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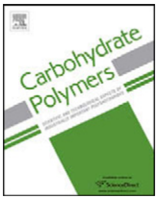

Characteristics of amine-crosslinked wheat straw and its adsorption mechanisms for phosphate and chromium (VI) removal from aqueous solution

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ABSTRACT

A new adsorbent was prepared from wheat straw (WS) after the crosslinking of amine groups. Its adsorption characteristics and operating parameters for phosphate and chromium (VI) removal were studied. BET surface area, elemental content and zeta potential analysis illustrated the physicochemical change between amine-crosslinked wheat straw (AC-WS) and WS. Significant variation in Raman shift of phosphate/chromium (VI)-loaded AC-WS was observed, and the results suggested the differential adsorption mechanisms for phosphate and chromate (VI) removal by AC-WS. The adverse effect of ionic strength on phosphate and chromate (VI) uptake suggests the possibility of ion exchange mechanisms being active in the adsorption process. The regeneration capacities for phosphate-loaded AC-WS and chromium (VI)-loaded AC-WS were 98.1% and 74.8%, respectively, which validated a potential chemical bonding between chromium (VI) and AC-WS. In addition, the adsorption capacities of AC-WS for phosphate and chromate (VI) were 1.71 and 5.68 mmol/g, respectively, providing a potential application of AC-WS for toxic heavy metals and nutrient substances removal from aqueous solutions.

1. Introduction

Increasing industrialization and urbanization worldwide had substantially ravaged our aquatic environment through the discharge of industrial and domestic wastes. These wastewaters are frequently laden with toxic heavy metals or nutrient substances in which significant amounts are deposited into the natural aquatic and terrestrial ecosystems (Wang, Chen, Chen, Wan, & Tang, 2010). Among these heavy metals, chromium is one of the priority contaminants in the environment which originates from the emissions of industry including electroplating, pigment, metal cleaning, leather processing and mining (Dinesh, Charles, & Pittman, 2006; Kalidhasan, Ganesh, Sricharan, & Rajesh, 2009). Chromium exists in natural water in two stable oxidation states, chromium (VI) and chromium (III). Chromium (VI) occurs as highly soluble and toxic chromate anions ($HCrO_4^-$ or $Cr_2O_7^{2-}$), which causes epigastric pain, nausea, vomiting, severe diarrhea, hemorrhaging and is suspected to be carcinogens and mutagens (Cheremisinoff, 2000; Gibb & Chen, 1989; Suksabye, Thiravetyan, & Nakbanpote, 2008; Wiegand, Ottenwälder, & Bolt, 1984). Phosphate is one of the major nutrients for plant growth and widely distributed in agricultural soils. Though phosphate is an essential nutrient for growth of microorganisms in aquatic environments, concentration in an excess of the desired limit is a major cause for eutrophication of lakes, rivers and sea thereby posing serious concern (Bell, 1992; Hasegawa et al., 2010). Therefore, removal of chromium (VI) and phosphate from water is significantly important from the environmental and health point of view.

Despite the environmental and health benefits of limiting chromium (VI) and phosphate release, there is a continuous need to supply them to industry and agriculture. Thus, development of treatment methods that facilitate the removal of the pollutants from wastewaters prior to discharge into the environment becomes inevitable. A wide range of physical and chemical processes is available to eliminate chromium (VI) and phosphate from water, such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, reverse osmosis, elecrodialysis, and solvent extraction (Anandkumar & Mandal, 2009; Emslie, 2010; Lakshmipathiraj, Raju, Basariya, Parvathy, & Prabhakar, 2008; Sun, Chang, Li, & Huang, 2007). However, these methods are not widely practiced due to their high operational costs and problems in the disposal of the residual sludges. In contrast, the adsorption method uses inexpensive adsorbents as an economically feasible alternative for chromium (VI) and phosphate removal due to its efficiency, low operational costs and clean operation (Šćiban, Klašnja, & Škrbić, 2008).

Recently, numerous attempts have been made in finding inexpensive and effective adsorbents produced from agricultural by-products. Adsorbents originated from agricultural by-products are particularly advantageous due to their low-cost and high availability as starting materials. In addition, the appropriate chemical composition in agricultural by-products with high contents of car-

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bohydrate polymers (e.g. cellulose and hemicelluloses) suggests a broad potential application to adsorbent production; this is due to the existence of large amount of easily available hydroxyl groups in cellulose and hemicelluloses, which can easily make a series of chemical reactions, such as esterification, etherification and copolymerization (Farag & Al-Afaleq, 2002).

