



Removal of hexavalent chromium ions from aqueous solution by amidoxime functionalized wool fibers

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ABSTRACT

Amidoxime functionalized wool fibers were used as the adsorbent for removal of hexavalent chromium (Cr(VI)) ions from aqueous solution. Effect of various process parameters like initial pH, contact time, initial Cr(VI) concentration, adsorbent dosage and temperature was investigated in batch experiment. The changes of the adsorbent during adsorption were determined by FT-IR and EDS-SEM. The results showed that the optimal pH for adsorption of Cr(VI) is at 3.0, the adsorption equilibrium would be achieved after 300 min. The adsorption capacity increases with the increasing of the initial concentration of Cr(VI). The adsorption process could be well described by pseudo-second-order kinetic model. The adsorption isotherm fitted well with the Langmuir model. Compared with the reported biomass adsorbents, the prepared Wool-g-AO showed excellent adsorption capacity for removal of Cr(VI) from aqueous solution.

Keywords: Amidoxime; Wool fiber; Hexavalent chromium; Adsorbent; Adsorption; Biomass

1. Introduction

Chromium is widely used in electroplating, leather tanning, coatings, dyes, pigments and other industries [1]. The two oxidation states of chromium, Cr(III) and Cr(VI), have different chemical, biological and environment properties. Cr(VI) is a primary contaminant because of its toxicity to human beings and the environment. The World Health Organization limits the value of Cr(VI) to 0.05 mg L⁻¹ in drinking water [2]. In order to reduce the concentration of Cr(VI) in industrial effluents, the ways to remove Cr(VI) from waste water include ion exchange, chemical precipitations, reduction, and adsorption [3,4], among which, adsorption has been considered to be an effective and economic method.

A variety of biosorbents have been reported for the removal of Cr(VI). Such as rice husk [5,6], coconut shell [7], *Hevea Brasilinesis* sawdust activated carbon [8], *Daucus carota L.* waste biomass [8], rice straw and neem leaves [9], *Rhodococcus* sp. AL03Ni [10], cork waste [11], fly ash [12], cone biomass [13], peanut shell [14] and *Carupta urens* inflorescence waste [15] and so on. Most of the above-mentioned adsorbents were used after some type of pretreatment.

Wool fibers, composed of α -keratin, are an abundant renewable natural polymer. About one million tons of wool fibers are produced every year world widely [16]. Although, the fine quality wool fibers are almost used by textile industry, there are still tons of poor quality wool fibers are not suitable for garment manufacturing. Moreover, tons of the used wool textiles are disposed as waste every year. Wool fibers

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have been used as an economical and eco-friendly adsorbent material for removal of heavy metal ions like Cu(II), Pb(II), Hg(II), Ni(II), Co(II), Cr(III) and U(VI) [17–21]. The multiple hydrophilic functional groups (–OH, –NH₂, –SH and –COOH) on the surface impart wool fibers with good hydrophilicity and easy modification [18]. Moreover, keratin is a major structural fibrous protein with better mechanical and chemical stability than most of other natural polymers.

In this work, amidoxime functionalized wool fiber (Wool-g-AO) was prepared for recovery of Cr(VI) from aqueous solutions. The effects of the initial pH, contact time, temperature and initial concentration of Cr(VI) on the adsorption were discussed. The isotherm equilibrium was investigated by Langmuir isotherm model. The adsorption kinetics was investigated using pseudo-second-order model. The changes of FT-IR spectra and elements on the surface of Wool-g-AO in the process of adsorption were analyzed.

2. Experimental

2.1. Materials

Wool fibers were collected from local tannery and degreased by acetone, and then were dried to a constant weight at 40°C. The stock solution of Cr(VI) (1,000 mg L⁻¹) was prepared by dissolving 2.829 g K₂Cr₂O₇ in 1,000 mL deionized water (18 MΩ). K₂Cr₂O₇, Acrylonitrile, hydroxylamine hydrochloride and N,N-dimethyl formamide (DMF) were purchased from KeLong Chemicals, China. All reagents were analytically pure and used as received without further treatment.

2.2. Preparation of amidoxime functionalized wool fibers

The amidoxime groups introduced onto wool fibers were prepared in two steps and described elsewhere [17]. Briefly, polyacrylonitrile was grafted onto wool fibers by using KMnO₄/oxalic acid redox initiation system and then the polyacrylonitrile-grafted wool fibers (Wool-g-PAN) were reacted with hydroxylamine hydrochloride solution to obtain amidoxime functionalized wool fibers (Wool-g-AO). The graft yield of the Wool-g-AO used for this study is at 78%.

