

Adsorption behavior of heavy metal ions in the solutions of clay minerals under various conditions

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The adsorption rates and characteristics of heavy metal ions (Cd, Cr, and Zn) were examined with solutions mixed with red clay, white clay, a mixture of red & white clay and zeolite under various pHs and initial concentrations. As expected, adsorption rates of heavy metal ions generally increased with increasing pH; however, Cr showed a particular behavior. A mixture of red & white clay among the clay minerals tried in this study showed the highest Cr adsorption rate at the low pH conditions (lower than pH 5) and red clay with additions of Cu, Fe and Pb ions at pH 5 showed above an 85% adsorption rate of Cr which was far from expectations. From the result, it is concluded that the adsorption characteristics of heavy metal ions depend not only on the physical properties of the absorbent itself such as the cation exchange capacity (CEC) but also on the concentration and existence of exchangeable cations, pH, ligands, etc..

Key words: Heavy Metal Adsorption Rate, Cation Exchange Capacity, Red Clay, White Clay, Zeolite.

Introduction

The total amount and types of waste have increased due to rapid industrial development in recent years. A focus on environmental problems caused by industrial wastes, especially those containing heavy metals, has increased and studies on their safe treatment have been intensively investigated [1-5]. One of the prospective methods for safe treatment of inorganic industrial wastes is to make ecological construction materials such as light weight aggregates, bricks, etc. with an appropriate treatment before or after ceramic processing.

Ecological construction materials recycled from inorganic wastes containing heavy metals (which are strictly controlled by most governments and expensive to treat properly or safely reclaim) may have a leaching problem for long term use if the wastes are not properly treated. The leaching problem of heavy metals in inorganic wastes can be resolved by using several steps of ceramic processing such as ion exchange, hydration, and sintering processes which can stabilize heavy metals in the wastes [2, 3].

It is known that there are three processes which show how to move heavy metal ions to a solid phase in an aqueous solution state [4]. The first process uses both physical adsorption by an ion exchange reaction or van der Waals forces and chemical adsorption by the bonding between the surface of clay minerals and ions containing different charges. The second is to make

mixtures by bonding with ligands and the third is to make a new solid phase by sedimentation on the surface of clay minerals. The above three processes do not occur independently; however, all three processes are simultaneously present and they are in competition in most cases. However, the dominant process can be changed by altering the conditions.

The surfaces of clay minerals are commonly charged because of incomplete ionic exchange; therefore, electrical neutralization of the surface can be achieved by the adsorption of differently charged ions from the outside. Clay minerals are known to be good adsorption materials for cations because they have a large specific surface area and their surfaces are negatively charged [5]. The heavy metal adsorption properties of clay minerals are dependant not only on the physical and chemical characteristics of the clay minerals themselves such as the existence and amount of organic materials within them, exchangeable cations, amorphous oxides, etc. but also on the chemical compositions and conditions of heavy metal solutions such as the pH, competing cations, ionic strength, and types of ligand [6-12]. Generally, the adsorption of heavy metal is activated under high pH conditions.

In this study, 3 heavy metal (Cd, Cr, and Zn) standard solutions with concentrations of 5, 10, 15, and 20 ppm under a fixed pH (pH 5) and red clay (red clays are usually called simply "clay"), white clay, a mixture of red clay and white clay, and a zeolite as adsorbing materials were used to investigate the behavior of heavy metal ions in the forming process for recycling inorganic wastes containing heavy metals. Also, another 3 standard solutions with concentration of 10, 20, 30 ppm with a from pH 3.0 to 9.0 conditions

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were selected to investigate in more detail the behavior of ionic adsorption characteristics according to pH with the same absorbing materials. The effect of selective adsorption characteristics and co-existent ions on the adsorption ability of absorbing materials was also examined by adding the corresponding ions to the solutions.

