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Removal of Cr(VI) from aqueous solution using activated carbon modified with nitric acid

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ABSTRACT

The adsorption processes of Cr(VI) from aqueous solution onto a granular activated carbon (GAC) and a modified activated carbon (MAC) with nitric acid have been investigated. The surface characteristics of these two activated carbons were measured. The results showed that the MAC has a lower surface area, lower pH_{IEP} and more oxygen functional groups compared with the GAC. Adsorption parameters such as adsorbent dosage, pH of solution, contact time and temperature of the adsorption onto the GAC or MAC have been investigated in a batch adsorption experiment in order to obtain the optimum conditions for the Cr(VI) adsorption process. Experimental equilibrium data have been obtained and correlated with Freundlich and Langmuir isotherms for the determination of the adsorption potential. The results have shown that the Langmuir isotherm model better fits the experimental data compared with the Freundlich isotherm for both MAC and GAC. It was found that the MAC has a higher Cr(VI) adsorption capability, with 16.1 mg g^{-1}, compared with GAC, which has a capacity of 6.40 mg g^{-1}. Furthermore, the separation factor R_L for the Langmuir isotherm indicated that the adsorption process is most favourable for the MAC. The breakthrough curve for the adsorption column test was obtained in a continuous adsorption bed experiment, and it would need, under continuous adsorption conditions, a minimum amount of 4.39 g l^{-1} for MAC, whereas under batch conditions, 2 g l^{-1} is enough for MAC to achieve the same removal of Cr(VI) with an initial concentration of 25 mg l^{-1}.

1. Introduction

With the rapid development of the galvanization industry in China recently, the amount of hexavalent chromium Cr(VI) containing wastewater generated by the industry has increased dramatically. Due to its high solubility and toxicity to living organisms, Cr(VI) containing wastewater has been classified as a top-priority toxic pollutant by the USEPA, as well as the Chinese EPB. Various methods have been used for treating Cr(VI) containing wastewater, including electro-chemical precipitation [1], ion exchange [2], membrane ultrafiltration [3], and reverse osmosis [4]. The adsorption method is widely used for wastewater treatment because of its convenient operation, its effectiveness and relatively low cost [5–7]. Activated carbon is the main adsorbent material used in the adsorption process because of its high specific surface area, which is normally in the range of 1000–1500 $m^2\,g^{-1}$ [8]. It has also been used as an adsorbent to remove Cr(VI) from aqueous solutions and/or wastewaters [9,10]. However, the low adsorption capacity of Cr(VI) on activated carbon has restricted its wide application [11]. Recently, surface modification of activated carbon has been recognized as an attractive approach to improve and/or enhance Cr(VI) removal from wastewater [12].

Activated carbon surface oxidation with HNO_3 is a typical modification method, which can increase the number of acidic function groups on the surface of the activated carbon, and this in turn can very effectively increase the Cr(VI) adsorption capacity [13,14]. Zhao [15] reported that, by using various oxidizing agents such as HNO_3, H_2O_2 and $Fe(NO_3)_3$, a commercially available activated carbon modified in such a way was used for the treatment of Cr(VI) containing wastewater. The results showed an improvement in the Cr(VI) adsorption capacity compared with untreated carbons. Liu [16] have reported that activated carbon with excellent Cr(VI) adsorption performance especially at low concentrations was prepared by an acid–base surface modification method. Raw activated carbon was first oxidized in boiling HNO_3, then treated with a mixture of NaOH and NaCl. The results revealed that the modified AC exhibited excellent Cr(VI) adsorption performance in terms of adsorption capacity. El-Sheikh [17] investigated the effect of oxidation of activated carbon with various oxidizing agents (nitric acid, hydrogen peroxide, and ammonium persulfate) on

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preconcentration of metal ions from environmental waters. The highest recoveries and adsorption capacities towards metal ions were achieved when using nitric acid-oxidized as preconcentrating sorbent at pH 9.

