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DEVELOPMENT OF ADSORBENT USING BYPRODUCTS FROM KOREAN MEDICINE FOR REMOVING HEAVY METALS

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Abstract : Most of the herb residue producing from oriental medical clinics(OMC) and hospitals(OMH) is wasted in Korea. To develop of adsorbent for removing heavy metal from wastewater, the various pre-treatment methods of the herb residue were evaluated by potentiometric titration, Freundlich isotherm adsorption test and the kinetic adsorption test. The herb residue was pre-treated for increasing the adsorption capacity by cleaning with distilled water, 0.1 N HCl and 0.1 N NaOH and by heating at 370°C for 30 min. It showed a typical weak acid-weak base titration curve and a short pH break like commercial activated carbon during photentiometric titration of pre-treated herb residue. The log-log plots in the Freundlich isotherm test were linear on the herb residue pre-treated with NaOH or HCl like commercial activated carbon. The adsorption capacity(qe) in the Freundlich isotherm test for Cr^{6+} was 1.5 times higher in the pre-treated herb residue with HCl than in activated carbon. On the other hand the herb residue pre-treated with NaOH showed the good adsorption capacities for Pb^{2+}, Cu^{2+} and Cd^{2+} even though those adsorption capacities were lower than that of activated carbon. In kinetic test, most of heavy metals removed within the first 10 min of contact and then approached to equilibrium with increasing contact time. The removal rate of heavy metals increased with an increase of the amount of adsorbent. Likewise, the removal rates of heavy metals were higher in the herb residue pre-treated with NaOH than in that pre-treated with HCl. The adsorption preference of herb residues pre-treated with NaOH or HCl was $Pb^{2+}>Cu^{2+}$ or $Cd^{2+}>Cr^{6+}$ in the order. Conclusively, the herb residue can be used as an alternative adsorbent for the removal of heavy metals depending on pr-treatment methods.

Key Words : Adsorption, Herb residue, Heavy metal, Pre-treatment, Korean medicine

INTRODUCTION

Sewage or wastewater is including various kinds of heavy metals and these pollutants have been treated by precipitation resulting in the production of much sludge. Ion exchange or adsorption processes are very effective for removing heavy meals but high cost is required for purchasing ion exchange resin and adsorbent.[1] For coping with these disadvantages, the materials from animal or plant such as rice-straw, orange peer, green tea and husk of lobster or crap have been developed as adsorbent by many researchers.[2-11] A few researchers have studied the effect of binary and multi-component adsorption for removing the heavy metals using the animal and plant materials.[9-12]

On the other hand, from ancient times,

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Korean has used many kinds of herbs for remedying. Usually, these medical herbs are boiled down for extraction causing the production of lots of residue (called "herb residue"). There are many oriental medical clinics and hospitals producing lots of herb residue in Korea. Most of herb residue, however, is wasted rather than reused. It was reported that some medical herbs can effectively adsorb heavy metals. Thus, the purpose of this study was to evaluate the potential of the herb residue as adsorbent for treating wastewater containing heavy metals.

MATERIALS AND METHODS

Materials

For using as adsorbent, the residue from extraction of medical herbs was collected from oriental medical clinics (OMC) or hospital (OMH). It was pre-treated for increasing the adsorption capacity by various activation methods (Table 1). The pre-treated residue was separated from solution and then dried at 90-95°C at constant weight. The dried residue was crushed smaller than 65 meshes for adsorption test. Pb^{2+}, Cr^{6+}, Cu^{2+} and Cd^{2+} (Sigma Chemical Co.) were used as target heavy metals and prepared by standard chemical preparation method. pH was controlled using 0.1 N HCl or 0.1 N NaOH during adsorption test. Commercial activated carbon was used as a control adsorbent.

