



## Removal of hexavalent chromium from aqueous solution using canola biomass: Isotherms and kinetics studies

Davoud Balarak<sup>1</sup>, Yousef Mahdavi<sup>2</sup>, Fardin Gharibi<sup>3</sup>, Shahram Sadeghi<sup>4</sup>

1 Health Promotion Research Center AND Department of Environmental Health, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran

2 Department of Environmental Health, Student Research Committee, Mazandaran University of Medical Sciences, Sari, Iran

3 Deputy of Research, Kurdistan University of Medical Sciences, Sanandaj, Iran

4 Department of Environmental Health Engineering, Student Research Committee, Kurdistan University of Medical Sciences, Sanandaj, Iran

### Original Article

#### Abstract

The removing of hexavalent chromium from wastewater or decreasing its chromium (VI) content up to the permitted levels is important due to its non-biodegradation, bioaccumulation, and cancer-causing and toxic effects. In the present study, biosorption of Cr (VI) from aqueous solutions using canola was investigated. The various physicochemical parameters such as pH, initial Cr (VI) ion concentration, adsorbent dose, and equilibrium contact time were optimized in batch adsorption system. The results showed that the optimum amount of each parameter was as follows: initial concentration = 10 mg/l, pH = 3, contact time = 75 minutes, and adsorbent dosage = 5 g/l. The maximum adsorption efficiency was about 99.1%. The maximum adsorption capacity was calculated and was about 10.67 mg/g of adsorbent. Moreover, the sorption data was best fitted on the Langmuir isotherm model and adsorption kinetic is adopted with the pseudo-second-order model. The results of the present study suggest that canola can be used beneficially in treating aqueous solutions containing heavy metal ions.

**KEYWORDS:** Adsorption, Biomass, Chromium (VI), Kinetics

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#### Introduction

Due to the specific characteristics of heavy metals, they are considered as major pollutants which reduce the water quality.<sup>1-3</sup> Chromium (Cr) is a heavy metal which can be found mainly in two forms, including hexavalent and trivalent.<sup>4-6</sup> The discharge of wastewater by various industries, including electroplating,

leather tanning processes, chromite ore processing, wood preservation, alloy making, corrosion control, pigment and dyes, and metal finishing industries, is the main source of Cr in the environment.<sup>7,8</sup> Cr is introduced as a toxic element due to its adverse effects, such as irritation of lungs and stomach, cancer in the digestive tract, low growth rates in plants, and death of animals.<sup>9</sup> Therefore, the elimination of Cr from water and wastewater is an important subject. Various techniques

#### Corresponding Author:

Shahram Sadeghi

Email: shahram.snaa@yahoo.com

such as electrodeposition, membrane filtration, ion exchange, and biological processes have been proven to remove Cr from effluents.<sup>10,11</sup> However, the disadvantages of these techniques can limit their application in Cr removal.<sup>12</sup> Among the aforesaid methods, adsorption is known as an efficient and reliable method.<sup>13</sup> Although activated carbon is widely used for Cr removal, problems associated with activated carbon decrease the attraction of its application. Therefore, researchers are trying to find a low-cost and effective adsorbent. Recently, various natural material, such as red mud, banana peel, apple residues, orange peel, and azolla, have been used as effective adsorbents for the removal of heavy metals.<sup>14-16</sup> The canola stalk is a lignocellulosic waste widely produced in Iran and around the world due to the growth of canola for the production and consumption of vegetable oils. Therefore, the canola stalk is easily available and, due to its characteristics, has been used in several studies for pollutant removal.<sup>17,18</sup> The aim of the present study was the investigation of the ability of canola in Cr removal from aqueous solution and the effect of various parameters on this process, and isotherm and kinetic studies.

## Materials and Methods

In this study, canola was used as low-cost natural or agricultural waste for Cr (VI) removal from aqueous solutions. The canola stalks were collected from the research farm of the School of Agriculture, University of Tabriz, Iran. The stalks were washed several times with water to remove any contaminants and dried in the oven at 105 °C for 5 hours. Subsequently, the biomass were treated with 0.1 M H<sub>2</sub>SO<sub>4</sub> for 2 hours, washed with distilled water, and then, oven dried at 105 °C for 3 hours.<sup>19</sup> After drying, the adsorbents were sieved to obtain particle size of 18 mesh prior to being used for adsorption studies.

