



Sorption of Ni(II) and Cr(III) ions by the *Chironomus yoshimatsui* larvae from wastewater

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ABSTRACT

In this study, *Chironomus yoshimatsui* larvae were applied to remove Ni(II) and Cr(III) ions from wastewater. The sorption studies were carried out using laboratory-reared *C. y.* larvae. It was found that *C. y.* larvae are very susceptible to Cr(III) as compared to Ni(II). The survival capacity of *C. y.* larvae was sharply reduced when exposed to even low Cr(III) concentration. Sorption isotherm and kinetics of *C. y.* larvae for Ni(II) were determined by means of controlled experiments in a batch system. It was observed that sorption efficiency of Ni(II) was largely concentration dependent and more effective at lower concentration. At each equilibrium, Ni(II) was removed up to roughly 44~80%. Sorption data were better fitted to the *Langmuir* isotherm model because of its correlation coefficient R^2 value greater than that of the *Freundlich* isotherm model. The sorption kinetics by *C. y.* larvae for Ni(II) was well described a pseudo-first-order rate expression. *C. y.* larvae have enormous potential for application in wastewater treatment technologies because they are widespread and abundant all around the world and can be easily kept in culture.

Keywords. *Chironomus yoshimatsui* larvae ; Ni(II); Sorption; Kinetics; Isotherm

1. INTRODUCTION

Water bodies including reservoirs, lakes, streams, rivers and oceans have been contaminated with a large quantity of toxic metals due to the rapid industrialization. The presence of toxic metals in water is actually harmful to the humans and aquatic life. Chromium and its compounds have been used for electroplating, leather tanning and metal finishing in various industry field [1]. Nickel has been widely used for the several industrial purposes like electroplating, production of batteries, manufacturing of slufate and porcelain enameling [2]. However, if these toxic metals are into the human body at higher level, it has been known that they causes various diseases like dermatitis, nausea, chronic bronchitis, gastrointestinal distress and reduced lung function to humans. Therefore, lots of methods have been proposed for the removal of toxic metals from wastewater. These include adsorption, chemical precipitation, ion exchange, membrane filtration, coagulation, biological and electrochemical treatment [3-24].

C. y. larvae are widely distributed in Korea and have been used as a model species to assess the quality of freshwater and sediments [25]. They inhabit the sediments and feed on organic detritus from fish and plants in water. *C. y.* larvae are abundant in sediments and water contaminated by certain metals. It has been demonstrated that *C. y.* larvae are less susceptible to exposure to metals at metal-polluted sites [26]. They acclimate themselves to metals by either regulating body burdens or sequestering them in selected tissues. Until now, many researchers have focused on evaluation of *C. y.* larvae as a test organism for use in sediment toxicity bioassays [27-29]. However, as far as author know, no studies have dealt with *C. y.* larvae for sorption of toxic metals in wastewater.

The objective of this study is to investigate the feasibility of *C. y.* larvae for sorption of Ni(II) and Cr(III) ions in wastewater. *C. y.* larvae were chosen because they is one of the species able to survive in heavily metal-polluted streams in Korea. The experiments were carried out using aqueous solution contaminated with selected toxic metals like Ni(II) and Cr(III). The sorption performance of Ni(II) and Cr(III) was done with contact time and different initial concentrations. Moreover, isotherms and kinetics were also analyzed to reveal the sorption characteristics.

2. MATERIALS AND METHODS

2.1. Materials and reagents

In this study, *C. y.* larvae were used as the sorbent for sorption of Ni(II) and Cr(III) from aqueous solution. *C. y.* larvae were acquired from sediments in organic rich urban streams in Korea. Mass larval rearing of *C. y.* larvae 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) was provided as feed for the larvae. Adult *C. y.* were retained using a plastic cage covered with steel wire mesh and reproduced continuously. Detailed rearing method of *C. y.* was presented in Baek et al [30]. Anhydrous NiCl₂ and Cr(NO₃)₃·9H₂O were purchased from Sigma-Aldrich, USA. The reagents are of analytical grade and were used without further purification.

