ISSN 2321-807X

A study on Biosorptive Removal of Cd from Wastewater using Chironomid Larvae (Diptera: Chironomidae)

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ABSTRACT

Cadmium (Cd) has caused serious public health problem due to its toxic nature. It is necessary to find a cost-effective method to dispose of wastewater containing Cd. Chironomid larvae as an alternative to conventional adsorbents were applied to remove Cd from wastewater. The sorption studies of Cd were carried out using laboratory-reared *Glyptotendipes tokunagai* (Diptera: Chironomidae) larvae. Kinetic and sorption capacity of chironomid larvae for Cd were determined by means of controlled experiments in a batch system. It was observed that removal efficiency of Cd was largely concentration dependent and more effective in lower concentration. At equilibrium, Cd was removed up to roughly 53 %. The sorption kinetics were found to conform to the pseudo-first-order kinetic model with a good correlation. Equilibrium sorption data were best fitted to the both Freundlich and Langmuir isotherm models owing to their correlation coefficient R^2 values greater than 0.99. Considering the values obtained from isotherm constants $1/n$ and r, it is confirmed that Cd is sorbed favorably by chironomid larvae. With its relatively high removal capability for Cd, Chironomid larvae have enormous potential for application in wastewater treatment technologies.

Keywords

Chironomid larvae; Cd removal; Wastewater; Kinetic; Isotherm

Council for Innovative Research
Peer Review Research Publishing System
Journal: Journal of Advances in Chemistry
Vol. 10, No. 3
editorjaconline@gmail.com
www.cirjac.com

1. INTRODUCTION

With the increase in industrial activities, a large amount of heavy metals have been continually brought into water bodies including reservoirs, lakes, streams, rivers and oceans. In the present, the presence of heavy metals in aqueous environments has been of great concern due to the disturbance of aquatic ecosystem. Cd is a non-essential element for human health and well-known as one of the most toxic heavy metals [1]. The major sources of Cd accumulation in the environment are originated from metallurgical alloying, ceramics, metal plating, pigment work, lead-zinc mining and alkaline batteries [2]. When the level of Cd in human body reaches a specific value, it causes severe damage to kidney, lung, and liver [3]. Therefore, it needs to be paid more attention to the solution of Cd contamination problem.

Biological methods by means of bacterial biomass [4-8] have been used to eliminate heavy metals in wastewater. However, they have shown unstable and insufficient efficiencies in removing heavy metals from wastewater. Moreover, they experience considerable difficulty in controlling microorganism for a long time by nature. As alternatives to biological methods, chemical precipitation, membrane filtration, ion exchange, liquid extraction and electro-dialysis methods have been widely used for the removal of heavy metals form wastewater over the decades [9-13]. Nevertheless, their applicability of wastewater treatment is limited in terms of the high cost and the low efficiency.

Adsorption is a quite popular method due to the simplicity and the absence of sludge, as well as the availability of a wide range of adsorbents. Activated carbon may become a favorite choice for removal of heavy metals from wastewater [14, 15] because of its high surface area and pore volume, along with convenient regeneration of spent carbon. However, the high cost of activated carbon makes its use limited. Therefore, many studies have described the adsorption abilities of various low-cost adsorbents as the potential replacement. So far, adsorbents that have been studied for the adsorption of heavy metals are fly ash, peat, zeolite, kaolinite, goethite and loess soil [16, 17]. However, these adsorbents, in many cases, suffer from the poor adsorption capacities for target heavy metals.

Benthic macroinvertebrates are a primary component of food-web in freshwater ecosystems [18, 19]. The dipteran family Chironomidae or non-biting midges represent one of the most important groups of benthic macroinvertebrates, and are distributed broadly with high density in almost all types of freshwater habitats such as rivers, streams, lakes, and wetlands, including polluted environments [20]. They also play a significant role in the nutrient and other inorganic cyclings in the freshwater ecosystem. Owing to these reasons, the chironomid larvae have been used as a test species in various ecotoxicological researches including a cadmium toxicity experiment [21-23]. The chironomid midge *Glyptotendipes tokunagai* Sasa is frequently a dominant benthic macroinvertebrate in organic rich urban streams in Asia, and has been suggested as a new test species for ecotoxicological studies [24].

The objective of this study is to investigate the feasibility of chironomid larvae as a bio-sorbent material for Cd removal in wastewater. The effects of operating factors such as contact time and initial concentration were systematically studied. Sorption kinetics and isotherms were also analyzed to reveal the sorption mechanisms.

2. MATERIALs AND METHODs

2.1. Cd solution

The synthetic Cd bearing wastewater solutions were prepared by diluting 1000 mg L^{-1} of analytical grade Cd standard solution (Kanto Chemical Co., Inc, Japan) into distilled water.