All the chemicals used in the present study were of analytical grade and were obtained from Merck & Co., White House Station, NJ, USA. The

specific surface area of dried canola was determined through the BET-N<sub>2</sub> method using a BET surface area analyzer (Model ASAP 2020, Micromeritics Instrument Corporation, Norcross, GA, USA) based on nitrogen adsorption-desorption isotherms at 77 K. The surface images of dried canola before and after the adsorption process were captured by a scanning electron microscope (SEM) (XL30, Philips, Amsterdam, Netherlands). An ultraviolet-visible spectrophotometer (DR5000 spectrophotometer, Hitachi, Tokyo, Japan) was used to determine the Cr (VI) content of standard and treated solutions after adsorption experiments.

The stock Cr (VI) solution (1000 mg/l) was prepared by dissolving 3.73 g of K<sub>2</sub>CrO<sub>4</sub> · 2H<sub>2</sub>O in 1000 ml of double distilled water. The desired initial concentrations for experiments were prepared by appropriate dilution of the stock Cr (VI) solution.

The batch adsorption experiments were carried out by 100 ml of Cr (VI) solution in a series of 250 ml stopper conical flasks. The pH of solution was adjusted by the addition of 0.1 N HCl or 0.1 N NaOH solutions, as required. Then, the flasks were shaken for the desired contact time in an electrically thermostated reciprocating shaker (Model LSI-3016R, Daihan LabTech Co., Ltd, Korea) at 120-125 rpm and 30 °C. The literature review indicated that the most important variables which are effective on adsorption include pH, adsorbent dose, contact time, and pollutant concentrations. Therefore, 10-100 mg/l was selected as the initial Cr (VI) concentration. The effect of adsorbent dosage (0.1-1 g), contact time (10- 180 minutes), and pH (3-8) were studied.<sup>20</sup>

The equilibrium time was estimated by sampling at regular time intervals. The samples were filtered through the Whatman no.1 paper filter (Whatman International Ltd., Maidstone, England). The UV-visible spectrophotometer was employed to determine the remaining Cr (VI) concentration in the sample solution using 1,5-diphenylcarbazide.<sup>21</sup> All the experiments were carried out in triplicate.

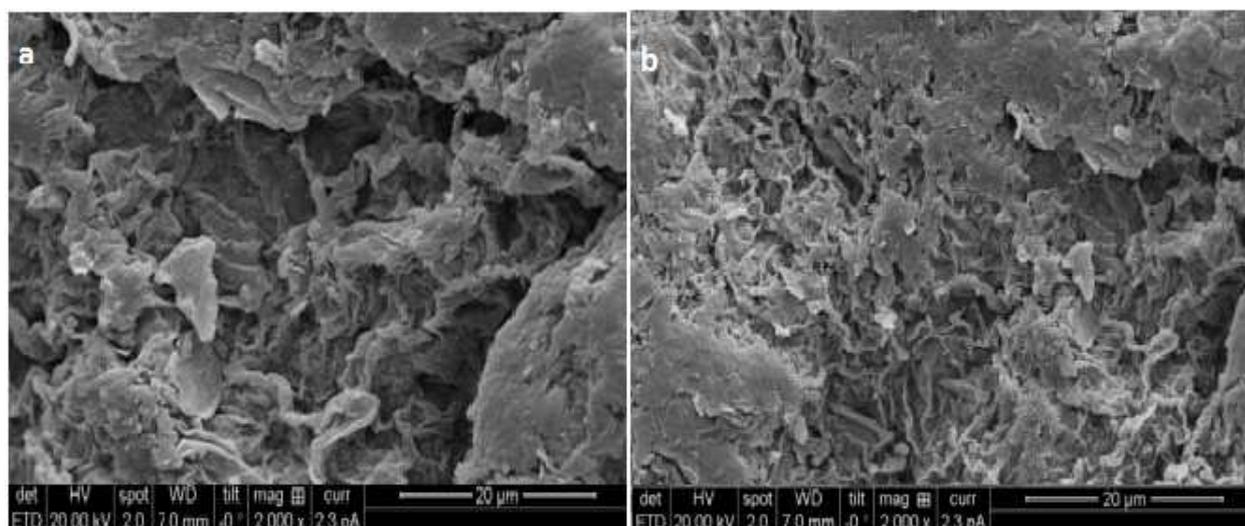


Figure 1. The Scanning electron microscopy (SEM) image of dried canola: (a) before use; (b) after use

