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A kinetic study of heavy metals removal from contaminated marine sediment with chelating agents

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ABSTRACT

Batch sediment washing experiments were conducted to remove six metals (Cu, Zn, Ni, Cd, Cr, and Pb) from contaminated sediments. The effect of different operating parameters such as: type of washing solutions, reaction time, solution concentration, pH, and liquid/solid ratio were investigated. Besides, the kinetic of the extraction process was also studied. In the proposed work, cheating agent, i.e., di-sodium salt of ethylenediamine tetraacetate (Na_2EDTA), was applied for extraction of heavy metals from contaminated sediment and showed significantly high efficiency compared with other agents. The extraction efficiency was 33%, 73%, 29%, 88%, 13%, and 83% for Cu, Zn, Ni, Cd, Cr, and Pb, respectively, at a 0.1 M Na_2EDTA washing solution, liquid/solid ratio of 10, pH 4.0, and 2 h washing time. The chelant extraction process was a first-order reaction. The k_1 (apparent rate constant for metal desorption) values were 0.0822–0.5598 h^{-1}, and the order was Pb > Zn > Cd > Ni > Cu > Cr. Moreover, the results indicated that the extraction efficiency of metals is directly proportional to the liquid/solid ratio and concentration of washing solution while inversely proportional to the pH in the range of 3–10. The results will be useful as preliminary evaluation of the removal of heavy metals from the contaminated sediments using chelating agents in washing operation.

Keywords: Sediments; Extraction; Heavy metals; Chelating agents

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1. Introduction

Recently, there are concerns over the contamination of marine sediments with metals and organic pollutants due to potential toxicological hazard. For instance, metals can bioaccumulate in food chains, induce high mortality rates, and disturbance of reproductive processes in marine organisms [1]. Conventional marine sediments remediation approaches such as in situ capping, landfill disposal, and dumping at sea are becoming unsustainable, due to problems associated with contaminant transport pathways and environmental compatibility. Even a low load of pollutants in marine sediments can cause secondary environmental pollution and bring various environmental changes in aqueous systems. Hence, environmentally friendly approaches should be developed in order to remove pollutants from sediments.

Heavy metals cannot be degraded but are infinitely persistent in the environment and cannot be subjected to treatment with biological and chemical degradation processes. Heavy metals can only be transformed from soluble to insoluble forms and vice versa and/or to less toxic species. Accordingly, many remediation technologies have been attempted to increase either metal solubility (mobilization) or stability, as to reduce the bioavailability (immobilization). Recently, various remedial techniques for heavy metal contaminated

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soils/sediments have been reported, including stabilization/solidification [2], electrokinetic remediation [3], bioremediation [4], and soils/sediments washing [5–7]. Stabilization/solidification technology can stabilize the contaminants and reduce the solubility, but may not meet regulation standard [8,9]. Although electrokinetic remediation has high metals removal efficiency, it probably has high energy consumption. Indeed, metal mobilization can be mediated microbially, but may take long time to meet the regulation standard.

In Taiwan, soil/sediment washing is often considered as a promising remedial technique for heavy metals contaminated sites over a relatively short time period compared with other remedial techniques. Numerous studies have been investigated over the use of different types of washing solutions (e.g., inorganic salts, inorganic acids, organic acids, alkaline agents, and chelating agents) for the remediation of soils and sediments contaminated by heavy metals. Hydrochloric acid and sulfuric acid, and other inorganic acids are known to be effective in extraction of heavy metals from soils/sediments [10]. For example, Moon et al. [11] reported that a Zn removal of approximately 92% and 90% was attained with a liquid/solid (L/S) ratio of 10 after 1 h treatment by using 2 M HCl, and H_2SO_4, respectively. Even though strong acids are expected to be more effective for soil/sediment washing, these strong acids tend to destruct the soil/sediment composition, which prompted researchers to apply weak acids. For example, Polettini et al. [12] have studied the efficiency of four chelating agents: ethylenediamine tetraacetate (EDTA), *S*,*S*-ethylene-diaminedisuccinic acid (EDDS), nitrilotriacetic acid (NTA), and citric acid, for heavy metal removal from a marine contaminated sediment. The results showed that Cd, Cu, Pb and Zn were adequately removed by both EDTA and EDDS. Wuana et al. [13] tested citric acid, tartaric acid, and EDTA for the removal of Ni, Cu, Zn, Cd, and Pb, from artificially contaminated soils and demonstrated that the washing efficiency varied in the order: EDTA > citric acid > tartaric acid.

Soil/sediment washing by chelating agents is a suitable technique for the removal of metals from contaminated soils/sediments, and selection of the suitable chelating agents is the most important decision action. The selection of chelating agents mainly depends on the target pollutants, the bonding/chelating strength of the extraction agents, and the soil/sediment characteristics (including pH, particle size distribution, and mineral composition) [5]. Besides, the success of chelating agents in removing metals from contaminated sediments also depends on the combination of many parameters such as extraction time, chelating agent/metal molar ratio, solution pH, L/S ratio, and chelating agent concentration. However, the kinetics of trace metals adsorption and desorption on soil/sediment plays important role, which were demonstrated by Polettini et al. [12]. In their study, they described the kinetics of chelant-assisted remediation for contaminated dredged sediment. Whereas EDTA and EDDS exhibited higher k_1 (apparent rate constant for metal desorption) and lower k_2 (apparent rate constant for metal adsorption) values for Cd, Cu, Pb, and Zn. Labanowski et al. [14] investigated the kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil. The results suggest that Zn and Cu displayed similar kinetics behaviors and had a more homogeneous binding strength compared with Cd and Pb. These kinetic results are useful for the determination of the optimal treatment duration and can be used to assess in situ remediation strategies.

