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Ex situ remediation technology for heavy metals in contaminated sediment

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ABSTRACT

The importance of metal mobile fractions rather than total contents in environmental matrices is increasing in the risk assessment evaluation of contaminated sites. Ethylenediaminetetraacetic acid (EDTA), aimed at the measurements of metals mobile fractions, was used to extract the metals from the contaminated dredged sediments based on chemical extraction technology. This work examined the influences of contact time and EDTA concentration on the extraction efficiency for metals from polluted dredged sediment. In addition, the sequential extraction method was carried out to show the change in distribution pattern of metals in sediment before and after EDTA extraction. The dredged sediment from Helwan area (H) was mainly polluted by Pb (685 mg/kg), and the dredged sediment from Talkha area (T) was significantly polluted by Cd (236 mg/kg), Cu (229 mg/kg), and Zn (2,888 mg/kg). For sediment (H), the maximum lead removal of 72.54% was achieved using EDTA under the optimum conditions. While For sediment (T), the maximum cadmium removal of 53.58% was achieved under the same conditions. Finally, EDTA can be used as washing solution for contaminated sediment as well as single-step extraction to identify non-residual metal content (the anthropogenic fraction) and to evaluate the potential bioavailability of metal.

Keywords: Chemical extraction technology; Ethylenediaminetetraacetic acid; Heavy metals; Sequential extraction; Sediments

1. Introduction

Nowadays, heavy metals originating from anthropogenic activities are frequently detected in sediments and water columns of river/lake, which cause a considerable number of the worlds' rivers/lakes severely contaminated. Therefore, heavy metals pollution had gradually become a major concern worldwide. Since, sediments constitute the principal sink for trace metals in aquatic systems, where heavy metals are usually distributed as follows: water-soluble species, colloids, suspended forms, and sedimentary phases [1–10].

Heavy metals usually are enriched in sediment by organisms or some other compounds. In some conditions, more than 99% of heavy metals entering into river can be stored in river sediments and can be bound to various compartments in different ways: occluded in amorphous materials; adsorbed on clay surfaces or iron/manganese oxyhydroxides; presented in lattice of secondary minerals such as carbonates, sulfates, or oxides; complexed with organic matter or lattice of primary minerals such as silicates [11–13]. Since each form has different remobilization potentials, and

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then affects its respective bioavailability and toxicity, so the measurement of total metals may not be able to provide exact information about the characteristics of pollution [14].

Thus, heavy metals cannot fix in sediment forever. Any variation of environmental conditions can lead to the release of the mobile fractions for these metals into the sediment water phase. From the sediment water phase, the metals can become available to organisms living in the water system. Therefore, heavy metals content in sediment has greater importance due to the fact that sediment often acts as both carriers and potential sources for metals in aquatic environment. Heavy metals usually possess significant toxicity to aquatic organisms, and then affect human health through food chain [15,16]. Therefore, sediment analyses are useful tools in investigating the history of effluent contamination, the processes involved in the removal of pollutants from the water column, and the stability and future pollution potential of the sediments [8,16,17].

In recent years, the importance of trace metal mobile fractions rather than total contents in environmental matrices is increasing in the risk assessment evaluation of contaminated sites. Therefore, investigating the transformation and distributions mechanisms of heavy metals in sediment becomes necessary [18–21].

The factors which affect the removal efficiency of metals from sediment include not only the contact time and EDTA concentrations, but also the content and fractional distribution of heavy metals in the sediment. Where the total concentration of heavy metals provides little indication of environmental impact, because they do not provide detailed information on potential environmental mobility or bioavailability. Therefore, the sequential extractions could give the information needed to explain different extraction efficiencies for different heavy metals [10,22,23]. Among various sequential extraction techniques, Tessier sequential extraction [12], which modified by Elsokkary and Müller [24], was used to determine the fractional distribution of heavy metals in sediment.

Chemical extraction is an essential process for the abatement of heavy metals contaminated sites to reduce the environmental and health risks. This means chemical extraction involves the dissolution of contaminants in extractant, firstly, and then separation of the soluble contaminants from the solid phase to a liquid matrix, usually implemented as an *ex situ* process [25].

Sediment washing is a relatively simple and useful *ex situ* remediation technology, which involves through adding washing water, heavy metals can be transferred from the dredged sediment to wash solution. To enhance the performance of sediment washing, various additives can be employed, such as acid washing (e.g. H_2SO_4 and HNO_3), chelating agents, or surfactants (e.g. rhamnolipid). These additives can assist in the solubilization, dispersal, and desorption of metal from dredged sediments. On the other hand, various chelating reagents, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), etc., can form strong soluble complexes with most divalent and trivalent metal contaminants resulting, thus, in the recovery of these contaminants in the aqueous solution [10,26].

