



Biosorption of hexavalent Chromium by the agricultural wastes of the cotton and barberry plants

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ABSTRACT

Hexavalent chromium, a highly toxic metal ion employed in industrial activities, is considered as a first priority pollutant. In this study, the capsule walls of the boll of cotton (cotton waste, CW) and the waste obtained from pruning barberry bushes (barberry waste, BW) were investigated as cheap and locally available adsorbents for Cr (VI) removal. The adsorption behavior, equilibrium, and kinetic properties have been studied through batch experiments. Specifically, the sample pH showed a significant effect and an initial pH of 2.0 was most favorable for the effective removal of chromium. The equilibrium adsorption data were well fitted to the Langmuir adsorption equation with the maximum adsorption capacities of 20.7 and 15.5 mg/g for CW and BW, respectively. The kinetic evaluations showed a rapid rate of adsorption (within 10 min) that followed the pseudo-second order kinetic model. In competitive adsorption tests, Cl⁻ had the least effect on the adsorption efficiency of Cr (VI), especially for CW. The results indicate the potential for the application of the studied agricultural wastes as adsorbents to reduce Cr (VI) concentration in aqueous samples.

1. Introduction

Mining, metal casting, leather tanning, production of fertilizer and pesticides, and electroplating are some examples of industrial activities that result in heavy metal leakage in the environment [1]. Industrial effluents have different side effects on human health; also, water resources may be polluted through inappropriate disposal or remediation [2]. Chromium, as a first priority pollutant, has a unique chemistry with three common oxidation states in the environment. Zero and hexavalent chromium are produced through industrial activities or the erosion of natural chromium deposits. Chromium (III) is a biologically active ion recognized as an important dietary element, which is essential to normal glucose, cholesterol,

carbohydrate and fat metabolism. However, hexavalent chromium is a more toxic form and its relationship with certain kinds of the cancers as well as its potential to damage vital organs has been demonstrated [2-4]. The world health organization (WHO) set the maximum residual limit of total chromium to 0.05 mg/L while the Environmental Protection Agency (EPA) proposes 100 µg/L of Cr (VI) for drinking water [5,6]. Different physicochemical and biological methods are widely used for the removal of toxic heavy metals from aqueous solutions [1,3]. Many of the existing technologies with their high capital and operational costs are not adequately efficient and this restricts their widespread application. Chemical precipitation and electrochemical methods produce a large quantity of sludge and are inefficient with a high content of

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metal ions. On the other hand, ion exchange and membrane processes are better alternatives but have high operating costs [3,7]. Adsorption, even with very low contaminant concentrations, has been widely studied as an effective technology for the removal of heavy metals from water samples. Activated carbons, mineral oxides, polymeric resins and biological materials are used as adsorbents [2,3,8]. Recently, bio-technology has also been considered as one of the most attractive areas for the treatment of polluted waters. Bio-sorption is capable of removing metal ions from dilute solutions via living systems (bacteria, fungi, yeast, algae) and certain natural materials of biological origin such as dead biomass [3,8-10]. Agricultural by-products or waste materials (wood, leaves, brans, seedspod, and compost) are also suitable examples of bio-sorbents. In contrast with expensive conventional sorbents, low-cost bio-sorbents are much more suitable for high metal ion concentrations [2,9,11]. The application of different materials such as rice straw [12], pine fruit coat [13], coffee husk [14], rice bran [15], and sawdust [16] have been reported for the removal of Cr (VI) from water samples. South Khorasan, a province located in eastern Iran, is the main producer of saffron, barberry, and jujube. Cotton is also another important agricultural product and the capsule wall of the boll of the cotton plant (CW) is a by-product. A similar situation exists in the case of the pruned branches of barberry bushes (BW). Generally, large quantities of these materials are burned annually, which leads to a reduction of the organic matter in the soil content followed by a reduction in fertility. In the present study, the role of raw CW and BW as a cheap, locally available, and biodegradable material for hexavalent chromium removal from aqueous solutions was evaluated. The experimental results were also considered to find better theoretical models to explain the adsorption kinetics and isotherms.

