Kinetic evaluation of chromium(VI) sorption by water lettuce (Pistia)

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ABSTRACT

An investigation was performed to evaluate the uptake capacity of Pistia in living condition for adsorptive removal of chromium(VI) from spiked solution for examining a remedial measure for disposal of chrome-laden wastewater in an urban wetland system. Kinetics results show about 78% removal was achieved for 3 mg/L initial concentration of Cr(VI). Experimental data showed that the root portion absorbed more Cr(VI) (28.54 μg/g) compared to accumulation in leaf (5.73 μg/g). It was also noted that the plant could effectively remove Cr(VI) from the solution with minor damage up to an initial Cr(VI) concentration of 3 mg/L, for which the adsorption isotherm studies were conducted. The maximum uptake capacity of the plant was recorded as 0.05 mg/g of Cr(VI) at the equilibrium level after a contact period of 7 days for an initial concentration of 8 mg/L, although severe physiological damage occurred. The experimental results were plotted in Langmuir and Freundlich isotherm models and both were found to be well fitted ($r^2 = 0.979$ and $r^2 = 0.974$ respectively). The high value of $n$ (2.16) reveals a strong bond between the plant root and dissolved Cr(VI), which favours the adsorption process. The order of the reaction was also examined on the basis of uptake capacity and it was found that the second order model fitted best.

Key words | chromium(VI), isotherm, reaction kinetic, sorption, water lettuce

INTRODUCTION

The ecological water environment in Kolkata (India) wetland area is contaminated due to discharge of chromium-laden wastewater from at least 538 tannery industries. Most of the drainage outfall and combined urban sewage disposal channel of the surrounding area receive such wastes (Chatterjee et al. 2012). Several ill effects to plankton and fish and carcinogenic potential to human health due to chromium contamination are being noted (Guha et al. 2010). Therefore, it is very much necessary to decontaminate Cr(VI) from tannery effluent before discharging the effluent in natural or constructed water bodies. Conventional methods are extensively used for removing soluble chromium (Elangovan et al. 2008) from the water environment. However, such methods suffer several drawbacks, due to high capital and operational cost and an expensive monitoring system, and because of the secondary problem of the generation of toxic sludge or other waste products that further impose complication in disposal of such materials (Volesky & Holan 1995). In this context, a great interest has been prompted to explore the development of alternative economic technologies for the removal of Cr(VI) in industrial liquid waste including tannery effluent. Biotic adsorbents using aquatic plants for cleaning up a contaminant-laden water stream are gaining high interest in this perspective as such plants are profusely grown in the Indian subcontinent.

The bioremediation of chromium from water using aquatic plants for cleaning up the hydrospheric environment is an emerging technology and a sustainable approach, which is gaining high interest for field application as reported by several researchers (Maine et al. 2004; Oporto et al. 2006; Sufie et al. 2007; Elangovan et al. 2008).

Most of the earlier investigations in this context were carried out to examine the removal potential of various macrophytes for heavy metal remediation to treat different industrial wastewater. A limited number of such research works have been done to determine the reaction order based on kinetic results.

The present work was undertaken to study the chromium uptake potential of water lettuce (Pistia) in living condition...
by evaluating its kinetics and reaction order models for successful treatment of chromium-laden wastewater.

**MATERIALS AND METHODS**

**Stock solution of Cr(VI)**

The stock solution of Cr(VI) (100 mg/L) was prepared in the laboratory by dissolving oven dried K$_2$Cr$_2$O$_7$ salt (analytical reagent grade) in deionised water. Different intermediate strengths of varying concentration were prepared by diluting the stock with the necessary volume of deionised water.

**Water lettuce (Pistia)**

The aquatic plants were collected from a nearby pond situated in the vicinity of the campus of Jadavpur University, Kolkata, India. After collection, young plants were thoroughly washed with distilled water to remove all suspended impurities and other plankton. The plants were acclimatised with 10% Hoagland solution (Hoagland & Arnon 1950). Once the plants became matured, the adult ones similar in size (28–30 mm long) and 4.0–4.5 g as wet mass were picked up as adsorbent.

**Batch kinetic studies**

Batch kinetic experiments were conducted in multi-cell aquaria made of Perspex sheet. The capacity of each cell was 3 L. The plants were kept in different cells with varied initial concentration of Cr(VI) in 1.5 L volume. The experiments were accomplished at an average room temperature of 298 °K in the presence of 2 × 40 W fluorescent tubes for a photoperiod of 10 h in each day. A photograph of the experimental set-up is shown in Figure 1.

