Removal Characteristics of Heavy Metal by Na-P1 Zeolite Synthesized from Coal Fly Ash

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This study was conducted for an efficient utilization of waste fly ash obtained from the power plant. Fly ash was used for synthesizing zeolite. Na-P1 zeolite could be easily synthesized from waste fly ash and showed the potential to remove heavy metal ions. The synthetic zeolite showed good adsorption property for heavy metal much better than raw fly ash and natural zeolites. Na-P1 exhibited the high adsorption efficiency with a maximum value of 260 Pb mg/g and strong affinity for Pb^{2+} ion. The metal ion selectivity of Na-P1 was determined in a decreasing order : $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}>Fe^{3+}$.

1. Introduction

Nowadays as economics have been developed and life quality is improved, the needs of energy are rapidly increased. The usage of coal fuel is increased in our country. The burning of coal, however, causes an air pollution by poisonous gases such as SO_x and NO_x and generates huge wastes of fly ash. The fly ash is produced when the coal is burned in a chamber and is mainly composed of fine carbon powder and fly ash. According to Ferraiolo et al.(1990) and Singh et al.(1993), the ratio of ash to coal buried in the whole world is almost 10~15 wt%, of which 20% are bottom ash and the others are fly ash.

The domestic generating amount of fly ash in 1996 became over 4.0×10^6 tons and more than 5.5×10^6 tons will be in 2006. The huge amount of fly ash has no application and most of them is disposed of by landfill(Shon, 1996).

One major utilization of the fly ash is to use as adsorbent for removal some substances such as phenol(Singh and Rawat, 1994), oxalic acid (Jain, 1978) and organic compounds(Teuney and Echelberger, 1970; Hung, 1983). Banerjee et al(1995) examined the dynamic behavior of the fly ash in a batch experiment. They found that the fly ash exhibited a good adsorbing property with organic compounds in water. Other applications have been reported. Most of them were related with heavy metal removal such as Cr(Panday, 1984), Cu(Panday, 1985), Cd(Yadara, 1987), Ac(Sen and De, 1987), Hg(Kapoor and Viraraghavan, 1992), Pb(Mathur and Rupainwar, 1988), Ni and Zn(Viraraghavan and Dronamraju, 1993).

However, a new approach for application of the fly ash is to convert it into zeolites. As the chemical composition of fly ash is similar to that of zeolites(Lee, 1993), many researches have been

focused on the synthesis of various zeolites by basic treatment of the fly ash.

The synthesized zeolites exhibit an improved adsorbing property and a selectivity for substances, such as heavy metal ions, gases and other poisonous materials. There are some reports in this promising field. Christopher(1996) performed the synthesis of zeolites using NaOH, KOH, KF and NH_4HF_2. Shigemoto(1995) converted fly ash to zeolites by hydrothermal and fusion treatment with NaOH and studied the structure of the synthesized zeolites with IR, NMR and XPS methods. Cheng-Fang Lin(1995) treated fly ash basically resulting in improvement the adsorbing property, with increase of cation exchange capacity and specific surface area.

In this study, an efficient utilization of fly ash by synthesizing various zeolite and by evaluating the potential for using the synthesized fly ash to remove heavy metals was presented. the chemical compositions, metal ion selectivities of the raw fly ash and the synthesized zeolites were investigated. For comparison, natural zeolites were also used. Adsorbing isothermal equation, rate of adsorption, heat of adsorption and diffusion coefficients were determined.

2. Experimental

The fly ash sample used in this work was obtained from a power plant located at Boryung in Chungnam, Korea. The sample was pretreated by HGMS(high gradient magnetic separator) to remove Fe_2O_3 and TiO_2 which were known to be undesirable for zeolite synthesis(Tazaki, 1989). To synthesize zeolites, the fly ash was reacted with 1 to 10 M NaOH at a 1 :10 ash(g) to a solution(mL) ratio in 125 mL or 750 mL capped Teflon tubes in stainless steel vessels in a digital-type forced-convection electric oven at 70

~200°C for 1~2 days without stirring(Kim, 1997). The same batch sample was used in all the experiments.