2.3. Batch adsorption experiments

The initial pH of Cr(VI) solution was adjusted to the desired value by adding 0.1 M NaOH or HCl. Adsorption processes were carried out in a HZS-H thermostatic water bath shaker (Donglian Electronic, China). Briefly, 0.1 g of Wool-g-AO and 100 mL of Cr(VI) solution were placed into a flask at a set temperature for a predetermined period of time. All the experiments were performed at least three times. The values used in calculations were the average of the experimental data. The concentration of Cr(VI) before and after adsorption was measured by a 2100 DV inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer, USA). The amount of the adsorption (q_e) and the removal efficiency (%) were calculated by Eqs. (1) and (2):

$$q_e = \frac{(C_i - C_e) \times V}{M} \quad (1)$$

$$\text{removal efficiency} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where, q_e is the equilibrium adsorption capacity (mg g⁻¹), C_i and C_e are the initial and equilibrium concentration of Cr(VI) (mg L⁻¹), V is the volume of Cr(VI) solution (L), and M is the amount of Wool-g-AO used (g).

Kinetic studies were performed at 30°C using 300 mL of Cr(VI) solution at pH 3.0. Samples were withdrawn at regular intervals and the concentrations of Cr(VI) were determined to plot the amount adsorbed vs. time. The data obtained were fitted to the pseudo-second-order model Equation [22] that is shown in Eq. (3):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (3)$$

where, k is the adsorption rate constant of pseudo-second-order equation (g mg⁻¹·min). q_e and q_t are the adsorption capacities (mg g⁻¹) at equilibrium and time t (min), respectively.

The isotherm experiments were investigated at 30°C using different concentrations (20–180 mg L⁻¹) of Cr(VI) solution at pH 3.0 for 300 min. The adsorption data obtained were fitted to the Langmuir isotherm [23] that is shown in Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

where, K_L is the Langmuir constant (L mg⁻¹), q_m is the maximum adsorption capacity formed monolayer on the adsorbent (mg g⁻¹).

2.4. Characterization

The FT-IR spectra of Wool-g-AO before and after adsorption of Cr(VI) were recorded on a Nicolet IS10 FT-IR spectrophotometer (Thermo Scientific, USA). The morphology of the surface of Wool-g-AO before and after adsorption was analyzed by a JSM-F7500 Scanning electron microscope (SEM) (Japan Electron Optical Laboratory Co., LTD, Japan). The elemental composition of the Wool-g-AO was determined by a 51-XXM0019 X-Max EDXS analyzer (Oxford Instruments, UK).

3. Results and discussion

3.1. Characterization of Wool-g-AO

The FT-IR spectra of Wool-g-AO before and after adsorption of Cr(VI) are shown in Fig. 1. The band at 3,433 cm⁻¹ corresponds to the stretching vibration of –O–H; the bands at 1,649, 1,539 and 1,388 cm⁻¹ correspond to the stretching vibration of –C=O (amide I), bending vibration of –N–H (amide II) and stretching vibration of –C–N (amide III), respectively. The band at 929 cm⁻¹ is the characteristic of stretching vibration of –N–O of amidoxime group [24]. When Cr(VI) ions has been combined with amidoxime groups, the symmetry of the group will be broken, which leads the band at 929 cm⁻¹ disappearing, and the bands of amide I and amide II shifting to 1,122 and 1,135 cm⁻¹ [25]. Similar results were reported in other literatures [26]. SEM-EDS profiles give the information

about the elements on the surface of materials. The element on the surface of Wool-g-AO contains C, N, O, S, and a small amount of Ca and Al Fig. 2(a). After adsorption, Cr could be observed on the surface of the adsorbent Fig. 2(b) which illustrated that Cr(VI) ions were absorbed by the Wool-g-AO. It has been shown that, the smooth surface of natural wool became rough and the grafted polymers could be observed after copolymerization. The scale layer on Wool-g-AO has already broken [17]. More damages appeared on Wool-g-AO adsorbed Cr(VI), which may due to the oxidation susceptibility of Cr(VI) at low pH conditions [27].

