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Extraction of heavy metals from water-stable soil aggregates using EDTA

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Abstract

Surface soil samples (0-15cm) were collected from a lead/zinc tailing site in Nanjing, China, and separated into four size fractions of water-stable aggregates. Metal contents in the bulk soil were 7479 ± 370 mg·kg^{-1} for Zn, 4189 ± 82 mg·kg^{-1} for Pb, 58.0 ± 0.4 mg·kg^{-1} for Cd and 544 ± 22mg·kg^{-1} for Cu, respectively. Contents of Zn, Pb, Cd and Cu in 0.02-0.002 mm fractions were lower than them in other size fractions. Extraction of heavy metals from each size fractions of aggregates as function of extraction time and pH value of EDTA was performed. Also, the effects of the extraction process on metal fractions in the samples were investigated. The molar ratio of EDTA/total heavy metals (Zn+Pb+Cu+Cd) was adopted as 1 for all extraction experiments. The extraction kinetics of the four metals in each fraction could be well fitted with Elovich formula. Pb had the highest extraction efficiency at time 24h, 82.7% (2-0.2 mm), 73.6% (0.2-0.02 mm), 75.0% (0.02-0.002), and 72.2% (<0.002 mm), among the four tested metals. The highest desorption rate for four metals in different size fractions was Zn in <0.002 mm fraction and Pb, Cd, and Cu in 2-0.2 mm fraction. Extraction of the tested metals negatively depended on the original pH value of extraction solution and the relationship could be described linearly. Exchangeable/acid soluble Zn, exchangeable/acid soluble and reducible fraction of Pb, Cd and Cu were influenced greatly by the extraction using EDTA.

1. Introduction

Soil contamination with heavy metals is one of the major environmental problems in the world,

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considering their almost indefinite persistence in the environment and the danger they pose [1-2]. Mining/smelting is one of the main sources of heavy metal pollution in the environment, and the tailings generally contain higher concentration of heavy metals. Therefore, many researches have been done on different metal mining tails and surroundings on the behavior of the heavy metals, and how to remove or immobilize them to relieve the risks [3-6].

Soil aggregates are the basic units of soil constructer, formed by the cohesion and adhesion of soil mechanical composition of different organic matter, mineral and other materials. Many important reactions occur on the interface of soil aggregates, e.g. the deposition and release of heavy metals from/into soil solution. Soil aggregates of different sizes separated from contaminated soil are distinct in the heavy metals contents [7-9]. Furthermore, sorption/desorption of heavy metals by them is also distinct due to their different physicochemical properties [10]. Chelating agents can improve soluble metal contents in soil solution and have been widely used in leaching/washing remediation techniques for contaminated soils [11-13]. However, most of the researches were carried out for bulk soil. Only a few concerns the release of heavy metals from soil aggregates of contaminated soil with chelating agents.

The objective of the present study is to investigate the effects of EDTA, a typical chelating agent, on release of heavy metals (Zn, Pb, Cd and Cu) from water-stable soil aggregates collected at a lead/zinc tailing site. Extraction kinetics and extraction with EDTA at different pH value were performed. Fractionation of Zn and Pb in samples after extraction with EDTA was also analyzed to help the understating of the reaction between EDTA and heavy metals in soil aggregates.

2. Materials and methods

2.1. Soil preparation

Surface soil sample (0-15cm) (S0) was collected from the lead/zinc tailing site at Qixiashan in Nanjing, P.R. China. The sampling site was bare, no plantation. The soil sample was air-dried, and sieved through a 2mm nylon mesh. Soil aggregates were separated using methods described by Balabane (2004) [14], slightly modified. The soil was immersed by distilled water for 10min, and than was shaken laterally for 4h for dispersion. After dispersed, the sample was wet-sieved to 0.02mm and mass of <0.02mm were separated through centrifugation/sedimentation. The size fractions were 2-0.2mm (S1), 0.2-0.02mm (S2), 0.02-0.002mm (S3), <0.002mm (S4). The sample pH was measured using a pH meter (PHs-2F, Relax, China) with 0.01 M $CaCl_2$ at a 1:5 ratio (w/v). Soil organic matter content, free iron/aluminum oxide (Fe_d, Al_d) were measured by the method described by Lu (2000) [15]. Soil samples were digested with HNO_3+HClO_4+HF before determine of the heavy metal contents [15]. Concentrations of Zn, Cu and Pb in the solution of the digested samples were determined by ICP-OES (Optima 5300DV, PerkinElmer, USA) and Cd by ICP-MS (Elan 9000, Perkin–Elmer, USA). The contents of Si and some mineral elements (expressed as the contents of the corresponding oxides) in the aggregates were analyzed with X-ray fluorescence instrument (ARL-9800, ARL, Switzerland). XRD spectrum of the aggregates was also analyzed with X-ray Diffraction instrument (X'TRA, ARL, Switzerland). The results are shown in Table 1 and Fig .1.

