Chemical remediation of heavy metals-contaminated soils by the"ASP" eluent

Hui-Min Liu[1,a], Gui-Wu Wang[1,a], Ke-Lin LI [1,a], De-Liang LI[1,a*], Dan XU[2,b]

[1]College of Forestry, Central South University of Forest and Technology, Changsha, China

[1]College of Material Science and Engineering, Central South University of Forest and Technology, Changsha, China

[1]College of Forestry, Central South University of Forest and Technology, Changsha, China

[1]College of Material Science and Engineering, Central South University of Forest and Technology, Changsha, China

[2]College of Material Science and Engineering, Central South University of Forest and Technology, Changsha, China

[a]liuhuimin0924@163.com,[a]wgwsuper21@aliyun.com,[a]csfuklli@163.com, [a]*globalize100@vip.163.com,[b]842078405@qq.com

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Abstract. A chemical remediation of heavy metals-contaminated soils by using the ASP (2-Amino-3-sulfhydrylpropanoic acid) as the key role was studied in this paper. The initial soil characterization shows its heavy metals index were: Pb15.6, Cd8.6, Cu47 and Ni54 ($mg.kg^{-1}$), respectively. By using the single-factor method, remediation related technical index were screened and they are: ASP concentration 2~3.5g/L, working pH 5~10, SLS dosage 0.2~0.5g/L and temperature (20±5C), respectively. The sensitivity analysis shows the parameters are in the order of: [ASP]≥pH ≥temperature ≥SLS, respectively. It is optimistic that the remediated soils can meet the agricultural standards and back to cultivation use.

Introduction

Heavy-metals related contamination in the cultivated land-fields is a food-safety challenge in mainland, China[1,2].Up to now there are a variety of decontamination methodologies involving physical[3,4], chemical[5,6], thermal, and(or) biological processes for soil treatment. However the chemical washing[7] method is applied widely for its wide adaptability for different lands and excellent removal efficiency of metals. The traditional lixiviants(washing agents)are limited in acids, EDTA and related salts, however they show several disadvantages such as lower leaching kinetics, higher residual index of the heavy metals in the soils [8,9]. And because their washing pH is limited in weak acidic media(for example: pH=3.5~5.5), another risk of the substantial destruction of the soil material will exist forever. Another challenge of the EDTA-type extraction comes from its slow kinetics and lower depth in the soil[10]. In fact decontamination can be an economically competitive alternative, particularly in instances if the pregnant solution can be collected efficiently and the extracted heavy metals are recovered in site. In this paper a novel eluent based on using ASP(2-Amino-3-sulfhydrylpropanoic acid)as the key ingredient was reported, and related processing parameters including ASP concentration, temperature, pH and SLS((sodium lignin-sulfonate, a wetting agent) dosage were discussed to understand the remediation in details .

Materials and methods

Initial soil characterization. The test soil was obtained from the a typical contaminated soil of RuCheng, Hunan Province mine area. The soil was passed through a No. 4 sieve 4.75mm.Rocks and other large material not passing through the sieve were removed. The soil was then thoroughly mixed to ensure uniformity and stored in a plastic barrel at room temperature for subsequent use in

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experiments. Its physical and chemical properties were shown in Table1:

Table1 Physical and chemical index of the tested soils before remediation (mg.kg^{-1})

pH	Organic matter	Total Metal Content				Exchangeable Species Index			
		Pb	Cd	Cu	Ni	Pb	Cd	Cu	Ni
6.2	9340	15.6	8.6	46	54	6.5	4.5	15	27

Experimentals. Batch tests agitation studies were performed to get appropriate ranges of concentration and dosage of the washing solutions to extract the heavy metal pollutants from the contaminated soil. ASP(2-Amino-3-sulfhydrylpropanoic acid)was selected as the main ingredient in the extraction composition to stabilize the heavy metals ions ,and keep them in a stable state of aqueous "Mercapta- Heavy Metals" complex in the extracts. DI water washes were performed to provide a baseline for the removal obtained by chemical washing. The leaching process was accomplished by placing certain amounts of soil in 150 ml plastic bottles followed by addition of varying volumes of the washing solution. The samples were then placed on a shaker table operated at 150 rpm at room temperature. A 6-h extraction time was deemed sufficient to extract the heavy metal ions from the contaminated soils. The leaching samples were allowed to settle for about 45 min and then filtered through a 0.45-mm membrane filter. Following S/L separation, the filtrate was acidified to a pH of 2.0 by use of 1:1 HNO_3 for heavy metal analysis. It was assumed that the metal concentration of the filtrate represents that released from the contaminated soil. Removal efficiency were determined by dividing the heavy metal release quantities by the initial data.

