[Article ID] 1003-6326(2002)03-0540-05

Elution of lead from vermiculite with environmentally benign reagents①

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[Abstract] The elution of lead from vermiculite was investigated by using a novel biodegradable chelating reagent, L-asparagic-N, N-diacetic acid (ASDA) and water soluble depolymerized pectic acid and comparing with a conventional chelating reagent, EDTA, as well as acetic acid. The influences of the reagent concentration, equilibrium pH and the suspension contact time on Pb extraction were examined. It is concluded that the acetic acid is not effective for Pb removal in any case due to its weak complexing ability with Pb. Although Pb is easier to be released by EDTA with stoichiometric amount, it is by no means the preferable alternative for the purpose because of its low biodegradability. On the other hand, ASDA and depolymerized pectic acid have the potential application because they are not only effective for Pb elution but also environmentally friendly.

[Key words] elution; lead; vermiculite; chelating reagents; pectic acid
[CLC number] X 53 **[Document code]** A

1 INTRODUCTION

The contaminated soil by heavy metals in environment has attracted much attention because it is a threat for human and wild life. Among the heavy metals polluting soil, lead is ranked as the No. 1 priority hazardous substance by assessment from its polluted site, toxicity and potential for human exposure. Source of lead contaminants is generally anthropogenically derived. Lead is often added to the soil as a pesticide or as an impurity in commercial fertilizer. Mining and smelting operation can be major sources of soil contamination. Reprocessing facilities of automobile battery may be very significant, albeit localized, contributors to soil pollution by lead. Emissions from motor vehicles also contribute significantly to soil contamination. Although, at present, lead emissions from gasoline have been largely eliminated due to strict environmental regulation, an estimated 4~5 million metric tones of lead previously used in gasoline still remain in soil and they are extreme threat against human life. Consequently, it is an important and urgent task to develop appropriate and economical technologies to remediate such contaminated soil[1, 2].

Cation exchange characteristics of clay minerals in soil with heavy metals in environments play an important role for metals fixation[3]. Vermiculite is one of the most important clay minerals, which contribute to cation exchange in soil. It is reported that vermiculite possesses the highest cation exchange capacity (CEC) among clay minerals due to its special structure and chemical compositions[4].

Several methods have been proposed for the remediation of soils contaminated with heavy metals, which are based on two principles: 1) immobilization of metals by increasing the retention of metals in soil or by decreasing the mass transfer rate of metals, or 2) removal of metal from soil matrix[5~8]. Regarding the fact that first method is not the permanent approach to resolve the problem of heavy metal pollution, consequently, solubilization of metal from contaminated soil by flushing and washing is a promising method. However, the exploration of novel reagents which achieve this purpose is significant to promote this route into actual application. Actually, a series of works have been conducted by the authors on this topic[9~11].

In this work, the attention is focused on exploring the effective and environment friendly reagents for the remediation of soil from lead pollution. Vermiculite preferentially loaded with lead is selected as representative of clay mineral for this investigation.

2 EXPERIMENTAL

The crude vermiculite sample purchased from Kinseimatec Co., Ltd., was crushed and sieved. The fractions of 208~104 μm (Sample B) and < 37 μm (Sample S) which were dried after saturated with lead were used in this study. The amount of lead adsorbed on the sample was measured as 817 mmol/kg for Sample B and 1 574 mmol/kg for Sample-S.

Elution tests were carried out batch-wise. In each experiment, 20 mg of vermiculite sample was mixed together with 20 mL of aqueous solution in a flask and shaken in a water bath incubator maintained at 30 ℃ for 24 h except for especially stated. Initial pH of the solution was adjusted by adding either concentrated HCl or NaOH. After certain hours, the suspended solution was filtrated and the concentration

① [Received date] 2001-10-16; [Accepted date] 2002-01-24

of lead was measured using flame atomic absorption spectrophotometer (SAS 7500, Seiko Instrument). Initial and equilibrium pHs after elution were measured by using a pH meter (Beckman model Φ45).