To determine the optimum amount of water lettuce, a separate study was undertaken with 1, 2 and 3 mg/L of Cr(VI) in different troughs with water lettuce, viz. 20, 30, 40, 50, 60, 80 and 100 g, respectively. The batch kinetic study was conducted using different initial concentrations (2, 3, 5, 8 mg/L) of Cr(VI) using 60 g/L amount of water lettuce as doses. The samples were withdrawn after 1, 2, 3, 4, 5, 6 and 7 consecutive days of contact period and residual concentration of Cr(VI) was measured after pipetting out the sample solution.

The residual concentration of Cr(VI) in samples was estimated as per the protocol described in *Standard Methods* (APHA 1998). The diphenyl carbazide method was followed to determine Cr(VI) content in the sample with the help of a UV-visible spectrophotometer at 540 nm. The amount of Cr(VI) accumulated in different plant parts was estimated using an atomic absorption spectrophotometer after digesting the sample as described in *Standard Methods* (APHA 1998).

**Isotherm studies**

Batch isotherm experiments were conducted with 3 mg/L of initial concentrations of Cr(VI). *Pistia* plants were taken in varying amount from different compartments of the multi-cell aquaria (Figure 1). The equilibrium time was considered
as 7 days as it was noticed that beyond this contact period the removal was very much marginal and led to physical damage. The pH of the solution was maintained at 6.5 ± 0.2. All the experiments were conducted in triplicate and average values are reported.

RESULTS AND DISCUSSION

Effect of water lettuce on removal efficiency of Cr(VI)

In the batch kinetic experiment, it is important to examine the optimum amount of water lettuce as dose and also the contact time for maximum plausible removal of solute as adsorbate. The removal of Cr(VI) was found to increase with the increase of *Pistia* dose and maximum removal was attained at 60 g/L of plant dose, which was selected as the optimum amount for Cr(VI) removal for initial Cr(VI) concentration of 1–3 mg/L. The removal was found to be 94, 87 and 78% for 60 g/L of dose for 1, 2 and 3 mg/L of initial Cr(VI) concentrations, respectively.

Batch sorption kinetics

The batch kinetic results are plotted in Figure 2, which shows that the sorption by *Pistia* reached a maximum level for 2 to 3 mg/L of initial Cr(VI) concentration and declined progressively at higher initial Cr(VI) concentration (5 and 8 mg/L). After a contact period of 7 days, with an initial Cr(VI) concentration of 3 mg/L, approximately 78% removal was observed, whereas 77% Cr(VI) removal was observed with an initial Cr(VI) concentration of 2 mg/L. When initial concentration exceeds 5 mg/L, although sorption takes place, the plant structures were found to be damaged considerably. The trend of removal reveals a biphasic nature of uptake with rapid sorption initially up to a period of 4 days, reaching almost equilibrium after 5 days. The sorption has been accomplished through plant root membrane and the rate was diffusion controlled triggering by the high concentration difference between the bulk solution and the root system. Similar removal patterns were also earlier noticed by Mukherjee & Kumar (2005a, b) for removal of arsenic using *Pistia* and *Salvinia* from spiked solution.

The rapid rate of removal for the earlier period of the experiment was also due to the higher removal capacity of the plant due to the high availability of active sites through root membrane structures but, as the time increases, the removal rate decreases because of density differences and non-availability of sites for the entrance of chromate ions. This decrease could be related to a sorption process at the root surface. Plant cells have an abundance of negatively charged sites on their walls and hence ion-exchange and other interactions between metals and carboxyl, sulphate, amino and other groups are likely to occur (Kratochvil & Volesky 1998).

The sorption kinetics as exhibited in the present investigation were limited to the uptake capacity of *Pistia* in living condition for removing Cr(VI) under the biologically active state prior to senescence or start of wilting. As such, 7 days equilibrium time was considered for the present experiment.

Translocation of Cr(VI)

Cr(VI) was mostly retained in the root and was translocated to the stem marginally in the plant. Zurayk et al. (2001) studied Cr accumulation in a number of hydrophytes and observed that metal accumulation varied within different plant parts of Cr-treated plants. The result of the present study found that the root portion showed more accumulation (28.54 μg/g) of Cr(VI) than the aerial part (5.73 μg/g) of the plant after a contact period of 7 days for initial concentration of 5 mg/L. The result showed that about 92% of the total uptake or that separated from the solution could be recovered.