Chelating agents used in sediment remediation usually possess higher chelating affinity for metal. They can combine with aqueous metal to form chelate complex, which subsequently lower the metal concentration in water. Through the adsorption/release balance between sediment and water, the toxic and bioavailability metals adsorbed on sediment will be transferred to chelate complex gradually, and finally removed with solution. This method is especially suitable for treating the dredged sediment contaminated concurrently by organic pollutants and heavy metal [27]. However, due to possible adverse health and environmental effects, EDTA is currently under scrutiny. Therefore, the optimization of chelating agents should be the research direction in future [26].

This technology is most appropriate for the weaker bound metals in the form of exchangeable, hydroxides, carbonates, and reducible oxides fraction. Residual fractions, the most difficult ones to remove, are not affected during the washing process [28–31]. Therefore, till date, EDTA, a very effective chelating agent, is used widely for heavy metal decontamination [32–35].

In this work, the chemical distribution of heavy metals with a sequential extraction procedure in contaminated sediment was determined before and after treating the sediment by an EDTA solution. The main objective of using EDTA was as a fast indicator to measure the availability of heavy metals as well as the extraction of metal contaminants through the formation of soluble metal chelates.

2. Material and method

2.1. Chemicals and reagents

Acetic acid (99.5 w/v %), hydroxylamine hydrochloride (99.0 w/w %), ammonium acetate (98.0 w/w %), hydrogen peroxide (30% w/v %), hydrochloric acid (37% w/v %), and nitric acid (99.5% w/v %) were used to prepare extracting solutions for sequential chemical fractionation. EDTA (99.0 w/w %) was used to prepare solutions meant for sediment washing.

All reagents were of Fluka and Riedel-de Haën patent supplied by Sigma–Aldrich.

2.2. Apparatus

Normal laboratory glassware (borosilicate), polyethylene vessels, Knick digital pH meter model "646" (Germany), Mechanical reciprocating shaker "Julapo-SW-20C," and a digitally operated high speed centrifuge (Model TGL-6G) were used. Atomic absorption spectrometer Varian SpectrAA (220) with graphite furnace accessory and equipped with deuterium arc background corrector was used for metal assay.

2.3. Sediment collection and analysis

The contaminated sediment samples were collected from Helwan area [in front of Iron and Steel Factory (H)] and from Talkha drain [in front of industrial discharge of Talkha fertilizer (T)]. Sediment samples were collected using an Eckman sampling device.

Samples were dried in air, ground, and sieved to 0.2 mm using stainless steel sieve to ensure homogenous sample. All experiments were performed in triplicate.

All reagents used for this study were of analytical reagent grade. Freshly prepared daily diluted solutions are prepared using deionized water and all glassware and plastic containers were washed with 15% nitric acid solution and rinsed thoroughly with deionized water.

2.4. Experimental procedure for metals remediation in sediment

Extraction of metals by EDTA was carried out as follows:

One gram of samples was diluted to approximately 10 ml with deionized water.

Using different volumes of 0.1 M stock standard solution of disodium salt of EDTA based on the calculated stoichiometric requirement for Cd, Cr, Cu, pb, Ni, and Zn in the initial sample, considering that one mole of metal requires 1 mol of EDTA at pH ranging from 5.33 to 7.2.

EDTA extraction was performed using different contact time and different EDTA concentrations.

The solid residue was separated by centrifuging for 10 min at 2,000 rpm, and then filtered through Whatman No. 4 filter paper.

The supernatant for metals concentrations was analyzed using Atomic absorption spectrometer according to Standard Methods [36].

The percentage of metals removal was calculated using the following equation [37,38]:

$$\text{Metals removal } (\%) = \left(V_f F \; / \; D \, I\right) \times 100$$

where F and I are the concentrations of metal in supernatant (in mg/L) and sediment (mg/kg), respectively, V_f is the volume of supernatant, and D is the dry mass of the sediment.

2.5. Sequential extraction procedure

The sequential extraction procedure was carried out according to Tessier et al. [12] that modified by Elsokkary and Müller [24] for sediment samples before and after EDTA extraction [39,40].

Subsequently, the solid residues after EDTA extraction were stored for a sequential extraction procedure to determine the transformations in the distribution and the chemical forms of metals affecting their mobility and availability.

