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# Heavy metal contaminant remediation study of western Xiamen Bay sediment, China: Laboratory bench scale testing results

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#### ABSTRACT

A surface sediment sample (<5 cm) was collected from a sewage sludge contaminated site (118°02.711′E, 24°32.585′N) within western Xiamen Bay, China, in July 2005 for a sediment decontamination study. A series of laboratory-based experiments under various conditions were performed using chemical complexation reagents (e.g.,  $H_2C_2O_4$ , EDTA–2Na, etc.) and their combination in order to provide information for sediment remediation technology development. In this study, the results suggest that aeration and agitation of the sediment samples in distilled–deionized water (DDW) have either no or weak (<30%) effect on metal removal, whereas agitation, aeration and rotation of the samples in chemical complexation solutions yield much better metal removal efficiency (up to 90%). A low pH condition (e.g., pH <3) and a low solid to liquid ratio (e.g., S:L = 1:50) could increase metal removal efficiency. The experimental results suggest that 0.20 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.025 M EDTA combination with solid:liquid ratio = 1:50 and 0.50 M ammonium acetate (NH<sub>4</sub>Ac) + 0.025 M EDTA combination with solid:liquid ratio = 1:50 are the most effective methods for metal removal from the contaminated sediments. This research provides additional useful information for sediment metal remediation technology development.

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#### 1. Introduction

The western Xiamen Bay is a semi-enclosed bay system in southeast coast of China and next to the Xiamen Economic Special Zone that was created in 1980. The water depth ranges from 6 m to 25 m with a deep-water coastline of about 30 km [1]. Thus, it has an excellent natural environment for navigation and shipping activities. Although the economic development in Xiamen Economic Zone speeds the industrialization and economic development of the region, it also brings environmental problems in the mean time. Similar to other urban coastal areas in the world with the population growth and industrialization, various contaminants (e.g., heavy metals) are being discharged into the estuarine and coastal environment along with sewage sludge, waste water, etc. and have raised serious concerns of human health and living environment (e.g., [2-9]). The rapid development of the Xiamen Economic Special Zone in past three decades has resulted in great environmental stress on the western Xiamen Bay and its adjacent areas [1]. To expand the Xiamen Harbor, navigation channel dredging in western Xiamen Bay has been operated every year since 1993. In the meantime, the municipality of Xiamen City has decided to restore the ecosystem of manmade lagoons adjacent to the western Xiamen Bay. Therefore, a large quantity of sediments (> $2 \times 10^7 \text{ m}^3$ ) is expected to be dredged during the project. Currently, a certain amount of dredged materials are dumped offshore outside of Xiamen Bay. This operation has raised environmental concerns around the dumping site. As a world-wide problem of sediment contamination, various sediment remediation technologies have been tested since 1990s based on physical or chemical principles in order to find a solution for this sediment contamination issue (e.g., [10–14]). Most of these technologies are still in the experimental or validation stages (e.g., [10,15–19]). It has been well known that development of sediment remediation methods is very critical to the economic development. In this study, a series of laboratory experiments on metal remediation were conducted on the dredged materials from western Xiamen Bay. The objectives of this laboratory study were to examine the metal removal efficiency from the contaminated sediments under various experimental conditions, evaluate the feasibility of the different techniques, and provide useful scientific information on metal remediation based on these experimental results for further development of applicable large-scale metal remediation technologies.

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Fig. 1. Map showing the study area and sampling locations.

#### 2. Methodology

The field sampling was conducted in July 2005 in western Xiamen Bay. Station X5 (118°02.711′E, 24°32.585′N) (Fig. 1) was chosen for the sediment remediation study because it was located next to the outlet of the Sewage Treatment Plant of Xinlin Industrial Area and metal concentrations at Station X5 were higher than that at other stations [20]. After the sediments were retrieved at this station, surface sediments (<5 cm) were collected and carefully transported to Environmental Science Research Center of Xiamen University for processing and analysis. The samples were initially dried naturally in the air in a controlled clean environment for a week. The subsamples for grain size analysis, trace metal concentration analyses and laboratory experiments were then transferred to an oven and dried at  $40 \pm 2$ °C. The samples were finally ground to a powder with a mortar and pestle, sieved through an 80 mesh sieve and kept in a pre-cleaned container for