2. Materials and methods

2.1. Cotton and Barberry Waste Preparation

Sunlight dried samples of CW and BW were collected in the fall of 2012 from local farms in Birjand, the capital of South Khorasan. The collected materials were washed several times with hot de-ionized water to remove any contamination and dried in a hot air oven at 105 °C for 12 h to reach a constant weight. The dried materials were ground and subsequently sieved; then, uniform size particles (60-80 µm) were collected for the characterization and bio-sorption tests without any pre-treatments. The final material was kept in desiccators at room temperature (25 °C) before further experiments.

2.2. Chemical Reagents and Materials

The 1, 5-diphenylcarbazide was purchased from the Sigma-Aldrich Corporation (Missouri, USA) and used as the indicator in the spectrophotometric determination of Cr (VI). The potassium salts of dichromate ($K_2Cr_2O_7$), chloride

(KCl), nitrate (KNO_3) and sulfate (K_2SO_4) along with the sodium hydroxide (NaOH) and other metal salts were obtained from Merck (Darmstadt, Germany). The acetone, hydrochloric acid (HCl), and nitric acid (HNO_3) were also purchased from Merck. All chemicals were of analytical grade and used as received without any purification.

2.3. Apparatus

The spectrophotometric determinations were performed by means of a Shimadzu 2501 PC UV-Vis spectrophotometer (Shimadzu, Japan). Metal ions other than chromium were analyzed via an atomic absorption spectrometer (Shimadzu AA-6300G, Japan). Infrared spectra ($4000-600\text{ cm}^{-1}$) were recorded using a Perkin-Elmer 781 infrared spectrophotometer (Perkin-Elmer Ltd, Buckinghamshire, England). All pH measurements were performed on a Schott CG 843 pH/ion meter (SCHOTT Instruments GmbH, Mainz, Germany) equipped with a combined glass-calomel electrode with a standard uncertainty of 0.1 mV.

2.4. Sorption experiments

The sorption experiments were carried out in batches as follows. The stock solution (1000 mg L^{-1}) of Cr(VI) was prepared via dissolving an appropriate amount of the potassium dichromate in de-ionized water. All other chromium working solutions were further prepared through proper dilution of the stock solution in de-ionized water. The initial sample pH was adjusted by the addition of small portions of the HCl or NaOH solution. The experiments were performed in 250 mL flasks and a certain amount of the adsorbent was equilibrated with the metal ion solution (100 mL). The flasks were sealed with a silicon cap to minimize sample evaporation and mixed at 200 rpm at room temperature (25 °C). After a specific time interval, the samples were filtered through Whatman filter paper and the Cr (VI) concentration in the filtrate was determined by the colorimetric standard method (EPA Test Method 7196A) with the 1, 5-diphenylcarbazide as the indicator and spectrophotometric determination at 540 nm. The adsorption percentage of Cr (VI) by the adsorbent and the amount of the metal ion adsorbed per unit mass of the adsorbent (q_e) were calculated according to Eqs. (1) and (2), respectively:

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e \text{ (mg g}^{-1}\text{)} = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are the initial and final equilibrium concentrations of the hexavalent chromium (mg/L), V is the solution volume (L) and m is the amount of the adsorbent (g) [1, 10]. Chromium adsorption as a function of the initial sample pH, sorbent weight, equilibrium time and initial Cr (VI) concentration was studied. All the batch sorption experiments were performed in triplicate and all the

reported results were an average value. Microsoft Excel 2010 software was used to plot the charts.