The present work focused on five different chelating agents and their metal removal efficiency from contaminated marine sediments. The optimization parameters were studied such as washing time, chelating agent concentration, pH of the washing solution, and L/S ratio. The effectiveness of the washing process was evaluated by measuring the residual metal concentrations after the washing process. In addition, the extraction efficiency of five metal fractions (exchangeable, carbonate, Fe–Mn oxides and hydroxides, organic matter, and residual) in the marine sediment was also investigated as to evaluate the change in bioavailability of the residual metals. As well as, the apparent rate constants and modeling of metal removal from contaminated sediment were also investigated in the proposed work.

2. Materials and methods

2.1. Sediment sampling

The contaminated marine sediment was collected from Kaohsiung harbor, Taiwan (Fig. 1). The contaminated sediment was further air-dried at room temperature (25°C–35°C) and sieved (<1 mm) to removed stones and large particles, then thoroughly mixed to ensure uniformity. Later, it was stored in a plastic box to analyzed the physicochemical properties and washing experiments.

2.2. Sediment washing experiments

Solutions of di-sodium salt of EDTA (Na_2EDTA; $Na_2C_{10}H_{16}N_2O_8$), EDDS ($C_{10}H_{13}N_2Na_3O_8$), potassium sodium tartrate (PST; $NaKC_4H_4O_6.4H_2O$), maleic acid (MA; $C_4H_4O_4$), and sodium citrate (SC; $C_6H_5O_7Na_3.2H_2O$) were used as washing agents. The washing process was performed with 2 g of dried sediment mixed with 10, 15, or 20 mL of washing solution in a 40-mL plastic bottle, and the mixture was shaken in a horizontal shaker at 200 rpm at room temperature

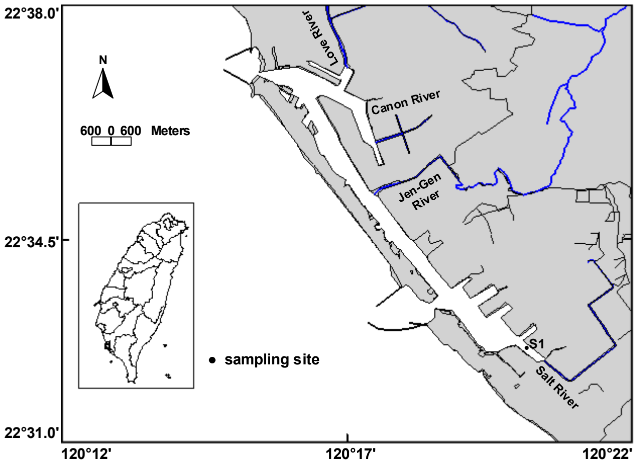

Fig. 1. Map denoting sediment sampling location.

(25°C ± 2°C). Afterward the each contact period, the slurries were centrifuged at 4,500 rpm for 30 min. The separated supernatant filtered through 0.45 μm membrane filters and analyzed for metal content. The solid remaining material was dried in oven at 60°C and thereafter subjected to the total metal digestion (incorporating HNO_3, $HClO_4$, and HF) extraction and sequential extraction procedure [15] to estimate the metal removal efficiency and speciation of residual contaminants. All experiments were carried out in duplicate.

2.3. Sequential extraction tests

A modified Tessier's sequential extraction methodology were applied to determine metals speciation (exchangeable, carbonate, Fe–Mn oxides and hydroxides, organic matter, and residual) and their distribution in washed and non-washed original sediments [16].

The exchangeable fraction (E1) was extracted from 1 g of air-dried remediated and original soils, with 8 mL of 1 M $MgCl_2$ at pH 7 for 1 h. The fraction bound to carbonates (E2) was determined after extraction with 8 mL of 1 M CH_3COONa adjusted to pH 5 with acetic acid for 5 h. The fraction bound to Fe–Mn oxides and hydroxides (E3) was determined after extraction with 20 mL of 0.04 M $NH_2OH{\cdot}HCl$ in 25 vol% acetic acid (pH 2) for 6 h at 96°C ± 3°C. The fraction bound to the sediment organic matter (E4) was determined after extraction with 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 (pH 2) for 2 h at 85°C ± 2°C, followed by 5 mL of 30% H_2O_2 (pH 2) for 3 h at 85°C ± 2°C and then 5 mL of 3.2 M CH_3COONH_4 in 20 vol% HNO_3 diluted to 20 mL at room temperature for 30 min. The residual fraction (E5) was determined after digestion of the residual samples with aqua regia.

2.4. Analysis

The pH of sediment was measured in 1:5 soil to water ratio by using pH meter. The organic matter was analyzed by Walkley–Black titration. Particle size of sediment was detected by laser particle size analyzer. All the heavy metal analyses were performed using an atomic absorption spectrophotometer (AAS). All reagents used in the experiments were of analytical grade. All plastic and glassware were soaked in a 5% HNO_3 solution overnight and rinsed with distilled water before use.

