The Effect of Humic Substances on Pb(II) Adsorption on Vermiculite

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Adsorption of lead ion from aqueous solutions containing humic substances on vermiculite was investigated. Humic substances exhibited a strong influence on lead adsorption on vermiculite. The adsorption of humic acids on vermiculite plays an important role in lead ion distribution between the clay mineral and aqueous solution. There are remarkable differences in adsorption behaviors of humic acid itself among the humic acids taken from different origins. Adsorption behaviors of lead from aqueous solution containing fulvic acids were found to be less dependent on their origins, which may be attributable to negligible adsorption of fulvic acids on vermiculite.

Humic substances are natural organic compounds found in soils, ground waters and coals. They play an important role in speciation and migration of heavy metals in the environment. Formation of stable metal humate can also adversely affect the removal of heavy metals by means of ion exchange, adsorption and precipitation. Humic substances are formed from the decomposition products of organic matter and they contain substituted aromatic rings, aliphatic acids, amino acids, heterocycles etc. For metal ion binding, carboxylic and phenolic hydroxyl groups are the most important constituents of humic substances.[1,2] Soluble humic substances can be classified into two main groups, humic acids (HA) and fulvic acids (FA). FA are compounds of lower molecular weight and are soluble in both basic and acidic solutions, whereas HA are those of higher molecular weight and are not soluble in acidic solutions (pH<2). HA in soil are strongly adsorbed on clay minerals.[3-5]

In this work, adsorption of lead from aqueous solutions containing various concentrations of FA or HA on commercial vermiculite was investigated in order to obtain fundamental information related to the effect of humic substances on the migration of heavy metals in soil and water environment in detail. Here, lead was selected as a representative heavy metal for its high affinity to humic substances.[2,6] Vermiculite was used as a representative clay mineral for its very high cation exchange capacity.[7] Vermiculite (Kinseimatec co.) was crushed and passed through the set of sieves to make the particle size uniform. The fraction 170-200 mesh was vacuum dried. HA and FA taken from different origins (Dando, Inogashira and Aso), prepared according to the International Humic Substances Society (IHSS) standard method were used.[8,9] Abbreviations DFA, IFA, AFA, DHA, IHA and AHA will be used hereafter, which denote Dando FA, Inogashira FA, Aso FA, Dando HA, Inogashira HA and Aso HA, respectively.

To an aqueous solution containing 0.1 mmol dm^{-3} Pb(II), 0.1 mol dm^{-3} HEPES buffer and 0.1 mol dm^{-3} HNO_3, FA or HA was added in the amount ranging from 125 to 500 ppm. Initial pH of the solutions was adjusted by adding a concentrated NaOH(10%wt.) solution. 5 ml portion of this solution was shaken together with 20 mg of vermiculite at 30 °C for 24 h. After shaking, the solution was filtrated and the concentrations of lead and FAor HA were measured by an atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100) and by UV-VIS spectrophotometer (Shimadzu UV-160), respectively.

Figure 1 illustrates the effect of FA from different origins on % adsorption. As seen from this figure, vermiculite exhibits a strong adsorption ability to lead. Adsorption increases with increasing pH, suggesting that lead adsorption competes H^+ ion binding to vermiculite. FA seriously impedes the adsorption of lead on vermiculite, and in all cases, the increase in FA concentration results in the decrease in adsorption. Effect of FA becomes significant at pH greater than about 3 which corresponds to the dissociation of carboxylic groups of FA.[10]

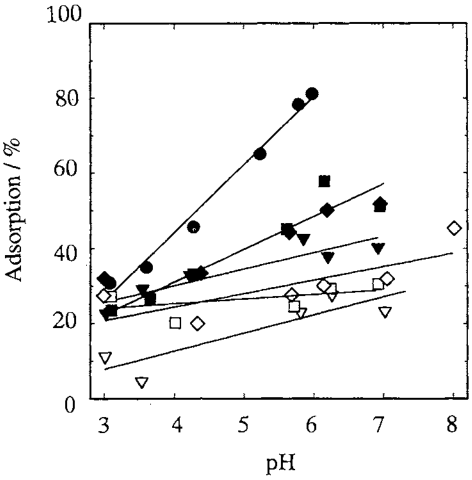

Figure 1. Effect of FA on the adsorption of Pb(II) on vermiculite. ● :Pb, ▼ : Pb+250 ppm DFA, ▽: Pb+500 ppm DFA, ■: Pb+250 ppm IFA, □: Pb+500ppm IFA, ◆: Pb+250 ppm AFA, ◇: Pb+500 ppm AFA.

Figure 2 illustrates the effect of HA. In contrast to the case of FA, there appears significant influence of HA on Pb adsorption, strongly dependent on their origin. This might be attributable to the adsorption of HA itself on vermiculite which may play an important role in the lead distribution between the solution and solid phases because lead is well known to give rise to stable complexes with HA as mentioned above.

Figure 3 illustrates the pH dependency of the adsorption of HA themselves on vermiculite, this figure demonstrates that adsorption of HA is strongly dependent on their origin.
Adsorption of DHA itself decreased from 70% down to 10%, with increasing pH ranging from ca. 4 to ca. 7, indicating that at the higher pH region main portion of DHA is in aqueous phase similar to FA. On the other hand, % adsorption of FA were negligible in all cases of DFA, IFA and AFA over whole pH.