Experimental

The raw materials used as absorbing materials for heavy metals were red clay (generally used for making red bricks), white clay, and zeolite as a reference material. All raw materials were dried at 100 °C for 24h and crushed under 80 mesh (425 μ m). No other pre-treatment of the raw materials was done. The chemical compositions of the raw materials are listed in Table 1 which were obtained by XRF (X-ray fluorescence spectrometer; Philips PW2400) and XRD (X-ray diffractometer; Philips PW1840). The CEC (cation exchange capacity) and amount of exchangeable cations were measured with barium chloride solutions at pH 8.1 by using reference KS M 9227 [13].

Standard solutions (1000 ppm) of Cd, Cr, Cu, Fe, Pb, and Zn from Aldrich Co. were diluted to 5-30 ppm with distilled water. The pH of these solutions was controlled to 3.0-9.0 with NaOH and CH₃COOH solutions. 100 ml of the pH-controlled solutions were put into beakers containing 5 g each of clay minerals (red clay, white clay, a 50/50 mixture of red and white clay, and zeolite). The solutions were mixed with a magnetic stirrer at 25 °C, 200 rpm for 2 h. After mixing, the solutions were filtered with GF/C (110 mm) filter paper and the remaining heavy metal concentrations in the filtered solutions were analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometer). The heavy metal adsorption rate of the clay minerals were determined by the following equation:

Adsorption rate =

$$= \frac{\begin{array}{l} \text{Concentration of heavy metal ions absorbed} \\ \text{on the surface of clay minerals} \\ \text{Concentration of heavy metal ions in the} \\ \text{standard solution} \\ \\ (\text{Concentration of heavy metal ions in the standard solution}) \\ - (\text{Concentration after filtering}) \end{array}}{\text{Concentration of heavy metal ions in the standard solution}}$$

Table 1. Chemical Composition of Raw Materials (wt. %).

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Ig.L.	Total
(Red) Clay	57.69	19.02	7.05	0.20	1.04	0.09	2.53	0.92	0.17	0.22	11.00	99.93
White Clay	51.43	30.52	1.79	4.76	0.85	2.39	1.03	0.15	-	-	6.93	99.85
Zeolite	67.24	14.63	2.70	2.29	1.26	2.37	2.73	0.35	0.08	-	6.28	99.93

A mixed standard solution of Cd, Cr and Zn was used to compare the preference of adsorption in the competitive conditions. A mixture of 30 ppm Cd, Cr, Zn, Cu, Fe, and Pb standard solution was also prepared by mixing the same amounts and it was controlled to pH 5. 1-20 ppm Cl⁻ and SO₄²⁻ ions were added to the 30 ppm Cd solution to compare the effect of the co-existing negative ions on the heavy metal adsorption.

Results and Discussion

The chemical compositions of the raw material are listed in Table 1. The composition of red clay is similar to that for making red bricks while the white clay has more Al₂O₃ than red clay. Zeolite has a little more of the SiO₂ component than the other clay minerals. The XRD analysis showed that red clay consists of quartz, albite and kaolinite, the white clay consists of anorthite and tremolite, and zeolite consists of anorthocalse, makatite, tridymite, and sanidine.

The cation exchange capacity (CEC) of clay minerals was measured by KS M 9727 and the measured values are listed in Table 2. Zeolite showed the highest CEC value of 15.72 meq/100 g; where the values for red clay and white clay were 5.58 and 3.21 meq/100 g, respectively. However, the amount of exchangeable cations in the solution is more important than the value of CEC to adsorb heavy metal ions effectively in the stabilization or in the forming process for making ecological products. Red clay has 0.17 meq/100 g of Mg which is a relatively higher value than the others and zeolite has 0.68 meq/100 g of Na which is the highest value of all. Therefore, it is expected that red clay will adsorb doubly charged heavy metal cations and zeolite will do so for singly or triply charged cations.