2.2. Preparation of chironomid larvae

For experiments, mass larval rearing of *G. tokunagai* was conducted in plastic containers (length 250, width 270, and height 170 mm) containing pre-aerated distilled water (depth 40–50 mm) and fine sand (depth 30–40 mm), which were placed inside a rearing cage (acrylic box with attached screen: length 420, width 550, and height 420 mm) for emerging adults. Tetramin® (< 0.2 mm) (TetraWerke, Melle, Germany) dissolved in pre-aerated distilled water was provided as feed for the larvae. Detailed rearing method of *G. tokunagai* was presented in Baek et al. (2012).

2.3. Sorption studies

Sorption studies were carried out by the batch system to obtain equilibrium data. For this studies, a series of flasks were employed. Each flask was filled with 500 mL of Cd solutions and then 0.5 g of chironomid larvae were added into flasks. Chironomid larvae were not fed during the sorption study. All flasks were aerated in order to maintain the dissolved oxygen levels. Studies were conducted without agitation at room temperature. At given time intervals, a fraction of the Cd solution was withdrawn from the flasks. Blank experiments were also performed without chironomid larvae to distinguish between possible Cd precipitation or sorption on the walls of flasks and actual Cd sorption. The concentrations of Cd in all samples were determined using ICP-AES (Flame Modula S, Spectro, Germany).

2.4. Sorption kinetics

The kinetic studies were carried out with initial Cd concentrations at different time periods varying between 1 and 10 day. The amount of Cd sorbed at time t, q_t (mg g^{-1}), was calculated as follows:

$$q_e = \frac{(C_i - C_t)V}{m} \tag{1}$$

where, C_i and C_t (mg L^{-1}) are concentrations of Cd at initial and a certain period of time, respectively. While V (L) is the initial solution volume and m (g) is the amount of chironomid larvae.

The well-known pseudo-first and pseudo-second kinetic models [25] were employed to analyze the kinetics of the sorption process.

2.5. Sorption isotherms

Sorption isotherms were measured by varying the initial Cd concentrations and keeping chironomid larvae constant. The initial concentrations of Cd in solution were in the range of 0.5 to 2 mg L^{-1} and the amount of chironomid larvae was 0.5 g. The amount of Cd sorbed by chironomid larvae at equilibrium, q_e (mg g^{-1}), was calculated according to the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{2}$$

where, C_e (mg L^{-1}) is concentration of Cd at equilibrium time.

In this isotherm study, Freundlich and Langmuir isotherm models [25] were used for comparison with experimental data.

3. RESULTS AND DISCUSSION

3.1. Effect of initial concentration and contact time

Sorption studies were carried out using different initial concentrations in the range of 0.25-2.0 mg L^{-1} of Cd for 0.5 g of chironomid larvae. In order to establish the equilibrium time, we measured the Cd concentration of samples, which were taken at specific time intervals. Fig. 1 represents amounts of Cd sorbed by chironomid larvae for initial concentrations plotted as a function of contact time. The contact time corresponding to the maximum sorption was considered as the equilibrium time.

As shown in Fig. 1, the amounts of Cd sorbed at the beginning of contact time were very low. However, the sorbed amounts of Cd were gradually increased with the passage of contact time until 10 day. After that time, the sorption rate approached constant. Additional contact time did not result in significant increase in sorption because the survival rate of chironomid larvae were lower as time went by. For this reason, the contact time of 10 day was chosen as the equilibrium time.

The sorbed amounts of Cd per unit weight of chironomid larvae decreased with increase of initial concentration. The percentage of Cd removal due to sorption was calculated as:

$$\%\ \text{Cd removal} = \frac{(C_i - C_e)}{C_i} \times 100\% \tag{3}$$

The process of Cd removal on chironomid larvae was highly concentration dependent. Depending on the initial concentrations, a roughly 31-53 % of Cd removal at equilibrium was achieved by chironomid larvae. Higher percentage of Cd removal in lower concentration ranges has a lot of industrial significance because it was reported that, in most cases, the wastewater has lower concentration of Cd compared to other heavy metal species [26]. By the way, according to the regulations by the United States Environmental Protection Agency (EPA) and World Health Organization (WHO), the maximum permissible concentration of Cd in wastewater is 0.26 mg L^{-1} [26].

3.2. Sorption kinetics

In order to investigate the sorption processes of Cd on chironomid larvae, two well known models, pseudo-first-order and pseudo-second-order kinetic model, were employed to describe the sorption process. The pseudo-first-order and pseudo-second-order kinetic models are based on the assumption that the rate of sorption is proportional to the number of free sites and the square of the number of unoccupied sites, respectively. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficient R^2. The relatively higher value is more applicable model to the kinetics of Cd sorption.

The pseudo-first-order kinetic model is given as:

$$\log \frac{q_e}{q_e - q_t} = \frac{k_1}{2.303} t \tag{4}$$

Eq. (4) can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

The values of q_e and k_1 are determined from the slope and intercept of the straight line.

