ELIMINATION OF Cr(VI) USING ACTIVATED CARBON PREPARED FROM MUSHROOM MEDIUM

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Mushroom medium, which is mainly composed of wood flour, is a kind of waste largely obtained from the mushroom cultivation industry. The typical method of reusing it is by burning it to generate heat. In the present paper, mushroom medium-based activated carbon was prepared and the removal for Cr(VI) through it was explored. The combined effect of five process parameters, *i.e.* contact time, pH, adsorbent dosage, initial concentration and temperature, on Cr(VI) adsorption were studied. The maximum adsorption capacity of activated carbon towards Cr(VI) was found under the following conditions: pH 2, contact time of 3 h, temperature of 60 °C and adsorbent dosage of 0.1 g. The adsorbed amount of Cr(VI) decreased with an increase in the initial concentration. In addition, the kinetics of Cr(VI) adsorption followed the pseudo-second-order rate expression. As regards the adsorption isotherms, the data were fitted better by the Langmuir model than by the Freundlich model.

Keywords: activated carbon, mushroom medium, adsorption, Cr(VI)

INTRODUCTION

The increasing contamination of urban and industrial wastewater by toxic metal ions causes important environmental pollution. Chromium (Cr) is one of the most toxic metals that finds wide spread use in various industries, including electroplating, metal finishing, leather tanning and pigments. Chromium exists almost exclusively in the Cr(III) oxidation state or in the Cr(VI) oxidation state. Cr(III) is sparingly soluble and less toxic in nature. However, Cr(VI) compounds are very toxic chemicals and genotoxic carcinogens.[1] Thus, the presence of Cr(VI) in the environment is posing serious problems and causing great public concern. Currently, the drinking water guideline of the Environmental Protection Agency (EPA) in the US has established the maximum contaminant level for chromium of 0.1 mg/L. To solve this serious problem for environmental and human health, an efficient elimination of Cr(VI) from polluted water is necessary.[2]

Several methods have been used for treating Cr(VI) containing wastewater, including precipitation, extraction, ion exchange, and adsorption.[3-4] Among all these methods, activated carbon (AC) adsorption is the most economically attractive and feasible, due to its easy operation and the development of various adsorbents.[5-8] However, commercially available AC may be expensive, for this reason, the production of low-cost, disposable sorbents for chromium removal is worth considering. There is a second largest mushroom cultivation base in China, which is located in Pingquan of Hebei Province. The mushroom culture medium, composed mainly of wood flour, is generally abandoned in landfills, amounting to a dozen tons per year. Most of the waste mushroom medium is burnt,

which releases toxic gases and pollutes the environment. Therefore, the waste mushroom medium could be used to prepare AC as a potential adsorbent for the removal of toxic pollutants from water, which will enlarge its application and help to deal with the emergent wastewater treatment challenge in China.

The objective of this paper is to prepare AC from mushroom medium and evaluate its capacity to adsorb Cr(VI) from aqueous solutions. Several important factors, such as contact time, adsorbent dose, initial concentration, pH and temperature, were investigated. Furthermore, the adsorption of Cr(VI) was characterized by kinetic models and adsorption isotherms.

EXPERIMENTAL
Materials

The mushroom medium was obtained from the Pingquan Mushroom Cultivation Company in Hebei Province (Hebei, China). The mushroom medium mainly consisted of wood flour. The chemical composition was the following: ash (GB/T 742-2008) 10.07%, lignin (GB/T 10337-2008) 28.39% and holocellulose (GB/T 2677.10-1995) 61.14%. Other chemicals of analytical grade were purchased from Beijing Lanyi Chemical Reagent (Beijing, China). Double distilled water was used for preparation of all required solutions.

Preparation of activated carbon

The process of preparing AC with KOH includes two steps. In the carbonization step, the mushroom medium was ground and then was heated to a carbonization temperature of 500 °C at a heating rate of 100 °C/h and was held at this temperature for 1 h. The carbonized samples were screened out with sieves to hold the 40-60 mesh fractions for further applications. In the activation step, 6 g of sample was soaked in a 50% KOH solution for 24 h at the impregnation ratio of 3:1. The soaked samples were then put in an electric furnace and heated up to about 850 °C at a heating rate of 10 °C/min and were held at this temperature for 50 min. Then, the AC was washed sequentially with a 50% HCl solution and with distilled water until the solution was neutral. Finally, the samples were dried at 105 °C in an oven for 6 h and kept as an adsorbent in a vacuum sealed beaker for the next experimental steps.

Characterization of activated carbon

Iodine number was determined at 303 K based on the Standard Test Method ASTM Designation: D4607-86. The nitrogen adsorption-desorption data were recorded at a liquid nitrogen temperature of 77 K.

