

original article

A batch study of hexavalent chromium removal from synthetic wastewater using modified Russian knapweed flower powder

Mohammad Taghi Ghaneian, Mahboobeh Dehvari, Behzad Jamshidi¹

Department of Environmental Health, Faculty of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran, ¹Department of Environmental Health Engineering, Abarkouh Paramedical School, Shahid Sadoughi University of Medical Sciences, Yazd, Iran

Address for correspondence:
Eng. Behzad Jamshidi, Department of Environmental Health Engineering, Abarkouh Paramedical School, Shahid Sadoughi University of Medical Sciences, Yazd, Iran
E-mail: BehzadJamshidi65@yahoo.com

ABSTRACT

Aims: In this research, modified *Acroptilon repens* (Russian knapweed) flower powder was used as a novel adsorbent for removal of Cr (VI) from synthetic wastewater.

Materials and Methods: The batch adsorption studies were performed under various laboratory conditions with initial chromium concentrations of 2, 10 and 15 mg/l, adsorbent dose of 0.05-0.2 g/100 ml, contact time of 30-240, min and pH of 2-9. The solution was mixed with a mechanical shaker with 120 r.p.m. at 20°C. The suitability of the adsorbent was evaluated using Langmuir, Freundlich and Temkin isotherm models. For kinetic study, pseudo-first-order and pseudo-second-order kinetics were used.

Results: The results indicated that maximum adsorption was achieved in acidic conditions. The optimum pH for the removal was 2. The capacity of chromium adsorption at equilibrium conditions increased by increasing the concentration of the adsorbate. The results also showed that the removal efficiency of Cr (VI) increased with increasing contact time. On increasing the initial concentration of the Cr (VI) solution, chromium removal reduced. The Freundlich and Langmuir isotherm models gave better accordance to the adsorption data in comparison with the Temkin equation. Adsorption of Cr (VI) followed pseudo-second-order kinetics rather than the pseudo-first-order kinetics.

Conclusion: This study showed that modified Russian knapweed flower powder can be used as an effective lignocellulosic biomaterial and biosorbent for removal of Cr (VI) from wastewater.

Key words: Adsorption, chromium, isotherm, kinetic, modified *Acroptilon repens*

INTRODUCTION

Heavy metals are known for their persistent biodegradation and accumulation in living organisms, causing serious health problems. One of these metals is chromium, which is a known environmental pollutant. The two predominant oxidation states of this metal in aqueous solutions are Cr (III)

Access this article online	
Quick Response Code: 	Website: www.ijehe.org
	DOI: 10.4103/2277-9183.133063

Copyright: © 2013 Ghaneian MT. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

This article may be cited as:
Ghaneian MT, Dehvari M, Jamshidi B. A batch study of hexavalent chromium removal from synthetic wastewater using modified Russian knapweed flower powder. Int J Env Health Eng 2014;3:16.

and Cr (VI).^[1,2] Cr (VI) is highly toxic and soluble in water in comparison with Cr (III).^[3] Hexavalent chromium is released into the receiving water from industrial effluents such as that from electroplating, pigment manufacturing, chromate preparation, leather tanning and fertilizer industries,^[2,4] and also naturally exists in water resources due to the geological structure of areas such as Birjand that are located in the eastern region of Iran and the Thiva — Tanagra — Malakasa basin, Eastern Sterea Hellas, Greece.^[5,6] This heavy metal affects human health and causes dermatitis, allergic skin reactions and ulceration of the intestine.^[7] Hexavalent chromium is known to be toxic to humans and animals, and the International Agency for Research on Cancer (IARC) has classified chromium (VI) in group-I as a human carcinogen.^[4] Its concentration in industrial wastewaters varies from 0.5 to 270 mg/l. The maximum permissible level of Cr (VI) in drinking water is 0.05 mg/l and the tolerance limit for Cr (VI) to be discharged into inland surface waters is 0.1 mg/l.^[3,8,9] Nevertheless, for most natural waters the Cr concentration is less than 50 µg/l, which is recommended for potable water by the World Health Organization (WHO) or the US Environmental Protection Agency (USEPA). In order to obtain this limit, it is crucial that industries treat their effluents to reduce Cr (VI) to a suitable level. Because of its high toxicity, Cr (VI) must be substantially removed from the wastewater before being discharged into the receiving waters.^[10] There are various methods for chromium ion removal from aqueous solutions such as chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction.^[11-13] These performance methods apart from being economically expensive have disadvantages such as energy requirements, incomplete metal removal, high reagent concentration, and generation of toxic sludge or other harmful waste products that must be managed. For these reasons efficient, cheap and environment friendly methods to reduce heavy metal content such as adsorption need to be developed. The most widely used adsorbent is activated carbon because it has a relatively higher surface area, but it is expensive and requires chelating agents to improve its performance. Therefore, there has been increased interest in the use of other adsorbent materials.^[3,14,15] In recent years considerable attention has been focused on the field of adsorption by agricultural wastes such as lignin,^[16] sawdust, walnut skin, coconut husks, biomass cone,^[10] exhausted coffee,^[17] waste tea^[18] and seeds of *Ocimum basilicum*.^[19] Also these biosorbents have some advantages such as very low or no cost, accessibility, simple operational process, etc.^[10]

Russian knapweed with the scientific name “*Acroptilon repens* (L.) DC.,” which is known as *Centaurea repens* in some literature, belongs to the family Asteraceae.^[20] This plant is herbaceous and perennial, and is native to Iran, Kazakhstan, Mongolia, Southern Ukraine and Southeast Russia. Only one species of this plant is known in Iran, which is found in the western Azarbaijan, Zanjan, Tehran and Yazd provinces.^[21,22]

The aerial parts of an *A. repens* plant are medicinal with antimicrobial and antipyretic properties,^[20,23,24] and are used for blood purification, curing stomach pain, fever and dysentery.^[20,24] The plant is reported to be allelopathic, but is not toxic to humans.^[25] There has not been any study about the adsorption characteristic of modified Russian knapweed flower powder, hence we introduce a new biosorbent for heavy metal removal. The aim of this research was evaluation of hexavalent chromium removal by using modified Russian knapweed flower powder as a new biosorbent from synthetic wastewater and the effect of reaction conditions on the adsorption process.