The objective of the present work was to determine an optimal way to modify activated carbon by using HNO_3 for adsorbing Cr(VI) from aqueous solution. A different modification method was introduced in this paper where a granular activated carbon was first oxidized with concentrated HNO_3, followed by calcination at 300 °C for 1 h. The Langmuir and Freundlich isotherms for Cr(VI) adsorption were measured to quantify the adsorption equilibrium. Furthermore, the breakthrough curve for adsorption in a continuous adsorption column was investigated to demonstrate the industrial application of the adsorbent, showing good potential for removing Cr(VI) from the wastewater generated by the galvanizing industry.

2. Experimental

2.1. Activated carbon modification with nitric acid

All activated carbon used in the study were in the granular form and from the Nan Feng Wood Processing Factory, China. The activated carbon was ground and sieved to retain the 40–60 mesh fractions. It was washed with distilled water (at 80 °C) to remove fine powder and contaminants, and then left to dry in an oven at 110 °C for 2 h before use. In this work, it is described as GAC (granular activated carbon).

The activated carbon used in the paper was modified by surface oxidation with concentrated nitric acid (1:1 dilution from 67% concentrated HNO_3 acid). The modification procedure was as follows. A known volume of 1:1 diluted nitric acid was heated at 110 °C. The appropriate amount of GAC was added to the boiling nitric acid solution at a ratio of 1 g GAC to 5 ml nitric acid solution. It was treated for 3 h to increase the formation of functional groups, such as carboxylic acids. The residual material was washed with distilled water until the conductivity of the water effluent was close to that of distilled water. The modified activated carbon by using nitric acid was then dried at 120 °C for 4 h. Finally, the oxidized activated carbon was placed in a tube furnace containing air at 300 °C for 1 h. After modification with HNO_3, MAC was found to contain some acidic groups, such as anhydride, ester and hydroxy aldehydes, during the calcination process at a temperature of 300 °C, giving the surface of the MAC a higher cation exchange capacity. It was cooled down to room temperature naturally and is referred to as MAC (modified activated carbon).

2.2. Surface characteristics of modified activated carbon

The specific surface area of the GAC/MAC samples was measured using a BET surface area analyzer (Micrometritics Instrument Corporation, Model ASAP-2000) based on the nitrogen adsorption and desorption method.

The Boehm titration method was used to measure the content of oxygen functional groups in the investigation of the surface characteristics [18,19]. This was achieved by neutralization experiments employing three kinds of base with 25 ml of 0.1 mol l^{-1} ($NaHCO_3$, Na_2CO_3, and NaOH) to estimate the acidic centres. According to Valdes [20], $NaHCO_3$ neutralizes carboxylic groups, Na_2CO_3 neutralizes carboxylic and lactone groups, and NaOH neutralizes carboxylic, lactone and phenol groups.

The Fourier transform infrared spectroscopes were recorded for the GAC and MAC on a Nicolet 380 FTIR spectrometer (Thermo Scientific Brand, America) by using pressed KBr pellets. The zeta potential measurements of the GAC and MAC were performed on a Zeta Probe (Colloidal–Dynamics, America).

2.3. Preparation of Cr(VI) solution

The Cr(VI) stock solution was prepared by dissolving 0.5657 g (±0.0001) $K_2Cr_2O_7$ dried at 105 °C for 2 h in a 1000 ml volumetric flask with deionized water to form a Cr(VI) stock solution with a concentration of 200 mg l^{-1}. According to the literature [11,16], low concentration wastewater containing Cr(VI) ions is best for the treatment with a modified activated carbon. Accordingly, our experimental solution was prepared at 25 mg l^{-1} by serial dilution from the stock solution of 200 mg l^{-1}.