Adsorption properties of synthesized zeolites for heavy metals were studied and compared in those of fly ash and natural zeolite. A stock solution was made with a concentration of 1000 mg/L and diluted for the further experiments. Analytical grades of $Pb(NO_3)_2$(Yakuri pure chemicals, Japan), $Cd(NO_3)_2 \cdot 4H_2O$(Junsei chemical, Japan), $Cr(NO_3)_3 \cdot 9H_2O$(Hayashi pure chemical, Japan), $Zn(NO_3)_2 \cdot 6H_2O$(Junsei chemical, Japan) and $Fe(NO_3)_3 \cdot 9H_2O$(Hayashi pure chemical, Japan) were used. for the experiments

Batch reactor experiments were carried out to investigate adsorption properties for heavy metals. The one liter of prepared aqueous solution containing heavy metal ion was placed in 2 L Erlenmeyer flask and the pH in the liquid was adjusted with NaOH or H_2SO_4 solution. Amount of an adsorbent such as zeolites, fly ash or natural zeolite was measured and added into the solution. The solution was stirred with a magnetic stirrer at the speed of more than 3000 rpm to get rid of mass transfer resistance. During the experiments, the same aliquots were taken from the solution at a given time interval, centrifuged at 6000 rpm, and the supernatants was decanted. The metal ion concentrations were obtained by using AA instrument(UNICAM 939 AA Spectrophotometer).

3. Results and Discussion

3.1. Synthesis of zeolites from raw fly ash

Most of the raw fly ash particles were hollow spheres in a different size. The particle size was distributed in a wide range of 0-180 μm, mainly between 10 and 50 μm. Fly ash is composed of

Table 1. Chemical compositions(%) of raw fly ash and synthesized product

Items Materials	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	MgO	MnO	P_2O_5	Na_2O	K_2O	LOI[a]
Raw Fly Ash	50.0	28.7	2.6	3.7	1.2	0.9	0.04	2.1	0.3	1.4	4.7
Synthesized Product[b]	37.0	30.3	2.5	2.5	1.2	1.3	0.03	0.2	6.8	0.6	17.4

[a]Loss on ignition
[b]Treated with 3M NaOH solution at 100oC for 24hr

aluminosilicate glasses in more then 60-80 %, which is an available source of zeolites(Kim, 1997).

The fly ash was transformed to zeolite with a hydrothermal treatment in a caustic solution. Product obtained after a 24 hour treatment in 3 M NaOH at 100℃ was fully analyzed. Table 1 shows the chemical compositions of raw fly ash and synthesized product. The chemical compositions of synthesized product represents a higher loss on ignition, 17.4 % and larger content of Na_2O than that of raw ash. These results indicate the formation of zeolite-like product from the raw ash, because these may be attributed to a desorption of the adsorbed water and a high degree of cation exchange.

3.2. Effects of adsorbent on metal removal

Fig. 1 shows removal efficiency of lead for raw fly ash, natural zeolites and the synthesized zeolite from raw fly ash. 0.2 g of each adsorbent was used in 20 mg/L lead solution at 25℃. The concentration of lead ion was measured at equilibrium and used for each adsorption efficiency.

Raw fly ash showed a relative small Pb^{2+} removal efficiency with a value of about 10%. Natural zeolites showed better removal efficiency, depending on produced place. For example, natural zeolite from Yongdong and Daesin exhibited the removal of 39% and 63%, respectively. The synthesized zeolite, Na-P1, showed the highest efficiency for lead removal with more than 98%.

