Analytical Methods

Use of modified wheat bran for the removal of chromium(VI) from aqueous solutions

K. Kaya [a], E. Pehlivan [b,*], C. Schmidt [c], M. Bahadir [c]

[a] Department of Chemistry, Süleyman Demirel University, Isparta, Turkey
[b] Department of Chemical Engineering, Selcuk University, Campus, 42079 Konya, Turkey
[c] Institute of Environmental and Sustainable Chemistry, Technische Universitaet Braunschweig, Germany

A B S T R A C T

Novel adsorbents, wheat bran (WB) and modified wheat bran (M-WB) with tartaric acid were developed and Cr(VI) adsorption was investigated by changing various parameters. The adsorption increased with contact time and become optimum at 180 min for WB and 200 min for M-WB. When the pH of the solution phase increased, some of toxic Cr(VI) reduced into less toxic Cr(III) on the WB surface. The maximum removal of Cr(VI) from the solution having an initial Cr(VI) concentration of 200 mg L^{-1} was obtained at pH 2.0 as 51.0% and 90.0% for WB and M-WB, respectively. Isotherm data of Cr(VI) adsorption on WB and M-WB was described by the Freundlich adsorption model. The adsorption capacity of 4.53 mg of Cr(VI)/g for WB and 5.28 mg of Cr(VI)/g for M-WB was obtained at pH 2 and 2.2 respectively.

1. Introduction

The removal of toxic metal ions from pollutant that comes from industry is an important matter. The scientific approach for the improving of cheaper and useful adsorbents has increased and many natural and modified adsorbents have been developed in last ten years (Kaya, Duranoglu, Beker, & Senkal, 2011; Wang et al., 2010). Different modified adsorbents are able to directly adsorb dissolved chromium from wastewater. Different treatment methods for the removal of chromium ions from wastewater streams has been used and they showed several disadvantages, such as high price of production, huge amount of toxic materials generated, and incomplete elimination of toxic metal from the wastewater (Kadivelu, Thamaraiselvi, & Namasivayam, 2001). A wide range adsorbents of agricultural residue such as barley, sugar cane have been developed and they represent a wide range of potentiality because of their individual chromium ion removing properties (Garg, Kaur, Sud, & Garg, 2009; Pehlivan, Altun, & Parlayici, 2012).

Hexavalent chromium, Cr(VI) is poisonous and carcinogenic more than the trivalent chromium, Cr(III). There are many types of chromium waste producing industries such as leather tanning salts, electroplating, metal processing, wood preservatives, batteries, reflective paints and pigments, textile dyes, surface coating, metal finishing, and canning industry.

The EPA has published a regulation for total chromium, called a maximum contaminant level, for effluents to be released to surface water is 0.1 mg L^{-1}. If industrial wastewater from any process may contain more than 0.1 mg L^{-1} chromium, the elimination all trace amounts of Cr(VI) from industrial wastes before discharging into sewerage or surface waters should be done. To solve this important problem for environmental and human health, an efficient elimination of Cr(VI) from polluted water is necessary.

Physical and chemical techniques including precipitation, extraction, adsorption, ion exchange, and membrane were used for removing toxic metal ions. Chemical precipitation is one of the traditionally most applied methods to remove the chromium from wastewater. The current existence of chromium in wastewater and their strong effect toxicity has been a research area in water treatment of research in environmental science for a long period. Major concern for the removal of metal ions from liquid waste has been concentrated upon agricultural by-products such as almond husk (Hasar, 2003), wheat bran (Singh, Hasan, Talat, Singh, & Gangwar, 2009), rice husk (Upendra & Manas, 2006), etc. Agricultural by-products consist of functional groups in the structure of lignin, cellulose, hemicellulose, ligno-humic, proteins, starch and polysaccharides (Demirbas, 2008; Mohan & Pittman, 2006). Sud researched the possible usage of agricultural wastes to remove toxic metal ions from polluted water (Sud, Mahajan, & Kaur, 2008). Agricultural by-products are preferred for the environment because they are abundant in nature, readily available and cheaper in prices (Park, Yun, & Park, 2005). The use of

* Corresponding author. Tel.: +90 332 2232127; fax: +90 332 2410635.
E-mail address: erolpehlivan@gmail.com (E. Pehlivan).

agricultural by-products as low-cost adsorbents can be thereby most advantageous.

