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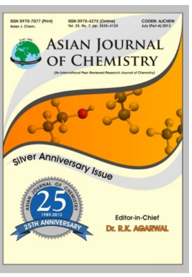

Adsorption/Ion Exchange of Metal ions on Clay Mineral Surfaces†

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This research aimed to investigate the removal of metal ions, such as Al^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+}, by adsorption or ion exchange on clay minerals. Refined natural bentonite (raw-bentonite), Ca^{2+} and Na^+ ion exchanged bentonite (Ca- and Na-bentonite) and commercial montmorillonite KSF and K10 from Sigma Aldrich, were used. The component of five inorganic clays was analyzed by XRF. The concentration of metal ions was measured by ICP. The cation exchange capacity and the particle charge of clay minerals were measured. The initial concentration range of metal ions was 10-100 ppm. From the experimental results, it was shown that the adsorption equilibrium was obtained within 1-2 h. The maximum percentage removals of Al^{3+}, Cu^{2+}, Pb^{2+} and Zn^{2+} on Na-bentonite was more than 98 % and that of Mn^{2+} was 66 %. Al^{3+} was leached out from KSF because of increased H^+ concentration. In general, the percentage removal of metal ions was decreased with increasing of the initial concentration of metal ions. The adsorption capacity of metal ions was in the order of Na-bentonite >> raw-bentonite ≅ K10 >Ca-bentonite > KSF. The Freundlich constant (K) of Na-bentonite was the largest for metal ions. The order of Freundlich constant (K) of Na-bentonite on metal ions was $Al^{3+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Mn^{2+}$ and the adsorption intensity (1/n) was determined to be 0.2 to *ca.* 0.39.

Key Words: Adsorption, Ion exchange, Metal ions, Clay mineral surfaces.

INTRODUCTION

If various types of dissolved heavy metals flow into the water system, they cause serious environmental problems such as critical hazard to the life of creatures. Even a very small amount of heavy metals exists in the water system, can enter and accumulate in the human body through various channels such as food chains to cause chronic poisoning symptoms. Thus it is required to process pollutants harmless to the human body.

Clay minerals, which exist affluently in the nature, are important composition of soil or geological feature media and since they have a relatively wide surface area and an excellent capability at ion exchange or adsorption, they play an important role in adsorbing pollutants. Bentonite, a reprehensive clay mineral, is widely used for a liner to prevent the soil or underground water around the landfill from being contaminated.

Therefore, this study was planed to compare and analyze differences in the degree of adsorption/ion exchange of metal ions such as Al^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+} on their surfaces between natural bentonite, calcium-type and sodium-type bentonites and KSF and K10 of montmorillonite under a certain pH and various experimental condition.

EXPERIMENTAL

Purifications of natural bentonite: The natural bentonite supplied by Südchemi, Korea was purified by sedimentation and centrifugation. The clay fraction with a diameter smaller than 63 μm was used in this study. The purified bentonite was ion exchanged with Na^+ and Ca^{2+} ions by stirring for 30 min and shaking with 150 rpm for 18 h in a 120 % concentration solution of Na_2CO_3 and $CaCl_2 \cdot 2H_2O$ compared with cation exchange capacity (CEC) of raw bentonite, then ion exchanged clays were separated by centrifugation with 3900 g of R.C.F from mixture of working clay slurry and deionized water (1:5). Centrifuged and separated clays were dried in 50 ºC for 48 h. After sieved again, they were stored in desiccators for use.

Characterization of clay minerals: The pH was measured with a 10 % solution after aging of 10 min using the pH meter (istek model 720 p, Korea). Swelling property was measured from the height of sediments after stabilization. The surface area was measured by EGME method[1]. Cationic exchange capacities of clays were measured by cations exchange method[2]. X-ray fluorescence data was collected on a Rigaku RIX 2100 spectrometer. Surface charges of clays were measured with particle charge detector (PCD O_3 pH, Mütek, Germany).