The pseudo-second-order kinetic model is presented as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{6}$$

Eq. (6) can be linearized as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The value of q_e and k_2 are determined from the slope and intercept of the straight line.

where, k_1 and k_2 are the equilibrium rate constants of the pseudo-first-order adsorption (min^{-1}) and the pseudo-second-order sorption (g mg^{-1} min^{-1}), respectively.

Fig. 2 and 3 show the pseudo-first-order and pseudo-second-ordre kinetic model fitting to the experimental data for chironomid larvae at different initial concentrations. The experimental amount of sorption equilibrium ($q_{e,exp}$), the rate constants of pseudo-first-order and pseudo-second-order kinetic (k_1 and k_2), the calculated amount of sorption equilibrium ($q_{e,cal}$) and the correlation coefficients (R^2) are shown in Table 1.

From Table 1, it was observed that the calculated amounts of sorption equilibrium ($q_{e,cal}$) from pseudo-first-order kinetic model are relatively close to the experimental amounts of sorption equilibrium ($q_{e,exp}$). The q_e values obtained experimentally and from the pseudo-first-order kinetic model for each initial concentration were found to be 0.13, 0.25, 0.43, 0.67 and 0.08, 0.14, 0.24, 0.45 mg g^{-1}, respectively. Meanwhile, the pseudo-first-order kinetic model, as shown clearly in Table 1, appeared to be the better-fitting model because it has higher R^2 than that of the pseudo-second-order kinetic model for chironomid larvae. The correlation coefficients (R^2) for the pseudo-first-order kinetic model are higher than 0.90 in all cases. This result suggests the Cd sorption on chironomid larvae can be approximated more appropriately by the pseudo-first-order kinetic model. This high applicability of the pseudo-first-order kinetic model to our result was contrary to results of other studies for Cd removal from wastewater in most cases. The rate constant k_1 of pseudo-first-order kinetic model was slightly decreased when increasing the initial Cd concentration from 0.25 to 0.5, 1.0 and 2.0 mg L^{-1}. This implies that the solution with smaller solute concentration is likely to reach equilibrium in a shorter time period.

3.3. Sorption isotherms

The sorption of Cd was carried out at different initial concentration ranging from 0.25 to 2.0 mg L^{-1} while maintaining 0.5 g of chironomid larvae. Two widely used isotherm models, Freundlich and Langmuir isotherms, were employed to investigate the Cd sorption behavior.

Freundlich isotherm, which is an empirical equation for a mono-layer sorption with a heterogeneous energetic distribution of active sites, and/or interaction between sorbed species. can be expressed as follows:

$$q_e = k_f (c_e)^{1/n} \quad (8)$$

where, k_f and $1/n$ are the Freundlich constants related to sorption capacity and the sorbent affinity for the sorbate, respectively. For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (9)$$

A linear plot of log q_e versus log c_e, yields a slope $1/n$ and an intercept of log k_f. The value of k_f is an indicative of the relative sorption capacity. The value of $1/n$, ranging in between 0 and 1, is a measure of the sorption intensity.

The Langmuir isotherm model takes an assumption that the sorption occurs at specific homogeneous sites within the sorbent without interaction between adjacent sorbed solutes. The Langmuir isotherm is written as follows:

$$\frac{c_e}{q_e} = \frac{1}{Qb} + \frac{c_e}{Q} \quad (10)$$

where, Q and b are empirical constants representing mono-layer capacity and energy of sorption, respectively, and can be evaluated from the slope and intercept of the linear plot of c_e/q_e against c_e.

The choice between Freundlich and Langmuir isotherms depends on mainly the constants obtained from equilibrium data.

Fig. 4 and 5 show Freundlich and Langmuir adsorption isotherms for curve fitting of the present experimental results. Corresponding isotherm constants from the linear plots were calculated and listed in Table 2. The correlation coefficient R^2 value of Freundlich isotherm for Cd sorption was very close to 1, which revealed the extremely good applicability of the Freundlich isotherm model to this sorption. Compared with Freundlich isotherm, R^2 value of Langmuir isotherm model was also greater than 0.99. These results suggest that the experimental data of Cd sorption experiments can be adequately described by both isotherm models mentioned above. Similar results were obtained on their studies of heavy metals biosorption from wastewater using *Pseudomonos* sp [27].

The value of $1/n$, one of the Freundlich isotherm constants, explains the type of isotherm. When $0 < 1/n < 1$, the sorption is favorable. Whereas, when $1/n > 1$, the sorption is unfavorable [28]. The value of $1/n$ obtained from experimental data indicates that Cd is sorbed favorably by chironomid larvae during the study.