Cellulose and lignin are the main parts of agricultural products and able to catch chromium ions. But their binding capacity for chromium differs from the origin of relevant functional groups. Hemicellulose and pectin have a general ability to bind toxic metals with their functional groups. X-ray diffraction and IR studies of wheat bran have proved that it contains various organic functional groups. The surface area of WB is 441.0 m^2/g and fixed carbon percentage is 31.78 (Singh et. al., 2009). WB contains various groups including aliphatic and phenolic hydroxyl groups, methoxyl and carbonyl groups that offer the capability to catch metal ion by donation of an oxygen electron pair to form complexes with chromium ions exist in liquid phase (Ravat, Dumonseau, & Monteil-Rivera, 2000).

Since WB is readily available and degradable material, they can be used for the Cr(VI) removal from polluted water. Citric acid, tartaric acid and oxalic acid may be used as modifiers and surface modification with them establishes carboxylic acid functional groups (–COOH) by esterification reaction, resulting in an increase of the adsorption capacity of agricultural by products (Altun & Pehlivan, 2007). Chemical modification of agricultural by-products by citric acid, epichlorohydrin and different modificators, can improve the exchange capacity and usability of them (Laszlo & Dintzis, 1994; Marshall, Wartelle, Boler, Johns, & Toles, 1999). There are some articles related to the removal of heavy metal from the aqueous phase by natural and modified WB (Ozer & Ozer, 2004; Singh, Singh, & Hasan, 2006).

WB that is a by-product of agricultural, can be used for the removal of Cr(VI) from aqueous solution because of it is abundant in nature. WB is an agricultural by-product obtained from the shell of wheat seed from the flour mill and it is economically viable, and biodegradable. WB is the place of the most nutrients of wheat that has protein, mineral, and fatty acids, and dietary fibre.

The present work was focused on developing a new modified adsorbent and an application of this with a series of experiments to remove Cr(VI) from aqueous solutions. The effects of pH, interaction time, initial Cr(VI) concentration and adsorbent quantity on the sorption of chromium ion from bulk solution were studied in this investigation.

2. Materials and methods

2.1. Materials

All the chemical substances used in the experiments were of analytical grade and deionised water was used to prepare all solutions throughout the experimental procedures. A stock solution of Cr(VI) ions with a concentration of 1×10^{-3} M was prepared by dissolving K$_2$Cr$_2$O$_7$ salt (analytical reagent grade from Merck) in deionized water. Concentrated NaOH, HCl and tartaric acid were purchased from (Merck). A series of of calibration standards were prepared by dilution of the Cr(VI) stock solution for each adsorption experiment.

2.2. Adsorbent preparation

2.2.1. Preparation of (WB)

WB was obtained from a flower milling in Isparta/Turkey. The collected adsorbent was milled and then washed with deionized water, and moisture in the WB was removed in an oven at 60 °C till constant weight. Dried WB was sieved to hold the 40–50 mesh fractions for further applications. The sieved WB was washed with deionized water and 0.1 M NaOH solution. The slurry was stirred in a magnetic stirrer for 1 h at 20 °C. After base treatment, WB was

rinsed with pure water. WB suspension was filtrated and then was left to dry overnight at 60 °C.

The chemical modification was realized by using citric acid as earlier stated (Gong, Guan, Zhao, Liu, & Ni, 2008). After washing, purified WB was mixed with 0.5 M tartaric acid (TA) at a ratio of 1.0 g to 12 ml TA. Next, the slurry was stirred at 600 rpm for 30 min at 20 °C. Then WB slurries were placed in a forced air oven and dried at 50 °C for 24 h. The thermo-chemical interaction between acid and WB was continued with increasing the temperature of the oven to 120 °C for 90 min. The TA-modified WB was washed with pure water several times and then filtered. The residue was suspended in 0.1 M NaOH and stirred for 60 min more and then washed thoroughly with pure water to remove residual alkaline material. Then the wet M-WB was dried at 50 °C until constant weight and kept as an adsorbent in a vacuum sealed beaker for the next experimental steps.

2.3. Sorption studies

A rotary shaker (Retsch, Germany) at 120 rpm and magnetic stirrer (IKAMAG RET-G) were used for the adsorption experiments. Contact time adsorption experiments were realized at room temperature (23 °C) in a plastic bottle. The solutions were agitated in the shaker for 24 h. The pH of the solution was measured using a pH meter. The effect of pH on Cr(VI) adsorption was inquired by adjusting the pH of initial solution within the range of 1.5–6. The pH of each solution was adjusted to the certain level with 0.01 M NaOH and HCl. The effect of the adsorbent amount for adsorption of Cr(VI) was studied in the batch reactor by varying the adsorbent from 0.5 to 2.5 g in the certain contact time intervals.