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TABLE-1
PHYSICOCHEMICAL PROPERTIES OF CLAYS

	Raw-B	Purified- B	Ca-B	Na-B	KSF	K10
pH	8.45	7.03	8.00	10.63	1.82	7.90
Swelling volume (mL/^{2}g)	7	11	10.5	85	4.5	5.5
Surface area (m^2/g)	496.9	660.8	501.5	657.9	448.7	512.5
CEC (meq/100g)	55.42	45.34	47.31	145.52	65.19	64.09
Specific charge density (μeq/g)	-10.43	- 5.73	- 8.53	- 180.50	- 1.25	- 6.33

TABLE-2
CHEMICAL COMPOSITIONS OF CLAY MINERALS

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	Na_2O	P_2O_5
Raw -B	63.2	23.1	4.54	4.01	3.84	0.627	0.431	0.183	0.064
P- B	61.2	25.10	5.25	4.53	2.88	0.542	0.394	0.067	0.029
Ca-B	61.1	25.2	5.32	3.89	3.59	0.512	3.384	0.061	0.027
Na-B	58.7	23.3	4.83	3.86	5.05	0.637	0.421	3.230	0.031
K10	54.4	26.9	7.36	5.42	4.12	1.170	0.436	0.146	0.062
KSF	55.6	26.8	7.32	5.14	3.16	1.330	0.427	0.128	0.079

*P-B: Purified Bentonite

Adsorption procedure: The adsorption experiments were carried out using the batch equilibrium technique and adsorption condition was simulated in advance by chemical equilibrium software (MINEQUL+, USA). For each isotherm for metal ions, a given amount (1 g) of clays was weighed into 250 mL Erlenmeyer flask and 200 mL of mixed metal solutions of given concentrations (10, 25, 50 and 100 mg/L as Zn^{2+}, Pb^{2+}, Cu^{2+}, Al^{3+}, Mn^{2+} respectively) were added. And pH values of solutions were adjusted by using 0.1 N NaOH to pH 5 in advance. The suspensions were shaken with 150 rpm in a shaking incubator (JEIO TECH SI-900R, Korea) of 25 ºC for 2 h and each 10 mL of samples were drown with intervals of 5 min, 30 min, 1 h and 2 h. After phase separation by centrifugation with 4000 rpm for 20 min, the concentrations of metal ions in the supernatant were determined by ICP (Thermo elemental, Model IRIS DUO, USA).

RESULTS AND DISCUSSION

Physicochemical properties of clay minerals: Table-1 shows the physicochemical properties of clay minerals. With the exception of the acid-treated KSF (pH 1.82), a montmorillonite-based clay mineral, most of clay minerals showed a pH value range of 7.03 to 10.63.

Na-bentonite showed a swelling capacity of 85 mL, while other clay minerals showed a swelling volume of 4.5 to 11 mL. The surface areas of clays were in the range of 449-661 m^2/g.

The CEC of Na-bentonite was 145.52 meq/100 g, the highest among clay minerals. The CEC of other bentonite-based clay minerals was between 47 and 55 meq/100 g. The CECs of montmorillonite-based KSF and K10 were approximately 65 and 64 meq/100 g, respectively. XRF data were represented in Table-2.

Adsorption/ion exchange of metal ions: The equilibrium state of adsorbates in solution was simulated using MINEQL+. And it was found that when five types of adsorbates (Al^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}) were mixed together, no reaction occurred between adsorbates.

Adsorption equilibrium on Pb^{2+} and Zn^{2+} by using raw-bentonite 1 g was plotted in Fig. 1. From these results, it appropriate to set the contact time required to 2 h and to range the initial concentration of adsorbates from 10 to 100 mg/L.