3 RESULTS AND DISCUSSION

3.1 Effect of reagent concentration

3.1.1 EDTA

Ethylenediaminetetraacetic acid (EDTA) has been commonly employed for investigation of the remediation of contaminated soil due to its strong complexation power with metal ions. The concentration of EDTA.2Na used in this study ranged from 0.02 to 20 mmol/L. The effect of EDTA concentration on the elution of Pb is shown in Fig. 1. It is clear that EDTA is effective for lead removal from both samples and there is a positive correlation between EDTA concentration and the release of Pb. This is imaginable since EDTA may form strong water-soluble complexes with Pb; logarithm of the stability of constant is 18 for the formation of $PbEDTA^{2-}$. It can be calculated that all the lead can be released in accordance with the chemical stoichiometry with EDTA with formation of 1∶1 reagent/Pb complexes. The same phenomenon had been also observed by Elliott et al[12, 13] in investigation of extraction of lead from a grossly contaminated soil (PbT= 21%).

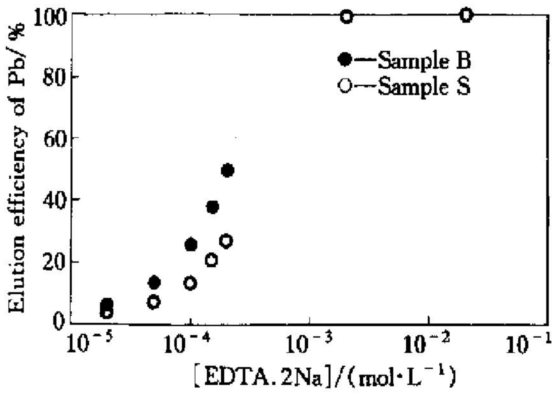

Fig. 1 Effect of EDTA.2Na concentration on elution of lead from vermiculite

3.1.2 ASDA

The formal chemical title of ASDA.4Na ($C_8H_7NO_8Na_4$) is L-Asparaginic-N-N-diacetic, tetrasodium salt, which has a chemical structure similar to EDTA. ASDA is a novel biodegradable chelating reagent which was recently developed by Mitsubishi Rayon Co., Ltd..

The effect of ASDA concentration on Pb elution from vermiculite is shown in Fig. 2. In general, ASDA is much effective for Pb extraction, especially from the sample with small particle size. In the low concentration region of ASDA ranging from 0.02 to 2 mmol/L, the removal of Pb increases with increasing concentration of ASDA; while the release of Pb is not enhanced with further increase of ASDA concentration, contrarily a little bit decreases. This phenomenon may be ascribed to the increase in viscosity of the solution at relatively high ASDA concentration, resulting in preventing the ASDA solution from contacting with the Pb-loaded vermiculite powder. The obtained result suggests that a stoichiometrically excess amount of ASDA is required to release the same amount of Pb compared with EDTA. The difference is probably due to the fact that the original solution of ASDA.4Na is alkaline.

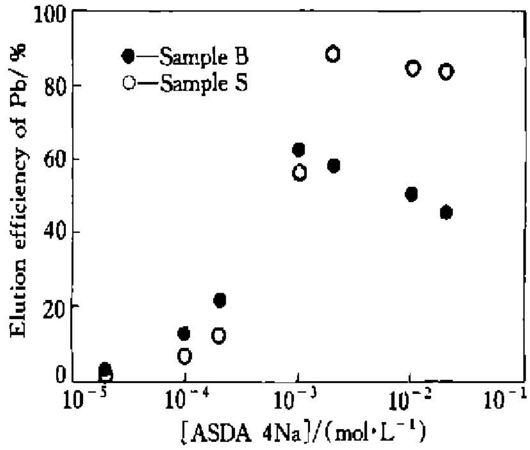

Fig. 2 Effect of ASDA.4Na concentration on elution of lead from vermiculite

3.1.3 Acetic acid

Although acetic acid is not a chelating reagent, the existence of the same functional group, carboxyl group, suggests the authors to compare its performance with EDTA and ASDA on Pb extraction from vermiculite. From the results shown in Fig. 3, it is seen that the acetic acid is not effective for Pb removal both from Sample B and Sample S. Although the elution increases with acetic acid concentration, it tends to become constant in high concentration region, indicating that excessive acetic acid is not effective for Pb removal.

