Remediation of Heavy Metal Contaminated Soil by Leaching with Na_2EDTA and STPP

ZHANG Xiaowen[1,a] YANG Rong[1,b] LI Mi[1,c] LIU Lifen[2,d]
YAO Ya[1,e] PENGYing[1,f]

[1] Key Laboratory of Radioactive Waste Treatment and Disposal, University of South China, Hengyang 421001, China

[2] College of Urban Construction, University of South China, Hengyang 421001, China

[a] shawn_zhang@sina,com, [b] yrwk322@163.com, [c] enemy_1983@163.com, [d] 964747289@qq.com, [e] 1195021995@qq.com, [f] pengying415@163.com

Keywords: STPP;Na_2EDTA;Lead;Cadmium;Copper;Composite leaching

Abstract. The contamination of soils with heavy metals has become a major environmental concern. Extractive-decontamination of the toxic metals (Pb, Cd and Cu) from the contaminated soil using N_2EDTA and STPP was evaluated by batch extraction. The influences of mixed liquid concentrations, oscillating time, pH of solutions on leaching efficiency were investigated. Pb, Cd and Cu fractions characteristics were compared before and after leaching to reveal the leaching of them. The extraction efficiencies increased in the order of Pb > Cd > Cu for Na_2EDTA, and Cd > Pb>Cu for STPP. Na_2EDTA and STPP can coordinate with metal ions in the soil, but the complexing ability of STPP is relatively weak. Synergistic effects on metal leaching with contaminated soil were observed in low solution. However, antagonistic effects on metal leaching were found at higher than 0.01 mol/L. The heavy metal removal efficiency from soil increases with concentrations of mixed solutions and leching time. Metal fractionation analysis showed that the leaching metal was mainly from acid exchangeable, reduction state, oxidation state, while residual state metals were almost unchanged.

Introduction

Soil contamination of our country is becoming increasingly serious, especially the heavy metal mining in the South. In the mining or smelting process of heavy metals in tailings and heavy metals produced thereafter, slag can cause soil contamination. Heavy metals in soil can cause directly to the surface water, groundwater and air pollution, More seriously the heavy metal pollution of soil has long-term and hysteresis characteristics, can enter the food chain to accumulate enlarge by a variety of ways, seriously affect human health and life[1]. Chemical leaching repair is considered as technology which can efficient and completely control heavy metal pollution[2]. The commonly used leaching agents are inorganic acid[3], chelating agents[4], surfactants[5], salt[6]. Studies have shown that different agents have a big difference in heavy metals leaching results. EDTA can effect with the most toxic heavy metals and form a stable complex but it’s not easy to be degraded to produce environmental risk that is likely to continue for a long time. Sodium tripolyphosphate (STPP) is a chelating agent which have very small impact on the environment.

In this study, we used STPP and Na_2EDTA mixture to study the leaching effects of Pb, Cd and Cu in polluted soil, analyzed the leaching effect and heavy metals remove mechanism with different leaching agent by comparing the extraction of heavy metals speciation before and after leaching.

Materials and Methods

Soil and soil analysis

Experimental soil used in the experimental comes from a lead-zinc mine (Shuikoushan, Hengyang city, China). All of the soil samples were air-dried and passed through 2 mm mesh sieve before chemical analysis. The content of organic carbon was determined by Nelson and Sommers method. The total contents of Pb, Cd and Cu in the soil were determined by acid digestion method(HNO_3+HF) on Atomic absorption spectrophotometer (PE-900H). Soil characteristics are as follows: pH value of 5.5-6.1, organic matter content of 2.33%, heavy metals lead 1115 mg / kg, Cd 25.05 mg / kg and copper 121.22 mg / kg.

methods

Soil-leaching with Na_2EDTA and STPP Single leaching solution

5 g soil samples was placed into a 250 ml plastic container and added 50 mL different conceration STPP or Na_2EDTA leaching solution. The ratio of sample weight to washing solution volume was 1 g:10 ml. The plastic container were shaken at about 160 rpm and 30˚Cfor 2 h on a rotary shaker. After that, centrifuged at 5200 rpm for 15 min then filtered through Whatman No.42 paper, and analyzed on Atomic absorption spectrophotometer (PE-900H).