RAW : Raw fly ash   YD : Youngdong(Natural)
DS   : Daesin(Natural) Na-P1 : Sythesized zeolite
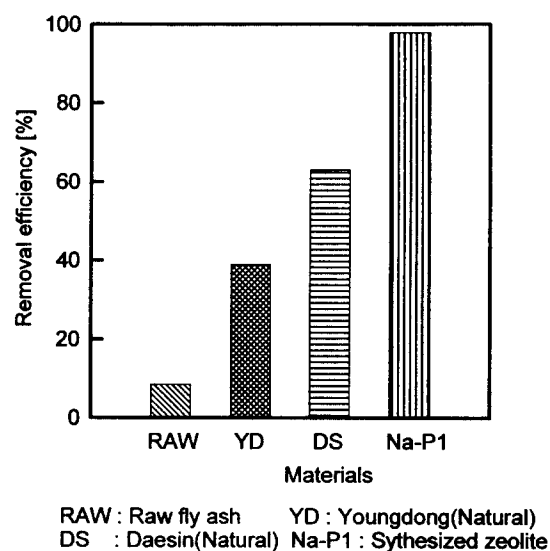
Fig. 1. Comparison of lead removal efficiency for each material.

3.3. Effects of heavy metal ion on its removal

Fig. 2 shows the metal removal efficiency of Na-P1 for various metal ions. The adsorbent, 0.1 g of Na-P1, was used and the initial metal ion concentration was 20 mg/L at 25℃. When equilibrated, the reduced metal concentration was measured and used for removal efficiency.

Lead ion was the most efficiently removed cation for Na-P1, showing more than 90% value. Cd, Cu, Zn, Fe were removed by 60, 30, 20 and 10%, respectively. Therefore the cation affinity for Na-P1 is shown in a decreasing order as follows: $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Fe^{3+}$. It is likely that the removal efficiency differences

among the various cations can be attributed to differences in their sizes and charges. As hydration radius of Fe^{3+} is largest among the metals, it is hard to get into zeolite pore and cation exchange occurs only on limited sites.
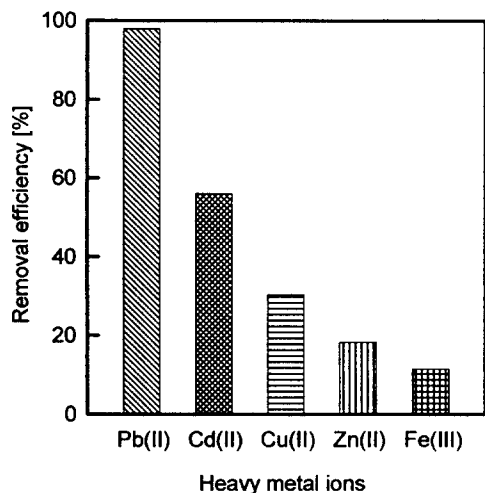

Fig. 2. Comparison of removal efficiencies of Na-P1 for each heavy metal.

3.4. Effects of adsorbent amount and initial lead concentration

Effects of adsorbent amount on metal removal were determined. A various amount of 0.1 g, 0.15 g and 0.2 g Na-P1 was added to a lead solution of 50 mg/L at 25℃. As the amount of adsorbent increased, lead removal efficiency increased as shown in Fig. 3. This result indicates that the larger surface area in large amount of adsorbent can give metal ions more adsorption sites.

Fig. 4 shows the effect of lead concentration on adsorption efficiency. 0.1 g of adsorbent Na-P1 was added to a lead solution of various concentration, 25, 50, 70 and 100 mg/L. As shown in Fig. 4, the higher concentration of lead solution was added, the lower metal removal efficiency was obtained.
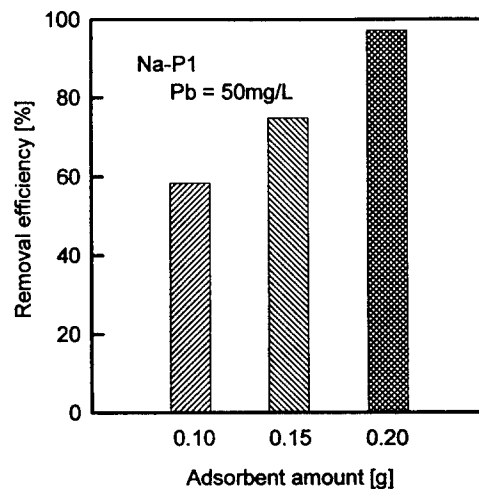