3. Results and discussion

3.1. Characterization of contaminated sediment

The bulk chemistry of contaminated sediment was provided in Table 1. The sediment pH value was measured at 6.95, and the contaminated sediment was composed of 7.2% sand, 83.1% silt, and 9.7% clay. The organic content was 7.7%, and the total Zn and Cu concentration were 1,914 and 599 mg/kg, respectively. Among all metals, the concentration of Cu was over the soil control regulation standard in Taiwan.

3.2. Kinetics of metal extraction

The study of sediment washing kinetics provided useful information on the relationship between metal extraction efficiency and contact time. Therefore, a kinetic study was carried by washing sediment with 0.1 M Na_2EDTA (Fig. 2). In Fig. 2, the heavy metals removal efficiency shows drastic increase in the initial 2 h, which was similar with previous reports [16,17]. And further increase in reaction time from 2 to 48 h shows insignificant removal efficiency, which were also noted by earlier researchers in their study [5,12,18]. For example, Zou et al. [5] observed that the extraction of five metals (As, Cd, Cu, Pb, and Zn) with EDTA was rapid, reaching equilibrium within a contact time of 1.0 h, then further increased the contact time; the removal efficiency reached a plateau and remained almost constant. Abumaizar and Smith [18] also reported a rapid uptake of Cd, Pb, and Zn from contaminated soil by 0.1 M Na_2EDTA, and an optimum soil–chelant contact time of 2 h was considered feasible because of no appreciable amount of metal was extracted beyond this time. Therefore, the optimal extraction time of 2 h was chosen for the following experiments.

Table 1
Characteristics of the sediment sample used in the study

Property	Value
Clay (%)	9.7
Silt (%)	83.1
Sand (%)	7.2
Soil pH	6.95
Organic matter (%)	7.7
Cr (mg/kg)	186
Ni (mg/kg)	65
Cu (mg/kg)	599
Zn (mg/kg)	1,914
Cd (mg/kg)	2
Pb (mg/kg)	106

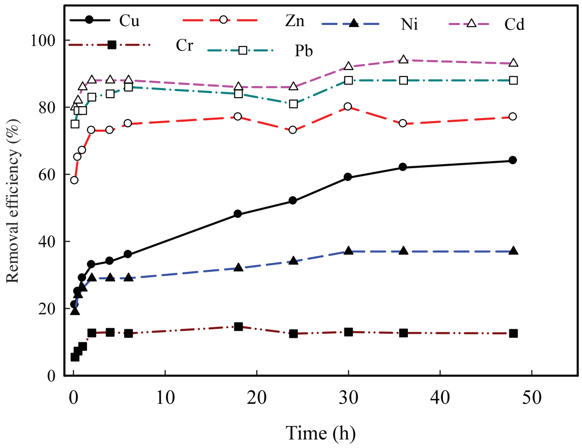

Fig. 2. Effect of washing time on metals removal with 0.1 M Na_2EDTA (liquid/solid ratio = 10; pH_0 = 4.0).

The removal efficiency order was Cd > Pb > Zn > Cu > Ni > Cr. After 2 h contact time, the removal efficiency for Cd, Pb, Zn, Cu, Ni, and Cr was 88%, 83%, 73%, 33%, 29%, and 13%, respectively. Among the heavy metals studied Cd, Pb, and Zn exhibit high removal efficiency (73%–88%) while Ni, Cr, and Cu shows low removal efficiency (13%–33%). The sequential extraction may give the information to explain different extraction efficiency for different heavy metals [16]. Table 2 shows the solid phase speciation of the target metal ions in the contaminated sediment sample. The Cd in contaminated sediment existed mainly in exchangeable and carbonate fraction; the content was approximately 39% and 35%, respectively. The Pb and Zn was mostly bound to Fe–Mn oxides and hydroxides; the content was approximately 91.7% and 92.2%, respectively. According to Polettini et al. [12], the extracted metals by EDTA mainly came from exchangeable, carbonate, and Fe–Mn oxides and hydroxides fraction. Furthermore, results also showed a significant reduction in the metal contents of exchangeable, carbonate, and Fe–Mn oxides and hydroxides fraction (Fig. 3). Hence, as expected, Cd, Pb, and Zn exhibited high removal efficiency.

Conversely, among the investigated metals, Cu, Cr, and Ni exhibited low removal efficiency. The Cu was mostly present in the organic fraction of the sediment (>83% of the total content); the difficulty in extracting copper can be attributed to the strong association between humus organic substances and Cu in sediments [19], which may form insoluble metal complexes [20]. The content of Cr and Ni, existed mainly in the residual fraction, was approximately 40% and 37%, respectively (Table 2). Metals in the residual fraction were persistent and could not be extracted easily, which resulted in low extraction efficiency (Fig. 3). Polettini et al. [12] reported that Ni and Cr were the most difficult to extract from the sediment matrix. Low removal efficiency (11%) for Cr with 0.2 M EDTA was reported. Begum et al. [21] also reported that it was difficult to extract Ni compared with other metals (Cd and Pb) with 0.5 M EDTA under an acidic condition (pH 4), due to strong bounding with the sediment particles [12,21].