The partitioning is a common strategy of the plants in living condition, which concentrate harmful ions in the roots to avoid toxicity to the leaves, the site of photosynthesis and other metabolic activities, as stated by Sinha et al. (2002). The results of the present investigation were in agreement with their observations.
Sorption isotherm studies

The batch kinetic results demonstrated no apparent textural damage to plant species up to 3 mg/L Cr(VI). For this reason, an isotherm study was carried out for 3 mg/L of initial Cr(VI) concentration. The isotherm data were plotted in Figures 3 and 4. Equilibrium data were tested for fitting in Langmuir and Freundlich equations as standard isotherm models along with standard errors and regression coefficient ($r^2 = 0.979$ for Langmuir isotherm and $r^2 = 0.974$ for Freundlich isotherm). Figures 3 and 4 illustrate both the models are fitted reasonably well.

The equilibrium data were used to plot the linear form of both the Langmuir and Freundlich isotherm models, as referred to in the Sips equations (Sips 1948). The linear form Langmuir equation is

$$\frac{C_e}{X/M} = \frac{1}{X_m} + \frac{K}{X_m} C_e$$

where $K$ is the Langmuir constant, $C_e$ is the equilibrium concentration (mg/L), $X/M$ is the mass of sorbate adsorbed per unit mass of sorbent (mg/g), $X_m$ is the adsorption capacity (mg/g).

The Freundlich equation in linear form is

$$\ln\left(\frac{X}{M}\right) = \ln K + \frac{1}{n} \ln C_e$$

where $1/n$ is the sorption intensity, and $K$ is the measure of sorption capacity.

However, the Langmuir model ($r^2 = 0.979$) was fitted marginally better than the Freundlich ($r^2 = 0.974$) for initial Cr(VI) concentrations of 3 mg/L.

For initial Cr(VI) concentration of 3 mg/L, the following equation was derived for the Langmuir model.

$$\frac{C_e}{X/M} = 10.20 C_e + 8.217$$

The corresponding Freundlich isotherm equation is expressed as

$$\ln(X/M) = 0.464 \ln C_e - 2.939$$

The adsorption parameters $K$ and $n$ are the key indicators for measuring preferential adsorption in Langmuir and Freundlich models. The $K$ value is moderate (0.805) and not very high. The high value of $n$ (2.16) denotes a strong bond between the plant root and existing Cr(VI) ions in dissolved chromate, which may be the driving force for adsorption of Cr(VI) by Pistia. The accumulated amount of Cr(VI) near the root zone as described earlier also corroborated the postulates of the Freundlich model.

Sorption kinetic model studies

The batch kinetic results were also tested in four kinetic models: first order reaction model based on the solution concentration, pseudo-first order equation on the basis of adsorbent uptake capacity, second order reaction model based on the solution concentration and pseudo-second order reaction model based on the solid-phase sorption (Ho & Mckay 1999; Adak et al. 2005; Ahmad et al. 2011). The experiment was carried out to evaluate the best fit sorption reaction order and mechanism. Kinetic constants obtained from different sorption kinetic models for Cr(VI) removal by Pistia at initial Cr(VI) concentration of 3 mg/L are presented in Table 1.
First order reaction model

The linear form of the first order rate equation is expressed as cited in Benefield & Randall (1993).

$$\ln C_t = \ln C_0 - K_1 t$$  \hspace{1cm} (5)

where $C_t$ = residual concentration of solute at time $t$, $C_0$ = initial concentration, and $K_1$ = first order reaction rate constant.

Although kinetic investigations were carried out for a wide variation of initial Cr(VI) concentration in the solution, the order of the reaction was tested for 3 mg/L only, because, at this initial concentration, the removal was found to be maximum for the 60 g/L plant dose. Figure 5 shows the plot between $\ln C_t$ with $t$ as line 1. A best fit line was drawn and $r^2$ was found as 0.923, which revealed that the adsorption followed reasonably the first order model.

