*Polish Journal of Chemical Technology, 15, **2,** 40 — 47, 10.2478/pjct-2013-0022*

Equilibrium and kinetic studies of Cr (VI) removal from synthetic wastewater by *Acroptilon repense* flower powder

Mohammad Taghi Ghaneian[1], **Mohammad Hasan Ehrampoush**[1], **Asghar Mosleh Arany**[2], **Behzad Jamshidi**[1*], **Mahboobeh Dehvari**[1]

[1]*Department of Environmental Health Engineering, Faculty of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran*
[2]*Department of Environmental Engineering, Yazd University, Yazd, Iran*
[*] *Corresponding author: e-mail: behzadjamshidi65@yahoo.com*

In this study the removal of Cr (VI) from synthetic wastewater was investigated using *Acroptilon repens* (Russian Knapweed) flower powder under various conditions (pH, contact time and initial concentration of Cr). The capacity of chromium adsorption at equilibrium conditions by this biosorbent was increased by adsorbate concentration. The results also showed that the removal efficiency of Cr (VI) was increased by increasing the contact time. By increasing the initial concentration of Cr (VI) solution, chromium removal was reduced. The suitability of adsorbents and their constants was tested or evaluated with the Langmuir, Freundlich and Temkin isotherms models. The results indicated that the Freundlich and Langmuir models ($R^2 > 0.99$) gave a better concordance to the adsorption data in comparison with the Temkin equation ($R^2 = 0.97$). The adsorption of Cr (VI) followed the pseudo-second-order kinetics ($R^2 = 0.991$). The study showed that Acroptilon repens flower powder can be used as an effective lignocellulosic biomaterial and biosorbent for the removal of Cr (VI) from wastewater.

Keywords: *Acroptilon repens*, Biosorbent, Hexavalent Chromium, Adsorption kinetic and isotherm.

INTRODUCTION

The chromium is one of the heavy metals and environmental pollutants. It is present in aqueous solution mainly in Cr (III) and Cr (VI) oxidation states. Cr (III) is more stable and less toxic whereas Cr (VI) is highly toxic and soluble in water[1–2]. Cr (VI) exists in the effluents of electroplating, paint, dyeing, pigment, mining, fertilizer and photography industries[3] and causes acute environmental and health problems. Exposure to Cr (VI) causes dermatitis, allergic skin reactions and ulceration of intestine[4–5]. Hexavalent chromium has been reported to be toxic to humans and animals and it is known to be carcinogenic[6]. The maximum permissible level of Cr (VI) in drinking water is 0.05 mg/L and the tolerance limit for Cr (VI) to discharge into inland surface waters is 0.1 mg/L[2, 5, 7]. Nevertheless, for most natural waters the Cr concentration is below the 50 μg/L value recommended for drinking water by the World Health Organization or the US Environmental Protection Agency. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr (VI) to acceptable levels. Because of its high toxicity, Cr (VI) must be substantially removed from the wastewater before being discharged into the aquatic system[8]. Different techniques used for chromium ions removal from industrial wastewater include bioremediation, chemical precipitation, ion exchange, reverse osmosis and solvent extraction[9, 10]. These methods, apart from being economically expensive, have disadvantages like high energy requirements, incomplete removal, high reagent and generation of toxic sludge or other harmful wastes that must be managed. For this reasons efficient, cheap and environmental friendly methods to reduce heavy metals content need to develop. The most widely used adsorbent is activated carbon because it has relatively higher surface area, but it is expensive and requires chelating agents to enhance its performance. Therefore, there has been increased interest in the use of other adsorbent materials[8, 11, 12]. In recent years considerable attention has been focused on the field of adsorption by lignocellulosic solid wastes such as lignin[13], sawdust, walnut skin, coconut husks, Biomass Cone[8], exhausted coffee[14], waste tea[4], seeds of Ocimum Basilicum[15]. Although agricultural wastes have adsorption capacity comparable to other natural sorbents, they have the advantage of very low or no cost, great availability, simple application and the fact that through their use as biosorbents, added value is provided to products that otherwise would be considered as a waste[8].

Acroptilon repens (L.) DC. (Russian Knapweed), known as *Centaura repens* in some literature, belongs to the family of Asteraceae[16]. This plant is herbaceous and perennial. *Acroptilon repens* is native to southern Ukraine, southeast Russia, Iran, Kazakhstan and Mongolia. Only one species of this plant is known in Iran, which is found in western Azarbayjan, Zanjan, Tehran and Yazd provinces[17, 18]. The aerial parts of *Acroptilon repens* plant is medicinal with antimicrobial and antipyretic properties[16, 19, 20] and used for blood purifiction, stomach pain, fever and dysentery[16, 21]. The plant is reported to be allelopathic, but is not toxic to human[21]. There isn't any study about adsorption characteristic of *Acroptilon repens* flower powder, so we introduce a new biosorbent for heavy metals removal. The aim of this research was evaluating the Hexavalent Chromium Removal by *Acroptilon repens* flower powder as a new biosorbent from synthetic wastewater and the effect of different parameters on the adsorption process.

EXPERIMENTAL

Preparation of Chromium solution

Stock solution was prepared by dissolving a definite amount of potassium dichromate ($K_2Cr_2O_7$) in distilled water[1, 13]. The chromium solutions with concentrations of 2 and 10 mg/L were prepared by dilution of the stock solution with distilled water. The pH of the solutions was adjusted by using 0.1 N HCl or NaOH. pH of the samples was measured using pH meter Mi 151. All the chemicals used were of analytical reagent grade and were obtained from Merck. Fresh dilutions were used for each study.

Preparation of biosorbent

Acroptilon repens were collected from nearby locality of Yazd city, Iran and then flowers of plant were separated[17]. Flowers were washed with distilled water to remove impurities and surface adhered particles and then dried at 102°C. In our study, adsorbent was pulverized by standard ASTM sieves with the range of 40 to 60 meshes (0.25–0.4 mm particles) and used as a new biosorbent in the experiments[22].

