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Kinetic Study of Lead Adsorption to Composite Biopolymer Adsorbent

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(Abbreviated title: KINETICS OF LEAD ADSORPTION TO BIOPOLYMER ADSORBENT)

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ABSTRACT

A kinetic study of lead adsorption to composite biopolymer adsorbents was carried out. Spherical and membranous adsorbents containing two kinds of biopolymers, humic acid and alginic acid, were used for lead adsorption in dilute acidic solutions. The shrinking core model derived by Rao and Gupta was applied to describe the rate process of lead adsorption to spherical adsorbents (average radii of 0.12, 0.15, and 0.16 cm). Furthermore, the shrinking core model was modified and adapted for the description of the rate process of lead adsorption to membranous adsorbent (an average thickness of 0.0216 cm). The adsorption rate process for the both cases was well-described and the average apparent lead diffusion coefficients of about 6×10^{-6} and $7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ were found for the spherical and membranous adsorbents, respectively.

Key Words: diffusivity; lead; composite biopolymer adsorbent; humic acid; alginic acid

INTRODUCTION

The adsorptive separation of heavy metal ions from aqueous environments is an emerging field of interest from both a resource conservation standpoint and an environmental remediation standpoint. Many biopolymers, such as cellulose, carrageenans, lignins, proteins, chitin derivatives, alginates, and humic substances, are known to bind heavy metal ions strongly (1-8). The use of biopolymers as adsorbents for the recovery of valuable metals or the removal of toxic metal contaminants has been a topic of intense research in recent years (1, 3-11). Biopolymers are capable of lowering heavy metal ion concentrations to part per billion concentrations (2). Moreover they are widely available and are ecologically acceptable.

We previously developed a composite biopolymer adsorbent which comprised two kinds of biopolymers, that is, humic acid and alginic acid (6,8). Both of them are widely and abundantly available biopolymers, and have high complexing ability with various heavy metal ions (1-11). In our previous studies, the adsorption mechanism of divalent heavy metal ions to the composite biopolymer adsorbent and the effect of immobilization on the metal complexation ability of the biopolymers were elucidated (6,8).

The aim of this paper is to report the adsorption kinetics of lead ions to

composite biopolymer adsorbents. For this purpose, spherical adsorbents which had average radii of 0.12, 0.15, and 0.16 cm, and a membranous adsorbent which had an average thickness of 0.0216 cm were prepared. Based on the shrinking core model (1, 9-12), the rate process of lead adsorption to the composite biopolymer adsorbents will be discussed.

MATERIALS

Chemicals

Lead nitrate, sodium nitrate and sodium alginate (AA) were obtained from Wako Pure Chemical Industries (Japan) and sodium salt of humic acid (HA) from Aldrich Chemical Co. They were used as received. Activated carbon powder (ACP) was purchased from Wako Pure Chemical Industries. It was screened by a 100-mesh (0.149-mm) sieve, and the undersize fraction was used.

Spherical Composite Biopolymer Adsorbent (HA-gel)

ACP (2.0 g) was added to an aqueous solution (0.045 dm^{-3}) containing HA (2.0 g) and AA (1.0 g), and the mixture was well mixed. It was dispensed down into a CaCl_2 solution ($0.1 \text{ mol} \cdot \text{dm}^{-3}$) in a stirred vessel and was converted to the gel particles. After 1 h the formed adsorbent (HA-gel) was removed from the solution and it was washed repeatedly with distilled water. The shape of the particles was nearly spherical. The diameters of randomly chosen ten particles were measured. The HA-gels which had average radii of 0.12, 0.15, and 0.18 cm (standard deviations were 0.021, 0.054, and 0.073, respectively) were used in this study.

Membranous Composite Biopolymer Adsorbent (HA-M)

A mixture of ACP, HA, and AA was prepared in the same manner as HA-gel preparation. It was extruded, dropwise, on a plastic (poly(vinyl chloride)) plate and dried at 60°C. Randomly chosen twenty samples were weighed, and the average weight of a membranous adsorbent in a dry state, m , was determined as 0.0034 g. Then it was immersed in an excess of CaCl₂ solution (0.1 mol·dm⁻³). The membranes of HA-entrapped calcium alginate (HA-M) were left to harden in the CaCl₂ solution for 1 h. The formed HA-M was removed from the solution, and it was washed repeatedly with distilled water. The diameters of randomly chosen ten membranes were measured. The HA-M had an average radius, r_M , of 0.35 cm (standard deviation was 0.017).

