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Heavy metal adsorption by a formulated zeolite-Portland cement mixture

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Abstract

Large amounts of fine zeolite by-product were produced when natural zeolite was processed into a powder with a specific particle size. In Korea, large piles of this by-product exist with no disposal options. We conducted studies to determine whether mixtures of this by-product with other materials could be used as a substitute to activated carbon for wastewater treatment. A granular material was formulated by mixing zeolite by-product with Portland cement (ZeoAds), and this material was tested for its efficiency for heavy metal removal from aqueous solutions. The ZeoAds removed Pb and Cu in an aqueous solution up to 27.03 and 23.25 mg g^{-1}, respectively. Adsorption kinetics of the ZeoAds for heavy metals was first-order, and the ZeoAds removed about 90% of the Cu within 30 min. At solution pH lower than five, the adsorption specificity of the ZeoAds for metals was Pb > Cu > Cd ≥ Zn. Langmuir isotherms adequately described the adsorption, and adsorption capacity increased as the particle size decreased to 2 mm in diameter. The maximum adsorption capacities of the metals for the ZeoAds were, irrespective of the kinds of metals, about two times greater than those of activated carbon. Column experiments demonstrated that the ZeoAds was more efficient and had a higher sorptive capacity than activated carbon for removing metals from industrial wastewater.

Keywords: Zeolite; Activated carbon; Adsorption; Heavy metals; Portland cement

1. Introduction

Zeolite is a naturally occurring crystalline aluminosilicate mineral consisting of a framework of tetrahedral molecules, linked with shared oxygen atoms. Zeolite has a large surface area and high cation exchange capacity (CEC), and provides an exchange complex that can adsorb variably-sized ions [1], which promotes its use as a selective adsorbent for oil and gas pollutants, pesticides, and metals [2–4]. During the 1970s, natural zeolite was shown to preferentially remove heavy metals such as Sr and Cs from wastewater [1], and this property made zeolite a preferred adsorbent for wastewater treatment systems. The selectivity of zeolite species, such as clinoptilolite and chabazite, for heavy metals based on the ionic radius and dissociation constant was in the order: $Pb^{2+} > Ni^2 > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+}$ [5–7]. Langella et al. [8] reported that the ion selectivity of clinoptilolite was in the order: $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} = Zn^{2+}$.

Activated carbon is the standard adsorbent used for treating wastewater containing heavy metals. Previous research demonstrated that zeolite performed better and was less expensive than activated carbon for removing heavy metals from wastewater [9,10]. Performance of zeolite for adsorption can be improved by decreasing zeolite particle size, but finer particles may reduce permeability of the column for wastewater treatment [11].

Since generation of commercial zeolite is expensive, mixtures of zeolite and other less-costly organic and inorganic materials, such as fly ash, Portland cement, clays, and polymers, have been formulated for specific pollutants and to reduce material cost [6,12,13]. Portland cement is one of the most common materials for solidification and stabilization and has been used as a supplement to zeolite for adsorption purposes [4,14].

A commercial-grade zeolite with a specific particle size has been produced in the Yeongil area of Korea for several decades

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[12]. As a result of this production, a powdery zeolite by-product, which contains primarily clinoptilolite, was created and placed in large piles with no plan for disposal. The objective of this research was to investigate the adsorption properties of this zeolite by-product mixed with Portland cement (mixture is called ZeoAds) and to compare this mixture to activated carbon, the industry standard, for heavy metal removal in wastewater.

2. Materials and methods

2.1. Formulation of the ZeoAds

The by-product zeolite was collected from the zeolite processing plant in Yeongil County in Southeastern Korea. The ZeoAds was made by mixing the by-product zeolite with Portland cement using a vacuum extruder equipped with various pore size nozzles ranging from 0.04 to 3.00 mm in diameter. The extruded samples were dried for 24 h at ambient temperature and aged for 30 days in water at 23 ± 2 °C, then heated for 3 h at 400 °C in the furnace, and cooled to ambient temperature. The ratio of zeolite by-product to Portland cement was 75:25, which was selected because this ratio provided the maximum compressive strength of the mixture.