Characterization of the biosorbent

In order to survey the particle properties of the adsorbent and see the surfaces of particle before and after adsorption, the powder texture was observed by the scanning electron microscope (SEM). The surface morphologies of the samples were examined using a Scanning Electron Microscopy (SEM) (KYKY-EM3200, China). SEM apparatus operated at a 25kV accelerating potential.

To obtain the information on the main chemical groups present on the surface of the Acroptilon repense flower powder particles, Fourier transform infrared spectroscopy (FTIR) was performed at the range of 4000–450 cm^{-1} with FT-IR-8400S-Shimadzu, Japan.

Chromium detection

The Cr (VI) is estimated by colorimetric technique. The samples were acidified with phosphoric acid, and then complexed with a solution of 1.5 diphenyl carbazide (DIPC) in acetone, tested in a spectrophotometer set (UV/VisibleSP-3000 Plus-Japan) at 540 nm according to standard methods[23, 24].

Adsorption experiments

Adsorption experiments were done by initial chromium concentrations of 2 and 10 mg/L, adsorbent dose of 0.05–0.2 g/100ml, contact time of 30–240 and pH of 2–11. The experiments were carried out by a mechanical shaker (INNOVA 40R, England) with shaker (120 rpm at 20°C). After shaking, samples were filtered through 0.45 μm filter paper and the filtrate was analyzed[2, 3]. The amount of adsorbed Cr (VI) was calculated by the difference of the initial and residual amount in the solution. The amount of Cr (VI) adsorbed in mg/g at time t (q_e) and the percentage of removed Cr (VI) ions (R) in solution were computed using formulae (1) and (2), respectively:

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

$$R\,(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

Where C_o and C_t are the 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; M is the weight of adsorbent in g[3, 13].

The results also were evaluated by various adsorption isotherms including the Langmuir, Freundlich and Temkin isotherms. To determine isotherm models, adsorbent doses of 0.05–0.2 g added to 100 ml of chromium solutions with concentration of 10 mg/L. Adsorption tests were performed in the optimal amount of contact time and pH factors. Adsorption kinetics study also was carried out with the pseudo-first-order and pseudo-second-order kinetics. The chromium concentration was 10 mg/L and 0.2 g of adsorbent material was added to 100 ml of chromium solution. The temperature and pH were constant. Adsorption kinetic was determined by analyzing adsorptive uptake of the chromium from synthetic wastewater at different time intervals.

RESULTS AND DISCUSSION

Characterization of the biosorbent

The SEM images of Acroptilon repense flower powder before and after adsorption are shown in Fig. 1 and 2. It can be observed that Acroptilon repense flower powder have irregular surface structure, a situation which favors the adsorption of Cr (VI) on different parts of biosorbent. It can be clearly seen that these samples do not indicate well-defined pore structures.

The construction of complexes between ions species in the solution and the functional groups of biosorbents enables them to play a role in biosorption. Since plant

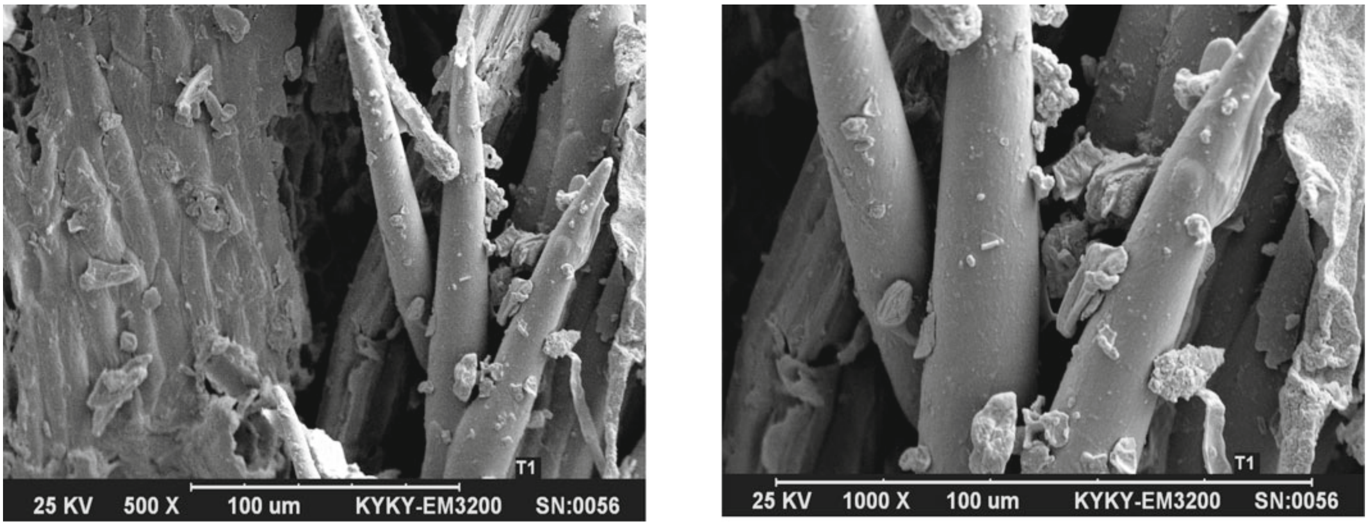

Figure 1. Scanning electron microscope (SEM) of *Acroptilon repens* flower powder in deferent magnifications