Isotherm studies for equilibrium were performed in completely covered 100 ml polyethylene bottles at room temperature 23 °C. The adsorption of Cr(VI) from aqueous solution onto WB and M-WB were carried out using batch containers. For the determination of the adsorption isotherms, 50 ml of Cr(VI) solution of known initial concentration was put into the beaker and mixed with a certain amount of the adsorbent on a shaker for 6 h. Initial Cr(VI) concentrations were changed in the range of 0.2×10^{-4}–2×10^{-3} M and the volume of the solution was taken as 50 ml. Following a 24 h reaction period on a shaker, the samples were taken at 15-min intervals, and adsorbent was separated from solution by filtration. Then, pH was measured and acidified samples were analyzed for equilibrium liquid phase concentration with the Varian Inc.-Vista-MPX inductively coupled plasma-optical emission spectrometer (ICP-OES) and then the residual Cr(VI) concentrations remaining in the solution phase were determined. The amount of Cr(VI) ion adsorbed was calculated using the Eq. (1).

$$q_e = (C_0 - C_e)V/M \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) ion (in mg/L), M is the mass of adsorbent (g) and V is the volume of solution (L).

Total chromium before and after adsorption was analyzed using ICP-OES. Meanwhile, the amount of Cr(VI) remaining in the solution was determined by using UV–Vis at 540 nm using 1,5 diphenyl carbazide as complexing agent (ASTM., 2009). The 1,5 diphenyl carbazide was used for the reduction of Cr(VI) ion to Cr(III) and the determination of Cr(III) in aqueous phase was realized with spectrophotometric determination at 540 nm, UV–visible Spectrophotometer.

After the mixture come to the equilibrium, it was filtered and analyzed for Cr(VI) ion content. The total chromium was measured using ICP-OES. The analysis of Cr(VI) remained in the solution phase was analyzed by using an UV–Visible Spectrophotometer, (UV–Vis Spectrophotometer, CADAS 100), based on the reaction of 1,5-diphenyl carbazide with Cr(VI) at a pH of 1.0 ± 0.2. The pink

complex was formed when 1,5-diphenyl carbazide was added into the solution phase. The determination of functional groups present in the adsorbent was realized by A Fourier transform infrared spectrometer (FT-IR) (BRUKER Tensor 27. IR). Fig. 1 and Table 1a show some functional groups in raw WB and M-WB at different wave numbers.

3. Results and discussion

3.1. Effect of contact time

The time-dependent concentrations of chromate ion were tested in a batch reactor. Fig. 2a and b shows the effect of contact time concerning the rate of adsorption. The contact time was in the range of 15 min to 24 h for the adsorption of Cr(VI) ion by using the WB and M-WB. The equilibrium between solution and solid phase reached after 180 min for WB and 200 min for M-WB respectively. The adsorption time to reach the equilibrium was chosen 200 min for WB and for M-WB respectively in the each set of experiment. The removal percentage of Cr(VI) ions increased in the initial adsorption period and it became slowly at the end of the equilibrium adsorption stage. The majority of Cr(VI) ions taken from the solution phase were accomplished between 5 and 180 min for both adsorbents. The initial rate speed of Cr(VI) ion adsorption was fast and may be explained by the large number of adsorption sites of the WB. The slower adsorption rate at the final stage of the adsorption was apparently due to the saturation of active sites of the WB with Cr(VI) ion in the solution phase. This result could be attributed to the instantaneous utilization of the available adsorbing sites on the WB lattice.

3.2. Effect of pH on Cr(VI) removal

The result of adsorption experiments gave valuable information on the mechanism of Cr(VI) adsorption. Different opinions for the Cr(VI)-binding mechanisms have been presented in the adsorption process such as: ion exchange, electrostatic attraction, chelation, complexation, chemisorption and coordination between Cr(VI) and M-WB. There is probable oxidation/reduction reaction occurrence on the surface of M-WB. Because of the complexity of using M-WB, some mechanisms were happening at the same time in different ways which depend upon the adsorbent and the solution environment. M-WB exhibits several molecular groups known to

Table 1a
IR values.

Groups	Absorbance (cm^{-1})
O–H	3330 stretching vibration
C–H	2900–2830 stretching
COOH	1728–1181 stretching
C=O	1707 stretching
C=C	1600 and 1500 aromatic skeletal vibration
CH$_2$	1430 asymmetric deformation
C–O–C	1060-1018 etching

offer ion exchange sites such as: carboxyl, hydroxyl and etc. The pH of the suspension influenced chromium adsorption on the surface of the M-WB and the dissociation of active functional groups (–OH, –COOH). WB has carboxyl groups and they have a binding capacity for Cr(VI) ion. The functional groups on the structure of the M-WB were protonated and limit the approach of cationic species as the result of repulsive forces at lower pH (pH < 2.0). As the pH of suspension increased, the degree of protonation of functional groups in the adsorbent matrix decreased, and the functional groups became more negatively charged.