In case of Langmuir isotherm model, the type of adsorption can be classified by a dimensionless constant r, which is given by the following equation:

$$r = \frac{1}{1+bc_i} \quad (11)$$

The *r* values greater than 1 indicate unfavorable nature of adsorption while the values between 0 and 1 represent favorable adsorption. In this study, the *r* values for the adsorption of Cd on chironomid larvae lie within 0.2969-0.7707 for initial concentrations ranging from 0.25 to 2.0 mg L^{-1}. It shows that the sorption process of the present Cd-chironomid larvae in aqueous solution is favorable.

4. CONCLUSIONS

The current study has provided a lot of useful information for the sorption of Cd from wastewater using chironomid larvae. As far as we know, any sorption studies have not dealt with chironomid larvae as a sorbent material up to date. In this study, the removal efficiency of chironomid larvae for Cd was highly concentration dependent, and the maximum removal efficiency of Cd at equilibrium was approximately 31-53 % at the studied Cd concentration ranges. The sorption kinetic studies demonstrated that the process for sorption of Cd followed the pseudo-first-order kinetic model, which provided the best fit for the experimental data. Isotherm studies revealed that both Freundlich and Langmuir isotherm model were suitable for describing the sorption system of Cd-chironomid larvae. Moreover, the isotherm constants, 1/*n* and *r* values, obtained from experimental data indicated that Cd is sorbed favorably by chironomid larvae. Chironomid larvae can be a good candidate as a bio-sorbent for removal of Cd in wastewater because they are environmentally friendly and easily obtained in nature.

ACKNOWLEDGEMENTS

This work is supported by the Eco-Innovation project of the Ministry of Environment, Korea (416-111-009).

REFERENCES

(1) Wang, Y., Tang, W., Chen, Y., Zhan, L., Li, Z., Tang, Q., 2009. J. Hazard. Mater. 172, 30-37.

(2) Mohapatra, M., Anand, S., 2007. J. Hazard. Mater. 148, 553-559.

(3) Bedoui, K., Berki-Abbes, I., Srasra, E., 2008. Desalination 223, 269-273.

(4) Zaki, S., Farag, S., 2010. Int. J. Environ. Sci. Technol. 7 (3), 553-560.

(5) Bueno, B.Y., Torem, M., de Carvalho, M.L., Pino, G.A.H., de Mesquita, L.M.S., 2011. Miner. Eng. 24, 1619-1624.

(6) Luo, S.L., Xiao, X., Xi, Q., Wan, Y., Chen, L., Zeng, G.M., Liu, C.B., Guo, H.J., Chen, J.L., 2011. J. Hazard. Mater. 190 (1-3), 1079.

(7) Mo, B.B., Lian, B., 2011. World J. Microbiol. Biotechnol. 27 (5), 1063-1070.

(8) Huang, W., Liu, Z., 2013. Colloids Surf. B. 105, 113-119.

(9) Walton, H.F., Rocklin, R.D., 1990. CRC Press, Boston, MA.

(10) Alfassi, Z.B., Wai, C.M., 1992. CRC Press, Boston, MA.

(11) Namasivayam, C., Ranganathan, K., 1995. Environ. Technol. 16, 851-860.

(12) Crini, G., Badot, P.M., 2007. Franche-Comte Univ. Press., France, 356.

(13) Nouri, L., Ghodbane, I., Hamdaoui, O., Chiha, M., 2007. J. Hazard. Mater. 149, 115-125.

(14) Fan, H.J., Anderson, P.R., 2005. Sep. Purif. Technol. 45, 61-67.

(15) Srivastava, V.C., Mall, I.D., Mishra, I.M., 2008. Chem. Eng. Proc. 47, 1269-1280.

(16) Tang, X., Li, Z., Chen, Y., 2009. J. Hazard. Mater. 161, 824-834.

(17) Kirkelund, G.M., Damoe, A.J., Ottosen, L.M., 2013. J. Hazard. Mater. 250-251, 212-219.

(18) Rosenberg, D.M., Resh, V.H., 1993. Chapman and Hall., New York.

(19) Bae, Y.J., Kil, H.K., Bae, K.S., 2005. KSCE J. Civil Engineering 9, 55-63.

(20) Ferrington, L.M.B. Berg, Coffman, W. P., 2008. Kendall/Hunt Press, Dubuque, Iowa, USA.

(21) Williams, K.A., Green, J., Pascoe, D., Gower, D.E., 1986. Oecologia (Berlin) 70, 362-366.

(22) Suedel, B.C., Jr. Rodgers, J.H., Deaver, E., 1997. Arch. Environ. Contam. Toxicol. 33, 188-193.

(23) Fargašová, A., 2001. Ecotoxicol. Environ. Safety 48, 1-5.

(24) Baek, M.J., Yoon, T.J., Bae, Y.J., 2012. Environ. Entomol. 41 (4), 950-958.