2.4. Batch adsorption experiment

Batch adsorption experiments were carried out by using the GAC or MAC as the adsorbents. A series of conical flasks containing Cr(VI) solutions with initial concentrations of 25 mg l^{-1} and a known dosage of the GAC (1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, and 5.5 g l^{-1}) or MAC (0.2, 0.5, 1.0, 1.5, 2.0, and 2.5 g l^{-1}). The pH value of the solution was adjusted with 0.5 M H_2SO_4 or 0.5 M NaOH to cover a range from 2.0 to 9.0, which was measured using a PHS-3C pH Meter (Hangzhou, China). After pH adjustment, the conical flasks were shaken in a SHA-C shaking machine (Changzhou, China) for 3 h at ambient temperature. The suspensions were centrifuged and the supernatant was then analysed by a standard spectrophotometric method (China National Standards, QB/T7467) for the Cr(VI) concentration change.

The percentage adsorption E and adsorption capacity q_e were calculated as

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{C_0 - C_e}{M} \times 100\% \tag{2}$$

Here C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) in mg l^{-1}, respectively, and M is the mass of adsorbent in g l^{-1}.

2.5. Continuous adsorption bed experiment

The packed bed breakthrough curve was measured by a continuous adsorption experiment. A glass column with a diameter of 30 mm (ID) was packed with 25 g GAC or MAC. There was a distributor on the top of the column in order to allow a homogeneous flow distribution. Porous organic plastic supports were used to hold the carbons in the column. A Cr(VI) initial concentration solution of 25 mg l^{-1} was pumped through the carbon bed at the rate of 20 ml min^{-1} using a BT-100 peristaltic pump (Shanghai, China). Effluent samples were taken at various times for Cr(VI) concentration analysis.

3. Results and discussion

3.1. The evaluation of the surface characteristics for MAC

Since adsorption is a surface phenomenon, the rate and extent of adsorption specific to a given adsorbent are influenced by the physiochemical characteristics of the adsorbent, such as surface area and the presence of surface functional groups [18]. Compared with the surface area of 853 m^2 g^{-1} for the GAC, the surface area of the MAC has a lower value of 681 m^2 g^{-1}. The decrease in the surface area is mainly due to the decrease in the micropore volume resulting from pore blockage by the surface oxide groups existing in some of the micropores. Similar results have been reported by Liu and Chen [21,22].

However, this oxidation treatment process greatly increased the total acidity of the surface that resulted from the increase in sur-

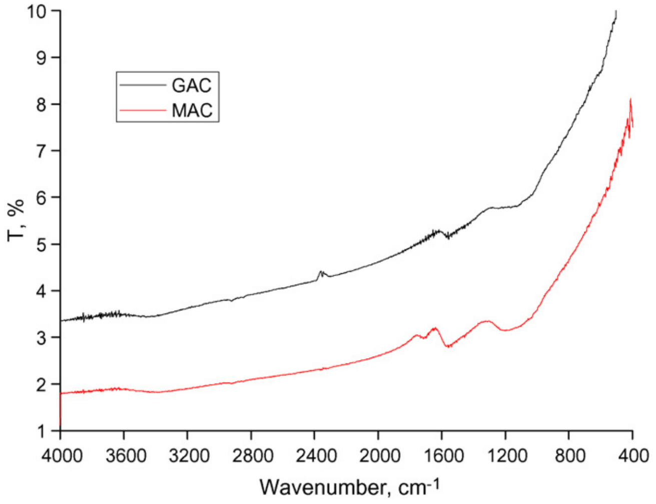

Fig. 1. The FTIR spectrum of GAC and MAC.

face acidic functional groups, such as carboxylic, lactone and phenol groups. The activated carbon used in the study was the measured amounts of carboxylic, lactone and phenol groups were 0.23, 0.5 and 0.38 mmol g^{-1}, respectively. After modification, the measured numbers of carboxylic groups, lactone groups and phenol groups on MAC increased to 1.37, 4.16 and 7.46 mmol g^{-1}, respectively. These acidic function groups could transform into –COOH^{2+}, –OH^{2+} or =C=OH^{+} by reaction with H^{+} in the solution. The more that these cations existed on the treated MAC surface, the better the removal of Cr(VI) via adsorption from the wastewater [20,21,23,24].

