Removal of Lead from Vermiculite by Using L-Asparaginic-*N*,*N*-diacetic Acid, a Novel Biodegradable Chelating Reagent, and Depolymerized Pectic Acid

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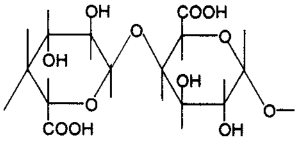
(Received Feburuary 15, 2001; CL-010128)

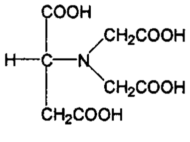
The removal of lead from vermiculite by means of elution with two kinds of novel chemical reagents L-asparaginic-*N*,*N*-diacetic acid and depolymerized pectic acid, was investigated. The effects of contact time, concentration of the reagents and equilibrium pH of solution on elution of lead were examined by batch-wise technique. It was found that both of the reagents are effective for the removal of lead and have the potential application for the remediation of soil polluted by heavy metals.

In recent years, there have been reported many sites, especially former sites of various plants such as chemical plants, which are polluted with oils, toxic organic materials such as PCB and heavy metals not only in the United States and Europe but also in Japan. Among the sites polluted with heavy metals, the most frequently observed contamination have been those with lead. Several methods have been proposed for remediating sites polluted with heavy metals. Among them, soil flushing and soil washing are promising methods.[1] In both cases, strong chelating reagents such as EDTA and NTA have been employed as the elution reagents for heavy metals. Although these chelating reagents are very effective for the purpose as such, they are too chemically stable and are not biologically decomposed by microorganisms in nature, which means that they have a high possibility to develop another pollution in soil or ground water. Actually, their uses were decided to be prohibited in near future in Europe.

Recently, Mitsubishi Rayon Co., Ltd. developed a novel biodegradable chelating reagent, L-asparaginic-*N*,*N*-diacetic acid, abbreviated as ASDA hereafter, which has a chemical structure similar to EDTA.[2] On the other hand, the authors found in the previous work that pectic acid contained in some fruits such as oranges and apples as well as alginic acid contained in brown sea weeds, acidic polysaccharides containing carboxylic groups, have very high affinity to lead and are suitable for selectively removing trace contamination of lead from water.[3] Although these polysaccharides are water insoluble under usual condition, we found that pectic acid can be depolymerized under high temperature and high pressure and the depolymerized products become water-soluble.



pectic acid



ASDA

Since these two reagents, ASDA and depolymerized pectic acid, may be environmentally benign chelating reagents alternative to EDTA or NTA, we conducted in the present work the elution tests of lead by employing them as elution reagents from vermiculite, a clay mineral with high loading capacity for lead, as first one of a series of fundamental investigations of removal of heavy metals from polluted soils.

The original crude vermiculite sample purchased from Kinseimatec Co., Ltd. was crushed and sieved. The fraction of 104 –208 μm was dried and used in this study after saturated with lead. The amount of lead adsorbed on the sample was measured and determined as 817 meq kg^{-1}.

The concentrated ASDA·4Na aqueous solution was kindly donated by Mitsubishi Rayon Co., Ltd. The depolymerized pectic acid, abbreviated as De-pectic acid hereafter, was prepared at 130 °C and 0.24 MPa for 60 min in an autoclave by depolymerizing sample of pectic acid, which has the molecular weight around 200000 and was purchased from Katayama Chemical Industries Co., Ltd. The concentration of De-pectic acid stated in the subsequent part denotes the total concentration of carboxylic groups measured by means of neutralization titration.

Elution tests were carried out batch-wise as follows. In each experiment, 20 mg of vermiculite was mixed together with 0.02 dm^3 of aqueous test solution in a flask and shaken in a water bath incubator maintained at 30 °C. 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 of lead was measured using a flame atomic absorption spectrophotometer (SAS 7500, Seiko Instrument). Initial and equilibrium pHs after elution were measured by using a pH meter (Beckman modelΦ45).

Although it was found that the equilibrium was not satisfactorily attained even by shaking for 25 h for the lead elution with 2 mM (M = mol dm^{-3}) ASDA and 2.8 mM De-pectic acid, the subsequent experiments were carried out by shaking for 24 h from the practical point of view.

Figure 1 illustrates the plots of the % elution of lead as well as equilibrium pH against reagent concentration in the elution with De-pectic acid and EDTA for comparison. Figure 2 illustrates the similar plots in the elution with ASDA and EDTA. It can be seen that increasing the reagent concentration favors the removal of lead from vermiculite, suggesting that both ASDA and De-pectic acid are effective for lead elution by giving rise to stable water-soluble complexes. However, the excess of stoichiometric amounts of these chemical reagents is required to achieve the complete removal of lead, while only the stoichiometric amount of the reagent was enough to accomplish the complete removal in the case of EDTA. The decrease in elution efficiency at higher concentration which is more remarkable for De-pectic acid may be due to increase in viscosity of solution, resulting in preventing the reagent molecules from penetrating into the inner parts of solid particles. On the other hand, the unsatisfactory removal by ASDA is owing to the fact that its alkaline sodium salt was employed in the elution test and, consequently, the pH increased