The total concentrations of heavy metals in each fraction step were determined after digestion according to Standard Methods [36].

Generally, all the results obtained for metal fractionation were calculated depending on the total amounts of metals determined in each sequential extraction scheme. The sum of the five sequential chemical extractions agreed within 10% with the total metal concentrations. All the results were expressed as the mean ± standard deviation of triplicate samples in mg/kg of dry solid sample.

3. Results and discussion

Indeed, sediments show a high capacity to accumulate and integrate on time the low concentrations of trace elements in water and therefore, they allow the determination of metals even when the levels in water are extremely low and undetectable with current methods of analysis. Particularly, from sample site Helwan area [in front of Iron and Steel Factory (H)] and from Talkha drain [in front of industrial discharge of Talkha fertilizer (T)]. The pH of the samples was found to be 6.8 ± 0.1 for H and 9.0 ± 0.1 for T. While, the high pH of (T) sample may be due to the fertilizer industries [41].

Heavy metal contents in contaminated sediments of collected samples were studied. Since, total metal concentrations for sample (H) were 3 ± 0.13, 90 ± 8.6,45 ± 5.7, 685 ± 22.7, 60 ± 10, and 262 ± 54 mg/kg for Cd, Cu, Cr, Pb, Ni, and Zn, respectively, and also for sample (T) were 236 ± 18, 229 ± 13.5, 36 ± 1.33, 24 ± 1.26, 28 ± 2.8, and 2,888 ± 262 mg/kg for Cd, Cu, Cr, Pb, Ni, and Zn, respectively.

These data showed that sediment of sample (H) was enriched with high concentration of Pb and sample (T) with high concentration of Cd, Cu, and Zn. These means the presence of pollution source in these areas coming from Iron and Steel Factory and Talkha fertilizers factory [42].

3.1. Remediation of heavy metals in sediments at different contact time and different EDTA concentrations

3.1.1. Different contact time

The dredged contaminated sediment samples of (H) and (T) were dosed with EDTA based on the stoichiometric requirement for concentration of investigated metals. EDTA extraction was performed using 1*X*, for different contact time of 2, 4, and 6 h, where *X* represents theoretically the required dose of the metal contents in sediment sample. After, liquid/solid separation procedures were executed.

Figs. 1 and 2 revealed that the metals remobilization percentages at different mixing time were slightly increased by increasing the length of mixing time from 2 to 6 h.

For sample (H), the results showed that by increasing the length of mixing time from 2 to 6 h, the metals remobilization percentages were slightly increased by 15.5, 3.33, 1.29, 3.89, 2.37, and 7.28% for Cd, Cu, Cr, Pb, Ni, and Zn, respectively. On the other hand, for sample (T), the metals remobilization percentages were slightly increased by 2.77, 0.98, 0.94, 2.15, 0.35, and 4.39% for Cd, Cu, Cr, Pb, Ni, and Zn, respectively.

From these results, the remobilization of metals was almost steady through 2–6 h intervals. Therefore, the less time that is required for achieving maximum metals solubilization is 4 h [38].

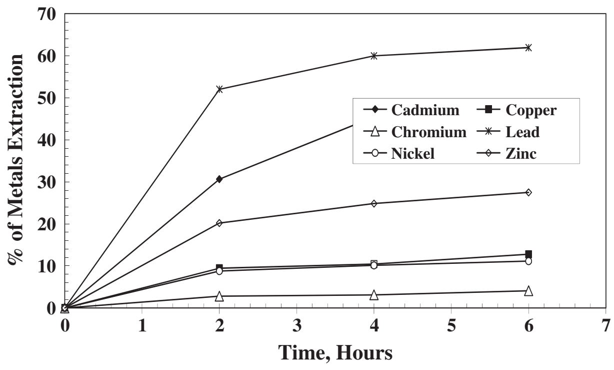

Fig. 1. Effect of extraction time on metals remobilization from Helwan sediment (H) using EDTA at 1*X* stoichiometric dose.

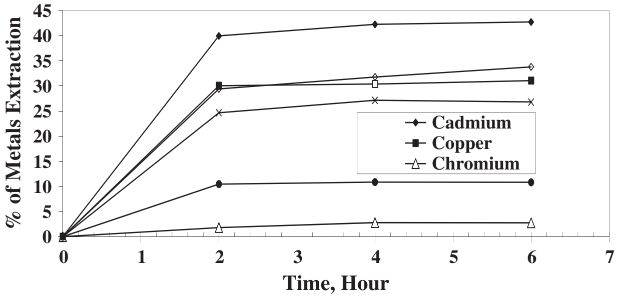

Fig. 2. Effect of extraction time on metals remobilization from Talkha sediment (T) using EDTA at 1*X* stoichiometric dose.

