Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Evaluation of PAN-TiO$_2$ Composite Adsorbent for Removal of Pb(II) Ion in Aqueous Solution

Hyung-Tae Kim[a]; Chang-Ha Lee[a]; Yong-Gun Shul[a]; Jei-Kwon Moon[b]; Eil-Hee Lee[b]
[a] Department of Chemical Engineering, Yonsei University, Seoul, Korea [b] Korea Atomic Energy Research Institute, Daejeon, Korea

To cite this Article Kim, Hyung-Tae , Lee, Chang-Ha , Shul, Yong-Gun , Moon, Jei-Kwon and Lee, Eil-Hee(2003) 'Evaluation of PAN-TiO$_2$ Composite Adsorbent for Removal of Pb(II) Ion in Aqueous Solution', Separation Science and Technology, 38: 3, 695 — 713

To link to this Article: DOI: 10.1081/SS-120016660

URL: http://dx.doi.org/10.1081/SS-120016660

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 3, pp. 695–713, 2003

Evaluation of PAN–TiO_2 Composite Adsorbent for Removal of Pb(II) Ion in Aqueous Solution

Hyung-Tae Kim,[1] Chang-Ha Lee,[1] Yong-Gun Shul,[1]
Jei-Kwon Moon,[2,*] and Eil-Hee Lee[2]

[1]Department of Chemical Engineering, Yonsei University, Seoul, Korea
[2]Korea Atomic Energy Research Institute, Daejeon, Korea

ABSTRACT

A polyacrylonitrile–TiO_2 composite adsorbent bead was prepared to remove Pb^{2+} ion in aqueous solution. The dual nozzle technique was applied to prepare a spherical bead. The prepared composite adsorbent was found to be highly porous and stable against strong acids. Adsorption tests showed that Pb^{2+} ion adsorption increased in proportion to pH and Pb^{2+} ion was completely removed at pH 5.60. The equilibrium and kinetic parameters such as equilibrium constant, adsorption capacity, film mass-transfer coefficient, and effective diffusivity were also evaluated by modeling the experimental data.

---

[*] Correspondence: Jei-Kwon Moon, Korea Atomic Energy Research Institute, Yuseong P.O. Box 105, Daejeon 305-600, Korea; E-mail: njkmoon@kaeri.re.kr.

DOI: 10.1081/SS-120016660 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

INTRODUCTION

Lead is a ubiquitous heavy metal which acts, even though the concentration is low, as a cumulative toxin and can cause mental retardation and brain damage in children. The pollution sources include mining and electronic industries and also happens in the manufacture and disposal of batteries, paints, polymers, and printing materials.[1–3]

To remove heavy metal ions from aqueous solution, the various methods such as ion exchange or adsorption, electrodialysis, chemical precipitation, reverse osmosis, and ultrafiltration have been applied case by case.[4–11] Recently, the possible application of TiO_2 for removal of heavy metal ions such as Pb, Cd, Cr, Ni, and U has been reviewed by several authors.[2,12–14] They confirmed that titanium dioxide could remove the heavy metal ions by surface adsorption without light source[2] or by photocatalytic deposition with light sources.[12–14] These studies mainly focused on the basic activity of titanium dioxide powders. However, for most cases, titanium dioxide powder, if used as is, can cause operational problems such as pressure drop and filtration. To solve this problem, the titanium dioxide powders, as in most inorganic adsorbent powders, have to be pelletized or immobilized to the other supporting materials. Even though some inorganic adsorbents such as zeolites are possibly pelletized, most inorganic powders are hard to pelletize. These reasons have recently expedited the study on the preparation of organic–inorganic composite adsorbent beads for industrial applications.[15–22] Many organic polymers have been proposed as a binder in preparing composite adsorbents. Among them, PAN(polyacrylonitrile) is reportedly one of the most favorable binding materials for any inorganic adsorbents due to its physico-chemical properties such as excellent pelletizing properties, strong adhesive force with inorganic materials, good solubility for organic solvents, and chemical stability.[15–16] Several authors reviewed the studies on PAN-based composite adsorbents.[17–18] Especially, John et al.[17] conducted chemical and radiation stability tests for PAN and AMP-PAN beads and proved that they had no limitation by chemical and radiation decomposition. Moon et al.[18] prepared the PAN-based composite ion-exchanger beads and applied them to the removal of radionuclides and heavy-metal ions in aqueous solution. In spite of some successful results on the preparation of PAN-based composite adsorbents, there is not enough data on the preparation conditions depending on the inorganic adsorbents, and even fewer on the equilibrium and kinetic performances.

Therefore, this study was focused on the preparation of spherical PAN/titanium dioxide composite adsorbent and then evaluation of its adsorption behaviors for Pb^{2+} ion.

EXPERIMENTAL

Preparation of PAN–TiO_2 Composite Adsorbent

The procedure of preparing spherical PAN–TiO_2 composite adsorbent was shown in Fig. 1. First, Degussa P-25 titanium dioxide was homogeneously dispersed by using DMSO (dimethylsulfuroxide) solvent in a 1-L three-neck flask furnished with mechanical stirrer at 50°C for 2 hr, and then mixed with PAN (polyacrylonitrile) powder and a few drops of TWEEN-80 surfactant at 50°C for another 3 hr to make the homogeneous composite dope. The viscosity of PAN–TiO_2 composite dope was measured by viscometer (Brookfield. Inc., Model DV-II). The composite dope, as described in previous study,[18] was passed through inside the dual nozzle by metering pump while the compressed air in the range of 0–6 psig was ejected through the outside annulus of the dual nozzle to adjust the sphericity and the size of the composite beads. The ejected composite beads were then dropped in distilled water, which was used as a gelation agent. Finally, the spherical composite beads were washed using demineralized water and dried in vacuum dryer for 2 days at 5 torr and 50°C, which is considered enough for evaporation of DMSO.[23] The other drying condition of 80°C, 5 torr was tested for comparison.