MATERIALS AND METHODS

Preparation of chromium solution

A stock solution (500 mg/l) was prepared by dissolving an accurately weighed amount (141.14 mg) of potassium dichromate (K₂Cr₂O₇) in 1 l of distilled water.^[11,16] Chromium solutions with concentrations of 2, 5, 10, 15 and 20 mg/l were prepared by dilution of the stock solution with distilled water. The tests were carried out in a 250-ml conical flask containing 100 ml of the chromium solutions. The pH of the solutions was adjusted using 0.1 N HCl or NaOH solutions. The pH of the samples was measured using the pH meter Mi 151. All chemicals used were of analytical reagent grade and were obtained from Merck, Germany. Fresh dilutions were used for each stage.

Preparation and modification of biosorbent

Russian knapweeds were collected from the nearby locality of Yazd city, Iran, and then the flowers were separated. The flowers were washed with distilled water to remove impurities and surface-adhering particles, and then dried at 102°C. The flowers were milled with an electric grinder.

For adsorbent modification, the Russian knapweed flower powder was boiled in de-ionized water at 300°C for 4 h and then treated with 1 N sulfuric acid and again washed for two times with distilled water. The residue was dried in an oven at 102°C for 24 h, and then pulverized by standard ASTM sieves with a range of 40 to 60 meshes (0.25-0.4 mm particles).^[26]

Chromium detection

For all experiments, the method of detection was by colorimetric techniques. Chromium was acidified with phosphoric acid and then complexed with a solution of 1,5-diphenyl carbazide (DIPC) in acetone, and was tested using a spectrophotometer set (UV/VisibleSP-3000 Plus, Japan) at 540 nm according to standard methods for examination of water and wastewater.^[10,27,28]

Adsorption experiments

Batch adsorption studies were performed using initial chromium concentrations of 2, 10 and 15 mg/l, adsorbent

doses of 0.05-0.2 g/100 ml, contact time of 30-240 min and pH of 2-9. The solution was mixed with a mechanical shaker (INNOVA 40R, England) at 120 r.p.m. at 20°C. After shaking, all sample solutions were filtered through a 0.45- μ m membrane filter paper (Sartorius, Germany) and the filtrate was analyzed.^[3,4] The amount of adsorbed Cr (VI) was calculated by estimating the difference between the initial and residual amount in the solution. The adsorption capacity (q_e) of Cr (VI) in mg/g at time t and the percentage of removed Cr (VI) ions (%R) in solution were computed using Eq (1) and Eq (2), respectively:

$$q_e = \frac{(C_o - C_t)V}{M} \quad (1)$$

$$R (\%) = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

Where C_o and C_t are Cr (VI) concentrations in mg/l initially and at a given time t , respectively. V is the volume of the Cr (VI) solutions in ml and M is the weight of adsorbent in gram.^[3,4]

The results were also evaluated by using various adsorption isotherms, including the Langmuir, Freundlich and Temkin isotherms. To determine isotherm models, adsorbent doses of 0.05-0.2 g were added to 100 ml of chromium solution with concentrations of 10 and 15 mg/l. Adsorption tests were performed using the optimal contact time span and pH factors. An adsorption kinetics study also was carried out using pseudo-first-order and pseudo-second-order kinetics. Chromium concentrations were 10 and 15 mg/l and adsorbent dose was 0.2 g/100 ml of chromium sample. Temperature and pH were constant. Adsorption kinetic was determined by analyzing adsorbate chromium from synthetic wastewater at different time intervals.

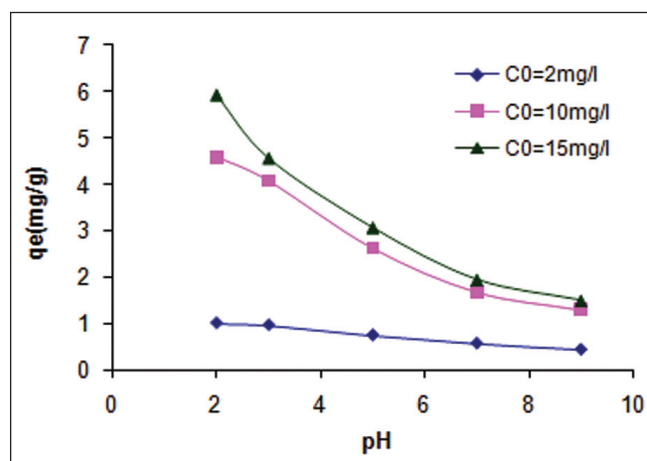


Figure 1: Effect of pH on Cr (VI) adsorption capacity (adsorbent dose=0.2 g/100 ml, contact time=24 h)

RESULTS

Effect of pH

The results of the effects of pH on hexavalent chromium removal by modified Russian knapweed flower powder in conditions of 20°C and 2, 10 and 15 mg/l chromium concentration are shown in Figure 1. In this stage, adsorbent dose and contact time were 0.2 g/100 ml and 24 h, respectively. The obtained results showed that as the pH of the solution was increased, adsorption capacity (q_e) and adsorption efficiency decreased. On increasing pH from 2 to 9, Cr (VI) adsorption capacity (removal efficiency) increased (decreased) from 1 to 0.43 mg/g (%100-%43), 4.58 to 1.3 mg/g (%91.7-%26) and 5.94 to 1.5 mg/g (%79.2-%20) for 2, 10 and 15 mg/l chromium concentration, respectively. The results showed that the maximum adsorption capacity of Cr (VI) was at pH 2.