The apparent density of HA-M was determined in the following manner. A certain amount (ca. 1 dry-g) of HA-M was gelated in CaCl₂ solution. After the gelation, the HA-M was collected and wiped the excess water on the adsorbent surface with a filter paper. The HA-M was introduced into a graduated cylinder (25 cm³) containing 20 cm³ of distilled water. The apparent volume of wet HA-M was determined from the difference between the volume of water in the absence and in the presence of HA-M. The apparent density of HA-M on a dry-weight basis, ρ_d , and wet-weight basis, ρ_w , were determined as 0.409 and 1.25 g·cm⁻³, respectively. Furthermore, the average thickness of HA-M in a wet

state, d , was determined from the following relationship:

$$d = m/(\rho_d \pi r^2) = 0.0216 \text{ cm.} \quad [1]$$

EXPERIMENTAL METHODS

Adsorption Experiment

A total of 900 cm³ of NaNO₃ (0.1 mol·dm⁻³) solution containing a certain amount of HA-gel or HA-M was prepared. The pH of the solution was adjusted to the desired value by HNO₃. After reaching thermal equilibrium at 30°C, a 100 cm³ of Pb(NO₃)₂ solution containing NaNO₃ (0.1 mol·dm⁻³) was added to the solution and mechanically stirred. Aliquots (3 cm³) of the solution were collected, periodically, for the determination of residual lead concentration. The lead concentration in liquid phase was determined by an atomic absorption spectrophotometer (Hitachi A-1800).

RESULTS AND DISCUSSION

Adsorption Kinetics of Lead Ions to HA-gel

Figures 1 and 2 show the time dependence of lead adsorption to HA-gel particles, which have average radii of 0.12, 0.15, and 0.18 cm, in different experimental conditions. The ordinate of the figures, X_t , denotes the adsorption amount of lead ions on 1 cm³ of the adsorbent at time t . The initial concentration of lead, C_i , and the equilibrium pH were indicated in the figures. The shrinking core model, which had been applied to find the apparent diffusivity of metal ions in ion exchange resins (9), calcium alginate beads (1, 10, 11), and a biosorbent (12), was applied to the rate process of lead adsorption to HA-gel particles. The model is based on the following assumptions: the adsorption rate process is controlled by the diffusion of adsorbate ions through the reacted shell in the adsorbent particles (particle diffusion control), and the shrinkage of unreacted shell is much slower than the mass transfer rate of adsorbate ions towards the unreacted shell surface.

The shrinking core model is described by the following equation (9):

$$1 - 3(1 - X_t/X)^{2/3} + 2(1 - X_t/X) = \frac{6D}{r^2 X} \int_0^t C dt \quad [2]$$

where C ($\text{mol}\cdot\text{cm}^{-3}$) is the concentration of lead ions in solution. D ($\text{cm}^2\cdot\text{s}^{-1}$), r (cm), and X ($\text{mol}\cdot\text{cm}^{-3}$) are the apparent diffusivity of lead ions, the average radius of adsorbent particles, and the active site concentration in adsorbents, respectively. If the adsorption process is controlled by the diffusion of lead ions through the reacted shell, a plot of $1 - 3(1 - X_t/X)^{2/3} + 2(1 - X_t/X)$ vs $\int_0^t C dt$ gives a straight line and the apparent diffusivity of lead ions in the adsorbent can be obtained from the slope of such a plot as follows:

$$D = AX \frac{r^2}{6}$$

or

$$r^2 = D \frac{6}{AX} \quad [3]$$

where A ($\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) represents the slope of the line obtained from the plot of Eq. [2].

The shrinking core model expressed by Eq. [2] was applied to the kinetic experimental data in Figs. 1 and 2. The results are shown in Figs. 3 and 4. The plot gives straight lines which pass through the origin and demonstrates a good

agreement of the experimental data with the shrinking core model. The apparent diffusivity of lead ions in HA-gel was estimated from Eq. [3], that is, from the plot of r^2 vs $6/AX$ using the slopes of the regression lines in Figs. 3 and 4. The result is shown in Fig. 5, and the plot gives a straight line which passes through the origin. The apparent diffusivity of lead ions was determined from the slope of the regression line as $5.85 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. This value is slightly lower than the ionic diffusivity of lead in aqueous medium at infinite dilution, $9.3 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ (9), and is in fair agreement with the apparent lead diffusivity in Chelex 100 resin determined by Rao and Gupta (9), $3 - 6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$.

Adsorption Kinetics of Lead ions to HA-M

Figure 6 shows the time dependence of lead adsorption to HA-M in different experimental conditions. The adsorption process of lead ions to HA-M is much faster than that of HA-gels. The shrinking core model was modified to describe the rate process of lead adsorption to HA-M. The area of unreacted shell surface in spherical adsorbents changes or shrinks with the extent of the adsorption process, while the area of unreacted layer surface in thin membranous adsorbents is kept constant through the adsorption process. In addition, the lead ions can diffuse into the membranous adsorbent from two

sides of the flat slab. In the case of membranous adsorbents, therefore, the shrinking core model can be modified or simplified to the following expression:

$$(X_t/X)^2 = \frac{2D}{(d/2)^2 X} \int_0^t C dt \quad [4]$$

Eq. [4] was applied to the kinetic experimental data in Fig. 6. The results are shown in Fig. 7. A good fit was found in all experimental trials.

The apparent diffusivity of lead ions in HA-M was estimated from the slopes of the regression lines in Fig. 7. The calculated apparent diffusivities are listed in Table 1. In this calculation, the thickness of HA-M determined from Eq.[1], $d = 0.0216$ cm, was used. The solid contents, that is, contents of HA, AA, and ACP in HA-gel and HA-M on a wet-weight basis are 5 and 33 %, respectively. Despite the solid content in HA-M is 6-fold higher than that in HA-gel, the apparent lead diffusivity in HA-M, about $7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, was almost the same as that in HA-gel.