In our previous work, natural wheat straw and corn straw were used as the original materials for the adsorbent production (Chen, Yue, Gao, & Xu, 2010; Wang, Gao, Yue, & Yue, 2007). However, these natural straws have a strong waxy coating which will prevent the reaction between chemical agents and carbohydrate polymers. In this work, wheat straw was pretreated by microbial fermentation, and a new adsorbent was prepared from fermented wheat straw by amination reaction. The physicochemical and sorption properties of amine-crosslinked wheat straw (AC-WS) were measured by BET surface area, elemental content, zeta potential and Raman spectrum techniques. The operating parameters that affected the adsorption, desorption and dynamic elution processes were investigated. In addition, characteristics and adsorption results were discussed and analyzed to elucidate the potential adsorption mechanisms for chromium (VI) and phosphate removal by AC-WS.

2. Materials and methods

2.1. Materials

WS was obtained from Liao Cheng, Shandong, China. The raw WS was pretreated in the biomass pool for three months so that the intertwined cellulose, semicellulose and lignin chains in WS could be degraded. The fermented WS was washed with water, dried at 60 °C for 6 h and sieved into particles with diameters from 100 to 250 μm.

2.2. Preparation of AC-WS

Ten grams of WS was reacted with 10 ml of epichlorohydrin and 9 ml of N,N-dimethylformamide in a three-neck round bottom flask at 85 °C for 60 min. Three milliliters of ethylenediamine was added and the mixture was stirred for 45 min at 85 °C, followed by adding 9 ml of triethylamine for grafting and stirring for 120 min at 85 °C. The product was washed with 250 ml of distilled water to remove the residual chemicals, dried at 60 °C for 12 h and sieved to obtain particles smaller than 250 μm in diameter (Orlando, Baes, Nishijima, & Okada, 2002; Xu, Gao, Yue, Zhong, & Zhan, 2010).

The synthetic scheme for the anion exchange resins utilizing WS as a starting material was emitted, which was shown in our previous work (Xu et al., 2010).

2.3. BET surface area, elemental, zeta potential and Raman spectroscopic analysis

Surface area measurements were performed with an automatic BET surface area analyzer (Model F-Sorb 2400, Beijing Jinaipu Technical Apparatus Co., Ltd., China). The detection limit of this instrument, using N_2, is 0.01 m^2/g. The nitrogen content of AC-WS was measured by element analyzer (Elementar Vario EL III, Germany) to evaluate the grafted amine groups in the AC-WS.

A microelectrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China) was used to determine the zeta potentials of AC-WS and WS. The AC-WS or WS samples were prepared in 25 mL of distilled water containing 0.1 g of AC-WS or WS and shaken for 15 min at 20 °C. In addition, the phosphate/chromium (VI)-loaded AC-WS samples were prepared by maintaining the suspensions contained with 0.1 g of AC-WS and 100 mg/L phosphate/chromium (VI).

Raman spectroscopic analysis was performed to provide insights into the mechanisms of phosphate/chromium (VI) interactions with AC-WS. In the Raman analysis, 0.1 g AC-WS was placed in 50 mL of phosphate solution with concentration of 0.5 mol/L. The wet solid samples and monopotassium phosphate solution (0.5 mol/L) were analyzed by Raman spectroscopy (Nicolet Almega XR Dispersive Raman, Thermo Electron Corporation, USA). The laser wavelength used in Raman measurement was 1050 nm. Similar operations were carried out for the Raman spectroscopic analysis of chromium (VI) using 0.5 mol/L of potassium dichromate solution.

2.4. Adsorption and desorption tests

The stock phosphate and chromium (VI) solutions (1000 mg/L) were prepared by dissolving 4.390 g of monopotassium phosphate (KH_2PO_4) (AR grade) and 2.829 g of potassium dichromate ($K_2Cr_2O_7$) (AR grade) in 1000 mL of distilled water. The stock solution was finally diluted to obtain standard solutions.

To investigate the effect of initial solution pH on adsorption performance, experiments were carried out at constant phosphate/chromium (VI) concentration (100 mg/L) and AC-WS dosage (2 g/L) with different initial pH from 2.0 to 12.0 at 20 °C. For the isotherm studies, 2 g/L of AC-WS was added to various concentrations of phosphate/chromium (VI) solutions at 20, 30 and 40 °C.

Salt effect experiments were carried out with NaCl, varying the concentration at 0.005 M, 0.01 M, 0.25 M, 0.05 M, 0.1 M, 0.2 M and 0.4 M. After 120 min, the samples were filtered and the remaining phosphate/chromium (VI) in the solution was determined.

A fixed-bed column with 200 mm length and 12 mm diameter was used in the column adsorption/desorption tests. The mass of AC-WS in the column is 1.0 g (bed height is 1.2 cm, after the column sorption tests, the bed height will be expanded to about 2.0 cm) and influent phosphate/chromium (VI) concentration was 200 mg/L, with flow rate of 5 ml/min. The effluent solutions were collected, and every 10 ml was selected as a sample to determine the residual concentrations in the effluent solutions. The pH values of the influent phosphate and chromium (VI) solutions were 5.12 and 4.67, respectively.

Regeneration of the AC-WS as well as recovery of adsorbate material was achieved by eluting the distilled water and hydrochloric acid (HCl) solution through the exhausted column (from top to bottom). The eluted phosphate/chromium (VI) concentrations and regeneration capacities were calculated.