Effect of adsorbent dose

The effect of adsorbent dose on removal efficiency of chromium (VI) by modified Russian knapweed flower powder has been investigated at the initial chromium concentrations of 2, 10 and 15 mg/l at pH 2. In this stage, shaker speed and reaction time were 120 r.p.m. and 24 h, respectively. The effect of adsorbent dose on chromium removal is shown in Figure 2. Results showed that chromium removal at an equilibrium condition increased with increasing adsorbent dose. So that upon increasing adsorbent dose from 0.05 to 0.2 g/100 ml, removal efficiency increased from 88% to 100%, 56.1% to 91.7% and 45% to 79.2% at concentrations of 2, 10 and 15 mg/l, respectively.

Effect of contact time

The effect of contact time on the chromium adsorption was tested at concentrations of 2, 10 and 15 mg/l Cr (VI) and 0.2 g/100 ml of adsorbent. The pH of the solution was 2 and detection of adsorption efficiency was done at 30, 60, 90, 120, 180 and 240 min. Results [Figure 3] showed that removal efficiency of Cr (VI) increases with increasing contact time. Adsorption of chromium ions by this biosorbent reached equilibrium in 180 min. At 180 min, removal efficiency at

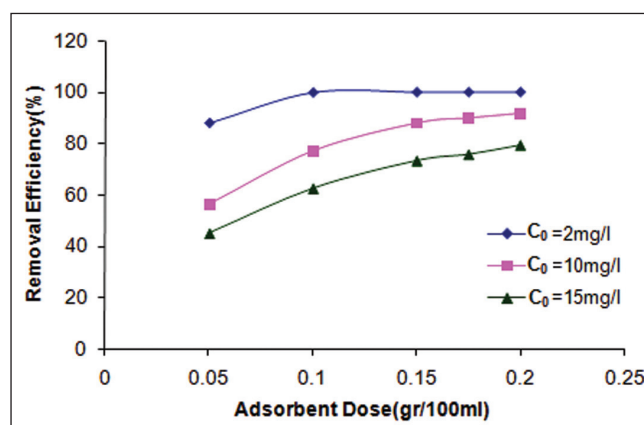


Figure 2: Effect of adsorbent dose on Cr (VI) removal efficiency (pH=2, contact time=24 h)

concentrations of 2, 10 and 15 mg/l was equal to 99.85%, 68.9% and 56.37%, respectively.

Effect of initial chromium ion concentration

As showed in Figure 4, with increasing initial concentration of Cr (VI) solution from 2 to 20 mg/l, chromium removal reduced, whereas removal efficiency for 2 and 20 mg/l were 99.85% and 39.41%, respectively.

Adsorption isotherm study

One of the major issues for appraisal of physicochemical aspects of estimation for the biosorption process are adsorption isotherms. Distribution of Cr (VI) between the liquid phase and the solid adsorbent phase is a measure of the position of the equilibrium in the adsorption process and can be declared by common isotherm models.^[7] The Langmuir, Freundlich and Temkin isotherms models are widely used to describe adsorption data in water and wastewater applications.^[29] In this study, the Langmuir, Freundlich and Temkin isotherm models were selected for assessment of Cr (VI) adsorption on modified Russian knapweed flower powder and equilibrium concentration in aqueous solutions.

Langmuir equation was fundamentally used for sorption of gases on a solid surface. However, it has been extended to include sorption of solutes at solid — liquid interfaces. The Langmuir isotherm is well founded for monolayer adsorption

onto surfaces having the limitation of identical sites.^[30] Langmuir equation is represented in the linear form as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_e C_e} \tag{3}$$

Where q_e is the amount of pollutant adsorbed on a unit mass of the adsorbent (mg/g) and q_m is the quantity of adsorbate needed to form a single monolayer on a unit mass of adsorbent (mg/g). The equilibrium concentration of metal ion solution is C_e (mg/l) and b (l/mg) is Langmuir constant, which is related to the apparent energy of adsorption. Eq (3) shows that a plot of $1/q_e$ versus $1/C_e$ should be a direct line if Langmuir equation complies by the adsorption equilibrium. The slope and the intercept of this line then yield the values of the constants q_m and b , respectively.^[14] The Langmuir isotherm is shown in Figure 5. The essential characteristic of Langmuir isotherm can be described by having the no-dimension constant called equilibrium parameter, R_L , defined as:

$$R_L = \frac{1}{1 + b C_0} \tag{4}$$

Where C_0 is the initial concentration of adsorbate (mg/l) and b is Langmuir constant.^[31] The determined parameters and their corresponding correlation coefficients (R^2) are listed in Table 1. The separation factor (R_L) indicates the

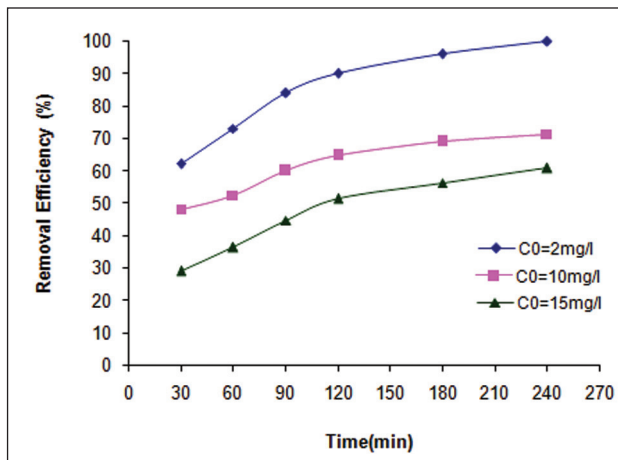


Figure 3: Effect of contact time on Cr (VI) removal (pH=2, adsorbent dose=0.2 g/100 ml)

