to remove from sediment, whatever the treatment considered, whereas Cr and Cu were often the most difficult to remove. The treatment with deionized water was not efficient for removing metals from sediment. Metals tended to accumulate near the cathode because of the apparition of the alkaline front, causing their precipitation as a result of the formation of hydroxides. The best removals were obtained in the order Zn>Cr>Cu>Pb>Cd with deionized water as a processing fluid. It has been shown that affinity of sediments to heavy metals increased in the order Zn<Pb<Cu<Cr, but the behavior of Cd strongly depends on the nature and content of organic matter, and on the respective total metal concentration in soils or sediments.

We can conclude from Table 1 that when Nitric Acid (NA) was used, the best recoveries were obtained in the order Zn>Cd>Pb>Cu>Cr. In the acidic medium, Zn which is generally predominantly found in the most accessible phases of the sediment (Kirkelund et al., 2010) can be completely removed after 15 days of treatment, and Cd also. If we compare the removal of Pb with water or with nitric acid, we can see that the absence of the basic front, when pH is stabilized around 2.0 by NA, promoted an efficient migration towards the cathode,

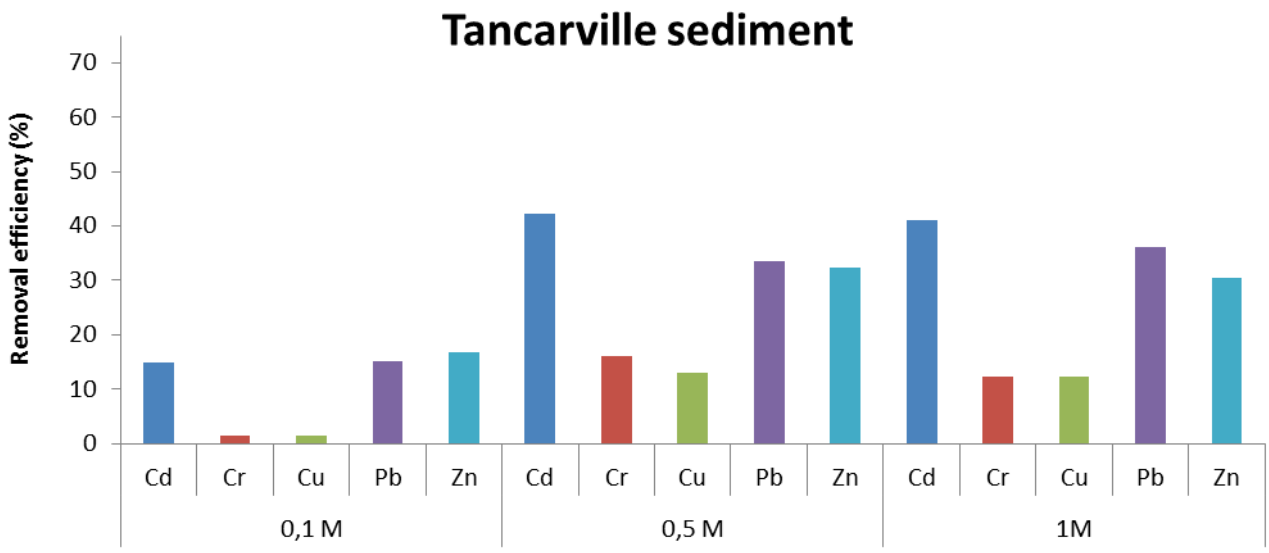

Fig. 3. Removal efficiency of heavy metals from natural sediment at various acid concentrations

whereas Pb was essentially found in the anodic effluents when deionized water was used. At last, Cu and Cr are less mobile when using NA in the processing fluid, because they are mainly found in the oxidisable fraction, less accessible for electromigration processes. As can be seen in Table 1, metal removal was better when adding the anionic surfactant SDS than using deionized water. The efficiency of the neutral surfactant Tween 20 for metal removal was worse than that of SDS. In the two cases, adding surfactants without any control of pH led to the apparition of the basic front, with a consecutive precipitation of metals and a poor metal removal. Consequently, it seemed more interesting to add these surfactants mixed with citric acid, in order to maintain an acidic pH (below pH=4) along the sediment specimen. Concerning the treatment with mixed CA and TW20, a significant improvement was noticed compared to the treatment using only TW20 in the processing fluid.

Figure 3 shows the removal efficiency of metals in Tancarville sediment, using different electrolyte (CA+TW20) concentrations. The removal efficiency start to be interesting with an optimal concentration close to 0,5 M, Cd and Pb being the best heavy metals removed. The amounts of metals removed are lower than that obtained in the model sediment because of the stronger and complex adsorption of heavy metals in natural sediment.

Conclusion

Laboratory electromigration experiments show the efficiency of such process in heavy metals removal from fine soils. The CA mixed with TW20 provides the best pollutant recovery when used as electrolyte enhancing-process. Zn and Cd are easy-removed from natural sediment which presents more metals-affinity than model sediment for which removal was more significant.

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