CONCLUSION

A kinetic study of lead adsorption to composite biopolymer adsorbents was carried out. Spherical and membranous adsorbents containing two kind of biopolymer, humic acid and alginic acid, were used for the lead adsorption in dilute acidic solutions.

The shrinking core model derived by Rao and Gupta was applied to describe the rate process of lead adsorption to the spherical adsorbents (average radii of 0.12, 0.15, and 0.18 cm). A good fit was found in all experimental trials. The lead diffusion coefficient in the adsorbents was estimated from the shrinking core model. An average apparent lead diffusion coefficient of about $6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ was found.

Furthermore, the shrinking core model was modified and adapted for the description of the rate process of lead adsorption to a membranous adsorbent (an average thickness of 0.0216 cm). The kinetic experimental data agreed well with the modified model. Despite the solid content in HA-M is 6-fold higher than that in HA-gel, the apparent lead diffusivity in HA-M, about $7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, was almost the same as that in HA-gel.

APPENDIX A: NOMENCLATURE

A	= slope of the line obtained from the plot of Eq. [2] or [4] ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)
C	= concentration of lead ions in solution ($\text{mol} \cdot \text{cm}^{-3}$)
d	= average thickness of HA-M in a wet state (cm)
D	= apparent diffusivity of lead ions in adsorbents ($\text{cm}^2 \cdot \text{s}^{-1}$)
m	= average weight of a HA-M membrane in a dry state (g)
r	= average radius of HA-gel (cm)
r_M	= average radius of HA-M (cm)
t	= time (s)
X	= active sites concentration in adsorbents ($\text{mol} \cdot \text{cm}^{-3}$)
X_t	= adsorption amount of lead at time t ($\text{mol} \cdot \text{cm}^{-3}$)
ρ_d	= apparent density of HA-M on a dry-weight basis ($\text{g} \cdot \text{cm}^{-3}$)
ρ_w	= apparent density of HA-M on a wet-weight basis ($\text{g} \cdot \text{cm}^{-3}$)

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Figure Captions

FIG. 1. Time dependence of lead adsorption to HA-gel which has an average radius of 0.12 cm at 30°C. Initial concentrations of $\text{Pb}(\text{NO}_3)_2$ were $2.0 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-3}$ (square) and $5.0 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-3}$ (circle).

FIG. 2. Time dependence of lead adsorption to HA-gels which have average radii of 0.15 cm (circles) and 0.18 cm (squares) at 30°C. Initial concentration of $\text{Pb}(\text{NO}_3)_2$ was $5.0 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-3}$.

FIG. 3. Fitting of the data of Fig. 1 to the shrinking core model described by Eq.[2].

FIG. 4. Fitting of the data of Fig. 2 to the shrinking core model described by Eq.[2].

FIG. 5. Plot of $6/AX$ versus r^2 for the slopes, A , of the lines in Figs. 3 and 4.

FIG. 6. Time dependence of lead adsorption to HA-M which has an average thickness of 0.0216 cm at 30°C. Initial concentrations of $\text{Pb}(\text{NO}_3)_2$ were $2.0 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-3}$, $3.0 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-3}$, and $5.0 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-3}$.

FIG. 7. Fitting of the data of Fig. 6 to Eq.[4].