Figure 1 shows the adsorption rate of cadmium ions in the various solutions containing four different clay minerals, which have different initial Cd concentrations (5-20 ppm). The adsorption rate of Cd linearly

Table 2. Cation exchange capacity and exchangeable cation of the clay, white clay and zeolite.

Raw Material	C.E.C (meq/100 g)	Exchangeable Cation (meq/100 g)			
		Na	K	Ca	Mg
(Red) Clay	5.58	0.58	0.03	0.24	0.17
White Clay	3.21	0.51	0.03	0.29	0.07
Zeolite	15.72	0.68	0.02	0.20	0.06

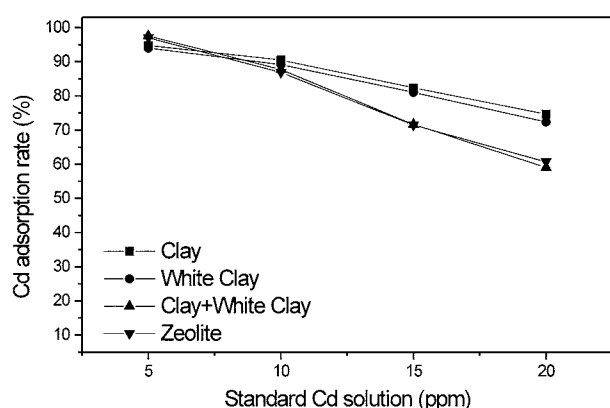


Fig. 1. The adsorption rate of cadmium ions in various solutions containing four different clay minerals, which have different initial Cd concentrations.

decreased with increasing initial concentration. The reason is an increase in competition among the Cd ions to occupy the remaining vacant sites on the surface of clay minerals by increasing the number of sites occupied by Cd ions and a decrease in binding energy caused by an increase in the activity coefficient of adsorbing surfaces [14, 15]. The average adsorption

rate was over 80% and adsorption rates of red and white clay were slightly higher than those of the red & white clay mixture and zeolite when the heavy metal concentration is higher than 10 ppm.

Figure 2 shows the adsorption rate of Cd ions in the four different solutions at different pHs and concentrations. The adsorption rate of Cd increased with increasing pH; however, there was little change above pH 5. At pH 3, red clay and white clay adsorb Cd ions more effectively than zeolite and the mixture of red & white clay; however, the adsorption rate of zeolite was the highest above pH 5. The adsorption rate of the mixture of red & white clay was lower than that of each clay separately, therefore, the elevating effect of the adsorption is not shown in the Cd ion case when red & white clays were mixed.

Figure 3 shows the adsorption rate of Cr ions in the various solutions containing four different clay minerals which have different initial Cr concentrations. The adsorption rate of Cr ions decreased with increasing initial concentration for the all the clay minerals except zeolite which kept a constant adsorption rate of 10%. The reason why zeolite shows a low adsorption rate of Cr may be because hydrogen ions with Cr ions in the