The spectra of the GAC and MAC samples were recorded between 4000 and 400 cm^{-1} using a Nicolet 380 FTIR and were depicted in Fig. 1. As seen from Fig. 1, the peak at 1750 cm^{-1} appears on the MAC only. The most logical explanation for the peak would be the existence of carboxyl groups that are formed as a result of nitric acid oxidation [25]. The more pronounced peaks for the MAC than GAC appearing at 1610, 1240 cm^{-1} are ascribed to the formation of, or to an increase in, the already available oxygen functionalities (highly conjugated C=O stretching, C–O stretching in carboxylic groups, and carboxylate moieties). These results also indicate that HNO$_3$ treatment gave rise to a greater increase in C=O phenol bonds in carboxylic acid and lactone groups.

The electrokinetic behaviour of the samples in solution is one of the most important properties in characterisation. The results for zeta potential measurements for the GAC and MAC are shown in Fig. 2. The results show that there is a marked difference in the isoelectric point (IEP) between the MAC (pH$_{IEP}$ = 1.8) and GAC (pH$_{IEP}$ = 6.3). The low IEP values for the MAC are due to the presence of acidic carboxylic functional groups. It is known that dissociation of the carboxylic groups in activated carbon lies between pH 2 and 6. Thus, the dissociation of the groups renders the carbon surface negative. The GAC sample may consist of weakly acidic functionality with a higher dissociation pH and that might have caused a higher isoelectric point when compared with the MAC. Meanwhile, the MAC sample also shows lower zeta potential than the GAC, which suggests the amphoteric nature of the sample.

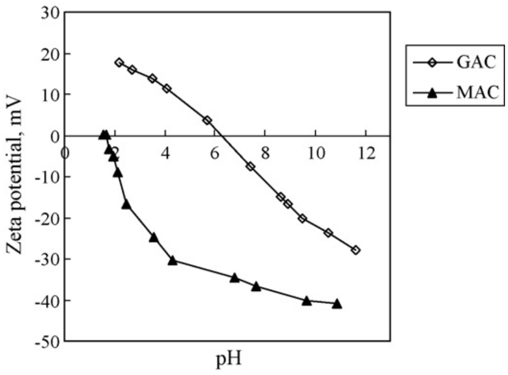

Fig. 2. Zeta potential measurements for the GAC and MAC.

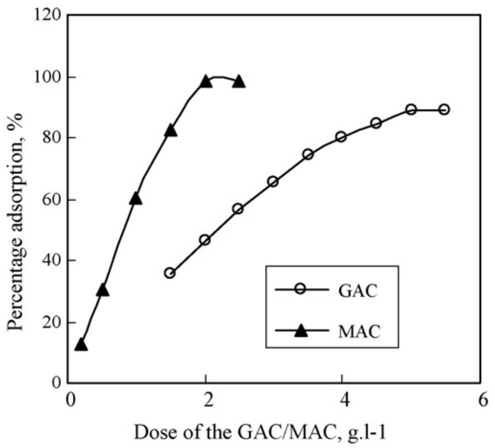

Fig. 3. Effect of MAC or GAC dosage on percentage adsorption (C_0 = 25 mg l^{-1}).

3.2. Effect of the MAC dosage

The effect of the GAC or MAC dosage on the adsorption was investigated in the range 200–6000 mg l^{-1}, while the pH value of the Cr(VI) solution was fixed at 4.0 and the contact time was fixed at 3 h at room temperature. The result is shown in Fig. 3.

Fig. 3 shows that the percentage adsorption generally increased with an increase in the MAC up to a certain value, and then remained constant above a MAC dosage of 2000 mg l^{-1}, which shows that those dosages were enough for Cr(VI) removal at an initial concentration of 25 mg l^{-1}. This indicates that the surface modification of the GAC with nitric acid significantly improved the Cr(VI) removal capacity compared with the GAC with a optimum dose of 5 g l^{-1}. Hence the optimal MAC dose for an initial concentration of Cr(VI) of 25 mg l^{-1} was 2 g l^{-1}.