2.2. Extraction experiment

Extraction of heavy metals with different extraction time. The EDTA / total heavy metals (Zn+ Pb+ Cu+ Cd) molar ratio was set as 1 for all extraction experiments. 5mL EDTA (Na_2EDTA in 0.01mol $L^{-1}KNO_3$) solution was added into 7 mL PE tube containing 0.1 g soil sample, followed by shaking on a rotary shaker. Extraction time (shaking time) was set as 3min, 5min, 10min, 20min, 40min, 1h, 2h, 4h, 8h,

and 24h. All the treatments were triplicate. Then the extraction tubes were centrifuged at 4000r min^{-1} for 15min. The supernate was filtered through 0.45 μm membrane and then kept in PE tube at 4℃ in refrigerator. Concentrations of heavy metals in the solution were determined by ICP-OES (Zn, Cu and Pb) or ICP-MS (Cd).

Extraction of heavy metals with EDTA solution of different pH value. The pH values of the EDTA extraction solutions were adjusted using NaOH solution and HNO$_3$ solution and set as 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, and 9.00. The extraction systems were shaken for 24h. Other treatments were the same as described above.

Metal fractionations in soil size fractions after EDTA extraction. 25mL EDTA (in 0.01mol L^{-1} KNO$_3$, pH7.0) solution was added into 50mL PE tube contained 0.5g soil or soil aggregate sample. The control treatments were set without EDTA. The extraction was the same as described above. After washed with distilled water, the residual soil samples were analyzed with modified BCR sequential extraction procedure described by Rauret et al (2000) to determine the heavy metals' fractionations [16]. All the treatments were triplicate.

Table 1. Properties of the test soil sample.

Bulk soil (S0) (mean ± standard deviation, n=3)							
pH	OM($mg·g^{-1}$)	Al$_d$($g·kg^{-1}$)	Fe$_d$($g·kg^{-1}$)	Zn($mg·kg^{-1}$)	Pb($mg·kg^{-1}$)	Cd($mg·kg^{-1}$)	Cu($mg·kg^{-1}$)
7.22±0.01	52.0±1.3	2.97±0.06	22.7±2.0	7479±370	4189±82	58.0±0.4	544±22

Soil aggregates (mean ± standard deviation, n=3)							
	Mass(%)	OM($mg·g^{-1}$)	Al$_d$($g·kg^{-1}$)	Fe$_d$($g·kg^{-1}$)	Zn($mg·kg^{-1}$)	Pb($mg·kg^{-1}$)	Cd($mg·kg^{-1}$)	Cu($mg·kg^{-1}$)
S1	31.4±3.5	59.8±0.6	2.49±0.13	15.8±2.2	7720±164	4995±206	64.0±1.5	589±25
S2	32.6±2.8	36.7±0.0	1.81±0.04	11.5±0.8	7890±129	3483±49	62.5±0.2	422±11
S3	30.8±3.8	15.1±0.3	2.38±0.13	16.3±3.3	5451±58	2914±75	32.7±0.0	372±2
S4	5.21±2.74	17.0±0.3	5.78±0.84	35.5±6.7	7185±59	3350±50	37.5±0.0	582±6

	SiO$_2$(%)	Al$_2$O$_3$(%)	Fe$_2$O$_3$(%)	K$_2$O(%)	SO$_3$(%)	CaO(%)	MgO(%)	Na$_2$O(%)	P$_2$O$_5$(%)
S1	53.0	15.0	6.59	1.86	2.31	1.68	0.859	0.589	0.263
S2	63.2	12.7	5.77	1.78	2.01	1.32	0.648	0.820	0.273
S3	61.3	16.9	5.95	2.33	0.880	0.920	0.949	0.665	0.245
S4	42.9	22.3	9.23	2.91	1.40	1.34	1.35	0.100	0.159