Methods

The adsorption capacity of the pre-treated residues was evaluated by potentiometric titration and isothermal adsorption test. It was compared with activated carbon. For potentiometric titration, 1 g of pre-treated residue was mixed with 100 mL distilled water and then the change of pH was measured with adding 0.01 N HCl solution or 0.01 N NaOH solution. Two different types of adsorption test were conducted. Firstly, kinetic studies were performed to compare the adsorption rates of the pre-treated residues on heavy metals (Pb^{2+}, Cr^{6+}, Cu^{2+} and Cd^{2+}). Secondly adsorption isotherms were measured to obtain the adsorption capacities. For batch kinetic experiments, 100 mL aqueous solution containing 100 mg/L of single component or multi-component of heavy metal was stirred with 0.05 or 0.4 g of the pre-treated residue at 200 rpm for 0~120 min. During the adsorption test, temperature was maintained at 25°C. After adsorption test, the solution was filtered using GFB filter and the heavy metals from the filtrate were analyzed by atomic absorption spectrophotometer(AA). The adsorption isotherm test was conducted at 25°C by shaking the aqueous heavy metals solution containing the pre-treated residues at 200 rpm for 24 hrs.

RESULTS AND DISCUSSION

Potentiometric Titration

The potentiometric titration curves for the pre-treated residues collected from OMH and OMC and activated carbon in deionized water are shown in Figure 1. The titration curve for the deionized water is also included for comparison which itself exhibited a wide pH break between pH 4 and 10 with equivalence point at

Table 1. Pre-treatment methods of the residue of Korean medical herb from OHM and OMC

Pre-treatment method		Procedure
Cleaning		The residue is cleaned 2~3 times with primary distilled water
Chemical treatment	Acid	The residue is mixed with 0.1 N HCl at 1:10 volumetric ratio and then the mixture is agitated for 2 hr at 200 rpm
	Alkali	The residue is mixed with 0.1 N NaOH at 1:10 volumetric ratio and then the mixture is agitated for 2 hr at 200 rpm
Thermal treatment		The residue is activated in tube furnace of reductive condition by N_2 gas at 370°C for 30 min.

pH 7.0. The pH of aqueous solution containing 1g adsorbent was changed smoothly with adding 0.01 N HCl solution or 0.01 N NaOH solution unlike titration curve of deionized water. It showed a typical weak acid-weak base titration and a short pH break even though the equivalence points are different according to pre-treatment methods. In case of HCl pre-treated residue, untreated residue and cleaned residue, pH was more increased with NaOH addition than in case of NaOH pre-treated residue and activated carbon. On the contrary, pH was more decreased with HCl addition in case of NaOH pre-treated residue and activated carbon.

As a result, the residues derived from Korean medical herb can adsorb H^+ and OH^- ion like activated carbon which is a representative adsorbent. And also, the titration curves between the residues collected from OMH and OMC were similar. Thus, the residue of OMH was used for following experiments.

Adsorption Characteristics on Heavy Metals

Equilibrium adsorption isotherms or adsorption capacity studies are fundamentally important in the characterization of adsorbent since these indicate how the heavy metal ions are partitioned between the media and liquid phase with increasing concentration at equilibrium.

Equilibrium adsorption isotherm. It is generally possible to express the results of experimental adsorption measurements in the theory of the Langmuir isotherm or the Freundlich isotherm. However, the experimental adsorption isotherms were better fitted to Freundlich equation than to the Langmuir equation. Therefore, the Freundlich equation was used in this study. As shown in Figure 2, the typical Freundlich adsorption isotherms were obtained for heavy metals using the herb residue from OMH. Thus,