3.2. Batch adsorption

3.2.1. Effect of pH on the removal of Cr(VI)

The adsorption of Cr(VI) onto Wool-g-AO and natural wool was investigated by varying the initial pH of solution from 1.0 to 6.0 with 100 mg L⁻¹ Cr(VI). All experiments were carried out at 30°C for 300 min. The results show that the adsorption is sensitive to the initial pH of the solution (Fig. 3). It is clear that the uptake of Cr(VI) by natural wool was much

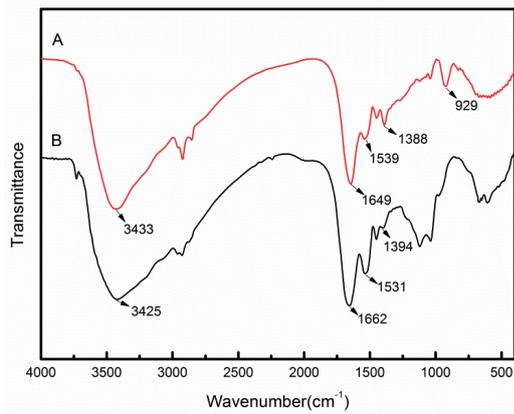


Fig. 1. FTIR Spectra of Wool-g-AO chelating fiber. (a) before adsorption; (b) after adsorption.

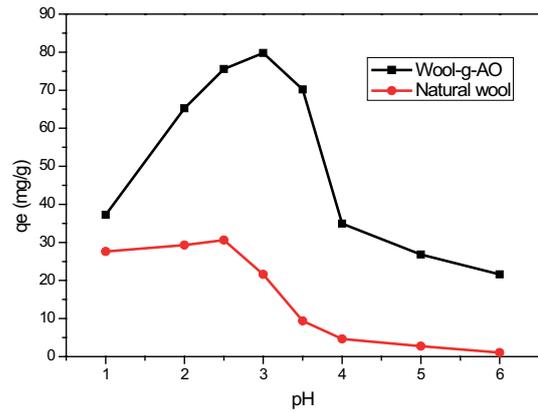


Fig. 3. Effect of pH on adsorption. Conditions: Temperature: 30°C; initial Cr(VI) concentration: 100 mg L⁻¹; time: 300 min; adsorbent dosage: 1.0 g L⁻¹.