3.3. Apparent rate constants and modeling of metal removal

The experimental rate constants were determined and plugged into numerical models to predict the metal removal along with time in the system. The prediction of time-dependent metal removal at controlled operating conditions will be quite useful in removal of heavy metals from contaminated marine sediments using chelating agents for washing process. Polettini et al. [12] studied the remediation of real heavy-metal-contaminated sediment by using four chelating agents. The results showed that the removal of metal by chelating agents may be considered as a simple first-order reaction model. Furthermore, re-adsorption of chelant–metal complexes onto the organic matter fraction of the soil has been shown by different investigators [22,23]. If the forward (metal desorption) and backward (metal sorption) reactions are expressed as $\mathrm{MS} \xrightarrow{k_1} \mathrm{ML}$ and $\mathrm{ML} \xrightarrow{k_2} \mathrm{MS}$, respectively, the rate equation may be written as:

$$-\frac{dC_{\mathrm{MS}}}{dt} = \frac{dC_{\mathrm{ML}}}{dt} = k_1 C_{\mathrm{MS}} - k_2 C_{\mathrm{ML}} \tag{1}$$

where C_{MS} and C_{ML} are the concentrations of metal on sediment and washing solution at time t, respectively, whereas k_1 and k_2 are the apparent rate constants for metal desorption and sorption at sediment surface during washing process, respectively. The k_1 can be obtained from the slope of $\ln[(C_{\mathrm{MS0}} - C_{\mathrm{MSe}})/(C_{\mathrm{MSt}} - C_{\mathrm{MSe}})]$ vs. time plots [24]:

$$\ln[\frac{(C_{\mathrm{MS0}} - C_{\mathrm{MSe}})}{(C_{\mathrm{MSt}} - C_{\mathrm{MSe}})}] = \left(\frac{1}{X_{\mathrm{MSe}}}\right) k_1 t \tag{2}$$

where C_{MS0} and C_{MSe} are the initial and equilibrium concentrations of MS, respectively, and X_{MSe} $(1 - (C_{\mathrm{MSe}}/C_{\mathrm{MS0}}))$ is the fractional removal at equilibrium, while the k_2 can be calculated using the equilibrium constant (K_c):

$$K_c = \frac{C_{\mathrm{MLe}}}{C_{\mathrm{MSe}}} = \frac{k_1}{k_2} \tag{3}$$

where $C_{\mathrm{ML}e}$ is the concentration of metal in washing solution at equilibrium. Incorporating the concentrations of MS and ML at 48 h as the C_{MSe} and C_{MLe}, respectively, the $\ln[(C_{\mathrm{MS0}} - C_{\mathrm{MSe}})/(C_{\mathrm{MS}} - C_{\mathrm{MSe}})]$ vs. time plots for the chelating agent washing cases were linear with $R^2 = 0.94$–0.99 (Fig. 4), verifying the first-order rate dependence of reaction. At 0.1 M $\mathrm{Na_2EDTA}$

Table 2
Total concentrations and solid phase speciation of the toxic metals in the contaminated sediment sample

Fractionation	Cu	Zn	Ni	Cd	Cr	Pb
Total metal concentrations (mg/kg)	599	1,914	65	2	186	106
Solid phase fractions (mg/kg)						
Exchangeable	3.0	18.0	0.4	0.9	0.0	0.0
Bound to carbonate	56.8	750.8	12.1	0.8	12.3	13.2
Bound to Fe–Mn oxides and hydroxides	3.4	592.1	20.1	0.3	78.9	73.1
Bound to organic matter	445.1	58.5	4.6	0.1	17.0	10.6
Residual	24.0	301.7	21.7	0.2	72.8	12.4
Recovery of total metal concentrations from the solid phase fractions (%)	88.9	89.9	90.6	114	97.3	103