3. Results and discussion

3.1. Characteristics of AC-WS and WS

3.1.1. BET surface area and elemental analysis

Results of specific surface area of AC-WS and WS are shown in Table 1. The specific surface area of AC-WS (5.3 m^2/g) is slightly lower than that of WS (6.5 m^2/g); this decrease in the specific surface area of AC-WS may be attributed to the grafting of the chemical reagents on the framework of WS, which leads to a constriction of the pore channels existing in the internal surfaces. Similar reduction in the specific surface area was reported in Krishna's work for montmorillonite (Krishna & Susmita, 2006). Pore-structure adsor-

Table 1
Change of elemental content and BET special surface area between AC-WS and WS.

	Elemental content change			BET special surface area
	N%	C%	H%	
AC-WS	6.2	42.14	8.11	5.3
WS	0.35	41.13	7.78	6.2

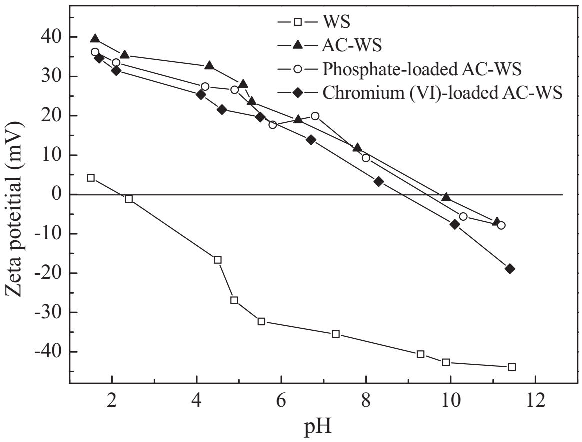

Fig. 1. Zeta potentials of WS, AC-WS and phosphate/chromium (VI)-loaded AC-WS as a function of pH.

bents such as active carbon have a specific surface area range of 500–2500 m^2/g. The low specific surface area of AC-WS illustrates the absence of surface adsorption in its potential adsorption mechanisms for various ions.

The elemental changes in carbon, hydrogen and nitrogen contents between AC-WS and WS are depicted in Table 1. As is shown in Table 1, no significant changes are observed in carbon and hydrogen contents after the amination reaction. In contrast, the nitrogen content of AC-WS is increased significantly from 0.35% to 6.20%. The sharp increase in nitrogen content of AC-WS sample suggests the large amounts of amine groups grafted in AC-WS (Orlando et al., 2002).

3.1.2. *Zeta potential analysis*

The pH–zeta potential curves of AC-WS and WS samples are presented in Fig. 1. It can be seen that the values of zeta potential in all suspensions decrease as pH increases. This may be interpreted in terms of the mechanisms of the variable charge generation. As the solution pH is increased, the surface positive charges of AC-WS and WS decrease while the surface negative charges increase due to the existence of pH-dependent functional groups in WS and AC-WS, such as hydroxyl and carboxyl groups (Jiang, Guan, Zhao, Li, & Yang, 2009). Surface hydroxyl and carboxyl groups will be protonized under the acidic conditions, resulting in the enhancement of positive charge cites in WS and AC-WS. As the pH increases, these groups will exhibit a greater negative charge and result in the decrease of the positive charge in WS and AC-WS.

The zeta potentials of AC-WS samples decrease from +39.3 mV to −7.0 mV with the increase in suspensions pH from 1.5 to 12.0; these data are relatively high as compared to those of WS samples with range of +5.2 to −45.8 mV. This illustrates the existence of increased positive-charge functional groups on the framework of AC-WS, which has been reported in our previous work for adsorbents production from agricultural by-products (Xu et al., 2010). The values of positive charges on the surface of phosphate/chromium (VI)-loaded AC-WS both decrease as comparison to those of AC-WS samples in the pH range of 1.5–12.0. The decreased zeta potential in phosphate/chromium (VI)-loaded AC-WS could be attributed to displacement of chloride ions by the adsorbed phosphate or chromium (VI) ions due to steric effects. This result was consistent with the studies of Wang for adsorption of Cr (VI) onto the modified bauxite tailings (Wang, Lan, & Hu, 2008).

3.1.3. *Raman spectrum analysis*

The Raman spectrum of phosphate/chromium (VI) solutions, AC-WS and phosphate/chromium (VI) loaded AC-WS are shown in Fig. 2. The peaks in 2961.1, 1610.7 and 1456.0 cm^{-1} are the characteristic peaks of cellulose/hemicellulose chains in AC-WS.