3.1.2. Different EDTA concentrations

To study the effect of EDTA concentrations on metals remobilization, the dredged sediment samples were dosed by different concentrations of EDTA based on the stoichiometric requirement for concentration of heavy metals under investigation. EDTA treatments were performed using 0.5*X*, 1*X*, 2*X*, and 4*X* stoichiometric doses for 4 h contact time.

Figs 3 and 4 showed the percentages of metals remobilization at different stoichiometric EDTA amounts. The results, which revealed low solubilization of metal percentages, were achieved by gradual increasing of the EDTA stoichiometric dose. Such low metals solubilization percentages reflect that EDTA is capable of extracting metals from non-residual fractions as mentioned by several authors [43,44].

For sample (H), when EDTA stoichiometric doses were increased from 0.5*X* to 4*X* for mixing time of 4 h, all percentages of metals solubilization were slightly increased by 23.24, 2.85, 1.45, 4.93,12.77, and 11.44% for Cd, Cu, Cr, Pb, Ni, and Zn, respectively, and also for sample (T), all percentages of metal solubilization were slightly increased by 27.9, 10.74, 8.43, 20.59, 13.26, and 23.39% for Cd, Cu, Cr, Pb, Ni, and Zn, respectively.

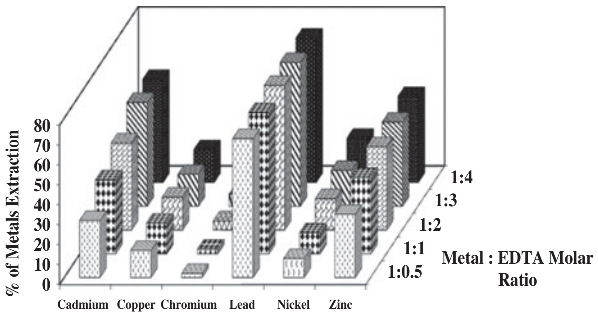

Fig. 3. Effect of different metals to EDTA molar ratio on metals extraction from Helwan sediment (H).

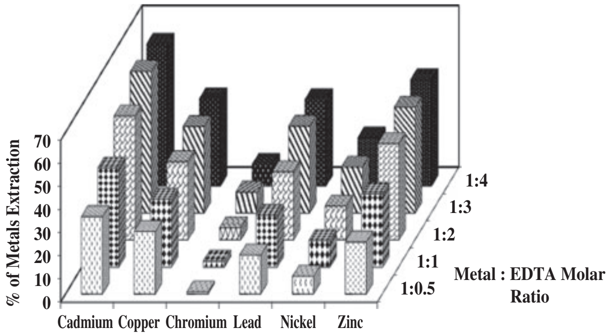

Fig. 4. Effect of different metals to EDTA molar ratio on metals extraction from Talkha sediment (T).

Such trend is confirmed by several authors [45–47] who reported that when EDTA dosages are increased from 0.5*X* to 4*X*, solubilization of all metals is slightly increased. On the other hand, increasing of EDTA concentrations above 2*X* does not cause much further extraction of metals from the sediment, pH change during extraction is nearly steady state, and a similar extraction pattern is observed for the examined metals.

3.2. *Relationship between extraction efficiency and distribution of metals in sediment*

The distribution of metal fractions in dredged sediments before and after EDTA extraction (2*X* Stoichiometric dose for 4 h) was examined using Tessier et al. [12] that modified by Elsokkary and Müller [24] method.

Before EDTA extraction, the data in Table 1 showed that most fractions of the examined metals were found in the potentially available form, especially Pb and Zn. Where the most concentrations of Pb

Table 1
The distribution pattern of heavy metals in sediment sample of Helwan (H) before and after EDTA extraction