2.5. Adsorption isotherms and kinetics

The amount of the adsorbed metal ion per unit mass of the adsorbent, q_e , was correlated with the liquid-phase concentration at equilibrium, C_e , using Langmuir and Freundlich equilibrium adsorption isotherms. In the Langmuir equation, the maximum adsorption capacity was obtained by fitting the experimental data to Eq. (3):

$$q_e \text{ (mg g}^{-1}\text{)} = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where, C_e is the equilibrium concentration (mg/L) of the metal ion in the liquid phase, q_e (mg g⁻¹), is the amount of chromium (VI) adsorbed per unit mass of the adsorbent at equilibrium, b is the equilibrium adsorption constant related to the affinity of the adsorption sites (L/mg) and q_{\max} is the maximum sorption capacity per the adsorbent weight (mg/g). Another useful equilibrium isotherm, based on the in-equivalent active sites, is the Freundlich isotherm and its linear form is presented in Eq. (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

In this equation, K_F (mg/g) and n are the Freundlich constants which indicate the adsorption capacity and the adsorption intensity, respectively [3,6,17-19]. The feasibility of the process was calculated by the dimensionless constant of separation factor (R_L) (Eq. 5).

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

In Eq. (5), b (L/mg) is the Langmuir constant and C_0 (mg L⁻¹) is the initial metal ion concentration. The $0 < R_L < 1$ values indicate the favorable sorption of the metal ions by the adsorbent [10,19,20]. To study the adsorption kinetics, the variation of the adsorption quantity in time was fitted to the pseudo first and second-order reaction kinetic models (Eqs. (6) and (7)):

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (7)$$

Here, q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t , respectively; K_1 (min⁻¹) and K_2 (g mg⁻¹ min⁻¹) are the first and second order rate constants [6,15,17].

3. Results and Discussion

3.1. Preliminary bio-sorption tests

The preliminary experiments were performed for the intended adsorbents and in similar conditions. Thus, CW and BW were equilibrated with different concentrations of

chromium when all other experimental conditions were identical. According to the results (Figure 1), the adsorption efficiency of about 40% was obtained with the initial concentrations of 20 and 40 mg/L for CW and BW, respectively, and these values were selected for the subsequent experiments.

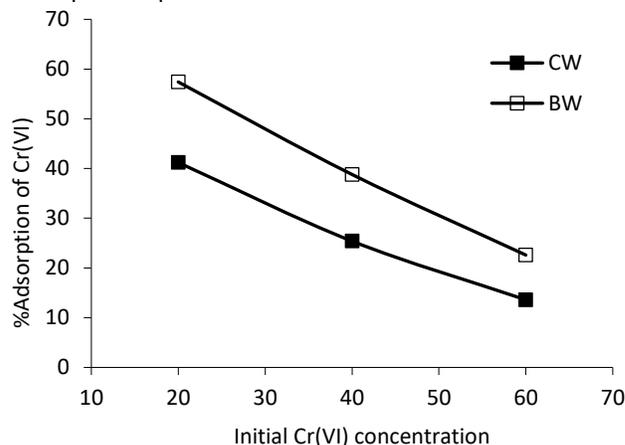


Fig. 1. Comparison of CW and BW in different initial concentrations of Cr(VI) (adsorbent = 0.1 g; contact time = 10 min; pH=3.0)

3.2. Effect of Initial Sample pH

Sample pH is one of the most important parameters in metal ion adsorption. The pH-dependence adsorption of the metal ions by bio-sorbents can be related to the surface functional groups. In fact, they can be protonated or deprotonated in respect to the sample acidity and their interaction ability with the metal ions can significantly change. The metal ion chemistry is also another parameter influenced by the solution pH. Chromium can exist in several stable forms depending on its concentration and In acidic solutions, Cr (VI) mainly exists as different anionic forms such as CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$; in the pH values between 2.0 and 6.0, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ are the dominant species [6,11,13,21]. The adsorption quantity of the hexavalent chromium was investigated in test solutions at different initial pH values (2-9). The adsorbent (0.1 g) was equilibrated with 100 mL of Cr (VI) solution and after 10 minutes, the mixture was filtered and the filtrate was analyzed for the remaining Cr(VI).