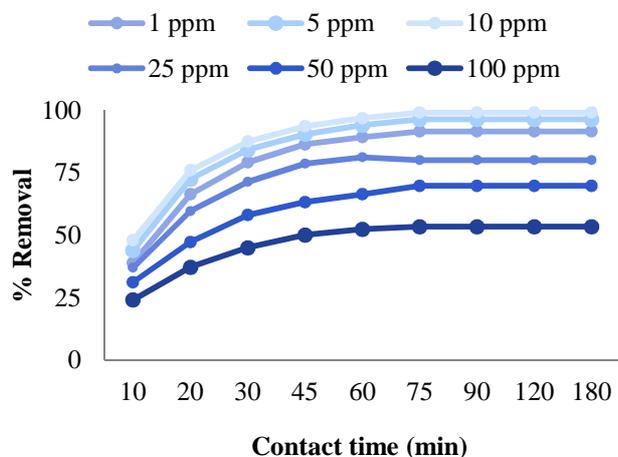
## Results and Discussion

Scanning electron microscopy (SEM) images were applied to analyze the surface structure of canola (Figure 1). Figure 1 (a) clearly shows the pore textural structure of dried canola before use. However, figure 1 (b) indicated that the clear pore textural structure is not observed on the surface of dried canola after use. This could be due to either agglomeration on the surface or the invasion of Cr into the pores of dried canola. In addition, it was found that the adsorbent has a heterogeneous surface structure with deep pores. The specific surface area of modified canola was determined and found to be 32 m<sup>2</sup>/g. Similar results were obtained for adsorption of Acid Blue 113 from aqueous solutions by canola.<sup>22</sup>

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

Among the desirable parameters, contact time is considered as a significant parameter for rapid sorption and successful practical application of biosorbents. Figure 2 shows the effect of contact time on the biosorption of Cr (VI) ions for several concentrations onto canola. The biosorption efficiency of Cr (VI) increased considerably with increasing of contact time up

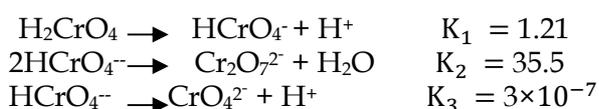
to 75 minutes, and then, it remained approximately constant. Therefore, 75 minutes was selected as optimum contact time for further experiments. Initially, the biosorption took place at a rapid rate due to the adsorption of Cr (VI) molecules on the upper surface of the biosorbent. Then, it reduced due to the slower diffusion of Cr (VI) molecules into the inner structure of the biosorbent.<sup>23</sup> The presence of a large number of exchanging sites at the start of biosorption is another reason which could help to improve the process.<sup>24</sup> Gupta et al. assessed the effect of contact time on Cr (VI) biosorption onto green algae *spirogyra* species.<sup>25</sup> The biosorption capacity (mg/g) increased quickly at the beginning, and equilibrium was attained after 90 minutes. The Cr (VI) removal efficiency decreased by increasing of initial concentration; therefore, the adsorption rate in a concentration of 10 mg/l wever, the removal efficiency decreased in higher initial concentration of Cr (VI) due to limitation of total available adsorption sites. Similarly, the biosorption of Pb<sup>+2</sup> by rice husk decreased with an increase in the Pb<sup>+2</sup> initial concentrations. It has been suggested that the available sites on the biosorbent can be the limiting factor for Pb<sup>+2</sup> removal.<sup>26</sup>



**Figure 2.** Effect of contact time and initial Cr (VI) concentration on removal efficiency (pH = 3, adsorbent dose = 5 g/L, temperature = 30 °C)

