



Batch adsorption and kinetics of chromium (VI) removal from aqueous solutions by *Ocimum americanum* L. seed pods

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ABSTRACT

In this paper batch removal of hexavalent chromium from aqueous solutions by *Ocimum americanum* L. seed pods was investigated. The optimum pH and shaker speed were found to be 1.5 and 121 rpm. The equilibrium adsorption data fit well with Langmuir isotherm. The maximum chromium adsorption capacity determined from Langmuir isotherm was 83.33 mg/g dry weight of seed pods at pH 1.5 and shaker speed 121 rpm. The batch experiments were conducted to study the adsorption kinetics of chromium removal for the concentrations of 100 mg/L, 150 mg/L and 200 mg/L chromium solutions. The adsorbent dosage was 8 g dry seed pods/L. The removal efficiency observed for all the three chromium concentrations was 100%. The equilibrium was achieved less than 120 min for all the three concentrations. The adsorption kinetic data was fitted with first and second order kinetic models. Finally it was concluded that the chromium adsorption kinetics of *O. americanum* L. seed pods was well explained by second order kinetic model rather than first order model.

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1. Introduction

The chromium related industries are now facing the problem of safest disposal of large quantity of chromium containing wastewater. This has become a serious issue because Cr⁶⁺ has been classified as a Group I human carcinogen by International Agency for Research on Cancer (IARC) and as a Group A inhalation carcinogen by US Environmental Protection Agency (EPA) [1]. The chromium pollution is increasing due to the generation of water from mining, leather tanning, cement, dying, electroplating and corrosive paint industries [2–7]. Chromium exists in two states as Cr (III) and Cr (VI). The hexavalent chromium is 500 times more toxic than the trivalent form [8]. The maximum Cr levels permitted in wastewater are 5 mg/L for trivalent chromium and 0.05 mg/L for hexavalent chromium [9].

Chromium-bearing industrial wastewater is typically treated by chemical means, which generally involves the reduction of Cr (VI) to Cr (III) by reductants like Fe (II) and the subsequent adjustment of the solution pH to near-neutral conditions to precipitate the Cr (III) ions produced [10–12]. Microbial reduction of Cr (VI) to Cr (III) is also possible and is becoming a promising alternative to the remediation of Cr (VI)-contaminated sites via chemical reduction [13–16]. Apart from the precipitation

method, lime coagulation, ion exchange, reverse osmosis and solvent extraction are some of other methods for chromium pollution abatement [17,18]. The aforesaid methods have many disadvantages like incomplete metal removal, high reagents and energy requirements, generation of toxic sludge that needs again safest disposal [6]. There is also considerable interest in the use of biopolymers, particularly the microbial exopolysaccharides. Several reports are available on metal biosorption using microbial exopolysaccharides [19–22].

Recently, use of natural materials for the treatment of heavy metal waste is gaining considerable importance as an alternative technology. Several chromium removal studies were carried out using naturally available biomaterials such as, Bengal gram husk [6], eucalyptus bark [9], saw dust, sugarcane bagasse, sugar beet pulp [23], coconut husk fibers [24], palm pressed fibers [25], waste tea [26] and *Ocimum basilicum* seeds [27]. The interesting features of the new adsorbents are their high versatility, metal selectivity and high uptake. The present investigation looks into a batch process, for the removal of toxic element, chromium by adsorption using low cost adsorbent developed from abundantly available *Ocimum americanum* L. seed pods, a plant material.

The adsorbent used for present investigation was obtained from the plant *O. americanum*. Locally it is called as “Naithulasi”. The plants are extensively grown in the state of Tamilnadu, India. The seeds of this plant are black in color and ovoid in shape with mean size, 2.05 mm (length) and 1.47 mm (width). In the maturation of the seed pod, the seeds grow within a jelly-like substance which

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is called as mucilage. The seeds grow within seed pods (the adsorbent material used for this study), each of which contains 4–8 small (1–1.5 mm diameter) seeds. As the seeds mature, the mucilage dries on to the outer hull of seeds. The seed mucilage of *O. americanum* can be used as tablet disintegrant [29], food hydrocolloids. The essential oil obtained from the seed was active against several tested microorganisms [30]. The seed mucilage can also be used for effluent treatment applications [31]. After removing the seeds, large quantity of seed pods are left as waste material. In the present investigation this wasted material was taken as biosorbent for the chromium removal applications.

