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Effects of Inorganic and Organic Acids on Heavy Metals Leaching in Contaminated Sediment

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Abstract Leaching properties of Pb, Cd, Zn, Cu at pH of 2-6 using different inorganic acids (hydrochloric acid, sulfuric acid, nitric acid) and organic acids (acetic acids, citric acid, malic acid, succinic acid) aiming at polluted sediment at downstream of a non-ferrous metal smelting enterprise is discussed. Results showed that leaching concentrations of 4 metals decreased with increasing pH. Among all the organic acids, the acetic acid showed exceptional leaching ability in a wide pH range of 2-5. Organic acids leached more heavy metals than inorganic acids did. Leaching concentration of heavy metals followed the descending order: Zn>Cd>Pb>Cu.

Key words sediment, heavy metal, inorganic and organic acid, pH, leaching concentration

Introduction

A non-ferrous metal smelting enterprise in Henan province discharging a large amount of contaminated wastewater has caused large enrichment of Pb, Cd, Zn, Cu in local river sediment, which is very dangerous for that the gathering heavy metals being apt to release and induce the secondary pollution.

It has been well recognized that pH is an important factor affecting metal leaching (Temminghoff et al. 1997). This article studies the leaching properties of different pH of inorganic acids (sulfuric acid, nitric acid and hydrochloric acid) and organic acids (citric acid, malic acid, succinic acid and acetic acid) on Pb, Cd, Zn, Cu existing in the sediment.

Materials and methods

Sediment sample

The sediment sample was collected from the downstream of sewage outfall of a non-ferrous metal smelting enterprise in Henan province using a tubular sand core sampler with the sampling depth of 4m. After being air dried and sorted out of macadam, gravel and plant residue, the sediment sample was grinded to pass through a 100-mesh sieve, and cryopreserved for subsequent analysis. The specification distributions of major heavy metals of the sediment are listed in table 1.

Table 1 *The specification distributions of the heavy metals of the experimental sediment (mg/kg)*

Item	Exchangeable form	Carbonate bound form	Fe-Mn oxide form	Organic form	Residual form	Total content
Pb	16.44	103.68	293.70	655.40	987.28	2056.50
Cd	85.90	172.65	459.36	70.99	10.15	799.05
Zn	13.64	294.50	416.47	1125.52	1049.86	2900.00
Cu	0.90	196.83	10.80	169.50	151.88	529.91

Experimental methods

The inorganic acids (sulfuric acid, nitric acid and hydrochloric acid) with pH of 2, 2.5, 3, 4, 5, 6 were added in a series of 2 L polyethylene bottles containing 100g sediment sample with the solid-to-liquid ratio of 1:10 (m/V). After being agitated at 23±2 ℃ for 20h using rotary agitator (30±2 r/min), the suspensions were filtered in a filter press with the filter membrane of 0.6μm-0.8μm. The filter liquor were collected and stored at 4℃ for subsequent test. The different organic acids (citric acid, malic acid, succinic acid and acetic acid) with the pH of 2, 2.5, 3, 4, 5, 6 were added in a series of 2 L polyethylene bottles containing 50 g sediment sample with the solid-to-liquid ratio of 1:20 (m/V). The subsequent operation followed the procedures detailed for inorganic acids.

Analytical method

The specification distributions of sediment were analyzed by the Tessier method(Tessier et al. 1979). The contents of heavy metals were determined by inductively coupled plasma atomic emission spectrometry (Agilent7700x). All the containers were soaked for more than 24 h in 10% HNO_3 solution and cleaned by ultrapure water before used, and all the experiments were in duplicate.