3.3. Effect of the pH

With a selected GAC or MAC dosage of 5 or 2 g l^{-1}, respectively, the effect of the solution pH on the adsorption behaviour was investigated in the range 2.0–9.0, while the contact time was fixed at 3 h at room temperature. The results are shown in Fig. 4.

Fig. 4 shows that the chromium adsorption onto the MAC and GAC is strongly pH dependent. The percentage adsorption kept constant at lower pH values from 2.0 to 4.0 for MAC. Above a pH of 4.0, the percentage adsorption began to decrease. This finding suggests that the optimal pH of solution for adsorption of Cr(VI) should not exceed a value of 4.0 below the precipitation pH (4.5–5.5). This phenomenon is mainly related to changing the surface charge of MAC, due to the increased number of acid function groups on the surface. The increased pH value of the solution may partially neutralize these acid function groups and lead to a decrease in the Cr(VI) removal rate. Similar results have been reported by Babel [16]. Modified carbon can adsorb Cr(VI) with a good removal rate compared with the GAC in a pH range of 2.0–4.0 shown in Fig. 2. It is also postulated that, under acidic conditions, Cr(VI) is easily or spontaneously reduced to Cr(III) by positively charged functional groups, and subsequently adsorbed by available carboxyl groups, because Cr(VI) has

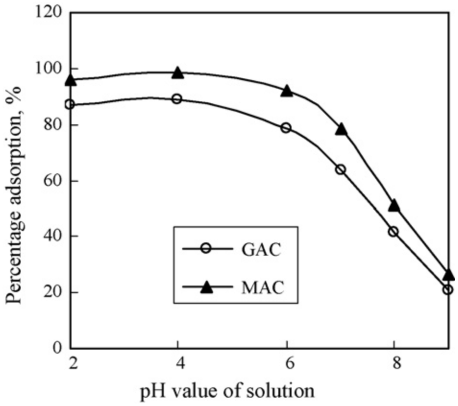

Fig. 4. Effect of pH value of solution on percentage adsorption ($C_0 = 25\,mg\,l^{-1}$).

a high redox potential value (above +1.3 V) [26], and the adsorption of the Cr(III) aqua complex occurs onto the carbon surface [27].

Under acidic conditions, Cr(VI) in the wastewater will be reduced to Cr(III):

$$3C + 2Cr_2O_7{}^{2-} + 16H^+ = 3CO_2 + 4Cr^{3+} + 8H_2O \qquad (3)$$

$$C + Cr_2O_4{}^{2-} + 4H+ = CO_2 + Cr^{3+} + 2H_2O \qquad (4)$$

3.4. Effect of the contact time

With a selected GAC and MAC dosage of 5 and 2 g l^{-1}, respectively, and a pH value for the solution of 4.0, respectively, the effect of the contact time on the adsorption was investigated in the range from 20 to 150 min at room temperature. The results are shown in Fig. 5.

Sufficient contact time is needed for the adsorption process to reach equilibrium for the maximum Cr(VI) adsorption on GAC or MAC. Fig. 5 indicated that the equilibrium time for Cr(VI) adsorption on GAC and MAC is about 120 and 100 min, respectively. The equilibrium results also indicated that the surface modified MAC can remove Cr(VI) more effectively from the solution compared with untreated GAC. Hence 100 min appears to be the optimum contact time for MAC.

3.5. Effect of temperature

Temperature is an important parameter in the context of adsorption on solid phase. In the present case the effect of temperature on the extent of solute adsorption was investigated in the range from 10 to 60 °C under the selected adsorption above. The results are shown in Fig. 6.

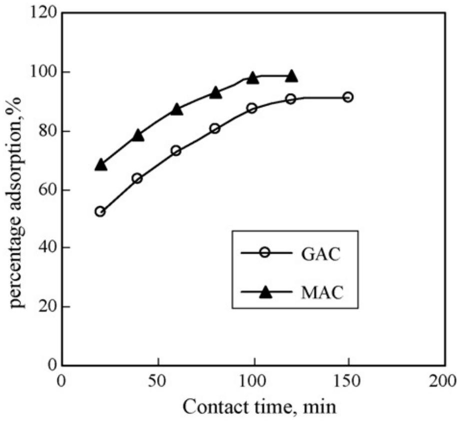

Fig. 5. Effect of contact time on percentage adsorption ($C_0 = 25\,mg\,l^{-1}$).