In both cases, maximum adsorption was achieved at the pH of 2.0 (Figure 2a) and significantly decreased with the increase of the sample pH. Many previous studies also showed complete removal of Cr (VI) at highly acidic solutions [1,2,11-16,21]. The dependence of the metal ion adsorption ability to the solution pH could be related to the ionic state of the functional groups in a bio-sorbent. As presented in Figure 2b, the pH value of about 6.0 can be considered as the point of zero charge (pHzpc) for BW and CW. In the solutions with pH values lower than 6.0, the adsorbent surface is positively charged, mainly due to the protonation of the surface functional groups. This effect is more pronounced at low pH values due to the presence of

a high concentration of H^+ ions. On the other hand, chromium exists as an anionic form which enhances electrostatic interactions between the adsorbent surface and metal ions. There is no significant adsorption at pH values higher than 6.0, probably due to the competition of the Cr(VI) anions with OH^- for the active sites [6,11].

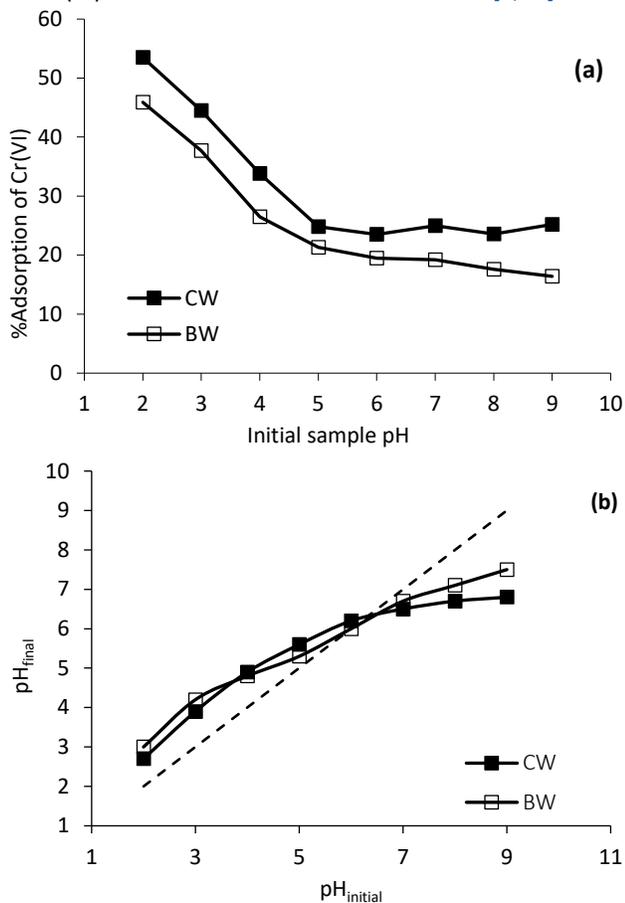


Fig. 2. (a) Effect of sample pH on the Cr (VI) adsorption (b) Determination of pHPZC (a: adsorbent = 0.1 g; contact time = 10 min; Cr(VI) initial concentration: CW=20 mg/L; BW= 40 mg/L) (b: adsorbent = 0.1 g; contact time = 10 h; NaCl=0.01 mg/L)

3.3. Effect of adsorbent weight

The effect of the adsorbent weight on the removal of Cr (VI) was investigated using different masses of CW and BW in 100 mL Cr(VI) solutions at the pH of 2.0. The quantitative removal of chromium was obtained for at least 0.3 and 0.5 g for CW and BW, respectively (Figure 3).

An improvement in the efficiency of chromium removal proportional to the adsorbent weight could be attributed to the increases in the adsorbent surface area and also the number of available active sites [22].

3.4 Kinetic studies

The rate required to establish chemical equilibrium between metal ions in the solution and adsorbent surface is another important parameter in the evaluation of a new adsorbent. Certainly, sufficient time is needed for the proper contact between metal ions and surface functional

groups. To evaluate the kinetics of Cr(VI) adsorption by the introduced adsorbents, the uptake amounts of chromium were examined at different incubation times (2-120 min). The adsorbent mass was constant and several similar experiments were performed with different initial concentrations of Cr (VI). For CW, equilibrium was established very quickly and more than 95% of initial chromium was adsorbed within 10 minutes (with an initial concentration of 20 mg//L), but longer contact times were needed for the higher concentrations. The results indicated that adsorption efficiency decreased to 65% when the chromium concentration increased to 80 mg L⁻¹ (contact time 10 min).