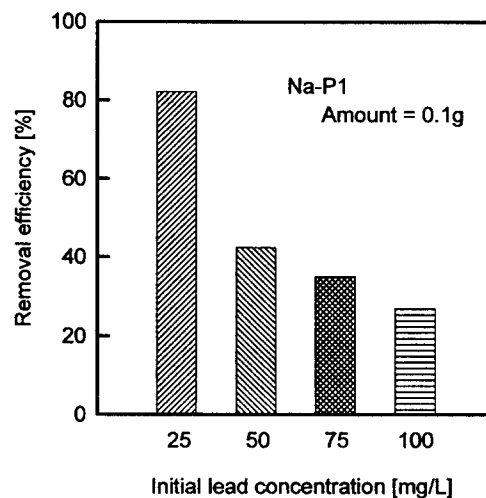**Fig. 3.** Effect of adsorbent amount on lead removal efficiency.

Fig. 4. Effect of initial lead concentration on lead removal efficiency.

3.5. Effects of reaction temperature

Effect of reaction temperature on lead removal was investigated. The reaction of 0.1 g Na-P1 and 50 mg/L lead solution were carried out at various temperature, 15, 25 and 50℃. As temperature went up, lead removal efficiency

increased. The removal for the metal ion is actually cation exchange process, in which activation energy is small as it is not involved in bond formation or dissociation. Fig. 5 is an Arrhenius plot and apparent activation energy obtained from the slope, 2.72 kJ/mol, is smaller than Yamashita's result, 6.48 kJ/mol(1978). The difference of the activation energy may be originated from those of synthetic condition of adsorbents and adsorption mechanism.
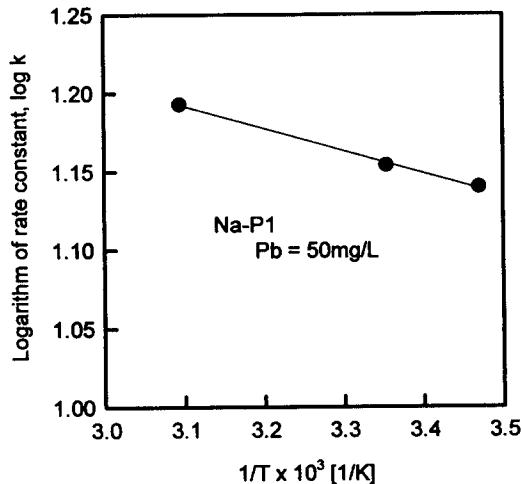

Fig. 5. Arrhenius plot of apparent reaction rate constant for Na-P1.

3.6. Adsorption isotherm

Generally, it is usual to apply the Langmuir and Freundlich adsorption isotherm equations to calculate the adsorption quantity. The adsorption isotherm equation is expressed by constants which indicate the surface property and affinity of absorbent (Al-Duri, 1992).

In Fig. 6 an adsorption isotherm is shown. The range of initial lead concentration is 10~200 mg/L and the quantity of synthesized zeolite and natural zeolite at 25℃ is 0.1g, respectively. In Fig. 7, a comparative adsorption isotherm of

heavy metal ion is shown. The results suggest that the maximum adsorbed ion in Na-P1 is Pb^{2+}, and Cd^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{3+} followed in order.
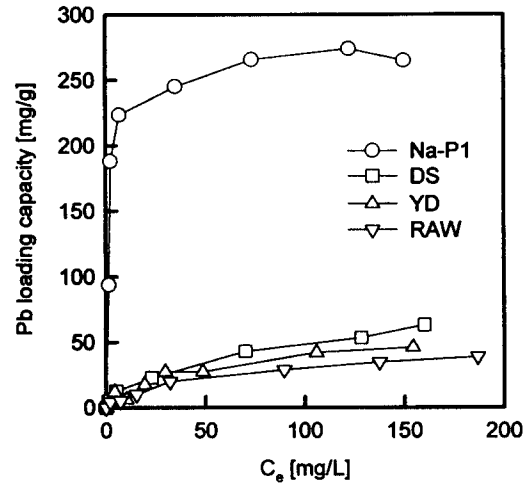