A commercial activated carbon material (Eulim Co. Ltd., Korea) was compared to the ZeoAds in heavy metal adsorption. The physical and chemical properties of the ZeoAds and activated carbon are shown in Table 1. The pH was measured in a 1:1 water suspension using a combination glass electrode. The CEC was determined by 1 M ammonium acetate (pH 7.0) extraction. Bulk density was measured by extracting cores and determining mass and volume. Specific surface area was determined by N_2 adsorption with the Carlo-Erba SORPTY 1750 at 77 K [15].

2.2. Adsorption kinetics of ZeoAds

A batch kinetic experiment was performed by adding the ZeoAds (2 mm in diameter) to an aqueous solution containing 100 mg L^{-1} of Cu at 1:25 of the ZeoAds for the solution ratio. The mixed solutions were shaken at 150 rpm in a reciprocal shaker at 10 °C and 20 °C for 10, 20, 30, 60, 90, 120, 150, 180, 210, and 240 min. After the reaction, the supernatant was collected by a syringe and filtered through a 0.2 μm membrane filter to measure the Cu concentration using ICP-AES (Optima 3100XL, Perkin-Elmer). Calibration standards were prepared using standard solutions certified by the supplier. Five calibration standards and blank solutions were used to calibrate the ICP-AES. A linear calibration curve was obtained, and if the correlation coefficient R^2 was less than 0.999, the equipment was recalibrated to ensure the accuracy of results. All instrumental conditions were optimized for maximum sensitivity as indicated by the manual of the manufacturer.

A first-order kinetic equation was employed for the adsorption of Cu onto the ZeoAds (Eq. (1)). Among several kinetic models, first-order kinetic equation was selected based on the highest coefficient of determination and the lowest standard error for the models [16,17]. The adsorption kinetics of the ZeoAds was also compared with those of the commercial activated carbon.

$$\ln \frac{[\mathrm{Cu}]_t}{[\mathrm{Cu}]_0} = -kt \tag{1}$$

where $[Cu]_0$ is initial molar concentration of Cu; $[Cu]_t$ is molar concentration of the remaining Cu after time t; t is reaction time (minutes); k is rate constant.

2.3. Adsorption capacity of the ZeoAds

Batch experiments were conducted by adding 5 g of ZeoAds (2 mm in diameter) or activated carbon to an aqueous solution containing Pb, Cu, Zn, or Cd in which the initial metal concentrations varied from 50 to 1600 mg L^{-1}. The ratio of the ZeoAds to the solution was 1:25. Each sample was shaken at 25 °C for 24 h in a reciprocal shaker. Effects of the initial pH on the adsorption of heavy metals by the ZeoAds were determined at a metal concentration of 600 mg kg^{-1} as nitrate salts with the estimated values of pH_{50} and pH_{100}, where 50% and 100% of the metals adsorbed onto the ZeoAds, respectively. All the reactions were conducted in a 0.01 mM $NaNO_3$ background solution to maintain a constant ionic strength during the experiment. The mass of the adsorbed metal per unit weight of the ZeoAds was calculated (Eq. (2)) [18,19].

$$q = \frac{(C_\mathrm{i} - C_\mathrm{e}) \times V}{m} \tag{2}$$

where q is mass of the adsorbed metal per unit weight of sorbent (mmol g^{-1}); V is volume of the reacting solution (L); C_i is initial concentration of the metal (mmol L^{-1}); C_e is equilibrium concentration of the metal (mmol L^{-1}); m is weight of the ZeoAds (g).