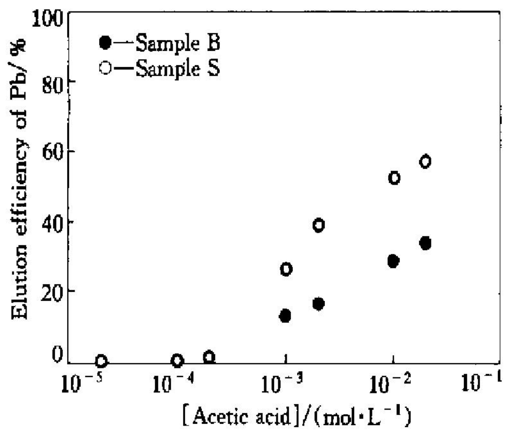

Fig. 3 Effect of acetic acid concentration on elution of lead from vermiculite

3.1.4 Depolymerized pectic acid

It was found in the previous work that pectic acid contained in some fruits such as oranges and apples has very high affinity to Pb and is suitable for selectively removing trace contamination of Pb from water[14]. Because pectic acid is water insoluble polysaccharide under usual condition, in this study, the water-soluble de-polymerized pectic acid, abbreviated as De-pectic acid hereafter, was prepared by depolymerizing pectic acid under high temperature and high pressure using an autoclave. The influence of the concentration of De-pectic acid on Pb extraction is illustrated in Fig. 4. From this figure, it was found that the increase in the concentration of De-pectic acid favors the removal of Pb. Under the optimum condition, 88.47% and 93.61% removal was achieved for Sample B and Sample S, respectively, proving that De-pectic acid may form strong water-soluble complexes with Pb. A little bit decrease in elution efficiency at 28 mmol/L, the highest concentration used in this study, may be attributed also to the increase in viscosity of the solution, thereby resulting in preventing the sample particle from contacting with the solution. It was also found that De-pectic acid cannot extract equivalent amount of Pb, namely excess of De-pectic acid is necessary to release all Pb from vermiculite.

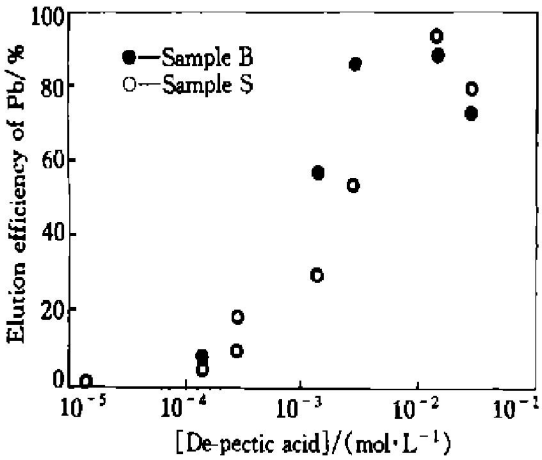

Fig. 4 Effect of De-pectic acid concentration on elution of Pb from vermiculite

3.2 Effect of equilibrium pH

3.2.1 EDTA

The effect of equilibrium pH on Pb elution by EDTA is shown in Fig. 5, where 2 mmol/L of EDTA.2Na was employed. The results shown in Fig. 5 demonstrates that the recovery of Pb favors acidic condition and decreases modestly as pH toward alkaline.