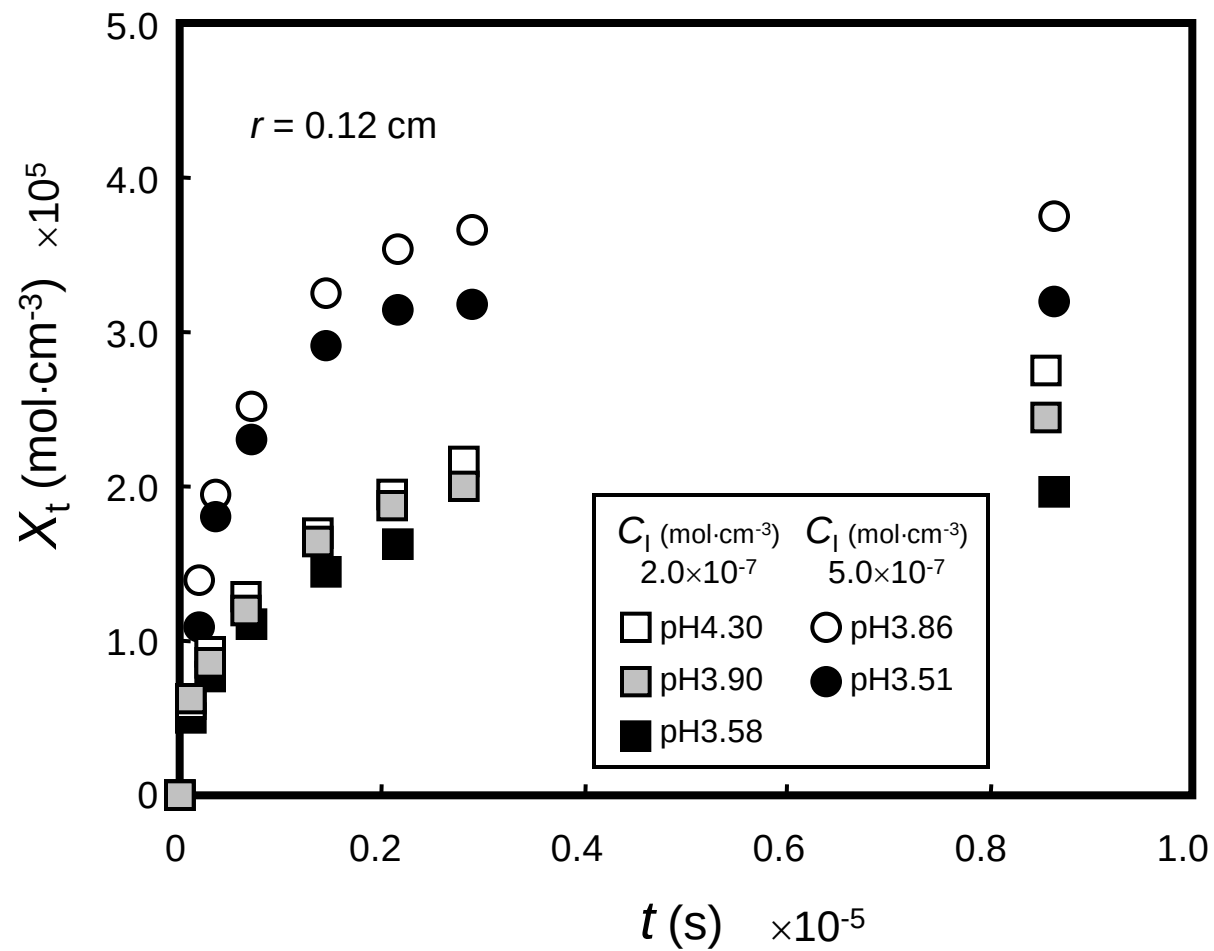


FIG.1 SEKI & SUZUKI

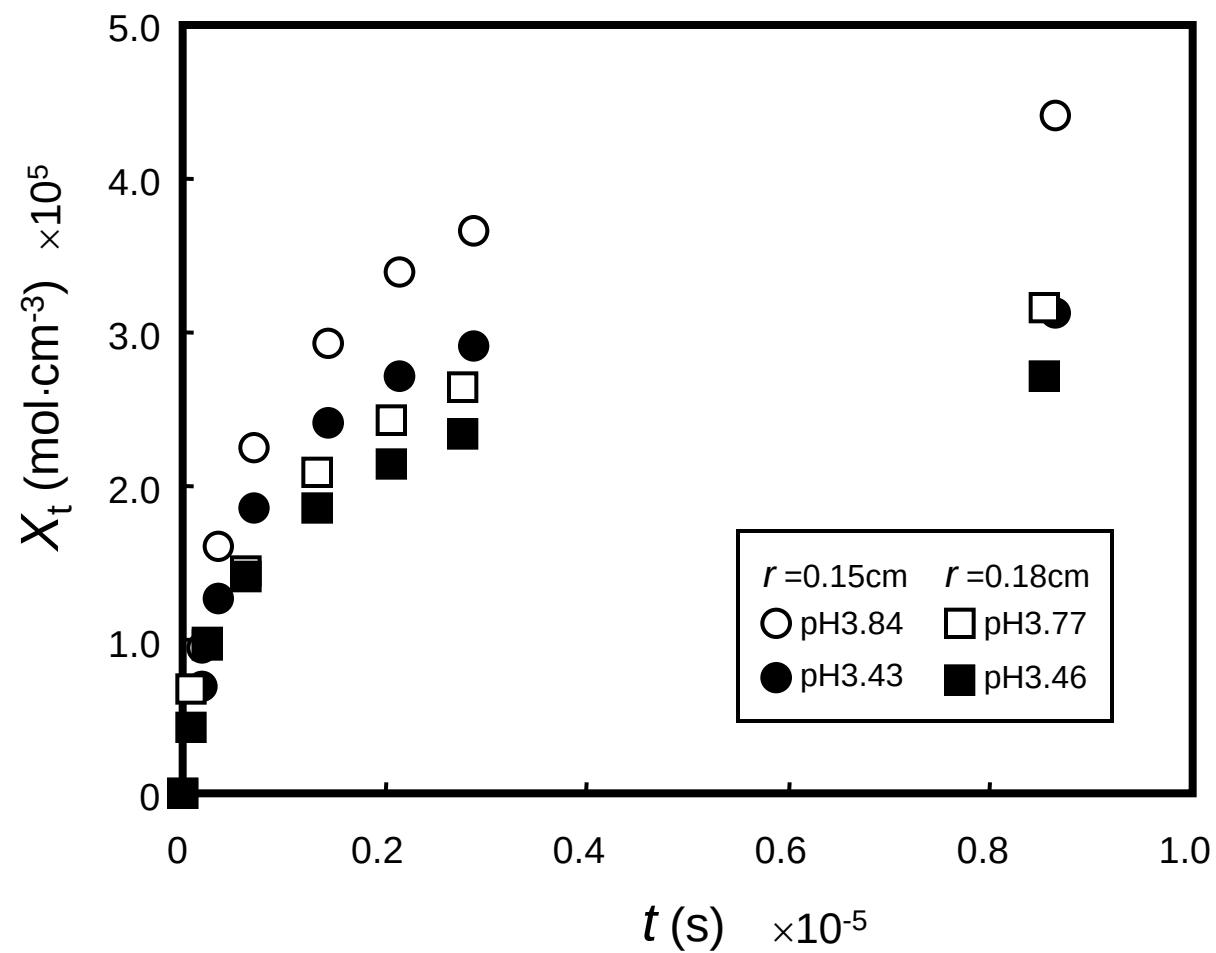