Scanning electron microscope (JEO. Co., JSM 5200) was used to observe the pore structure and the distribution of P-25 TiO_2 powder in the beads. Pore size distribution and porosity of the composite bead were measured by using mercury porosimeter (Micromeritics, AutoPoreIII). Its morphology was observed by digital camera (Olympus Co., Model 2500).

The stability of the composite adsorbent was evaluated on its chemical and mechanical stabilities. In order to confirm the chemical stability, PAN–TiO_2 composite bead was immersed into the nitric acid solutions of pH 1–3 for 3 days and then the weight losses by the dissolution of PAN and TiO_2 powder imbedded in the beads were measured. For mechanical stability evaluation, the deformation of the beads was determined by contacting the composite adsorbent with the solution stirred at 500 rpm for 5 days.

Adsorption of Pb^{2+} Ion on PAN–TiO_2 Composite Bead

The distribution coefficients and adsorption isotherms were determined to evaluate the equilibrium performances of the composite adsorbents. The two different PAN–TiO_2 composite beads, which contain 71% and 50% TiO_2, respectively, were compared with the TiO_2 powder.

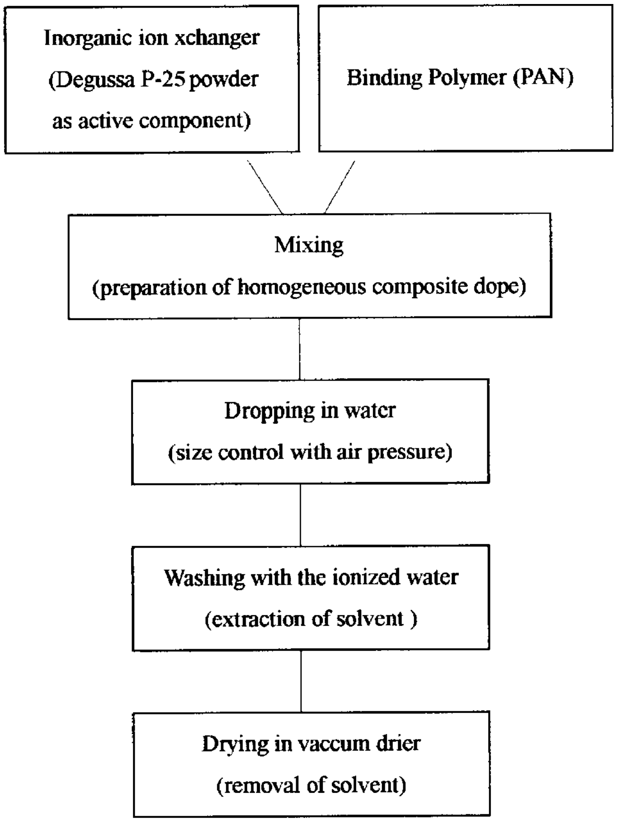

Figure 1. Procedure for preparing the PAN–TiO_2 composite bead.

First, the distribution coefficients were determined by contacting 0.1 g of Degussa P-25 TiO_2 powder and PAN–TiO_2 composite beads with 50 mL of 10^{-5} N Pb(II) solutions for 24 hr at room temperature. $Pb(NO_3)_2$ was used for Pb^{2+} ion source and the pHs of the solutions were varied in the range of 2–6. Then the adsorption isotherms of Degussa P-25 TiO_2 powder and PAN–TiO_2 composite beads for Pb^{2+} ion were determined in a batch reactor where the mass of the composite adsorbent was varied. The other variables such as solution concentration, volume, and pH were held constant at 1.0 ppm, 50 mL, and 5.60, respectively. The tests were performed in triplicate and averaged to obtain each isotherm point.

Uptake rate for Pb^{2+} ion was determined in a finite batch reactor by contacting 2 g of PAN–TiO_2 composite adsorbents with 1 L of 10^{-5} N Pb(II) solution at 500 rpm. The samples were then filtered using a 0.2 μm syringe filter (Millipore), and the decanted solutions were analyzed using an atomic-absorption spectrophotometer (PERKIN ELMER, Model 1100B) for Pb^{2+} ion.

RESULTS AND DISCUSSION

Preparation and Characterization of PAN–TiO_2 Composite Adsorbent Beads

In the previous study on the preparation of composite ion-exchanger beads,[18] it was confirmed that sphericity of composite bead was greatly affected by viscosity of the composite dope, even though the optimum viscosity ranges would be somewhat different from the kinds and contents of the inorganic materials.

In this experiment for preparing a composite adsorbent containing about 71% of Degussa P-25 TiO_2 powder, the optimum viscosities for spherical beads were found to be at around 950 cP as shown in Fig. 2. The bead sphericity was somewhat improved by the airflow outside channel of the dual nozzle.