The maximum adsorption quantity of the metal by ZeoAds was obtained from the Langmuir isotherm as shown in the Eqs. (3) and (4) [16].

$$q = \frac{k \times C_\mathrm{e} \times b}{1 + k \times C_\mathrm{e}} \tag{3}$$

Table 1
Physical and chemical properties of the granular zeolite-Portland cement adsorbent (ZeoAds) and the activated carbon used in the experiment

Adsorbent	pH	CEC ($cmol_c\ kg^{-1}$)	Surface area ($m^2\ g^{-1}$)	Particle size (mm)	Bulk density ($g\ cm^{-3}$)
ZeoAds[a]	12.1	52.2	17.3	2.0	1.38
Activated carbon[b]	9.4	16.3	897.7	0.5–1.0	0.38

[a] The granular adsorbent formulated from the by-product powdery zeolite and Portland cement with a mixing ratio of 75:25.
[b] The commercially available product from Eulim Co. Ltd., Korea.

Table 2
Experimental conditions of the column leaching experiment using the ZeoAds and the activated carbon for the treatment of semiconductor industry wastewater

Parameter	ZeoAds	Activated carbon
Adsorbent (g)	25	25
Flow velocity ($L\,h^{-1}$)	1.42	1.42
Linear flow velocity ($m^3\,m^{-2}\,h^{-1}$)	2.68	2.68
Volume (cm^3)	34.5	69.4

$$\frac{C_e}{q} = \frac{1}{kb} + \frac{C_e}{b} \quad (4)$$

where q is mass of the adsorbed metal per unit weight of sorbent ($mmol\,g^{-1}$); C_e is equilibrium concentration of the metal ($mmol\,L^{-1}$); b is maximum adsorbable concentration of the metal ($mmol\,g^{-1}$); k is constant related to the binding strength.

2.4. Metal removal efficiency of the ZeoAds

The static mode of column leaching experiments with an internal diameter of 1 cm was conducted to investigate the metal removal efficiency of the ZeoAds as compared to those of the activated carbon. Throughout the experiment, the ratio of column diameter to height was maintained at 1:25 to avoid the edge effect during the experiment [20]. The column was packed by pouring glass beads into the bottom to 1 cm in height, followed by 25 cm of the ZeoAds with a bulk density of $1.2\,g\,cm^{-3}$. The experimental conditions maintained during the experiment are listed in Table 2. Prior to wastewater addition, over 25 pore volumes of distilled water were eluted through the column in order to remove the suspended particles and stabilize the pH of the column system. Wastewater from the semiconductor industry, which was contaminated with metals and sulfate (Table 3), was introduced to the top of the column at a flow rate of $1.42\,L\,h^{-1}$. Leachate was collected from the base of the column in polypropylene test tubes using a fraction collector, and the concentration of the metals was determined by the ICP-AES (Optima 3100XL, Perkin-Elmer).

3. Results and discussion

3.1. Physical and chemical characteristics of ZeoAds

The pH, particle size, and bulk density of the ZeoAds were higher than those of the activated carbon (Table 1). The CEC of the ZeoAds was three times higher than that of the activated carbon, even though the surface area of the ZeoAds, $17.3\,m^2\,g^{-1}$, was much lower than that of the activated carbon, $897.7\,m^2\,g^{-1}$.

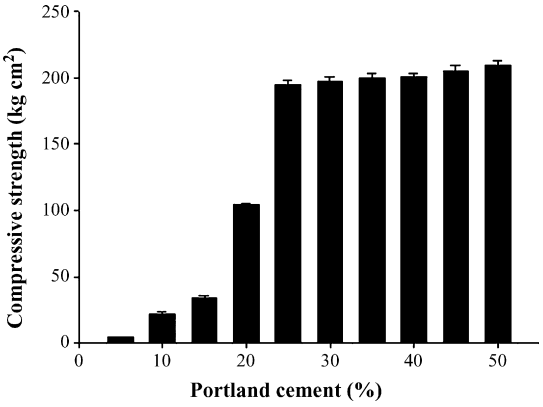

Fig. 1. Effect of mixing ratio of Portland cement over the by-product powdery zeolite on compressive strength of the granular adsorbent formular (ZeoAds).