FIG.2 SEKI & SUZUKI

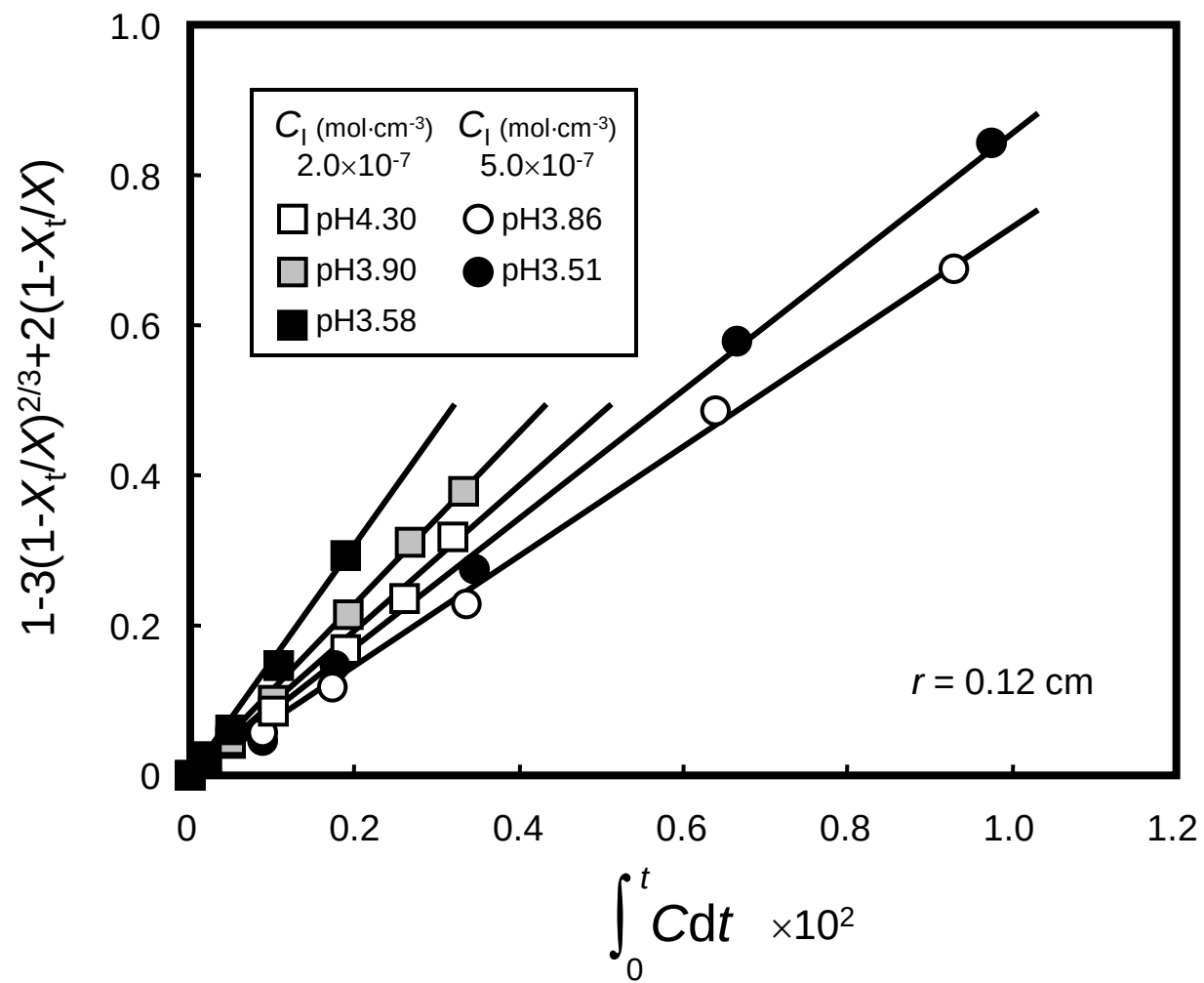


FIG.3 SEKI & SUZUKI

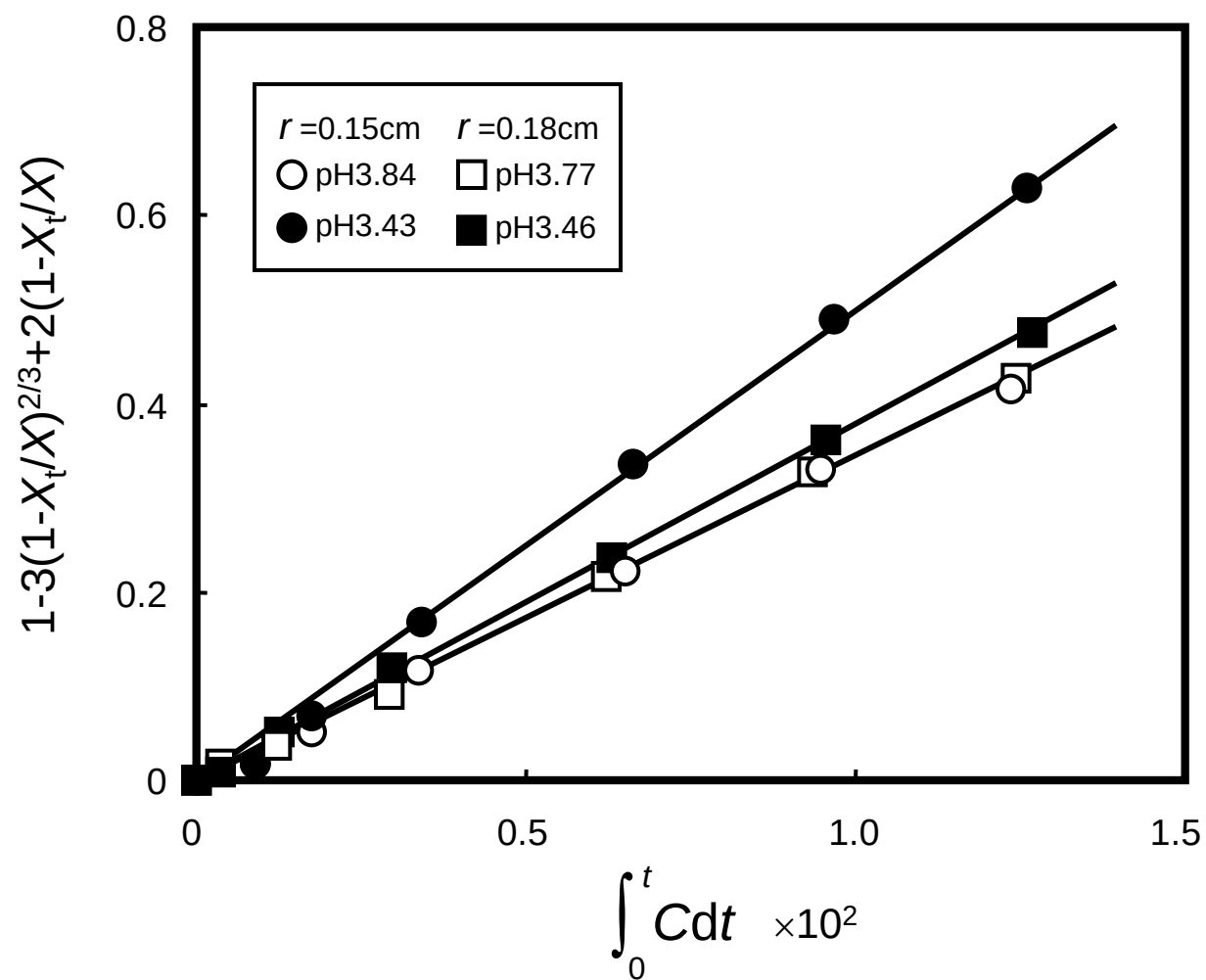