3.2.2 ASDA

Fig. 6 illustrates the influence of equilibrium pH on Pb elution in the case of ASDA, where the ASDA concentration adopted was 2 mmol/L. Although the original ASDA.4Na solution is alkaline, the result

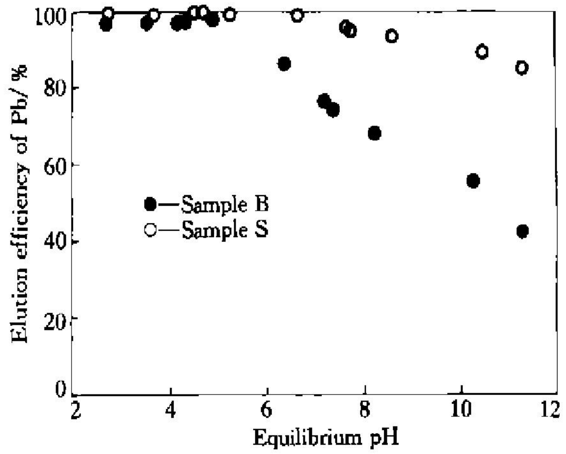

Fig. 5 Effect of equilibrium pH on elution of Pb from vermiculite by EDTA.2Na

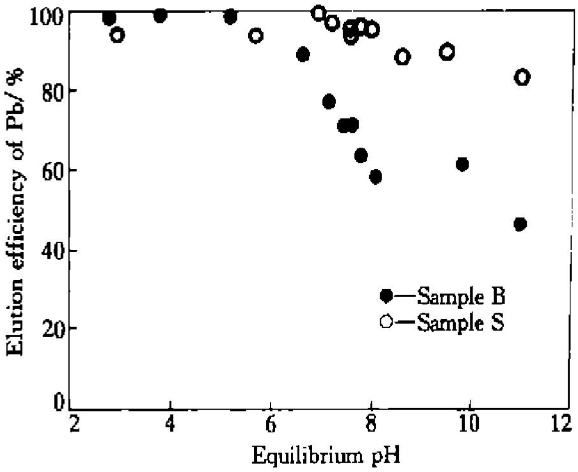

Fig. 6 Effect of equilibrium pH on elution of Pb from vermiculite by ASDA.4Na

demonstrates that, for Sample S, the effective Pb extraction may be achieved over wide pH range, while a little bit low elution was observed in strong alkaline media. On the other hand, in the case of Sample B, the Pb elution is quite pH sensitive, from which it can be concluded that the elution of Pb from Sample S seems easier than that from Sample B.

3.2.3 Acetic acid

Fig. 7 illustrates the result of lead removal by acetic acid at different equilibrium pH, where 2 mmol/L acetic acid solution was adopted. From this result, it is found that, in acidic media, the elution of Pb by acetic acid is pH dependent, while, in neutral and alkaline media, Pb extraction is not so sensitive to equilibrium pH. Similar to the extraction by ASDA, the elution from Sample S seems to be easier than that from Sample B. Conclusively, acetic acid cannot be considered as an effective reagent for Pb elution from vermiculite due to its weak coordination with Pb.

3.2.4 De-pectic acid

The effect of equilibrium pH on Pb removal from vermiculite by De-pectic acid is shown in Fig. 8. It is clear from this figure that De-pectic acid is quite