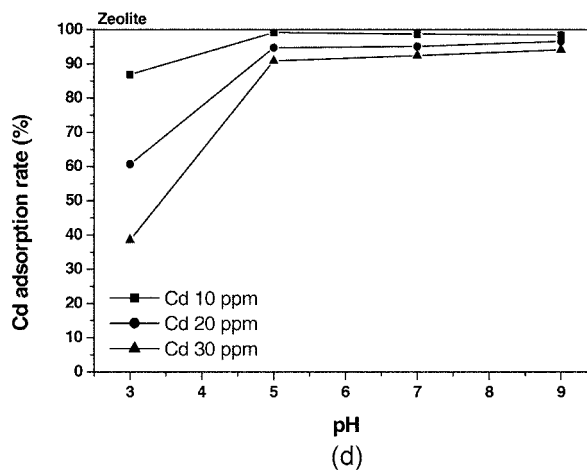
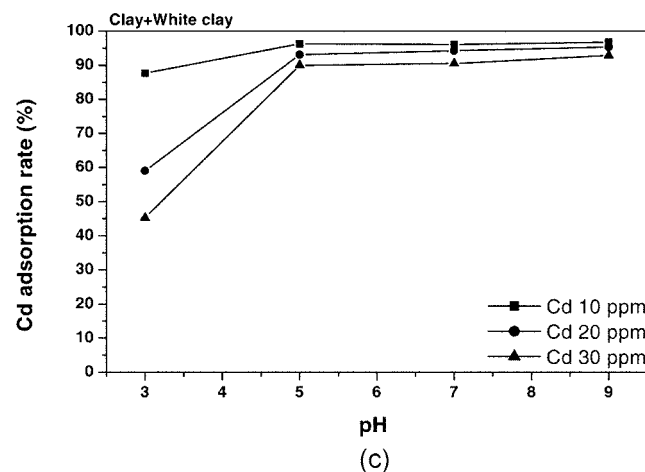
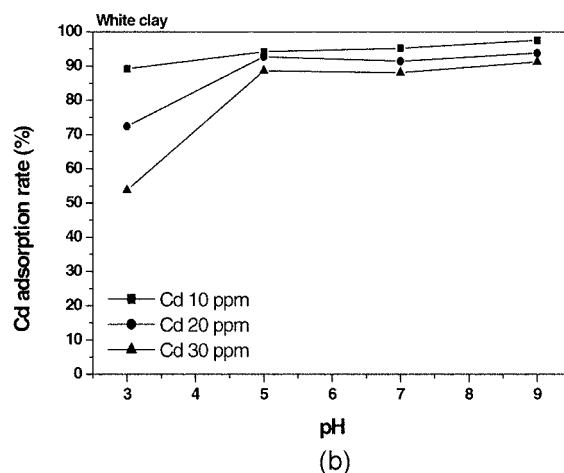
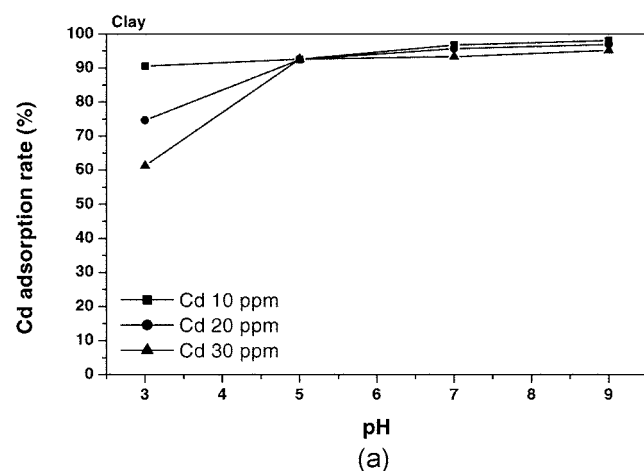


Fig. 2. The adsorption rate of Cd ions in the four different solutions at different pH levels and concentrations: (a) red clay, (b) white clay, (c) red clay & white clay mixture, and (d) zeolite.

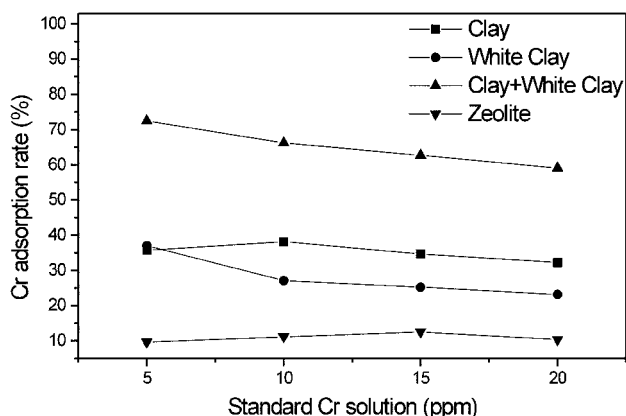


Fig. 3. The adsorption rate of chrome ions in various solutions containing four different clay minerals, which have different initial Cr concentrations.

low pH solutions will be competitively adsorbed on the surfaces of zeolite.

