Speciation Analysis and Removal of Heavy Metals Zn, Cu, Cd from Sludge by Organic Acid

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ABSTRACT: A chemical extraction procedure for removing extractable heavy metals Zn, Cu, Cd using organic acid as extractant has been applied to wastewater sediments collected from wastewater treatment plant. The Tessier's five-stage sequential extraction procedure for extractable heavy metals determination is applied to sludge samples. The results show that the extractable content of tested heavy metals exhibits a positive correlation with increasing acid concentration, reaction temperature and time. After the extraction process, citric acid is more efficient in removing Zn, oxalic acid exhibits higher extractability in removing Cu but inefficient in Zn and Cd. Zn removed by citric acid is mainly in stable form, resulting in a relative increase of its unstable and exchangeable form in sludge. Though the removal rate of Cu and Cd are lower, their exchangeable form has still increased after the action of tested organic acid.

The analysis of heavy metals is of paramount important to assess soil pollution problems associate with sludge coming from wastewater treatment plants. Untreated sludge enters to environment will bring secondary pollution and pose a serious threat for ecological environment. However, the determi-nation of total concentration of heavy metals does not give an accurate estimation of potential environmental impact. It is crucial that heavy metals are removed or transferred to other active speciation with less biological toxicity[1]. For this reason, chemically polarity method has become of growing importance in repairing sludge polluted by heavy metals. Among chemical extractant, organic acid has been widely studied[2-4].

According to Tessier's work, heavy metals are extracted into exchangeable form, carbonates, iron/manganese oxides, substances/sulfide and residuals. Exchangeable form, carbonates, iron/ manganese oxides are unstable state. Substances/ sulfides and residuals form are stable state. The environmental effects of above chemical forms are as follows: exchangeable form is more sensitive to environmental changes, which is easy to migrate, transfer and be absorbed by plants. Carbonates form with more sensitivity to pH value may co-precipice with the increase of pH, and is easy to re-release to environment. When pH value of soil decreases, iron/manganese oxides, substances and sulfides are relatively stable, but can be released and absorbed by biology. The difference lies in iron/manganese oxides show higher biological effectiveness in reducing condition, but substances and sulfides exhibit more activities under oxidizing condition. The metal in residue state is stable, and is uneasy to release or be absorbed by plants under normal condition[5].

In the present work, Extraction process is conducted with organic acid to investigate the rules of speciation and transformation of Zn, Cu and Cd in sludge. The environmental behavior and biological toxicity of tested sludge are studied indicating the suitability of sludge samples for agricultural use in relation to current international legislation.

EXPERIMENT

Apparatus and chemical reagents

Microwave digestion instrument(MDS-2003F, Sineo Microwave Chemistry Technology limited company, Shanghai, China), Atomic absorption spectrometry (AA-6300C, Shimadzu Corporation, Japan), pHS-3C digital ionalizer (Shanghai fine victory scientific instrument limited company, China).

Chemicals are of analytical grade. Elements of the standard solution are prepared according to the standard method proposed by the national standard material research center. Experimental water is

for its ultra pure water. Experiment using glass instruments are soaked in 4% HNO_3 for 24h and rinsed with ultrapure water.

Pretreatment of sludge samples and Tessier's experiments

Sludge samples collected from wastewater treatment plant of Yan'an city, Shaanxi province, China are firstly dewatered and dried in 105˚C for 24h. After grinding and homogenizing, the sludge of 100 mesh fraction is used for the test. The Tessier's five-stage sequential extraction procedure is used (Table1)[6] in anglicizing the concentration of heavy metals before and after extraction procedure. The extract and digestion solutions are analyzed by AAS.

Table 1 Tessier's sequential extraction procedure

Sediment form	Extraction conditions
Exchangeable form	1mol/L $MgCl_2$(30mL), 25˚C 1h
Carbonates	1mol/L NaAc-HAc(30mL pH 5.0), 25˚C 8 h
Iron/manganese oxides	0.04mol/L NH_4Cl in 25% HAc, 20mL, 96˚C 6h
Substances/ sulfide	0.02mol/L HNO_3(6mL)+30%H_2O_2 (10mL), pH 2.0, 85˚C 2h
	3.2mol/L NH_4Ac diluted with 20% HNO_3, 10mL, 25˚C 0.5h
Residuals	Digestion: HNO_3 8mL+HF 4mL+ H_2O_2 3mL

* Centrifugal solution at 4000 rpm for 30 min after each step.

Extraction of heavy metal from sludge

The extraction experiment is performed using following procedure: 0.5g sludge is mixed with 50mL water, citric acid and oxalic acid range from 0.1 to 1.0mol/L and acetic acid between 9% and 36%, respectively. pH is adjusted to 6.8 to keep the original soil acidity. Then the mixture is placed in an oscillator under test temperature and time.

DISSCUSSION

Heavy metal concentration and form in sludge

Table 2 shows the total content of heavy metals, which are lower than maximum permitted levels for agricultural use in relation to current international legislation. The concentrations of heavy metal in percent(%) determined in each extraction step are illustrated in Figure1, and the regulations of three heavy metals in sludge are concluded as follows.