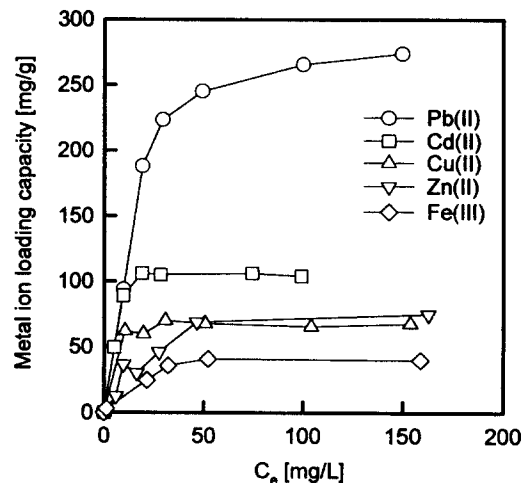**Fig. 6.** The adsorption isotherms of various materials.

Fig. 7. The adsorption isotherms of Na-P1.

The results for adsorption isotherm of lead are shown in Fig. 8 as Langmuir model and in Fig. 9 as Freundlich model. From the figures, it is verified that the results fit well with Freundlich model than Langmuir model.
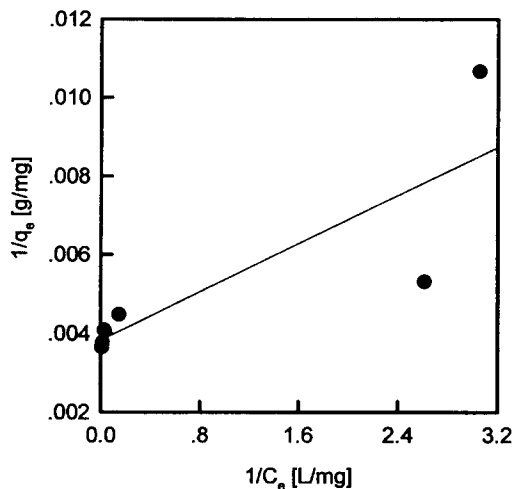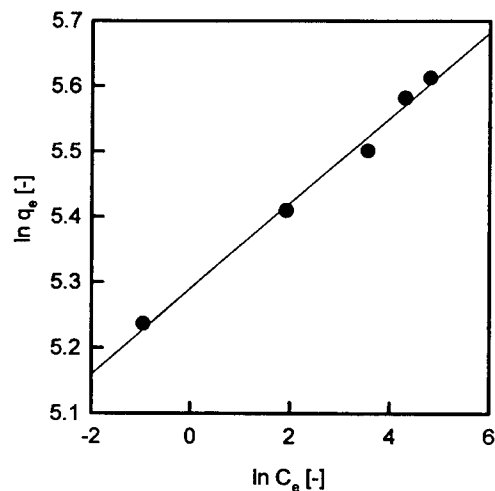
Fig. 8. Langmuir isotherm for lead of Na-P1.

Fig. 9. Freundlich isotherm for lead of Na-P1.

Table 2. Langmuir and Freundlich isotherm parameters of various adsorbents for lead adsorption.