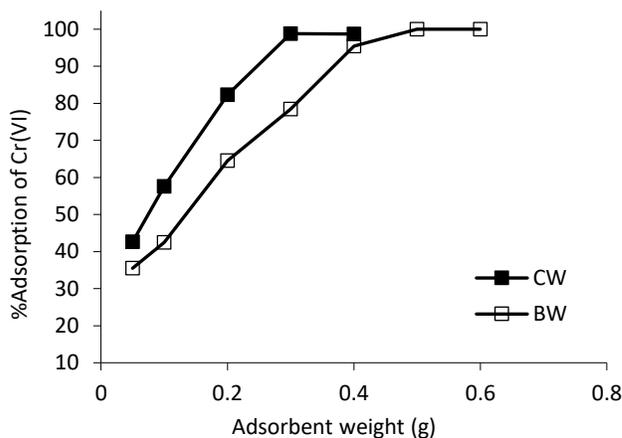


Fig. 3. Effect of adsorbent weight on the Cr (VI) adsorption (contact time = 10 min; pH=2.0; Cr (VI) initial concentration: CW=20 mg/L; BW= 40 mg/L)

A similar assessment was carried out for the BW and showed that in the initial concentration of 40 mg/L, equilibrium was established in 10 minutes; however, for higher concentrations (80 mg/L), only 75 percent of Cr (VI) was adsorbed and chromium was not completely removed even after one hour. For kinetic evaluations, the results were fitted to the pseudo-first and second order models. The straight-line plots of $\log (q_e - q_t)$ and t/q_t against time (min) were analyzed in the first and second order models, respectively. The kinetic constants and correlation coefficients are summarized in Table (1). Better R^2 values were obtained in the second-order model (for all initial concentrations) and the calculated values of equilibrium adsorption capacities showed good agreement with the experimental values (q_{exp}).

Table 1. The kinetic parameters obtained in Cr(VI) adsorption by the CW and BW

	Initial cons. (mg/L)	q_{exp} (mg/g)	pseudo-first-order			pseudo-second-order		
			r^2	q_e (mg/g)	K_1 (min^{-1})	r^2	q_e (mg/g)	K_2 ($g\ mg^{-1}min^{-1}$)
CW	20	6.75	0.9935	2.02	0.24	0.9999	6.87	0.28
BW	40	7.89	0.9557	1.54	0.15	1	7.94	0.26

CW: (adsorbent mass = 0.3 g; pH=2.0).

BW: (adsorbent mass = 0.5 g; pH=2.0).

3.5. Study of Bio-sorption Isotherms

In various reports, the primary increase of the capacity of the bio-sorbents with an increase in the initial concentration of metal ions is reported, which finally approaches a saturation value [22]. The adsorption efficiency of CW and BW was studied in different initial concentrations of Cr (VI) with the conditions of other experimental parameters constant. The results (Figure 4) show a significant decrease in the removal efficiency along with an increase in the initial metal ion concentration. At high concentrations, the number of binding sites is not sufficient and Cr (VI) ions cannot be completely adsorbed due to the saturation. On the other hand, the electrostatic repulsions between the free and adsorbed metal ions lead to a further decrease of metal ion adsorption.