FIG.4 SEKI & SUZUKI

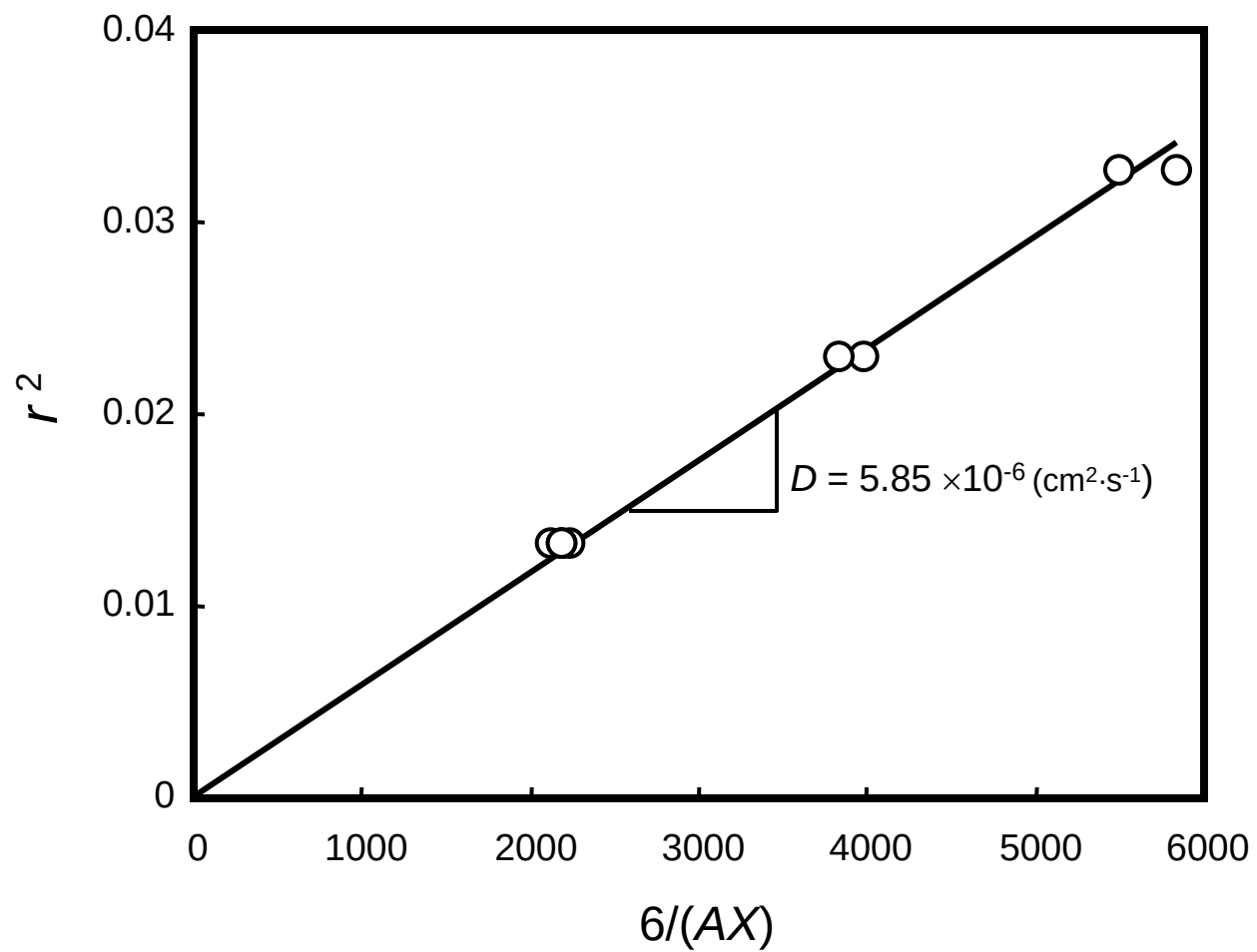


FIG.5 SEKI & SUZUKI