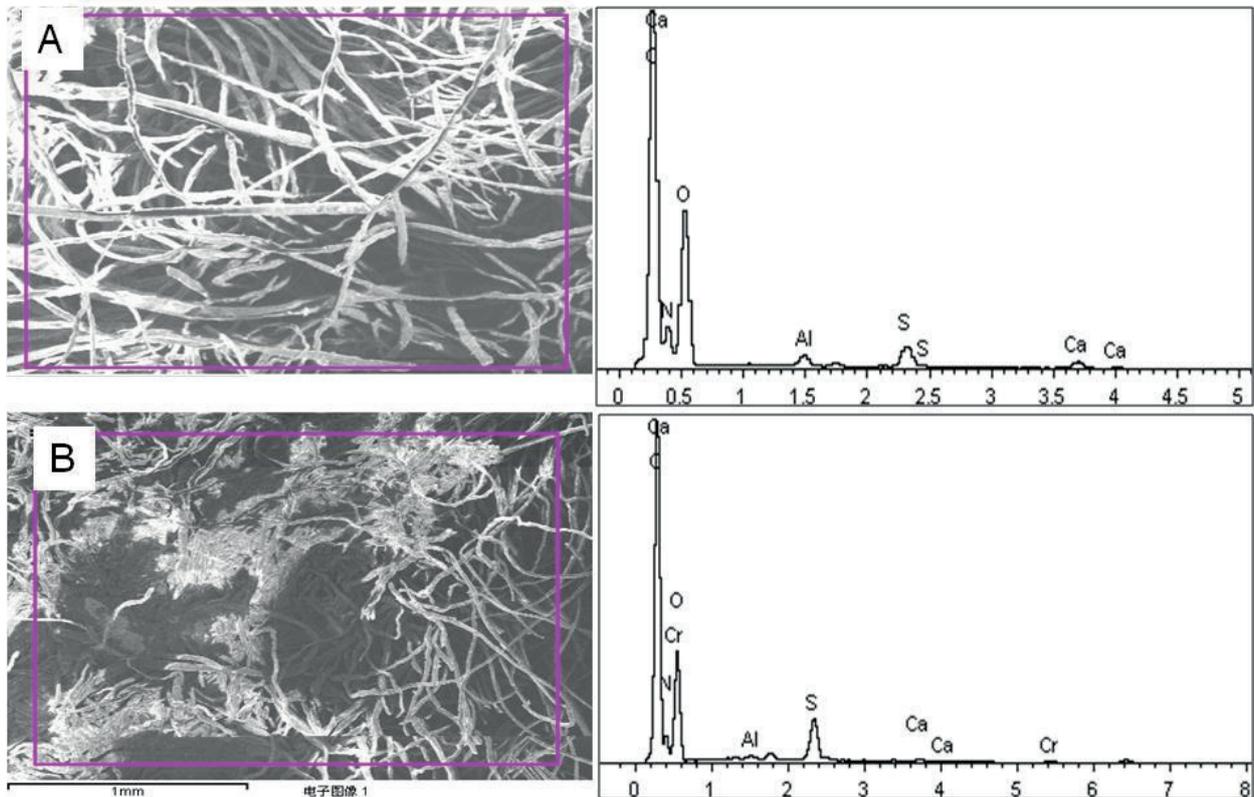


Fig. 2. The SEM-EDS spectra of Wool-g-AO fibers adsorption of Cr(VI). (a) before adsorption, (b) after adsorption.

lower than by Wool-g-AO at the same pH. The uptake of Cr(VI) by Wool-g-AO increased from 37.26 to 79.96 mg g⁻¹ as the initial pH was raised from 1.0 to 3.0. After that the uptake amount of Cr(VI) decreased when the initial pH was increased to 6.0. The adsorption capacity decreased to 21.62 mg g⁻¹ when the initial pH was at 6.0. The initial pH of the solution plays a role in the surface charge of the adsorbent and in the forms of Cr(VI) in the solution as well. When the pH is lower than 2.0, the amidoxime groups on the adsorbent could be oxidized easily [27], resulting in them a poor binding capacity to metal ions. While pH of the solution increases to 3.0, the amidoxime groups are protonated and positively charged, which will be attracted with the anion forms of Cr(VI) in the solution. Coordination of an amidoxime to a metal center is accompanied by O-ligation, and thus the species formed are stabilized by generation of a five-membered chelate ring [28]. With pH continued to increase, the amidoxime group should be gradually deprotonated, thus the binding ability to Cr(VI) would be decreased, leading poor adsorption capacity [29]. Furthermore, when the pH is lower than 3.0, Cr(VI) is predominately in the form of H₂CrO₄ and HCrO₄⁻. H₂CrO₄ is an uncharged form which is hard to combine with amidoxime groups. The fraction of HCrO₄⁻ increases when the initial pH of the solution increases, in turn leading the uptake amount increases [30]. When the pH value is over 4.0, the proportions of CrO₄²⁻, Cr₂O₇²⁻ and OH⁻ increase [31].

3.2.2. Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Cr(VI) onto Wool-g-AO was investigated at different dosages with the initial Cr(VI) concentration of 100 mg L⁻¹ at 30°C and pH 3.0. The equilibrium uptakes and percent removal are shown in Fig. 4. When the adsorbent dosage was increased from 0.5 to 8.0 g L⁻¹, the removal increased from 21.6% to 94.6%. It is clear that the Cr(VI) adsorbed increases but the amount adsorbed per unit mass decreases by increasing the adsorbent dosage. Such phenomenon is obvious because with an increase in adsorbent dosage, the number of active sites available in the adsorbent for the removal of Cr(VI) will

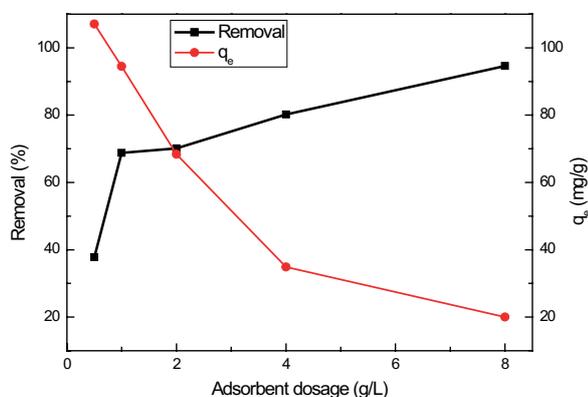


Fig. 4. Effect of adsorbent dosage. Conditions: pH: 3.0; Temperature 30; initial Cr(VI) concentration 100 mg L⁻¹; time 300 min.

be more due to the progressive saturation of the active sites. The decrease in adsorption uptake with increasing adsorbent dosage is mainly due to unsaturation of adsorption sites through the adsorption reaction [13].