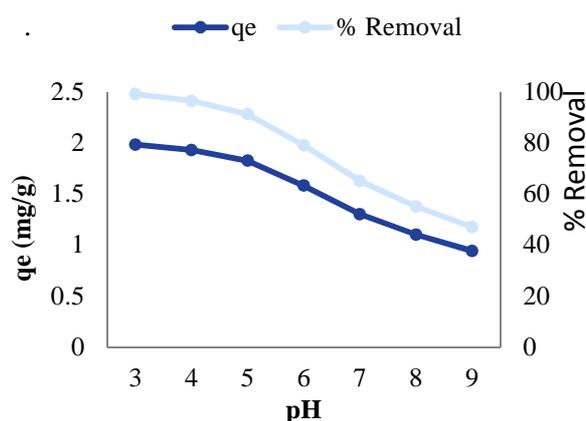
#### Effect of pH

Metal sorption depends on the solution pH. The pH of the system determines the adsorption capacity due to its influence on the surface of the canola and formation of different ions in chromium solutions. The variation of the adsorption capacity of Cr (VI) on canola with pH is shown in figure 3. The chromium ions exist in the form of  $\text{HCrO}_4^-$  at very low pH values; however, there are different forms such as  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{HCrO}_4^-$ , and  $\text{Cr}_3\text{O}_{10}^{2-}$  at pH values of higher than 6. The predominant form is  $\text{HCrO}_4^-$ . By increasing of pH value, equilibrium shifted from  $\text{HCrO}_4^-$  to  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$ .<sup>27</sup> At lower pH values, the surface of adsorbent is surrounded by hydronium ions which enhance the Cr (VI) interaction with binding sites of the biosorbent. As the pH increased, the overall surface charge on the biosorbents became negative and adsorption decreased.<sup>21</sup> The following equilibrium may be written for the Cr (VI) anions present in aqueous solutions.<sup>20</sup> The equilibrium that exists between different ionic species of chromium is as follows:



Adsorption of Cr (VI) was not significant at

pH values of more than 6 due to dual complexation of the anions  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ , and  $\text{OH}^-$  which can be adsorbed on the surface of the adsorbents; however, the predominant form in these pH values was  $\text{OH}^-$ .<sup>28</sup> Hence, it can be concluded that other mechanisms, such as physical adsorption, have played an important role and ion exchange mechanism might have reduced at lower pH values.<sup>29</sup>

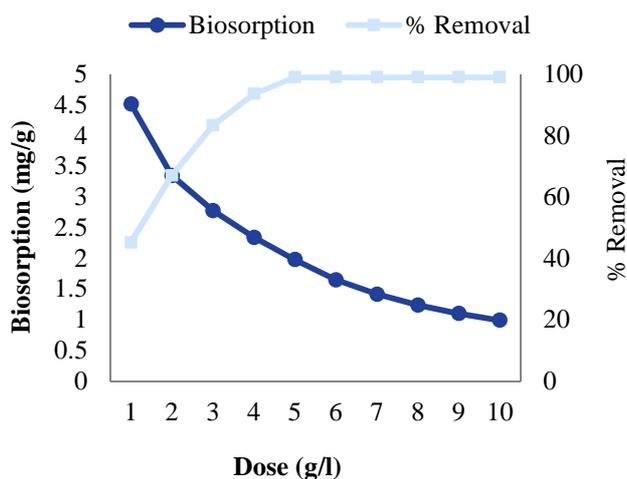


**Figure 3.** Effect of pH on Cr (VI) removal efficiency and adsorption capacity ( $C_0 = 10 \text{ mg/l}$ , adsorbent dose = 5 g/l, contact time = 75 minutes, and temperature = 30 °C)

#### Effect of biomass dosage

The effect of biomass dosage on the biosorption of Cr (VI) ions was studied using different biomass dosages in the range of 1–10 g/l (Figure 4). The results showed that biosorption efficiency is significantly dependent on the increase of biomass dosage in the solution. The percentage of metal biosorption steeply increases with biomass loading up to 5 g/l. Moreover, it was observed that the adsorption capacity decreases by increasing of biosorbent dosage. These results can be describe by the fact that although the number of available sites for biosorption increases by increasing of the biosorbent dose, biosorption sites remain unsaturated during the biosorption reaction.<sup>30,31</sup> Similarly, Kumar and Bandyopadhyay investigated the effect of biosorbent dose on the removal of  $\text{Cd}^{+2}$  by rice husk from aqueous solution.<sup>32</sup> The results showed that an increase in the biosorbent dose from 1 to 5 g/l leads to the increasing of the removal efficiency from 38% to