The adsorption rates of Cr were quite different according to the absorbing material, which is not the same tendency as the case for Cd. The mixture of red & white clay shows the best absorption rate of Cr. This is a very interesting phenomenon if we consider there are few suitable and effective absorbent materials

especially for Cr ions. The mixture of red & white clay may constructively interact and supply more sites for absorbing +6 and +3 valence ions. Therefore, adsorption rates of Cr ions were kept over 60% regardless of the initial concentration of the solutions.

Schulthess and Huang reported that high concentrations of hydrogen ions in the low pH solutions compete with heavy metal ions, so that the adsorption rate of Cr decreases in a low pH condition [16]. Therefore, it is necessary to see the effect of pH change on the adsorption rate of Cr.

Figure 4 shows the adsorption rate of Cr ions in the four different solutions at different pHs and initial concentrations of solutions. The adsorption rate of Cr ions in the solutions containing red clay, white clay, and zeolite decreased with an increase in the initial concentration as similar to Fig. 3; however, there is little effect of the pH of the solutions. This proves that Cr ions (Cr^{6+} and Cr^{3+}) are independent of the concentration of H^+ ions and they do not compete. Hence, the adsorption rate of the mixture of red & white clay decreased with an increase in pH of solutions which is a result very different from the expectation of Schulthess and Huang [16]. Anyway, the mixture of red & white clay was the best absorbent material for Cr

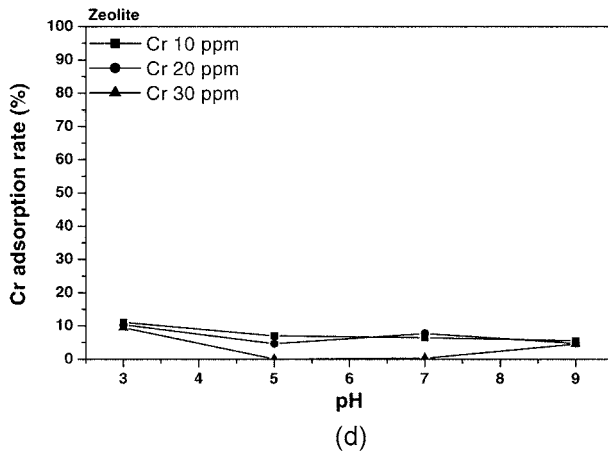
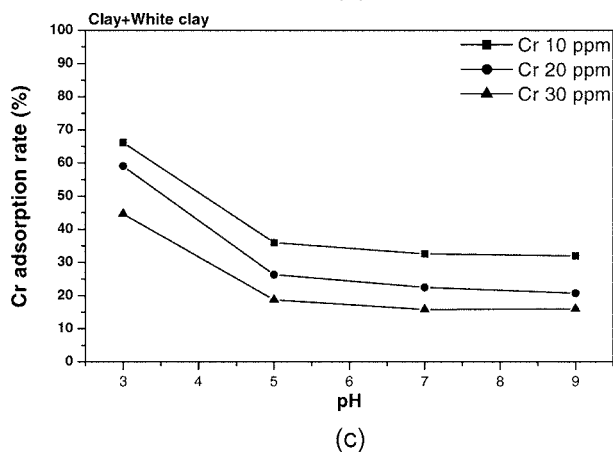
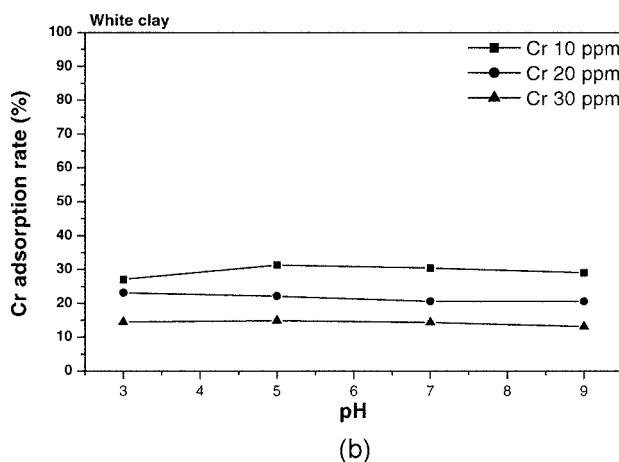
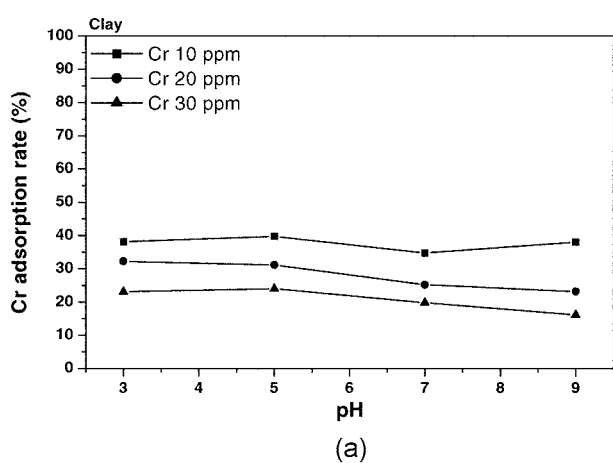