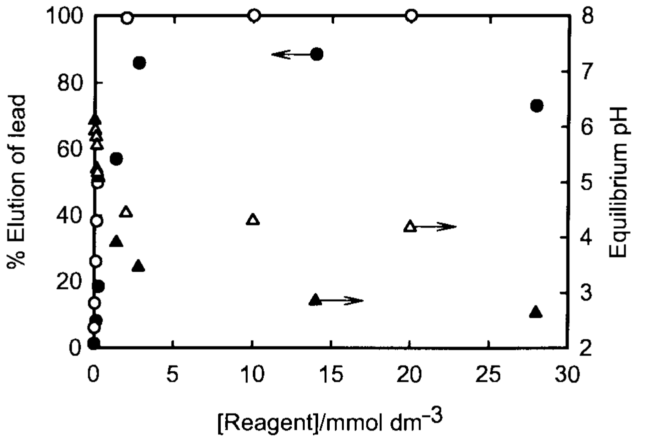


Figure 1. Effect of reagent concentration on elution of lead from vermiculite: ●, % elution vs concentration for De-pectic acid; ○, % elution vs concentration for EDTA; ▲, equilibrium pH vs concentration for De-pectic acid; △, equilibrium pH vs concentration for EDTA.

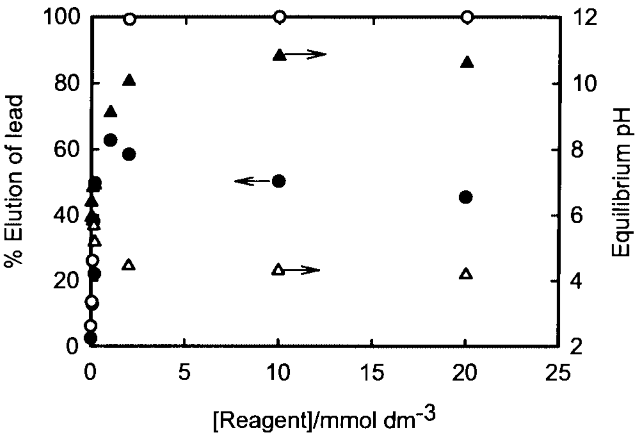


Figure 2. Effect of reagent concentration on elution of lead from vermiculite: ●, % elution vs concentration for ASDA; ○, % elution vs concentration for EDTA; ▲, equilibrium pH vs concentration for ASDA; △, equilibrium pH vs concentration for EDTA.

with increasing the reagent concentration.

The effect of equilibrium pH on the lead elution from vermiculite by these two chemical reagents in comparison with EDTA and acetic acid are shown in Figures 3 and 4. In this case, 2.8 and 1.4 mM De-pectic acid were employed while the concentrations of ASDA, EDTA and acetic acid were 2 mM. From these figures, it is evident that acetic acid is not effective for the removal of lead from vermiculite while high elution of lead may be achieved over a wide pH range by using 2 mM ASDA, suggesting strong complexing ability of ASDA similar to EDTA. On the other hand, De-pectic acid is quite effective for lead elution under acidic condition and the optimum pH range is between 3 and 6.

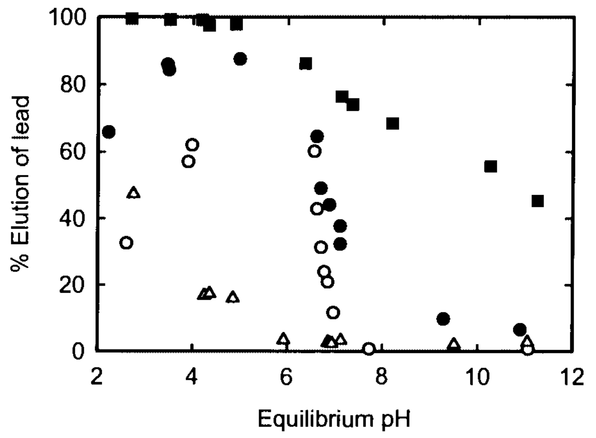


Figure 3. Effect of equilibrium pH on elution of lead from vermiculite: ■, 2 mM EDTA; ●, 2.8 mM De-pectic acid; ○, 1.4 mM De-pectic acid; △, 2 mM acetic acid.

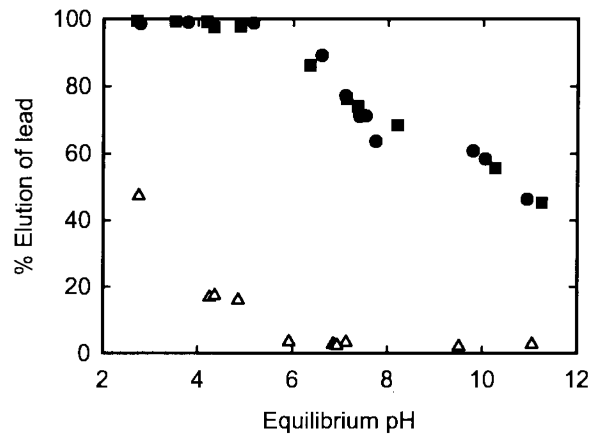


Figure 4. Effect of equilibrium pH on elution of lead from vermiculite: ●, 2 mM ASDA; ■, 2 mM EDTA; △, 2 mM acetic acid.

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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