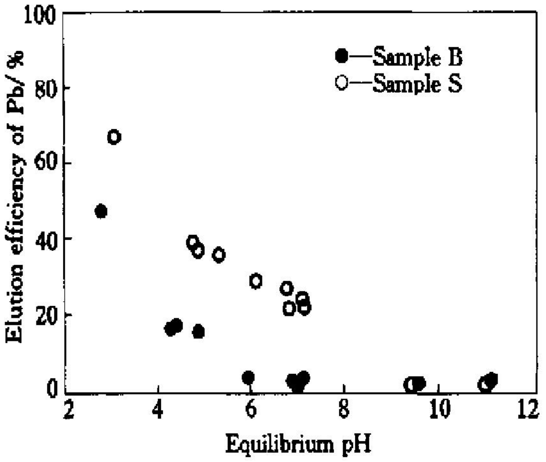

Fig. 7 Effect of equilibrium pH on elution of Pb from vermiculite by acetic acid

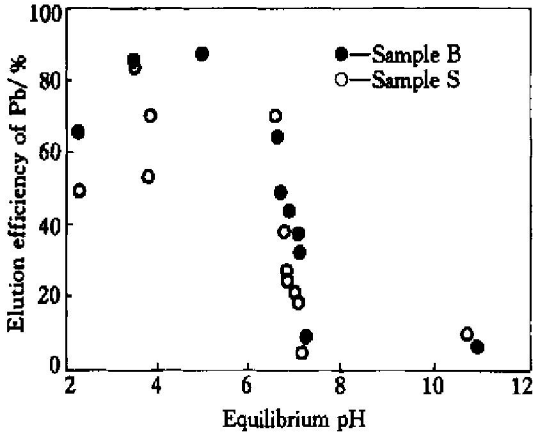

Fig. 8 Effect of equilibrium pH on elution of Pb from vermiculite by De-pectic acid

effective for Pb extraction under acidic media, that is, the optimum pH range for this reagent is 3~ 6. It is striking that the elution of Pb is suppressed in much strongly acidic region.

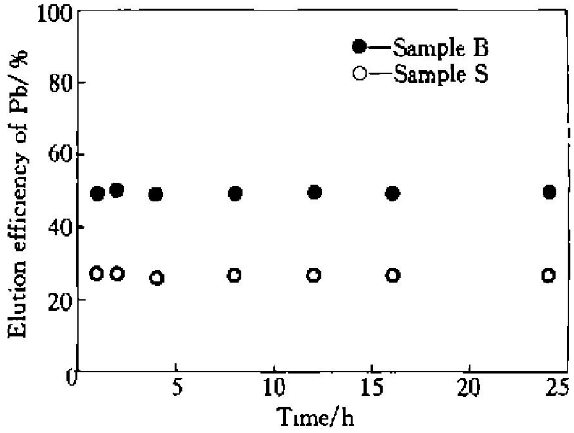

Fig. 9 Time dependence of lead elution from vermiculite by EDTA. 2Na

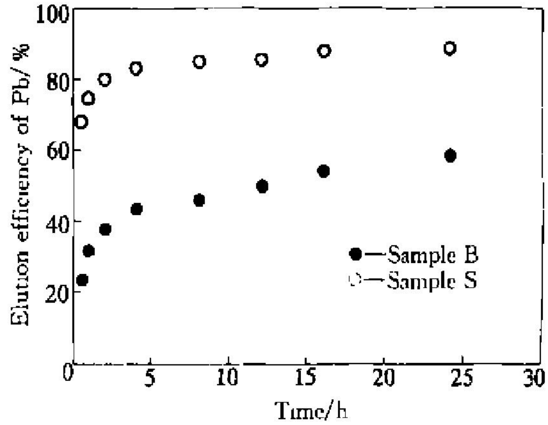

Fig. 10 Time dependence of lead elution from vermiculite by ASDA. 4Na

3. 3 Effect of suspension contact time

3. 3. 1 EDTA

The influence of suspension contact time on the elution by EDTA is shown in Fig. 9, where 0. 2 mmol/ L EDTA. 2Na was employed. It is quite clear that no matter the sample particle size, big or small, the elution process is rapid and independent on suspension contact time.

3. 3. 2 ASDA

In this case, 2 mmol/ L of ASDA. 4Na was employed. The results shown in Fig. 10 prove that the removal of Pb by ASDA is time dependent, i. e. with extending suspension contact time, the removal of Pb increases, especially, at the beginning of first several hours. From the result that under the same ASDA concentration, larger amount of Pb was released from Sample S than from Sample B, it is suggested that the process of Pb elution by ASDA from vermiculite is diffusion limited.