Adsorbents	Langmuir			Freundlich		
	q_{max} (mg/g)	b	r^2	K	n	r^2
Na-P1	260.3	0.62	0.294	165.1	9.016	0.862
DS	79.2	0.019	0.878	5.01	2.016	0.977
YD	58.6	0.023	0.822	4.65	2.16	0.965
Raw fly ash	38.5	0.12	0.714	0.827	1.244	0.987

In Table. 2, the isotherm parameters obtained by the linear regression method are shown. As seen in Table 2, the maximum adsorption of raw fly ash is about 38.5 mg/g and that of natural zeolite is 60~80 mg/g, however, the maximum absorption of Na-P1 is 260 mg/g. Therefore, it is known that the synthesized zeolite has an excellent adsorption capacity compared with raw fly ash and natural zeolites.

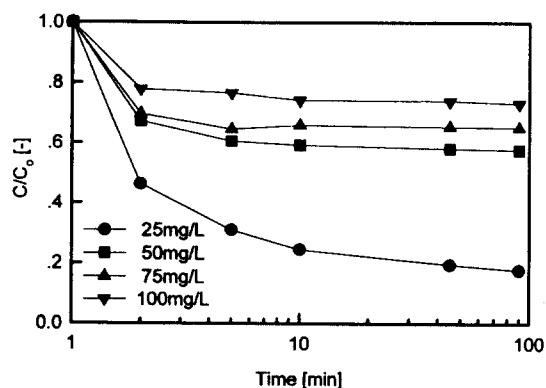## 3.7. Diffusion coefficient in particles.

The process to reach adsorption equilibrium depends on the adsorbing solute, adsorbent, and the condition of adsorption. In order to obtain the important parameters for the design of adsorptive facility, the coefficients of surface diffusion and pore diffusion into zeolite channel are essential, which can be calculated by the graphical method of Suzuki and Kawazoe(1974a, 1974b).

In Fig. 10, it is shown that the ratio of equilibrium concentration to initial concentration, C/C_0, decreases as the initial concentration decreases. In addition, up to 10 minutes of adsorption it decreases, however, after 15 minutes, it reaches at equilibrium. By the graphical method of Suzuki and Kawazoe, the diffusion coefficients in particles were obtained from the theoretical curve fitting, which are close to n value of Freundlich constant, 9.016 shown in Table 2. They are shown in Table 3.

Table 3. Pore diffusion and surface diffusion coefficients for the various initial lead solution concentrations.

Initial concentration C_o [mg/L]	Pore diffusion coefficient $D_p \times 10^3$ [cm²/sec]	Surface diffusion coefficient $D_s \times 10^{10}$ [cm²/sec]
25	8.22	1.50
50	7.06	1.67
75	6.42	2.00
100	5.83	2.33

Fig. 10. Effect of initial solution concentration on concentration profile.

4. Conclusion

Zeolite could be produced from fly ash by heating in basic solution. Synthesized zeolite showed a high affinity for metal ion and better removal efficiency than raw fly ash and natural zeolites. Na-P1 exhibited high affinity for lead ion with a maximum adsorption capacity of 260 Pb mg/g, which was corresponding to 98% removal efficiency. While raw fly ash showed 10% removal efficiency with 38.5 Pb mg/g capacity and naturel zeolite from Yongdong showed 39%, from Daesin 63% with 60~80 Pb mg/g capacity.

Selectivity of Na-P1 for metal removal was determined in a decreasing order : $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}>Fe^{3+}$. Adsorption equilibrium of lead by Na-P1 was consistent in Freundich isotherm rather than Langmuir. It is considered that this high metal ions removal properties of Na-P1 can be applied to reduce heavy metal ions from waste water.

Nomenclatures

b   constant related to the energy of net enthalpy of adsorption

C_o initial lead concentration in solution, mg/L

C_e measured concentration of lead in solution at equilibrium state, mg/L

D_P pore diffusion coefficient, cm²/sec

D_S surface diffusion coefficient, cm²/sec

K   indicator of adsorption capacity

1/n   adsorption intensity

q   amount of lead adsorbed per unit weight of adsorbent at equilibrium time, mg/g

q_{max} amount of lead adsorbed per unit weight of adsorbent, mg/g

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