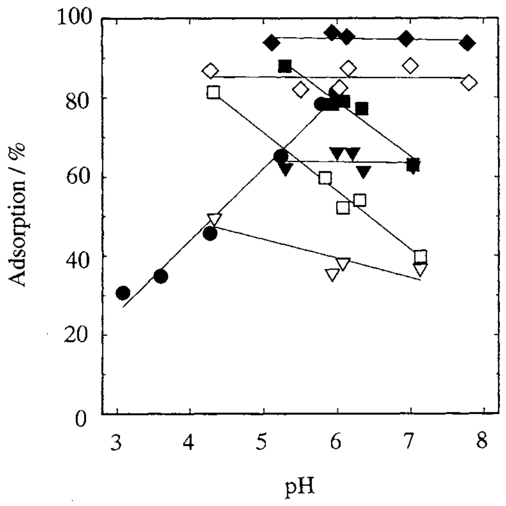

Figure 2. Effect of HA on the adsorption of Pb(II) on vermiculite. ● :Pb, ▼ : Pb+125 ppm DHA, ▽: Pb+250 ppm DHA, ■: Pb+125 ppm IHA, □: Pb+250ppm IHA, ◆: Pb+125 ppm AHA, ◇: Pb+250 ppm AHA.

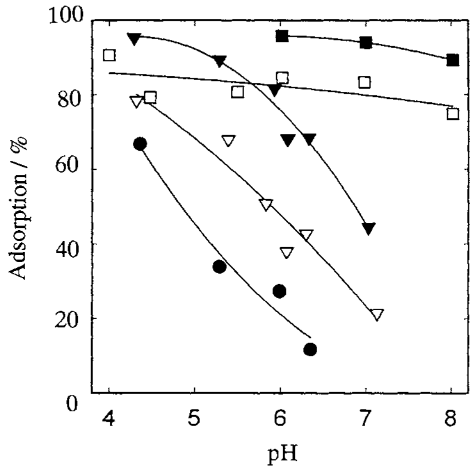

Figure 3. Adsorption of HA itself on vermiculite. ● :125 ppm DHA, ▼ : 125 ppm IHA, ▽: 250 ppm IHA, ■: 125 ppm AHA, □: 250ppm AHA.

In Figure 2, the effect of IHA on the adsorption of lead is much more different from that of DHA. IHA was more strongly adsorbed on vermiculite than DHA, as shown in Figure 3. When the concentration of IHA was 125 ppm, about 95% of HA was adsorbed at lower pH (4-5), while with increasing pH, % adsorption decreased down to 45% at pH 7. In Figure 2, lead adsorption from the solution containing IHA similarly decreased with increasing pH. At low pH where IHA is almost completely adsorbed, the amount of lead adsorbed from the solution containing IHA is higher than that from the solution without IHA, suggesting that lead may be co-adsorbed on vermiculite as lead humate together with HA, i.e., IHA is considered to be strongly adsorbed on vermiculite keeping lead within the solid phase. With increasing concentration of IHA, % adsorption of both lead and IHA itself decreases because adsorption of IHA itself has been saturated (at pH 4.5 maximum adsorption of IHA was about 16 mg/g dry vermiculite). Consequently, further increase of IHA concentration results in the increase of the portion of HA which is not adsorbed on vermiculite and keeps lead in the solution.

AHA is strongly or nearly quantitatively adsorbed on vermiculite over the whole pH investigated, which is different from the case of IHA. % adsorption of lead decreases with increasing AHA concentration and was nearly independent of pH similar to the adsorption of AHA itself.

The adsorption of HA on layered clay minerals from acidic and neutral solutions, is considered to occur on the edge surface of clay mineral due to opposite charge between negatively charged HA and positively charged edge surface.[5]

Since there is no remarkable difference in the functional group contents among DHA, IHA and AHA, the difference in the adsorption behavior on vermiculite among the HA samples can be ascribed not only to the electrostatic interactions but also to the hydrophobic interactions. The aromatic (hydrophobic) portion of HA molecules is strongly adsorbed on vermiculite whereas their hydrophilic portions are oriented to aqueous phase staying available for the lead binding. The aromaticity of IHA skeleton is higher than that of DHA, which can probably explain their different adsorption behavior.

Much more attention should be paid to the structures of HA skeleton which can significantly affect the metal ion migration in the environment through the adsorption to HA/clay mineral matrix.

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References

1 D. S. Gamble, J. A. Marinsky, and C. H. Langford, *Ion Exch. Solvent Extr.*, **9**, 373 (1985).
2 E. Tipping and M. A. Hurley, *Geochim. Cosmochim. Acta,* **56**, 3627 (1992).
3 H. Farrah and W. F. Pickering, *Proc. N. Z. Semin. Trau. Elem. Health,* **2nd**, 192 (1979).
4 M. D. Taylor and B. K. G Theng, *Commun. Soil. Sci. Plant. Anal.*, **26**, 765, (1995).
5 M. Koyama, *Soil Sci. Plant Nutr.*, **41**, 215 (1995).
6 S. Z. Zhrobekova, G. M. Mal'tseva, and K. A. Kydralieva, *Biol. Nauki (Moscow),* **10**, 571 (1991).
7 V. Jedinakova-Krizova, *J. Radioanal. Nucl. Chem.*, **208**, 559 (1996).
8 A. Watanabe, K. Itoh, S. Arai, and S. Kuwatsuka, *Soil Sci. Plant Nutr.*, **40**, 601 (1994).
9 S. Kuwatsuka, A. Watanabe, K. Itoh, and S. Arai, *Soil Sci. Plant Nutr.*, **38**, 23 (1992).
10 T. Miyajima and M. Mori, *Bunseki Kagaku*, **45**, 369 (1996).