The nitrogen adsorption isotherm was measured over a relative pressure (P/P$_0$) range, from approximately 10^{-6} to 1. BET surface area was calculated from N$_2$ adsorption isotherms using the Brunauer-Emmett-Teller (BET) equation. Pore size distribution in the micropore range was obtained by the Barrett–Joyner–Halenda (BJH) method.

Cr(VI) adsorption experiments

The Cr(VI) solution was prepared by dissolving 0.5660 g of potassium dichromate (K$_2$Cr$_2$O$_7$) in 2000 mL distilled water. Cr(VI) solutions were prepared by dissolving K$_2$Cr$_2$O$_7$ in distilled water. The Cr(VI) solution with a Cr(VI) concentration of 100 mg/L was prepared in the next work. At the end of the adsorption process, the supernatant liquids were filtered with 0.45-µm filter membranes. The concentration of Cr(VI) was determined by a UV/vis spectrophotometer with 1,5-diphenyl-carbazide in acid medium at a wavelength of 540 nm.

The amount of adsorption at equilibrium, q$_e$ (mg/g), was calculated by:

$$q_e = \frac{(c_o - c_e) \times v}{m} \tag{1}$$

where C$_0$ and C$_e$ are the initial and the equilibrium concentrations of Cr(VI) in solution (mol/L), respectively; v is the volume of the solution (L), and m is the mass of AC used (g).

RESULTS AND DISCUSSION
Characterization of the adsorbent

The optimum iodine number of the solution is of 1068 mg/g for Cr(VI) adsorption. The nitrogen adsorption–desorption isotherm of AC850 (Fig. 1(a)) was used to determine the surface area and pore-size distribution of the AC850. The isotherm of the AC sample resembles a combination of type-I and type-II isotherms, which is in accordance with the International Union of Pure and Applied Chemistry (IUPAC) classification. This adsorption behavior exhibits a combination of microporous-mesoporous structure. Meanwhile, the isotherm shows an almost flat plateau at higher relative pressure, indicating the presence of micropores.[9] Figure 1(b) shows the pore size distribution of the AC. As we know, micropores are less than 2 nm wide, mesopores are 2-50 nm wide, and macropores are more than 50 nm wide. As can be seen from Figure 1(b), the pores of the prepared AC included micropores and mesopores. The textural parameters of the AC at 850 °C show strictly mesopore surface area and significant micropore surface area, while the BET surface area could reach 977.4 m^2/g.
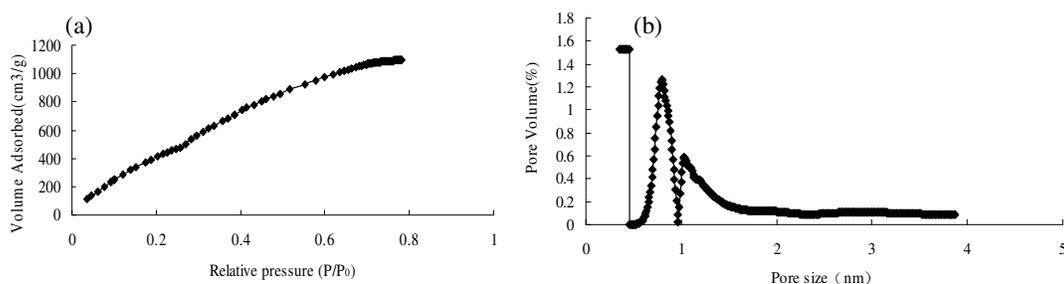
Figure 1: (a) AC850 nitrogen adsorption-desorption; (b) AC850 pore size distribution curves

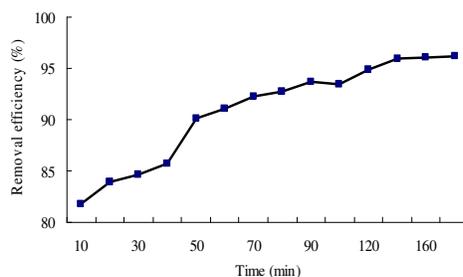Figure 2: Effect of contact time on adsorption efficiency (adsorbent dosage = 1.0 g/L, volume of Cr(VI) solution = 100 mL, c_0 = 100 mg/L, T = 40 °C, pH 2)

Effect of contact time

The effect of contact time was investigated to identify the rate of its removal by the proposed adsorbent. These experiments were carried out at an initial pH 2 in the presence of 100 mg/L $K_2Cr_2O_7$. The results are shown in Figure 2, wherefrom it is clear that the adsorption of Cr(VI) increased rapidly within the first 2 h and then levelled off. Therefore, the amount of Cr(VI) removed reached a maximum after 2 h. The percentage of adsorption of AC is up to 96.2%.