3.2.3. Effect of contact time

The effect of contact time on the adsorption of Cr(VI) onto Wool-g-AO was investigated at 30°C with the initial Cr(VI) concentration of 100 mg L⁻¹ at pH 3.0. It is clear that the adsorption rate of Cr(VI) by Wool-g-AO was high during the first 150 min, then slowed down slightly and reached equilibrium at around 300 min (Fig. 5). The adsorption capacity at equilibrium is 80.0 mg g⁻¹. At the beginning of adsorption process, active sites are available for binding with Cr(VI) ions, while the most of active sites are occupied by Cr(VI) ions, the adsorption process become difficult to continue [32].

3.2.4. Effect of initial concentration of Cr(VI)

The effect of initial concentration for adsorption of Cr(VI) onto Wool-g-AO was investigated by varying the concentration from 20 to 180 mg L⁻¹ for 300 min. All experiments were performed at 30°C and pH 3.0. The results show that the uptake amount of Cr(VI) onto Wool-g-AO increased with increasing initial concentration of Cr(VI) (Fig. 6). The adsorption capacity increases linearly from 37.3 to 116.1 mg g⁻¹, with the initial concentration of Cr(VI) increased from 20 to 180 mg L⁻¹, while the removal efficiency decreased from 96.5% to 25.2%.

3.2.5. Effect of temperature

The effect of process temperature for adsorption of Cr(VI) onto Wool-g-AO was investigated by varying the temperature at 20°C, 30°C, 40°C, 50°C, respectively. It is found that the adsorption amount for Cr(VI) by Wool-g-AO increases with increasing process temperature (Fig. 7). A highly temperature for adsorption will facilitate the diffusion rate of Cr(VI) onto the surface of the adsorbent in that increases the energy of the adsorption system to overcome the electrostatic attraction between Cr(VI) and the adsorbent [33,34].

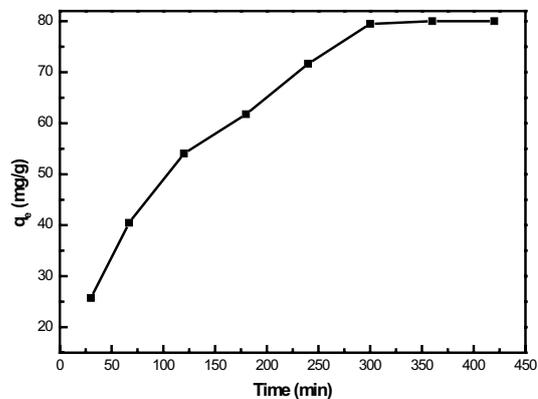


Fig. 5. Effect of contact time on adsorption. Conditions: pH: 3.0; Temperature: 30°C; initial Cr(VI) concentration: 100 mg L⁻¹; adsorbent dosage: 1.0 g L⁻¹.

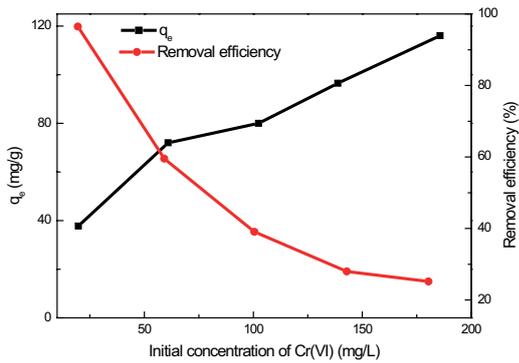


Fig. 6. Effect of initial concentration of Cr(VI) on adsorption. Conditions: pH: 3.0; Temperature: 30°C; initial Cr(VI) concentration: 100 mg L⁻¹; adsorbent dosage: 1.0 g L⁻¹.

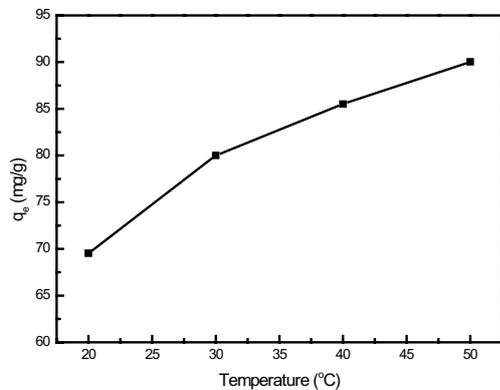


Fig. 7. Effect of temperature on adsorption. Conditions: pH: 3.0; initial Cr(VI) concentration 100 mg L⁻¹; time 300 min; adsorbent dosage 1.0 g L⁻¹.