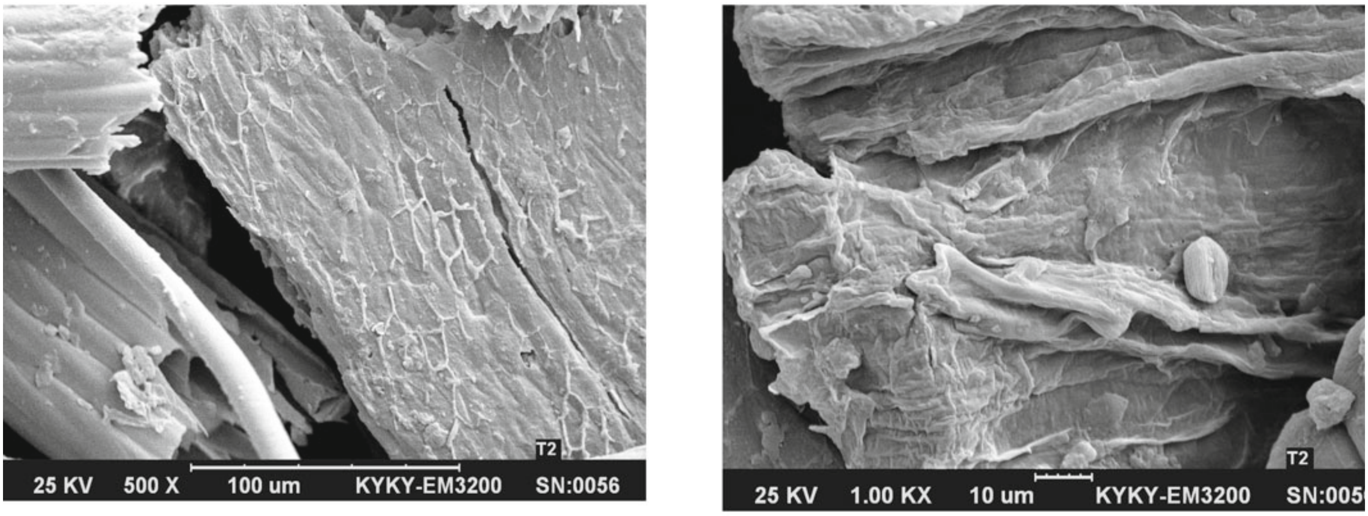

Figure 2. Scanning electron microscope (SEM) of *Acroptilon repens* flower powder loaded with Cr(VI) in deferent magnifications

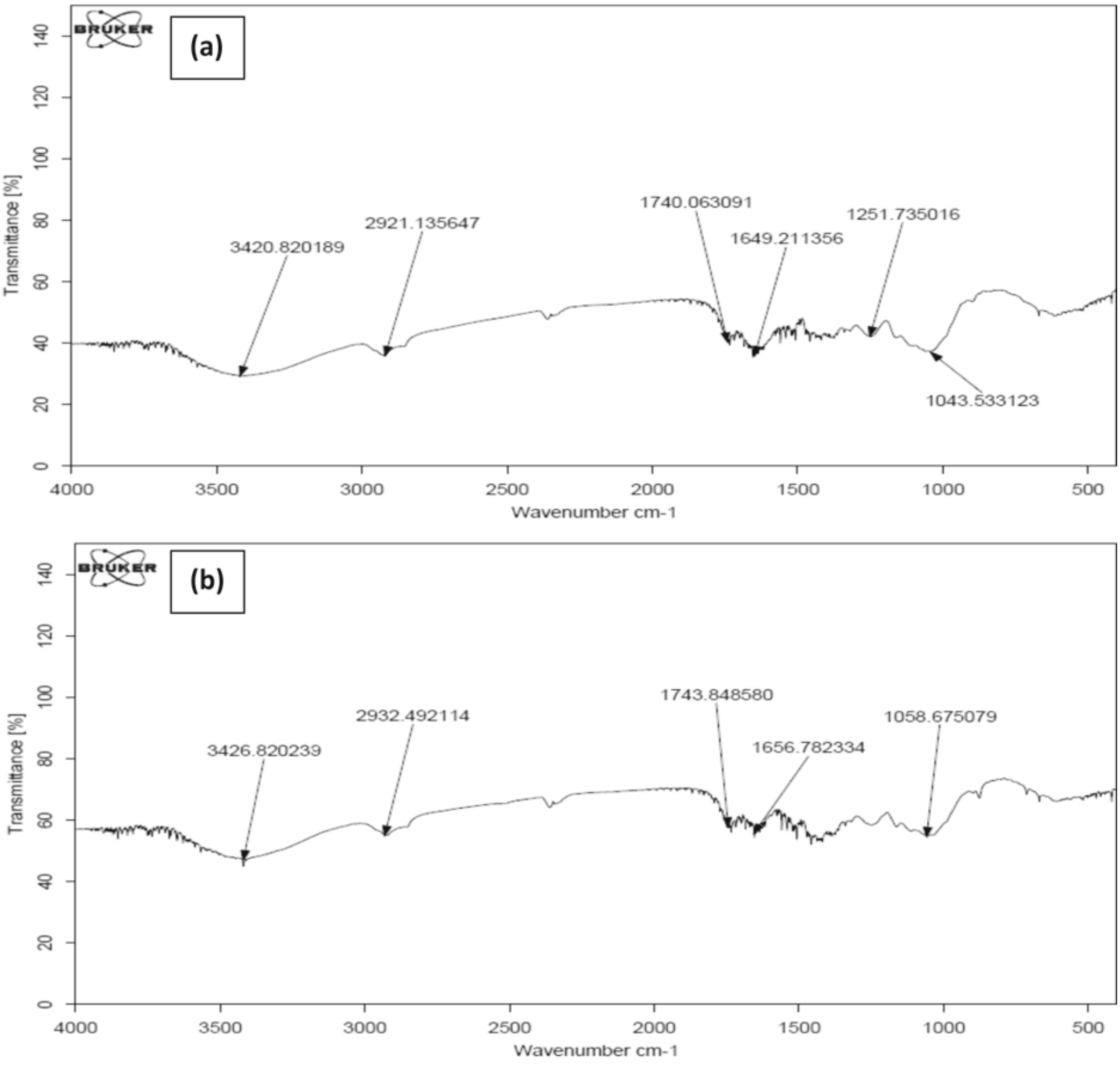

Figure 3. FTIR spectra of *Acroptilon repense* flower powder (a) before and (b) after the biosorption of Cr (VI)

fibers consist mostly of cellulose, hemicelluloses, lignin, pectin and extractives, ions sorb mainly to carboxylic (primarily present in hemicelluloses, pectin and lignin), phenolic (lignin and extractives) and to some extent hydroxylic (cellulose, hemicelluloses, lignin, extractives and pectin) and carbonyl groups (lignin, pectin)[25].