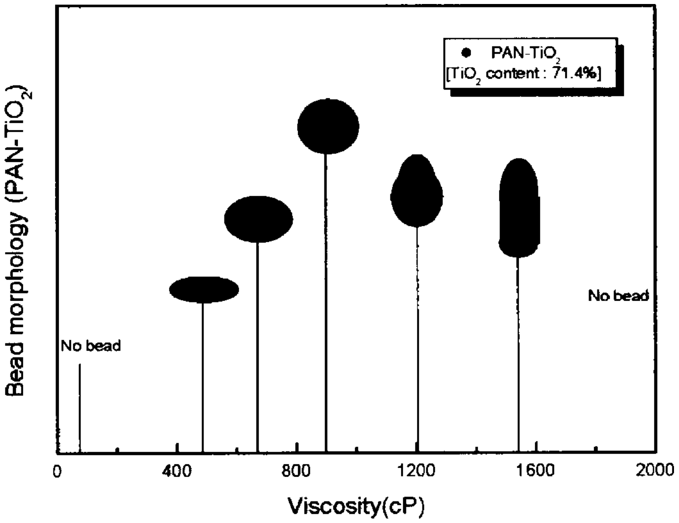

Figure 2. Change of PAN–TiO_2 composite bead morphology with viscosity.

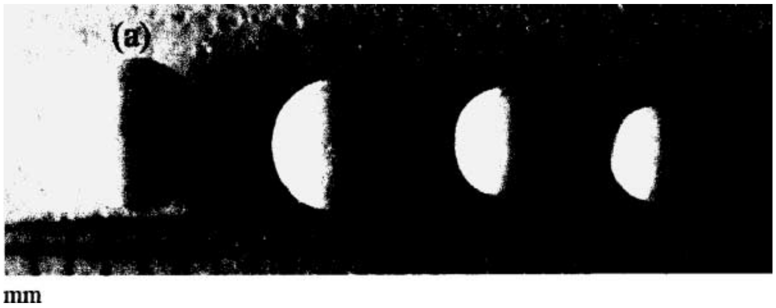

Figure 3. Effect of air pressure on the PAN–TiO_2 composite bead sizes; (a) Atmospheric pressure, (b) 2 psi, (c) 4 psi, (d) 6 psi.

Composite bead sizes are normally controlled by nozzle size variation. Even though the nozzle size is fixed, the bead size could be more or less controlled by air pressure flowing outside channel of the dual nozzle. The effect of air pressure on the bead sizes, for fixed nozzle size, was tested and the resulting morphologies of the beads were represented in Fig. 3. It shows that the bead sizes were varied in the range of 2.05–3.30 mm for the air pressure variations between atmospheric pressure and 6 psig.

Figure 4 is the SEM image for the cross-section of the composite bead, which is showing homogeneous distribution of P-25 TiO_2 powder and well-developed pores in the composite bead. The pore size distribution and average pore size of the composite beads were analyzed using a mercury

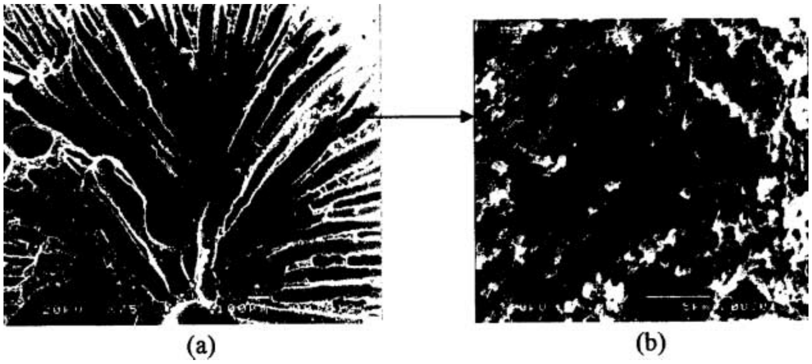

Figure 4. SEM images showing the fracture (a) and detailed pore structure (b) of the PAN–TiO_2 composite bead.

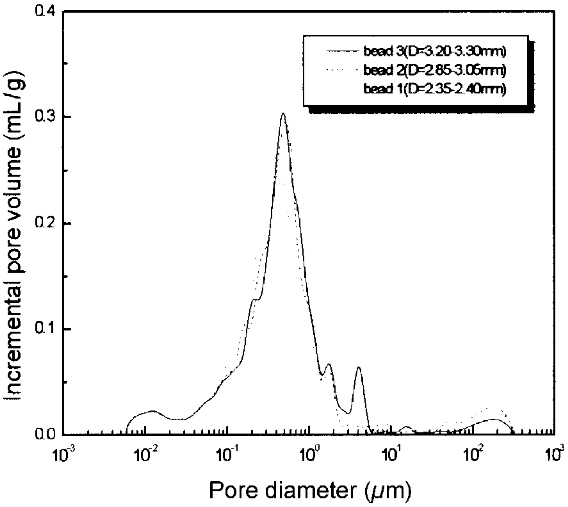

Figure 5. Pore size distribution of PAN–TiO_2 composite bead with the pressure change (bead 1: 6 psi, bead 2: 4 psi, bead 3: 2 psi).

porosimeter and the results were represented in Fig. 5 and summarized in Table 1.

The bead pores were mainly (>99.9%) composed of macropores larger than 0.05 μm and a minor portion (<0.1%) of mesopores were in the range between 0.002 μm and 0.05 μm.[24] The porosity of PAN/TiO_2 composite bead was more than 80%, which is an outright high value considering that the porosities of the other inorganic adsorbent beads such as zeolites are normally less than 50%. Such a high porosity would be one of the characterizing

Table 1. Summary of porosimetry data for PAN–TiO_2 composite beads.