(25) Do, D.D., 1998. Imperial College Press, London.

(26) Rita, F.L., Rebeiro, V.C., Soares, L.M., Costa, C.N., 2012. J. Hazard. Mater. 237-238, 170-179.

(27) Hussein, H., Farag, S., Kandeel, K., Moawad, H., 2004. Electron. J. Biotechnol. 7 (1), 38-46.

(28) Vasiliu, S., Bunia, I., Racovita, S., Neagu, V., 2011. Carbohydr. Polym. 85 (2), 376-387.

Table 1. Pseudo-first and pseudo-second order kinetic model parameters for different initial Cd concentration at 298 K

Bio-sorbent	Initial concentration (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			$q_{e,cal}$ (mg g^{-1})	k_1 (day^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} day^{-1})	R^2
chironomid larvae	0.25	0.13	0.08	2.00	0.897	0.62	2.17	0.392
	0.50	0.23	0.14	1.60	0.908	1.20	1.21	0.636
	1.00	0.43	0.24	0.43	0.931	2.63	0.51	0.607
	2.00	0.67	0.45	0.31	0.952	3.17	0.36	0.689

Table 2. *Freundlich* and *Langmuir* constants for sorption of Cd at 298 K

Langmuir constants *Freundlich* constants						
Bio-sorbent	*Q* (mg g^{-1})	*b* (L mg^{-1})	R^2	*1/n*	k_F (mg g^{-1})	R^2
chironomid larvae	1.05	1.19	0.9906	0.65	0.52	0.9957

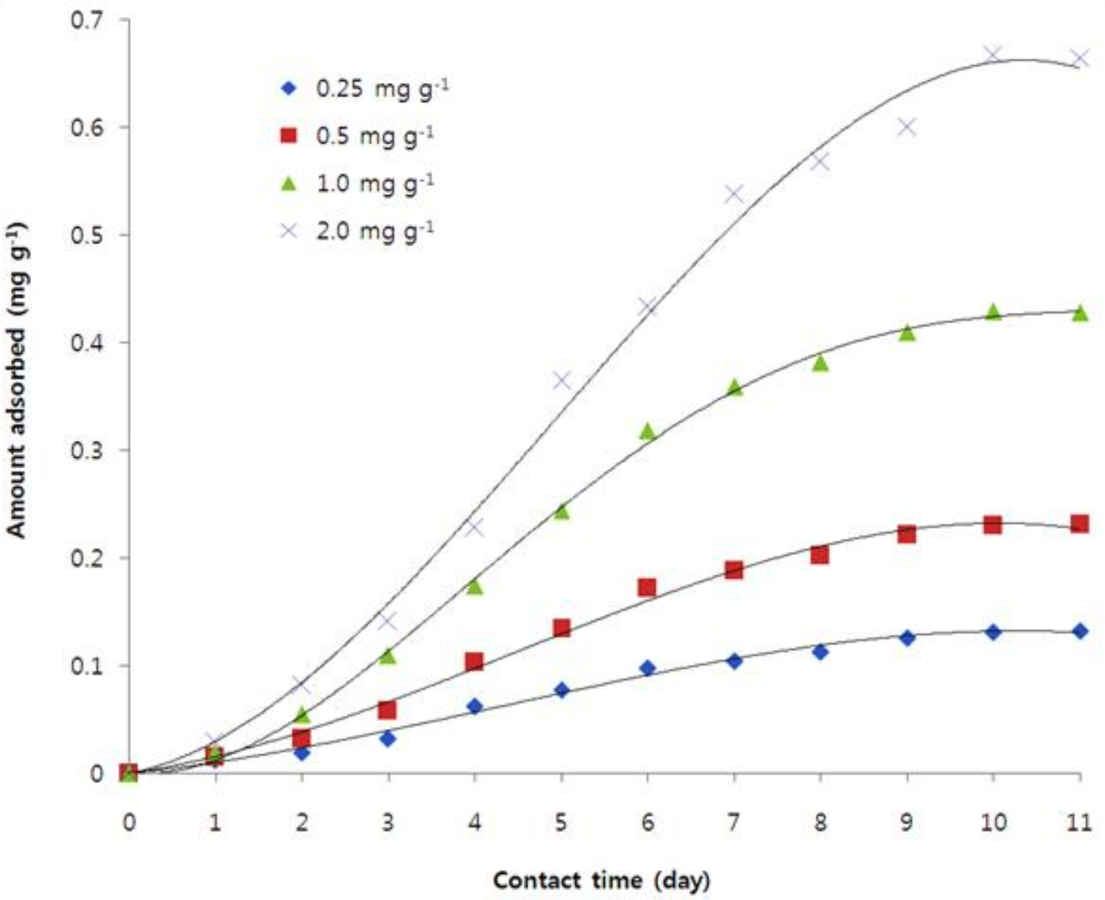


Fig. 1. Adsorption of Cd on chironomid larvae at 298 K.