3. Results and discussion

3.1. Desorption of Zn, Pb, Cd and Cu at different time

Fig. 2 shows the extraction of Zn, Pb, Cd and Cu with EDTA at different time. Extractable contents of metals with EDTA from the soil fractions follow the order of S4 > S1 ≈ S0 > S3 > S2 for Zn, S1 > S0 > S2 ≈ S4 > S3 for Pb, S1 > S4 ≈ S0 > S2 > S3 for Cd, and S1 > S0 > S4 > S2 > S3 for Cu, respectively. About 51.5% (S1), 33.5% (S2), 55.9% (S3) and 66.3% (S4) of Zn were extracted at time 24h. Pb had the highest extraction efficiency at time 24h, 82.7% (S1), 73.6% (S2), 75.0% (S3), and 72.2% (S4), among the four tested metals. For Cu, the extraction efficiency from S1 was much higher than from the aggregates of other size. For Cd, the extraction efficiency from S4 was the highest, while the lowest from S2.

The kinetic dependence of extraction of the four metals could be well described by Elovich formula (Table 2). Heavy metals may exist in soils as absorbed ions, simplex minerals of carbonates, hydroxide,
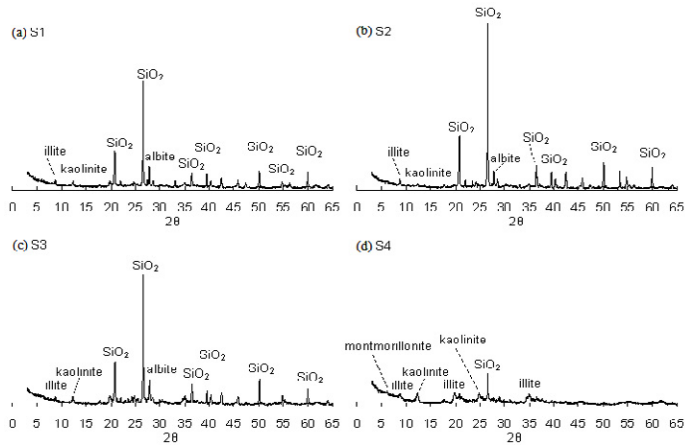
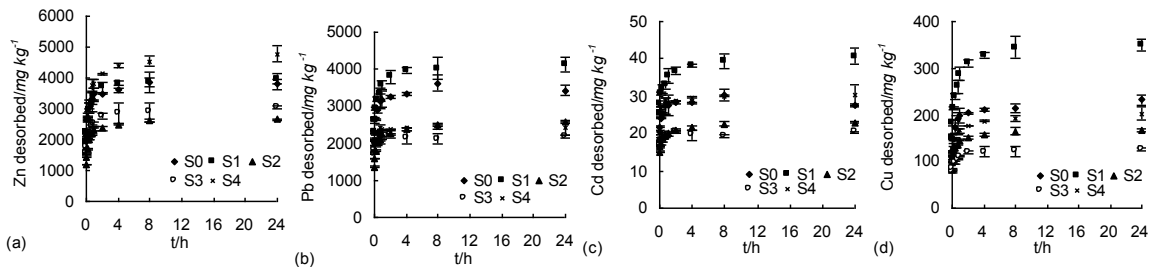Fig. 1. XRD spectrum of the aggregates separated .

Fig. 2. Contents of heavy metals extracted with different extraction time.

Table 2. Kinetic dependence of the desorption of the metals described by Elovich formula   (S=A+ Blnt).

	S0		S1		S2		S3		S4	
	R^2	B	R^2	B	R^2	B	R^2	B	R^2	B
Zn	0.880[**]	307±40	0.931[**]	346±33	0.913[**]	239±26	0.953[**]	247±19	0.951[**]	463±37
Pb	0.859[**]	238±34	0.944[**]	304±26	0.934[**]	191±18	0.794[*]	71.0±12.8	0.768[*]	56.3±11.0
Cd	0.747[*]	1.35±0.28	0.964[**]	2.48±0.17	0.968[**]	1.29±0.08	0.758[*]	0.529±0.106	0.951[**]	0.851±0.068
Cu	0.906[**]	19.6±2.6	0.956[**]	33.5±2.5	0.925[**]	13.7±1.4	0.938[**]	7.84±0.71	0.974[**]	15.1±0.9