	Adsorbents		
Physical properties	Bead 1	Bead 2	Bead 3
Average pore diameter (μm)	0.1074	0.1145	0.1155
Bulk density (g/mL)	0.3631	0.3451	0.3463
Apparent density (g/mL)	2.3298	2.2287	2.1471
Porosity (%)	84.42	84.52	83.87

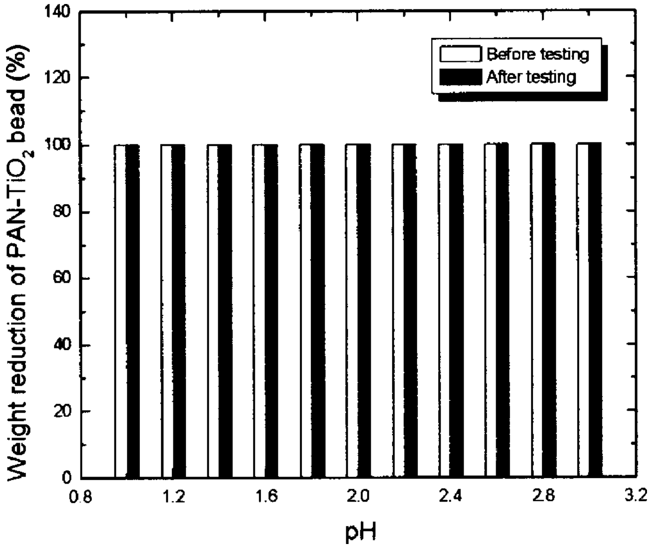

Figure 6. Stability of PAN–TiO_2 composite bead in nitric acid solution.

features of organic binder-based composite beads, which might improve the kinetics.

The stability of the PAN–TiO_2 composite bead against acid solution was tested for the pH range of 1 and 3. It was confirmed that the PAN–TiO_2 composite beads were so acid resistant that no weight loss was observed for the solutions with pH above 1.0, as shown in Fig. 6.

Figure 7 shows the mechanical stability test results for the composite beads. The prepared composite adsorbent was mechanically stable for five days without destruction and deformation of the beads in the stirring condition of 500 rpm.

Pb^{2+} Ion-Adsorption Characteristics of PAN–TiO_2 Composite Adsorbent

Equilibrium Behavior

The effect of pH on the Pb^{2+} ion adsorption was represented in Fig. 8. Adsorption of Pb^{2+} ion increased with pH and complete removal was achieved at pH 5.60. Such a trend was also reported by Vohra and Davis.[2] They reported

Marcel Dekker, Inc. • 270 Madison Avenue • New York, NY 10016

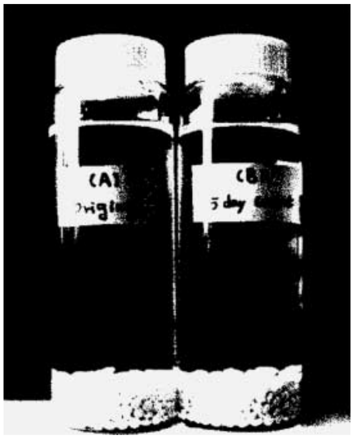

Figure 7. Photographs of PAN–TiO_2 representing the mechanical stability test result; (A) Original, (B) 5-day contact.

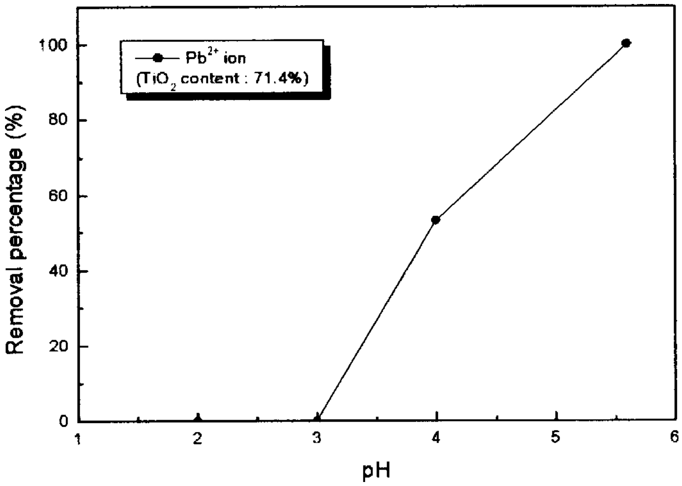

Figure 8. Effect of pH on the Pb^{2+} ion adsorption onto PAN–TiO_2 composite adsorbent.

that the possible mechanism for the removal of Pb^{2+} ions with TiO_2 would be a monodentate inner-sphere-type surface complexation as follows;

$$\mathrm{Ti{-}OH} + \mathrm{Pb}^{2+} \leftrightarrow \mathrm{Ti{-}O{-}Pb}^{+} + \mathrm{H}^{+} \tag{1}$$

When pH increases, the protonation-dissociation equilibria of the TiO_2 surface hydroxy groups make the surface more negatively charged. Consequently, the positively charged Pb^{2+} ions interact favorably with the surface.

Adsorption isotherms were obtained to evaluate the equilibrium parameters such as adsorption capacity and equilibrium constant for kinetic calculations. PAN-adsorbents that contain the different TiO_2 contents were tested to confirm the effect of TiO_2 on the adsorption capacities. The experimental data were modeled by the Langmuir equation given by

$$q = \frac{Bq_m c}{1 + Bc} \tag{2}$$

where c (meq/mL) and q (meq/g) are equilibrium concentrations of Pb^{2+} ion in aqueous and solid phases, respectively, q_m (meq/g) is the maximum adsorption capacity, and B (mL/meq) is the Langmuir constant.