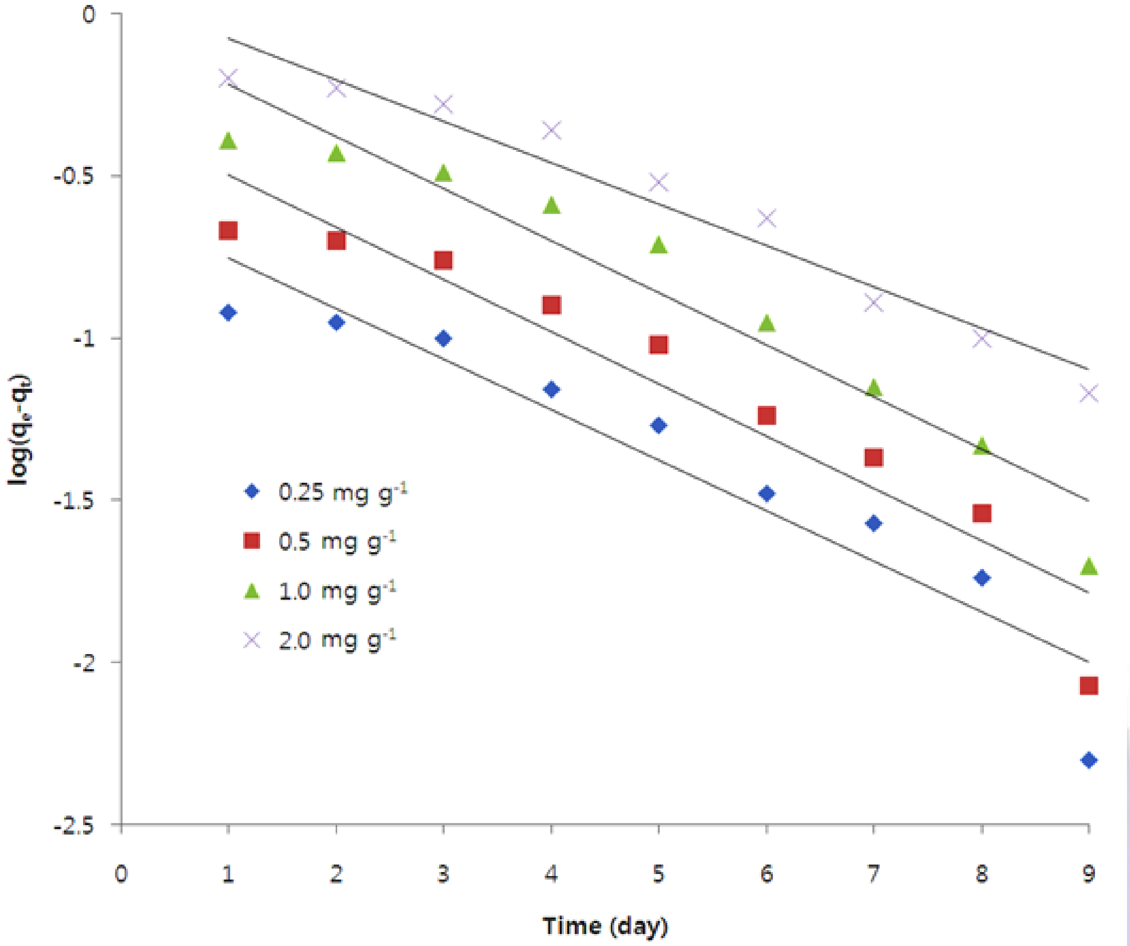


Fig. 2. Plots of pseudo-first-order kinetics of Cd sorption on chironomid larvae at 298 K.