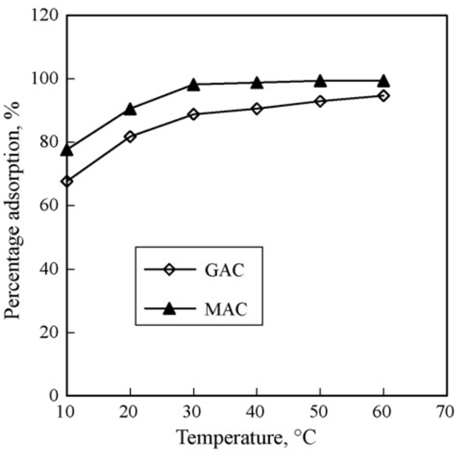

Fig. 6. Effect of temperature on percentage adsorption ($C_0 = 25\,mg\,l^{-1}$).

The temperature has main effects on the adsorption process. An increase in temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and within the pores. Furthermore, changing the temperature will modify the equilibrium capacity of the adsorbent for a particular adsorbate. Fig. 6 shows that the percentage adsorption increases as the temperature increases for the MAC and the GAC. The adsorption process in this study was that the Cr(VI) is reduced to Cr(III) in the aqueous phase by contact with the functional groups of the MAC and GAC. Since a redox reaction is endothermic, the reduction rate of Cr(VI) increased with increasing temperature. It also can be noted that the increase in percentage uptake was not obvious from 30 to 60 °C. So our experiments were carried out at room temperature, which was about 30 °C.

3.6. Adsorption isotherms

In order to determine the adsorption potential, an adsorption isotherm is essential. The experimental data for Cr(VI) onto MAC obtained with an initial Cr(VI) concentration of 25 mg l^{-1} was correlated with the Freundlich and Langmuir isotherms. The Langmuir isotherm is expressed as

$$q_e = \frac{a_m b C_e}{1 + bC_e} \qquad (5)$$

The Freundlich isotherm is expressed as

$$q_e = KC_e^{1/n} \qquad (6)$$

Here q_e is the amount of adsorbed Cr(VI) per gram of modified activated carbon and C_e is the equilibrium concentration of Cr(VI) in the bulk of the solution. The constants a_m and b are characteristics of the Langmuir equation; while K and n are the constants of the Freundlich equation, incorporating adsorption capacity and intensity.

The Langmuir (C_e versus C_e/q_e) and Freundlich ($\ln C_e$ versus $\ln q_e$) isotherms for the adsorption of Cr(VI) from aqueous solutions onto MAC were plotted in Figs. 7 and 8, respectively, and the adsorption isotherm parameters, along with the correlation coefficients, are presented in Table 1.

Table 1 shows that the correlation coefficients are high, which indicates the applicability of these two adsorption isotherms and the monolayer coverage of Cr(VI) onto the MAC surface. This result for the adsorption capacity of MAC indicated that the surface modification process with nitric acid has significantly improved the

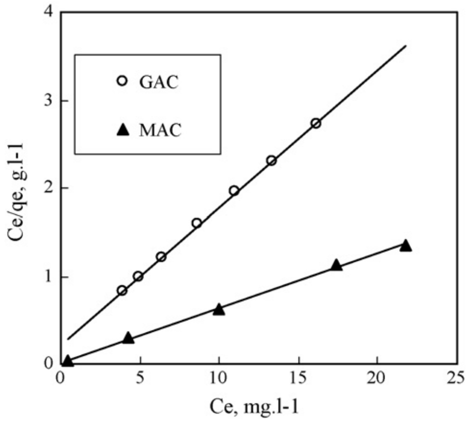

Fig. 7. The Langmuir adsorption isotherm for GAC and MAC.