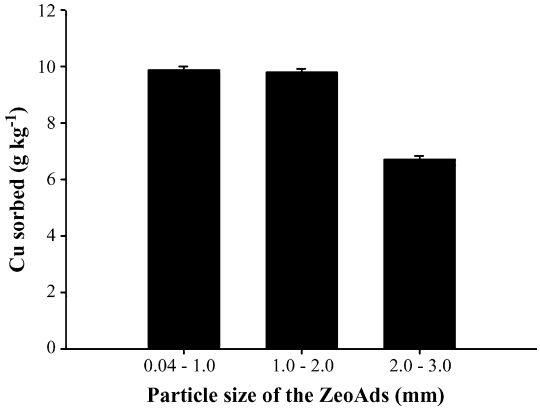

Fig. 2. Effect of particle size of ZeoAds on adsorption capacity of Cu in aqueous solution (conditions: 5 g ZeoAds, 125 mL 1000 mg L^{-1} Cu solution, pH 3.0, background electrolyte: 0.01 M $NaNO_3$, contact temperature: 25 °C, reaction time: 24 h).

The compressive strength of the ZeoAds reached about $200\,kg\,cm^{-2}$ at 25% of the mixing ratio of the Portland cement over the by-product zeolite, above which no significant difference was observed (Fig. 1). Fig. 2 shows the effect of particle size of the ZeoAds on the adsorption capacity of Cu in an aqueous solution. The Cu removal efficiency of the ZeoAds with 0.04–2.0 mm diameter was $9.9\,g\,kg^{-1}$, but decreased significantly to $6.7\,g\,kg^{-1}$ as the particle size of the ZeoAds increased to 2.0–3.0 mm in diameter. Based on the compressive strength and adsorption capacity of Cu, the mixing ratio of 1:3 (Portland cement to by-product zeolite) with 2 mm in diameter was the optimum physical criterion for the formulation of the ZeoAds.

Table 3
Characteristics of the experimental wastewater used in the column leaching experiment

	pH	EC ($dS\,m^{-1}$)	COD ($mg\,L^{-1}$)	SO_4 ($mg\,L^{-1}$)	Cd ($mg\,L^{-1}$)	Cu ($mg\,L^{-1}$)	Pb ($mg\,L^{-1}$)	Zn ($mg\,L^{-1}$)
Wastewater[a]	8.8	1.21	720.9	200.8	0.03	0.16	2.08	0.24
Standard[b]	5.8–8.6	–	150	–	0.10	3.00	1.00	5.00

[a] Wastewater was collected from the semiconductor industry, Seoul, Korea.
[b] Water quality standards for discharging wastewater in Korea.

Table 4
The first-order kinetic equations for Cu adsorption by the ZeoAds at 10 and 20 °C

Metal	Temperatures (°C)	Regression equation[b]	r^2
Cu[a]	10	$Y=-1.2e{-}03X+4.530$	0.890[c]
	20	$Y=-1.8e{-}03X+4.541$	0.969[c]

[a] Initial Cu concentration: 100 mg L^{-1}, 1:25 of the ZeoAds for the solution ratio; reaction time: 10, 20, 30, 60, 90, 120, 150, 180, 210, and 240 min.
[b] Y: ln (molar % of the remaining Cu); X: time (minute).
[c] $p<0.01$.

3.2. Adsorption kinetics of the ZeoAds

Adsorption of Cu by the ZeoAds followed first-order kinetics to a significant extent (Table 4), indicating the adsorption of the metal onto the ZeoAds was dependent on the concentration of the reacting metal. Among the kinetic models, first-order kinetics gave the best fit based on the highest coefficient of determination (r^2) and the lowest standard error. The rate constant for Cu adsorption at 20 °C was about 50% greater than that at 10 °C. Adsorption kinetics also occurred rapidly, showing about 90% of the Cu removed within 30 min and reaching a pseudo-equilibrium state within an hour (Fig. 3). The proportional increase of Cu removal with increased temperature demonstrated that adsorption of Cu onto the ZeoAds occurred by chemisorption and was thermodynamically favorable as proposed by Poots et al. [21] and Yang and Skogley [22].