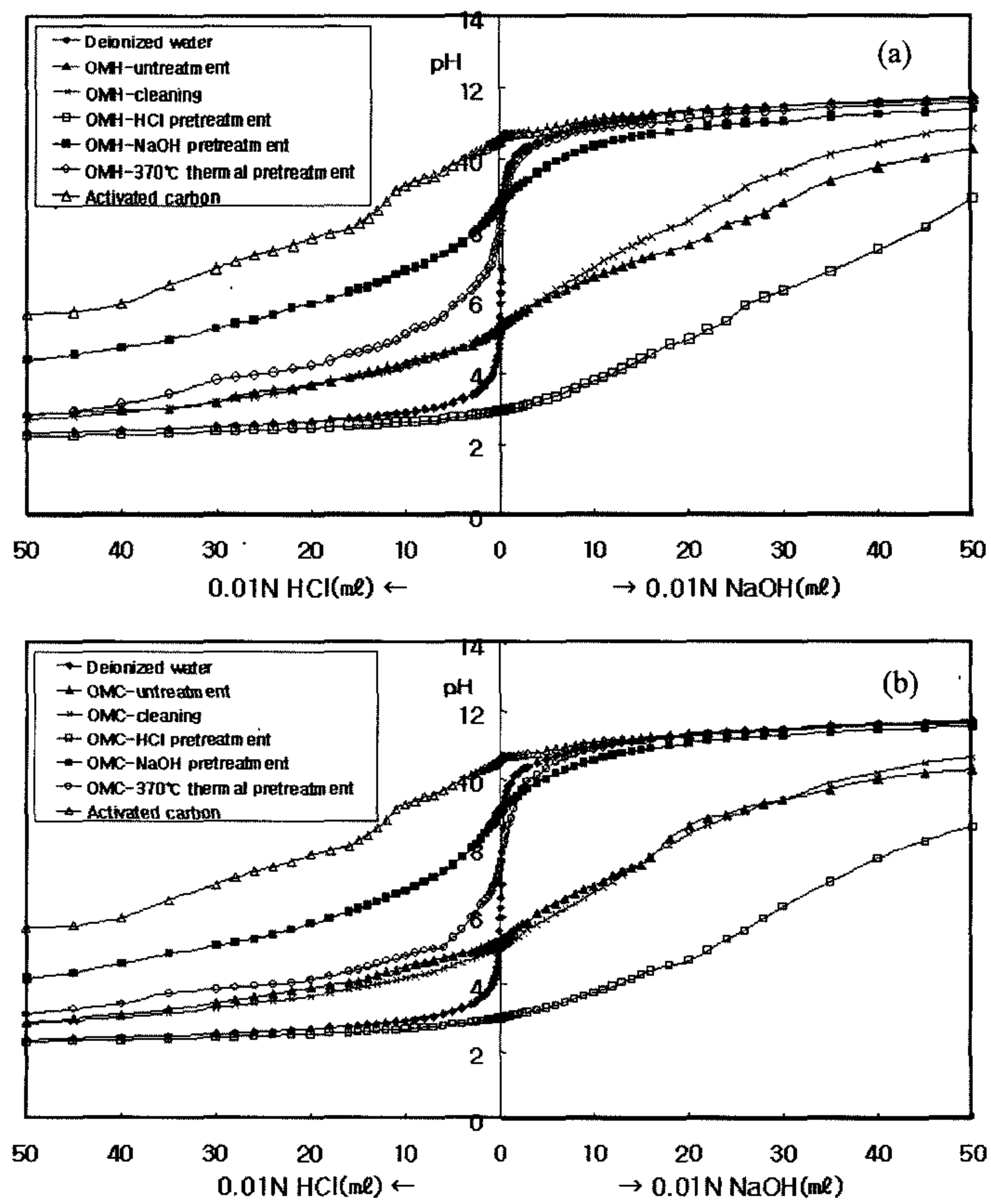


Figure 1. Photentiometic titration curves for pre-treated residues from OMH(a) and OMC(b).