The result shows that the experimental data can be modeled successfully by Langmuir equation as in Fig. 9. The adsorption capacities are increased as the contents of TiO_2, the active component. It is obvious that the differences in adsorption capacities are due to the difference in inorganic contents in PAN–TiO_2 composite bead. It also indicates that the PAN binder provides a smooth pathway for Pb(II) ion adsorption onto TiO_2 without blocking the adsorption sites. The obtained parameters were summarized in Table 2.

Kinetic Behavior

Experimental studies of the kinetics of adsorption processes were performed in batch reactor, which is known to have the advantage of easy control of the film mass-transfer resistance by stirrer speed. Uptake data for Pb^{2+} ion onto P-25 TiO_2 powder and the prepared PAN–TiO_2 composite adsorbents were obtained to determine the impact of pore diffusion. And the results were represented in Fig. 10.

The uptake rate for the 0.075 mm diameter P-25 TiO_2 powder was significantly faster than the other two composite adsorbents, which have much larger particle diameters of 1.19 and 1.46 mm, respectively. It is obvious that the rate of adsorption onto the surfaces of P-25 TiO_2 powder is much faster

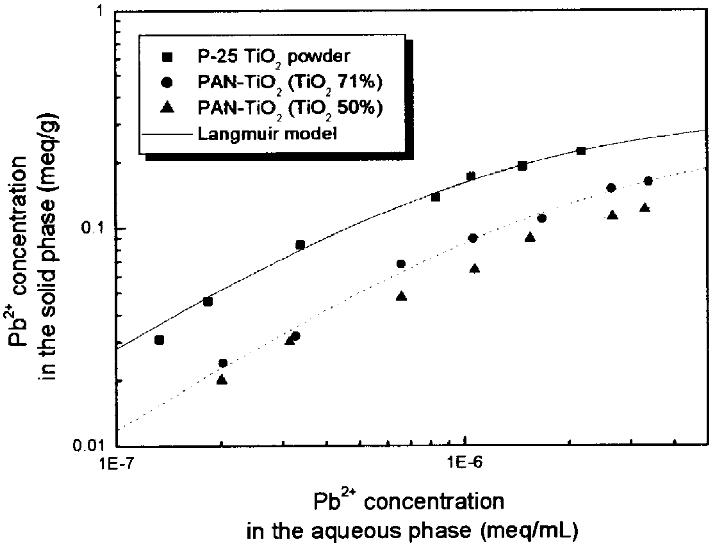

Figure 9. Pb^{2+} ion adsorption isotherm on Degussa P-25 TiO$_2$ powder and PAN–TiO$_2$ composite adsorbents.

than the pore diffusion. Therefore, the surface adsorption rate does not affect the kinetics of the system while the pore diffusion significantly contributes to the mass-transfer resistance.

Figure 11 shows the effect of drying condition on the uptake rate of Pb^{2+} ions. The two drying conditions of 50°C at 5 torr and 80°C at 5 torr were compared. It shows that the elevated drying temperature resulted in the decrease in the uptake rate. In our previous study,[18] it was reported that the drying conditions affect the bead morphology and pore structures of the beads. This is due to the shrink of the beads by elevating the drying temperature.

Table 2. Langmuir model parameters for Pb^{2+} ion adsorption isotherm.

	Absorbents		
Parameters	P-25 TiO$_2$ powder	PAN–TiO$_2$ (71%)	PAN–TiO$_2$ (50%)
q_m (meq/g)	0.336	0.265	0.187
B (mL/meq)	9.904×10^5	4.679×10^5	5.54×10^5
R^2	0.995	0.993	0.991

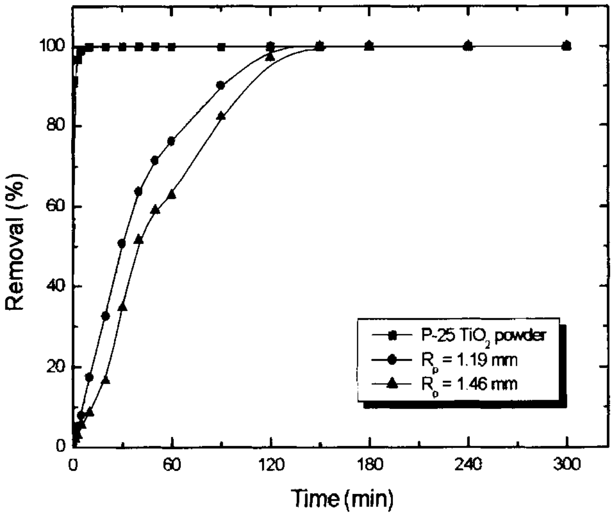

Figure 10. Effect of particle size on uptake rate for Pb^{2+} ion by Degussa P-25 TiO_2 powder and PAN–TiO_2 composite adsorbents.