Pseudo-first order reaction model

The linearised form of the pseudo-first order kinetic model is based on the solid capacity for the sorption analysis as proposed by Lagergren (1898).

$$\ln \left( \frac{q_e}{C_0} \right) = \ln \left( \frac{q_e}{C_t} \right) - K_{s1} t$$  \hspace{1cm} (6)

where $q_e$ = amount of solute adsorbed per unit weight of adsorbent at equilibrium, $q_t$ = amount of solute adsorbed per unit weight of adsorbent at time $t$, $K_{s1}$ = pseudo-first order reaction rate constant.

The above equation gives a straight line relationship by plotting $\ln \left( \frac{q_e}{C_0} \right)$ versus $t$. The experimental data are plotted in Figure 5 (line 2). The $r^2$ value was found to be 0.979, which indicates that the pseudo-first order reaction model is a better match than the first order model.

Second order reaction model

The second order rate equation is widely used for metal ion sorption in the literature (Ho & McKay 1999) and is expressed in the following linearised form.

$$\frac{1}{C_t} - \frac{1}{C_0} = K_2 t$$  \hspace{1cm} (7)

where $K_2$ = second order reaction rate constant.

A linear plot of $1/C_t$ against $t$ gives the reaction rate of second order.

The plot is shown in Figure 6 (line 3). The linear fitting of kinetic data demonstrates that $r^2 = 0.969$.

Pseudo-second order reaction model

The linear form of the pseudo-second order equation as per Ho & McKay (1999) is presented as

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K t$$  \hspace{1cm} (8)

where $K$ = proportionality rate constant.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Equation</th>
<th>$r^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order</td>
<td>$Y = -0.1003 X + 0.4567$</td>
<td>0.9237</td>
</tr>
<tr>
<td>Pseudo-first order</td>
<td>$Y = -0.6388 X - 2.714$</td>
<td>0.979</td>
</tr>
<tr>
<td>Second order</td>
<td>$Y = 0.1957 X + 0.1925$</td>
<td>0.9698</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>$Y = 9.8428 X + 95.612$</td>
<td>0.6474</td>
</tr>
</tbody>
</table>

Table 1 Kinetic constants obtained from different sorption kinetic models for Cr(VI) removal by Pistia at initial Cr(VI) concentration of 3 mg/L.
The above equation is the integrated rate law for a pseudo-second order reaction, which after rearrangement is expressed in the following form

\[
\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t
\]  

where \( h = K_s q_e^2 \) (\( K_s \) = pseudo-second order reaction rate constant).

The equation indicates that the rate of reaction would follow pseudo-second order kinetics for a linear plot of \( t \) versus \( t/q_t \). A plot of \( t/q_t \) versus \( t \) (Figure 6, line 4) for the present experimental study shows that \( r^2 \) value is close to 0.647, which indicates a poor fitting of the pseudo-second order model. The linear fit of data indicates that the reaction follows the second order reaction model, although the pseudo-first order was very close to the second order. The reaction rate constant was found to be based on the second order kinetic reaction model as 0.194 mg/L per min.

In the real-life treated tannery effluent sample, Cr(VI) was found to be present with minimum, maximum and average values of 0.48, 8 and 2.75 mg/L, respectively out of 12 samplings throughout the year (Chakraborty & Mukherjee 2013). In most of the cases, the amount of Cr(VI) present in the samples was detected in the range 2–3 mg/L. Considering all these, the kinetic study was carried out with 2, 3, 5 and 8 mg/L of Cr(VI) in the synthetic solution. Therefore, this result can be successfully used in field conditions in real-life cases with a unit flow of 9.51 L/(m²·d).

### CONCLUSION

The present investigation demonstrated that water lettuce (Pistia) possesses potential as a living biosorbent for the removal of chromium(VI) from wastewater when the pollutant is present in low concentration (2–3 mg/L). Batch kinetic results demonstrated that the equilibrium time and optimum plant dose were 7 days and 60 g/L, respectively. Under optimised condition, a maximum of 78% removal for a 3 mg/L of initial Cr(VI) concentration was achieved. The removal of Cr(VI) by Pistia followed close to the second order reaction kinetics, and also isotherm models were well fitted with the experimental data. The plant was inhibited beyond 5 mg/L of initial Cr(VI) concentration and started to get wilted beyond this concentration. From the present investigation, it is revealed that chromium sorption by water lettuce would be an effective scientific and engineering tool for toxic metals emanating from wastewater treatment plants.

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### REFERENCES


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