Raman spectrums of different forms of phosphate are presented in Fig. 2a. A new peak at 895.8 cm^{-1} is observed in the spectrum of phosphate-loaded AC-WS as compared to that of AC-WS, attributed to the adsorbed phosphate ions on the surface of AC-WS. Phosphate in a 0.5 mol L^{-1} of monopotassium phosphate solution at pH 5.0 has a characteristic peak at 898.4 cm^{-1}, which is similar to the adsorbed phosphate on the AC-WS. The results indicate that there is no strong chemical interaction between the adsorbed phosphate and the AC-WS. It suggests that phosphate is adsorbed onto the AC-WS surface through electrostatic attraction between the phosphate ions and the positively charged amine sites.

When it comes to the Raman spectrums of different forms of chromium (VI), it is observed that the characteristic peak of chromium (VI) solution (903.3 cm^{-1}) is significantly shifted to a lower wave number (845.6 cm^{-1}) after the adsorption of chromium (VI) onto AC-WS (Hu, Chen, & Lo, 2005). The significant shift of peaks between different forms of chromium (VI) as compared to those of phosphate indicates that the bonding environment between chromium (VI) and AC-WS is quite different from that of phosphate. This finding was consistent with the work of Yoon for the adsorption of perchlorate onto active carbon, which suggests that the chromium (VI) is associated on the AC-WS surface through interactions stronger than electrostatic forces (Yoon et al., 2009).

Raman shift of different forms of chromium (VI) illustrates a potential chemical bonding between chromium (VI) ions and AC-WS, which will be validated in the following adsorption and desorption tests.

3.2. *Adsorption and desorption tests*

The adsorption and desorption tests were performed to validate the adsorption mechanisms of chromium (VI) and phosphate by AC-WS. The operating parameters such as contact time, pH, temperatures and breakthrough volumes were conventional and important controlling data in the ion adsorption processes and their effects on the removal of chromium (VI) and phosphate were determined as follows.

Adsorption of ions onto any adsorbents can be by physical, chemical bonding, ion-exchange or combination of all. If adsorption is by physical bonding then the loosely bound ions can be easily desorbed with distilled water. However, if the adsorption process is by chemical bonding or ion exchange or combination of both, then desorption can be affected by stronger eluents like acid or alkali solution. Thus, desorption study can give a clear idea about the mechanism of adsorption along with the stability of the adsorbent for further use.

3.2.1. *Effect of contact time*

The adsorption capacities of AC-WS for chromium (VI) and phosphate versus the contact time are shown in Fig. 3a. The experimental data were measured at 3 h to make sure that full equilibrium was attained. As is shown in Fig. 3a, the adsorption capacity of AC-WS for chromium (VI) increases with contact time and attains a maximum value at 35 min and thereafter, it reaches a constant value. The equilibrium time for phosphate adsorption is found to be around 15 min; this illustrates a faster adsorption process for phosphate as compared to chromium (VI). When the adsorption processes reaches the equilibrium time, the adsorption capacities for phosphate and chromium (VI) are about 1.15 and 0.98 mmol/g, respectively.

Fig. 3a also shows the adsorption capacities of WS for chromium (VI) and phosphate. The WS almost has no effect on the adsorption of phosphate, and its phosphate adsorption capacity is only

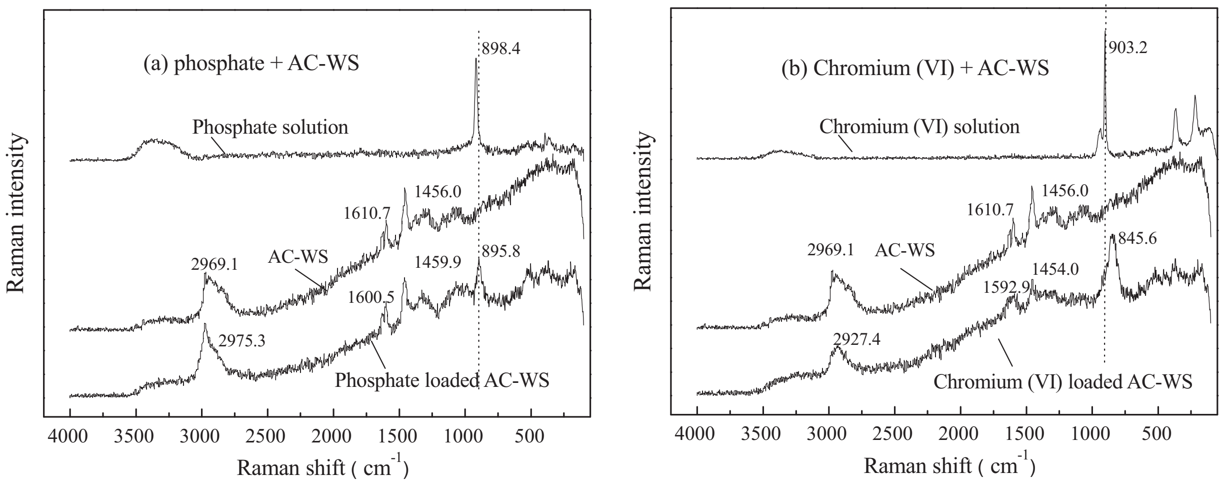

Fig. 2. Raman spectrums of phosphate/chromium (VI)-loaded AC-WS.