The FTIR spectra analyses for the Acroptilon repense flower powder before and after biosorption of Cr (VI) were undertaken and the results are demonstrated in Fig. 3. The FTIR spectra indicate that there is a move of some functional group bands, which indicates changes in biosorbent functional groups and surface properties. the infrared absorption wavelengths of each peak and

Table 1. The FTIR spectral characteristics of *Acroptilon repense* flower powder before and after biosorption of Cr (VI)

Wavelength range (cm^{-1})	Before adsorption	After adsorption	Differences	Assignment
3500–3200	3420	3426	−6	Bonded hydroxyl groups(OH)
3000–2850	2921	2932	−11	C–H methyl and methylene groups
1750–1680	1740	1743	−3	C=O carbonyls
1670–1640	1649	1656	−7	Carboxylic groups
1350–1000	1251	Absent	–	O–H alcohols (primary and secondary) and aliphatic ethers
1300–1000	1043	1058	−15	C–O stretching of COOH

the related functional groups are presented in Table1. The results exhibited biosorbent heterogeneity, proved by diverse attribute peaks with the possible presence of phenolic, carboxylic, hydroxyl and carbonyl groups[26].

Effect of initial pH

The results for the effects of pH on Hexavalent chromium removal by the *Acroptilon repens* flower in condition of 25°C and 2 mg/L chromium concentration are shown in Fig. 4. At this stage, adsorbent dose and contact time were 0.2 g/100 ml and 24 h, respectively. The results of this study showed that as the pH of solution was increased the adsorption capacity (q_e) and adsorption efficiency decreased ($r = -0.96, P = 0.001$). By increasing pH from 2 to 11, Cr (VI) percentage removal decreased from %99.95 to %18.2. It was observed that the maximum percentage of removal of Cr (VI) was at pH 2. In low pH solutions, hydronium ions associates to functional groups such as carboxyl, phenolic, hydroxyl, and carbonyl, thus increasing the affinity for Cr (VI) ions because they are positively charged ions[13, 27]. At lower pH, the surface will be surrounded by high quantities of hydronium ions. At pH 2 the predominant Cr (VI) was $HCrO_4^-$ and as a result, electrostatic attraction took place between the positively charged adsorbent and the negatively charged $HCrO_4^-$ [8, 13]. According to Gupta et al. (2010), at high pH there will be abundance of negatively charged hydroxyl ions in aqueous solution, causing hindrance between the negatively charged ions $Cr_2O_7^{2-}$; CrO_4^{2-}, etc. and the negatively charged adsorbent, resulting in a decrease of adsorption. Accordingly, the optimum pH for the maximum adsorption of Cr (VI) was 2 [28]. Similar results were demonstrated by Wu et al. (2008) who studied adsorption of chromium (III) on lignin[12].

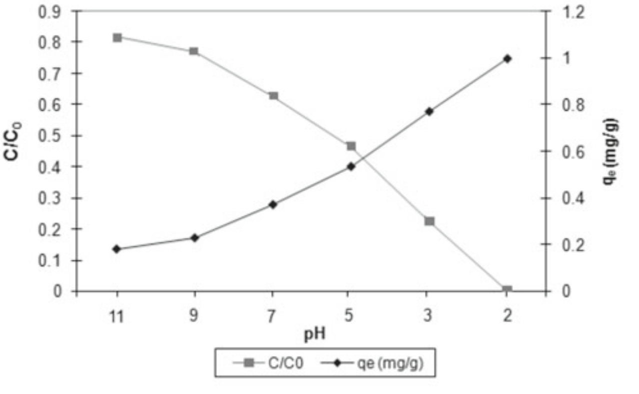

Figure 4. Effect of initial pH on Cr (VI) removal and adsorption capacity

Effect of adsorbent dose

The effect of adsorbent dose on removal efficiency of chromium (VI) by *Acroptilon repens* flower powder has been investigated in the initial chromium concentrations, 2 and 10 mg/L at pH=2. In this stage shaker speed and reaction time were 120 rpm and 24 h, respectively. The effect of adsorbent dose on the chromium removal is shown in Fig. 5. Results showed chromium removal at equilibrium condition was increased with the increasing of adsorbent dose from 0.05 to 0.2 g/100 ml; this can be attributed to increased surface area and the availability of more binding sites for adsorption. The same results were reported by Mor et al. (2007). They indicated that adsorption of Cr (VI) increased with increasing the dose of the activated alumina and activated charcoal[1]. According to the results of the present study, by increasing the adsorbent dose from 0.1 to 0.2 gr/100 ml, the removal efficiency of chromium increased for the initial concentration 2 mg/L from 76.5% to 99.95% and for the initial concentration 10 mg/L from 35.1% to 58.6%, respectively. The maximum adsorption capacity (q_e) for the initial concentration of chromium 2 and 10 mg/L were 1.66 and 5.72 mg/g, respectively. Similar results for the effect of adsorbent dose on Cr (VI) adsorption capacity was reported for other sorbents[11]. The results of the present study showed that the optimal adsorbent dose was 0.2 g/100 ml.