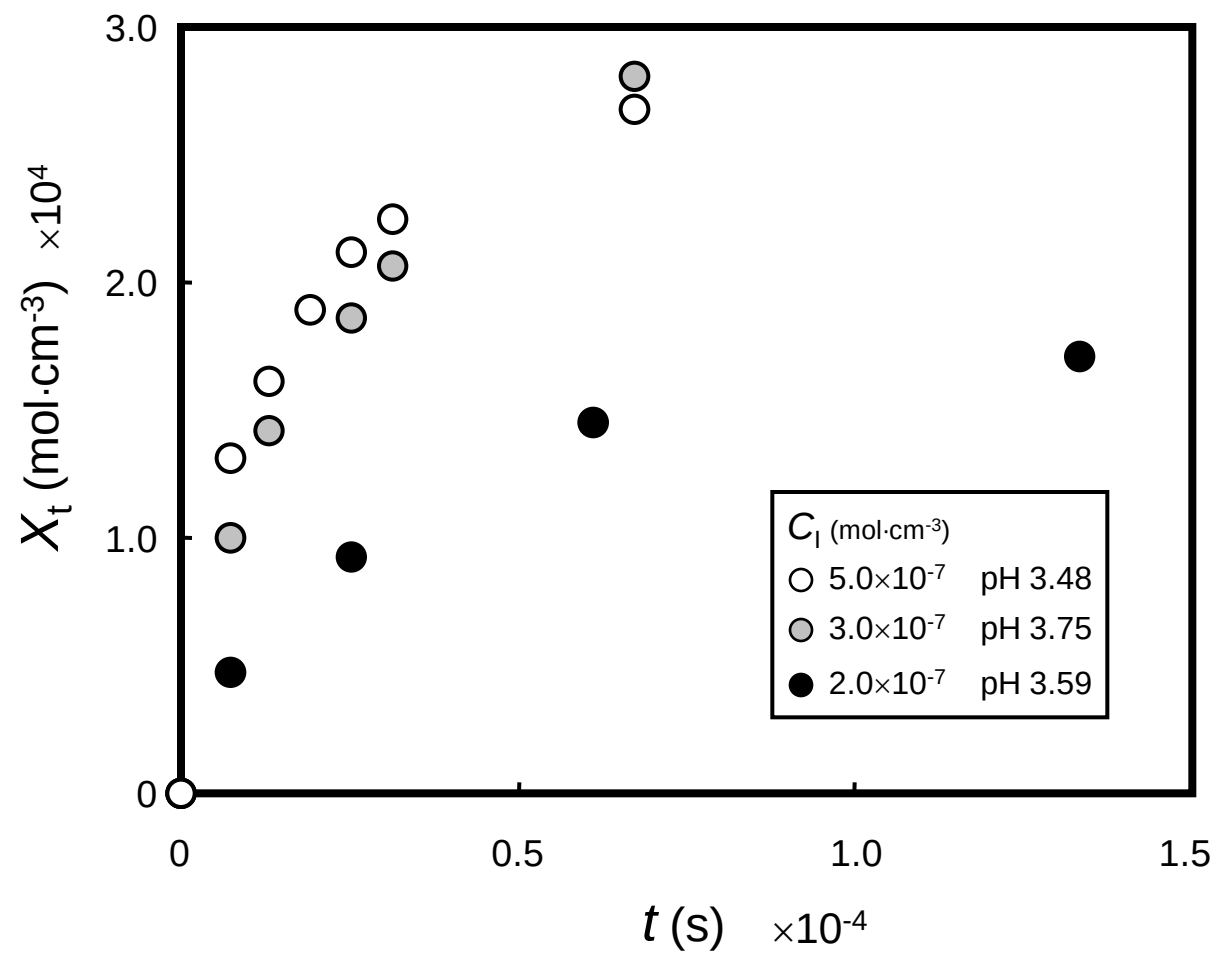


FIG.6 SEKI & SUZUKI

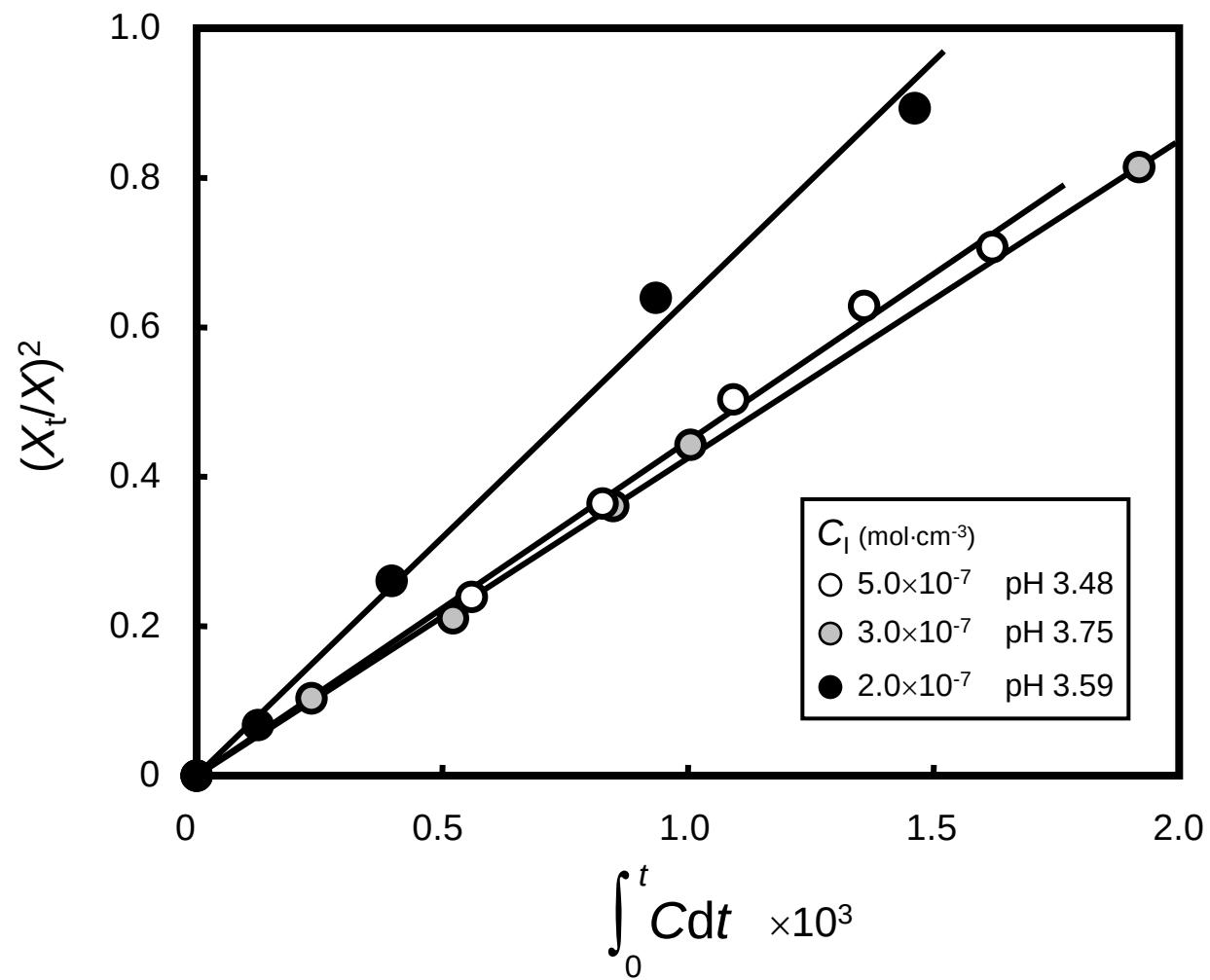


FIG.7 SEKI & SUZUKI

Table 1. Apparent diffusivity of lead ions in HA-M.

pH	D (cm ² ·s ⁻¹)
3.75	7.97×10 ⁻⁶
3.59	6.94×10 ⁻⁶
3.48	7.23×10 ⁻⁶