0.03 mmol/g. As compared to that of phosphate, a relatively high adsorption capacity of WS for chromium (VI) is observed and the adsorption capacity at equilibrium time (40 min) is about 0.35 mmol/g. Wang has reported the adsorption of chromium (VI) onto natural biomaterials such as sugarcane bagasse (0.26 mmol/g), almond shell (0.42 mmol/g), ground nut shell (0.11 mmol/g) and so forth (Wang et al., 2010). The capacity of natural biomaterials in binding of the chromium (VI) ions may be due to the partial conversion of chromium (VI) to the reduced form of chromium (III) on the surface of the biomaterials as proposed by Park, Yun, and Park (2005). According to their reaction mechanism, $HCrO_4^-$ is converted to Cr^{3+} on the surface of non-living biomass through reduction by adjacent electron-donor groups. The resulting Cr^{3+} can be then bound to anionic groups such as the hydroxyl and carboxyl groups and form complexes with the Cr-binding groups present in the WS. This complex interaction will also exist in the adsorption of chromium (VI) onto AC-WS (Miretzkya & Cirelli, 2010; Park, Lim, Yun, & Park, 2008).

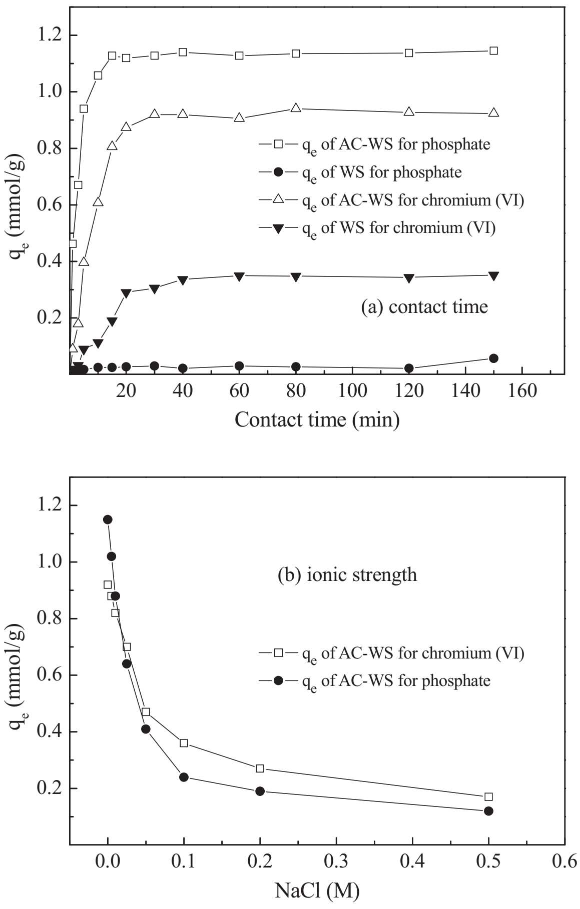

Fig. 3. Effect of contact time (a) and ionic strength (b) on the adsorption capacities for phosphate/chromium (VI).

Based on the discussion above, it is suggested that the adsorption mechanism for chromium (VI) onto AC-WS could be related to the complicated interactions including complexation, electrostatic force and so forth, as comparison to the electrostatic attraction mechanism for phosphate. Further researches on their differential adsorption mechanisms will be discussed in the following sections.

3.2.2. *Salt effect*

Wastewaters from industries contain various types of suspended solids and salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the adsorption process. The adsorption of chromate (VI) from the solution with initial concentration of 100 mg/L decreases from 0.92 mmol/g to 0.16 mmol/g as the ionic strength is increased from 0 M to 0.5 M (Fig. 3b). It is noted that the salt concentration also influences the phosphate adsorption process. The adverse effect of ionic strength on phosphate and chromate (VI) uptake suggests the possibility of ion exchange mechanisms being active in the adsorption process. As ion strength increases, the active sites on the surface of AC-WS and the active concentration of phosphate/chromate (VI) will decrease. The interaction between positive charge and negative charge (coulomb attraction) becomes weak, which inhibits the AC-WS particles and phosphate/chromate (VI) species from approaching each other.

3.2.3. *Effect of pH*

The aqueous solution pH is an important controlling parameter in the ion adsorption processes. Its role on the removal of chromium (VI) and phosphate is shown in Fig. 4a. An examination of the solution pH indicates that the equilibrium pH of the chromium (VI) and phosphate solutions keep almost constant with the initial solution pH when the initial pH is below 6.0. In contrast, a significant decrease in the equilibrium pH is observed as the initial pH increases from 7.0 to 12.0. This could be attributed to the weakly acidic carboxyl inherently in AC-WS, which would decrease the pH of solutions in mild alkali conditions.