Fig. 3a and b shows the influence of the equilibrium pH on the percent adsorption of Cr(VI) ions on the WB and M-WB. All pH experiments were carried out with varying pH from 1.5 to 6.05 at 23 °C and initial concentration of 200 mg L^{-1} Cr(VI). The adsorption of Cr(VI) was increased with increase of pH up to 2.2 at the beginning and then reduced with an increase in the value of pH from 2.2 to 5.0 at the end of adsorption.

Cr(VI) exists as five different species in aqueous medium: H_2CrO_4; $HCrO_4^-$; CrO_4^{2-}; $HCr_2O_7^-$; $Cr_2O_7^{2-}$ which based on pH and total Cr concentration of the suspended solution. The reduction of Cr(VI) to Cr(III) occurred after Cr(VI) was adsorbed with the M-WB under acidic circumstances of the solution due to its high redox potential value (greater than 1.3 V at standard condition). Effect of pH pointed out that WB was not only attacking Cr(VI) ion from aqueous solution but also reducing it into less toxic Cr(III) ions on the adsorbent surface. Thus, during adsorption of Cr(VI) into the lattice of WB, the reduction of Cr(VI) into Cr(III) was apparent from the feature or behaviour of Cr(VI) in aqueous solution at a low pH value. The optimum pH for the maximum adsorption of Cr(VI) was founded 2.0 for WB and 2.2 for M-WB. This situation could describe that since Cr(VI) happens in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}, in acidic solution and if the
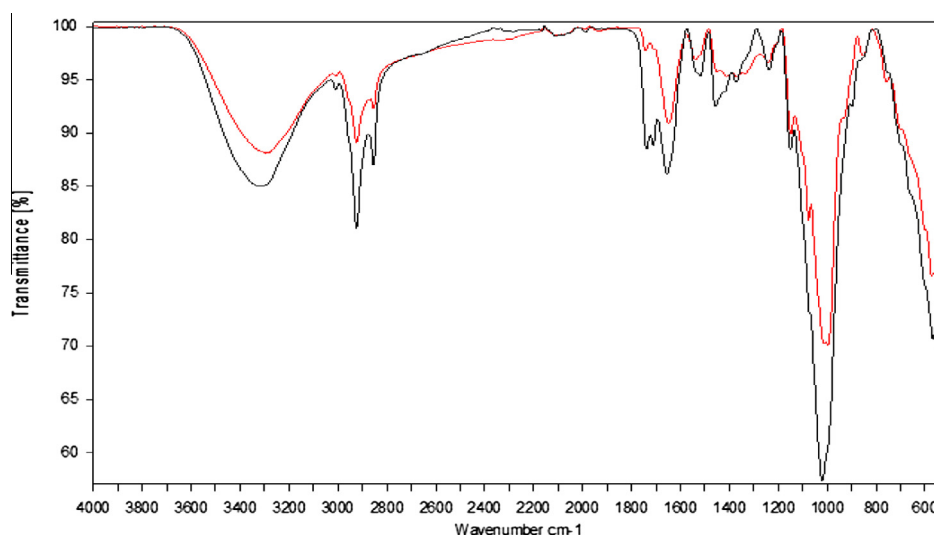

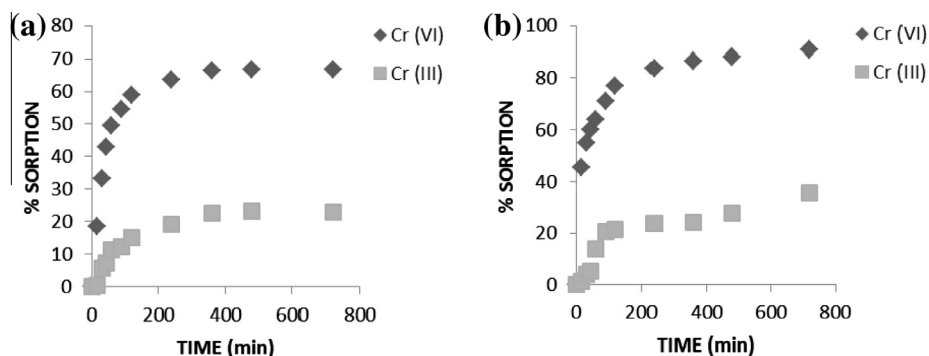**Fig. 1.** FT-IR spectra of WB and M-WB.