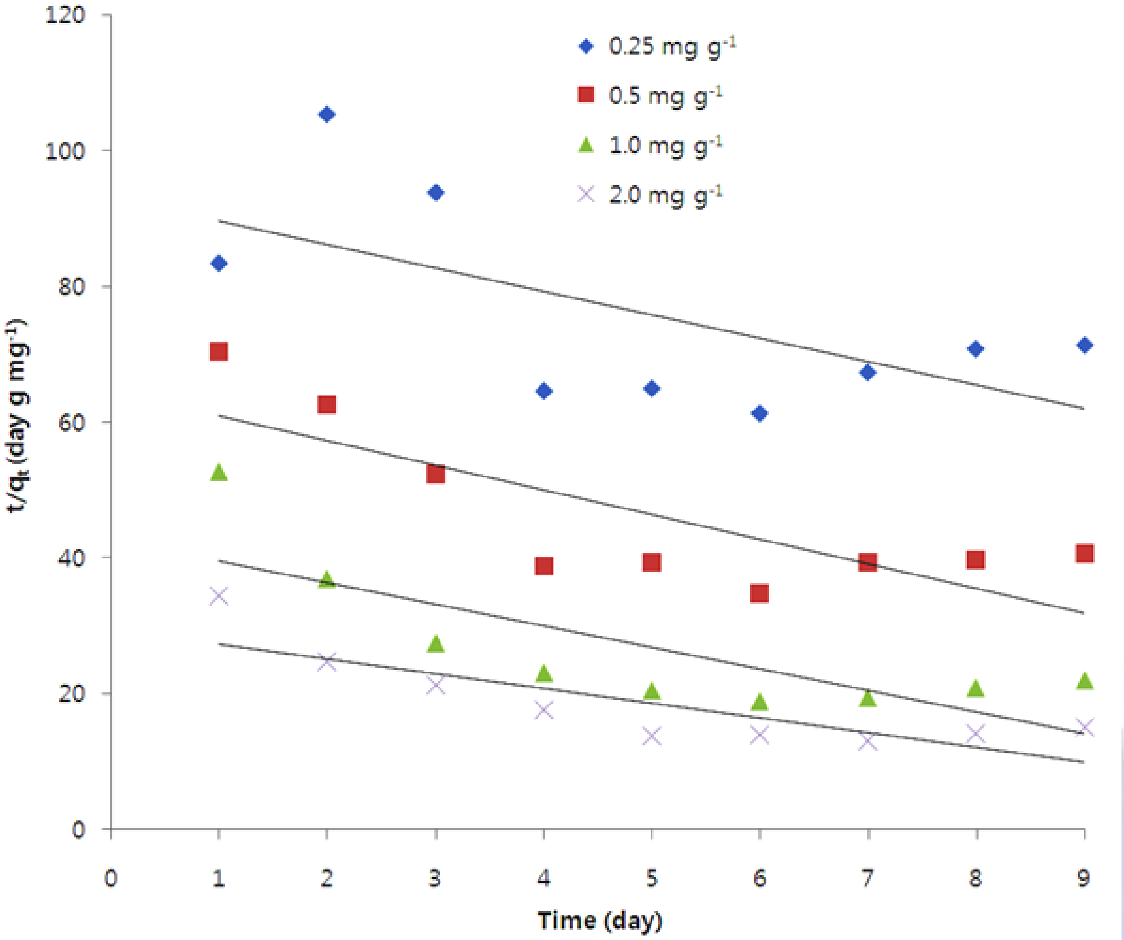
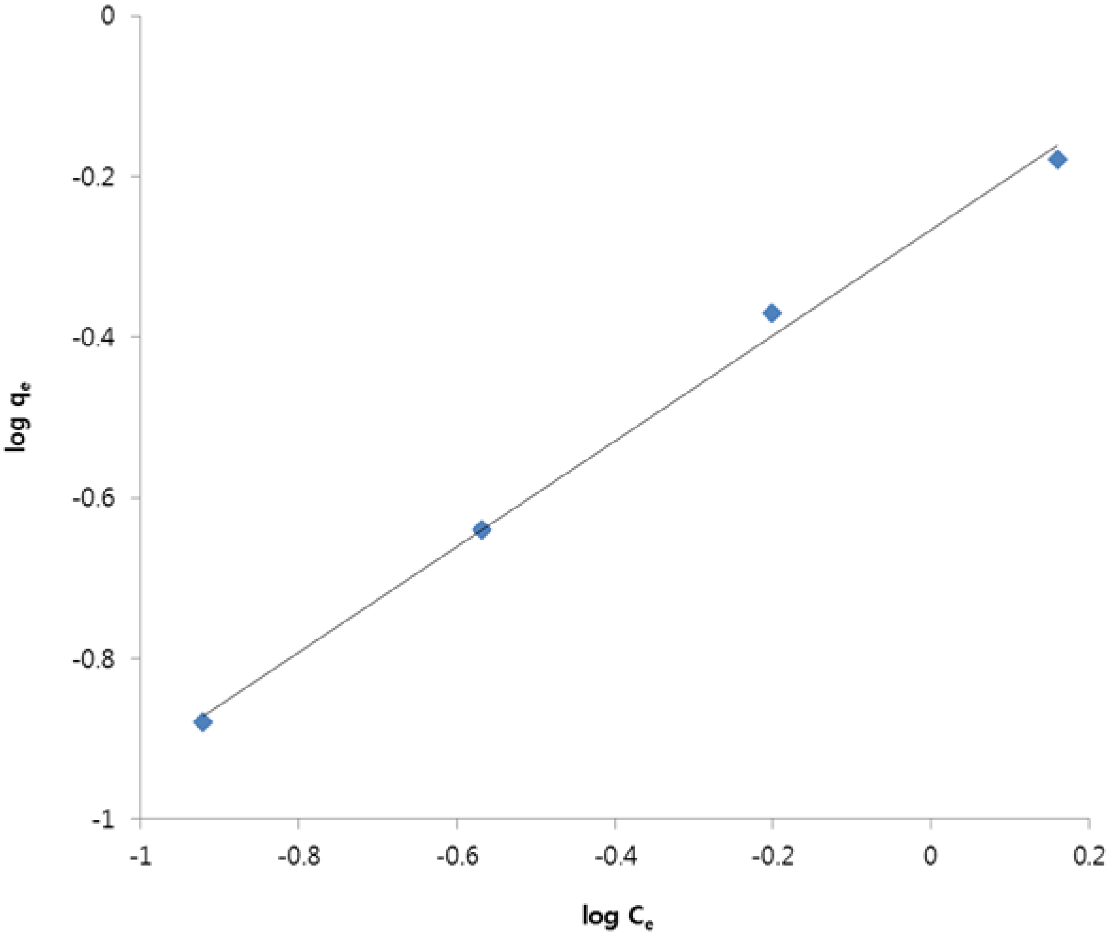