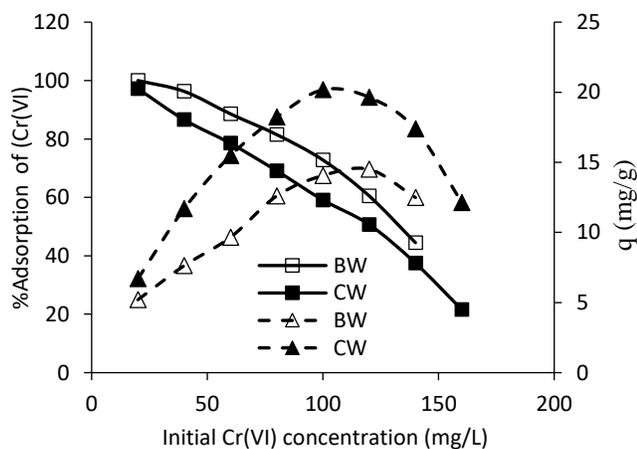


Fig. 4. Variation of the adsorption quantity (solid lines) and adsorption capacity (dotted lines) for the sorption of Cr (VI) (contact time= 10 min; pH=2.0; adsorbent, CW= 0.3 g; BW=0.5 g)

The adsorption capacity and also the feasibility of the process were evaluated by the theoretical equilibrium isotherms. The experimental data were compared by the widely applied Langmuir and Freundlich isotherm equations. The Langmuir isotherm is based on three assumptions: (a) a mono layer adsorption (b) independent adsorption ability and (c) equivalent active sites [3]. In this equilibrium isotherm, the values of q_{max} and b are obtained from the slope and the intercept of the plot C_e/q_e vs. C_e . In the Freundlich isotherm equation, the logarithmic decrease in the adsorption energy with the increasing of surface

coverage is investigated and can be attributed to surface heterogeneity. The Freundlich isotherm parameters, K_F and n , are the slope and intercept values of the plot of $\log q_e$ vs. $\log C_e$. The regression coefficients and respective isotherm parameters are summarized in Table (2). The calculated values for q_{max} by the Freundlich equilibrium isotherm were lower than the experimental adsorbed amount (q_{exp} : the flat region in Figure 4). Additionally, R^2 values were lower than the Langmuir equation. The good correlation of coefficients obtained through the Langmuir equation demonstrates the suitability of this isotherm and supports the homogeneity of surface active sites. The results show higher adsorption capacity and more favorable sorption (R_L) for CW compared with BW. The effectiveness of the suggested adsorbents was compared in terms of their adsorption capacity with some of the similar ones reported in the literature. The results are given in Table (3), and it is evident that CW and BW show good adsorption capacity for hexavalent chromium.

3.6. Interference study of the other ions

The actual water or wastewater samples usually contain a complex mixture of various ions. The presence of other ions is expected to cause interference and competition phenomena for adsorption sites. Chromium adsorption was studied in binary solutions of Cr(VI) with different concentrations of co-existing ions and under optimized conditions. In regard to the anionic form of Cr(VI), the effect of the anions Cl^- , SO_4^{2-} and NO_3^- on the removal efficiency of Cr(VI) was investigated. The results showed higher interference for BW than CW, but in both cases, Cl^- showed the lowest effect on the adsorption efficiency of chromium. The presence of chloride with concentrations of up to 10 and 20 times higher than Cr(VI) have no significant effect on the chromium removal by the BW and CW, respectively. The nitrate and sulfate ions at concentrations of 5 and 10 times higher than chromium (for BW and CW, respectively) also showed no significant interferences. The observed loss in adsorption efficiency at higher co-existing anion concentrations may result from the competition of other anions with Cr(VI) to occupy positively charged surface sites.

Table 2. Adsorption isotherm parameters obtained for the Cr(VI) adsorption by CW and BW

	q_{exp} (mg/g)	Langmuir				Freundlich		
		r^2	b (L/mg)	q_{max} (mg/g)	R_L	r^2	n	K_F (mg/g)
CW	20.2	0.9980	0.35	20.7	0.13	0.9837	4.1	7.82
BW	14.5	0.9956	0.29	15.5	0.08	0.9335	4.9	6.72

Table 3. Comparison of CW and BW with similar adsorbents in term of their adsorption capacity