future use. The subsample for organic content measurement was oven dried at 105 °C in our laboratory at Xiamen University after dried naturally. Then, an aliquot of 20g of sample was determined for organic content by loss on ignition (LOI) method, i.e., the sample was combusted at 450 °C for 8 h [21,22]. The grain size of the sediment sample was analyzed using Mastersizer MS 2000 Particle Size Analyzer (Malvern Instruments Ltd., UK) [23]. For the laboratory tests under different physical experimental settings (e.g., aeration, agitation and rotation), aliquots of 3-20 g of dried sediment samples were used with and without additions of various chemical complexation reagents. After rotation, aeration or agitation of the samples in the various solutions, the sediment samples were allowed to settle down for a certain time period. Then, the overlying liquid was filtered using a vacuum pump and collected in pre-cleaned bottles. Finally, the filtered solutions were analyzed on an Agilent 7500i Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) for metal concentrations. The chemical reagents chosen



**Fig. 2.** Metal removal efficiency comparison among physical processes. An aliquot of 5 g of sediment was added to 250 mL of (a) distilled–deionized water (DDW) under three different experimental conditions: (i) standing still, (ii) aeration and (iii) agitation; and (b) 0.20 M oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) solution under four different experimental conditions (i) standing still, (ii) aeration and (iv) agitation. In these sets of experiments, aeration rate is set at 5 L/min, agitation rate is 300 rpm, and the reaction time is 16 h.

for this study included ethylenediamine tetra acetic acid, disodium salt (EDTA–2Na), sodium dodecylsulphate (SDS), acetic acid (HAc), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), ammonium acetate (NH<sub>4</sub>Ac), ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) and trace metal standard stock solutions, which are all optima grade. All the containers, bottles and glassware for the experiments were pre-cleaned with 1:3 (v/v) nitric acid (HNO<sub>3</sub>) and rinsed with milli-pore water. To examine the reproducibility of the experimental results, we selectively conducted

certain ( ${\sim}20\%)$  duplicate experiments. The reproducibility of the results was better than 10% of variance.

## 3. Results

The physical and chemical parameters of sediment at Station X5 are listed in Table 1. Due to physical treatment processes solely (e.g., aeration, agitation and rotation) alone could not yield high



**Fig. 3.** Metal removal efficiency comparison under various experimental conditions using 5 g of sediment and oxalic acid  $(H_2C_2O_4)$  solution: (a) at varying aeration flow rate with concentration = 0.20 M, solution = 250 mL and time = 16 h; (b) at different solid to liquid (S:L) ratios with aeration rate = 5 L/min and time = 16; (c) at different pH conditions with concentration = 0.20 M, solution = 250 mL and agitation time = 8 h at 300 rpm; and (d) at different  $H_2C_2O_4$  concentrations with solution = 250 mL and agitation time t = 36 h at 300 rpm.



Fig. 4. EDTA leaching results under varying EDTA-2Na concentrations and solid (sediment) to liquid (EDTA-2Na solution) ratios. An aliquot of 20 g of naturally dried sediments was used in each batch of experiment. Reaction time is 16 h.

metal removal efficiencies, several sets of combinations of physical treatment with various chemical extractions were performed to enhance the metal removal. The results are presented in the following sections.

## 3.1. Physical and chemical parameters of sediments

Sediments at Station X5 were mainly fine grain materials (grain size: 0.0015–0.42 mm), of which sand fraction (grain size:

#### Table 1

Sediment physical and chemical properties at Station X5 (118°02.711′E, 24°32.585′N) in western Xiamen Bay, China.

Parameters	Concentration	Units
Sand	0.8	%
Fine sand	70.7	%
Silt and clay	28.5	%
Organic content	3.75	%
Cd	0.19	mg/kg
Cr	122	mg/kg
Cu	78.9	mg/kg
Ni	64.8	mg/kg
Pb	52.2	mg/kg
Zn	129	mg/kg

0.063–0.5 mm) accounted for 0.8%, fine sand faction (grain size: 0.0039–0.063 mm) accounted for 70.7%, and silt-clay fraction (grain size: 0.00049–0.0039 mm) accounted for 28.5% (Table 1). Organic content was 3.75% (Table 1). Heavy metal concentrations at Station X5 were 0.19 mg/kg for Cd, 122 mg/kg for Cr, 78.9 mg/kg for Cu, 64.8 mg/kg for Ni, 52.2 mg/kg for Pb, and 129 mg/kg for Zn (Table 1).