S: amount of the metals desorbed at time t ($mg\ kg^{-1}$); t: time (*min*)
   [*]: $p<0.01$; [**]: $p<0.001$

and sulfide and so on, or are combined in the matrix of other minerals and organics [17-18]. Therefore, desorption of the metals from the contaminated soil is controlled by different processes: diffusion of the ions in the solid particulates or on the solid surface, reactions of the minerals and the extractor. Elovich formula is an empirical equation, useful in describing reactions composed of a series of complex processes, especially reactions occurring on the solid/liquor interface of soil/water and sediment/water. In current study, though specific complex forms of the tested metals in the samples were unknown, it was obvious that the tested metals appeared in the samples with various forms of different mobility (Fig. 4). So desorption of the heavy metals from both the bulk soil and the soil aggregates could all fit the Elovich formula well. Value of constant B implied the reaction rate – bigger B, higher reaction rate [19-20]. The

highest desorption rate appeared in the extraction of S4 for Zn and S1 for Pb, Cd, and Cu, and the lowest desorption rate appeared in extraction of S2/S3 for Zn, S4/ S3 for Pb, and S3 for Cd and Cu.

3.2. Extraction of heavy metals with EDTA solution of different pH value

Fig. 3 shows the extraction of Zn, Pb, Cd and Cu with EDTA solution of different pH. There were significant decreases of Zn and Cu contents extracted when pH of EDTA solution changes from 3 to 4 for aggregates of all sizes investigated. When pH value of EDTA solution increased from 5 to 9, the contents of Zn and Cu extracted decreased gradually for S2, S3 and S4, and Pb the same. There were no significant differences ($P>0.05$) between the contents of Zn or Cu extracted at pH 4 and pH5 from S2, S3 or S4. The contents of Cd extracted varied slightly when pH of EDTA solution exchanged from 3 to 9 for S2, S3 or S4. The four metals extracted from S1 decreased significantly when pH of EDTA solution exchanged from 3 to 5. Then Cd or Pb extracted from S1 increased at pH6, while Zn or Cu extracted from S1 at pH6 were close to their contents extracted at pH 5. From pH 6 to pH 9, contents of the four metals extracted from S1 decreased gradually. Generally, desorption of the heavy metals will decrease when pH value of the extractor goes up, as many metal compound has lower solubility at higher pH. Consequently, the extraction amount of the four target metals decreased when pH of EDTA solution increased, although EDTA may have higher the extraction ability at higher pH. The extracted contents of the metals and pH value of EDTA solution were linearly correlated. However, it may be more suitable to describe the relationship between Cd or Pb amount extracted and EDTA pH value with different equations at pH3 to pH5 and pH 6 to pH9 for S1 (Table 3).
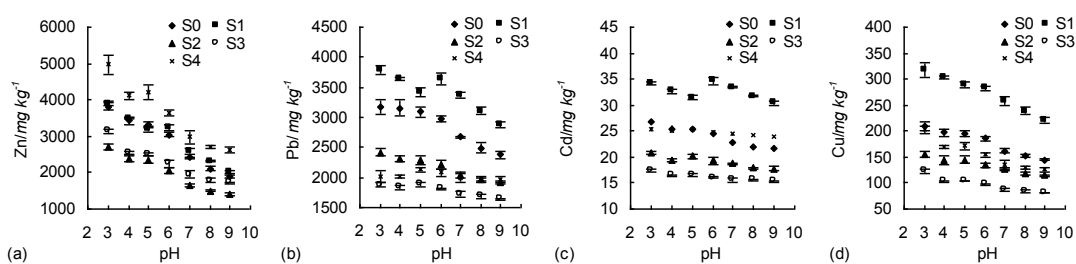

Fig. 3. Content of Zn, Pb, Cd and Cu extracted with EDTA solution of different pH.

Table 3. Regression using linear equation(x – pH; y –amount of heavy metals extracted, *mgkg⁻¹*).

	S1 pH3-9		S1 pH3-5		S1 pH6-9	
Zn	$y = -308x + 4808$	$R^2 = 0.966$	$y = -346x + 4913$	$R^2 = 0.993$	$y = -394x + 5489$	$R^2 = 0.951$
Pb	$y = -136x + 4218$	$R^2 = 0.836$	$y = -186x + 4353$	$R^2 = 0.986$	$y = -256x + 5165$	$R^2 = 0.999$
Cd	$y = -0.380x + 34.9$	$R^2 = 0.295$	$y = -1.32x + 38.0$	$R^2 = 0.998$	$y = -1.42x + 43.2$	$R^2 = 0.996$
Cu	$y = -16.0x + 369$	$R^2 = 0.983$	$y = -14.5x + 361$	$R^2 = 1.00$	$y = -20.3x + 402$	$R^2 = 0.993$
	S2 pH3-9		S3 pH3-9		S4 pH3-9	
Zn	$y = -228x + 3374$	$R^2 = 0.973$	$y = -226x + 3622$	$R^2 = 0.940$	$y = -395x + 5979$	$R^2 = 0.943$
Pb	$y = -87.8x + 2695$	$R^2 = 0.967$	$y = -41.6x + 2027$	$R^2 = 0.878$	$y = -14.9x + 2116$	$R^2 = 0.281$
Cd	$y = -0.489x + 22.1$	$R^2 = 0.876$	$y = -0.316x + 18.0$	$R^2 = 0.909$	$y = -0.234x + 26.2$	$R^2 = 0.899$
Cu	$y = -6.89x + 176$	$R^2 = 0.973$	$y = -6.263x + 135$	$R^2 = 0.909$	$y = -12.4x + 230$	$R^2 = 0.930$