2. Materials and methods

2.1. Materials

The chemicals used for this study were of analytical reagent grade and procured from the standard source. The water used in all the experiments was obtained from the Millipore make unit in our laboratory.

2.2. Preparation of stock solution

An aqueous solution (2000 mg/L) of Cr (VI) ions was prepared using $K_2Cr_2O_7$ salt. For pH adjustments, 6 N H_2SO_4 /1 N NaOH was used. Fresh dilutions were used for each study.

2.3. Preparation of adsorbent

The seed pods used in this study were obtained from local area. The seed pods are washed with distilled water to remove dirt and other particulate matter. The washing procedure was continued till the wash water contained no color. The washed seed pods were dried in hot air oven at $105^\circ C$ for 24 h. The dried seed pods were ground using a domestic mixer. The ground materials were then sieved through standard sieve (mesh no 25 (ASTM), 0.6 mm) to the pan. The product collected in the pan was stored in plastic bottles for further use.

2.4. Adsorption studies

The adsorption isotherm experiments were conducted at $27 \pm 1^\circ C$ for the concentrations varying from 20 mg/L to 400 mg/L. A volume of 50 mL of the chromium solution of different concentrations was taken in a 150 mL conical flasks and pH was adjusted to 1.5. The adsorbent dosage equivalent to 0.2 g dry weight was added in to each conical flask. In this study a volume of 50 mL of the chromium solution in a 150 mL flask adjusted to pH 1.5 without adsorbent was taken as control. Then the flasks including the control were placed in a rotary shaker and shaken for 24 h by maintaining the speed at 121 rpm.

The effect of pH on chromium adsorption rate was studied by varying the pH from 1 to 6. The concentration of chromium solution used for this study was 50 mg/L. The volume of chromium solution was 50 mL. The adsorbent dosage was 0.2 g dry weight of adsorbent. The shaker speed was 121 rpm and time contact was about 90 min.

To study the effect of speed on chromium removal from solution by the adsorbent, experiments were conducted by varying the shaker speed from 80 rpm to 180 rpm. The concentration of chromium solution used for this study was 50 mg/L. The adsorbent dosage was 0.2 g dry weight of adsorbent. The effect of chromium removal by 0.2 g of adsorbent for the same experimental conditions was done using a non-agitated system as the control.

The equilibrium kinetic studies were conducted for three different concentrations 100 mg/L, 150 mg/L and 200 mg/L of chromium

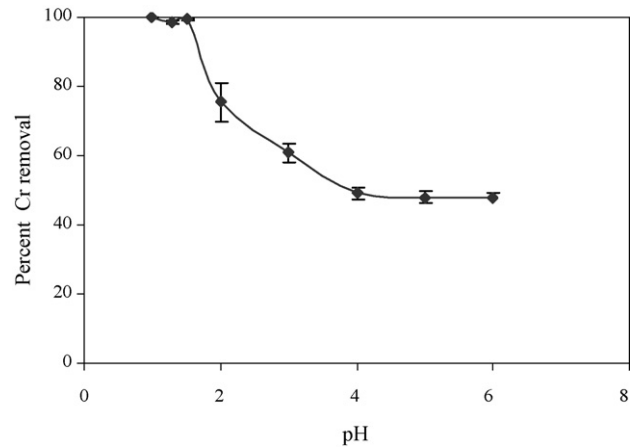


Fig. 1. Effect of pH on the chromium removal efficiency. Initial concentration of chromium is 50 mg/L and adsorbent dose 4 g/L. The contact time was 90 min.

solutions adjusted to the pH value 1.5. The adsorbent dosage was 0.4 g dry weight of seed pods. 50 mL of distilled water adjusted to pH 1.5 taken in a 150 mL conical flask. Then 0.4 g of adsorbent was added in to the flask. This was used as a control for this experiment. The flasks were kept in a shaker and agitated with 121 rpm.

2.5. Estimation of chromium: diphenyl carbazide complex method

The residual concentration of chromium was determined spectrophotometrically (Hitachi U 2000, Japan) at 540 nm using the diphenyl carbazide reagent. A standard graph of absorbance vs concentration was obtained for known chromium concentrations. The absorbance value of sample was used to determine the unknown concentration [28].