# 3.2. Metal removal efficiency comparison with and without oxalic acid

Metal removal efficiencies in distilled–deionized water (DDW) and 0.20 M oxalic acid ( $H_2C_2O_4$ ) solution were tested under the conditions of no action (still solution), aeration, agitation and rotation. The results showed that, in pure DDW matrix, both still solution and aeration of solution had no detectable removal of the metals (As, Cd, Cr, Cu, Ni and Zn) from sediment, whereas agitation of the solution yielded a very low metal removal efficiency (<30%) (Fig. 2a). In contrast, when 0.20 M oxalic acid ( $H_2C_2O_4$ ) was used instead of DDW, the metal removal efficiency was greatly improved, ranging from 33% to 67% for As, from 27% to 48% for Cr, from 15% to 62% for Cu, from 33% to 59% for Ni and from 24% to 65% for Zn under the experimental conditions of still solution (no action),



Fig. 5. EDTA leaching results under different pH conditions and solid (sediment) to liquid (EDTA-2Na solution) ratios. Concentration of EDTA-2Na used in this experiment remains 0.025 M. An aliquot of 20 g of naturally dried sediments was used in each batch of experiment. The reaction time is 16 h.

rotation, aeration (5 L/min) and agitation (300 rpm), respectively (Fig. 2b).

#### 3.3. Oxalic acid extraction

Oxalic acid  $(H_2C_2O_4)$  is a relatively strong organic acid. Many metal ions form insoluble precipitates with oxalate. In our study,

oxalic acid was used in a series of experiment to examine the metal removal efficiency from the contaminated sediments. As shown in Fig. 3a, when aeration rate increased from 5 L/min to 30 L/min in 0.20 M oxalic acid ( $H_2C_2O_4$ ) solution the metal removal efficiencies were changed from 44% to 48% for As, from 13% to 28% for Cd, from 26% to 32% for Cr, from 40% to 52% for Cu, from 43% to 44% for Ni and from 42% to 44% for Zn. The results suggest that within the range

#### Table 2

Summary of the experimental results using EDTA-2Na as complexation reagent with varying pH conditions and solid to liquid rations. The metal removal efficiencies vary from metal to metal.

Metal	Result
Cd	Varying pH values and solid to liquid ratios did not affect Cd removal efficiency significantly.
Cr	Decreasing pH value and decreasing solid to liquid ratio improved Cr removal efficiency by up to 5%. In general removal efficiency of Cr by EDTA–2Na was low ranging from 6.8% to 13% under various experimental conditions.
Cu	Decreasing pH value from 7 to 3 and decreasing solid to liquid ratio from 1:20 to 1:50 increased extraction efficiency by as much as 15%.
Ni	Similar to Cr, decreasing pH value and decreasing solid lo liquid ratio improved Ni removal efficiency by up to 5%. However, EDTA-2Na had better removal efficiency for Ni than that for Cr, ranging from 24% to 35% under various experimental conditions.
Pb	Decreasing solid (sediment) to liquid (complexation solution) ratio from 1:20 to 1:50 increases Pb removal efficiency by 8% to 18%. Decreasing pH values from pH = 7 to pH = 3 does not improve removal efficiency significantly.
Zn	Under a low pH condition (pH 5) and decreasing solid to liquid ratio (e.g., 1:50). Zn removal efficiency was improved by up to 7%.



**Fig. 6.** Results of extraction using various complexation reagent combination and solid (sediment) to liquid (complexation reagent solution) ratios. An aliquot of 20 g of naturally dried sediments was used in each batch of experiment. The reaction time is 16 h.

of experimental aeration rates (5–30 L/min) increasing oxygen content have no significant impact on the removal efficiencies of As, Cd, Cr, Cu, Ni and Zn from the contaminated sediment. This observation is consistent with other studies in metal remediation [24–27], although aeration shows effectiveness on removing volatile organic carbon due to oxidation [28–31].