Table 2 Concentration of heavy metal in sludge (mg/kg)

Heavy metal	Concentration			Average concentration	RSD/ %
Cu	103.5	109.1	107.4	106.7	2.12
Zn	91.2	94.3	92.6	92.6	1.06
Cd	20.6	20.6	20.5	20.5	0.86

Acid soluble form (exchangeable and carbonates form)

Cu in acid soluble form (exist only in exchangeable form) is 23.7%. Cd mainly exists in exchangeable (66.5%) and carbonates form(15.01%), which indicates Cd in the sludge probably occurs in acid soluble form.

Iron/manganese oxides

About 42% Zn in sludge exists in reducible form. For Cu and Cd, the concentrations in percent are 11.25% and 6.12%, respectively.

Substances and sulfide

Cu and Zn are relative high in the forth extraction procedure (42.9% and 17.9%). This indicates that the above heavy metals exist in oxidize complexes. As reported before, extractable Cu is dominantly associate with the oxidize phase, where it is likely to exist as organically metal species[7]. Cd find at the fourth stage is probably in metal sulfides and bound to organic substances, which indicating its existent in oxides and bound to organic matter[8].

Residual form

Cu and Zn is about 15.1% and 21.2% in the fifth extraction step and Cd extracted from this procedure is 5.1%, which indicates Cd rarely exists in insoluble form and is easy to migrate to the environment. The relatively high proportion of Cu and Zn in residual form and the generally low levels of extractable metals indicate that the sediment is relatively unpolluted[7].

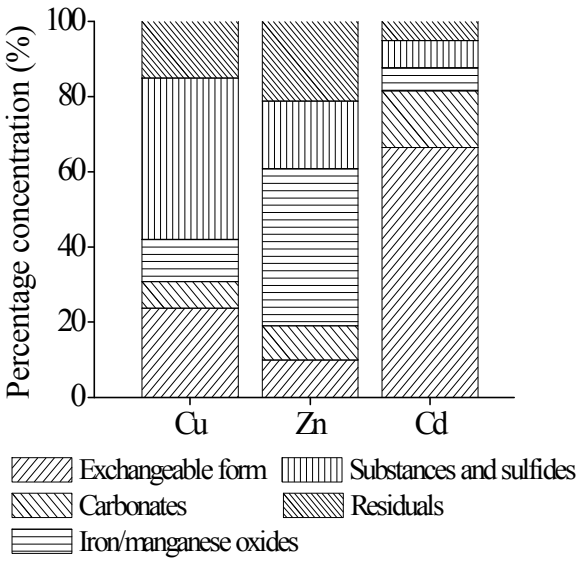

Figure 1. Heavy metals percentage concentration in sludge

Effect of organic acid concentration

In order to investigate the transfer characteristics of heavy metals with organic acid concentration, citric acid and oxalic acid concentration are chosen as 0.1, 0.3, 0.5, 0.7 and 1.0mol/L, acetic acid ranges from 9% to 36% under the temperature of 25˚C for 24h(Figure2). Owning to the complexation and adsorption of heavy metals in water and sludge, water soluble content of heavy metals are lower than organic acid extractable form, which are 0.22, 0.48 and 0.12mg/kg for Cu, Zn and Cd.

Compare with water, organic acid solution with lower pH shows weaker adsorption complexing capability, resulting in the incensement of heavy metal in sludge[9]. Therefore, heavy metals in organic acid exhibit higher activity in the migration and transformation process. Additionally, extractable concentration increases with citric acid and oxalic acid value up to 0.7mol/L follow by a decrease. Zn increases from 20.36 to 60.56mg/kg when citric acid concentration is increase. On the contrary, oxalic acid shows poor extraction effects towards heavy metal. With the increasing of organic acid changes of extraction efficiency is unobvious, indicating that the efficiency of organic acid on heavy metal extraction depends on ion[9].

In the experiment, the maximum removal rates on Cd are 8.1%, 8.6% and 5.6% correspond to citric acid, oxalic acid and acetic acid. Compared with Huang' work(91.5%)[10], great difference is possible because of the differ of Cd concentration in sludge samples, Cd in Huang' group(4.68×10^4mg/kg) is far greater than the present paper(20.53mg/kg). The removal rate of Cd in Huang' group[9] is 9.5% and Cd(16.51mg/kg) is similar to our result. Such phenomenon indicates that the migration and transformation of heavy metals in sludge correlation with sludge properties, extraction agent and the physicochemical properties of extractant. The poor extraction effect of Cu owns to its non ion existing form. The increase of Cd concentration in sludge treated by oxalic acid is in spite of poor effect of organic acid on Cd.