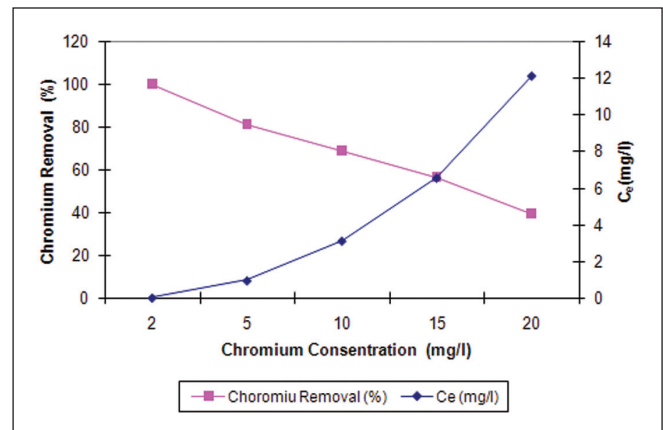


Figure 4: Effect of initial chromium ion concentration on Cr (VI) removal (pH=2, adsorbent dose=0.2 g/100 ml, contact time=180 min)

Table 1: Characteristics of adsorption isotherms (time = 24 h, pH = 2)						
Initial chromium ion concentration	Isotherm					
	Langmuir		Freundlich		Temkin	
10 mg/l	B (l/mg)	1.94	K_f (mg/g)	5.11	K_t (l/g)	3.891
	q_{max} (mg/g)	7.8	$1/n$	0.524	B_T (kJ/mol)	5.088
	R^2	0.991	R^2	0.995	R^2	0.979
	R_L	0.049				
15 mg/l	B (l/mg)	28.41	K_f (mg/g)	2.201	K_t (l/g)	7.822
	q_{max} (mg/g)	2.07	$1/n$	0.851	B_T (kJ/mol)	3.479
	R^2	0.992	R^2	0.994	R^2	0.973
	R_L	0.002				

isotherm shape and whether adsorption is favorable or not: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible.^[32] According to obtained results, the R_L parameter rate for both concentrations 10 mg/l (0.049) and 15 mg/l (0.002) is between 0 and 1, which confirms that adsorption of chromium by modified Russian knapweed flower powder is favorable.

The Freundlich isotherm model assumes multilayer adsorption and it is suitable for adsorption of metal ions on a heterogeneous adsorbent surface.^[7] It can be expressed in the linear form as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

Where q_e is the amount of Cr (VI) adsorbed per gram of adsorbent (mg/g), C_e is solute concentration (mg/l), K_f (mg/g) is related to the relative adsorption capacity and n (g/l) is related to the intensity of adsorption.^[33] The values of K_f , $1/n$ and R^2 are reported in Table 1. The value of $1/n$ obtained from the Freundlich isotherm for adsorption of Cr (VI) on modified Russian knapweed flower powder was found to be less than 1 for both initial chromium concentrations 10 and 15 mg/l ($1/n = 0.524$ and 0.851 , respectively), which specifies that the adsorption is favorable.

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent — adsorbate repulsions. Also adsorption of adsorbate is uniformly distributed and the decrease in the heat of adsorption is linear rather than logarithmic.^[33] The Temkin isotherm equation is given as:

$$q_e = B_T \ln K_t + B_T \ln C_e \quad (6)$$

Where $B_T = RT/b$. The constant B_T is related to the heat of adsorption (kJ/mol), K_t is the equilibrium binding constant (l/mg) corresponding to the maximum binding energy. The slope and the intercept from the plot of q_e versus $\ln C_e$ determine the isotherm constants K_t and B_T , respectively.^[14] The values of Temkin isotherm constant in the present study are shown in Table 1.

Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficient (R^2). The results indicated that the Freundlich and Langmuir models ($R^2 > 0.99$) gave better fit to the experimental results in comparison with Temkin equation ($R^2 = 0.97$). The values of R^2 obtained for Langmuir isotherm were 0.991 and 0.992 for concentrations of 10 and 15 mg/l, respectively, indicating heterogeneous surface conditions may exist [Figure 5]. R^2 rate for Freundlich isotherm at concentrations of 10 and 15 mg/l was equal to 0.995 and 0.994 [Figure 6].

Adsorption kinetics

In order to further expose the adsorption mechanism and rate of adsorption reaction, kinetic models are very useful.^[34] In this study, for survey of adsorption kinetics of Cr (VI) onto Russian knapweed flower powder, pseudo-first and pseudo-second-order kinetic models were used.

The pseudo-first-order reaction equation of Lagergren was widely used for adsorption of liquid/solid systems on the basis of solid capacity.^[35] Its linear form is generally expressed as the following:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

Where q_e and q_t (mg/g) are adsorption amount at equilibrium and time (minutes), respectively. k_1 (min^{-1}) is the rate constant in the pseudo-first-order reactions. The constant and adsorption capacity were determined experimentally by plotting of $\log(q_e - q_t)$ versus time and are listed in Table 2. The results showed that the correlation coefficient (R^2) of the data for the pseudo-first-order reaction were 0.95 and 0.972 for initial concentrations 10 and 15 mg/l, respectively, and the theoretic values ($q_{e,\text{calc}}$) are far lower than the experimental data ($q_{e,\text{exp}}$), implying that the adsorption process does not follow the pseudo-first-order reaction expression.