Variation in solid (sediment) to liquid (solution) ratio (S:L ratio) on metal removal efficiency was tested using  $0.20 \text{ M H}_2\text{C}_2\text{O}_4$  under aeration (5 L/min) for 16 h. When S:L ratio decreased from 1:10 to 1:50, metal removal efficiencies increased from 9% to 27% for Cd, from 21% to 35% for Cr, from 28% to 52% for Cu, from 23% to 46% for Ni and from 19% to 47% for Zn (Fig. 3b). The results suggest that a low

S:L ratio (or a high dilution) may result in a better metal removal efficiency.

The effect of pH on metal removal efficiency was also tested by using 0.20 M  $H_2C_2O_4$  solution and agitating the solution at a rate of 300 rpm for 8 h under S:L = 1:50. An aliquot of 5 g of sediment was used for the experiment. When pH value was decreased from 7 to 1 by adding 0.10 M nitric acid (HNO<sub>3</sub>), the metal removal efficiencies increased generally from 0% to 52% for As, from 4% to 30% for Cr, from 13% to 50% for Cu, from 11% to 42% for Ni and from 13% to 40% for Zn. However, the removal efficiency for Cd showed a fluctuation between 18% at pH 3 and 36% at pH 1 (Fig. 3c). The reason is not clear. Nevertheless, the results demonstrated that a low pH condition (pH  $\leq$  3) could yield a high metal removal efficiency although a condition of pH 1 would be better for As and Cd removal. The results also suggest that the metal solubility be controlled by the acidity of the solution.

The effect of different oxalic acid concentrations on metal removal efficiency was tested on an aliquot of 5 g of sediment in 250 mL of oxalic acid ( $H_2C_2O_4$ ) solution (S:L=1:50) under an agitation rate of 300 rpm and reaction time of 36 h. When  $H_2C_2O_4$  concentrations increased from 0.05 M to 0.70 M, the metal removal efficiencies increased from 22% to 63% for As, from 16% to 55% for Cr, from 38% to 66% for Cu, from 26% to 63% for Ni, and from 15% to 56% for Zn (Fig. 3d). Removal efficiency for Cd showed some a fluctuation from 8.3% at a 0.10 M  $H_2C_2O_4$  concentration to 52% at a 0.40 M  $H_2C_2O_4$  concentration (Fig. 3d). Nevertheless, it still showed a general increase with a high  $H_2C_2O_4$  concentration.

#### 3.4. EDTA–2Na extraction

Ethylenediamine tetra acetic acid, disodium salt (EDTA–2Na) is a water soluble complexation reagent. It can react with heavy metals and form very stable metal complexes [17,32–34]. Therefore, heavy metals can be extracted from sediments to solution. As a complexation reagent, EDTA–2Na was used to examine metal removal efficiency from the contaminated sediments under various conditions including changing EDTA–2Na concentrations, pH values and solid (sediment) to liquid (EDTA–2Na solution) ratios. The results from these experiments are shown in Fig. 4. It is seen that doubling the amount of EDTA–2Na increased Cd, Cu, Pb and Zn extraction efficiency by 10–20%, but only 3–5% for Cr and Ni (Fig. 4). Under various experimental conditions, removal efficiency for Cr was the lowest ranging from 6% to 13% reproducibly, while removal efficiency for Cd, in contrast, was the highest ranging from 41% to 68%.

#### Table 3

Summary of the experimental results in metal remediations using various complexation reagents and their combinations with different solid to liquid (S:L) ratios.