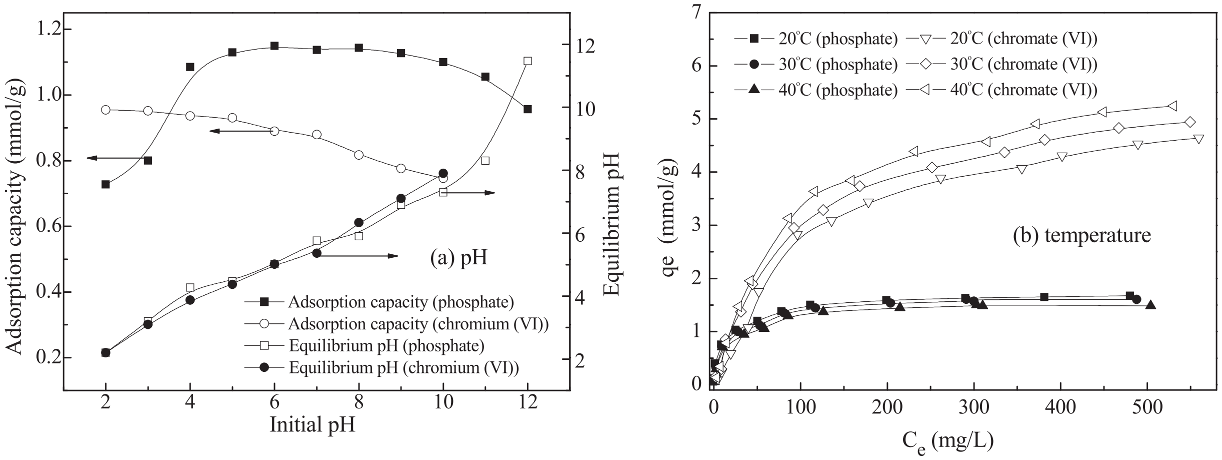

Fig. 4. Effect of pH and temperature on the adsorption capacities of AC-WS for various anions.

It is apparent that the phosphate adsorption capacity gradually increases as the initial pH increases from 2.00 to 10.0, and then decreases with the further increase in pH from 10.0 to 12.0 (Fig. 4a). As shown in some literatures, the adsorption process of some adsorbents with positive surface charges often displayed a general trend of decrease as the solution pH value increases (Krishna & Susmita, 2006; Park et al., 2008; Xu et al., 2010); this may be attributed to the less attractive or more repulsive electrostatic interaction resulting from the increased negatively charged surface sites at higher solution pH values. What is more, when the pH increases beyond 10.0, the OH^- will increase significantly, and the exchange sites for phosphate adsorption will decrease on the outer surface of AC-WS due to the presence of excess OH^- ions competing with phosphate ions for adsorption sites and a result of the adsorption capacity decreases (Ong, Lee, & Zainal, 2007).

As shown in Fig. 4a, the adsorption capacity of chromium (VI) decreases with the increase in solution pH. The result demonstrates that the removal of chromium (VI) is mainly dependent on the proton concentration. The higher the proton concentration, the higher the adsorption capacity of AC-WS for chromium (VI). Such a dependence is also observed in other studies (Bai & Abraham, 2001; Baral & Engelken, 2002). It has been explained by two potential mechanisms as follows: (i) electrostatic attraction between chromate (VI) and positively charged amine groups, which favors chromate adsorption in acidic media. (ii) Reduction process of chromium (VI) to chromium (III), which requires a large amount of proton (Miretzkya & Cirelli, 2010; Park et al., 2008). The adsorption capacity of chromium (VI) is high in acidic condition which is in agreement with the previous results in zeta potential analysis.

3.2.4. Adsorption isotherm

Temperature is an important parameter for the adsorption process. Fig. 4b illustrates the effect of temperature (20, 30 and 40 °C) on the adsorption of phosphate and chromate (VI) by AC-WS. The adsorption capacity of AC-WS for phosphate decreases as the temperature increases, while it is observed that the adsorption capacity for chromate (VI) increases with the increase in temperature; this indicates that the adsorption of chromate (VI) onto AC-WS is an endothermic process by contrast with the exothermic nature in the phosphate adsorption process. Similar results were observed in the work of Singh for the removal of chromium (VI) with rice bran and Tian for the adsorption of phosphate onto montmorillonite, which validate the differential adsorption mechanisms between the adsorption processes of phosphate and chromate (VI) by AC-WS (Singh, Rastogi, & Hasana, 2005; Tian, Jiang, Ning, & Sua, 2009).

The adsorption results were analyzed by the Langmuir and Freundlich isotherm model equations, and the data are shown in Table 2.

Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{bQ_{\max}}\frac{1}{C_e}. \tag{1}$$

Freundlich equation:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{2}$$

where C_e, the equilibrium concentration in solution (mg/L); Q_{max}, the monolayer capacity of the sorbent (mmol/g); b, the Langmuir constant (L/mol) and related to the free energy of adsorption; K_F, the Freundlich constant; n (dimensionless), the heterogeneity factor.