3.3. Effect of pH on metal adsorption by the ZeoAds

The pH is a critical criterion for determining the surface characteristics of adsorbents and the adsorption equilibrium of adsorbates. Adsorption of Cd, Cu, Pb, and Zn onto the ZeoAds generally increased as the pH increased (Fig. 4). At pH values higher than six, the percent of adsorbed metals significantly increased, possibly due to precipitation of metal complexes, which is indicative of typical sorption edges [16]. Sorption edge is the narrow range of pH, where adsorption of the metals onto the adsorbents jumped completely to 100%.

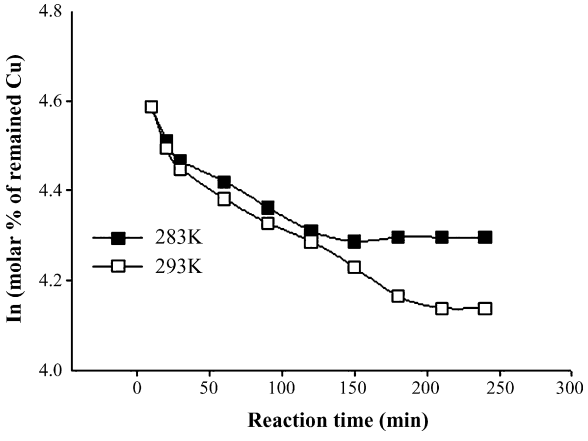

Fig. 3. The rate curves of the first-order kinetic model for adsorption of Cu by the ZeoAds at 10 °C and 20 °C (conditions: 5 g ZeoAds, 125 mL 100 mg L^{-1} Cu solution, background electrolyte: 0.01 M $NaNO_3$).

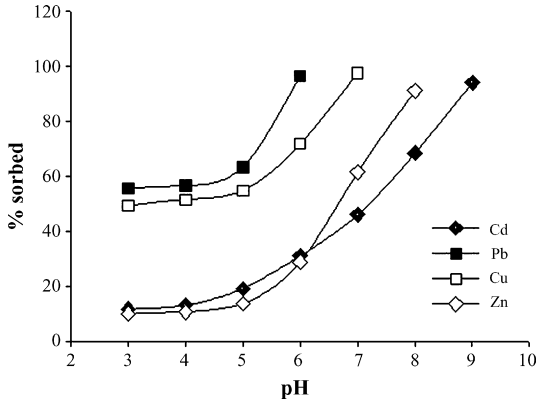

Fig. 4. Effects of initial pH on adsorption of heavy metals by the ZeoAds in aqueous solution (conditions: 5 g ZeoAds, 125 mL 600 mg L^{-1} metal solution, background electrolyte: 0.01 M $NaNO_3$, contact temperature: 25 °C, reaction time: 1 h).

The values of pH_{50} and pH_{100}, where 50% and 100% of the Pb were sorbed onto the ZeoAds, were three and six, respectively. The values for Cu were three and about seven. However, the pH_{50} values for Zn and Cd were about seven, where pH_{100} values ranged from 8 to 9.5. At pHs lower than five, the adsorption specificity of the ZeoAds followed the order of Pb > Cu > Cd ≥ Zn. Similarly, An et al. [9] reported that the order of affinity of the commercial zeolite was Pb > Cd ≥ Cu in an aqueous solution. They showed that zeolite was more efficient for metal sorption capacity than both the granular activated carbon and the powdered activated carbon (PAC) made from coconut shell char.