Metal	Result
Cd	The best removal efficiency, 96%, was resulted from a combination of 0.20 M $(NH_4)_2C_2O_4 + 0.025$ M EDTA with solid:liquid ratio (S:L) = 1:50. A combination of 0.50 M NH <sub>4</sub> Ac + 0.025 M EDTA with S:L = 1:50 ranked in the second place with the removal efficiency of 90%. A 0.20 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> solution with S:L = 1:50 was the next and yielded 84% removal efficiency.
Cr	Except for 0.20 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> solution with S:L 1:50 that yielded 39% removal efficiency, the rest of complexation reagents and combinations yielded low removal efficiency (0.2–22%) in removing Cr from sediments.
Cu	The highest removal efficiency (70%) was produced by a combination of $0.50 \text{ M NH}_4\text{Ac} + 0.025 \text{ M EDTA}$ with S:L = 1:50. With S:L = 1:50, a $0.20 \text{ M H}_2\text{C}_2\text{O}_4$ solution and a combination of $0.20 \text{ M}$ (NH $_4$ ) $_2\text{C}_2\text{O}_4 + 0.025 \text{ M EDTA}$ yielded essentially the same removal efficiency, which are 61% and 62%, respectively. A 0.010 M SDS solution had the least removal efficiency, <7%.
Ni	All the complexation reagents and combinations yielded a relatively low removal efficiency, varying from nearly zero (0.010 M SDS solution with S:L = 1:20) to 23% (0.025 M EDTA + 0.010 M SDS combination with S:L = 1:20 and 0.20 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 0.025 M EDTA combination with S:L = 1:50).
РЬ	A combination of $0.50 \text{ M NH}_4\text{Ac} + 0.025 \text{ M EDTA}$ with S:L = 1:50 had the highest removal efficiency (76%) A combination of $0.20 \text{ M (NH}_4)_2\text{C}_2\text{O}_4 + 0.025 \text{ M EDTA}$ with S:L = 1.50 was the second most effective method, giving 68% removal efficiency. A 0.010 M SDS solution with S:L = 1.20 had essentially no effect on removing Pb contaminant (1%).
Zn	A combination of $0.20 \text{ M} (\text{NH}_4)_2 \text{C}_2 \text{O}_4 + 0.025 \text{ M}$ EDTA solution with S:L = 1:50 yielded the best removal efficiency, 69%. This was followed by a combination of 0.50 M NH <sub>4</sub> Ac + 0.025 M EDTA with S:L = 1.50 that yielded the second best removal efficiency, 62% A 0.010 M SDS solution with S:L = 1.20 yielded the lowest removal efficiency, 6%



Fig. 7. Extraction efficiency comparison between aeration (2.5 L/min) and rotation using different chemical complexation reagents. An aliquot of 5 g of sediment was used in each batch of experiment and the reaction time is 16 h.

However, when the solid to liquid ratio was changed from 1:10 to 1:20, i.e., more complexation solution was added, an increase in metal removal efficiency was observed (Fig. 4). Effects of changing pH values and solid to liquid ratios on metal removal efficiency were tested in the laboratory experimental scale in this study. Several trends with respect to the metal removal were observed (Fig. 5) and the results are summarized in Table 2.

### 3.5. Removal efficiency comparison

Further laboratory experiments involving more complexation reagents (e.g., ethylenediamine tetra acetic acid, disodium salt (EDTA–2Na), sodium dodecylsulphate (SDS), acetic acid (HAc), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), ammonium acetate (NH<sub>4</sub>Ac), ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) continued with different experimental settings and reagent combinations. The results showed that the removal efficiency varied with each individual metal (Fig. 6) and are summarized in Table 3. The metal removal efficiencies under aeration at a rate of 2.5 L/min and rotation, respectively, with and without additions of various chemical complexation reagents were

examined. Solid (sediment) to liquid (complexation solution) ratio was  $1:50 \text{ g/cm}^3$  in all the experiment. The comparisons of the results from these two conditions (i.e., aeration and rotation) are shown in Fig. 7. In this set of experiment, we found that a 0.20 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution under aeration and with S:L = 1:50 yielded the best removal efficiency (79% for Cd, 45% for Cr, 93% for Cu, 66% for Ni, and 89% for Zn, respectively), but the least removal efficiency for Pb (3%). However, we found that using a 0.025 M EDTA solution under aeration and with S:L = 1:50 resulted in 73% removal efficiency for Pb besides moderate to high removal efficiencies for other metals (except for Cr) ranging from 37% (Ni) to 94% (Cu) (Fig. 7).