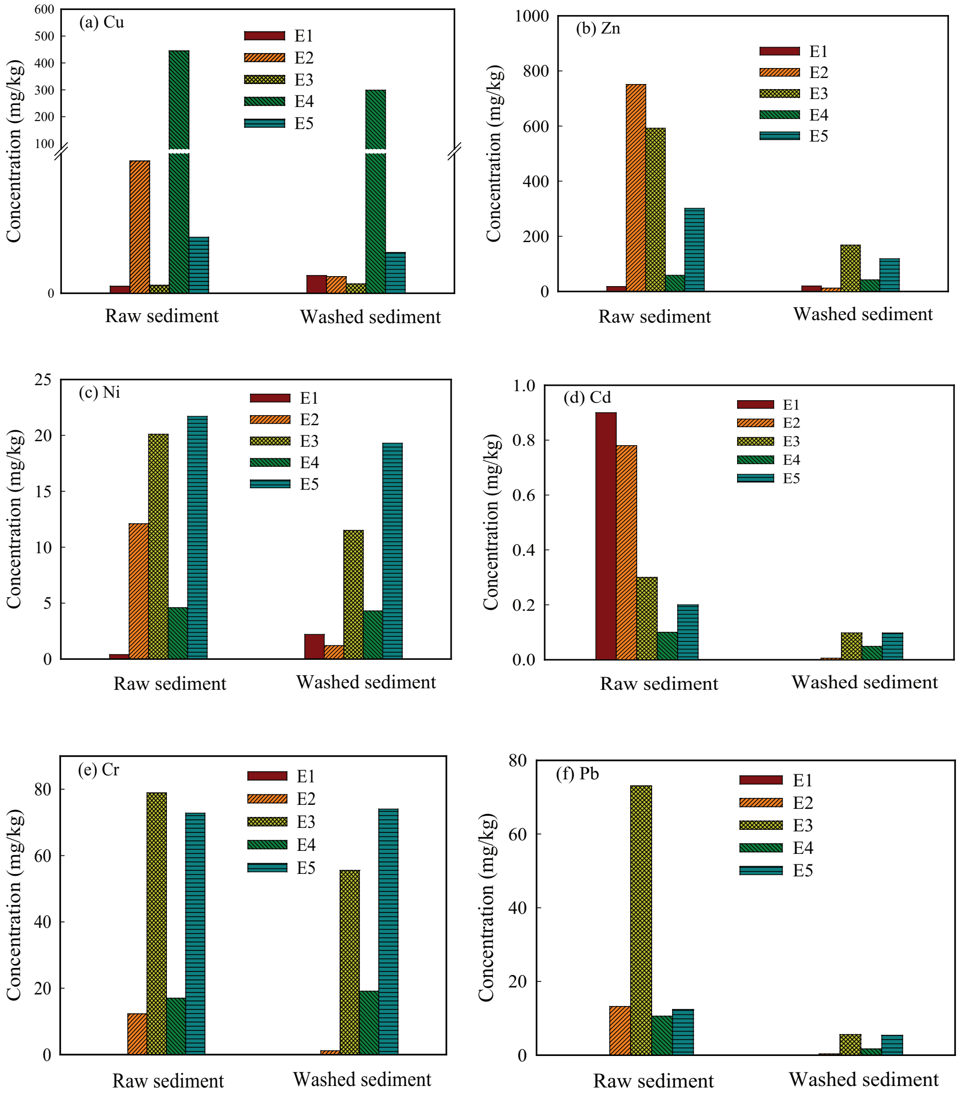

Fig. 3. Comparative concentration of metals in the solid phase of contaminated sediment before and after washing treatment (0.1 M Na_2EDTA; liquid/solid ratio = 15; pH_0 = 4.0; reaction time = 2 h).

(L/S ratio = 10; pH_0 = 4.0), the k_1 values obtained from the plots were 0.0822–0.5598 h^{-1}, corresponding to k_2 values of 0.0282–0.5502 h^{-1} (Table 3). The k_1 was in the order: Pb > Zn > Cd > Ni > Cu > Cr revealing that Pb has the maximum desorption rate constant, and Cr was the most difficult to extract from the sediment matrix. However, if plugging the determined k_1 and k_2 values into the following equation obtained from the integration of Eq. (1):

$$C_{MS} = \frac{C_{MS0}k_2}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) + C_{MS0}e^{-(k_1+k_2)t} \tag{4}$$

The modeled metal removal curves for the 0.1 M Na_2EDTA case matched the experimental data in 4–48 h but the experimental data before 4 h were higher than the modeled curves (Fig. 5). This is because a simple batch reactor, by its nature, operates in an unsteady state, and the MS and ML concentrations are time-dependent.

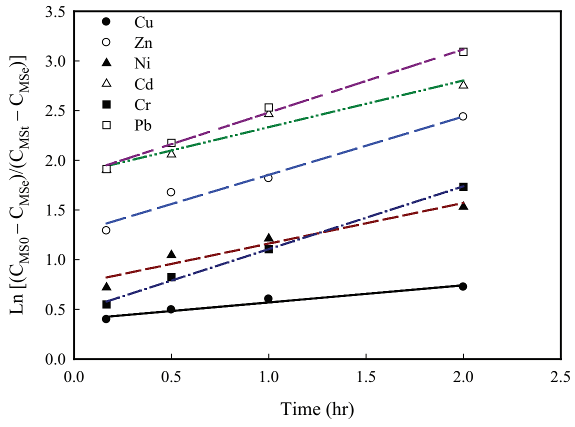

Fig. 4. Plots of $\ln[(C_{MS0} - C_{MSe})/(C_{MSt} - C_{MSe})]$ vs. time (with regression lines) for the metal removal in 0.1 M Na_2EDTA (liquid/solid ratio = 10, pH_0 = 4.0).

Table 3
Kinetic of metal desorption/sorption with 0.1 M Na_2EDTA washing solution

Element	k_1 (h^{-1})	k_2 (h^{-1})	R^2
Cu	0.1105	0.0622	0.96
Zn	0.4695	0.1174	0.97
Ni	0.1514	0.2578	0.94
Cd	0.4416	0.0282	0.95
Cr	0.0822	0.5502	0.99
Pb	0.5598	0.0763	0.99

Note: pH = 4.0, and L/S = 15.

3.4. Influence of liquid/soil ratio

In soil/sediment washing, the L/S ratio plays an important role on metal removal. Fig. 6 shows the effect of L/S ratio on metal extraction efficiency. It exhibits that increasing the liquid/soil ratio had a positive effect on the metals extraction efficiency. The removal percentage increased steadily with increases in L/S ratio from 5 to 10. Further increase in the L/S ratio from 10 to 15 led to only a slight increase in the metal removal efficiency. At the same concentration (0.1 M), increasing the liquid/soil ratio increases the mass of Na_2EDTA. In general, washing solution contains more EDTA ions that will enhance formation of metal–EDTA complexes and result in better removal efficiency. However, as the liquid/soil ratio is