All heavy metal analyses were performed according to the standard GB/T17138-1997 and CB/T17140-1997, and they were detected by using a SHIMADZU AAS-6300 spectrometer. Standard concentrations including Pb, Cd, Ni and Cu were provided by Sigma-Aldrich Corp.Ltd., and 1N sodium hydroxide and 0.5N Hydrochloric acid were chosen as the pH adjustants. To get the optimum extracting parameters, a set of batch experiments were conducted at room temperature and fixed 1:10 soil–solution ratios. Effects of the eluent(ASP)concentration, leaching pH ,temperature and the dosage of the SLS(sodium lignin-sulfonate, wetting agent) were discussed to understand the metal-extracting characteristics.

Results and Discussion

Effect of the ASP concentration on the metal-extraction. Effect of the ASP concentration on the metal-extraction was shown in Fig.1, and related processing factors were: pH(7.5), temperature(20C), SLS dosage (0.50g/L) and time 48 hour, respectively.

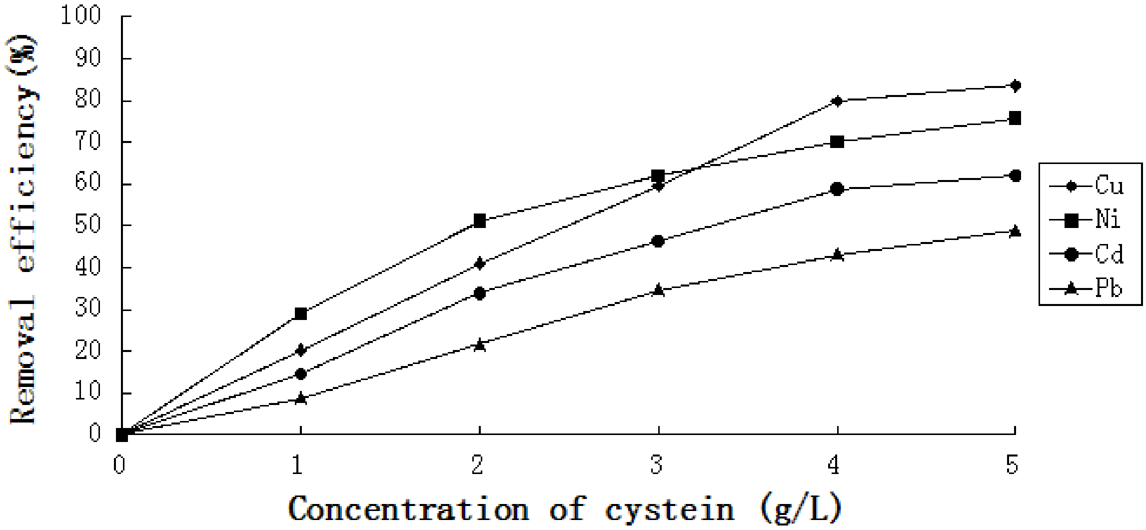

Fig.1 Relationship between ASP concentration and metals extraction

It is easy to find that ASP is an active extractant even at room temperature and weak alkaline media. By comparing the table 1,it is very clear that not only the exchangeable-state metals can be extracted fully, but also the heavy metals in the species of oxide, carbonate, chloride&sulfate can be transformed extracted efficiently. A preferable ASP dosage should be in the range of 2~3.5 g/L.

Effect of the leaching pH on the metal-extraction. Effect of the working pH on the metal-extraction was shown in Fig.2, and related processing factors were: SLS dosage(0.50g/L), ASP concentration(1.5g/L),temperature(20C)and leaching time 48 hour, respectively.