Soil-leaching with the mixed solutions

The mixed washing solutions were prepared by STPP-to-Na_2EDTA molar ratios of 1. Experement conditions are the same as described in 1.2.1. The pH of solutions were adjust with 0.1 mol/L NaOH or 0.1 mol/L HNO_3 in the range of 4.0-11.0.

Sequential extraction of contaminated soil before and after leaching

A modified BCR sequential extraction procedure was used to assess the fractionation of Pb, Zn and Cd in the soil into four forms. All experiments described were performed twice using ultra-pure water.

Results and discussions

Effects of Na_2EDTA and STPP on the leaching efficiency

Figs. 1, 2 show leaching efficiency of heavy metals from contaminated soil in the presence of different concentrations of Na_2EDTA and STPP (mol/L) at room temperature (30˚C). The removal rate of Pb was increased significantly from 37% to 75% with an increase of Na_2EDTA concentration from 0.005 to 0.16 mol/L at room temperature (30˚C). It increased from 42% to 67% for Cd and 10% to 34% for Cu at the same condition. The removal rate of Cd and Cu increased from 17% to 38%, 4% to 10% in STPP concentration from 0.005 to 0.16 mol/L. That confirmed that Na_2EDTA can form coordination complexes with heavy metals more easily.

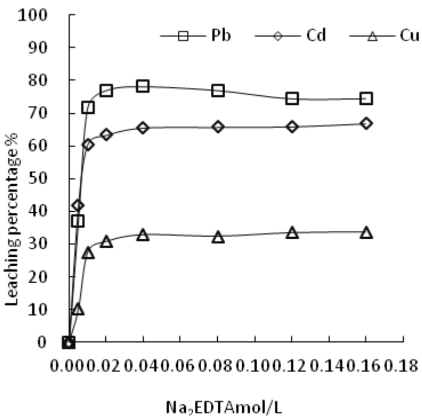

Fig.1 Leaching efficiency of heavy metals from contaminated soil with different Na_2EDTA concentration at room temperature (30˚C).

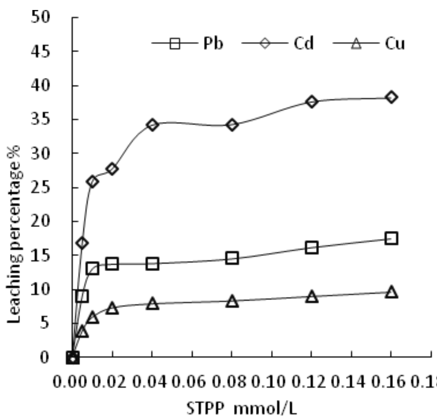

Fig.2 Leaching efficiency of heavy metals from contaminated soil with different STPP concentration at room temperature (30˚C).

The extraction efficiencies increased as the order: Pb > Cd > Cu for Na_2EDTA, and Cd > Pb>Cu for STPP, which is inconsistent with stability constants of the chelates. The form of heavy metals and the stability constants of complex will impact on heavy metal removal. There are various forms of metal ions in soil, each form has a big difference in the ability to move, has a different ability to form complexes with the chelating agents. The reactivity and behavior of the metals in the soil sample towards the extracting solutions depend on the partitioning of metals within the soil, and can be used to explain the varied extraction efficiencies for different metals. However, extraction efficiencies of metals the contaminated soil depends not only on the stability constants of complex, but also on the chemical speciation of heavy metal.