Results shown in Table 2 indicate that Langmuir isotherm generates the better agreement with experimental data for adsorption systems in comparison with Freundlich isotherm. The Q_{max} for phosphate and chromate (VI) at ambient temperature condition (20 °C) are 1.71 and 5.68 mmol/g, respectively, which suggests the more effective interaction between amine groups and chromate (VI) ions. Table 3 shows the comparison of the Q_{max} of various adsorbents/resins for phosphate and chromate (VI). Experimental data shown in Table 3 indicate that AC-WS is excellent in the

Table 2
Adsorption isotherms parameters.

Anions	T, K	Langmuir equation			Freundlish equation		
		Q_{max}, mmol/g	K_L	R^2	K_f	1/n	R^2
	293	1.71	0.0715	0.998	7.23	2.72	0.985
Phosphate	303	1.65	0.0472	0.993	7.50	2.90	0.971
	313	1.58	0.0371	0.998	6.38	2.25	0.954
	293	5.38	0.104	0.999	24.5	7.73	0.973
Chromium (VI)	303	5.52	0.171	0.999	26.3	6.75	0.984
	313	5.68	0.266	0.998	28.7	4.14	0.967

Table 3
Comparison of the Q_{max} of AC-WS with other adsorbents.

Anions	Resins/adsorbents	Q_{max} (mmol/g)	References
PO_4-P	AC-WS	1.71	This work
	Polystyrene PA308	0.58–0.71	Park and Na (2006)
	Calcined alunite	1.54	Özacar (2003)
	Amberlite IRA-900	1.20	Orlando et al. (2002)
	Activated carbon	0.19	Park and Na (2006)
Cr (VI)	AC-WS	5.68	This work
	Bagasse fly-ash	5.00	Gupta, Morhan, Sharma, and Park (1999)
	Amberlite IRA-400	8.46	Marshall and Wartelle (2006)
	Amberlite IRA-900	2.88	Baes, Okuda, and Nishijima (1997)
	Activated carbon	0.11	Baes et al. (1997)

adsorption of phosphate and chromate (VI), and can be in competition with some commercially available adsorbents; this provides strong evidence of the potential applications of AC-WS for toxic heavy metals or nutrient substances removal from aqueous solutions.

3.2.5. Column adsorption and desorption

When the sorption zone moves up and the upper edge of this zone reaches the bottom of the column, the effluent concentration starts to rise rapidly. This is called the breakthrough point. The desired breakthrough point is determined to be 0.1 C_t/C_0. The point where the effluent concentration reached 95% ($C_t/C_0 = 0.95$) of its influent value is called the point of column exhaustion. The results in Fig. 5a present the column adsorption of AC-WS for phosphate and chromate (VI). The breakthrough points for phosphate and chromate (VI) occur at the breakthrough volumes of 170 and 710 ml, respectively. As the phosphate and chromate (VI) solutions continue to flow into the column, the two fixed columns gradually become saturated with phosphate and chromate (VI) ions and become less effective for further adsorption. The points on the S-shaped curve at which the phosphate and chromate (VI) concentrations approach their exhaustion values are about 490 and 1170 ml, respectively. When the effluent phosphate and chromate (VI) concentrations reach the influent concentrations, the calculated q_{ed} at these points are 1.62 and 5.17 mmol/g, respectively.

The dynamic desorption experiments for AC-WS adsorbing phosphate and chromate (VI) in a saturated state were conduced using distilled water and 0.1 mol/L of HCl solution as eluents. The desorption capacities of AC-WS eluted by distilled water are only 3.5% and 3.2% for phosphate and chromate (VI), respectively; this illustrates the insignificance of physical bonding in the adsorption of phosphate and chromate (VI) onto AC-WS. The dynamic desorption curves of HCl solution are given in Fig. 5b. From the experiments, it is observed that the desorption efficiencies of phosphate and chromate (VI) are about 98.1 and 74.8%, respectively. The high desorption efficiency of phosphate indicates that the desorption of phosphate ions from the surface of AC-WS is most probably through a reaction of ion-exchange with high concentration of Cl^- from the HCl displacing phosphate ions from AC-WS. In addition, the main specie of phosphate and chromate in 0.1 mol/L HCl solution is H_3PO_4 and H_2CrO_4, phosphate/chromate (VI) can be desorbed from surface of AC-WS due to the weakening of the interaction between amine groups and H_3PO_4/H_2CrO_4.

Desorption of chromium (VI) from AC-WS is a complicated process with potential interactions between the bonding sites and ions. The desorption of chromium (VI) fails to reach the utmost as compared to that of phosphate because some amount of adsorbed chromium (VI) gets reduced to chromium (III) in the biosorbent surface and bonds to the hydroxyl and carboxyl groups in a stable interaction. The chromium (III) complexes form the chemical bonding with the Cr-binding groups, which cannot be desorbed in the solution (Suksabye et al., 2008). HCl solution plays a role of ion-exchange (chromium (VI) ion is exchanged by Cl^- ion) and can effectively elute the unreduced chromium (VI) ions from the cationic surfaces of AC-WS. This results were consistent with the desorption data reported by Suksabye et al. (2008) and Baral et al. (2009).