Fig. 3. Plots of pseudo-second-order kinetics of Cd sorption on chironomid larvae at 298 K.



. Fig. 4. Freundlich sorption isotherm curve for Cd at 298 K.

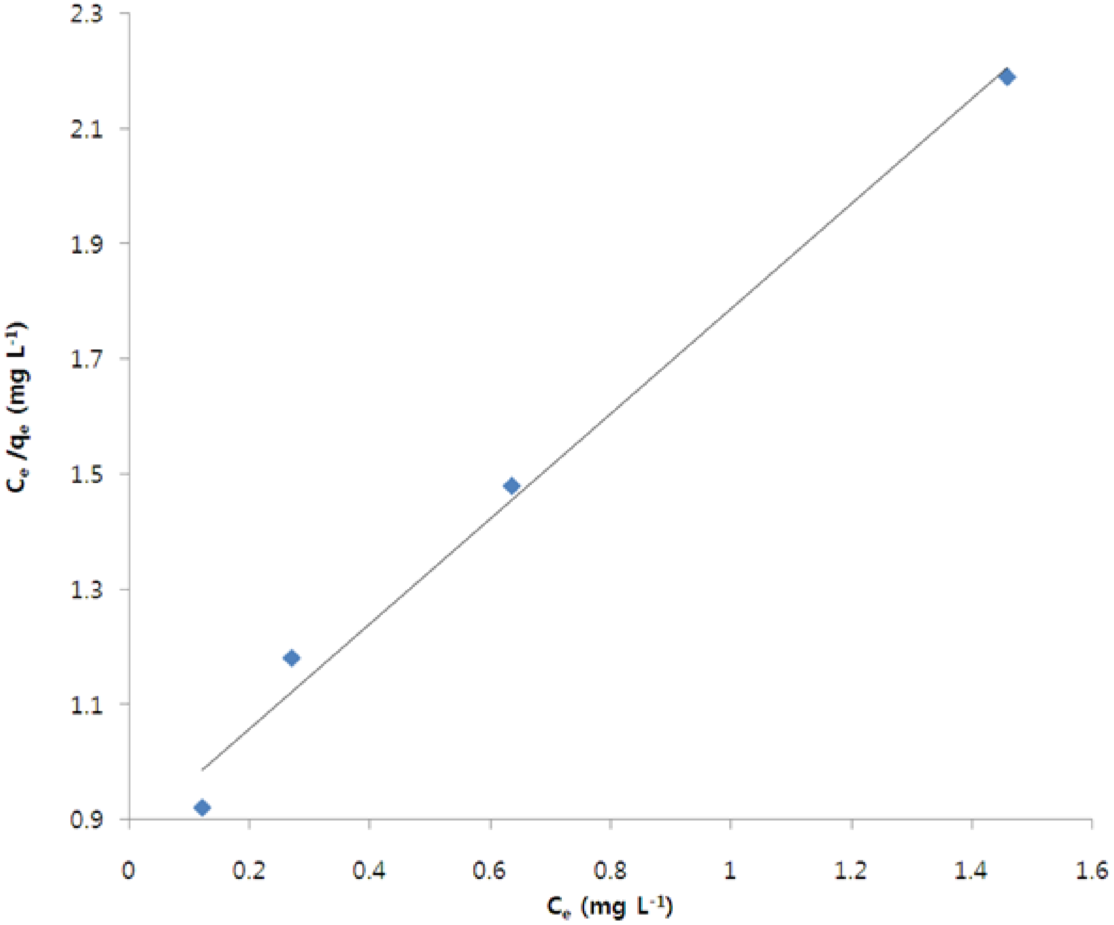


Fig. 5. Langmuir sorption isotherm curve for Cd at 298 K.