3.3. Effects of EDTA extraction on the fractionation of the tested metals

Extraction with EDTA resulted in the significant reduction of exchangeable/acid soluble Zn, exchangeable/acid soluble and reducible fraction of Pb, Cd and Cu (Fig. 4). It has been reported that exchangeable/acid soluble fraction and reducible fraction are the main fractions that affected by chelating agents during column extraction and batch experiment [21-23]. In present study, most of the extracted Zn or Cd by EDTA was from exchangeable/acid soluble fraction, while most of the extracted Pb was from reducible fraction. Both exchangeable/acid soluble fraction and reducible fraction contributed significantly to the amount of EDTA extracted Cu. According to the modified BCR sequential extraction procedure, metals liberated in step 1 (0.11M acetic acid) (B1) consisted of exchangeable ions and carbonates, and reducible fraction (B2) comprised hydroxide or oxide related to Fe/Mn oxides [18, 24]. Of course, exchangeable ions can be desorbed by chelating agents. Solubility of the carbonates will greatly increase at the presence of chelating agents [25]. Therefore, exchangeable/acid soluble fraction is more easily extracted by EDTA. Metal oxide can also react with chelating agents, resulting in the release of the associated metals [11]. Compared with B1 and B2 fraction, it is rather difficult for B3 fraction (associated with the sulfide and the organics) and the residual fraction (combined in the matrix of the crystal) to release at the presence of chelating agents, considering their combined phase.
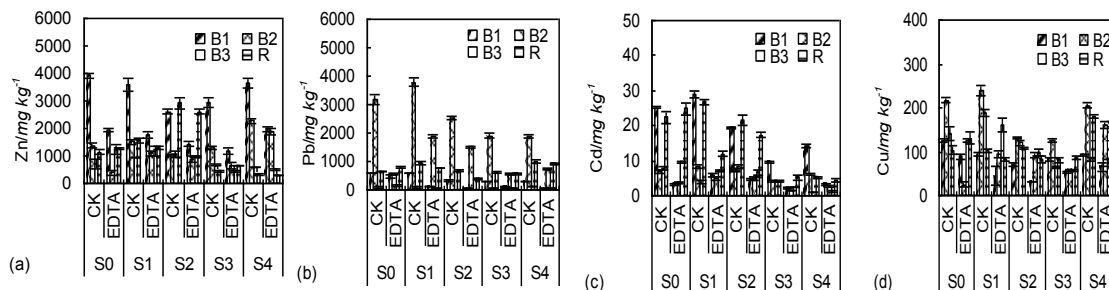

Fig. 4. Fractions of Zn, Pb, Cd and Cu in soil samples analyzed with BCR sequncial extraction procedure after extraction with EDTA (B1 – exchangeable/acid soluble fraction, B2 – reducible fraction, B3 – oxidizible fraction, R – residual fraction).

4. Conclusions

Desorption of heavy metals from soil aggregates of a lead/zinc tailing soil with EDTA was carried out. Extraction of heavy metals with different extraction time shows that extractable content of heavy metals was the highest in S2 for Zn or S3 for Pb, Cd and Cu, while lowest extraction efficiency was found in S2 for Zn, Pb and Cd or S3 and S4 for Cu, considering the total amount of the concerned metals in the aggregates. The extraction kinetics of the four metals could be well fitted with Elovich formula. The highest desorption rate appeared in the extraction of S4 for Zn and S1 for Pb, Cd, and Cu, and the lowest appeared in extraction of S2 and S3 for Zn, S4 and S3 for Pb, and S3 for Cu. The extraction of the tested metals strongly depended on the original pH value of EDTA extraction solution. Extractable metal contents decreased with pH value. Exchangeable/acid soluble fraction and reducible fraction of four soil metals were mainly affected by EDTA extraction.

Acknowledgements

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