2.6. Statistical analysis

All the data represent the mean of three independent experiments. The errors during the measurement were indicated by error bars. All the statistical analysis was done using Microsoft excel 2003, ANOVA statistical tool.

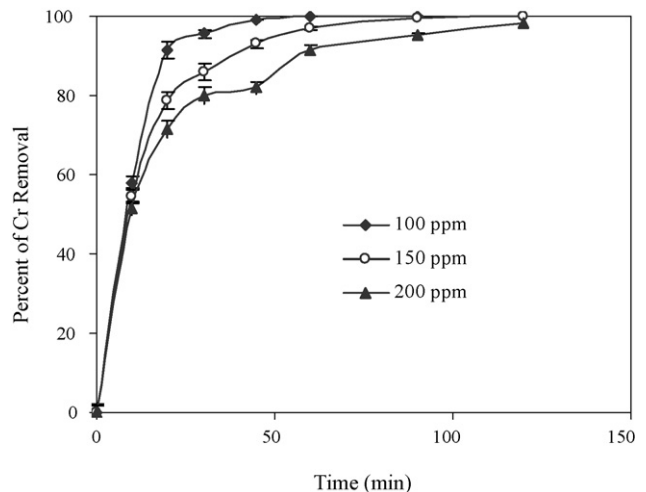


Fig. 2. Adsorption kinetics of chromium on *Ocimum americanum* L. seeds with shaker speed 121 rpm, pH 1.5 and adsorbent dose 8 g/L.

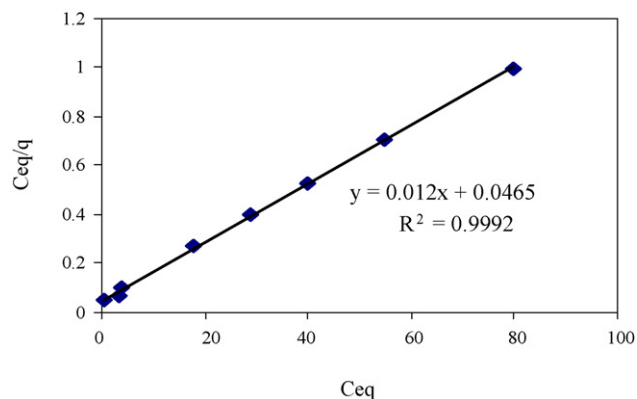


Fig. 3. Langmuir isotherm for adsorption of chromium on powdered *Ocimum americanum* L. seed pods at pH 1.5, shaker speed 121 rpm and adsorbent dose 4 g/L.

3. Results and discussion

3.1. Effect of pH

The chromium removal efficiency of *O. americanum* L. seed pods at different pH values at an initial concentration of 50 mg/L are shown in Fig. 1. The chromium removal efficiency was 100%, 98.5% and 99% for the pH values 1, 1.3 and 1.5, respectively. But it decreased to 75% when the initial value of pH of the Cr solution is 2. The efficiency was 60% when the initial pH was kept at 3. At pH 4, the efficiency decreased to 49%. After this pH there was no appreciable change observed for pH values 5 and 6. The optimum removal takes place at the pH range 1–1.5. The reason for the high uptake of chromium at lower pH range was explained below. The Cr (VI) exists in different forms such as H_2CrO_4 , HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ in aqueous solution and the stability of these forms is dependent on the pH of the system. The active form of Cr (VI) adsorbed on the adsorbent is HCrO_4^- . This form is stable at only lower pH range which leads to high uptake of chromium. But the concentration of this form decreases when there is an increase in pH. Hence chromium uptake at higher pH decreases [7,9].

3.2. Adsorption kinetics

The percentage removal of chromium with respect to time was plotted in a graph shown Fig. 2. It was observed that there was no appreciable change in control measurements. From the graph, it is clear that 100% chromium removal was achieved for the chromium concentrations 100 mg/L, 150 mg/L and 200 mg/L for the shaking times of 30 min, 60 min and 120 min, respectively. There is no appreciable change in control observed.