Fig. 2. Effect of contact time on the sorption of Cr(VI) by (a) (WB) and (b) (M-WB). (Conditions; initial concentration of Cr(VI) 1×10^{-3} M; amount of adsorbent 1 g; volume of adsorption medium, 50 ml; temperature 25 ± 1 °C; stirring rate 180 rpm; pH 2 for (WB) and pH 2.2 for (M-WB)).
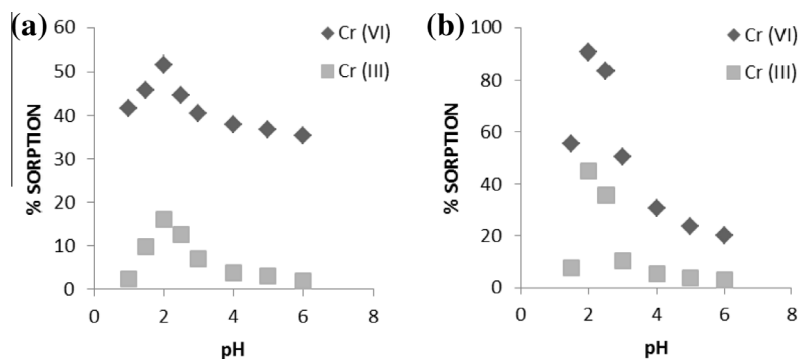

Fig. 3. Effect of pH on the sorption of Cr(VI) by (a) (WB) and (b) (M-WB). (Conditions; initial concentration of Cr(VI) 1×10^{-3} M; amount of adsorbent, 1 g; volume of adsorption medium, 50 ml; temperature, 25 ± 1 °C; stirring rate 180 rpm; stirring time, 24 h).

pH was lowered, the surface of the adsorbent to become more protonated and then a strong attraction force occurs between these oxyanions of Cr(VI) and positively charged exterior face of WB. Another phenomena was observed at low pH (2.0 and 2.2) was that the colour of the surface of adsorbent turned into greenish during the adsorption. That was the result of adsorption of Cr(III) (greenish) in a reduced form of chromium on the M-WB surface.

Park et al., reported that Cr(VI) could be eliminated from the aqueous liquid phase by natural adsorbents with two reduction mechanisms (Park, Yun, Lee, & Park, 2008): (i) Direct reduction mechanism: The reduction of Cr(VI) to Cr(III) takes place in the solution by interaction with the electron-donor groups of the adsorbent that having little reduction potential size than that of Cr(VI) ion. Cr(III) ions remain in the aqueous solution or reacts with the Cr-binding groups present in the adsorbent. The solution pH increased from initial 2.0 to the final 2.7 and a large amount of hydrogen ion was consumed accompanied by the reduction of Cr(VI) to Cr(III). (ii) An indirect reduction mechanism that describes the binding of anionic Cr(VI) ion to the positively charged groups on the adsorbent surface such as hydroxyl and carboxyl groups and the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups. Then, allowing Cr(III) into an aqueous medium due to repulsion between positively charged Cr(III) and positively charged groups in the adsorbent lattice, or complexation of Cr(III) ions with adjacent functional groups can be suggested as a mechanism for removal of chromium. Removal of Cr(VI) ion with a lignocellulose substrate extracted from WB was studied by Dupont and Guillon (2003). They showed that carboxylic and phenolic groups as the main part of the lignocellulose material and the adsorption reaction of Cr(VI) ion onto the adsorbent used up a large amount of H$^+$ ions along with the reduction of Cr(VI) to Cr(III) ion. The adsorbent surface was negatively charged at high pH and as the result of this, the large amount of negatively charged hydroxide ions in the aqueous phase existed. Both of these factors can lead to the restriction in the adsorption of negatively charge ions; $Cr_2O_7^{2-}$, CrO_4^{2-} and caused the decrease in the adsorption of Cr(VI) at a high pH value.