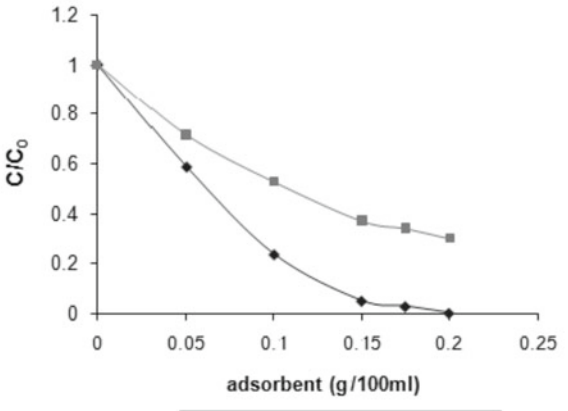

Figure 5. Effect of adsorbent dose on Cr (VI) removal

Effect of contact time and the initial Cr (VI) concentration

The effect of contact time on chromium adsorption tested with 2 and 10 mg/L Cr (VI) and 0.2 g/100 ml adsorbent. The pH of the solution was 2 and detection of adsorption efficiency was done at 30, 60, 120, 180 and 240 min. The results showed that the removal efficiency of Cr (VI) increased by increasing the contact time. The adsorption of chromium ions by this biosorbent reached equilibrium in less than 180 minutes. The experiments showed that the removal rate of Cr (VI) reaching equilibrium within the first three hours of adsorption. The same as our results, Altun et al. (2012) showed that the equilibrium time was 120 min and the results were independent of initial Cr (VI) ions concentration[29]. As is shown in Fig. 6, with increasing the initial concentration of Cr (VI) solution from 2 to 10 mg/L, chromium removal decreased. While at equilibrium time (180 min) removal efficiency for chromium concentration 2 and 10 mg/L was 74.5% and 55.6% respectively. Removal efficiency between 2 and 10 mg/L was also significantly different ($P = 0.05$). This can be explained by the fact that for the sorption a limited number of active sites available, which would have become saturated above a certain concentration[30]. The results of Suman Mor et al. study (2007) were in agreement with our results, they indicated that Cr (VI) removal decreased as the initial concentration of Cr (VI) was increased[1].

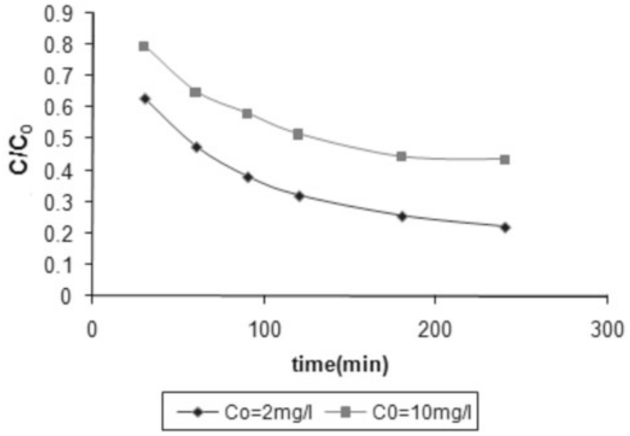

Figure 6. Effect of contact time and initial Cr (VI) concentrations

Adsorption isotherm study

One of important physico-chemical aspects for the evaluation of the biosorption process is the adsorption isotherms. The distribution of Cr (VI) between the liquid and the adsorbent phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the most popular isotherm models[7]. The Langmuir, Freundlich and Temkin isotherms models are widely used to describe adsorption data in water and wastewater treatment[31]. In this study, Langmuir, Freundlich and Temkin isotherm models were selected for an assessment of Cr (VI) adsorption on *Acroptilon repens* flower powder and the equilibrium concentration in aqueous solutions. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites[28]. The model takes the following linear form:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_eC_e} \qquad (3)$$

Where q_m is the quantity of an adsorbate required to form a single monolayer on the unit mass of the adsorbent (mg/g); q_e is the amount pollutant adsorbed on the unit mass of the adsorbent (mg/g); C_e is the equilibrium concentration of metal ions solution (mg/L) and b (L/mg) is Langmuir constant that is related to the apparent energy of adsorption. Equation 3 shows that a plot of $1/q_e$ versus $1/C_e$ should yield a straight line if the Langmuir isotherm model is obeyed by the adsorption equilibrium. The slope and the intercept of this line then yield the values of constants qm and b respectively[32, 33]. The Langmuir isotherm is shown in Fig. 7. The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant R_L, which is represented by:

$$R_L = \frac{1}{1+bC_0} \qquad (4)$$

Where C_0 is the initial concentration of adsorbate (mg/l) and b is the Langmuir constant[29]. The determined parameters and their corresponding correlation coefficients (R^2) are listed in Table 2. The separation factor (R_L) indicates the isotherm shape and whether the adsorption is favorable or not: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible[34]. The R_L value obtained in the present case is less than 1 that indicated a favorable adsorption of Cr (VI). Similar results were reported by Neagu et al. (2010)[5].

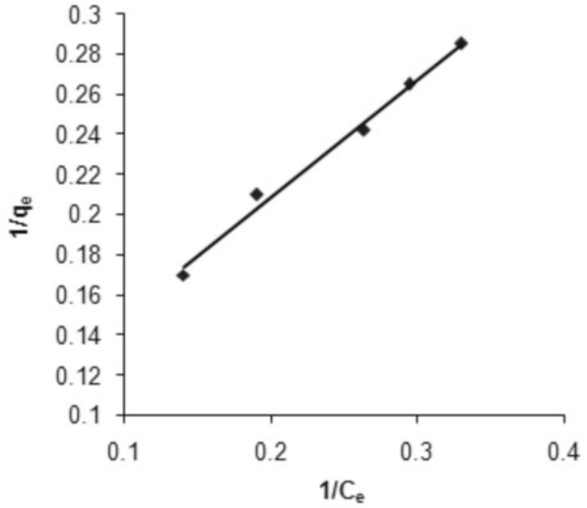

Figure 7. Langmuir adsorption isotherms on Cr (VI) removal

The Freundlich isotherm model is applicable to adsorption of metal ions and occurs on a heterogeneous adsorbent surface[5]. The Freundlich's model can be described by the following equation:

$$Ln\, q_e = Ln\, K_f + \frac{1}{n}\, Ln\, C_e \qquad (5)$$

Where q_e is the amount 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[11]. The values of K_f, 1/n and R^2 are reported in Table 2. The value of R^2 obtained was 0.993, indicating that heterogeneous surface conditions may exist (Fig. 8). The value of 1/n obtained for the adsorption of Cr (VI) on *Acroptilon repens* flower powder was found to be less than one (1/n = 0.547) that specifies that the adsorption is favourable. Similar results were found by Cimino et al. (2000), who studied the removal of toxic cations and Cr (VI) from aqueous solution on hazelnut shell[35].

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 [32]. The Temkin isotherm equation is represented by:

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

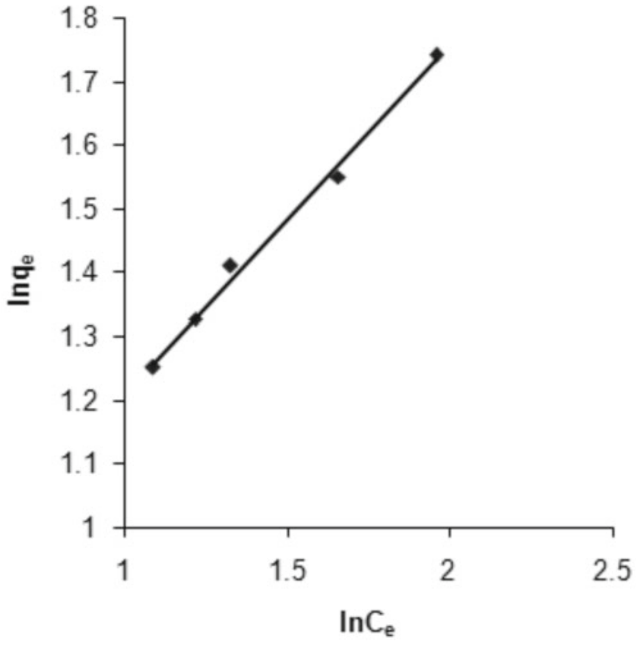

Figure 8. Freundlich adsorption isotherms on Cr (VI) removal

Where B_T = RT/b. The constant B_T is related to the heat of adsorption (kJ/mol), K_t is the binding constant which represents the maximum binding energy (L/mg). The isotherm constants of K_t and B_T are determined by slope and the intercept from the plot of q_e versus ln C_e, respectively[11]. The results of temkin isotherm constant in the present study are shown in Table 2. The values of B_T and K_T constant were 0.760 kJ/mol and 248.7 L/g, respectively. Zhang et al. (2010) investigated the hexavalent chromium removal from aqueous solution by algal bloom residue derived from activated carbon[11].

Values of the correlation coefficient (R^2) are a measure of the goodness-of-fit of the experimental data on the isotherm models. The results indicated that the Freundlich and Langmuir models ($R^2 > 0.99$) data in comparison with the Temkin equation ($R^2 = 0.97$) gave a better fit to the experimental. The results of Neagu et al.[5] and Zhang et al.[11] studies also have good concordance with Langmuir and Freundlich isotherm models.

Adsorption kinetics

A kinetic investigation was conducted in order to further expose the adsorption mechanism of hexavalent chromium onto *Acroptilon repens* flower powder and rate controlling steps. For testing the experimental data Pseudo-first and the pseudo-second-order kinetic models were used.

The pseudo-first-order reaction equation was used for the adsorption of liquid/solid system on the basis of solid capacity[36]. Its linear form is described by the following equation:

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

k_1 (1/min) is the rate constant in the pseudo-first-order adsorption process. The constant and adsorption capacity were determined experimentally by plotting of the log $(q_e - q_t)$ versus time and listed in Table 3. The results showed that the correlation coefficient (R^2) of the data for the pseudo-first-order reaction was 0.941 and the theoretic value ($q_{e,cal}$) is lower than that experimental data ($q_{e,exp}$) which specifies that the adsorption process does not follow the pseudo-first-order reaction. The same results were also obtained by Muthukumaran et al. (2011). According to the results, adsorption of Cr (VI) did not follow the pseudo-first-order kinetic[2].

In the pseudo-second-order model, adsorption follows the second-order chemisorptions[37]. The linear form is represented by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

Where k_2 (g/mg·min) is the adsorption rate constant. By plotting a curve of t/qt versus time, q_e and k_2 can be evaluated (Fig. 9). The values of q_e, k_2 and R^2 are listed in Table 3. The R^2 value obtained was 0.991 which confirmed the applicability of the pseudo-second-order equation. On the other hand, there was a little difference between the $q_{e,exp}$ and $q_{e,cal}$, that indicated the applicability of this model. The pseudo-second-order model equation provided a good fit between the experimental values and the predicted curves, whereas the first-order kinetics did not fit well to the experimental data. Anandkumar et al. (2011) studied adsorption of chromium (VI) and Rhodamine B on the surface modified tannery waste. The calculated q_e values were closely fitted with the experimental data. Thus, the pseudo-second-order kinetics was predominant[34]. Thamilarasu et al. studied the feasibility of the removal of hexavalent chromium ions from aqueous solutions and reported that the metal ion adsorption using the activated carbon produced from Cajanus Cajan (L) Milsp followed the pseudo-second order kinetic model[38].