3.3. Adsorption isotherm

The adsorption isotherm experimental data obtained was fitted to Langmuir isotherm. The following linear form of Langmuir

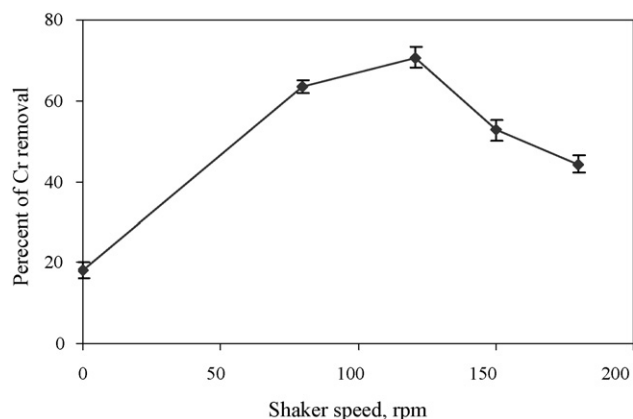


Fig. 4. Effect of speed on the chromium removal efficiency. Initial concentration of chromium is 50 mg/L, pH 1.5, adsorbent dose 4 g/L and time of adsorption 30 min.

isotherm was used to fit the data.

$$\frac{C_{eq}}{q_m} = \frac{C_{eq}}{q_m} + \frac{1}{bq_m} \quad (1)$$

where C_{eq} is the equilibrium concentration in mg/L, q_m is maximum adsorption capacity in mg/g dry seed pods and b is the ratio of adsorption and desorption rates [5].

The correlation coefficient for the above data is shown in Fig. 3 as 0.9992 indicates that the adsorption isotherm data fit well with Langmuir isotherm. From the slope of Langmuir isotherm linear Eq. (1), the maximum chromium adsorption capacity, q_m was found to be 83.33 mg/g of dry seed pods. This value is comparable with adsorption capacity of many natural materials like eucalyptus bark, saw dust, coconut husk fibers, sugar beet pulp, wool and sugar cane bagasse which have been reported earlier in the literature which is shown in Table 1.

3.4. Effect of speed

The speed of shaker also plays an important role in the mass transfer of chromium from the solution to the surface of adsorbent. For a non-agitated system the removal efficiency was only 18%. The effect of speed on chromium removal efficiency was shown in Fig. 4. When the speed was 80 rpm, the chromium removal efficiency was obtained as 63%. This value increases to 70% when the speed was 121 rpm. The efficiency decreased to 53% and then 44% when the speed was maintained at 150 rpm and 180 rpm, respectively. This may be due to the fact that at higher speed the influence of desorption made the adsorption process highly reversible one. So the adsorbed ions will be immediately desorbed which decreases the net rate of adsorption of chromium ions on adsorbent surface. The optimum speed obtained from the above experiments is 121 rpm.

Table 1

Comparison of adsorption capacity of *Ocimum americanum* seed pods with other adsorbents

Adsorbent	Maximum absorption capacity (mg/g) q_0	Optimum pH	Maximum concentration (ppm)	References
Bengal gram husk	91.64	2	600	[6]
Eucalyptus bark	45	2	250	[9]
Saw dust	39.7	2	1000	[23]
Coconut husk	29	2.05	–	[23]
Palm pressed fiber	15	2	–	[25]
<i>Ocimum basilicum</i> seeds	205	1.5	2000	[27]
<i>Ocimum americanum</i> seed pods	83.33	1.5	400	[27]

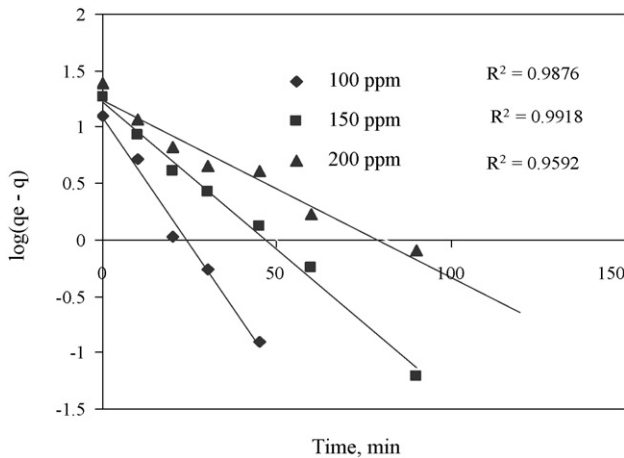


Fig. 5. Pseudo-first order kinetics of powdered *Ocimum americanum* L. seed pods for different initial concentrations at optimum pH 1.5.