		Before extraction		After extraction		EDTA extraction	
Metals	Fractions	mg/Kg	%	mg/Kg	%	mg/Kg	%
Cadmium	Exchangeable	n.d.	0.0	n.d.	0.0	1.24 ± 0.046	43.66
	Carbonate	0.52 ± 0.078	18.31	n.d.	0.0		
	Fe/Mn oxide	0.46 ± 0.028	16.20	0.21 ± 0.015	7.39		
	Organic and sulfide	0.71 ± 0.05	25.00	0.16 ± 0.027	5.63		
	Residual	1.16 ± 0.055	40.85	1.24 ± 0.046	43.66		
Copper	Exchangeable	1.42 ± 0.23	1.42	4.11 ± 0.7	4.11	16.42 ± 0.39	16.44
	Carbonate	4.62 ± 0.33	4.62	2.46 ± 0.34	2.46		
	Fe/Mn oxide	3.18 ± 0.28	3.18	1.98 ± 0.21	1.98		
	Organic and sulfide	61.57 ± 7.52	61.63	36.57 ± 3.3	36.61		
	Residual	29.11 ± 3.3	29.14	38.35 ± 5.85	38.39		
Chromium	Exchangeable	n.d.	0.0	1.27 ± 0.13	2.92	1.97 ± 0.32	4.53
	Carbonate	0.19 ± 0.014	0.44	0.43 ± 0.025	0.99		
	Fe/Mn oxide	0.09 ± 0.014	0.21	0.51 ± 0.07	1.17		
	Organic and sulfide	3.58 ± 0.138	8.23	3.23 ± 0.32	7.43		
	Residual	39.64 ± 4.66	91.13	36.09 ± 8	82.97		
Lead	Exchangeable	128.1 ± 10.7	17.74	30.66 ± 4	4.25	523.76 ± 10.6	72.54
	Carbonate	123.2 ± 13.2	17.06	3.7 ± 0.5	0.51		
	Fe/Mn-oxide	177.95 ± 16	24.65	3.94 ± 0.6	0.55		
	Organic and sulfide	79 ± 15	10.94	4.03 ± 0.5	0.56		
	Residual	213.7 ± 12.6	29.60	155 ± 3.7	21.59		
Nickel	Exchangeable	1.75 ± 0.63	2.87	4.5 ± 1.1	7.38	9.57 ± 0.23	15.69
	Carbonate	2.75 ± 0.16	4.51	1.02 ± 0.07	1.67		
	Fe/Mn oxide	5.26 ± 0.28	8.62	3.071 ± 0.095	5.03		
	Organic and sulfide	14.81 ± 0.49	24.28	8.19 ± 0.6	13.43		
	Residual	36.43 ± 5.38	59.72	34.64 ± 4.4	56.79		
Zinc	Exchangeable	16.73 ± 1.52	6.11	14.92 ± 1	5.45	114.56 ± 9	41.81
	Carbonate	11.37 ± 1.3	4.15	5.33 ± 0.6	1.95		
	Fe/Mn oxide	39.54 ± 1.3	14.43	29.31 ± 0.9	10.70		
	Organic and sulfide	125.5 ± 1.5	45.82	39.3 ± 3.6	14.34		
	Residual	80.8 ± 10.6	29.23	70.6 ± 4.1	25.77		

and Zn (more than 70%) are mainly distributed in the mobile forms. This potential availability of these metals indicates that metals have contamination risk in this area (Helwan). But after EDTA extraction, the results (Table 1) showed that metals concentrations in non-residual forms were decreased from 1.69 to 0.37 mg/kgm for Cd, from 70.79 to 45.12 mg/kg m for Cu, from 508.25 to 42.33 mg/kg m for Pb, from 24.57 to 16.78 mg/kg m for Ni, and from 193.14 to 88.86 mg/kg m for Zn. These were equivalent to approximate extraction yields of 43.66% Cd, 16.44% Cu, 72.54% Pb, 15.69% Ni, and 41.81% Zn. These mean that EDTA washing of the contaminated sediment enhanced metal extraction from mobile and available fractions where the available forms of metals are the sum of first four fractions and non-available form is residual fraction [27,44,48]. However, there is no change in the chemical forms of Cr after EDTA extraction, because most concentration of Cr was mainly present in the residual fraction.

Also, the data in Table 2 showed that most fractions of the examined metals were found in the potentially available form especially Cd, Cu, and Zn. This potential availability of these metals indicates that metals have contamination risk in this area (Talkha). But after EDTA extraction, the results (Table 1) showed that metals concentrations in non-residual forms were decreased from 212.06 to 93.04 mg/kg m for Cd, from 82.52 to 30.9 mg/kg for Cu, from 7.93 to 1.59 mg/kg for Pb, from 12.04 to 7.89 mg/kg for Ni, and from 2,002.69 to 862.31 mg/kg for Zn. These mean that EDTA washing of the contaminated sediment enhanced metal extraction from mobile and available fractions. These data are confirmed by several authors [27,43,44,48] who mentioned that EDTA extracts weakly held heavy metals from a variety of phases and effectively dissolves exchangeable, carbonate, Mn/Fe oxide, and organic and sulfide fractions.