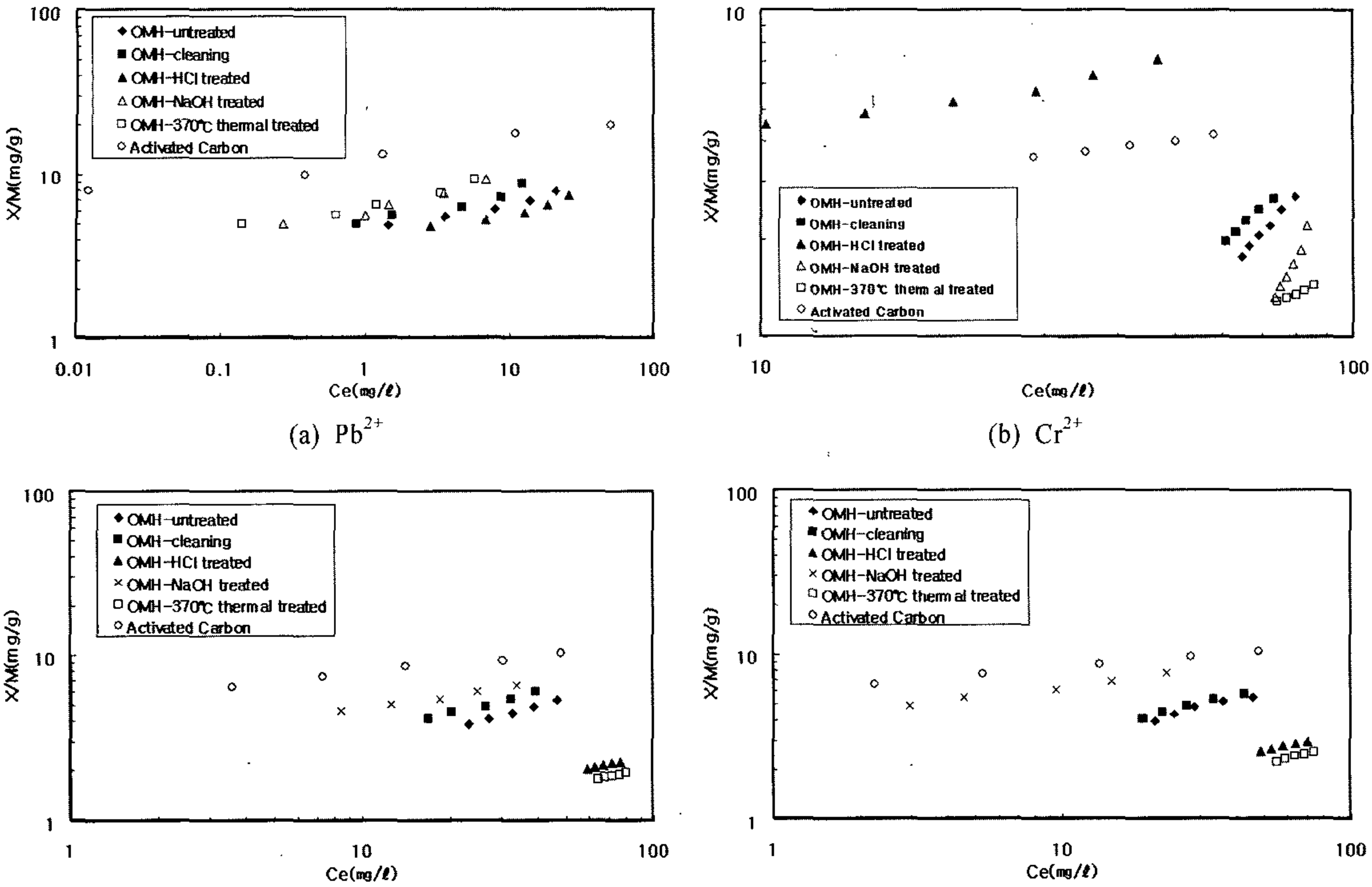


Figure 2. Freundlich adsorption isotherms on heavy metals with various pre-treatment methods.