Results

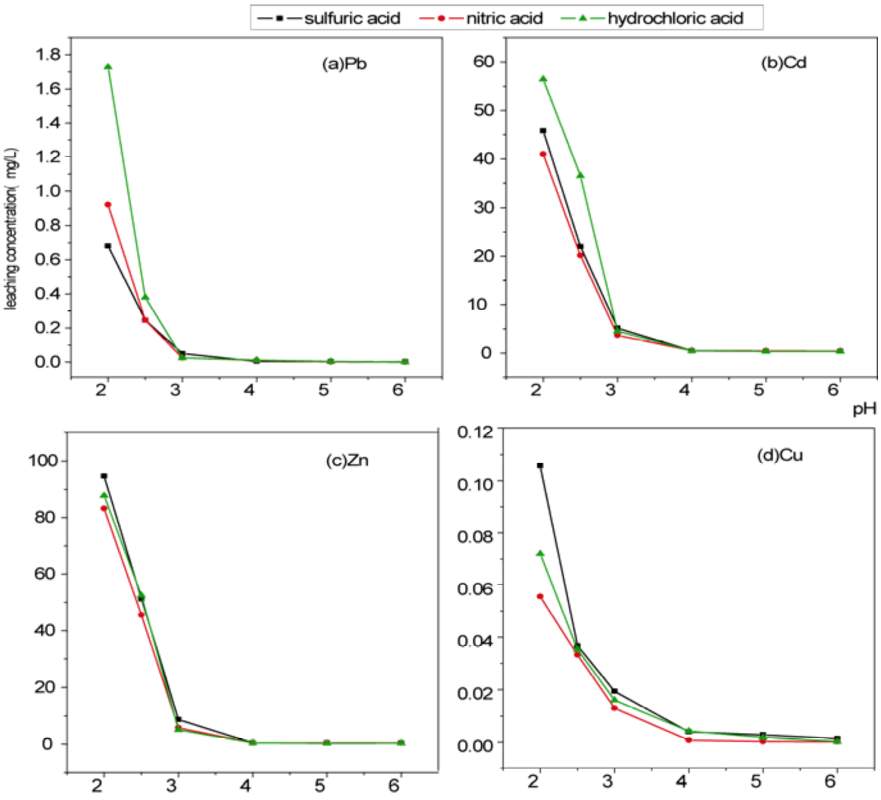

Fig.1 *Effects of different inorganic acids and pH on the heavy metals leaching*

Effects of inorganic acids on the heavy metals leaching

Leaching effect of Pb, Cd, Zn, Cu by three kinds of inorganic acids all decreased with increasing pH (fig.1). For all the experimented metals, the leaching concentration declined dramatically at pH=2-3, and flattened out at pH>3. However, the leaching ability of each kind of inorganic acid was different for each metal. Furthermore, the leaching concentration of 4 metals followed the descending order: Zn>Cd>Pb>Cu, among which the leaching concentration of Zn, Cd and Pb was 50-100 times, 400-600 times and 10-15 times as large as Cu.