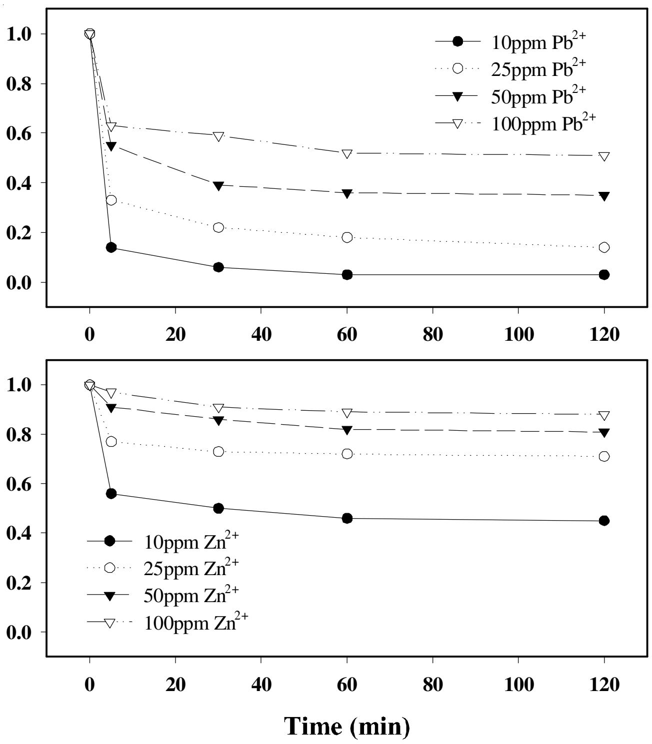

Fig. 1. Residual concentration variations of Pb^{2+} and Zn^{2+} ions according to contact time under the different initial concentrations for the raw-bentonite

To compare the percentage removal of Al^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+} by using clay minerals, as well as their adsorption capacity, adsorption experiments for 2 h were performed. For example, Fig. 2 shows the percentage removal of the Al^{3+} ion by using clay minerals and its adsorption capacity. With the exception of KSF, using clay minerals resulted in a higher percentage removal of above 98 %, regardless of initial concentrations. In addition, with the initial concentration of metal ions increasing, the adsorption quantity of Al^{3+} per 1 g-clay continuously increased in a range between 2 mg/g and 19 mg/g. On the other hand, KSF showed no percentage removal of Al^{3+} and rather, the use of KSF as an adsorbent caused Al^{3+} to be leached out at the low initial concentration.

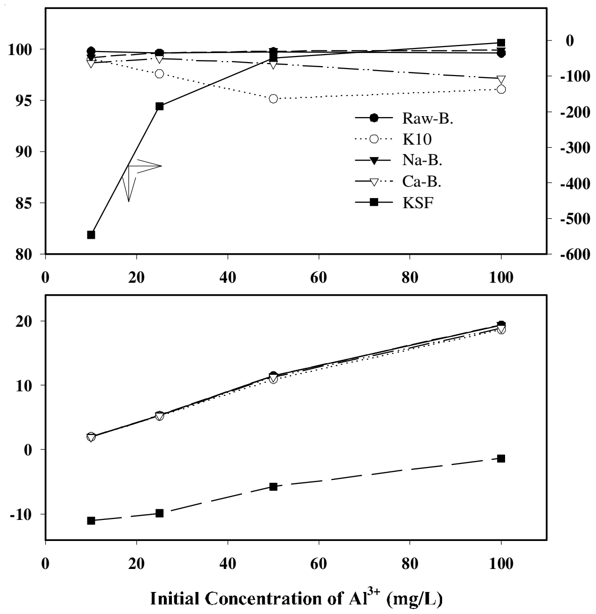

Fig. 2. Removal and adsorbed amount of Al^{3+}

The use of Na-bentonite also resulted in a continuously higher percentage removal (above 98 %) of Cu^{2+}, regardless of initial concentrations. It was also observed that the adsorption capacities of clay minerals on Mn^{2+} were significantly smaller than that on Cu^{2+}. In particular, the adsorption capacity of KSF was very small (below 1 mg/g).