Table 2. Freundlich adsorption isotherm constants for the adsorption of heavy metals

Activation methods	Pb^{2+}			Cr^{6+}			Cu^{2+}			Cd^{2+}		
	K_F	1/n	r^2	K_F	1/n	r^2	K_F	1/n	r^2	K_F	1/n	r^2
Untreatment	1.922	0.172	0.961	0.033	2.022	0.995	0.942	0.472	0.999	1.059	0.417	0.968
Cleaning	2.021	0.193	0.937	0.071	1.649	0.993	1.109	0.420	0.983	1.067	0.431	0.986
HCl pretreatment	1.795	0.184	0.921	1.536	0.296	0.967	0.733	0.423	0.991	0.807	0.372	0.994
NaOH pretreatment	2.198	0.196	0.957	0.003	3.697	0.973	1.628	0.268	0.990	1.796	0.215	0.984
Thermal pretreatment	2.265	0.167	0.943	0.265	2.075	0.972	0.662	0.368	0.970	0.676	0.427	0.972
Activated carbon	3.012	0.117	0.961	1.248	0.435	0.993	2.046	0.177	0.986	2.149	0.151	0.998

the variation of adsorption capacity(q_e), i.e., the amount of heavy metals adsorbed per gram herb residue or activated carbon, as a function of equilibrium concentration of heavy metals(C_e) followed the Freundlich adsorption model($q_e = K_F C_e^{1/n}$). The Freundlich isotherm constants K_F and 1/n which indicate the relative adsorption capacity of adsorbent and the intensity of the adsorption, respectively are presented with correlation coefficient (r^2) in Table 2.

Generally, the adsorbent showing the larger K_F and the smaller 1/n whose value ranges between 0 and 1 is the better adsorbent.[5,8,9] The values of K_F and 1/n of the herb residues for Pb^{2+} were similar regardless of the pre-treatment methods although the two values(K_F, 1/n) of the herb residues were lower and higher than those of activated carbon, respectively. The K_F of Cr^{6+} was very low except for the herb residue pre-treated with HCl which showing lower value of 1/n than that of activated carbon. Among them, the residue pre-treated with NaOH showed the highest K_F and the lowest 1/n for Cu^{2+} and Cd^{2+} and these values ranged from 80% to 150% of activated carbon, respectively. Table 3 shows the adsorption capacity after adsorbing

Table 3. Adsorption capacity for single heavy metal (100 mg/L contact time: 2 hr; adsorbent : solution=1 : 100 (w:w))

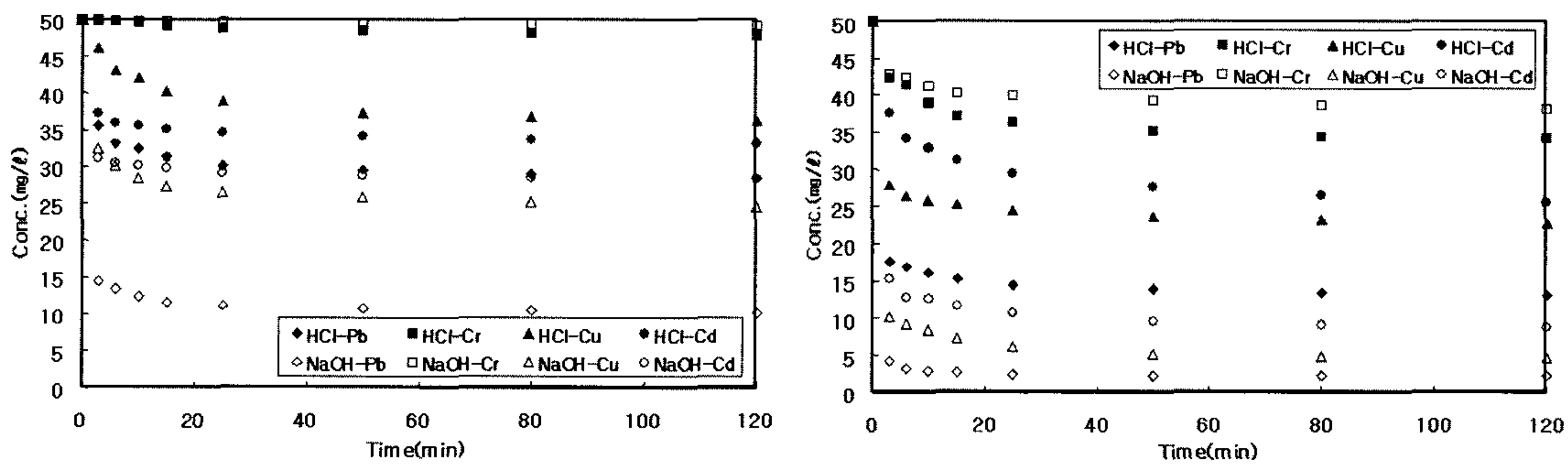
Activation methods	Adsorption capacity, q_e (mg/g)			
	Pb^{2}	Cr^{6+}	Cu^{2+}	Cd^{2+}
Untreated	7.95	2.45	5.35	5.46
Cleaning	8.80	2.66	6.06	5.75
HCl pretreatment	7.46	6.37	2.28	2.96
NaOH pretreatment	9.32	1.85	6.62	7.70
Thermal pretreatment	9.43	1.44	1.95	2.54
Activated carbon	9.96	4.18	8.59	8.66