#### 4. Discussion

To develop technically feasible and cost effective ex-situ sediment remediation technologies, a series of laboratory experiments under various conditions, including using different chemical complexation reagents and their combinations, were performed in this study. Due to chemical reaction and complexation, metal removal efficiencies with addition of chemical complexation reagent (e.g., 0.20 M oxalic acid  $(H_2C_2O_4)$  solution) under aeration, agitation and rotation were better than that in distilled-deionized water (Fig. 2). In the meantime, a low solid to liquid (S:L) ratio (or high dilution) in 0.20 M oxalic acid  $(H_2C_2O_4)$  solution resulted in a better metal removal efficiency due partly to increasing interaction sites between particles and solution or increasing chances of solidsolution reaction (Fig. 3b). Although a high  $H_2C_2O_4$  concentration generally yielded high metal removal efficiency, an increase of metal removal efficiency from 0.40 M  $H_2C_2O_4$  to 0.70 M  $H_2C_2O_4$  was not significant (Fig. 3d). From a cost effectiveness and safety stand point of view, the study shows that a 0.40 M oxalic acid ( $H_2C_2O_4$ ) concentration yielded optimum metal removal efficiency.

When EDTA-2Na was used as a chemical complexation reagent in the experiment, changing EDTA-2Na concentrations under the same solid (sediment) to liquid (complexation solution) ratio (i.e., either 1:10 or 1:20) did not show obvious impact on the removal efficiency of individual heavy metals of interest in general, although significant differences in removal efficiency were observed between the heavy metals (Fig. 4). The impact of acidity of the solution (pH values) and solid to liquid (S:L) ratios on metal removal efficiency in EDTA-2Na solution varied from one metal to another, although relatively better metal removal efficiencies were observed in most cases with a decrease of S:L ratio (e.g., S:L = 1:50) (Fig. 5 and Table 2). These observations suggest that adding more EDTA-2Na complexation solution to the system dilute the particle concentration, increase the interaction opportunity between particles and complexation agent and, hence, increase metal removal efficiency from the particles. The consequence is that the low S:L ratio promotes the complexation reaction towards formation of metal complex in solution and removal of metals from solids, as demonstrated in the experiment.

When several chemical complexation reagents were combined for metal extraction, the results showed that 0.20 M  $(NH_4)_2C_2O_4 + 0.025 M$  EDTA combination with S:L=1:50 and 0.50 M NH<sub>4</sub>Ac + 0.025 M EDTA combination with S:L = 1:50 were the recommended methods for metal remediation because these combinations yielded relatively high metal removal efficiency (Fig. 6). Using 0.010 M SDS solution with S:L=1:20 should be avoided because it yielded a lower efficiency in removing metals from sediments (Fig. 6). Although aerating pure DDW resulted in no or a very low metal removal efficiency, the results showed that both aeration and rotation yielded better metal removal efficiency in chemical complexation solutions (Fig. 7). Although it varied with each metal and reagent used, an even better (up to 50%) metal removal efficiency by aeration was observed (Fig. 7). The results suggest that the chemical complexation agents increase the metal solubility or partitioning in these solutions.

#### 5. Conclusions

The remediation of metals in the sediments with and without chemical complexation reagents was evaluated in this study. The results from our laboratory-based experiments provide useful information for metal remediation, although further validation of these methods in larger-scale experiments should be conducted. The key findings from our laboratory-based experiments are summarized below:

 Without addition of chemical complexation agents (i.e., in distilled-deionized water matrix), neither still solution nor aeration had a detectable effect on metal removal whereas agitation of the solution had a low metal removal efficiency (<30%) (Fig. 2a). In contrast, agitation, aeration and rotation of the samples in 0.20 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution yielded better metal removal efficiencies (15–67%) (Fig. 2b). Even in still 0.20 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution, the metal removal efficiencies ranged from 15% to 33% depending on individual metal (Fig. 2b).