Metal removal using mixed solutions

Effects of different concentrations of mixed solutions

The washing solution, which was a mixture of STPP and Na_2EDTA, was an economically optimum solution for Pb, Cd and Cu removal. Fig. 3 shows Leaching efficiency of heavy metals from contaminated soil in the presence of different concentrations of mixed solutions (mol/L) at room temperature (30˚C). The removal efficiencies of Pb, Cd and Cu increased from 57%-71% , 61%-69% and 20%-25% with an increase in mixed concentration from 0.005 to 0.08 mol/L. Synergistic effects on metal leaching were observed in 0.005 mol/L. however, antagonistic effects on metal leaching were found at higher than 0.01 mol/L. Synergistic effects on Pb, Cd and Cu leaching in contaminated soil more than the leaching effect of the single leaching agent were observed in different concentrations of mixed solution（0.05 mol/L）. STPP can chelated with a part of metal ions and adjusted the pH of solution. However, with the increasing concentration of anionic surfactant, micelles will become increasingly large, easily generated precipitation upon binding with metal ions. As a result, antagonistic effects on metal leaching were observed at higher than 0.01 mol/L.

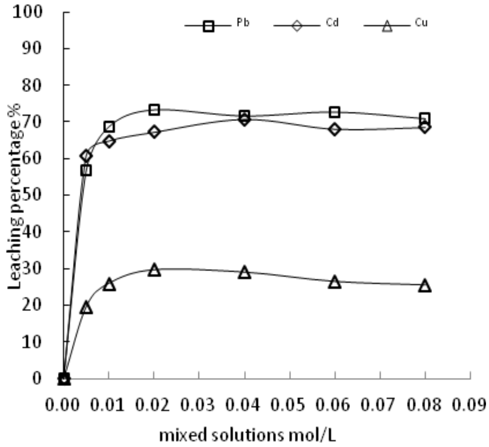

Fig.3 Leaching efficiency of heavy metals from contaminated soil in mixed solutions concentration from 0.005 to 0.08 mol/L at room temperature (30˚C).

Effects of different time and pH

Oscillating time and pH plays important role in the foam fractionation removal process. The experiments clearly indicated that the removal of Cd decreased from the range of 67% to 63% and the removal of Cu decreased from the range of 29% to 25% with increased in pH from 4 to 11 at mixed solutions at 0.01 mol/L (in Fig. 4). The removal of Pb was increased from 75% to 76% with pH increase from 4 to 5, whereas it decreased from 76% to 63% with pH increase from 4 to 5 at the same leach solution. The reason is that particle surface of soil were protonated and positively charged reduced the cation adsorption and heavy metal cation desorption with the increase of H^+ concentration. In alkaline conditions, Metal ions can form hydroxide precipitates, so the extraction of Pb, Cd and Cu decreased. Fig. 5 shows the extraction efficiency of Cu, Zn and Pb from the contaminated soil by

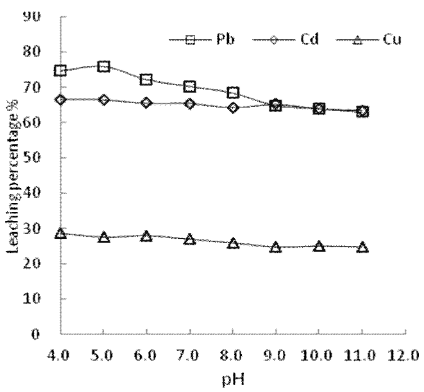

Fig.4 Effects of pH on metal leaching efficiency

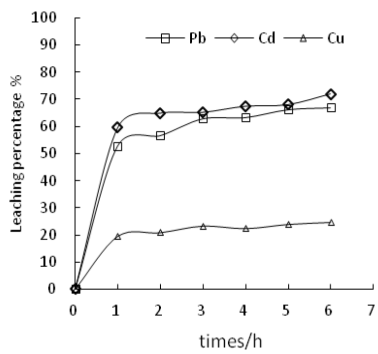

Fig.5 Effects of oscillating time on metal leaching efficiency

solutions at different oscillating time. About 53% , 60% , 20% of Pb, Cd ,Cu was extracted in 1 h respectively, then increased slowly in the next 5 hrs.