3.3. Effect of initial Cr(VI) ion concentration

The effect of Cr(VI) concentration on the adsorption of WB and M-WB was examined by changing the Cr(VI) concentration in the
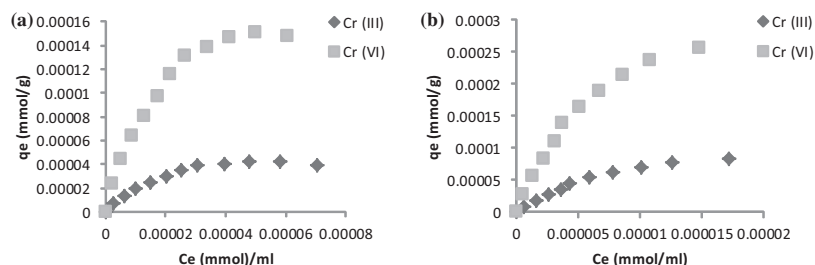

Fig. 4. Sorption isotherms of Cr(VI) on (a) (WB) and (b) (M-WB). (Conditions: initial concentration of Cr(VI), 0.2×10^{-4}–2×10^{-3}M; amount of adsorbent, 1 g; volume of adsorption medium, 50 ml; temperature, 25 ± 1 °C; stirring rate 180 rpm; stirring time, 24 h; pH 2 for (WB) and pH 2.2 for (M-WB)).

Table 1b
Freundlich and Langmuir adsorption isotherm parameters.

Adsorbent	Freundlich Isotherm			Langmuir Isotherm		
	K_f[a]	n	R^2	K_b	A_s[a]	R^2
WB	4.53	1.573	0.988	3.73	2.32×10^{-5}	0.915
M-WB	5.28	1.278	0.992	16.18	4.6×10^{-4}	0.927

[a] mmol/g dry adsorbent.

range of (0.1–1.0 mM) at a pH of 2.0 and 2.2 respectively for 200 min equilibrium time (Fig. 4a and b). The percent Cr(VI) ion adsorption on M-WB increased by raising Cr(VI) ion concentration, more Cr(VI) ions stayed in the solution phase at higher concentrations of metal because of the saturation of binding sites of M-WB. Cr(VI) removal by both adsorbents was 60% at a concentration of 0.5 mM.

Isotherm study provides information on the capacity of the adsorbent and characterization of the adsorption process was described by using a number of different isotherm models developed by researchers (Altun & Pehlivan, 2012; Graciela, Silva, & Flores, 2005; Arief, Trilestari, Sunarso, Indraswati, & Ismadji, 2008). Langmuir (Eq. (2)) and Freundlich equation (Eq. (3)) were being used for the equilibrium. The Langmuir adsorption isotherm expresses the surface as homogeneous and assumes that all the adsorption sites in the adsorbent skeleton have equal metal affinity and also marks out that adsorption of metal ion at one surface bounding part does not affect the adsorption at an adjacent part. The linear form of the Langmuir isotherms may be indicated as:

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{A_s} + \frac{1}{A_s K_b} \qquad (2)$$

where A_s (mol g^{-1}) and K_b (L mol^{-1}) are the coefficients of the equation, q_e is the weight adsorbed per unit weight of adsorbent and C_e is the chromium concentration in bulk solution at the equilibrium stage.

The Freundlich adsorption isotherm gives an empirical expression representing the equilibrium on heterogeneous surfaces and does not assume monolayer coverage.

Freundlich equation:

$$\left(\frac{x}{m}\right) = kC_e^{1/n} \qquad (3)$$

where n and k are Freundlich isotherm constants. The values of n and k can be determined from the slope and intercept of the plot respectively. By taking logs and rearranging Eqs. (3) and (4) can be written.

$$\log(\frac{x}{m}) = \log k + \frac{1}{n} \log C_e \qquad (4)$$

The adsorption curves shown in the Fig. 4a and b were single smooth and implies the formation of monolayer of Cr(VI) on the surface of M-WB. The Freundlich model has been suitable for the equilibrium hence it has the two useful parameters (n and k) (Altun & Pehlivan, 2007; Arief et al., 2008). Cr (VI) adsorption capacity was 4.53 and 5.28 mg/g for WB and M-WB respectively (Table 1b.). Various adsorbents has been used by several investigators for Cr(VI) uptake and their adsorption capacities for chromium were illustrated in Table 2.

3.4. Effect of adsorbent quantity on the adsorption

The quantity of WB was varied from 0.25 to 2.0 g and mixed for 200 min by using 0.001 M Cr(VI) solution at pH 2.0. It was seen that the equilibrium concentration of chromium in the solution phase decreased with the increasing adsorbent amount for a given

Table 2
Maximum adsorbent capacity of various commercial and low-cost adsorbents.