Adsorbent	Adsorption system	pH	Equilibrium isotherms	q_{max} ($mg\ g^{-1}$)	Reference
Rice bran	Batch	2	Freundlich	0.07	[23]
Sawdust	Batch	3	Freundlich	1.5	[16]
Rice straw	Batch	2	Langmuir	3.15	[12]
Almond shell	Batch	3.2	Langmuir	3.4	[24]
Walnut shell	Batch	3.5	Langmuir	8.01	[24]
Hazelnut shell	Batch	3.5	Langmuir	8.28	[24]
Almond shell	Batch	2	Langmuir	10.62	[25]
Sawdust	Batch	2.5	Langmuir	12.97	[26]
Maze comb	Batch	1.5	Langmuir	13.8	[26]
Sawdust	Batch	2	Langmuir	15.82	[25]
Coconut husk	Batch	2.05	Langmuir	29	[27]
Coffee husk	Batch	2	Langmuir	44.95	[14]
CW	Batch	2	Langmuir	20.7	this work
BW	Batch	2	Langmuir	15.5	this work

3.7. Analysis of infrared spectra

The presence of various surface functional groups in bio-sorbents is a key parameter in their ability to adsorb metal ions. Direct information of the functional groups can be obtained from infrared (IR) studies. The IR spectra of CW and BW before chromium adsorption are presented in Fig. 5. The strong and broad band at $3350\ cm^{-1}$ in Figure 5a is attributed to the O-Hs stretching vibration. The width of this band indicates the presence of strong hydrogen bonds. The peak observed at $2900\ cm^{-1}$ is ascribed to the aliphatic C-H stretching vibrations. The absorption bands at 1730 and $1610\ cm^{-1}$ belong to the C=O and C=C stretching vibrations. The other band of $1510\ cm^{-1}$ confirms the presence of aromatic or rings with C=C bands. Several bands in the range of 1310 - $1010\ cm^{-1}$ refer to the C-O stretching vibrations of phenols, ethers or esters. All of these assigned bands indicate that there are different functional groups such as –OH, C=O and aromatic rings in CW. Similar bands are also observed for BW (Figure 5b).

Infrared spectra were also acquired after the bio-sorption of chromium (data are not reported here) that shows a slight change in some vibration frequencies. The main changes occurred in the frequencies of the hydroxyl and carbonyl groups; also, a decrease is clearly seen in C=C stretching vibrations and different bands in the 1310 - $1010\ cm^{-1}$ region. These changes can be attributed to the

interaction of surface functional groups, especially hydroxyl and aromatic rings, with chromium through bio-sorption.

3.8. Evaluation of the bio-sorbents in real water Samples

The adsorption efficiency of CW and BW was evaluated in the water samples polluted with Cr(VI). The ground water sample (Amir-Abad Qanat, Birjand, South Khorasan, Iran) was initially filtered with Whatman filter paper. The concentration of some of the metal ions was determined by the atomic absorption method. Its hardness was determined based on the EDTA titration method at the presence of Eriochrom Black T as the indicator. The results are listed in the caption of Table (4). The filtered water samples were spiked with Cr(VI) at different concentration levels. After sample pH adjustment, adsorption experiments were carried out under optimized conditions and each experiment was repeated three times. The average adsorption percentages and the relative standard deviation values (%RSD) are presented in Table (4). The average removal percentage of Cr(VI) at three spiked levels ranged from 92.2-98.5% with RSD < 0.2% for CW and 85.5-95.5 with RSD<0.5% for BW. The results showed the proposed adsorbents had the ability to remove Cr(VI) from water samples and can be used in the treatment of wastewater samples.