2.2. Adsorption procedures

The Ni(II) and Cr(III) stock solutions with concentration of 100 mg L⁻¹ were prepared by using NiCl₂ and Cr(NO₃)₃·9H₂O as a source of Ni(II) and Cr(III), respectively. Experimental solutions of the desired concentration were obtained by diluting the stock solutions successively. Batch sorption studies were carried out in a series of 500 mL of volumetric flasks filled with 100 mL Ni(II) solution and Cr(III) as well as the required amounts of *C. y.* larvae. The flasks were tightly closed with a silicone stopper. *C. y.* larvae were not fed during the sorption study. All flasks were aerated in order to maintain the dissolved oxygen levels. Sorption studies were conducted without agitation at room temperature. The samples were drawn from the flasks at regular intervals for determining the residual Ni(II) and Cr(III) concentrations. All experiments were

performed in triplicate and the average was taken for subsequent calculations. The concentrations of Ni(II) and Cr(III) in samples were determined using ICP-AES (Flame Modula S, Spectro, Germany).

Sorption isotherms were measured by varying the initial Ni(II) and Cr(III) concentrations and keeping *C. y. larvae* constant. The initial concentrations of Ni(II) and Cr(III) in aqueous solutions were in the range of 0.5 to 5.0 mg L⁻¹ and the amount of *C. y. larvae* was 0.1 g. The sorption capacity of Ni(II) and Cr(III), q_e (mg g⁻¹), of *C. y. larvae* was evaluated by using the following expression:

$$q_e = \frac{(c_i - c_e)V}{m} \quad (1)$$

Where, c_i and c_e (mg L⁻¹) are the concentrations of metals at initial and equilibrium time t , respectively. V (L) is the volume of the solution and m (g) is the weight of *C. y. larvae*. In this isotherm study, the *Freundlich* and *Langmuir* isotherm models were used for comparison with experimental data.

The sorption kinetic studies were performed with initial metal concentrations at different time periods varying between 1 day~11 day. The amount of metals adsorbed at time t , q_t (mg g⁻¹), was calculated using the following relationship:

$$q_t = \frac{(c_i - c_t)V}{m} \quad (2)$$

Where, c_t (mg L⁻¹) is the concentration of metals at a certain period of time t . The pseudo-first-order and pseudo-second-order models were selected to analyze the kinetics of the sorption process.

3. RESULTS AND DISCUSSION

3.1. Effect of initial Ni(II) concentration and contact time

Generally, the sorption of sorbate on sorbent is dependent on both contact time and the initial sorbate concentration. The effect of contact time on the sorption of sorbate at different initial concentrations represents the sorption pattern. The contact time corresponding to the maximum sorption is considered as the equilibrium sorption time.

The sorption study was conducted in the concentration range from 0.5~5.0 mg L⁻¹ for each Ni(II) and Cr(III) while maintaining 0.1 g L⁻¹ of *C. y. larvae* at room temperature. The sorption patterns corresponding to four different initial Ni(II) concentrations are presented in Fig. 1. It is observed that for all initial Ni(II) concentrations, there is an increase in the amount sorbed by increasing the contact time. Sorption reached equilibrium in 7 day at low concentrations of 0.5 and 1.0. mg L⁻¹. On the other hand, at higher concentrations, equilibrium time was 11 day. After equilibrium, the remaining concentration of Ni(II) in solution remained nearly constant.

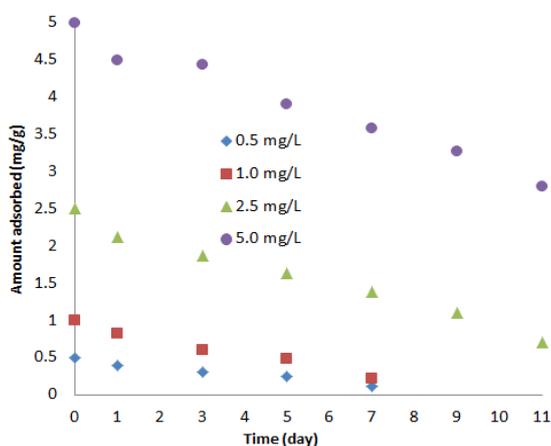


Fig. 1. Sorption pattern of Ni(II) by *C. y. larvae* with contact time at room temperature.

The percent of Ni(II) sorption and the distribution ratio, K_d (mg g⁻¹), can be correlated by the following equations:

$$\text{Sorption (\%)} = \frac{1000K_d}{K_d + \frac{V}{m}} \quad (3)$$

$$K_d = \frac{\text{amount of solute in adsorbent}}{\text{amount of solute in solution}} \times \frac{V}{m} \quad (4)$$

Where, V is the volume of the solution (mL) and m is the weight of *C. y. larvae* (g). The sorption percent of Ni(II) at equilibrium was found to be lower with increased initial concentration from 0.5 to 5.0 mg L⁻¹. Depending on the initial concentrations, approximately 44~80 % of Ni(II) sorption at equilibrium was achieved by *C. y. larvae*.

