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Removal of aqueous heavy metals (Pb, Cu, Zn, Cd) by scoria from Jeju, Korea

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<요 약 문>

Heavy metal release from wastewater is a serious environmental problem, and therefore, various wastewater treatment techniques have been developed. Among the techniques, sorption technique is most attractive. Considerable researches have been recently focused on finding out inexpensive sorbents, especially from various natural materials. In order to evaluate the applicability of the scoria taken from the Jeju Island, Korea to remove heavy metals (Pb, Cu, Zn, Cd) from aqueous solutions, equilibrium sorption experiments were conducted in this study. In equilibrium tests, powdered activated carbon (PAC), one of the most commonly used sorbents, was also tested to compare the effectiveness of the Jeju scoria with that of PAC. The Jeju scoria had larger adsorption capacity and affinity for metal ions (Pb(II), Cu(II), Zn(II), Cd(II)) than PAC. The sorption parameters of the two sorbents were evaluated by using both the Langmuir and Freundlich isotherms, and the sorption data were better fitted to the Freundlich isotherm. In addition, the sorption behavior of metal ions (Pb(II), Cu(II), Zn(II), Cd(II)) onto the scoria displayed a typical characteristic of the cation sorption. The removal of metal ions decreased at a lower pH condition due to competition with hydrogen ions for the sorption sites of Jeju scoria, while the removal increased at a high pH condition due to hydroxide precipitation.

Key words : Scoria, Heavy metal removal, Sorption, PAC, Langmuir and Freundlich isotherms

1. Introduction

Human activities introduce heavy metals to the hydrosphere in many ways such as burning of fossil fuels, smelting of ores, municipal sewage, industrial effluent, mining activities, landfill, underground toxic waste disposal, etc. High concentrations of heavy metals, regardless of their source, generally do not persist as the metals are transported through aquatic systems. The heavy metals such as Pb, Cu, Zn, and Cd in aqueous environments are accumulated not only in aquatic organisms but also in human body through physico-chemical and biological processes. In human body, these metals accumulate mainly in bones, brain, kidney and muscles, and may cause many serious disorders such

as anaemia, kidney disease, nervous disorders and sickness even death.

For these reasons, various treatment technologies have been developed for a cleanup of water and wastewater contaminated and polluted with heavy metals. Among the techniques, sorption is one of the most practical methods. The sorption technique based on ion exchange processes and physicochemical sorption has been applied to various studies.

In this study, Jeju scoria was used as a sorbent to remove the metal ions from aqueous solution. Scoria is a bomb-sized, generally vesicular pyroclast that is red or black in color and light in weight. The specific objectives of the present paper are (1) to estimate the affinity of four cations (lead, copper, zinc, and cadmium) onto Jeju scoria; (2) to compare the Jeju scoria with powdered activated carbon (PAC) for the sorption capacity, and (3) to evaluate the consistency between experimental data and theoretical adsorption capacity for the adsorption isotherms.

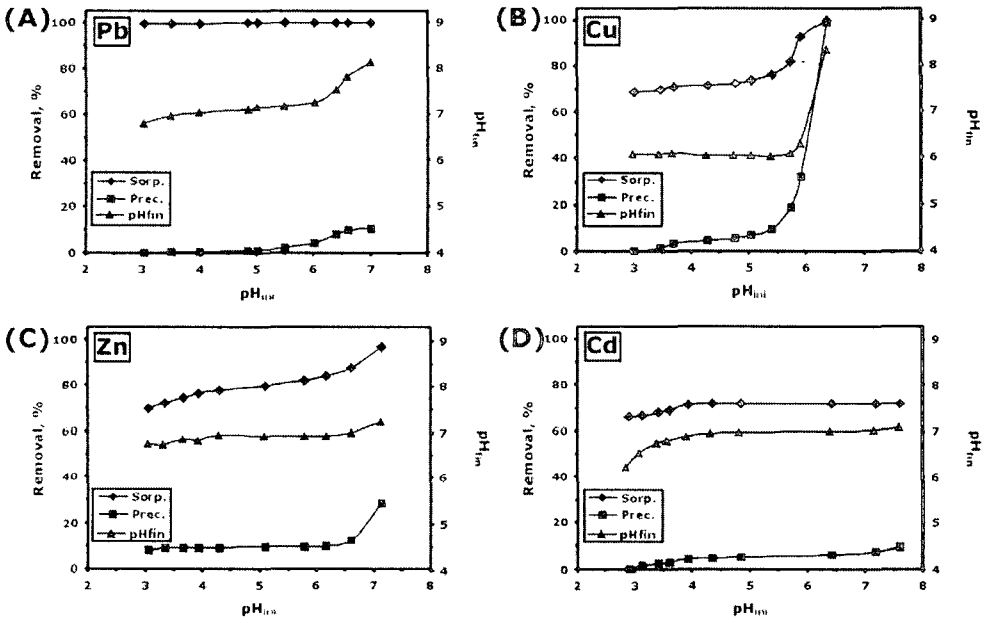

Fig. 1. Contribution of precipitation and the variation of pH on the removal of metals (A: Pb; B: Cu; C: Zn; and D: Cd) by the Jeju scoria (temp. = 25 C, particle size = 0.1-0.2 mm, initial metal concentration = 5.0 mM, and sorbate/sorbent ratio = 20 mL g^{-1}).