3. 3. 3 Acetic acid

In this case, the concentration of acetic acid used was 2 mmol/ L and the result is shown in Fig. 11. A little bit difference from other reagents employed, at the beginning of several hours, the Pb elution appears to slightly decrease and then tends to become constant. It is considered that Pb extraction process by acetic acid is just acid dissolution of vermiculite matrix, which is strongly controlled by the acidity of solution. With the consumption of acid increase during the elution, especially at the beginning of several hours, the pH of aqueous solution increases, resulting in re-precipitation of the once dissolved Pb as hydroxide due to weak coordination ability of acetic acid. Thereafter, since pH is kept constant, Pb will be no longer eluted.

3. 3. 4 De-pectic acid

The effect of suspension contact time on Pb elution by De-pectic acid is shown in Fig. 12, in which the concentration of Sample S1 was 2. 8 mmol/ L, and that of Sample S2 14 mmol/ L. Similar to the case of ASDA, Pb removal increases with suspension contact time in the cases of Sample B and Sample S2, suggesting that the elution process is diffusion controlled. The irregular results for Sample S 1 may be attributed

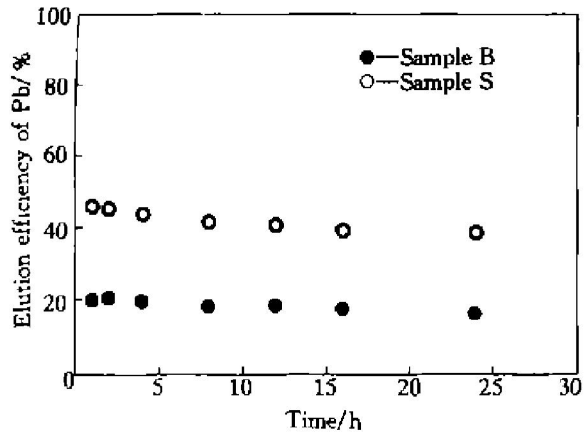

Fig. 11 Time dependence of lead elution from vermiculite by acetic acid

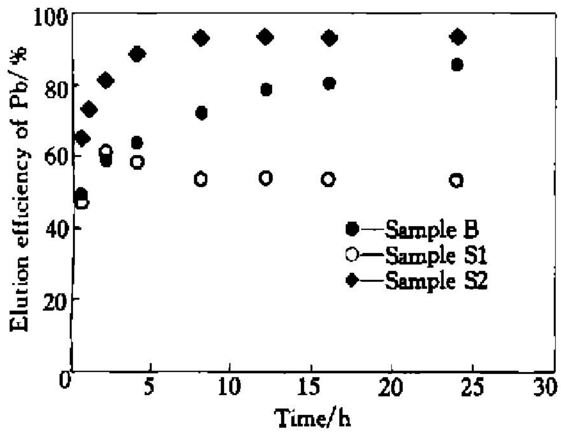

Fig. 12 Time dependence of lead elution from vermiculite by De-pectic acid

also to the re-precipitation of Pb because of the relatively low concentration used for Sample S, which may be evidenced by the observation that the filtrate become turbid and there appeared colloid formation after the filtration.

4 CONCLUSIONS

1) Removal of lead from contaminated vermiculite was found to be possible by applying some chelating reagents. Lead may be easily released by stoichiometric amount of EDTA. ASDA and De-pectic acid are effective reagents for Pb removal in acidic media, however excessive stoichiometric amount is necessary for Pb extraction and the elution process is diffusion limited. Acetic acid is not effective due to its weak coordinating ability with Pb.

2) EDTA is by no means the preferable alternative for the purpose because of its low biodegradability while ASDA and De-pectic acid have the potential application because they are effective for Pb elution and environment friendly. The achievements in this study may provide a fundamental knowledge for the lead removal and recovery from contaminated soil.

Acknowledgement

This work was financially supported in part by grant in aid for exploratory research by JSPS (No. 11678102) and by Kurita Water Industries Ltd. The authors are also grateful to Mitsubishi Rayon Co., Ltd. for providing the sample of ASDA.

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(Edited by YUAN Sai-qian)