Fig. 4. The adsorption rate of Cr ions in the four different solutions at different pH levels and concentrations: (a) red clay, (b) white clay, (c) red clay & white clay mixture, and (d) zeolite.

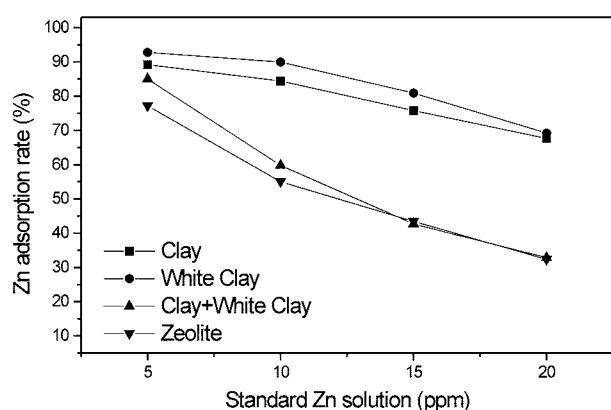


Fig. 5. The adsorption rate of zinc ions in various solutions containing four different clay minerals, which have different initial Zn concentrations.

ions at low pH conditions. Additional experiments will be required to explain why zeolite shows such a low absorption rate and how mixtures of red & white clay constructively interact and supply additional absorbing sites for +6 and +3 valence ions.

Figure 5 shows the adsorption rate of zinc ions in various solutions containing the four different clay minerals, which have different initial zinc concentrations

from 5 to 20 ppm. The adsorption rate of red clay and white clay slowly decreased with increasing initial concentration; however, those of the clay mixture and zeolite decreased rapidly up to 30% with increasing initial concentration. The adsorption rates of zinc ions in the four different solutions at different pH levels and initial concentrations were also observed to show the effect of pH as shown in Fig. 6. When the initial concentration was low such as 10 ppm, the adsorption rate of zinc was so saturated above pH 5 that there was little change with increasing pH. However, the adsorption rate of zinc increased almost linearly with increasing pH when the initial concentration was high (20 and 30 ppm) and the pH was lower than 5. Heavy metal ions having +2 valence will compete with hydrogen ions to adsorb in low pH conditions as already shown for Cd ions.