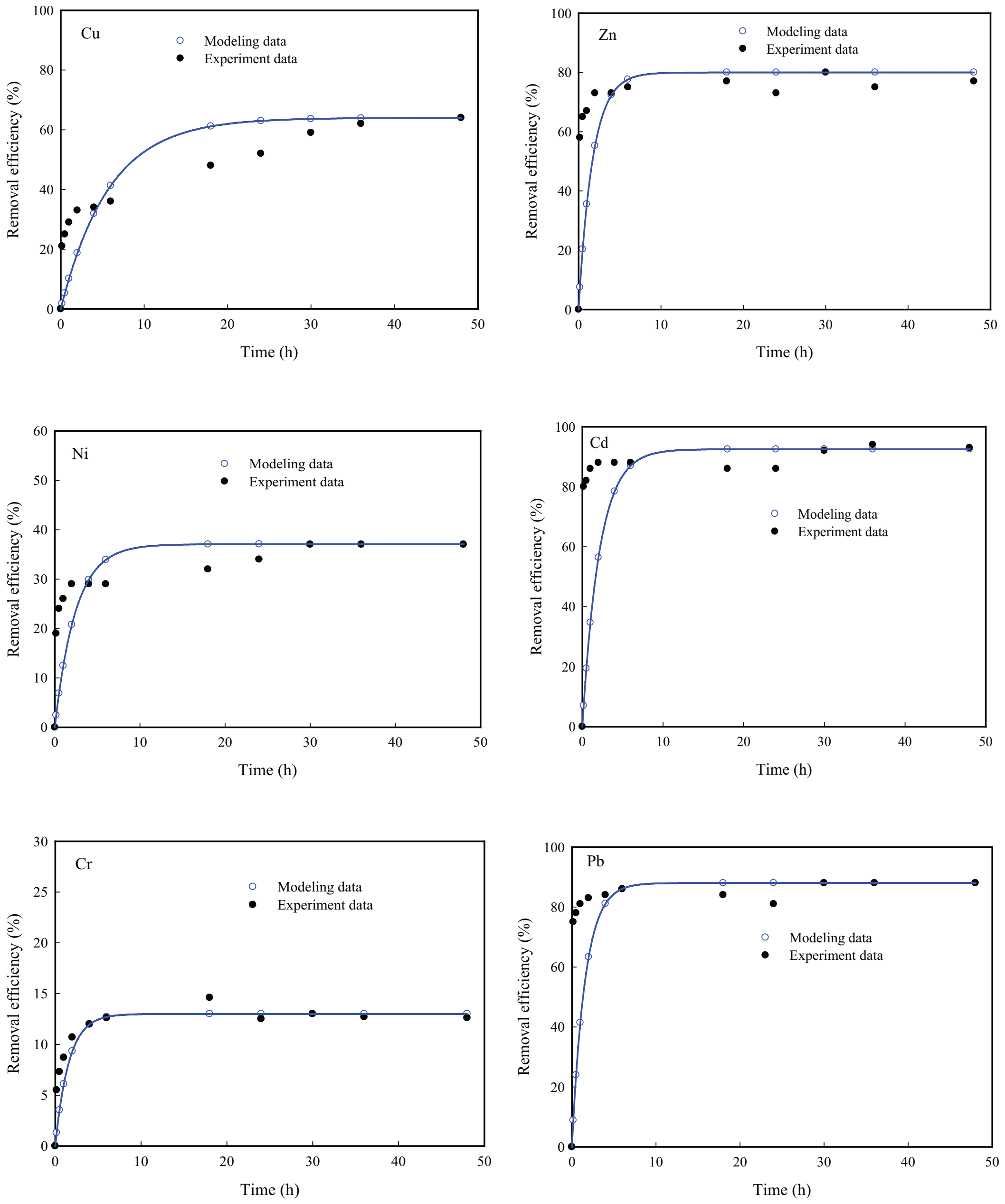

Fig. 5. Metal removal efficiency of modeling and experiment data (0.1 M Na_2EDTA, liquid/solid ratio = 10, and pH = 4.0).

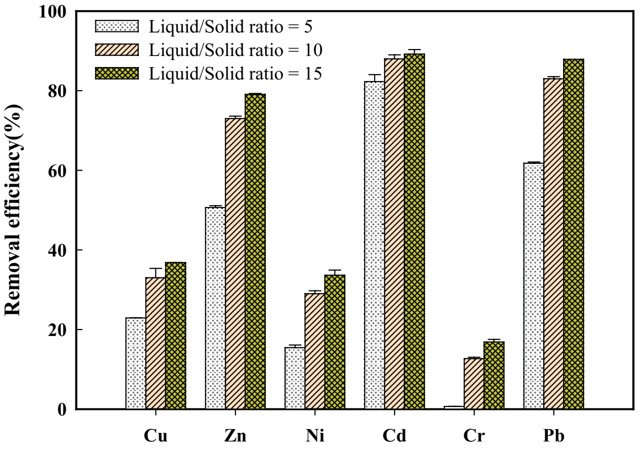

Fig. 6. Removal efficiency (%) of metals from the contaminated sediment as a function of liquid/solid ratio (0.1 M Na_2EDTA; pH_0 = 4.0; reaction time = 2 h).

too large, only a small portion of EDTA ion was effectively reacted with target metals to form metal–EDTA complexes, while the excess EDTA remained in free form in the solution or might form complexes with major cations in the sediment (Ca, Mg, Fe and Al). Hence, although increasing the liquid/soil ratio had a positive effect on the removal efficiency of metals from contaminated sediment, larger liquid/soil ratio may increase leachate volume and operating cost, and reduce treatment capacity. Andrade et al. [25] reported that reducing the liquid/soil ratio would produce smaller amounts of leachate and be easier for scaling up. Therefore, the liquid/soil ratio of 10 was used to carry out the subsequent tests in this study.