96%, and decreasing of the biosorption capacity from 7.5 to 1.24 mg/g. Similar results were reported for cadmium biosorption in an aqueous solution by *Saccharomyces cerevisiae*. Therefore, the optimum biomass dosage was determined as 4 g/l for further experiments.<sup>33</sup>



**Figure 4.** Effect of biomass dose on Cr (VI) biosorption on dried canola ( $C_0 = 10$  mg/l, pH = 3, contact time = 75 minutes, and temperature = 30 °C)

### Biosorption isotherm models

The capacity of a biomass can be described by equilibrium biosorption isotherm, which is characterized by certain constants which can express surface properties and affinity of the biomass. The biosorption isotherms were investigated using 3 equilibrium models, which are the Langmuir, Freundlich, and Temkin models. The applicability of the isotherm equations was compared by investigating the correlation coefficients,  $R^2$ .

The Langmuir biosorption isotherm has been successfully applied for various pollutant biosorption processes and has been extensively used for the biosorption of a solute from a liquid solution. Biosorption onto specific homogeneous sites within the adsorbent is the basic assumption of the Langmuir theory. This model can be written as follows:<sup>34</sup>

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L} \times \frac{1}{C_e}$$

where  $q_e$  is the equilibrium Cr (VI) ion concentration on the adsorbent (mg/g),  $C_e$  the equilibrium Cr (VI) concentration in the solution (mg/l),  $q_m$  the monolayer biosorption capacity of the adsorbent (mg/g), and  $K_L$  the Langmuir biosorption constant (mg/l) related to the free energy of biosorption.

The significant feature of the Langmuir isotherm model can be defined by the dimensionless constant separation factor ( $R_L$ ) which is expressed by the following equation:<sup>35</sup>

$$R_L = \frac{1}{1 + K_L C_0}$$

where  $C_0$  is the initial Cr (VI) concentration (mg/l) and  $K_L$  is the Langmuir constant (mg/l).  $R_L$  shows the nature of biosorption mechanism. Values of  $R_L$  specify the shapes of isotherms as either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or favorable ( $0 < R_L < 1$ ).

The Freundlich isotherm is an empirical relationship which shows the interaction between adsorbate molecules and heterogeneous surfaces.

The linear equation is expressed as follows:<sup>36</sup>

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where  $q_e$  is the equilibrium Cr (VI) concentration on the adsorbent (mg  $g^{-1}$ ),  $C_e$  the equilibrium Cr (VI) concentration in solution (mg  $l^{-1}$ ), and  $K_F$  is the Freundlich constant.

The Temkin isotherm model suggests an equal distribution of binding energies over the number of the exchanging sites on the surface. The linear form of the Temkin isotherm equation is represented by the following equation:<sup>35</sup>

$$q_e = B \ln A + B \ln C_e$$

where  $B = RT/b$ ,  $T$  is the absolute temperature in K,  $R$  the universal gas constant (8.314  $JK^{-1} mol^{-1}$ ),  $A$  the equilibrium binding constant, and the constant  $B$  is related to the heat of adsorption. Values of band  $A$  were calculated from the plot of  $q_e$  against  $\ln C_e$ .

The values of various isotherm constants are described in table 1. The results show that the Cr (VI) adsorption equilibrium was best defined by

the Langmuir isotherm model, which indicated that the chemisorption mechanism is involved in the adsorption of Cr (VI) on canola. In this study, the value of  $R_L$  was obtained in the range of 0–1, and this shows that the biosorption process is favorable.

Finally, the correlation coefficients ( $R^2$ ) for the Freundlich and Temkin isotherm models were lower than that of the Langmuir isotherm model.