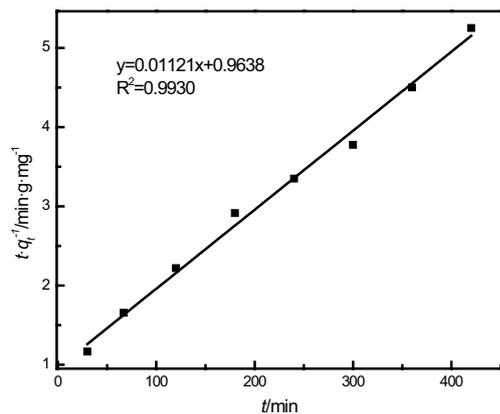


Fig. 8. The plot of pseudo second order model.

3.3. Adsorption kinetics

The main role of adsorption kinetics is to understand the adsorption mechanism [35]. The adsorption of Cr(VI) on Wool-g-AO fitted well with pseudo-second-order model (Fig. 8), with the correlation coefficient R^2 at 0.993 (Table 1). The calculated equilibrium adsorption capacity based on

Table 1
Kinetics parameters of pseudo second order model

k_1 (g mg ⁻¹ ·min)	q_e (mg g ⁻¹)	R^2
0.000126	89.21	0.993

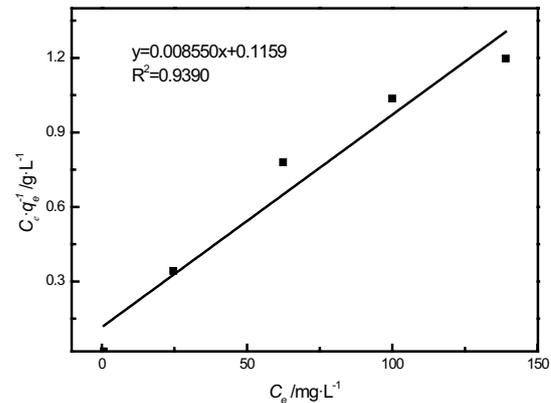


Fig. 9. The plot of Langmuir isotherm model.

Table 2
Parameters of Langmuir isotherm

k_L (L mg ⁻¹)	q_m (mg g ⁻¹)	R^2
0.07377	117.0	0.939

pseudo-second-order model is 89.2 mg g⁻¹, which is close to the experimental data (80.0 mg g⁻¹). The results indicate that the adsorption of Cr(VI) onto Wool-g-AO is dominant by chemical adsorption [36].

3.4. Adsorption isotherm and equilibrium

The adsorption isotherms reflect the metal ions between solid phase and aqueous phase which provides important parameters and better understanding on the adsorption mechanism. The data are fitted well with Langmuir isotherm model (Fig. 9, Table 2). The correlation coefficient R^2 is 0.939 and the maximum adsorption capacity of monolayer adsorption was 117.0 mg g⁻¹. A dimensionless constant R_L can predict whether an adsorption system is favorable or not, which is defined in Eq. (5).

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

When the value of R_L is between 0 and 1, the adsorption process is favorable [37]. The values of R_L were between 0 and 1 (Table 3), indicating that the adsorption of Cr (VI) onto Wool-g-AO was favorable. Different biomass adsorbents from the literature were compared in terms of the maximum adsorption capacity (q_m) of Cr(VI) (Table 4). The Wool-g-AO shows a relative higher adsorption capacity than most of

Table 3
The values of R_L at different initial Cr(VI) concentration

C_i (mg L ⁻¹)	R_L
20	0.4040
60	0.1843
100	0.1194
140	0.08828
180	0.07004

Table 4
Adsorption capacity of Cr(VI) by different adsorbents

Adsorbent	q_m (mg g ⁻¹)	References
Wool-g-AO	117.0	This work
Rice husk treated by formaldehyde	10.4	[6]
Coconut shell	23.0	[7]
<i>Hevea Brasilinesis</i> sawdust activated carbon	65.8	[8]
Rice straw	12.2	[9]
Neem leaves	15.9	[9]
<i>Rhodococcus</i> sp. AL03Ni	107.5	[10]
Cork waste	140	[11]
<i>Caryota urens</i> inflorescence	100	[14]
Peanut shells	147	[15]
<i>Pistachio</i> hull	116.3	[26]
chitosan/polypyrrole	78.6	[34]

other adsorbents, indicating that Wool-g-AO is an effective adsorbent for removal of Cr(VI) from aqueous solution.