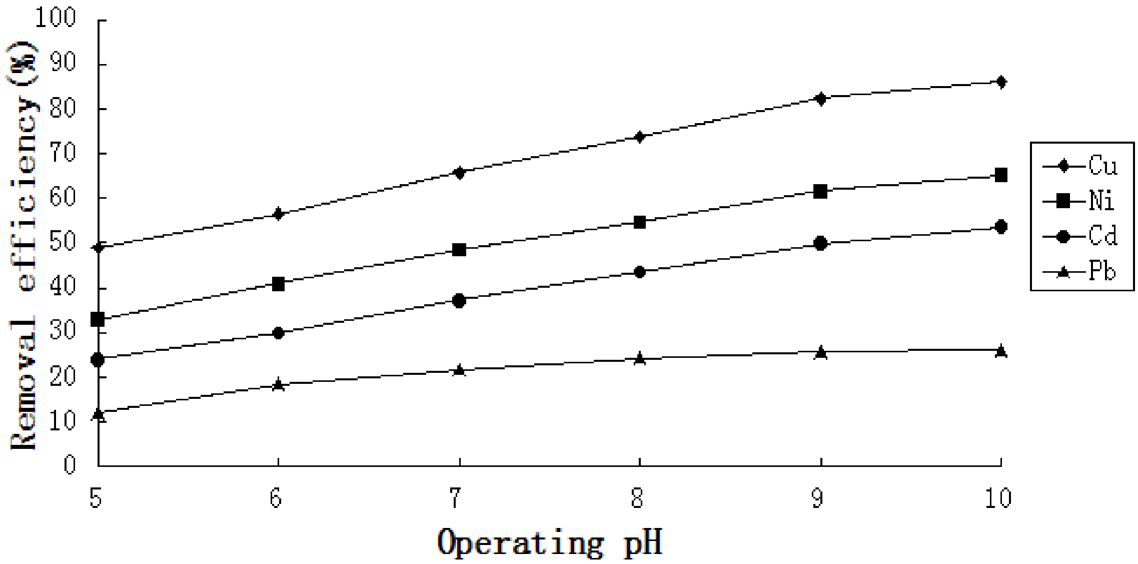

Fig.2 Relationship between working pH and metals extraction

It is easy to find that the extracting efficiency is sensitive to the working pH. However the heavier metal (Pb) is not so sensitive as that of copper and nickel. Obviously the extraction efficiency of the heavy metals is closely reliant on the working pH. and heavy-metals can be transformed to aqueous-species complex even at higher pH. It is optimize to get a clean soil on no risks of resulting in acidic lands. Another advantage of cysteine comes from its organic-sulfur characteristic, because sulfur-bearing fertilizer is necessary and need supplemented periodically for crops harvest .

Effect of the SLS dosage on the metal-extraction. Effect of the SLS(sodium lignin-sulfonate) dosage on the metal-extractions was shown in Fig.3, and related processing factors were: pH(7.5),temperature(20C),ASP concentration 2.0 g/L and leaching time 48 hour, respectively.

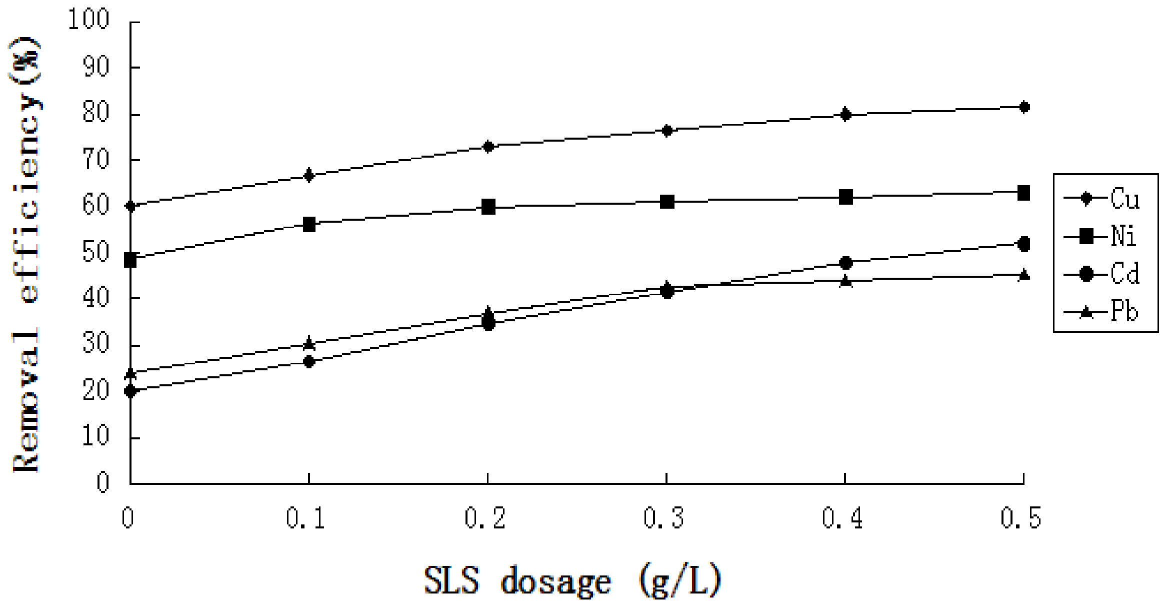

Fig.3 Relationship between SLS dosage and metals extraction

It is easy to find that SLS(a typical wetting agent)is a good assistant lixiviant in the the extracting process, but its removal role is not so powerful as that of ASP. Generally the extractive growth can reach 10~20% by controlling the SLS dosage in the scope of 0.2~0.5 g/L .