Table 2
The distribution pattern of heavy metals in sediment sample of Talkha (T) before and after EDTA extraction

Metals	Fractions	Before extraction mg/Kg	%	After extraction mg/Kg	%	EDTA extraction mg/Kg	%
Cadmium	Exchangeable	28.21 ± 2	12.71	9.05 ± 0.44	4.08	118.95 ± 3.3	53.58
	Carbonate	103.7 ± 3	46.71	42.62 ± 4	19.20		
	Fe/Mn oxide	54.32 ± 5	24.47	40 ± 1.3	18.02		
	Organic and sulfide	25.83 ± 2.5	11.64	1.37 ± 0.1	0.62		
	Residual	9.93 ± 0 .4	4.47	10 ± 0.12	4.50		
Copper	Exchangeable	9.35 ± 1.09	4.58	5.47 ± 0.4	2.68	69.06 ± 1.2	33.85
	Carbonate	13.55 ± 1.28	6.64	5.23 ± 0.5	2.56		
	Fe/Mn oxide	9.49 ± 0.25	4.65	7.47 ± 0.4	3.66		
	Organic and sulfide	50.13 ± 3	24.57	12.73 ± 0.5	6.24		
	Residual	121.51 ± 15.5	59.55	104.05 ± 3.3	51.00		
Chromium	Exchangeable	n.d.	0.0	n.d.	0.0	1.7 ± 0.04	5.33
	Carbonate	0.41 ± 0.05	1.29	0.50 ± 0.04	1.57		
	Fe/Mn oxide	12.52 ± 1.4	39.25	12 ± 1.31	37.62		
	Organic and sulfide	7.7 ± 0.7	24.14	7 ± 0.14	21.94		
	Residual	11.27 ± 0.045	35.33	10.71 ± 0.6	33.57		
Lead	Exchangeable	0.88 ± 0.15	3.70	n.d.	0.0	7.03 ± 0.25	29.54
	Carbonate	0.88 ± 0.15	3.70	n.d.	0.0		
	Fe/Mn oxide	5.38 ± 0.15	22.61	1.41 ± 0.14	5.92		
	Organic and sulfide	0.79 ± 0.10	3.32	0.18 ± 0.025	0.76		
	Residua	15.87 ± 1.74	67.26	15 ± 1.29	63.03		
Nickel	Exchangeable	n.d.	0.0	n.d.	0.0	4.09 ± 0.08	14.66
	Carbonate	0.64 ± 0.125	2.29	n.d.	0.0		
	Fe/Mn oxide	1.74 ± 0.16	6.24	5.13 ± 0.14	18.39		
	Organic and sulfide	9.66 ± 0.15	34.62	2.76 ± 0.14	9.89		
	Residual	15.86 ± 1.74	56.85	15.92 ± 2.08	57.06		
Zinc	Exchangeable	11.27 ± 1.67	0.41	94.86 ± 8.9	3.47	1,140.51 ± 24.4	41.71
	Carbonate	802.79 ± 30	29.36	209.52 ± 22	7.66		
	Fe/Mn oxide	651.7 ± 33	23.84	524.9± 13.8	19.20		
	Organic and sulfide	536.93 ± 36.8	19.64	33.03 ± 2.6	1.21		
	Residual	731.44 ± 45	26.75	731.3 ± 55	26.75		

4. Conclusion

Sequential extraction provides information on different fractions of metals in sediment to understand their mobility and availability. The availability is related to solubility of metals and then, the availability decrease in order: exchangeable > carbonate > Fe/Mn-oxide > organic > residual. Most metals discharged into the river would store in sediment and become available to living organisms for a long time. Therefore, remediation of contaminated sediment was done by *ex situ* remediation technology. The data showed that the percentages of metals remobilized at 2*X* stoichiometric dose through 4 h mixing time from Helwan (H) sediment sample did not exceed ~34%. However, remobilization of Pb reached 72.54% at the same conditions. On the another hand, the percentages of metals remobilized at 2*X* EDTA stoichiometric dose through 4 h mixing time from Talkha (T) sediment sample did not exceed ~36.39%. However, remobilization of Cd reached 53.58% at the same condition. EDTA can be used as faster indicators to assess the mobility and the availability of heavy metals on various types of sediments. Also, EDTA can be used as washing solution for contaminated sediment to reduce the risk assessment of metals on ecosystem.

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