4. Conclusions

Amidoxime functionalized wool fibers were used as a biomass adsorbent for removing hexavalent chromium ions from aqueous solution.

The optimal pH of adsorption of Cr(VI) by Wool-g-AO is at 3.0, and the adsorption capacity would increase with the increases of initial concentration of metal ion and temperature. The adsorption process reaches equilibrium after 300 min at 30°C with the initial concentration of Cr(VI) at 100 mg L⁻¹ and adsorbent dosage at 1.0 g L⁻¹.

Kinetic studies showed that the experimental data for adsorbing Cr(VI) onto Wool-g-AO fitted well with a pseudo-second-order model. Chemical adsorption was the rate-limiting step of adsorption process.

The adsorption isotherms showed well correlation with Langmuir isotherm model. In accordance with the Langmuir equation, the monolayer adsorption capacity of Cr(VI) by Wool-g-AO was found to be 117.0 mg g⁻¹. The adsorption process is favorable.

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References

- [1] D. Mohan, K.P. Singh, V.K. Singh, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, *J. Hazard. Mater.*, 135 (2006) 280–295.
- [2] X. Guan, H. Dong, J. Ma, I. Lo, Simultaneous removal of chromium and arsenate from contaminated groundwater by ferrous sulfate: batch uptake behavior, *J. Environ. Sci.*, 23 (2011) 372–380.
- [3] M. Owlad, M.K. Aroua, W.A. Daud, S. Baroutian, Removal of hexavalent chromium-contaminated water and wastewater: a review, *Water Air Soil Pollut.*, 200 (2008) 59–77.
- [4] S. Kalidhasan, N. Rajesh, Simple and selective extraction process for chromium (VI) in industrial wastewater, *J. Hazard. Mater.*, 170 (2009) 1079–1085.
- [5] S. Sugashini, K.M. Meera Sheriffa Begum, Optimization using central composite design (CCD) for the biosorption of Cr(VI) ions by cross linked chitosan carbonized rice husk (CCACR), *Clean Technol., Environ Policy*, 15 (2013) 293–302.
- [6] M. Bansal, U. Garg, D. Singha, V.K. Garg, Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk, *J. Hazard. Mater.*, 162 (2009) 312–320.
- [7] S. Kumar, B.C. Meikap, Removal of Chromium(VI) from waste water by using adsorbent prepared from green coconut shell, *Desal. Wat. Treat.*, 52 (2014) 3122–3132.
- [8] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea Brasilinesis* sawdust activated carbon, *J. Hazard. Mater.*, 124 (2005) 192–199.
- [9] G. Moussavi, B. Barikbin, Biosorption of chromium(VI) from industrial wastewater onto pistachio hull waste biomass, *Chem. Eng. J.*, 162 (2010) 893–900.
- [10] Z. Xie, F. Ji, X. Qiu, H. Huang, Adsorption performance of orange residue adsorbent to hexavalent chromium, *J. Chongqing Univ.*, 32 (2009) 192–196.
- [11] Z. Sfaksi, N. Azzouz, A. Abdelwahab, Removal of Cr (VI) from water by cork waste, *Arab. J. Chem.*, 7 (2014) 37–42.
- [12] H. Singh, V.K. Rattan, Comparison of hexavalent chromium adsorption from aqueous solutions by various biowastes and granulated activated carbon, *Indian Chem. Eng.*, 56 (2014) 12–28.
- [13] S. Mittal, U. Vaid, N.G. Nabi, Removal of hexavalent chromium from aqueous solution: a comparative study of cone biomass of "*Picea smithiana*" and activated charcoal, *Desal. Wat. Treat.*, 57 (2016) 11081–11095.
- [14] M. Ossman, M. Mansour, M. Fattah, Peanuts shell and talc powder for removal of hexavalent chromium from aqueous solutions, *Bulgarian Chem. Commun.*, 3 (2014) 629–639.
- [15] S. Rangabhashiyam, N. Selvaraju, Evaluation of the biosorption potential of a novel *Caryota urens* inflorescence waste biomass for the removal of hexavalent chromium from aqueous solutions, *J. Taiwan Inst. Chem. Eng.*, 47 (2015) 59–70.
- [16] A. Patnaik, M. Mvubu, S. Muniyasamy, A. Botha, R.D. Anandjiwala, Thermal and sound insulation materials from waste wool and recycled polyester fibers and their biodegradation studies, *Eng. Build.*, 92 (2015) 161–169.
- [17] Z. Yin, M. Chen, S. Hu, H. Cheng, Carboxylate functionalized wool fibers for removal of Cu(II) and Pb(II) from aqueous solution, *Desal. Wat. Treat.*, 57 (2016) 17367–17376. doi: 10.1080/19443994.2015.1084484
- [18] Z. Yin, J. Xiong, M. Chen, S. Hu, H. Cheng, Recovery of uranium(VI) from aqueous solution by amidoxime functionalized wool fibers, *J. Radioanal. Nucl. Chem.*, 307 (2016) 1471–1479.
- [19] Z. Yin, B. Chen, M. Chen, S. Hu, H. Cheng, Recovery of chromium(III) ions from aqueous solution by carboxylate functionalized wool fibres, *J. Soc. Leather Technol. Chem.*, 99 (2015) 101–106.
- [20] C. Ki, E. Gang, I. Um, Y. Park, Nanofibrous membrane of wool keratose/silk fibroin blend for heavy metal ion adsorption, *J. Membr. Sci.*, 302 (2007) 20–26.
- [21] M. Monier, N. Nawar, D.A. Abdel-Latif, Preparation and characterization of chelating fibers based on natural wool for removal of Hg(II), Cu(II) and Co(II) metal ions from aqueous solutions, *J. Hazard. Mater.*, 184 (2010) 118–125.