Fig. 2 represents amounts of Cr(III) sorbed by *C. y.* larvae with contact time for initial Cr(III) concentrations. As shown in Fig. 2, any sorption of Cr(III) by *C. y.* larvae was not observed through the contact time. Furthermore, additional contact time did not show the increase in sorption. The significant sorption difference for Ni(II) and Cr(III) can be explained by change in the survival capacity of *C. y.* larvae. A large number of *C. y.* larvae survived in all Ni(II) concentrations. Whereas, the survival of *C. y.* larvae declined sharply within the first day at all Cr(III) concentrations. The result indicates that *C. y.* larvae is capable of tolerating for Ni(II) compared with Cr(III) in solution.

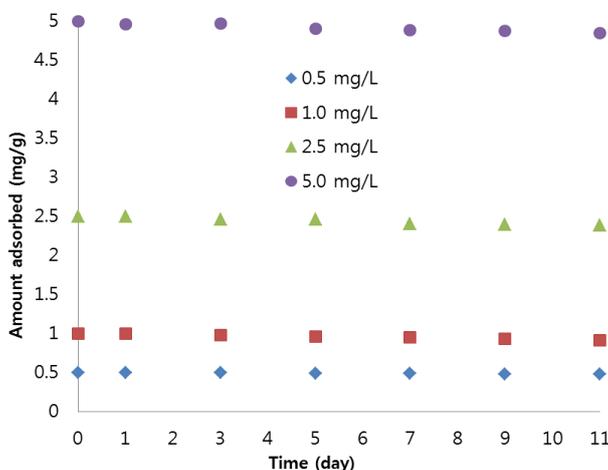


Fig. 2. Sorption pattern of Cr(III) by *C. y.* larvae with time at room temperature.

3.2. Sorption isotherms

Sorption isotherms provide essential data source for understanding of relation with sorbent and sorbate when sorption equilibrium is arrived at a constant temperature. It is important for sorption system because it can be used to compare the properties with different sorbents quantitatively. In this study, the most commonly used *Freundlich* and *Langmuir* isotherm models were employed to investigate the sorption behavior of Ni(II) by *C. y.* larvae in aqueous solution. The *Freundlich* isotherm is an empirical equation employed to describe heterogeneous system. Whereas, the *Langmuir* isotherm takes an assumption that the sorption occurs at specific homogeneous sites within the sorbent.

The *Freundlich* isotherm equation is given as:

$$q_e = k_f(c_e)^{1/n} \quad (5)$$

Where, k_f (mg g^{-1}) and $1/n$ are the *Freundlich* constants related to sorption capacity and the sorbent affinity for the sorbate, respectively. A linear form of the *Freundlich* isotherm equation can be described as:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (6)$$

A linear plot of $\log q_e$ versus $\log c_e$ yields a slope $1/n$ and an intercept of $\log k_f$.

The *Langmuir* isotherm equation is presented as:

$$\frac{c_e}{q_e} = \frac{1}{Qb} + \frac{c_e}{Q} \quad (7)$$

Where, Q (mg g^{-1}) is the maximum amount of sorbate per unit mass of sorbent and b (L mg^{-1}) is the equilibrium sorption constant which is related to the affinity of the sorbate. The *Langmuir* constants are determined from the intercept of the linear plot of c_e/q_e against c_e .

The choice between the *Freundlich* and *Langmuir* isotherms depends mainly on the nature of equilibrium data. The fittings of *Freundlich* and *Langmuir* isotherm of Ni(II) for *C. y.* larvae are presented in Figure 3 and 4. It was observed that the experimental data deviate more in the case of the *Freundlich* than *Langmuir* plot. This is verified by the correlation coefficient R^2 values of the linear plots, which revealed the extremely good applicability of the *Langmuir* isotherm model to the Ni(II) sorption by *C. y.* larvae.