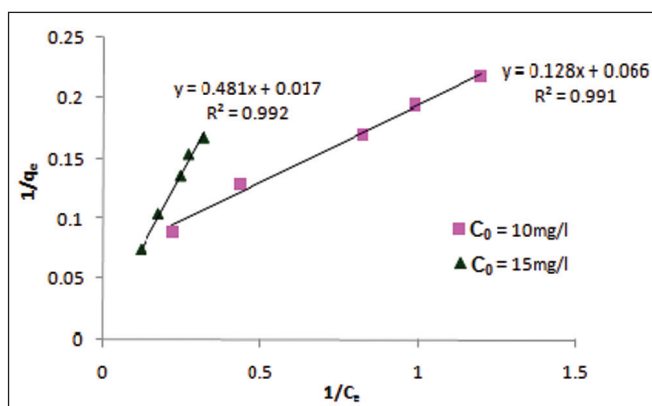


Figure 5: Langmuir adsorption isotherms (pH=2, contact time=24 h, temperature=20°C)

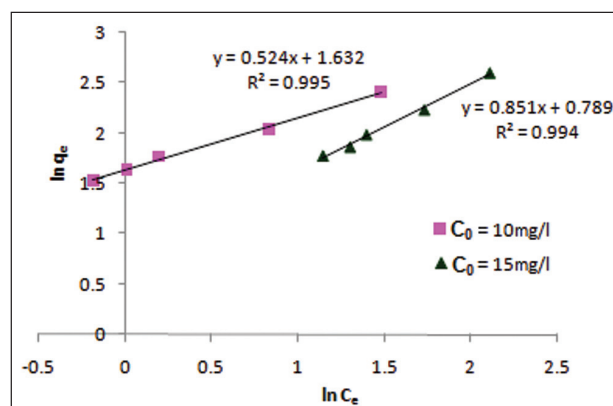


Figure 6: Freundlich adsorption isotherms (pH=2, contact time=24 h, temperature=20°C)

The pseudo-second-order model is based on the assumption that the adsorption follows second-order chemisorptions. The linear form can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Where k_2 (g/mg.min) is the adsorption rate constant.^[36] By plotting a curve of t/q_t versus time, q_e and k_2 can be evaluated [Figure 7]. The values of q_e , k_2 and R^2 are listed in Table 2. The correlation coefficient (R^2) values for initial Cr (VI) concentrations 10 and 15 mg/l in the pseudo-second-order model are equal to 0.997 and 0.995, respectively. Thus, pseudo-second-order model provides a good correlation for adsorption of Cr (VI).

Comparison with other adsorbents

The maximum adsorption capacities obtained in this study were compared to reports of other adsorbents and are presented in Table 3.

DISCUSSION

Effect of pH on Cr (VI) removal

At low pH, H⁺ associates with functional groups such as carboxyl, phenolic, hydroxyl and carbonyl, increasing affinity for Cr (VI) ions because they have positive charges. So the surface will be surrounded by hydronium ions (H⁺).^[16]

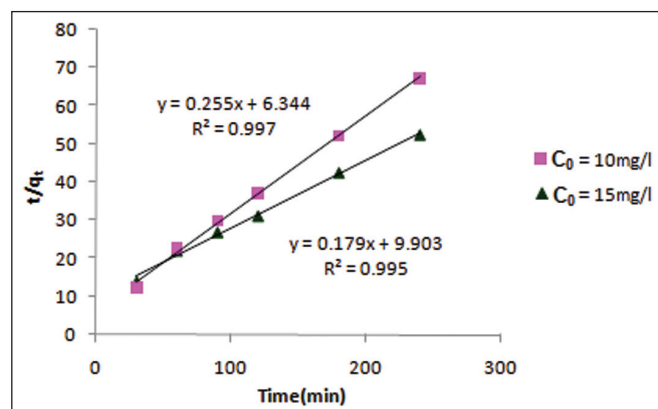


Figure 7: Pseudo-second-order kinetics for Cr (VI) removal (pH=2, adsorbent dose=0.2 g/100 ml, temperature=20°C)

The carboxyl groups are prorogated and as a result are positively charged, which will promote the approach of the negatively charged Cr (VI) ions. At pH 2, the predominant Cr (VI) species was HCrO_4^- and as a result, electrostatic attraction occurred between the positively charged adsorbent and negatively charged HCrO_4^- .^[10,16] According to Gupta *et al.*,^[30] at high pH there will be an abundance of negatively charged hydroxyl ions in aqueous solutions, causing hindrance between negatively charged ions $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , etc., and the negatively charged adsorbent, resulting in a decrease in adsorption capacity. Accordingly, the optimum pH for maximum uptake of Cr (VI) in the present study was found to be 2.0. Similar results were demonstrated by Malakootian *et al.*, who studied adsorption of chromium (VI) on dried activated sludge. Their investigation showed that at higher pH, the adsorbent surface will be surrounded by high quantities of hydroxyl ions and caused low chromium adsorption. They explained that at a pH above 7, metal ions precipitated.^[34] Jung Kim *et al.*, in their study of biosorption of chromium (Cr(III)/Cr(VI)) on the residual microalgae *Nannochloris oculata* after lipid extraction for biodiesel production found that Cr (VI) removal was highest at pH 2 and decreased as pH increased. The zeta potential value for biomass suspensions decreased as pH increased, indicating that the surface of the residual *N. oculata* is negatively charged at all pH ranges. At lower pH, protons would occupy the surface of the biomass, resulting in a less negative charge. At pH between 1 and 6, Cr (VI) is present mainly in a negatively charged form, that is, HCrO_4^- .^[37]