The adsorption rates of clay minerals were measured for single solutions of heavy metal ions. Now the more complex case of the adsorption rates of red clay in mixed solutions of three or six heavy metal ions will be discussed to see whether there were any ion(s) preferably absorbed. Mixtures of 5 g of red clay and 30 ppm each of Cd, Cr and Zn controlled to pH 5 were used to find the ion type preferably absorbed. Because

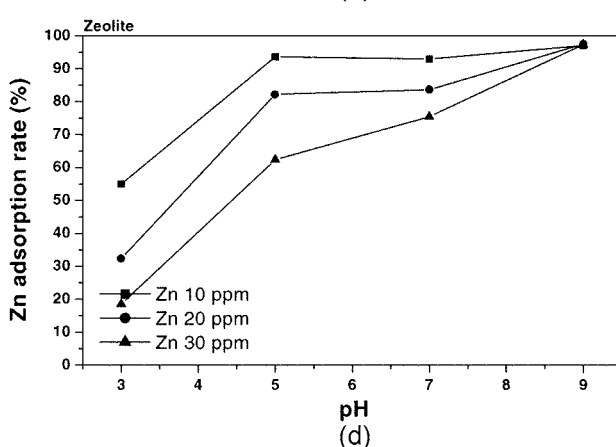
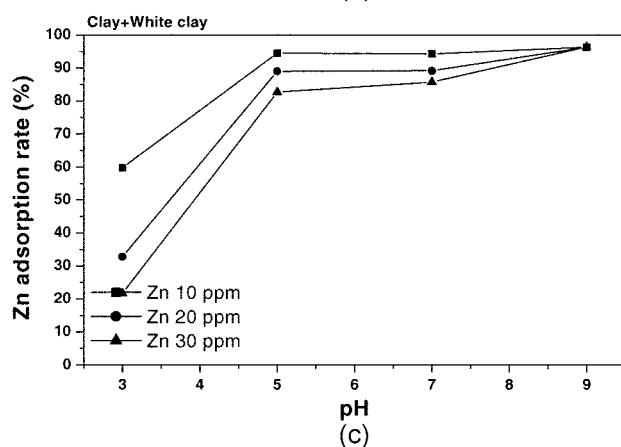
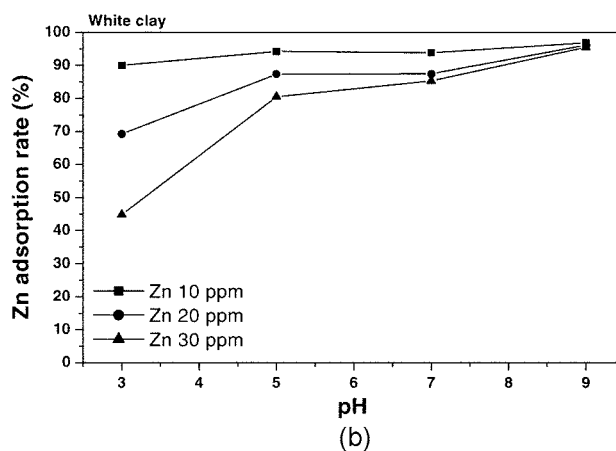
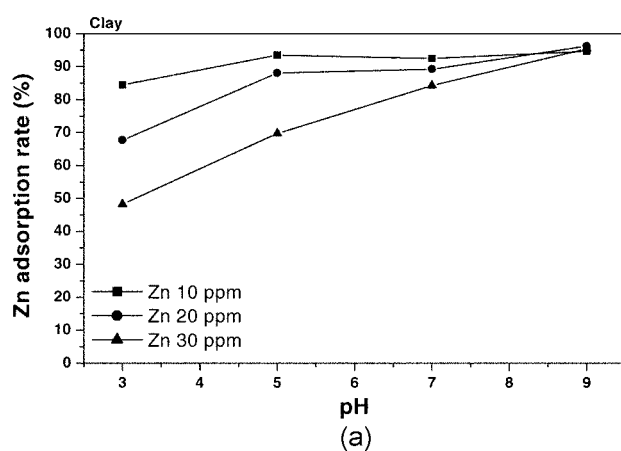


Fig. 6. The adsorption rate of Zn ions in the four different solutions at different pH levels and concentrations: (a) red clay, (b) white clay, (c) red clay & white clay mixture, and (d) zeolite.