Effect of the temperature on the metal-extraction. Effect of the temperature on the metal-extractions was shown in the column-diagram(Fig.4), and related processing factors were: pH(7.5),ASP concentration 2.0 g/L ,leaching time 48 hour, respectively.

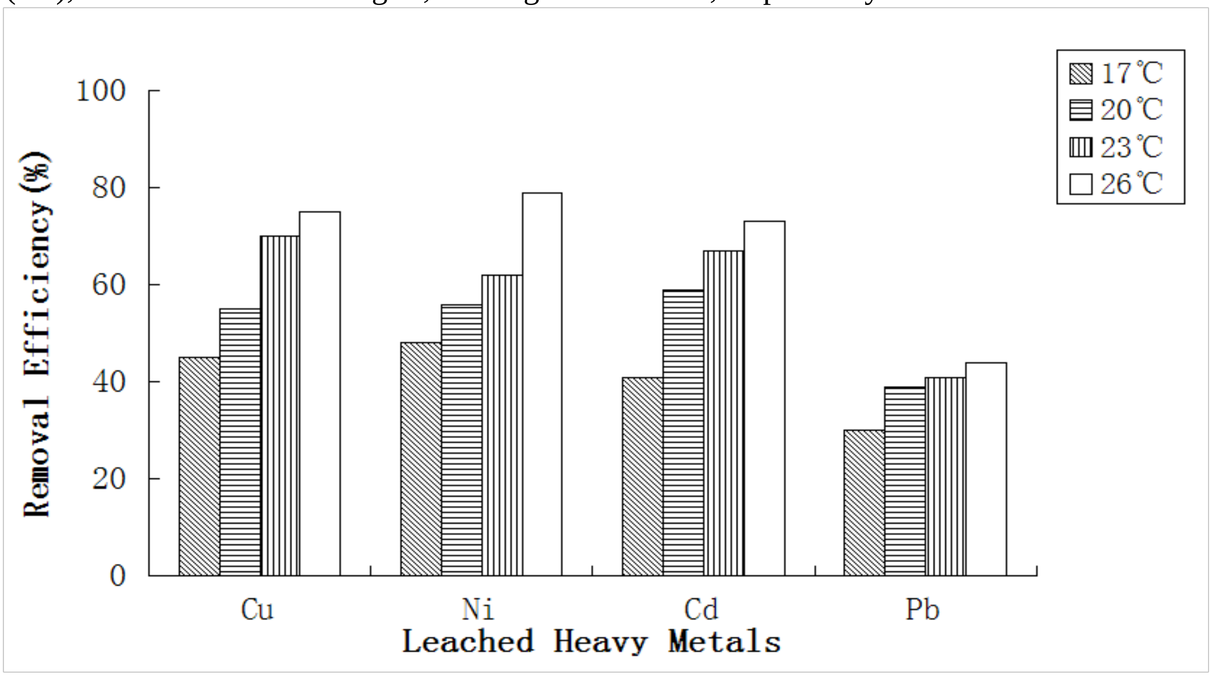

Fig.4 Column-diagram about the the operating temperature and the metal-removal efficiency

It is easy to find that the extracting efficiency is sensitive to the working temperature, however the heavier metal(Pb) is not so sensitive as that of copper or nickel. In fact decomposition and hydrolysis may take place for the aqueous transition compounds at higher temperature ,so room temperature (20±5C) is a good selection in the washing procedure especially taking the energy into consideration.

Sensitivity analysis on the parameters order. The Sensitivity-analysis method was employed to estimate the parameters order by the comparison method. By comparing the amplitude of variation in the Fig.1~Fig.4, it can be concluded the impact factors go down according to the order:

ASP concentration ≥operating pH≥temperature≥ SLS , respectively.

Summary

1)ASP(2-Amino-3-sulfhydrylpropanoic acid)can be used in the chemical remediation of the heavy metals contaminated soils even at very high pH.

2)SLS(sodium lignin-sulfonate) is an excellent assistant-agent in the removal of the heavy metals .

3)Not only the exchangeable-state heavy-metals can be extracted, but also those heavy metals in the form of un-exchangeable species can be removed efficiently .

4)The impact factors go down according to the order: ASP concentration≥operating pH≥temperature≥ SLS ,respectively .

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