Effect of adsorbent dose on Cr (VI) removal

According to the results of the present study, upon increasing adsorbent dose from 0.05 to 0.2 g/100 ml, removal efficiency of chromium will be increased for initial concentrations 2, 10 and 15 mg/l from 88% to 100%, 56.1% to 91.7% and 45% to 79.2%, respectively. This can be attributed to increased surface area and availability of more binding sites for adsorption. Similar behavior for the effect of adsorbent dose on Cr (VI) removal efficiency was reported for other types of adsorbents.^[13] Zubair *et al.*,^[31] found that the Cr (VI) removal efficiency by *Citrus reticulata* waste biomass increases with increasing adsorbent amount, which can be due to the large number of vacant adsorption sites and the greater surface area, hence favoring more Cr (VI) adsorption.^[31] In their study,

Table 2: Biosorption rate constants for Cr (VI) adsorption

Initial chromium ion concentration	Kinetic			
	Pseudo-first order		Pseudo-second order	
10 mg/l	$q_{e,calc.}$ (mg/g)	2.318	q_e (mg/g)	3.921
	$q_{e,exp.}$ (mg/g)	4.585	K_2 (g/mg.min)	0.01
	K_1 (min ⁻¹)	0.003	R^2	0.997
	R^2	0.95		
15 mg/l	$q_{e,calc.}$ (mg/g)	4.112	q_e (mg/g)	5.586
	$q_{e,exp.}$ (mg/g)	5.94	K_2 (g/mg.min)	0.003
	K_1 (min ⁻¹)	0.004	R^2	0.995
	R^2	0.972		

Table 3: Comparison of adsorption capacities of Cr (VI) with different sorbents

Adsorbent	Adsorption capacity (mg/g)
Raw rice bran ^[42]	0.07
Maize corn cob ^[43]	0.28
Fly ash – wollastonite ^[44]	2.92
Sawdust ^[45]	3.3
Maple sawdust ^[46]	5.1
Cactus leaves ^[17]	7.08
Carbon slurry ^[30]	15.24
<i>Citrus reticulata</i> waste biomass ^[31]	16.56
Lignin ^[15]	17.97
Mucilaginous seeds of <i>Ocimum basilicum</i> ^[19]	20.5
Algal bloom residue-derived activated carbon ^[14]	155.52
	5.94

Altun *et al.*, observed that the equilibrium concentration of Cr(VI) decreased with increasing the amount of citric acid-modified walnut shells (CA-WNSs), but changed slightly when the amount of CA-WNSs was more than 0.1 g/20 ml. Thus the optimum CA-WNS amount for adsorption of Cr (VI) was found as 0.1 g/20 ml of experimental solution.^[58] The results of present study showed that optimal adsorbent dose was 0.2 g/100 ml.

Effect of contact time and initial chromium ion concentration on Cr (VI) removal

The experiments showed that removal rate reached equilibrium within the first three hours of adsorption time. The participation of specific functional groups and active surface sites are the main reason for the initial rapid adsorption.^[34] As our results showed, Malakootian *et al.*, claimed that the equilibrium time was 180 min. In their study of biosorption of nickel (II) and chromium (VI) by dried activated sludge, the rate of Ni (II) and Cr (VI) removal was initially rapid and then there was no observed increase in rate removal.^[34] Altun *et al.*, studied removal of Cr (VI) from aqueous solutions by modified walnut shells. The results of their study showed that equilibrium time is 120 min, which is independent of initial Cr (VI) ion concentration.^[58]

In this study, removal efficiency between 2 and 20 mg/l was also significantly different. This can be explained by the facts that for sorption a limited number of active sites were available, which would have become saturated above a certain concentration.^[59] The results of the study by Mor *et al.*,^[11] are the same as our results; they indicated that Cr (VI) removal decreased as the initial concentration of Cr (VI) increased.^[11]

Adsorption isotherm study

According to the results of the present study, because of a higher R^2 value, adsorption data followed both Langmuir and Freundlich isotherm models. Similar results were reported by Zhang *et al.*, The results of their study indicated that adsorption of Cr (VI) follows the Langmuir and Freundlich isotherm models for algal bloom residue-derived activated

carbon. The values of regression coefficients obtained from these models were used as the fitting criteria to find out these adsorption isotherms. It was found that both plots portray the linear form of the isotherms and the extremely high correlation coefficients, thus both surface conditions of monolayer and heterogeneous may exist.^[14] Neagu *et al.*,^[7] studied the removal of hexavalent chromium by using a new quaternized, cross-linked poly-(4-vinylpyridines). In their study the adsorption plots fitted very well with both Langmuir and Freundlich isotherm models.^[7]

In this study, the R_L value of the Langmuir isotherm was between 0 and 1 and the $1/n$ value of the Freundlich isotherm was less than 1, which indicates favorable adsorption of hexavalent chromium. Neagu *et al.*, studied the removal of hexavalent chromium by using a new quaternized, cross-linked poly-(4-vinylpyridines). The R_L values were much less than 1 and almost close to 0, and therefore, indicated favorable adsorption of chromate ions by the resins.^[7]