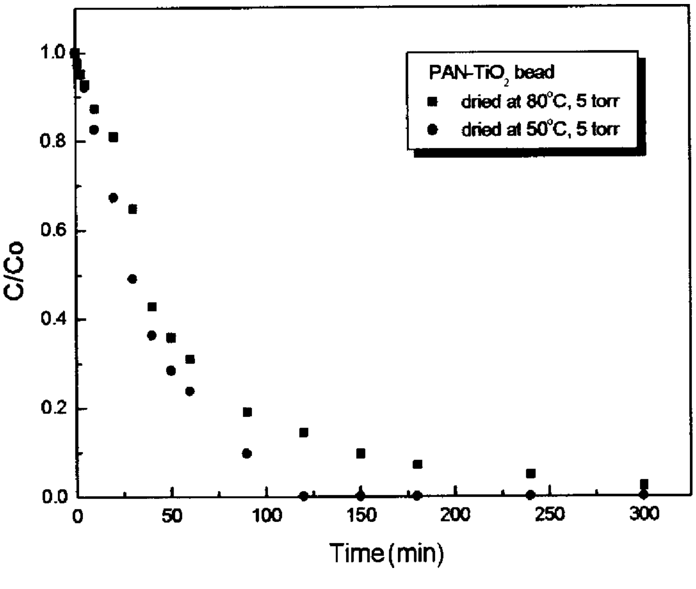

Figure 11. Effect of drying temperature on the uptake rate for Pb^{2+} ion.

Mass-Transfer Coefficient and Effective Pore Diffusivity

Kinetic parameters such as film mass-transfer coefficient and effective pore diffusivity were evaluated by modeling the data. Film mass-transfer coefficient is usually assumed to be negligible when the uptake curves in batch system are not a function of the stirrer speed. However, if the relative speed of the particles to a solution is unknown, this is not reportedly always valid.[25] Film mass-transfer coefficients are traditionally determined from correlations available in the literature or from modeling experimental data. Unfortunately, these correlations may be obtained experimentally from media that are significantly different from adsorption material. In the meanwhile, researchers have indicated that film mass-transfer dominates the initial uptake rate in batch reactor.[26] Since the initial portion of the uptake curve is insensitive to intraparticle mass transfer, it can be modeled by evaluating the equations for film mass-transfer.

In this study, the film mass-transfer coefficient, k_f, was estimated from initial concentration history in which the diffusion resistance does not prevail. When adsorption time, *t*, approaches zero, the initial concentration history can be approximated by the following equation, which is derived from the combination of the mass balance on each solute in liquid phase and the mass-transfer equation across the liquid film:

$$-\ln\left(\frac{c_i}{c_o}\right) = \frac{\kappa_f a}{V} t \tag{3}$$

where *V* is the volume of solution and *a* is the effective external surface area of adsorbent particles which is given by:

$$a = \frac{3w}{\rho_p R_p} \tag{4}$$

where w is the weight of adsorbent particle loaded and ρ_p is the particle density.

The calculated film mass-transfer coefficients were 0.0034 cm/sec for 1.19 mm bead and 0.003 cm/sec for 1.46 mm bead as shown in Table 3.

The effective pore diffusivity for the system of Pb^{2+} ion adsorption onto PAN–TiO_2 composite adsorbent was determined by modeling the experimental data with a homogeneous diffusion model.[27] This model has been widely used for adsorbent crystal or powder-types rather than particles. However, since the micropore structure of TiO_2 powder is not well developed and adsorption occurs on the external surface of it, TiO_2 powder-PAN composite adsorbent could be considered to have macropores only.

Table 3. Film mass-transfer coefficients and effective diffusivities estimated in batch reactor.

Particle radius (mm)	k_f (cm/s)	D_c (cm^2/s)
1.19	0.0034	1.0×10^{-8}
1.46	0.0030	1.0×10^{-8}

For this reason, a homogeneous diffusion model was used in this study. This model assumes that the particle is a homogeneous solid and the diffusion occurs through the liquid-filled pores with local equilibrium between the solid and the pore liquids. It is also assumed that the concentration of adsorbates is uniform throughout the batch reactor and the adsorbents are spherical particles with an identical radius. The system is also operated under isothermal conditions.

By assuming that the diffusion follows Fick's law, the differential mass balance in the adsorbent gives:

$$\frac{\partial q}{\partial t} = D_c\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{5}$$

Boundary conditions are given by:

$$\frac{\partial q}{\partial r} = 0 \quad at \quad r = 0 \tag{6}$$

$$q(r,0) = 0 \tag{7}$$

$$D_c\rho_p\frac{\partial q}{\partial r}|_{r=R_p} = k_f(c - c_S) \tag{8}$$

For bulk fluid, the material balance is given by:

$$V\frac{dc}{dt} = -w\frac{d\bar{q}}{dt} \tag{9}$$

$$c = c_0 \quad at \quad t = 0 \tag{10}$$

$$\bar{q} = \frac{3}{R_p^3}\int_0^{R_p} q(r,t)r^2 dr \tag{11}$$

Adsorption equilibrium equation relates the q and c_S. For the Langmuir isotherm, c_S can be represented as:

$$c_S = \frac{q|_{r=R_p}}{B(q_m - q|_{r=R_p})} \tag{12}$$

Equations (5) through (12) can be rewritten in dimensionless form by letting $C = c/c_0$, $Q = q/q_0$, $X = r/R_p$, $\tau = D_c t/R_p^2$, and $\lambda = k_f R_p c_0/\rho_p D_c q_0$, where q_0 is in equilibrium with c_0:

$$\frac{\partial Q}{\partial \tau} = D_c \frac{1}{X^2}\frac{\partial}{\partial X}\left(X^2 \frac{\partial C}{\partial X}\right) \tag{13}$$

$$\frac{\partial Q}{\partial X}|_{X=0} = 0 \tag{14}$$

$$Q|_{\tau=0} = Q_0 \tag{15}$$

$$\frac{\partial Q}{\partial X} = \lambda(C - C_S) \tag{16}$$

$$C_S = 1 - \alpha(\bar{Q} - \bar{Q}_0) \tag{17}$$

$$C|_{\tau=0} = 1 \tag{18}$$

$$\bar{Q} = 3\int_0^1 QX^2 dX \tag{19}$$

where, α is defined as:

$$\alpha = \frac{wq_0}{VC_0} \tag{20}$$

Equations (13) through (20) form a set of coupled second-order parabolic partial-differential equations with boundary conditions. The method of orthogonal collocation based on a Jacobi polynomial was used to reduce the partial-differential equations to a set of ordinary differential equations with the eight interior collocation points. These ordinary differential equations were solved by DGEAR in IMSL.