- A low pH condition (e.g., pH < 3) and decreased solid to liquid ratio (e.g., S:L=1:50) could increase metal removal efficiency although it would also depend on metals and chemical reagents.
- 3. A 0.20 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.025 M EDTA combination with solid:liquid ratio = 1:50 and a 0.50 M NH<sub>4</sub>Ac + 0.025 M EDTA combination with solid:liquid ratio = 1:50 could be the recommended methods for metal removal from the sediments.
- 4. A 0.20 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution under aeration with solid:liquid ratio = 1:50 yielded the best extraction efficiency for Cd (79%), Cr (45%), Cu (93%), Ni (66%) and Zn (89%). However, this method had very low removal efficiency for Pb (3.4%).
- 5. A 0.025 M EDTA solution under aeration and solid:liquid ratio = 1:50 had 73% removal efficiency for Pb besides moderate to high removal efficiencies for other metals (except for Cr) ranging from 37% (Ni) to 94% (Cu).

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#### References

- [1] Y. Wu, Y. Guo, H. Xie, D. Gu, H. Lin, X. Liu, W. Lin, ZhaoF D., The profile of Xiamen coastal zone, in: G. Chen (Ed.), Integrated Coastal Management in Xiamen. GEF/UNDP/IMO, Ocean Press, Beijing, 1998, pp. II-11–II-92 (chapter 2).
- [2] M.H. Bothner, M. Buchholtz ten Brink, F.T. Manheim, Metal concentrations in surface sediments of Boston Harbor-changes with time, Mar. Environ. Res. 45 (1998) 127–155.
- [3] S. Chen, A. Xu, B. Luo, Distribution and sources of heavy metals in sediments from the Xiamen Harbour, J. Oceanogr. Taiwan Strait 6 (1987) 139–145 (in Chinese with English abstract).
- [4] W. Chen, L. Zhang, L. Xu, X. Wang, L. Hong, H. Hong, Residue levels of HCHs, DDTs and PCBs in shellfish from coastal areas of east Xiamen Island and Minjiang Estuary, China, Mar. Pollut. Bull. 45 (2002) 385–390.
- [5] H. Feng, J.K. Cochran, H. Lwiza, B. Brownawell, D.J. Hirschberg, Distribution of heavy metal and PCB contaminants in the sediments of an urban estuary: the Hudson River, Mar. Environ. Res. 45 (1998) 69–88.
- [6] H. Feng, X. Han, W. Zhang, L. Yu, A preliminary study of heavy metal contamination in Yangtze river intertidal zone due to urbanization, Mar. Pollut. Bull. 49 (2004) 910–915.
- [7] L.-Y. Hong, H.-S. Hong, W.-Q. Chen, X.-H. Wang, L.-P. Zhang, Heavy metals in surface sediments from Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas, J. Environ. Sci. 15 (2003) 116–122.
- [8] K. Maskaoui, J.L. Zhou, H.S. Hong, Z.L. Zhang, Contamination by polycyclic aromatic hydrocarbons in the Jiulong River Estuary and Western Xiamen Sea, China, Environ. Pollut. 118 (2002) 109–122.
- [9] K. Maskaoui, J.L. Zhou, T.L. Zheng, H. Hong, Z. Yu, Organochlorine micropollutants in the Jiulong River Estuary and Western Xiamen Sea, China, Mar. Pollut. Bull. 51 (2005) 950–959.
- [10] J.N. Meegoda, R. Perera, Ultrasound to decontaminate heavy metals in dredged sediments, J. Hazard. Mater. 85 (2001) 73–89.
- [11] P. Cauwenberg, F. Verdonckt, A. Maes, Flotation as a remediation technique for heavily polluted dredged material. 1. A feasibility study, Sci. Total Environ. 209 (1998) 113–119.
- [12] M.M.A. Ferdinandy-van Vlerken, Chances for biological techniques in sediment remediation, Water Sci. Technol. 37 (1998) 345–353.
- [13] I. Muller, E. Pluquet, Immobilization of heavy metals in sediment dredged from a seaport by iron bearing materials, Water Sci. Technol. 37 (1998) 379–386.
- [14] M. Vanthuyne, A. Maes, P. Cauwenberg, The use of flotation techniques in the remediation of heavy metal contaminated sediments and soils: an overview of controlling factors, Miner. Eng. 16 (2003) 1131–1141.
- [15] H.D. Detzner, W. Schramm, U. Döring, W. Bode, New technology of mechanical treatment of dredged material from Hamburg harbour, Water Sci. Technol. 37 (1998) 337–343.
- [16] K.W. Jones, H. Feng, E.A. Stern, J. Lodge, N.L. Clesceri, Decontaminating and processing dredged material for beneficial use, J. Hazard. Mater. 85 (2001) 127–143.
- [17] C.N. Mulligan, R.N. Yong, B.F. Gibbs, An evaluation of technologies for the heavy metal remediation of dredged sediments, J. Hazard. Mater. 85 (2001) 145–163.