2. Results

The equilibrium isotherm for the sorption of metal ions (Pb(II), Cu(II), Zn(II), and Cd(II)) onto sorbents was determined by agitating 0.5 g sorbent (0.1-0.2 mm in particle size) with 10 mL of metal solutions of various concentrations at 25℃ for 24 h.

The solution pH has a significant effect on the sorption of metal ions onto Jeju scoria. Removal of the metal ions as a function of initial pH value, pH_{ini}, is presented in Fig. 1. All the experiments were carried out at the constant initial concentration of 5.0 mM of each metal ions. The sorption of metal ions on Jeju scoria increased with an increase of pH_{ini}. These results are consistent with a

typical characteristic of cation sorption. The order of the effective sorption onto scoria was found to be Pb > Zn = Cu = Cd at pH_{ini} < 5.6, and Pb > Cu > Zn > Cd at pH_{ini} > 5.6.

To evaluate the fraction of metal ions (Pb(II), Cu(II), Zn(II), and Cd(II)) removed by precipitation as a function of pH, the experiments were performed at the absence of sorbent in identical pH conditions. The results are presented in Fig. 1. The metal hydroxide precipitation increased with increase in pH_{ini}. These phenomena combined with metal hydroxide precipitation were controlled by the pH_{ini}. In summary, metal removal was low at low pH condition due to the competition with hydrogen ions for sorption sites, whereas it was enhanced at high pH condition due to the formation of hydroxide precipitation.

Also, the variation of the final pH value, pH_{fin}, as a function of pHini is shown Fig. 1. The removal of metal ions onto Jeju scoria increased with increasing pH_{ini}, but the pH_{fin} was more or less constant up to pH_{ini} 5.5. The pH_{fin} of aliquot increased beyond the pH_{ini} 5.5 (Pb), 5.7 (Cu), and 6.2 (Zn). The pH_{fin} were constant, while the amounts of precipitation increased with increasing H_{ini}.

The sorption capacity (mg g^{-1}) of Jeju scoria for metal ions (Pb(II), Cu(II), Zn(II), and Cd(II)) was compared with that of PAC, because PAC has been considered as one of the most commonly used sorbents. The results are shown in Fig. 2. The order of the metal affinity onto the two sorbents was Pb > Cu > Zn > Cd, approximately, and the results showed that the metal sorption capacity of the Jeju scoria is better than that of the PAC.

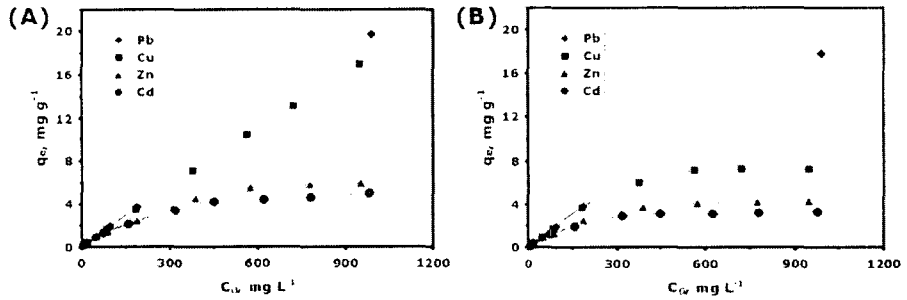

Fig. 2. Sorption capacity of the two sorbents (A: Jeju scoria; B: PAC) on the removal of divalent Pb, Cu, Zn, and Cd (temp. = 25℃, pH_{ini} = 3, and sorbate/sorbent ratio = 20 mL g^{-1}).

In addition, the sorption capacities of both the sorbents were determined from adsorption isotherms. The isotherms for the sorption of metal ions (Pb(II), Cu(II), Zn(II), and Cd(II)) onto the two sorbents were determined at pH_{ini} 3.0 for preventing their removal as a result of metal hydroxide precipitation. The studies were performed at 25℃ to determine the adsorption isotherms and isotherm parameters using linear Langmuir and Freundlich models, because the Langmuir and the Freundlich models are commonly used to fit experimental data when removal of metal ions occurs by a mono-layer sorption. Table 1 represents the Langmuir and Freundlich isotherm parameters. The results (Q and K_f values) indicate that Jeju scoria has larger adsorption capacity and affinity than PAC. Furthermore, the data on metal sorption onto Jeju scoria were applicable to the Freundlich model, which is based on an exponential distribution of sorption sites and energies, while that onto PAC were fitted well to the Langmuir model, which is based on the formation of layers on active sites.

Table 1. Langmuir and Freundlich isotherm constants for the sorption of metal ions (Pb(II), Cu(II), Zn(II), and Cd(II)) onto the Jeju scoria and PAC at pHini 3 and 25℃.

Sorbent	Metal	Langmuir			Freundlich		
		Q (mg g^{-1})	b	R^2	K_f	$1/n$	R^2
Scoria	Pb	42.37	0.2128	0.7222	6.081	0.8377	0.9988
	Cu	20.00	0.0423	0.9107	0.9305	0.6698	0.9971
	Zn	6.203	0.0263	0.9809	0.5698	0.3780	0.9864
	Cd	5.030	0.0275	0.9894	0.4200	0.4015	0.9827
PAC	Pb	18.66	0.3098	0.9973	2.341	0.5521	0.9000
	Cu	7.342	0.2867	0.9994	1.409	0.3104	0.8560
	Zn	4.431	0.0344	0.9967	0.3599	0.4118	0.9768
	Cd	3.323	0.0452	0.9976	0.3432	0.3728	0.9713