Sequential extraction

The modified BCR sequential extraction procedure for the chemical speciation of heavy metal, proposed by the commission of the European has been applied to the soils. The fractions extracted were acid exchangeable, reducible, oxidisable and residual fractions. Tab. 1 shows the changes of Pb, Cd and Cu fractions in contaminated soil before and after leaching. It revealed that 73.95% of all Pb was in reduction form, 39.67% of Cd was in acid exchangeable form, 28.24% was in reducible form, 24.37% was in oxidisable form, 16.22% was in residual form. 36.06% of all Cu was in acid exchangeable form and 37.71% of all Cu was in the residual form. Besides, it was found reducible and oxidisable form but very little.

Tab. 1 Changes of Pb、Cd and Cu fractions in contaminated soil before and after leaching

metal	Form of sample	before washing %	after washing %		
			Na_2EDTA	STPP	mixed solutions
Pb	acid exchangeable	14.85±0.17	10.34±0.12	5.42±0.06	5.52±0.06
	reducible	73.95±0.15	9.00±0.10	69.13±0.25	21.73±0.63
	oxidisable	1.03±0.04	1.99±0.18	2.15±0.27	0.96±0.26
	residual	12.60±0.24	12.24±1.23	12.15±1.27	12.18±1.18
Cd	acid exchangeable	39.67±1.31	8.36±0.34	6.10±0.54	2.15±0.10
	reducible	28.24±0.26	1.26±0.48	17.42±1.20	4.32±1.09
	oxidisable	24.37±4.03	10.91±2.17	14.17±0.66	13.03±1.16
	residual	16.49±0.73	16.08±1.37	16.28±0.85	15.85±1.34
Cu	acid exchangeable	9.95±0.54	9.37±0.36	6.49±0.21	6.50±0.06
	reducible	36.06±1.27	6.49±0.92	31.16±0.75	15.31±1.10
	oxidisable	13.10±0.12	5.94±0.07	10.51±0.16	6.81±0.06
	residual	37.71±0.01	37.59±0.45	37.29±0.40	37.40±0.27

Conclusions

Extractive-decontamination of the toxic metals (Pb, Cd and Cu) from the contaminated soil using N_2EDTA and STPP was evaluated. The extraction efficiencies increased in the order: Pb > Cd > Cu for Na_2EDTA, and Cd > Pb>Cu for STPP. Na_2EDTA and STPP can coordinate with metal ions in the soil, but the complexing ability of STPP is relatively small. Synergistic effects on metal leaching with contaminated soil were observed in low solution. however, antagonistic effects on metal leaching were found at higher than 0.01 mol/L. The heavy metal removal efficiency from soil increases with concentrations increasing of mixed solutions and leching time. Metal fractionation analysis showed that the leaching metal was mainly from acid exchangeable, reduction state, oxidation state, while residual state metals were almost unchanged.

Acknowledgements

This study was financially supported by the Natural Science Foundation of China (51404141, U1401231) and the Scientific Research Foundation of Hunan Education Department (15C1170).

References

[1] P. Conte, A. Agetto and R. Spaccini: Environ. Pollut., Vol.135(2005), p.515
[2] C. Y. Liu, Y. F. Zhang and J. Teng: Pollut. Control Technol., Vol.19(2006), p.42
[3] X. Liu, J. T. Wang and M. Zhang: Environ. Sci., Vol.34(2013), p.1590
[4] V. David and L. Domen: Chemosphere, Vol.91(2013), p.76
[5] C.N. Mulligan: Environ. Pollut., Vol.133(2005), p.183
[6] G. Dermont, M. Bergeron and G. Mercier: J. Hazard. Mater., Vol.152(2007), p.1