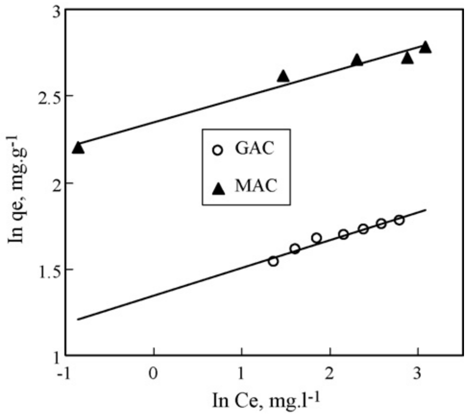

Fig. 8. The Freundlich adsorption isotherm for GAC and MAC.

Cr(VI) removal capacity compared with the material having no surface modification (GAC). The results have shown that the Langmuir isotherm model better fits the experimental data compared with the Freundlich isotherm for both MAC and GAC. The corresponding regression correlation coefficients ($R^2 = 0.9996, 0.9977$ for the Langmuir isotherm and $R^2 = 0.9669, 0.9680$ for the Freundlich isotherm) support this conclusion. The adsorption capacity obtained from the Langmuir isotherm was 16.1 mg Cr(VI) per gram MAC for a Cr(VI) concentration of 25 mg l^{-1}, which was in the range of 8.47–33.57 mg Cr(VI) per gram for Cr(VI) adsorption onto MAC published by other researchers [13,16].The Langmuir equations for adsorption of Cr(VI) on GAC and MAC, respectively are

$$q_e = \frac{4.61C_e}{1+0.72C_e} \qquad q_e = \frac{15.62C_e}{1+0.38C_e} \tag{9}$$

The Freundlich equations for adsorption of Cr(VI) on GAC and MAC, respectively are:

$$q_e = 3.84C_e^{0.16} \qquad q_e = 10.5C_e^{0.14} \tag{10}$$

Table 1
Langmuir and Freundlich isotherm constants.

Type of carbon	Langmuir isotherm				Freundlich isotherm		
	a_m	b	R^2	R_L	K	n	R^2
GAC	6.40	0.72	0.9996	0.053	3.84	6.25	0.9669
MAC	16.10	0.38	0.9977	0.095	10.50	6.93	0.9680

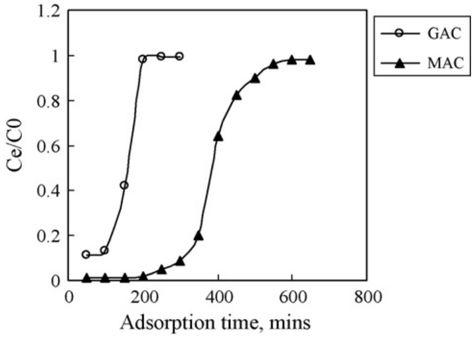

Fig. 9. Packed bed breakthrough curve for GAC and MAC.

Furthermore, the essential characteristics of Langmuir isotherm can be described by a separation factor, which is defined by the following equation [28]:

$$R_L = \frac{1}{1+bC_0} \tag{11}$$

The value of R_L indicates the shape of Langmuir isotherm and nature of the adsorption process. It is a favourable process when the value is within the range 0–1. In our study, Table 1 shows that the calculated values of R_L were found to be in the range of 0–1, indicating that the adsorption process was favourable for both GAC and MAC.

3.7. Packed bed breakthrough curve

The packed bed breakthrough curve was obtained by a continuous adsorption experiment. The adsorption process was carried out according to the method described in Section 2.5.