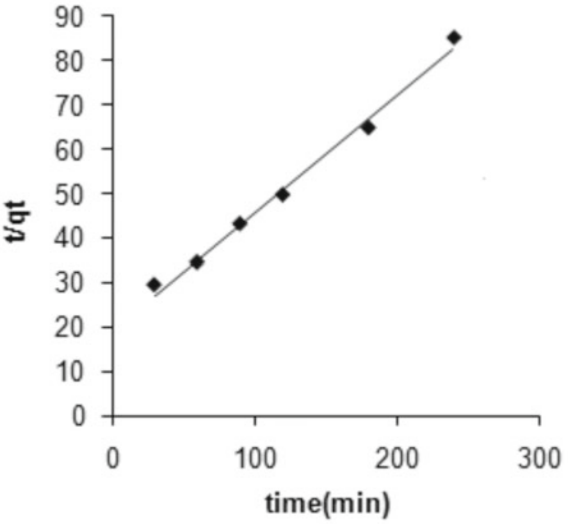

Figure 9. Pseudo second order kinetics for Cr (VI) removal

Table 2. Characteristics of adsorption isotherms

Langmuir		Freundlich		Temkin	
B (L/mg)	6.37	K_f (mg/g)	1.937	K_t (L/g)	248.7
q_{max}(mg/g)	1.7	1/n	0.547	B_T (kJ/mol)	0.760
R^2	0.990	R^2	0.993	R^2	0.97
R_L	0.0154				

Table 3. The biosorption rate constant for Cr (VI) onto *Acroptilon repens* flower powder

Pseudo-first-order		Pseudo-second-order	
q_e (calc.) (mg/g)	2.479	q_e (mg/g)	3.788
q_e (exp.) (mg/g)	3.5	K_2 (g/mg.min)	0.0036
K_1 (min^{-1})	0.006	R^2	0.991
R^2	0.941		

CONCLUSIONS

In recent years, increasing costs and environmental considerations caused the use of new low or no cost adsorbents derived from renewable resources. The present study indicated that lignocellulosic agricultural wastes such as *Acroptilon repens* flower powder can be used as an effective biosorbent for the removal of Cr (VI). The results showed that increasing the adsorption dose and contact time increased the removal efficiency and increasing the pH and the initial concentration led to a decrease of removal efficiency. The sorption data is fitted with the Freundlich and Langmuir isotherm models and follows the pseudo-second-order kinetics better than Pseudo-first order kinetics. Utilization of the *Acroptilon repens* flower powder for the treatment of aqueous solution containing Cr (VI) ions is gaining attention as a simple, effective and economical means of wastewater treatment.

Acknowledgement

Researchers would like to acknowledge and appreciate the financial support Shahid Sadoughi University of Medical Sciences. Yazd, Iran.

LITERATURE CITED

1. Mor, S., Ravindra, K. & Bishnoi, N. (2007). Adsorption of chromium from aqueous solution by activated alumina and activated charcoal, *Bioresour Technol.* 98, 954–957. DOI: 10.1016/j. biortech.2006.03.018.

2. Muthukumaran, K. & Beulah, S. (2011). Removal of Chromium (VI) from wastewater using chemically activated Syzygium jambolanum nut carbon by batch studies, *Procedia Environ Sci*. 4, 266–280. DOI:10.1016/j.proenv.2011.03.032.

3. Demirbas, E., Kobya, M., Senturk, E. & Ozkan, T. (2004). Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, Water S.A. 30, 533–540.

4. Mahvi, A.H., Naghipour, D., Vaezi, F. & Nazmara, S. (2005). Tea waste as an adsorbent for heavy metal removal from industrial wastewaters, *Am. J. Appl. Sci.* 2, 372–375. DOI: 10.3844/ ajassp.2005.372.375

5. Neagu, V. & Mikhalovsky, S. (2010). Removal of hexavalent chromium by new quaternized crosslinked poly (4-vinylpyridines), *J. Hazard Mater.* 183, 533–540.

6. Cieslak-Golonka, M. (1996). Toxic and mutagenic effects of chromium (VI). *A. Review. Polyhedron*, 15, 3667–3689. DOI: 10.1016/0277-5387(96)00141-6.

7. Seyf-Laye, M., Sika, A., Liu, F. & Chen, H. (2010). Optimization of key parameters for chromium (VI) removal from aqueous solutions using activated charcoal, *J. Soil Sci. Environ Manage*. 1, 55–62.

8. Miretzky, P. & Cirelli, A.F. (2010). Cr (VI) and Cr (III) removal from aqueous solution by and modified lignocellulosic materials, *J. Hazard Mater*. 180, 1–19.

9. Yan, G. & Viraraghavan, T. (2001). Heavy metal removal in a biosorption column by immobilized M. rouxii biomass, *Bioresour Technol*. 78, 243–249. DOI: http://dx.doi.org/ 10.1016/ S0960-8524(01)00020-7.

10. Hafeza, A.I., Manhay, M.S. & Khedr, M.A. (2002). RO membrane removal ofunreacted chromium from spent tanning effluent a pilot-scale stud. *Desalination*, 144, 237–242.

11. Zhang, H., Tang, Y., Cai, D., Liu, X., Wang, X., Huang, Q. & Yu, Z. (2010). Hexavalent chromium removal from aqueous solution by algal bloom residue derived activated carbon: Equilibrium and kinetic studies, *J. Hazard Mater*, 181, 801–808. doi:10.1016/j.jhazmat.2010.05. 084.

12. Wu, Y., Zhang, S., Guo, X. & Huang, H. (2008). Adsorption of chromium (III) on lignin, *Bioresour Technol*. 99, 7709–7715.

13. Albadarin, A.B., Al-Muhtaseb, A.H., Al-Laqtah, N.A., Walker, G.M., Allen, S.J. & Ahmad, M.N.M. (2011). Biosorption of toxic chromium from aqueous phase by lignin: Mechanism, effect of other metals ions and salts, *Chem. Eng. J.* 169:20–30. DOI: 10.1016/j.cej. 2011.02.044.