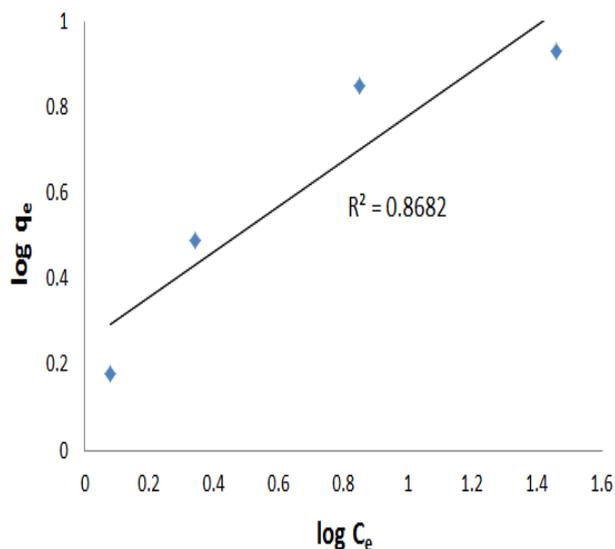


Fig. 3. Freundlich sorption isotherm curve for Ni(II) at 298 K.

The corresponding isotherm parameters were evaluated from the linear plot and listed in Table 1. The values of Q and b of *Langmuir* isotherm constants were 10.59 and 0.14, respectively. Generally, the sorbates having higher Q values have high affinity toward sorbents compared to others having lower Q values. If the value of b is smaller than 1, it indicates favorable sorption on sorbate to the surface of the sorbent. Whereas, if the value is larger than 1, the sorption is unfavorable.

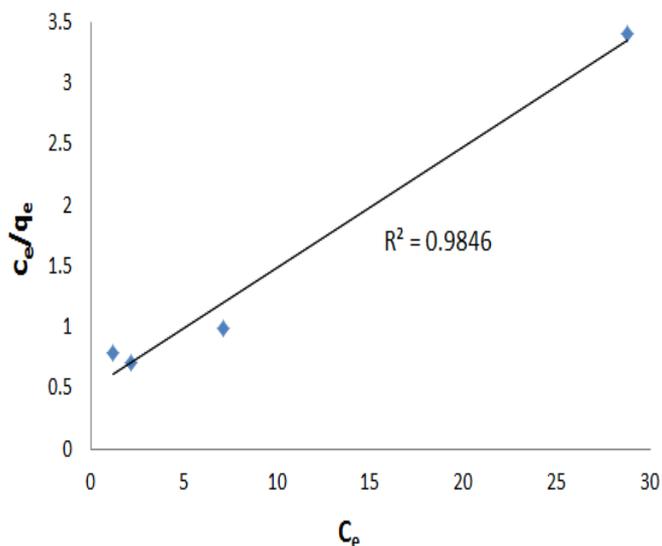


Fig. 4. Langmuir sorption isotherm curve for Ni(II) at 298 K.

Table 1. Langmuir and Freundlich constants for sorption of Ni(II) at 298 K

Sorbent	Langmuir constants			Freundlich constants		
	Q (mg g ⁻¹)	b (L mg ⁻¹)	R^2	$1/n$	k_F (mg g ⁻¹)	R^2
C. y. larvae	10.59	0.14	0.9846	0.54	1.38	0.8682

3.3. Sorption kinetics

In this study, two kinetic models were employed to evaluate the sorption processes of Ni(II) on *C. y.* larvae. The selected kinetic models are the *pseudo-first-order* and *pseudo-second-order* based on the assumption that the rate of adsorption 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 Ni(II) sorption.

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

$$\log \frac{q_e}{(q_e - q_t)} = \frac{k_1}{2.303} t \quad (8)$$

Eq. (8) can be rearranged to obtain the following linear relationship:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

Where, k_1 (min^{-1}) is the equilibrium rate constant of the *pseudo-first-order* kinetics. 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:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (10)$$

Eq. (10) can be linearized:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

Where, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the equilibrium rate constant of the *pseudo-second-order* kinetics. The values of q_e and k_2 are determined from the slope and intercept of the straight line.

Fig. 5 and 6 show the *pseudo-first-order* and *pseudo-second-order* kinetic model fitting to the experimental data for *C. y.* larvae at different initial concentrations. The experimental amounts of sorption equilibrium ($q_{e,\text{exp}}$), the rate constants of *pseudo-first-order* and *pseudo-second-order* kinetic (k_1 and k_2), the calculated amount of sorption equilibrium ($q_{e,\text{cal}}$) and the correlation coefficients (R^2) are shown in Table 2.