It can be seen from Fig. 9 that all Cr(VI) were initially retained in the packed bed because of full adsorption (no Cr(VI) in the effluent). With greater Cr(VI) solution flow through the bed, the Cr(VI) concentration in the effluent increases steadily until it reaches the same value as its inlet concentration (C_0), the so-called breakthrough point, when the packed bed is saturated. The measured breakthrough times for GAC and MAC are 150 and 200 min, respectively. Compared with the batch adsorption data, the packed bed adsorption results show less removal capacity. This is because the dynamic adsorption process (continuous adsorption) has less contact time comparing to static condition (batch adsorption). To remove 25 mg Cr l^{-1} onto the GAC or MAC, the minimum requirement for the continuous adsorption condition would be 6.25 g l^{-1} for GAC and 4.39 g l^{-1} for MAC; whereas in the batch condition, 5.0 g l^{-1} is enough for GAC and 2 g l^{-1} for MAC to achieve the same removal rate.

3.8. Desorption and reuse of modified activated carbon

The desorption of the adsorbed Cr(VI) from the modified activated carbon was investigated in a batch reactor. The adsorbed Cr(VI) has been reduced to Cr(III) first, and it then desorbed from MAC under acidic conditions, and the MAC was then regenerated. Finally, the Cr(III) was eluted with 20% H_2SO_4 in this study. The results showed that more than 95% of the adsorbed Cr(VI) was desorbed from the MAC. In order to assess the reusability of the MAC, the adsorption–desorption cycle was repeated eight times by using 0.2 g of the adsorbed MAC and 25 mg l^{-1} of Cr(VI) solution in a final volume of 100 ml. The adsorption conditions were a Cr(VI) concentration of 25 mg l^{-1}, a solution pH of 4.0, and a contact time of 100 min. The desorption conditions were a stripping solution of 20% H_2SO_4 and a contacting time of 4 h. The effect of recycling time on the adsorption capacity of MAC is shown in Fig. 10.

Fig. 10 indicates that the adsorption capacity did not noticeably change in first three cycles, in which the percentage adsorption

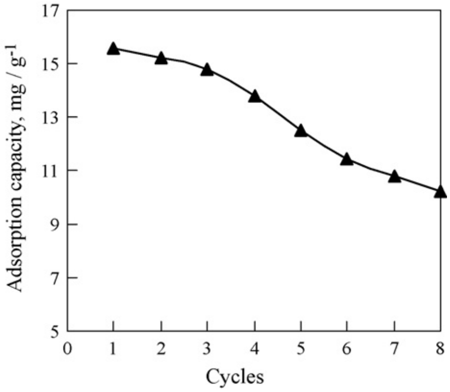

Fig. 10. The results of the adsorption/desorption investigation, showing the adsorption capacity as a function of time.

remained over 92%. Then the uptake capacity started decreasing from the fourth cycle steadily until the eighth cycle, reaching a level of 63% of the initial value. These results show that the adsorbed MAC can be repeatedly used for a number of cycles for Cr(VI) adsorption without losing its adsorption capacity completely. The washed out Cr(III) solution is normally neutralized first, and Cr(III) is then precipitated at the pH values of 4.5–5.5 as $Cr(OH)_3$ for reuse and disposal.

4. Conclusions

In this work, activated carbon, modified using nitric acid, has been found to have a lower surface area, lower pH_{IEP}, and more surface oxygen functional groups compared with untreated activated carbon. These oxygen functional groups improve the Cr(VI) adsorption capacity. The optimum Cr(VI) adsorption conditions onto the MAC were as follows: a MAC dosage of about $2\,g\,l^{-1}$, at a solution pH of about 4.0 and a contact time of about 100 min. Its maximum adsorption capacity was $16.1\,mg\,g^{-1}$ at room temperature. The Langmuir isotherm model correlated the experimental data slightly better than the Freundlich isotherm. The calculated separation factors (R_L) were found to be in the range of 0–1, indicating that the adsorption processes was favourable for both GAC and MAC adsorption. To remove $25\,mg\,Cr\,l^{-1}$ onto GAC or MAC, in the continuous condition, a minimum amount of 6.25 and $4.39\,g\,l^{-1}$ of the GAC or MAC would be required, respectively, whereas in the static condition, 5.0 and $2\,g\,l^{-1}$ are needed, respectively.

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