100 mg/L single component for 2 hr. As mentioned previously, among the herb residues, the herb residue pre-treated with NaOH showed the best adsorption capacities for Pb^{2+}, Cu^{2+} and Cd^{2+} even though those adsorption capacities were lower than that of activated carbon. Especially, the herb residue pre-treated with HCl was the best for adsorption of Cr^{6+}, thus the adsorption capacity of the residue was higher than that of activated carbon.

The adsorption capacities(mg/g) for Pb^{2+}, Cr^{6+}, Cu^{2+} and Cd^{2+} of the herb residue without any pretreatment were 7.95, 2.45, 5.35 and 5.46, respectively showing 40~60% of that obtained using activated carbon. By cleaning the herb residue, the adsorption capacities for heavy metals were increased. As a result, the residue pre-treated with NaOH can be used as alternative adsorbent of activated carbon for removing Pb^{2+}, Cu^{2+} and Cd^{2+} while the residue pre-treated with HCl can be used for removing Cr^{6+}. On the other hand, because only 10% (weight base) can be recovered after thermal pre-treatment of the herb residue, it cannot be considered as an efficient pre-treatment method.

Kinetic studies. The rate which adsorption takes place is an important factor for designing of adsorption system. Single or multi components adsorption kinetic curves were obtained by batch contact time studies for the herb residues pre-treated with HCl and NaOH which has shown high adsorption capacity for Cr^{6+} and Pb^{2+}, Cr^{6+} and Cu^{2+}, respectively. Figure 3 shows the adsorption kinetic curves for each heavy metal onto the different amount of media. Most of the total metal ion capture occurred within the first 10 min of contact time and then approached to equilibrium with increasing contact time. The removal rate of heavy metals increased with increasing an amount of adsorbent.

Especially, in case of the herb residue pre-treated with NaOH, about 72 and 92% of Pb^{2+} were removed within the first 3min by 0.05 and 0.2 g of adsorbent, respectively. Generally, adsorption reaction includes ion exchange reaction, adsorption in surface of adsorbent and hydrolysis.[6,7] Thus, it is supposed that the improvement of adsorption capacity by alkali treatment is due to the increase of anion on surface of adsorbent resulting in the formation of metal oxide precipitation. In case of acid treatment, the adsorption capacity for heavy metals decreased except for Cr^{6+}. The reason might be because the sites of adsorbent which



(a) 0.05g (b) 0.2g

Figure 3. Adsorption kinetic of single metal according to pre-treatment method (sample: 100 mL, adsorbent: (a) 0.05g, (b) 0.2g).