**Table 1. Adsorption isotherm constants for the adsorption of Cr (VI) onto canola at two biomass dosages**

Isotherm models	3 g/l	6 g/l
Langmuir		
$q_m$ (mg/g)	2.950	4.450
$K_L$ (mg/l)	0.071	0.014
$R_L$	0.190	0.340
$R^2$	0.998	0.999
Freundlich		
$K_F$ (mg/g)	9.170	14.720
$n$	1.260	2.440
$R^2$	0.941	0.962
Temkin		
$A$ (g/l)	0.350	0.570
$B$	15.410	26.340
$R^2$	0.914	0.944

$q_m$ : The monolayer biosorption capacity;  $K_L$ : The Langmuir biosorption constant;  $R_L$ : The nature of biosorption mechanism;  $R^2$ : correlation coefficients;  $K_f$ : The Freundlich constant

### Biosorption kinetics

Kinetic studies are necessary to optimize the different operation conditions of biosorption. Various kinetic models have been suggested for explaining the order of reactions.

The kinetics of Cr (VI) onto canola was analyzed using pseudo-first-order and pseudo-second-order kinetic models. The applicability of these kinetic models was determined by measuring the coefficients of determination ( $R^2$ ). The higher value of  $R^2$  indicates the best applicability of the model for obtained data.

The pseudo-first-order kinetic model can be expressed as follows:<sup>36</sup>

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

where  $q_e$  and  $q_t$  are the biosorption capacity (mg/g) at equilibrium and time  $t$ , respectively,

$k_1$  is the constant rate ( $L \text{ min}^{-1}$ ) of pseudo-first-order kinetic model.

The values of  $k_1$ , calculated  $q_e$ , experimental  $q_e$ , and  $R^2$  are presented in table 2. This table showed that calculated  $q_e$  is not equal to experimental  $q_e$ , although the values of  $R^2$  are satisfactory. Mostly, the first-order kinetic model is not fitted well for the whole data range of contact time and can be applied for the preliminary stage of the biosorption mechanism.<sup>37</sup> This suggests that the uptake of Cr (VI) probably does not follow the pseudo-first-order model. Roy et al. showed that the biosorption of heavy metals onto green algae and ground rice hulls does not follow the first-order kinetic model.<sup>38</sup>

Furthermore, the pseudo-second-order kinetic model can be described as follows:<sup>36</sup>

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

where  $q_e$  is the biosorbed amount of Cr (VI) at equilibrium (mg/g) for the pseudo-second-order biosorption,  $q_t$  is the amount of biosorbed Cr (VI) at time  $t$  (mg/g), and  $k_2$  is the pseudo-second-order kinetic constant rate (g/mg/min). The values of various pseudo-second-order constants are described in table 2. The values of calculated  $q_e$  and experimental  $q_e$  are quite close. The correlation coefficients ( $R^2 = 0.999$ ) are also significant which indicates that the pseudo-second-order kinetic model is well fitted for kinetic data. The results showed that the pseudo-second-order kinetic model is more appropriate and effective than the pseudo-first-order kinetic model. Wong et al. suggested that the removal of  $\text{Cu}^{+2}$  and  $\text{Pb}^{+2}$  onto rice husk obeyed the pseudo-second-order kinetic model.<sup>26</sup>

### Conclusion

This study demonstrated the potency of canola biomass in Cr (VI) removal from aqueous solution. The results indicated that the Langmuir model provided the best correlation of the experimental data. Pseudo-second-order model was best applicable for the sorption data.

**Table 2. Kinetic parameters for the adsorption of Cr (VI) onto canola at various concentrations**

Concentration (mg/l)	Experimental $q_e$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		$K_1$	$q_e$	$R^2$	$K_2$	$q_e$	$R^2$
10	1.98	0.341	6.19	0.965	0.0021	2.24	0.999
50	6.95	0.574	13.24	0.941	0.0043	7.36	0.998
100	10.67	0.922	18.45	0.972	0.0072	11.14	0.999

$q_e$ : The equilibrium;  $K_1$ : The constant rate;  $K_2$ : The pseudo-second-order kinetic constant rate

The BET surface area of biosorbent was 32 m<sup>2</sup>/g. Low pH value is favorable for the biosorption of Cr (VI). The removal efficiency is enhanced with an increase in contact time and biosorbent dosage. The results indicated that canola is a promising biosorbent in the removal of Cr (VI) from aqueous solution.

### Conflict of Interests

Authors have no conflict of interests.

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