3.5. Influence of washing solution concentration

Fig. 7 shows the effect of Na_2EDTA concentration on metal removal efficiency. The removal efficiency of six metals increased with increasing Na_2EDTA concentration from 0.01 to 0.2 M, but the increase was not proportional to the concentration. At low Na_2EDTA concentration (0.01 M), heavy metal removal efficiency was low except Cd, which may be due to low Cd concentration and existed mainly in exchangeable and carbonate fraction. The removal efficiency of Cu, Zn, Ni, Cr, Pb, and Cd was 14.7, 39.9, 5.6, 0.2, 37.3, and 84.0%, respectively, when the L/S ratio was 10 and initial solution pH is 4.0 with 2 h contact time. The removal efficiency of Cu, Zn, Ni, Cr, and Pb was obviously increased as the Na_2EDTA concentration was increased from 0.01 to 0.10 M. However, further increase in Na_2EDTA concentration from 0.1 to 0.2 M leads to only a slight increase in metal extraction. In this study, the L/S ratio was fixed at 10. However, as Na_2EDTA concentration was higher than 0.1 M, the removal efficiency was increased only slightly. The result implied that there was a critical EDTA level at which almost all mobile metals (exchangeable, carbonate, Fe–Mn oxides, and hydroxides fractions) in the sediment were extracted. It is well known that the residual fraction was difficult to be extracted. Hence, further increase in Na_2EDTA concentration only yielded a small increase in the metal release. This phenomenon was in agreed with the findings of some earlier studies [26,27]. Considering the cost of chelating agents and metal removal efficiency, the suitable washing solution concentration was 0.1 M in this study.

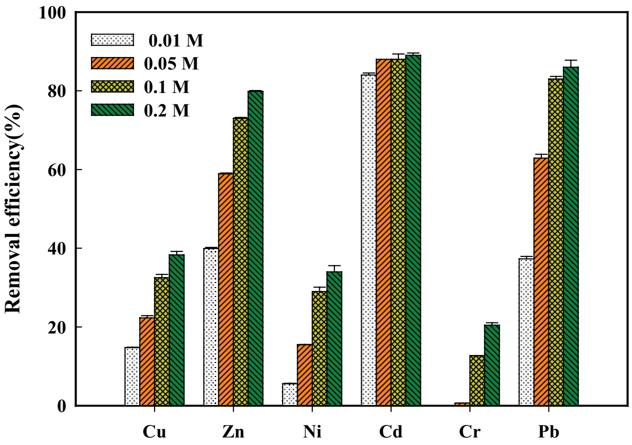

Fig. 7. Removal efficiency (%) of metals from the contaminated sediment as a function of Na_2EDTA concentration (pH_0 = 4.0; liquid/solid ratio = 10; reaction time = 2 h).

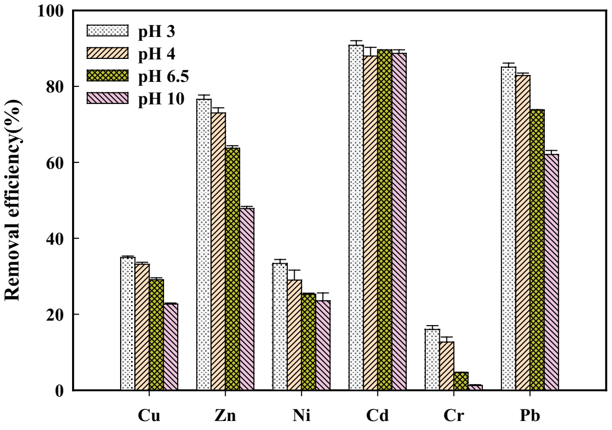

Fig. 8. Removal efficiency (%) of metals from the contaminated sediment as a function of pH (0.1 M Na_2EDTA; liquid/solid ratio = 10; reaction time = 2 h).

3.6. Effect of pH

Many studies showed that the solution pH was an important parameter affecting the metal extraction efficiency of soil and sediment [21,28,29]. Peters [28] indicated that solution pH can influence the soil retention of metals and affect the capability of chelating agents to extract the pollutants from soil. In this study, the solution pH range of 3.0–10.0 was carried out to investigate the removal efficiency of six metals from contaminated sediments. Fig. 8 shows the extraction efficiency of heavy metals from the sediment with Na_2EDTA at different solution pH. As can be seen, the removal efficiency decreased with increase in the solution pH. The highest removal efficiency was observed at pH = 3. The maximum removal efficiency was 34.9%, 76.6%, 33.4%, 90.8%, 16.0%, and 85.1% for Cu, Zn, Ni, Cd, Cr, and Pb, respectively. The similar trend was obtained by earlier studies [5,26,29]. Elliot et al. [26] performed a series of batch experiments to evaluate Pb extractive efficiency from Pb-polluted soil using EDTA. Results indicated that removal efficiency of Pb was generally greatest under acidic conditions and decreased steadily as the pH became more alkaline. Zou et al. [5] investigated the influence of pH on extraction of five metals (As, Cd, Cu, Pb, and Zn) using 0.01 M Na_2EDTA. The highest metals removal efficiency was obtained at pH = 1. In the pH range of 2.0–10.0, the removal efficiency of metals decreased with increase in pH. Peters [28] indicated that hydrogen ions can replaces the adsorbed heavy metals via a cation exchange mechanism, and as the solution pH decreases, the sediment particle surface generally becomes increasingly protonated and acquires a positive charge, thus promoting desorption of metals. Some studies also indicated that at the acidic condition, chelants interact with the metal constituents of the contaminated soil leading to the simultaneous release of retained ions and an exchange of the H^+ with the absorbed metal ions via the protonation of surface functional group on soil solids [30,31].