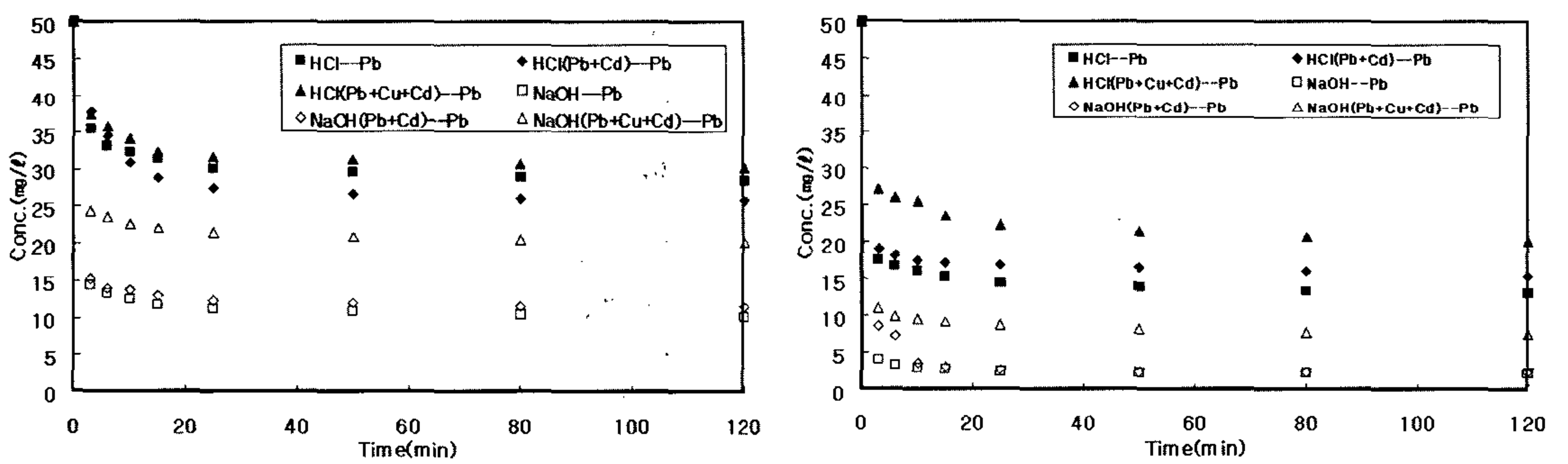
can exchange with heavy metal cation are already substituted with H^+ from HCl. That is, ion-exchange reaction involving heavy metals are in competition with H^+ in the solution.

Consequently, the order of preference of the herb residues for heavy metal ions was Pb^{2+}> Cu^{2+}>Cd^{2+}>Cr^{6+} in single - component systems. This preference might be explained on the basis of their ionic radii, hydration energy, ionic mobility and diffusion coefficient. Thus, it is supposed that a greater accessibility to the surface of certain pores of Pb^{2+} ion than the other metal ions is due to its relatively higher ionic mobility, smaller hydration energy and higher diffusion coefficient. And also, Ricordel and his coworker[10)] suggested that the lower extent in the adsorption of Cd^{2+} with regard to Pb^{2+} might be due to its smaller polarizing power. Thus, carbon-Cd^{2+} interaction forces will be weaker than those corresponding to Pb^{2+} and Cd^{2+} will be retained only on those surface centers with a density of negative charge higher than that necessary to retain Pb^{2+}.

Figure 4 and 5 show the adsorption kinetic curves for Pb^{2+} and Cr^{6+} in binary and ternary component systems onto the different amount of media. The results clearly reveal that the presence of other metal ions compete with Pb^{2+} and Cr^{6+} onto the herb residues pre-treated with NaOH and HCl, respectively. It is observed that Cd^{2+} has lower interfering tendency to Pb^{2+} than Cu^{2+} in the herb residue pre-treated with NaOH. And also, Cd^{2+} showed a little interference to Cr^{6+} adsorption in 0.4 g of the herb residue pre-treated with HCl.