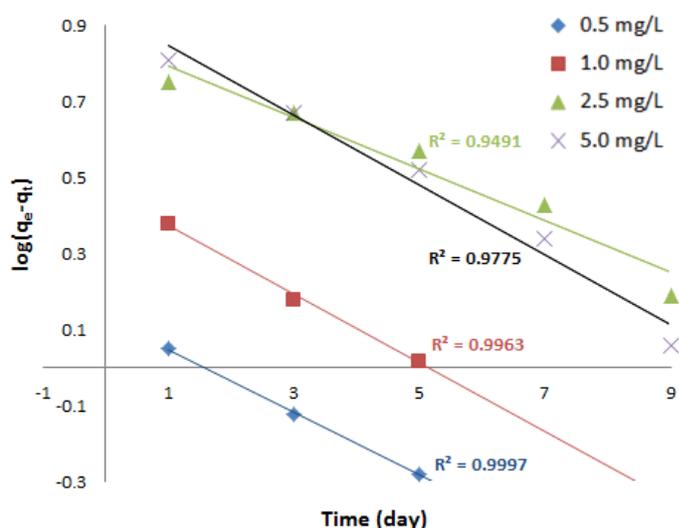


Fig. 5. Plots of pseudo-first-order kinetics of Ni(II) sorption on *C. y.* larvae at 298 K.

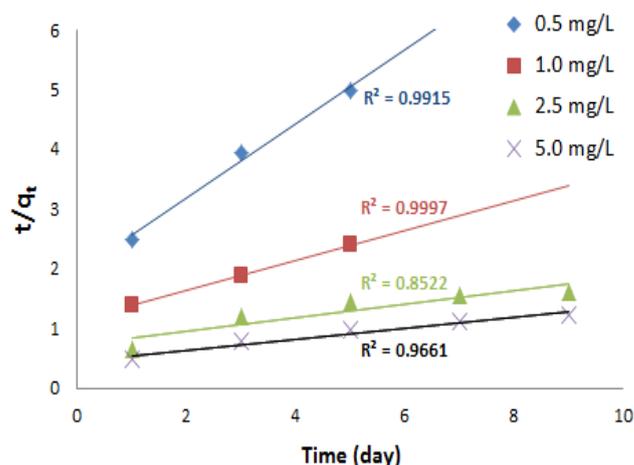


Fig. 6. Plots of pseudo-second-order kinetics of Ni(II) sorption on *C. y.* larvae at 298 K.

From Table 2, it was observed that the calculated amounts of sorption equilibrium ($q_{e,cal}$) from both *pseudo-first-order* and *pseudo-second-order* kinetic models deviated slightly from 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 3.80, 7.80, 17.9, 22.0 and 1.75, 3.68, 8.34, 9.60 mg g^{-1} , respectively. Meanwhile, the *pseudo-first-order* kinetic model, as shown clearly in Table 2, appeared to be the better-fitting model because it has higher R^2 than that of the *pseudo-second-order* kinetic model for 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 Ni(II) sorption on *C. y.* larvae can be approximated more appropriately by the *pseudo-first-order* kinetic model. The rate constant k_1 of *pseudo-first-order* kinetic model was almost same when increasing the initial Ni(II) concentration from 0.5 to 1.0, 2.5 and 5.0 mg L^{-1} .

Table 2. Pseudo-first and pseudo-second order kinetic model parameters for different initial Ni(II) concentrations at 298 K

sorbent	Initial concen- tration (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 ($\text{g mg}^{-1} \text{ day}$)	R^2
Chironomid midge larvae	0.5	3.80	1.75	0.19	0.9997	1.90	0.22	0.9915
	1.0	7.80	3.68	0.19	0.9963	3.78	0.11	0.9997
	2.5	17.9	8.34	0.12	0.9491	8.12	0.025	0.8522
	5.0	22.0	9.60	0.17	0.9775	10.66	0.033	0.9661

4. CONCLUSION

In this study, we have provided an useful information for the sorption of Ni(II) and Cr(III) from wastewater using *C. y.* larvae. As far as author knows, any sorption studies have not dealt with *C. y.* larvae as a sorbent material until now. It was found that the population of *C. y.* larvae declined sharply when exposed to Cr(III). However, *C. y.* larvae were less affected by exposure to the Pb(II). The sorption efficiency of *C. y.* larvae for Ni(II) was highly concentration dependent, and the maximum sorption efficiency of Ni(II) at equilibrium was approximately 44~80 % in the studied concentration ranges. Isotherm studies showed that the *Langmuir* isotherm model were more suitable for describing the sorption system of Ni(II) and *C. y.* larvae. The sorption kinetic studies demonstrated that the process for sorption of Ni(II) followed the *pseudo-first-order* kinetic model, which provided the best fit for the experimental data. It reveals that *C. y.* larvae can be a good candidate as a sorbent for removal of Ni(II) in wastewater.

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