Fig. 3 shows the percentage removal of Pb^{2+} and their adsorption capacity. Likewise, using Na-bentonite resulted in the highest percentage removal. What is particularly noteworthy is that KSF showed a relatively high percentage removal (70-88 %). This phenomenon can be found in studies conducted by Robert[3] and Gozen *et al.*[4]. For the adsorption capacity of clay minerals on Pb^{2+}, Na-bentonite and KSF showed a gradual as their initial concentrations increased.

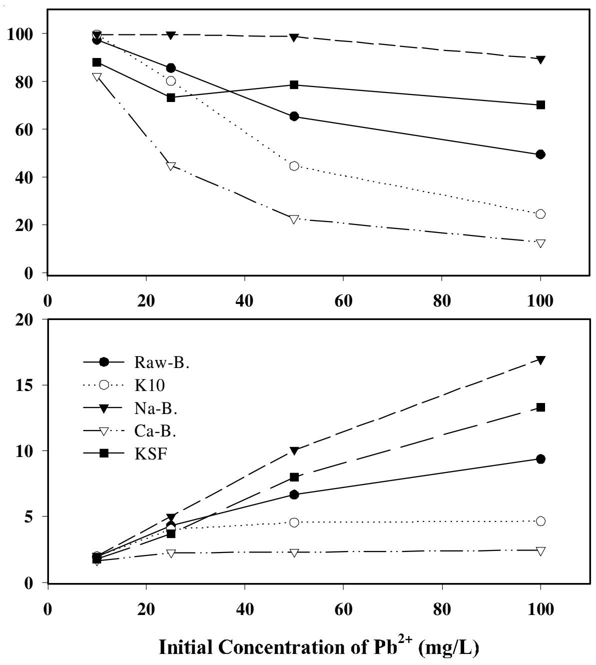

Fig. 3. Removal and adsorbed amount of Pb^{2+}

For Zn^{2+}, KSF showed different percentage removal with respect to the previous one. The adsorption capacity of raw-bentonite was smaller (below 2 mg/g), but that of other adsorbents increased linearly in a range between 1 mg/g and 10 mg/g, as a result of increasing initial concentrations.

To find the value of K and 1/n from the gradient and intercept on an adsorption isotherm, an algebraic expression was applied to the Freundlich equation through which graphs were drawn and the linear regression analysis equation was applied:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e$$

TABLE-3
CONSTANT (k) AND CORRELATION COEFFICIENTS (1/n)

		Raw-B.	K10	KSF	Na-B.	Ca-B.
Al^{3+}	K	42.5	7.1	-	$10^{6.3}$	10.7
	1/n	0.79	0.57	-	5.52	0.70
Cu^{2+}	K	3.0	3.1	0.02	15.4	1.2
	1/n	0.35	0.27	0.88	0.39	0.37
Mn^{2+}	K	0.43	0.83	0.007	1.07	0.76
	1/n	0.45	0.13	0.59	0.20	0.10
Pb^{2+}	K	2.88	3.02	1.41	8.71	1.62
	1/n	0.30	0.12	0.65	0.36	0.10
Zn^{2+}	K	0.83	0.35	$.8\times10^{-6}$	3.63	0.16
	1/n	0.21	0.86	4.09	0.28	1.04

Conclusion

Na-bentonite showed the highest percentage removal of Al^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+} more than 98 %, with the exception of Mn^{2+} (66 %). On the contrary, KSF was observed to leach out Al^{3+}. The largest amount of each adsorbed metal ion per 1 g was observed in the order of Na-bentonite >> raw-bentonite ≈ K10 > Ca-bentonite >> KSF. This tendency can be seen from the analytical results of cation exchange capacity (CEC), specific charge density and the hydrogen ion concentration. From the Freundlich adsorption isotherms, the value K of Na-bentonite on all metal ions was the largest and the value 1/n ranged from 0.2 to 0.39. The highest adsorption capacity on Na-bentonite was observed in the order of $Al^{3+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Mn^{2+}$.

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