In spite of the somewhat ideal assumption, the experimental data was modeled with some accuracy as in Fig. 12. The resulting parameters are summarized in Table 3.

As in the table, the calculated effective pore diffusivities for both composite beads are roughly in the order of 10^{-8} cm^2/sec.

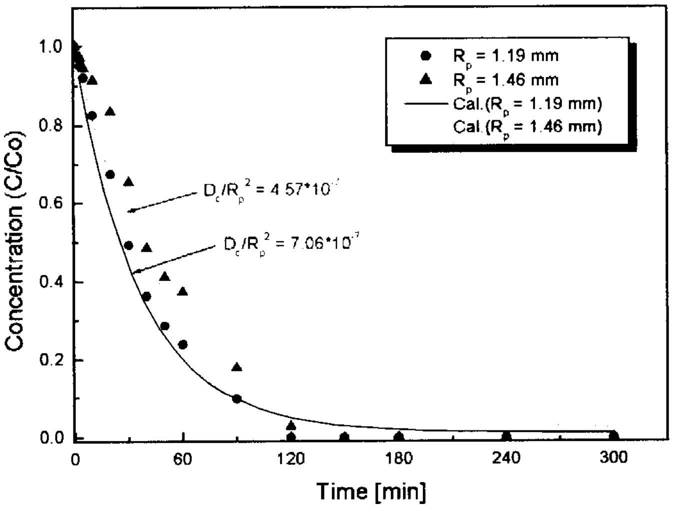

Figure 12. Experimental data and predicted uptake curve for Pb^{2+} ion adsorption by PAN–TiO_2 composite adsorbent.

CONCLUSION

A PAN–TiO_2 composite adsorbent bead containing about 71% TiO_2 was prepared to remove Pb^{2+} ion in aqueous solution. The optimum viscosity for the spherical bead formation was found to be at around 950 cP. The porosity of composite bead was about 80%, which is a much higher value compared with the other inorganic adsorbent beads such as zeolites. The composite adsorbent also showed very high stability against strong acids above pH 1. Adsorption tests using the PAN–TiO_2 composite adsorbent showed that Pb^{2+} ion adsorption increased in proportion to pH and complete removal of Pb^{2+} ion was achieved at pH 5.60. The effective diffusivity was also evaluated by modeling the uptake data with a homogeneous diffusion model and it was found to be about 10^{-8} cm^2/sec.

NOMENCLATURE

a	effective external surface area of adsorbent particles (cm^2)
B	Langmuir constant (mL/meq)
c	concentration of Pb^{2+} ion in liquid phase (meq/mL)
c_o	initial concentration of Pb^{2+} ion in liquid phase (meq/mL)

c_S	concentration of Pb^{2+} ion in liquid at particle surface (meq/mL)
C	dimensionless concentration of Pb^{2+} ion in liquid phase (c/c_o)
C_S	dimensionless concentration of Pb^{2+} ion at particle surface
D_c	effective pore diffusivity for Pb^{2+} ion (cm^2/s)
k_f	film mass-transfer coefficient (cm/s)
q	concentration of Pb^{2+} ion in solid phase (meq/g)
$\bar{q}$	average concentration of Pb^{2+} ion in solid phase (meq/g)
q_m	maximum adsorption capacity (meq/g)
q_o	concentration of Pb^{2+} ion in equilibrium with c_o (meq/g)
Q	dimensionless concentration of Pb^{2+} ion in solid phase (q/q_o)
$\bar{Q}$	dimensionless average concentration of Pb^{2+} ion in solid phase
$\bar{Q}_o$	dimensionless average initial concentration of Pb^{2+} ion in solid phase
r	radial coordinate for particle (cm)
R_p	particle radius (cm)
t	time (sec)
V	solution volume in batch reactor (mL)
w	amount of adsorbent (g)
X	dimension radial coordinate (r/R_p)
α	$\frac{wq_0}{VC_0}$
λ	$k_f R_p c_0 / \rho_p D_c q_0$
ρ_p	density of particle (g/cm^3)
τ	diffusion time constant ($D_c t / R_p^2$)

ACKNOWLEDGMENTS

This project has been carried out under the Nuclear R&D program by MOST, and was also supported by the Brain Korea 21 project.

REFERENCES

1. Ahmed, S.; Chughtai, S.; Keane, M.K. The removal of cadmium and lead from aqueous solution by ion exchange with NA-Y zeolite. Sep. Purif. Technol. **1998**, *13*, 57–64.