14. Dakiky, M., Khamis, M., Manassra, A. & Mer'eb, M. (2002). Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents, *Adv. Environ. Res.* 6, 533–540. DOI: http://dx.doi.org/10.1016/ S1093-0191(01)00079-X.

15. Melo, J.S. & D'souza, S.F. (2004). Removal of chromium by mucilaginous seeds of Ocimum Basilicu, *Bioresour Technol*. 92 (2) 151–155.

16. Tareen, R.B., Bibi, T., Khan, M., Ahmad, M. & Zafar, M. (2010). Indigenous knowledge of folk medicine by the women of Kalat and Khuzdar regions of Balochistan, Pakistan, Pakistan *J. Botany*. 42, 1465–1485.

17. Ghahremen A. (1995).Flora of Iran .Research Institute of Forest and Rangelends and Tehran University press: Tehran. 3: 606-607. [Persian].

18. Mozaffarian, V.A. (1996). Dictionary of Iranian plant Names. Farhange Moaser, 740.

19. Norouziarasi, H., Yavari, I., Chalabian, F., Kiarostami, V., Ghaffarzadeh, F. & Nasirian, A. (2006). Chemical constituents and antimicrobial activities of the essential oil of *Acroptilon repens* (L.) DC, *Flavour and Fragr. J.* 21, 247–249. DOI: 10.1002/ffj.1568.

20. Shamsa, F., Monsef, H., Ghamooshi, R. & Verdian-Rizi, M. (2008). Spectrophotometric determination of total alkaloids in some Iranian medicinal plants, *Thai J. Pharm. Sci.* 32, 17–20.

21. Khan, M.A., Ahmad, M., Zafar, M., Sultana, S., Marwat, S.K., Shaheen, S., Leghari, M.K., Jan, G., Ahmad, F. & Nazir, A. (2011). Medico-botanical and chemical standardization of pharmaceutically important plant of Tricholepis chaetolepis (Boiss) Rech, *J. Med. Plant Res*. 5(8) 1471–1477.

22. ASTM. (2007). Test Method for Particle Size Distribution of Granular Activated Carbon. Book of Standards.26th ed. Washington D.C. ASS, 15.01, 396–405.

23. AWWA, APHA. (2005). Standard Methods for the Examination of Water and Wastewater. Washington DC, USA, 3, 67–3, 68.

24. Rosales, E., Pazos, M., Sanromán, M. & Tavares, T. (2011). Application of zeolite Arthrobacter viscosus system for the removal of heavy metal and dye: Chromium and Azure B. Desalination. 284, 150–156. doi: 10.1016/j.desal.2011.08.049.

25. Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.* 30, 38–70. DOI: 10.1016/j.progpolymsci.2004.11.002.

26. Wahab, M.A., Jellali, S., Jedidi, N. (2010). Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption

isotherms modeling, *Bioresour Technol*. 101, 5070–5075. DOI: 10.1016/j.biortech.2010.01.121.

27. Lie, Y., Zhengfang, Y., ZhongYou, W. & JinRen, N. (2008). Characteristics of Pb^{2+} biosorption with aerobic granular biomass. *Chinese Sci. Bull*, 53 (6): 948–953.

28. Gupta, V.K., Rastogi, A. & Nayak, A. (2010). Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material, *J. Colloid Interface Sci*. 342, 135–141. DOI: 10.1016/j.jcis.2009.09.065.

29. Altun, T. & Pehlivan, E. (2012). Removal of Cr (VI) from aqueous solutions by modified walnut shells, *Food Chem*. 132, 693–700. DOI: 10.1016/j.foodchem.2011.10.099.

30. Owlad, M., Aroua, M.K. & Wan Daud, W.M.A. (2010). Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine, *Bioresour Technol*. 101, 5098–5103.

31. Foo, K. & Hameed, B. (2010). Insights into the modeling of adsorption isotherm systems, *Chem. Eng. J.* 156, 2–10.

32. Zhang, H., Tang, Y., Cai, D., Liu, X., Wang, X., Huang, Q. & Yu, Z. (2010). Hexavalent chromium removal from aqueous solution by algal bloom residue derived activated carbon: Equilibrium and kinetic studies, *J. Hazard Mater*. 181, 801–808.

33. Zubair, A., Bhatti, H.N., Hanif, M.A. & Shafqat, F. (2008). Kinetic and equilibrium modeling for Cr (III) and Cr (VI) removal from aqueous solutions by Citrus reticulata waste biomass, *Water Air Soil Pollut.* 191, 305–318.

34. Anandkumar, J. & Mandal, B. (2011). Adsorption of chromium (VI) and Rhodamine B by surface modified tannery waste: Kinetic, mechanistic and thermodynamic studies, *J. Hazard Mater.* 186, 1088–1096.

35. Cimino, G., Passerini, A. & Toscano, G. (2000). Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell, *Water Res.* 34, 2955–2962. DOI: 10.1016/S0043-1354(00)00048-8.

36. Ahmad, R. (2005). Sawdust: cost effective scavenger for the removal of chromium (III) ions from aqueous solutions, *Water Air Soil Pollute.* 163, 169–183. DOI: http://dx.doi.org/10.1007/ s11270-005-0217-x.

37. Elangovan, R., Philip, L. & Chandraraj, K. (2008). Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies, *J. Hazard Mater.* 152, 100–112.

38. Thamilarasu, P., Kumar, G.Vijaya, Tamilarasan, R., Sivakumar, V. & Karunakaran, K. (2011). Kinetic, Equilibrium and Thermodynamic studies on the removal of Cr (VI) by activated carbon prepared from Cajanus Cajan(L) Milsp seed shell, *Pol. J. Chem. Tech.* 13, 1–7. DOI: 10.2478/v100 26-011-0041-6.