Adsorbent	Adsorbent capacity, (mg g^{-1})	Optimum pH	Reference
Eucalyptus bark	45.0	2.0	Sarin and Pant (2006)
Coconut tree sawdust	3.46	3.0	Selvi, Pattabi, and Kadirvelu (2001)
Pine needles Ocimum	5.36	2.0	Dakiky, Khamis, Manassra, and Mer'eb (2002)
Ocimum americanum	83.33	1.5	Levankumar, Muthukumaran, and Gobinath (2009)
Bael fruit	17.27	2.0	Anandkumara and Mandalb (2009)
WB	4.53	2.0	This study
M-WB	5.28	2.2	This study

initial Cr(VI) ion concentration, but changed slightly when adsorbent amount was more than 1.0 g/20 ml. The maximum WB and M-WB amount for adsorption of Cr(VI) was obtained as 1.5 g/ 20 ml of Cr(VI) solution.

3.5. Effect of ionic strength on Cr(VI) adsorption

The ionic strength of the solution phase affects the equilibrium between chromium and M-WB. The effect of sulphate and nitrate anions was tried by changing the concentration of these ions from 0.01 M to 0.1 M. The adsorption of Cr(VI) was slightly decreased by increasing the salt ion concentration in the solution phase and the effect of these ions on the adsorption can be neglected.

3.6. Desorption studies

Desorption studies give the idea about reusability of the adsorbent and recovery of Cr(VI). Desorption of Cr(VI) experiments were completed using 0.5 M, 50 ml HCl solution as a stripping agent and Cr(VI) loaded M-WB was shaken in the container with this acid for 24 h. The filtrate was analyzed for desorbed Cr(VI) ion. Sequential adsorption–desorption cycles were repeated three times by using the same adsorbent. Desorption results indicated that 65.0, 77.0, 80.0, 84.0 and 99% of Cr(VI) were removed from the surface of the adsorbent by using solutions having different pH values such as 2, 5, 7, 10, 13 and 14.

Percent desorption (PD) varied with the pH of stripping solution which was used for the desorption process. The bonded Cr(VI) was removed slightly at acidic or neutral pH, while they were sharply desorbed in alkaline solution owing to the formation of soluble sodium chromate. Released Cr(VI) through the pores or from the surface of M-WB was calculated by using following equation:

$$PD = (\text{amount of Cr(VI) desorbed})/(\text{amount of Cr(VI) adsorbed}) \times 100 \qquad (5)$$

4. Conclusion

WB has been successfully applied for the removal of Cr(VI) from aqueous solution. The adsorption of Cr(VI) on WB and M-WB was investigated by changing many parameters during the experiment. The adsorption value of chromium was related to contact time and attained to the equilibrium at 180 min for WB and 200 min for M-WB. The initial Cr(VI) amount in the solution phase and the

pH value of bulk solution influenced the adsorption quantity. The optimum pH for the removal of Cr(VI) by WB and M-WB was found in between 2.0 and 2.2 at the equilibrium conditions. The maximum uptake of Cr(VI) percentages was obtained as 51.0% and 90.0% for WB and M-WB, respectively. Isotherm data of Cr(VI) adsorption on WB and M-WB was modelled by Freundlich adsorption model. WB and M-WB have removed 4.53 mg 5.28 mg of Cr(VI)/g from the solution respectively. When amount of adsorbent increased in the solution phase, the retention of Cr(VI) increased in the solid phase. The results showed that the holding of Cr(VI) increased with rising the quantity of solid phase amount but adsorption density decreases and then reached the equilibrium. 0.01–0.1 M KNO_3 and K_2SO_4 ionic concentration in solution phase were not changed the adsorption amount. Chemical modification of WB gave to the structure more resistance and M-WB has higher capacity compared to raw WB. Desorption studies was also carried out with different solutions. It was found that a complete desorption of Cr(VI) was occurred when 1 M NaOH solution applied as a stripping agent.

Acknowledgements

References

Altun, T., & Pehlivan, E. (2007). Removal of copper(II) ions from aqueous solutions by walnut-, hazelnut- and almond-shells. *Clean, 35*(6), 601–606.

Altun, T., & Pehlivan, E. (2012). Removal of Cr(VI) from aqueous solutions by modified walnut shells. *Food Chemistry, 132*, 693–700.

Anandkumara, J., & Mandalb, B. (2009). Removal of Cr(VI) from aqueous solution using Bael fruit (*Aegle marmelos correa*) shell as an adsorbent. *Journal of Hazardous Materials, 168*, 633–640.

Arief, V. O., Trilestari, K., Sunarso, J., Indraswati, N., & Ismadji, S. (2008). Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies. *Clean, 36*, 937–962.

ASTM. (2009). Annual Book of ASTM Standards, 'Standard Test Methods for Chromium in Water', D1687-02R07E01.