3.7. Effect of the type of chelating agent

The chelating agent has played a key role in the removal of toxic metals by washing. Hence, in order to compare the heavy metals extraction efficiency of different chelating agents, the extraction of six metals from the contaminated sediment with Na_2EDTA, EDDS, PTS, MA, and SC was conducted simultaneously under the same conditions with L/S ratio of 10 and pH = 4. As shown in Fig. 9, the Na_2EDTA exhibited the highest metal extraction, with 33%, 73%, 29%, 88%, 13%, and 83% for Cu, Zn, Ni, Cd, Cr, and Pb, respectively, followed by EDDS, while much lower removal efficiency was observed for PTS, MA, and SC. In general, Na_2EDTA was a more efficient extracting agent than other agents, because EDTA can form very stable complexes with metals [21,32]. This implies that Na_2EDTA acts as an effective washing agent for a variety of toxic metals. In EDDS solution, five metals (Zn, Ni, Cd, Cr, and Pb) extraction efficiency was lower than Na_2EDTA, but Cu extraction efficiency was similar to that of Na_2EDTA. This phenomenon can attributed to the similar stability constant of EDTA–Cu and EDDS–Cu (log$K$ =18.4 and 18.78) [33]. Although Na_2EDTA presented better metal removal efficiency than EDDS, EDDS is readily biodegradable and less toxic than Na_2EDTA to plants and microorganisms, which would keep the fertility and function of the raw soils [34,35]. Hence, recently, EDDS has been proposed as a safe and environment-friendly washing agent and gradually replace Na_2EDTA in soil/sediment washing.

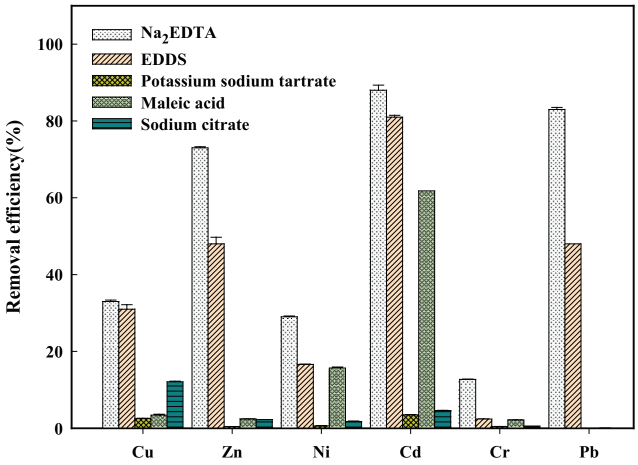

Fig. 9. Removal efficiency (%) of metals from the contaminated sediment as a function of chelants (chelant concentration = 0.1 M; pH_0 = 4.0; liquid/solid ratio = 10; reaction time = 2 h).

3.8. Heavy metals removal under the optimum operating conditions

In this section, the optimization of different operating parameters were considered based on the entire experiment as well as noticed soil control standard of Taiwan. The optimized conditions was L/S = 15, pH = 4.0, and washing time = 24 h with 0.2 M Na_2EDTA. These results revealed that the metal removal efficiency of the evaluated six metals were 62%, 78%, 26%, 100%, 21%, and 86% for Cu, Zn, Ni, Cd, Cr, and Pb, respectively. The residual concentration were 228, 421, 47, 0, 147, and 15 mg/kg for Cu, Zn, Ni, Cd, Cr, and Pb, respectively. The observed results from the experiment were complied with the standard parameters of soil control standard of Taiwan. Hence, the chelating agent washing method shows good potential to be used for the removal of heavy metals from contaminated marine sediments.

4. Conclusions

This study investigated the extractive-decontamination of the toxic metals (Cu, Zn, Ni, Cd, Cr, and Pb) from contaminated sediment using chelating agents. Several operating parameters including washing time, L/S ratio, concentration of washing agents, solution pH, and chelating agents were studied as to evaluate the metal removal efficiency. The results indicated that the heavy metal removal efficiency increased rapidly in the first 2 h; extending the reaction time from 2 to 48 h did not affect the removal efficiency significantly. The removal efficiency order was: Cd > Pb > Zn > Cu > Ni > Cr by using 0.1 M Na_2EDTA and 2 h of contact time. The chelant extraction process was a first-order reaction. The k_1 values were 0.0822–0.5598 h^{-1}, and the order was Pb > Zn > Cd > Ni > Cu > Cr revealing that Pb has the maximum desorption rate constant and Cr was the most difficult to extract from the sediment matrix. The extraction efficiency of toxic metals decreased with increasing pH in the range of 3.0–10.0. The removal of metals depended mainly on the speciation of the metal forms. The extracted metals mainly originated from the fractions of exchangeable, carbonate, and Fe–Mn oxides and hydroxides. Among the evaluated washing agents, Na_2EDTA was the most effective extracting agent. Moreover, the metal extraction efficiency increased with increasing L/S ratio and concentration of washing chemicals. The results will be useful to preliminarily evaluate the removal of heavy metals from contaminated sediments by chelating agents in sediment washing.

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