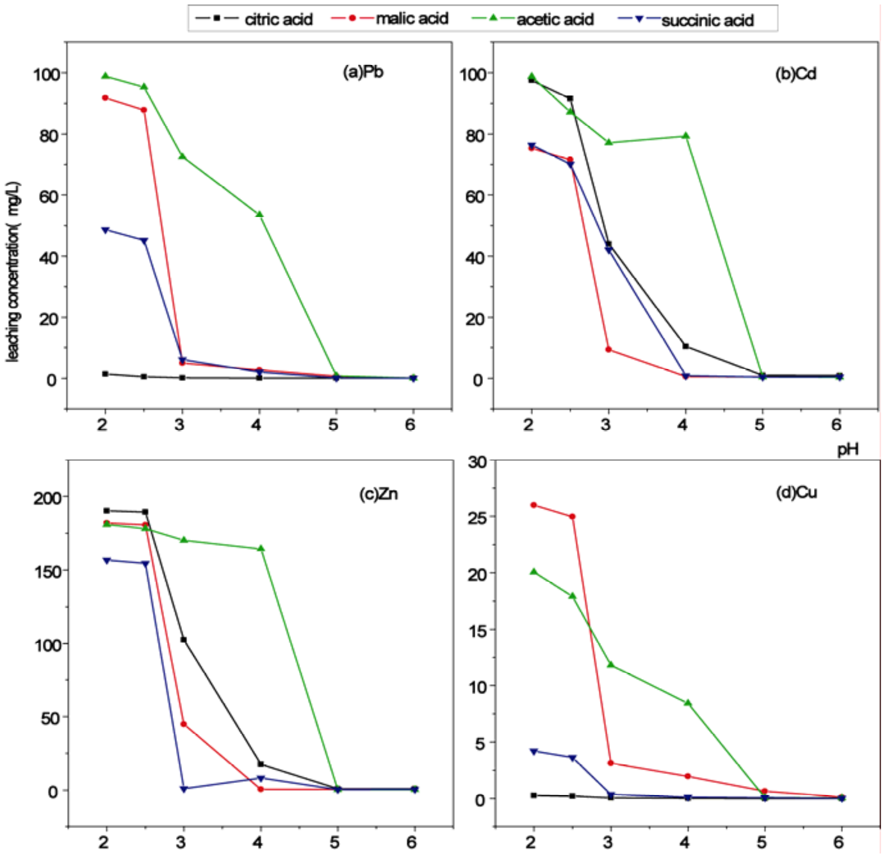

Fig.2 *Effects of different organic acids and pH on the heavy metals leaching*

Effects of organic acids on the heavy metals leaching

The downtrend of heavy metals leaching concentration with increasing pH using organic acids, which was consistent with that of inorganic acids, was observed as shown in fig.2. In contrast to the inorganic acids, the pH turning point of different organic acid varied for each kind of metal, and the acetic acid showed the most remarkable leaching ability in the wider pH range of 2-5 among all the organic acids. On the whole, the leaching concentration order of 4 heavy metals extracted by organic acids, which was consistent with that of the inorganic acids, was Zn>Cd>Pb>Cu, and the leaching ability of acetic acid for Zn was 2 times, 2 times and 10 times as many as Cd, Pb and Cu.

Discussion

With increase of pH, the leaching concentration of heavy metals by inorganic acids decreased(fig.1). Generally, the pH showed the effect from two aspects when no organic ligands existed in the extractants. On one hand, pH changed the affinity of sediments for heavy metals, which maybe caused by pH-dependent proton competition, surface potential and surface-charge density on colloids(Naidu et al. 1997). This change in affinity resulted in the decrease of heavy metal leaching concentration with increased pH. On the other hand, pH changed the ionic forms of metals. With increase of pH, the hydrolysis of metal cations increased. The hydrolyzed forms had lower solvation energies for surface binding than aquo metal ions did(James and Healy 1972). Therefore, the leaching concentration of metals decreased with increasing pH when inorganic acids were used as extractants.

Fig.2 showed that the heavy metal leaching concentration decreased with increasing pH when organic acids were employed as extractants. However, it showed much larger difference of leaching concentrations with different organic acid, heavy metal and pH value when compared with that of inorganic acids extractants. Except for above reasons for inorganic acids, the complicated stability adjustment of organic acids ligands binding heavy metals was the other important reason for metal leaching. Comparison of fig.1 and fig.2 showed that the organic acids had much stronger leaching ability than inorganic acids. When extracted by organic acids the leaching concentration of Pb, Cd and Zn was 50-200, 1.5-2.0, 1.8-2.0 times as large as that when extracted by inorganic acids. As to Cu, the inorganic acids did not show obvious extracting effect while the organic acids realized the effective leaching for it. Desorption of heavy metals in soil by low molecular-weight organic acids/salts (Song et al. 2010) revealed that the salts of organic acid had much more higher soil-heavy metal-release efficiency than organic acids at the same concentration. Therefore, the mechanisms for organic acids/salts to extract heavy metals should not be dominated by H^+ but the anionic reactions of organic acids. Consequently, the organic acids possessed more remarkable leaching efficiency compared with inorganic acids.