Dakiky, M., Khamis, M., Manassra, A., & Mer'eb, M. (2002). Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Advances in Environmental Research, 6*, 533–540.

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. *Journal of Hazardous Materials, 157*, 220–229.

Dupont, L., & Guillon, E. (2003). Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. *Environmental Science & Technology, 37*, 4235–4241.

Garg, U. K., Kaur, M. P., Sud, D., & Garg, V. K. (2009). Removal of hexavalent chromium from aqueous solution by adsorption on treated sugarcane bagasse using response surface methodological approach. *Desalination, 249*(2), 475–479.

Gong, R., Guan, R., Zhao, J., Liu, X., & Ni, S. (2008). Citric acid functionalizing wheat straw as sorbent for copper removal from aqueous solution. *Journal of Health Science, 54*(2), 174–178.

Graciela, R., Silva, J., & Flores, J. A. (2005). Adsorption of chromium onto cross-linked chitosan. *Separation and Purification Technology, 44*(1), 31–36.

Hasar, H. (2003). Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk. *Journal of Hazardous Materials, B97*, 49–57.

Kadivelu, K., Thamaraiselvi, K., & Namasivayam, C. (2001). Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology, 76*, 63–65.

Kaya, I. G. B., Duranoglu, D., Beker, U., & Senkal, B. F. (2011). Development of polymeric and polymer-based hybrid adsorbents for chromium removal from aqueous solution. *Clean, 39*(11), 980–988.

Laszlo, J. A., & Dintzis, F. R. (1994). Crop residues as ion exchange materials. Treatment of soybean hull and sugar beet fiber–pulp with epichlorohydrin to improve cation-exchange capacity and physical stability. *Journal of Applied Polymer Science, 52*, 531–538.

Levankumar, L., Muthukumaran, V., & Gobinath, M. B. (2009). Batch adsorption and kinetics of chromium (VI) removal from aqueous solutions by *Ocimum americanum* L. seed pods. *Journal of Hazardous Materials, 161*(2–3), 709–713.

Marshall, W. E., Wartelle, L. H., Boler, D. E., Johns, M. M., & Toles, C. A. (1999). Enhanced metal adsorption by soybean hulls modified with citric acid. *Bioresource Technology, 69*, 263–268.

Mohan, D., & Pittman, C. (2006). Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of Hazardous Materials, B137*, 762–811.

Ozer, A., & Ozer, D. (2004). The adsorption of Cr(VI) on sulphuric acid-treated wheat bran. *Environmental Technology, 25*, 689–697.

Park, D., Yun, Y. S., Lee, H. W., & Park, J. M. (2008). Advanced kinetic model of the Cr (VI) removal by biomaterials at various pHs and temperatures. *Bioresource Technology, 99*, 1141–1147.

Park, D., Yun, Y. S., & Park, J. M. (2005). Use of dead fungal biomass for the detoxification of hexavalent chromium: Screening and kinetics. *Process Biochemistry, 40*, 2559–2565.

Pehlivan, E., Altun, T., & Parlayici, Ş. (2012). Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution. *Food Chemistry, 135*(4), 2229–2234.

Ravat, C., Dumonseau, J., & Monteil-Rivera, F. (2000). Acid/base and Cu(II) binding properties of natural organic matter extracted from wheat bran: modeling by the surface complexation model. *Water Research, 34*(4), 1327–1339.

Sarin, V., & Pant, K. K. (2006). Removal of chromium from industrial waste by using eucalyptus bark. *Bioresource Technology, 97*, 15–20.

Selvi, K., Pattabi, S., & Kadirvelu, K. (2001). Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresource Technology, 80*, 87–89.

Singh, K. K., Hasan, S. H., Talat, M., Singh, V. K., & Gangwar, S. K. (2009). Removal of Cr (VI) from aqueous solutions using wheat bran. *Chemical Engineering Journal, 151*, 113–121.

Singh, K. K., Singh, A. K., & Hasan, S. H. (2006). Low cost bio-sorbent 'wheat bran' for the removal of cadmium from wastewater: Kinetic and equilibrium studies. *Bioresource Technology, 97*, 994–1001.

Sud, D., Mahajan, G., & Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. *Bioresource Technology, 99*, 6017–6027.

Upendra, K., & Manas, B. (2006). Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology, 97*, 104–109.

Wang, X. S., Tang, Y. J., Chen, L. F., Li, F. Y., Wan, W. Y., & Tan, Y. B. (2010). Removal of Cr(VI) by Zero-valent. Iron-encapsulated alginate beads. *Clean, 38*(3), 263–267.