Adsorption kinetics

The result shows that the adsorption process does not follow the pseudo-first-order reaction expression. Such similar results were also obtained by Muthukumaran *et al.*, They studied removal of chromium (VI) from wastewater using chemically activated *Syzygium jambolanum* nut carbon. The applicability of a reversible first-order equation was confirmed by their regression coefficient (R^2) values. It was found that the values of $q_{e,theo}$ calculated from the pseudo-first-order kinetic model differed appreciably from the experimental values $q_{e,exp}$. According to the results, adsorption of Cr (VI) does not follow pseudo-first-order kinetic.^[3] In the present study, the R^2 values were rather than 0.99 which confirmed the applicability of the pseudo-second-order equation. In addition, there was only a little difference between $q_{e,exp}$ and $q_{e,calc}$, reinforcing the applicability of second-order reactions. The pseudo-second-order model equation provided an excellent fit between the predicted curves and the experimental values, whereas the first-order kinetics did not fit the experimental data well. Anandkumar *et al.*, studied adsorption of chromium (VI) and Rhodamine-B on surface-modified tannery waste. The results of their study showed that the kinetic model was the best model fitting their experimental data with high R^2 value for the pseudo-second-order model. Moreover, the calculated q_e values closely fit the experimental data. Thus, the pseudo-second-order kinetics was predominant and the overall rate of the metal as well as dye adsorption processes was largely controlled by the chemisorption process.^[52] Researches such as Aranda-Garcia *et al.*, and Faraji *et al.*, also reached the same results.^[40,41] Ghanizadeh *et al.*, studied the adsorption kinetics and isotherms of Cr (VI) by using bone charcoal. The results of their study showed that adsorption of hexavalent chromium using this biosorbent complies with pseudo-first-order kinetics.^[2]

CONCLUSION

In this study, the efficiency of hexavalent chromium removal by modified Russian knapweed flower powder was investigated. Increasing costs and environmental considerations for industrial wastewater treatment containing heavy metals led to the use of new low- or no-cost adsorbents derived from renewable resources. The present study showed that agricultural wastes such as modified Russian knapweed flower powder can be used as an effective biosorbent for removal of Cr (VI). Removal of this carcinogenic toxicant depended on adsorbent dosage, initial concentration of Cr (VI) and contact time. The results showed that increasing adsorption dose and contact time led to increase in removal efficiency, and increasing pH and initial Cr (VI) concentration led to decrease in removal efficiency. The equilibrium sorption data are satisfactorily fitted with Freundlich and Langmuir equations, and follow the pseudo-second-order kinetics better than pseudo-first order kinetics. Utilization of the modified Russian knapweed flower powder for treatment of aqueous solution containing Cr (VI) ions is gaining attention as a simple, effective and economical means of wastewater treatment.

REFERENCES

- Mor S, Ravindra K, Bishnoi N. Adsorption of chromium from aqueous solution by activated alumina and activated charcoal. *Bioresour Technol* 2007;98:954-7.
- Ghanizadeh G, Asgari G, Mohammadi AM, Ghaneian MT. Kinetics and isotherm studies of hexavalent chromium adsorption from water using bone charcoal. *Fresen Environ Bull J* 2012;21:1296-302.
- Muthukumaran K, Beulah S. Removal of chromium (VI) from wastewater using chemically activated *Syzygium jambolanum* nut carbon by batch studies. *Procedia Environ Sci* 2011;4:266-80.
- Vasudevan S, Lakshmi J, Sozhan G. Studies on the Al-ZnIn-alloy as anode material for the removal of chromium from drinking water in electrocoagulation process. *Desalination* 2011;275:260-8.
- Tashauoei HR, Movahedian Attar H, Kamali M, Amin MM, Nikaen M. Removal of hexavalent chromium (VI) from aqueous solutions using surface modified nanozeolite A. *Int J Environ Res* 2010;4:491-500.
- Vasilatos C, Megremi I, Economou-Eliopoulos M, Mitsis I. Hexavalent chromium and other toxic elements in natural waters in the Thiva-Tanagra-Malakasa Basin, Greece. *Hellenic J Geosci* 2008;43:57-66.
- Neagu V, Mikhalovsky S. Removal of hexavalent chromium by new quaternized crosslinked poly(4-vinylpyridines). *J Hazard Mater* 2010;183:533-40.
- Cieslak-Golonka M. Toxic and mutagenic effects of chromium (VI). A review. *Polyhedron* 1996;15:3667-89.
- Seyf-laye M, Sika A, Liu F, Chen H. Optimization of key parameters for chromium (VI) removal from aqueous solutions using activated charcoal. *JSEM* 2010;1:55-62.
- Miretzky P, Cirelli AF. Cr (VI) and Cr (III) removal from aqueous solution by raw and modified lignocellulosic materials. *J Hazard Mater* 2010;180:1-19.
- Yan G, Viraraghavan T. Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass. *Bioresour Technol* 2001;78:243-9.
- Hafeza AI, Manhay MS, Khedr MA. RO membrane removal of unreacted chromium from spent tanning effluent a pilot-scale study. *Desalination* 2002;144:237-42.
- Konczyk J, Kozłowski C, Walkowiak W. Removal of chromium(III) from acidic aqueous solution by polymer inclusion membranes with D2EHPA and Aliquat 336. *Desalination* 2010;263:211-6.
- Zhang H, Tang Y, Cai D, Liu X, Wang X, Huang Q, Yu Z. Hexavalent chromium removal from aqueous solution by algal bloom residue derived activated carbon: Equilibrium and kinetic studies. *J Hazard Mater* 2010;181:801-8.
- Wu Y, Zhang S, Guo X, Huang H. Adsorption of chromium (III) on lignin. *Bioresour Technol* 2008;99:7709-15.
- Albadarin AB, Al-Muhtaseb AH, Al-Laqtah NA, Walker GM, Allen SJ, Ahmad MN. Biosorption of toxic chromium from aqueous phase by lignin: Mechanism, effect of other metals ions and salts. *Chem Eng J* 2011;169:20-30.
- Dakiky M, Khamis M, Manassra A, Mer'eb M. Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Adv Environ Res* 2002;6:533-40.
- Mahvi AH, Naghipour D, Vaezi F, Nazmara S. Teawaste as an adsorbent for heavy metal removal from industrial wastewaters. *Am J Appl Sci* 2005;2:372-5.
- Melo JS, D'Souza SF. Removal of chromium by mucilaginous seeds of *Ocimum basilicum*. *Bioresour Technol* 2004;92:151-5.
- Tareen RB, Bibi T, Khan M, Ahmad M, Zafar M. Indigenous knowledge of folk medicine by the women of Kalat and Khuzdar regions of Balochistan, Pakistan. *Pakistan J Bot* 2010;42:1465-85.
- Ghahreman A. *Flora of Iran Research Institute of Forest and Rangelands*. Tehran University Press 1995;3:606-7.
- Mozaffarian VA. *Dictionary of Iranian plant Names*. Farhange Moaser; 1996. p. 740.
- Norouzi Arasi H, Yavari I, Chalabian F, Kiarostami V, Ghaffarzadeh F, Nasirian A. Chemical constituents and antimicrobial activities of the essential oil of *Acroptilon repens* (L.) DC. *Flavour Fragr J* 2006;21:247-9.
- Shamsa F, Monsef H, Ghamooshi R, Verdian-Rizi M. Spectrophotometric determination of total alkaloids in some Iranian medicinal plants. *Thai J Pharm Sci* 2008;32:17-20.
- Khan MA, Ahmad M, Zafar M, Sultana S, Marwat SK, Shaheen S, Leghari MK, Jan G, Ahmad F, Nazir A. Medico-botanical and chemical standardization of pharmaceutically important plant of *Tricholepis chaetolepis* (Boiss) Rech., F. *J Med Plant Res* 2011;5:1471-7.
- ASTM. Test method for particle size distribution of granular activated carbon. *Book of Standards*. 26th ed. Washington DC: ASS; 2007:15. p. 396-405.
- Greenberg AE, Clesceri LS, Eaton AD. *Standard methods for the examination of water and wastewater*. Washington DC: American Public Health Association; 1992.
- Rosales E, Pazos M, Sanromán M, Tavares T. Application of zeolite *Arthrobacter viscosus* system for the removal of heavy metal and dye: Chromium and azure B. *Desalination* 2011;284:150-6.
- Foo K, Hameed B. Insights into the modeling of adsorption isotherm systems. *Chem Eng J* 2010;156:2-10.
- Gupta VK, Rastogi A, Nayak A. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *J Colloid Interface Sci* 2010;342:135-41.
- Zubair A, Bhatti HN, Hanif MA, Shafiqat F. Kinetic and equilibrium modeling for Cr (III) and Cr (VI) removal from aqueous solutions by *Citrus reticulata* waste biomass. *Water Air Soil Pollut* 2008;191:305-18.
- Anandkumar J, Mandal B. Adsorption of chromium (VI) and rhodamine B by surface modified tannery waste: Kinetic, mechanistic and thermodynamic studies. *J Hazard Mater* 2011;186:1088-96.
- Cimino G, Passerini A, Toscano G. Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell. *Water Res* 2000;34:2955-62.
- Malakootian M, Ghadin SK, Yousefi N, Fatehizadeh A. Isotherms and kinetics studies of biosorption nickel (II) and chromium (VI) from aqueous solution by dried activated sludge. *Int J Environ Health Eng* 2012;1:8-13.