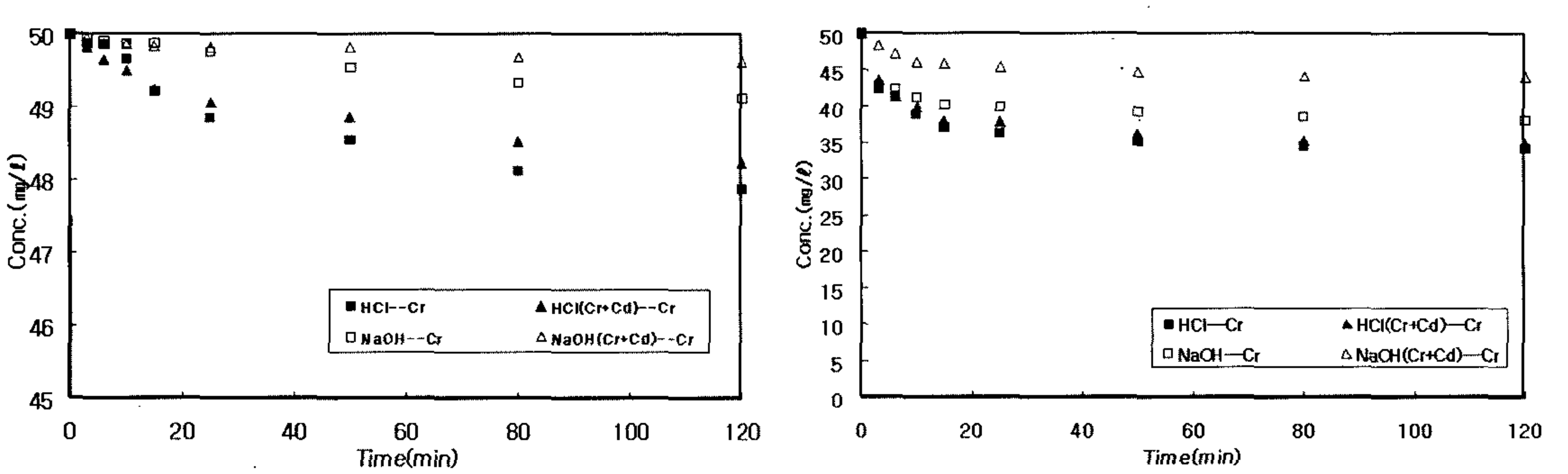
CONCLUSIONS

The potential of herb residue as adsorbent for removing heavy metals was evaluated in this



(a) 0.1 g (b) 0.4 g

Figure 4. Single, binary and ternary adsorption of Pb^{2+} on the herb residue from OMH pre-treated with NaOH and HCl (sample: 100 mL, adsorbent: (a) 0.1 g, (b) 0.4 g).



(a) 0.1 g (b) 0.4 g

Figure 5. Single and binary adsorption of Cr^{6+} on the herb residue from OMH pre-treated with NaOH and HCl (sample: 100 mL, adsorbent: (a) 0.1 g, (b) 0.4 g).

study. The herb residue pre-treated with HCl or NaOH showed the adsorption capability on H^+ and OH^- ion like commercial activated carbon during photentiometric titration. From the Freundlich isotherm adsorption test, it was demonstrated that NaOH and HCl pre-treatment are the most effective for removing Pb^{2+}, Cd^{2+} and Cu^{2+} and Cr^{6+}, respectively among the pre-treatment methods of herb residue.

The adsorption preference of the herb residues in single-component adsorption system was Pb^{2+}>Cu^{2+}>Cd^{2+}>Cr^{6+} while it was Pb^{2+}>Cd^{2+}>Cu^{2+}>Cr^{6+} in multi-components system. Especially, in case of the herb residue pre-treated with NaOH the removal rate of Pb^{2+} was distinguished and the presence of other metal ions compete with Pb^{2+} and Cr^{6+} onto the herb residues pre-treated with NaOH and HCl, respectively. The higher competitive adsorption occurred under the conditions of the less adsorptive heavy metal and the less amount of adsorbent.

In Conclusion, the herb residues collected from OMH or OMC can be used as an alternative adsorbent for the removal of heavy metal ions. Although their capacity is lower than that of the commercial activated carbon, it would be useful for the economic treatment of wastewater containing heavy metals. However, because the adsorption is highly dependent on pre-treatment (activation) methods and kinds of heavy metals, an appropriate pre-treatment method should be chosen for target heavy metal.

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