4. Modeling of adsorption kinetics

The experimental adsorption kinetic data was fitted with pseudo-first and pseudo-second order models.

4.1. Pseudo-first order kinetics

The sorption kinetics explained by pseudo-first order equation [7] is given as

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2)$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q is the amount of solute adsorbed at any time t per unit weight of adsorbent (mg/g) and k_1 is first order adsorption rate constant. When applying the boundary conditions $t=0$ to $t>0$ and $q=0$ to $q>0$ and rearranging the Eq. (2), it yields

Table 2
First order adsorption rate constants for different initial concentrations

Initial concentration (mg/L)	k_1 (min ⁻¹)	R^2
100	0.046	0.9876
150	0.026	0.991
200	0.015	0.9592

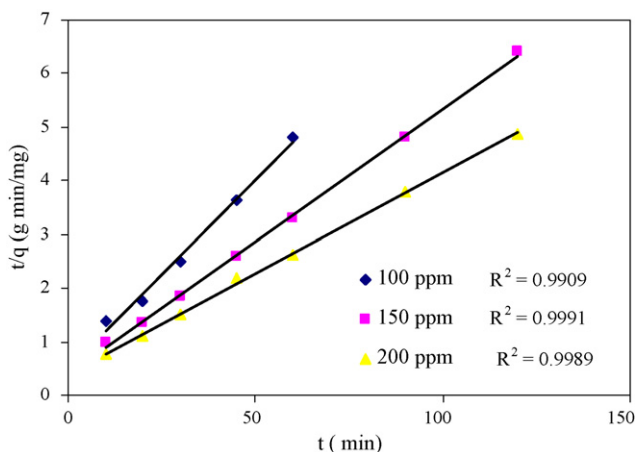


Fig. 6. Pseudo-second order kinetics of powdered *Ocimum americanum* L. seed pods for different initial concentrations at optimum pH 1.5.

Table 3
Second order adsorption rate constants for different initial concentrations

Initial concentration (mg/L)	k_2 (g/mg min)	h (mg/g min)	R^2
100	0.008	1.33	0.9909
150	0.006	2.22	0.991
200	0.005	3.13	0.9989

the following linear time dependence equation.

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303} t \quad (3)$$

The plots were drawn for Eq. (3) for the concentrations 100 ppm, 150 ppm and 200 ppm. Approximately linear plots were obtained for all the three concentrations which were shown in Fig. 5. The kinetic constant k_1 for the three different concentrations were obtained from the slopes of the plots and tabulated in Table 2. The smallest correlation coefficient obtained from the first order kinetic is 0.9592. The largest one is 0.9918.

4.2. Pseudo-second order kinetics

The sorption kinetics explained by pseudo-second order equation [7] is given as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (4)$$

where k_2 is the rate constant in g/mg min. Integration of Eq. (4) for the boundary conditions $t=0$ to $t>0$ and $q=0$ to $q>0$ and then rearrangement yields the following linear form

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t_1}{q_e} \quad (5)$$

$h = k_2 q_e^2$, where h is the initial sorption rate in mg/g min. The values of k_2 and h are determined from the intercept of second order Eq. (5) from graph shown in Fig. 6. The values of k_2 and h are tabulated in Table 3. The smallest and largest correlation coefficients obtained from the second order kinetics are 0.9909 and 0.9991 which are still better than the correlation coefficients of the first order kinetics.

5. Conclusion

The powdered *O. americanum* L. seed pods were reported as an effective adsorbent for the treatment of hexavalent chromium for the very first time. It was capable of removing 100% of chromium from the aqueous solutions of concentrations 100 mg/L, 150 mg/L and 200 mg/L. The predicted maximum chromium adsorption capacity as 83.33 mg/g showed that adsorbent prepared from the *O. americanum* L. seed pods have reasonable chromium removal efficiency. The adsorption kinetics was well explained by pseudo-second order kinetics rather than the first order kinetics. But further studies such as the effect of particle size and temperature on chromium adsorption, continuous column experimentation and adsorption process parameters optimization have to be carried out for complete understanding and scale up of the adsorption process.

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