35. Ahmad R. Sawdust: Cost effective scavenger for the removal of chromium (III) ions from aqueous solutions. *Water Air Soil Pollut* 2005;163:169-83.
36. Elangovan R, Philip L, Chandraraj K. Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies. *J Hazard Mater* 2008;152:100-12.
37. Oliveira EA, Montanher S, Andrade AD, Nobrega JA, Rollemberg MC. Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran. *Process Biochem* 2005;40:3485-90.
38. Garg UK, Kaur MP, Garg VK, Suda D. Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. *J Hazard Mater* 2007;140:60-8.
39. Pandey KK, Prasad G, Singh VN. Removal of Cr (VI) from aqueous solution by adsorption on fly ash-wollastonite. *J Chem Technol Biotechnol* 1984;34A:367-74.
40. Srivastava HC, Mathur RP, Mehrotra I. Removal of chromium from industrial effluents by adsorption on sawdust. *Environ Technol Lett* 1987;7:55-63.
41. Yu LJ, Shukla SS, Dorris KL, Shukla A, Margrave JL. Adsorption of chromium from aqueous solutions by maple sawdust. *J Hazard Mater* 2003;100:53-63.
42. Jung Kim E, Park S, Hong HJ, Choi YE, Yang JW. Biosorption of chromium (Cr (III)/Cr (VI)) on the residual microalga *Nannochloris oculata* after lipid extraction for biodiesel production. *Bioresour Technol* 2011;102:11155-60.38.
43. Altun T, Pehlivan E. Removal of Cr (VI) from aqueous solutions by modified walnut shells. *Food Chem* 2012;132:693-700.
44. Owwal M, Aroua MK, Wan Daud WM. Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine. *Bioresour Technol* 2010;101:5098-103.
45. Aranda-Garcia E, Del Carmen Cristiani-Urbina M, Netzahuatl-Munoz AR, Villegas-Garrido TL, Cristiani-Urbina E, Estela Barragan-Huerta B. Removal of hexavalent and total chromium from aqueous solutions by schinus molle bark. *Fresen Environ Bull J* 2010;19:2911-8.
46. Faraji M, Abooi Mehrizi E, Sadani M, Karimaei M, Ghahramani E, Ghadiri K, Taghizadeh MS. Isotherms and kinetics of lead and cadmium uptake from the waste leachate by natural and modified clinoptilolite. *Int J Environ Health Eng* 2012;1:1-7.

Source of Support: Shahid Sadoughi University of Medical Sciences,
Conflict of Interest: None declared.