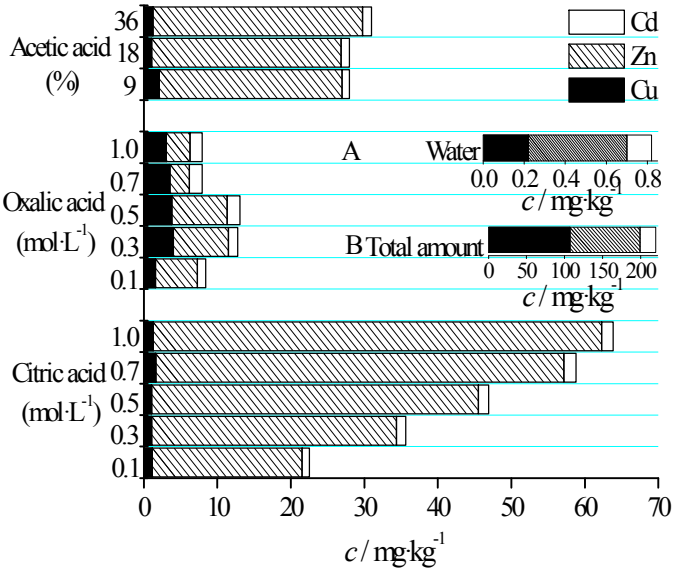

Figure 2. Removal of heavy metals affected by organic acids with different concentration

Effect of time and temperature on extracted concentration

As shown in the experiment, extractable content of tested heavy metals exhibit a positive correlation with action time and temperature, which indicate heavy metals in aqueous phase are influenced by adsorption. Phenomena of chemical and physical adsorption coexist in the extraction system. During the extraction process, physical adsorption plays a major role first then chemical adsorption enhance with the intensity of extraction time and temperature. Eventually, it shows an increase of heavy metals related to the transformation of metal ions into the solution together with high molecular colloidal solid compound.

Water soluble Cd is undetected in 15˚C-35˚C and low in 45˚C. Significant increase of Cd content in organic acids indicates the effect of H^+ on migration and transformation of Cd.

Effect of extraction on speciation transformation of heavy metals

Figure 3 shows the effect of citric acid and oxalic acid on the morphology of Zn. The content of stable and unstable Zn in untreated sludge is basically equivalent(Figure3, CK), which account for 49.31% and 50.69%, respectively. When treated by citric acid and oxalic acid, unstable Zn increases, and the phenomena is just opposite when extracted by oxalic acid. The unstable state of Zn account for the largest proportion with the treatment of 1.0mol/L citric acid(64.18%). The results show that higher citric acid results in higher concentration of unstable Zn in sludge. Cu mainly exists in last two forms(55.3% and 16.59%) in the absence of extraction.

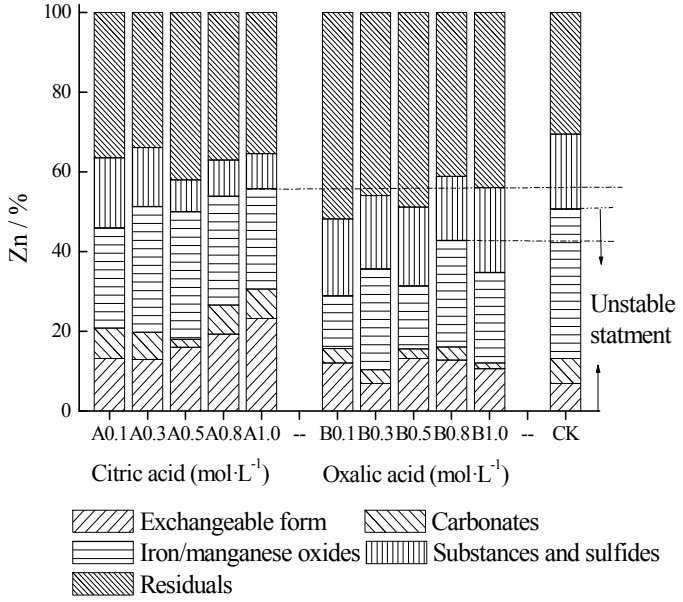

Figure 3. Percentage content of Zn after extracted by organic acid with different concentration

When treated by 1.0 mol/L citric acid, both Cu and Cd in exchangeable form increase and climbs gradually with the improvement of citric acid content, indicating that Cu and Cd in sludge mainly exist in non ionic form.

CONCLUSION

Chemically extraction procedure is significant in analysis extractable heavy metals and is valuable in giving estimations of potential environmental bioavailability. According to the experiment, it can be conclude as follows:

Concentration of heavy metals collected from wastewater treatment plant from high to low are Cu>Zn>Cd, which are all within the control range of agricultural use.

Before extraction process, Cd and Cu mainly exist in acid soluble form and organically metal species, Zn exists in organic substances and sulfides.

The extractable content of tested heavy metals exhibit a positive correlation with increasing acid content, reaction temperature and time.

Citric acid is more efficient in removing Zn, oxalic acid exhibits higher extractability in removing Cu but inefficient in Zn and Cd.

Zn removed by citric acid is mainly in stable form, and the unstable form in sludge increases. The exchangeable form of Cu and Cd increases after the extract procedure.

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