- [18] G.M. Nystrbm, L.M. Ottosen, A. Villumsen, Test of experimental set-ups for electrodialytic removal of Cu, Zn, Pb and Cd from different contaminated harbour sediments, Eng. Geol. 77 (2005) 349–357.
- [19] V.J. Urban, C. Block, J. Manem, Bioflocculation in activated sludge: an analytic approach, Water Res. 27 (1993) 829–838.
- [20] L. Zhang, X. Ye, H. Feng, Y. Jing, T. Ouyang, X. Yu, R. Liang, W. Chen, Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China, Mar. Pollut. Bull. 54 (2007) 974–982.
- [21] C.B. Craft, E.D. Seneca, S.W. Broome, Loss on ignition and Kjeldahl digestion for estimating organic carbon and total nitrogen in estuarine marsh soils: calibration with dry combustion, Estuaries 14 (1991) 175–179.
- [22] R.K. Lu, Soil and Agricultural Chemistry Analysis Method, China Agricultural Science and Technology Press, Beijing, 2000, 638 pp. (in Chinese).
- [23] J. Clifton, P. McDonald, A. Plater, F. Oldfield, Derivation of a grain-size proxy to aid the modelling and prediction of radionuclide activity in saltmarshes and mud flats of the Eastern Irish Sea, Estuar. Coast. Shelf Sci. 48 (1999) 511– 518.
- [24] J. Fajtl, M. Kabrna, R. Tichy, R. Ledvina, Environmental risks associated with aeration of a freshwater sediment exposed to mine drainage water, Environ. Geol. 41 (2002) 563–570.
- [25] Y. Filali-Meknassi, R.D. Tyagi, K.S. Narasiah, Simultaneous sewage sludge digestion and metal leaching: effect of aeration, Process Biochem. 36 (2000) 263–273.
- [26] N. Caille, C. Tiffreau, C. Leyval, J.L. Morel, Solubility of metals in an anoxic sediment during prolonged aeration, Sci. Total Environ. 301 (2003) 239– 250.

- [27] D. Dong, X. Zhao, X. Hua, J. Liu, M. Gao, Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China, J. Hazard. Mater. 162 (2009) 1261–1268.
- [28] R.L. Rhykerd, B. Crews, K.J. McInnes, R.W. Weaver, Impact of bulking agents, forced aeration, and tillage on remediation of oil-contaminated soil, Bioresour. Technol. 67 (1999) 279–285.
- [29] B.L. Hall, T.E. Lachmar, R.R. Dupont, Field monitoring and performance evaluation of a field-scale in-well aeration system at a gasoline-contaminated site, J. Hazard. Mater. 82 (2001) 197–212.
- [30] K. Paudyn, A. Rutter, R.K. Rowe, J.S. Poland, Remediation of hydrocarbon contaminated soils in the Canadian Arctic by landfarming, Cold Reg. Sci. Technol. 53 (2008) 102–114.
- [31] G.U. Balcke, H. Paschke, C. Vogt, M. Schirmer, Pulsed gas injection: a minimum effort approach for enhanced natural attenuation of chlorobenzene in contaminated groundwater, Environ. Pollut. 157 (2009) 2011–2018.
- [32] O.K. Júnior, L.V.A. Gurgel, R.P. de Freitas, L.F. Gil, Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD), Carbohyd. Polym. 77 (2009) 643–650.
- [33] M. Pociecha, D. Lestan, EDTA leaching of Cu contaminated soil using electrochemical treatment of the washing solution, J. Hazard. Mater. 165 (2009) 533–539.
- [34] W. Xia, H. Gao, X. Wang, C. Zhou, Y. Liu, T. Fan, X. Wang, Application of EDTA decontamination on soils affected by mining activities and impact of treatment on the geochemical partition of metal contaminants, J. Hazard. Mater. 164 (2009) 936–940.