3.4. Adsorption capacities of metals onto the ZeoAds

Adsorption isotherms of the ZeoAds and activated carbon for Cd, Cu, Pb, and Zn followed the Langmuir isotherm model, as shown in Table 5 and Fig. 5. The maximum adsorption capacities (Q_{max}) of the ZeoAds for Pb and Cu were 27.03 and 23.25 mg g^{-1}, respectively. The order of Q_{max} was Pb > Cu > Zn > Cd for both the ZeoAds and activated carbon (Table 5). The Q_{max} values of the ZeoAds for Pb, Cu, Zn, and Cd were 47, 89, 78, and 71% higher than those of activated carbon. In general, the order of heavy metal adsorption was known to correlate with the ionic radius [23] and the covalent index [24], which are functions of electronegativity and ionic radii. The ionic radii followed the order of Pb > Cu > Cd, which coincided with the adsorption capacities of the ZeoAds. Even though this selectivity may vary according to the sources of adsorbents, kinds of metals, and experimental conditions, many researches reported that zeolite had preferential adsorption for Pb over Cu and Zn [9,25–27]. The k value, a constant related to the binding strength of an adsorbent, of activated carbon was higher than that of the ZeoAds (Table 5). Sparks [16] reported that the calculation of binding strength (k) values seemed questionable, while it is admissible to calculate Q_{max} values for different adsorbents and to compare them in a qualitative sense.

Table 5
Langmuir model equations for adsorptions of Pb, Cu, Zn, and Cd by the ZeoAds and the activated carbon

Metals	Adsorbents	Regression equations[a]	r^2	Q_{max}[b]	k[b]
Cu	Activated carbon	$Y = 75.74X + 8.11 \times 10^{-2}$	0.986[c]	12.33	70.6
	ZeoAds	$Y = 2.22X + 4.30 \times 10^{-2}$	0.979[c]	23.25	51.5
Zn	Activated carbon	$Y = 17.42X + 13.86 \times 10^{-2}$	0.976[c]	7.20	125.0
	ZeoAds	$Y = 7.90X + 7.79 \times 10^{-2}$	0.912[c]	12.85	101.5
Cd	Activated carbon	$Y = 26.01X + 15.73 \times 10^{-2}$	0.957[c]	6.37	165.7
	ZeoAds	$Y = 15.07X + 9.25 \times 10^{-2}$	0.931[c]	10.87	163.0
Pb	Activated carbon	$Y = 6.30X + 5.45 \times 10^{-2}$	0.997[c]	18.35	115.7
	ZeoAds	$Y = 1.87X + 3.71 \times 10^{-2}$	0.984[c]	27.03	50.6

Conditions: 5 g ZeoAds, 125 mL, 50–1600 mg L^{-1} metal solution, background electrolyte: 0.01 M $NaNO_3$, contact temperature: 25 °C, reaction time: 24 h.
[a] Y: C_e/q; X: C_e.
[b] Q_{max}: maximum amount of adsorbate that adsorbed (mg/g); k: a constant related to the binding strength.
[c] $p < 0.01$.

3.5. Application of the ZeoAds into industrial wastewater

The column breakthrough curves for Pb removal by the ZeoAds are shown in Fig. 6 (curves for Cd, Cu, and Zn breakthrough were similar to Pb and therefore are not shown). The efficiency of the ZeoAds for Pb removal was higher than that of the activated carbon. Greater than 90% of Pb in wastewater was removed during the elution of about 90 pore volumes of the column, at which Pb concentrations were maintained at below