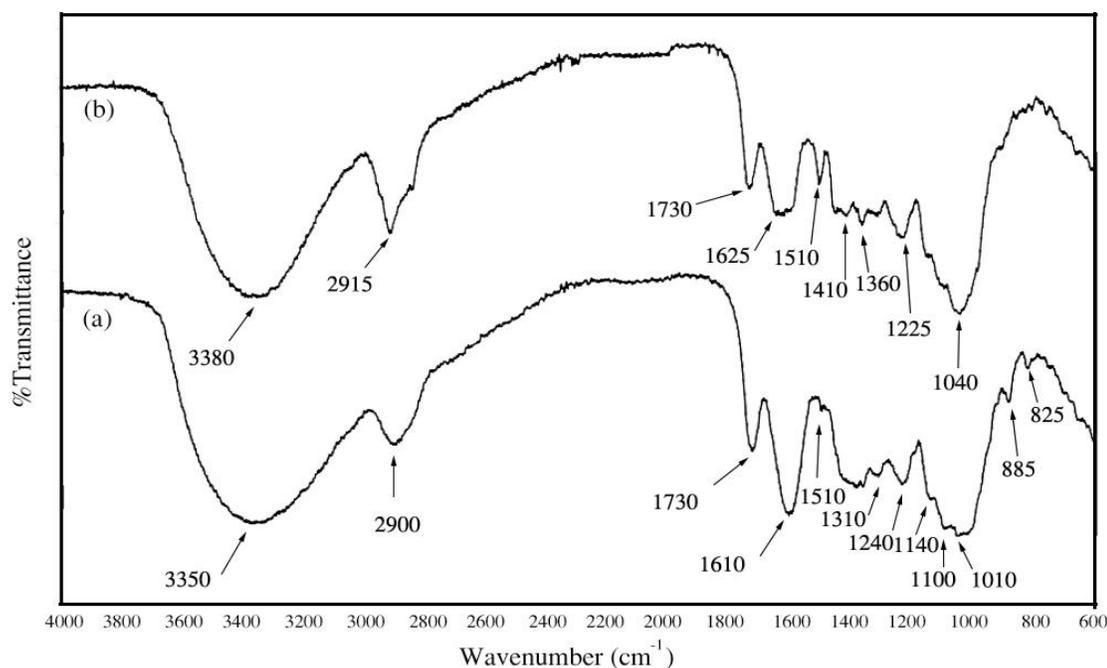


Fig. 5. The IR spectra of the CW (a) and BW (b)

Table 4. The adsorption quantity and relative standard deviation values in Cr(VI) removal from spiked Qanat samples

Sorbent	Sample No.	Spiked amount (mg/L)	% Removal	% RSD
CW	1	5	98.5	0.10
	2	10	95.2	0.17
	3	20	92.2	0.18
BW	1	20	95.5	0.02
	2	40	90.9	0.31
	3	60	82.5	0.47

Other specifications:

Temporary hardness: 132 mg/L CaCO₃, Permanent hardness: 88 mg/L CaCO₃ (Determined by the DETA titration method)

Mg=35 mg/L; Cu=0.95 mg/L; Zn=1.39 mg/L; Pb, Cr& Cd= N.d (Determined by the atomic absorption spectrometry)

5. Conclusions

Environmental pollution by heavy metal ions and their side effects on living organisms has been well demonstrated. The contamination of water by toxic heavy metals through the discharge of the industrial effluents is a worldwide environmental concern. Heavy metals are not biodegradable and tend to accumulate in the living organisms causing various diseases and disorders. In the present study, CW and BW from locally available agricultural by-products produced in South Khorasan were evaluated for the removal of Cr(VI) ions from contaminated water samples. Chromium as a common pollutant is introduced into natural waters from the discharge of industrial wastewaters. The study of various parameters indicates that sample pH plays an important role and therefore, electrostatic interactions of chromium ions with the charged surface are one of the possible mechanisms. However, reduction of the Cr(VI) to the less toxic form of Cr(III) can also be occurs at the surface functional groups. The kinetic studies indicate a rapid adsorption equilibrium that obeys the pseudo-second-order kinetic model. The

equilibrium data describes the Langmuir equilibrium isotherm well-defined adsorption behavior and the monolayer adsorption capacities (20.7 and 15.5 mg/g for CW and BW, respectively) are in good agreement with the experimental values (20.2 and 14.5 mg/g).

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