The heavy metal leaching is directly related to the coordinative ability of organic acids and metal ions. The more stable of the ligand formed, the more difficult for it to be adsorbed by the soil and sediment, and thus the metal leaching is much easier(Gao et al. 2002). A number of studies of heavy metal pollution of soil have verified that the reactions between organic acid and heavy metal is related to the amount and place of the carboxyl and hydroxyl groups(Ma et al. 2008; Gao et al. 2002; Qin et al. 2004; Schwab et al. 2008; Shan et al. 2002). Generally, the structure with more carboxyl is beneficial to the heavy metal leaching for the formed ligand being more stable. Therefore, the leaching ability of citric acid with 3 carboxyl is supposed to be higher than that of malic acid and succinic acid with 2 carboxyl; correspondingly, the acetic acid with only one carboxyl has the lowest leaching ability. In the area of heavy metal pollution of sediment, the similar conclusion was obtained when Pb and Zn were leached using citric acid, malic acid and tartaric acid(Li et al. 2010). However, our experiment showed that the acetic acid possessed the most remarkable leaching ability in the wider range of pH (pH=2-5), and citric acid did not even show obvious leaching effect for Pb and Cu. It was presumed that the difference of organic matter and the specification of heavy metals existed in the experimented sediment caused the entirely different conclusions.

For both inorganic acids and organic acids, the metals followed the leaching order: Zn>Cd>Pb>Cu. Meanwhile, the sum of carbonate bound form and Fe-Mn oxide form of Zn was 1.1, 1.8 and 3.4 times as many as Cd, Pb and Cu as shown in table 1. Since it is favourable for the carbonate bound form and Fe-Mn oxide form to be converted to exchangeable form under acidic condition, the metal leaching effect was positively correlated with the contents of these two forms.

Conclusions

The inorganic acids(sulfuric acid, nitric acid and hydrochloric acid) and organic acids(acetic acids, citric acid, malic acid, succinic acid) showed different leaching effect for Pb, Cd, Zn and Cu existing in the experimented polluted sediment. On the whole, the leaching ability of both inorganic and organic acids decreased dramatically with increasing of pH value. The leaching effects of inorganic acids for different metals generally flatted at pH>3, while large difference of pH turning points occurred when different organic acid used for different metals.

The acetic acid showed the maximum leaching ability in the wide pH range of 2-5 among all the organic acids.

At the same pH, the organic acids showed stronger leaching ability than inorganic acids. The leaching concentration of 4 metals followed the descending order: Zn>Cd>Pb>Cu for both inorganic and organic acids, which was positively correlative to the sum of carbonate bound form and Fe-Mn oxide form of 4 heavy metals.

References

Gao YZ, He JZ, Ling W T, Hu HQ, Liu F (2002) Effect of organic acids on Cu desorption in contaminated soils. China Environmental Science 22(3): 244-248

James RO, Healy TW (1972) Adsorption of hydrolyzable metal ions at the oxide—water interface. III. A thermodynamic model of adsorption. Journal of Colloid and Interface Science 40(1): 65-81

Li P, Zeng GM, Xu WH, Zhang C, Jiang M (2010) Effects of organic acids on zinc and lead leaching from contaminated sediments. China Environmental Science 30(9): 1235-1240

Ma YL, Zeng QR, Hu H, Pan J, Liu XY, Liao BH (2008) Effect of low molecular weight organic acids on desorptions of Pb, Cd, Cu and Zn from soils. Chinese Journal of Soil Science 39(6): 1419-1423

Naidu R, Kookana RS, Sumner ME, Harter RD, Tiller KG (1997) Cadmium sorption and transport in variable charge soils: A Review. Journal of Environmental Quality 26(3): 602-617

Qin FX, Shan XQ, Wei B (2004) Effects of low-molecular-weight organic acids and residence time on desorption of Cu, Cd, and Pb from soils. Chemosphere 57(4): 253-263

Schwab AP, Zhu DS, Banks MK (2008) Influence of organic acids on the transport of heavy metals in soil. Chemosphere 72(6): 986-994

Shan XQ, Lian J, Wen B (2002) Effect of organic acids on adsorption and desorption of rare earth elements. Chemosphere 47(7): 701-710

Song JF, Yang JY, Cui XY (2010) Effects of low molecular-weight organic acids/salts on availability of lead, zinc and arsenic in mixed metal-polluted soil. Journal of Soil and Water Conservation 24(4): 108-112

Temminghoff EJM, Vander ZS, Dehaan FAM (1997) Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. Environ. Sci. Technol 31(4):1109-1115

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51(7): 844-851