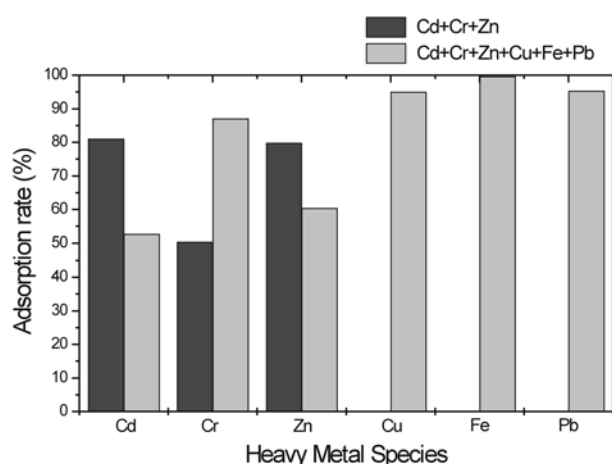


Fig. 7. The adsorption rate of heavy metals by red clay with various heavy metal ions co-existing.

the pH of solutions from the dust from electric arc furnaces and heavy metal sludges from the steel industry treated with water gives a pH of around 5, the solutions of mixtures studied here was controlled to be pH 5 [17]. Adsorption rates of Cd and Zn were the same at 80%; however, that of Cr was only 50%. This result could be expected from and is similar to the results of the single solution case.

When 30 ppm each of Cu, Fe and Pb were additionally mixed with the solution of the mixture of three ions (Cd, Cr, Zn), the adsorption rates of Cu, Fe, and Pb were more than 95% as shown in Fig. 7. However, the adsorption rates of Cd and Zn decreased to 50-60% and that of Cr surprisingly increased up to 85%. The decreasing order of adsorption rate is Fe > Pb, Cu > Cr > Zn > Cd. This result suggested that the preferentially absorbed ions existed when various ions are mixed in the solution simultaneously and the adsorption rate of a specific ion can be increased by controlling the species of co-existing ions. In this experiment, Fe, Pb and Cu turned out to be the preferentially absorbed ions and especially the adsorption rate of Cr ions was substantially increased by adding preferentially absorbed ions. Therefore, one assumes that the atmosphere of a solution, i.e. the type of co-existing ions as well as the absorbent material itself, is a very important factor for the control of the adsorption rate of specific heavy metal ions.

To see the effect of co-existing anions, Na₂SO₄ and NaCl (Cl⁻ and SO₄²⁻ anions) were added, up to 20 ppm, to a Cd solution with red clay; however, there was little change of the adsorption rate of Cd regardless of the anion existence.

Conclusions

It has been shown that there is no exact linear relationship between the adsorption rate of heavy metal ions and the cation exchange capacity (CEC) as seen

from the Fig. 1 to Fig. 6 and Table 2. Zeolite, which is known as the best absorbent material for heavy metals, has the highest CEC and shows high adsorption rates above pH 7; however, it shows relatively lower adsorption rates than the other clay minerals under acid conditions (below pH 5). Notably, zeolite shows the lowest adsorption rate of Cr. This result suggests that the characteristics of adsorption of heavy metals depends not only on the physical properties of the absorbent itself such as its CEC but also on the concentration and existence of exchangeable cations, pH, ligands, etc.. Co-existing anions had little effect on the change of the adsorption rate when they were added up to 20 ppm.

Because there are few effective absorbing materials for Cr ions, red clay, in which the pH was controlled and a few other ions were added to the solution, can selectively adsorb Cr ions if necessary.

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