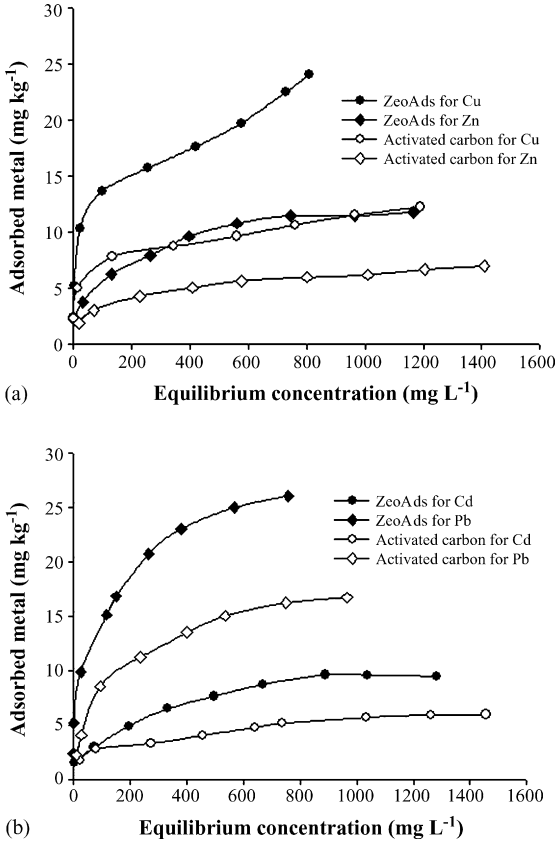

Fig. 5. Adsorption isotherms for (a) Cu and Zn and (b) Pb and Cd adsorptions by the ZeoAds and the activated carbon (conditions: 5 g ZeoAds, 125 mL 50–1600 mg L^{-1} metal solution, background electrolyte: 0.01 M $NaNO_3$, contact temperature: 25 °C, reaction time: 24 h).

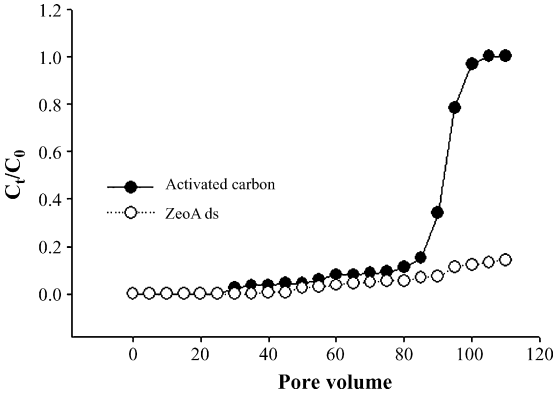

Fig. 6. Breakthrough curves for Pb removal by the ZeoAds and the activated carbon from the wastewater of the semiconductor industry.

0.075 mg L^{-1} Pb. The efficiency of Pb removal by the activated carbon declined considerably after the elution of about 90 pore volume and did not remove Pb after 100 pore volumes of the wastewater. Babel and Kurniawan [1] also showed that zeolite was effective for removal of metals such as Pb and Zn in contaminated wastewater in continuous column experiments. Our results showed that the ZeoAds in packed columns are feasible for wastewater treatment from a practical and economic point of view.

4. Conclusions

Adsorption kinetics of the ZeoAds followed first-order kinetics, showing about 90% of Cu removal within 30 min and reaching a pseudo-equilibrium state within an hour. Adsorption of metals onto both the ZeoAds and activated carbon followed the Langmuir-type isotherm. Adsorption capacities of the ZeoAds for the respective metal increased as the particle size decreased down to 2 mm in diameter, but no difference was observed for a diameter less than 2 mm. The order for the maximum adsorption capacities was Pb > Cu > Zn > Cd in both the ZeoAds and activated carbon. Maximum adsorption capacities of heavy metals for the ZeoAds were about two times greater than those of activated carbon irrespective of the kinds of met-

als. The weights of the adsorbed Pb and Cu per unit mass of the ZeoAds were 27.03 and 23.25 mg g^{-1}, respectively. The column experiment demonstrated that the ZeoAds was more efficient than activated carbon for removing metals from industrial wastewater. The overall results strongly supported the conclusion that the ZeoAds had a higher sorptive capacity than activated carbon and could be applicable to treatment of metal contaminated wastewater.

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