2. Vohra, M.S.; Davis, A.P. Adsorption of Pb(II), NTA, and Pb(II)–NTA onto TiO_2. J. Colloid Interface Sci. **1997**, *194*, 59–67.
3. Kaufman, A.S. Do low levels of lead produce IQ loss in children? A careful examination of the literature. Arch. Clin. Neuropsychol. **2001**, *16* (ER4), 303–341.
4. Ahmad, A.A.i.; Ribhi, E.B. Removal of lead and nickel ions using zeolite tuff. J. Chem. Technol. Biotechnol. **1997**, *69*, 27–34.
5. Husein, M.M.; Vera, J.H.; Webber, M.M. Removal of lead from aqueous solutions with sodium caprate. Sep. Sci. Technol. **1998**, *33* (12), 1889–1904.
6. Davis, M.L.; Cornwell, D.A. *Introduction to Environmental Engineering*; 2nd Ed. McGraw-Hill: New York, 1991.
7. Bailey, S.E.; Olin, T.J.; Bricka, R.M.; Adrian, D.D. A review of potentially low-cost sorbents for heavy metals. Water Res. **1999**, *33* (11), 2469–2479.
8. Pichtel, J.; Vine, B.; Kuula-Vaisanen, P.; Niskanen, P. Lead extraction from soils as affected by lead chemical and mineral forms. Environ. Eng. Sci. **2001**, *18* (2), 91–98.
9. Jianlong, W.; Xinmin, Z.; Decai, D.; Ding, Z. Bioadsorption of lead(II) from aqueous solution by fungal biomass of *Aspergillus niger*. J. Biotechnol. **2001**, *87* (ER3), 273–277.
10. Ho, Y.S.; Ng, J.C.Y.; McKay, G. Removal of lead(II) from effluents by sorption on peat using second-order kinetics. Sep. Sci. Technol. **2001**, *36* (2), 241–262.
11. Esalah, J.O.; Weber, M.E.; Vera, J.H. Removal of lead, cadmium and zinc from aqueous solutions by precipitation with sodium di-(n-octyl) phosphinate. Can. J. Chem. Eng. **2000**, *78* (5), 948–954.
12. Chen, J.; Ollis, D.V.; Rulkens, W.H.; Bruning, H. Photocalyzed deposition and concentration of soluble uranium(Vi) from TiO_2 suspension. Colloids Surf. A: Physicochem. Eng. Asp. **1999**, *151*, 339–349.
13. Tennakone, K.; Wijayantha, K.G.U. Heavy-metal extraction from aqueous medium with immobilized TiO_2 photocatalyst and a solid sacrificial agent. J. Photochem. Photobiol. A: Chem. **1998**, *113*, 89–92.
14. Colon, G.; Hidalgo, M.C.; Navio, J.A. Photocatalytic deactivation of commercial TiO_2 samples during simultaneous photoreduction of Cr(VI) and photooxidation of salicylic acid. J. Photochem. Photobiol. A: Chem. **2001**, *138*, 79–85.
15. Sebesta, F.; John, J.; Motl, A.; Watson, J. *Development of PAN-based absorbers for treating waste problems at U.S. DOE facilities*. Proc. the 5th International Conference on Radioactive Waste Management and

Environmental Remediation, ICEM 95; Slate, F., Feizollahi, F., Creer, J., Eds.; ASME: Berlin, New York, 1995.

16. Xue, T.J.; McKinney, A.; Wilkie, C.A. The thermal degradation of polyacrylonitrile. Polym. Degrad. Stab. **1997**, *58*, 193–202.
17. John, J.; Sebesta, F.; Motl, A. Composite absorbers consisting of inorganic ion-exchangers and polyacrylonitrile minding matrix: leaching of ^{137}Cs from cemented NiFC-PAN absorber. Radiochim. Acta **1997**, *78*, 131–135.
18. Moon, J.K.; Kim, K.W.; Jung, C.H.; Lee, E.H.; Shul, Y.G. Preparation of organic–inorganic composite beads for removal of radionuclides and heavy metal ions. J. Radioanal. Nucl. Chem. **2000**, *246* (2), 299–307.
19. Mariamichel, A.; Krishnamoorthy, S. Synthesis and characterization of new composite ion exchangers. J. Sci. Ind. Res. **1997**, *56*, 680–685.
20. Mardan, A.; Ajaz, R.; Mehmood, A.; Raza, S.M.; Ghaffar, A. Preparation of silica potassium cobalt hexacyanoferrate composite ion exchanger and its uptake behavior for cesium. Sep. Purif. Technol. **1999**, *16*, 147–158.
21. Pandit, B.; Chudasama, U. A new inorgano-organo ion exchanger; chromotropic acid anchored onto zirconium molybdate. Colloids Surf. A: Physicochem. Eng. Asp. **1998**, *132*, 145–151.
22. Simanova, S.A.; Belyaev, K.A.N.; Knyazkov, O.V.; Konovalov, L.V. Complexation of platinum in sorption of tetrachloroplatinate(II) ion by fibrous sorbent based on polyacrylonitrile modified with thiosemicarbazide. Russ. J. Appl. Chem. **1999**, *72* (8), 1344–1350.
23. Martha Windholz. *The Merck Index*, 10th Ed.; MERCK & CO., INC.: Rahway, NJ, 1983.
24. Yang, R.T. *Gas Separation by Adsorption Processes*; Butterworths: London, 1987.
25. Ruthven, D.M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons: New York, 1997.
26. McKay, G.; Bino, M.J. Adsorption of pollutants from wastewater onto activated carbon based external mass transfer and pore diffusion. Water Res. **1988**, *22* (3), 279–286.
27. Robinson, D.M.; Arnold, W.D.; Byers, C.H. Mass-transfer mechanisms for zeolite ion exchange in wastewater treatment. AIChE J. **1994**, *40* (12), 2045–2054.

Received July 2001
Revised April 2002