- [22] Y.S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.*, 136 (2006) 681–689.
- [23] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.*, 40 (1918) 1361–1403.
- [24] B. Gao, Y. Gao, Y. Li, Preparation and chelation adsorption property of composite chelating material poly(amidoxime)/SiO₂ towards heavy metal ions, *Chem. Eng. J.*, 158 (2010) 542–549.
- [25] J. Chang, Q. Dong, Principle and Analysis of Spectrum, Science Press: Beijing, 2012, pp. 53–97.
- [26] B. Singha, S.K. Das, Biosorption of Cr(VI) ions from aqueous solutions: kinetics, equilibrium, thermodynamics and desorption studies, *Colloid. Surf. B: Biointerfaces*, 84 (2011) 221–232.
- [27] J. Huang, M. Liu, Adsorption of Cr(e) on a novel cellulose chelation adsorbent, *J. Cell. Sci. Technol.*, 18 (2010) 7–11.
- [28] D.S. Bolotin¹, N.A. Bokach¹, V.Y. Kukushkin, Coordination chemistry and metal-involving reactions of amidoximes: relevance to the chemistry of oximes and oxime ligands. *Coordin. Chem. Rev.*, 313 (2016) 62–93.
- [29] N. Horzum, T. Shahwan, O. Parlak, M.M. Demir, Synthesis of amidoximated polyacrylonitrile fibers and its application for sorption of aqueous uranyl ions under continuous flow, *Chem. Eng. J.*, 213 (2012) 41–49.
- [30] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G. Lu, Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chem. Eng. J.*, 84 (2001) 95–105.
- [31] K. Muthukumaran, S. Beulah, Removal of chromium (VI) from wastewater using chemically activated syzygium jambolanum nut carbon by batch studies. *Proc. Environ. Sci.*, 4 (2011) 266–280.
- [32] Y. Lu, J. He, G. Luo, An improved synthesis of chitosan bead for Pb(II) adsorption, *Chem. Eng. J.*, 226 (2013) 271–278.
- [33] K. Mukherjee, Nandi, R. Nandi, D. Saha, B. Saha, Surfactant-assisted bioremediation of hexavalent chromium from contaminated water, *Desal. Wat. Treat.*, 53 (2015) 746–751.
- [34] R. Karthik, S. Meenakshi, Removal of hexavalent chromium ions from aqueous solution using chitosan/polypyrrole composite, *Desal. Wat. Treat.*, 56 (2015) 1587–1600.
- [35] S. Rengaraj, Y. Kim, C.K. Joo, J. Yi, Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: kinetics and equilibrium, *J. Colloid. Interface Sci.*, 273 (2004) 14–21.
- [36] D. Robati, Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube, *J. Nanostruct. Chem.*, 3 (2013) 55–60.
- [37] K. Hall, L. Eagleton, A. Acrivos, T. Vermeulen, Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, *Ind. Eng. Chem. Fundam.*, 5 (1996) 212–223.