3.2.6. Adsorption mechanism of phosphate and chromium (VI) onto AC-WS

Based on the analysis of characteristics, adsorption and desorption results, the differential adsorption mechanisms of phosphate and chromium (VI) onto AC-WS were evaluated and concluded as follows.Adsorption process of phosphate onto AC-WS proceeds due to the electrostatic forces between the phosphate species

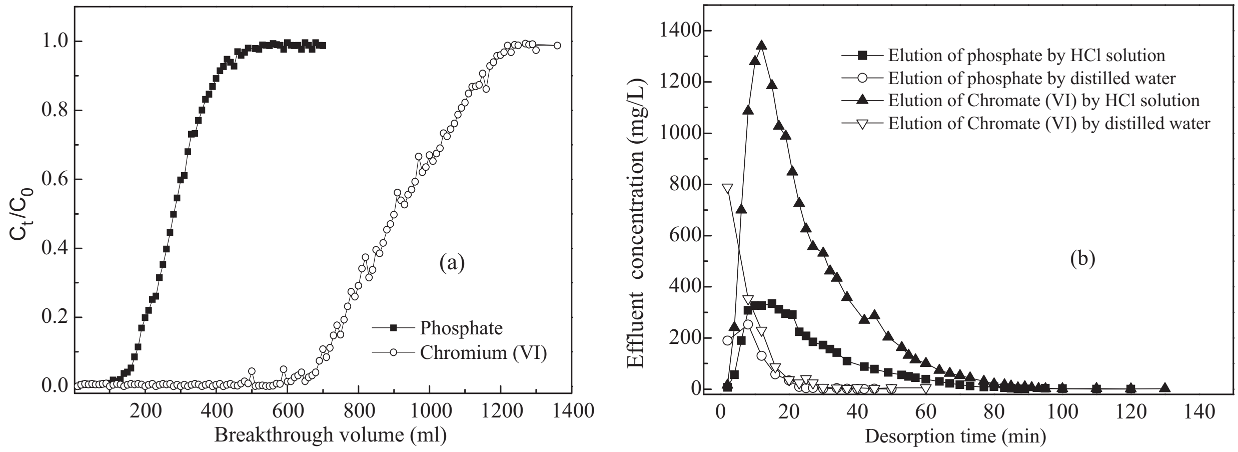

Fig. 5. Column adsorption and dynamic elution curves.

(e.g. $H_2PO_4{}^-$) and the positively charged amine groups ($R–N^+(CH_2CH_3)_3Cl^-$) in AC-WS (Eq. (3)).

$$R'–N^+(CH_2CH_3)_3Cl^- + H_2PO_4{}^- \rightarrow R'–N(CH_2CH_3)_3{}^+ \ldots H_2PO_4{}^- + Cl^- \qquad (3)$$

$$R'–N^+(CH_2CH_3)_3Cl^- + HCrPO_4{}^- \rightarrow R'–N(CH_2CH_3)_3{}^+ \ldots HCrO_4{}^- + Cl^- \qquad (4)$$

The chromium (VI) mechanism might be inferred as follows: (i) the negatively charged chromium (VI) species (e.g. $HCrO_4{}^-$) migrated to the positively charged AC-WS surface sites (e.g. amine groups) mainly due to electrostatic driving forces (Eq. (4)). (ii) Chromium (VI) is converted to chromium (III) on the surface of AC-WS through reduction by adjacent electron-donor groups at acidic conditions. The resulting chromium (III) can be then bound to anionic groups (e.g. hydroxyl and carboxyl groups) and form complexes with the chemical binding groups present in the AC-WS (Eq. (5)–(7)).

$$HCrO_4{}^- + 7H^+ + 3e- \leftrightarrow Cr^{3+} + 4H_2O \qquad (5)$$

$$Cr^{3+} + H_2O \leftrightarrow Cr(OH)^{2+} + H^+ \qquad (6)$$

$$R'–COOH + Cr(OH)^{2+} \rightarrow R'–COOCr(OH)^+ + H^+ \qquad (7)$$

4. Conclusions

AC-WS was prepared for the removal of phosphate and Chromium (VI) from water solution. BET surface area, elemental, zeta potential and Raman spectrum techniques were measured to elucidate the physicochemical change between AC-WS and WS. Characteristics of AC-WS and various adsorption and desorption tests validated a potential chemical bonding between chromium (VI) and AC-WS as comparison to the electrostatic forces between phosphate and AC-WS. In addition, the adsorption capacities of AC-WS for phosphate and chromate (VI) were calculated, and the high adsorption capacity data provided a potential application of AC-WS for toxic heavy metals or nutrient substances removal from aqueous solutions.

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