The rapid adsorption at the initial contact time is related to the availability of a higher number of active sites near the surface, which improves the flux of Cr(VI) diffusion to the adsorbent surface. The slower adsorption rate at the final stage of the adsorption was apparently due to the gradual saturation of the active sites on the less accessible internal pore surfaces of the AC. This result could be attributed to the instantaneous utilization of the available adsorbing sites in the AC lattice. Besides, the fast adsorption was due to the fast transfer of Cr(VI) ions to the surface of the AC, while the following slow adsorption was on account of the low concentration of the ions in the intra-particle pores of the AC.

It was reported that the removal of Cr(VI) using a cellulose microsphere-based adsorbent and activated weed *Slavonia cucullata* required 1 h and 12 h to obtain adsorption equilibrium, respectively.[10-11]

Effect of initial Cr(VI) concentration

The assessment of the effect of initial concentration on the adsorption of Cr(VI) on AC was carried out by varying the adsorptive concentrations from 50 mg/L to 280 mg/L for 180 min, and the results are shown in Figure 3. It was found that the adsorption of Cr(VI) was strongly dependent on the initial metal ion concentration. As shown in Figure 3, the equilibrium adsorption capacities increased when initial concentration of Cr(VI) ions increased. More Cr(VI) ions stayed in the solution phase at higher concentrations of metal because of the saturation of the binding sites of AC. At low initial concentration, the ratio of the surface active sites to the AC in the solution was high, and hence all AC may interact with the active functional groups on the surface of the carbon and be removed from the solution. In addition, with increased initial concentration, the number of active adsorption sites is enough to accommodate the AC.
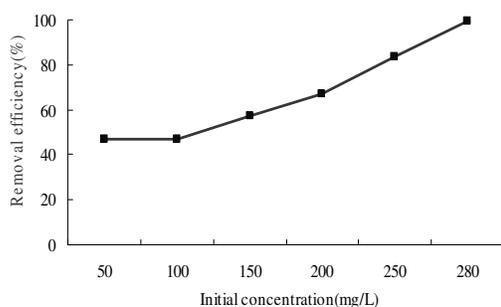
Figure 3: Effect of initial concentration on adsorption efficiency (adsorbent dosage = 1.0 g/L, volume of Cr(VI) solution = 100 mL, t = 180 min, T = 30 °C, pH 2)
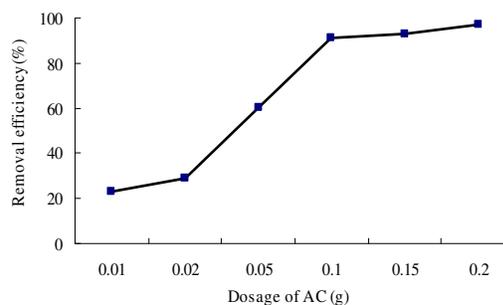
Figure 4: Effect of AC dosage on adsorption (experimental conditions: pH 2.0; initial chromium concentration = 100 mg/L; volume of solution = 100 mL; T = 40 °C)
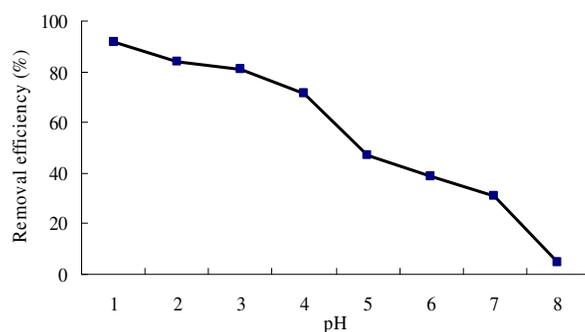

Figure 5: Effect of pH value on adsorption efficiency (carbon dosage = 0.1g; t = 3 h; Cr(VI) concentration = 100 mg/L; volume of solution = 100 mL; T = 40 °C)

Effect of adsorbent dosage

The effects of AC dosage on the removal of chromium are shown in Figure 4. In this study, experiments were carried out to examine the influence of adsorbent dosage (0.01, 0.02, 0.05, 0.10, 0.15 and 0.20 g) at an initial concentration of 100 mg/L and optimal pH value of the adsorbent for 180 min.

The result was determined as follows: with increasing adsorbent dosage, higher phase contact area, adsorption surface area and adsorption sites were provided. As shown in Figure 4, when the adsorbent dosage was as high as 1.0 g, the removal ratio of Cr(VI) was of nearly 90.9%. However, the efficiency did not increase linearly with the increase in the adsorbent dosage. The increase in the percentage of Cr(VI) adsorption when increasing the adsorbent dosage was due to the increase in the number of adsorbent sites available.

Similar phenomena were also observed by other researchers. Parinda and Paitip indicated that the optimum Cr(VI) concentration was 13 g/L (or 1.3% w/v), when 99.99% of Cr(VI) adsorption was achieved.[12]

Effect of pH

The pH is one of the most important factors affecting many adsorption processes.[13-14] From Figure 5, it can be seen that the Cr(VI) adsorption onto AC is dramatically decreased with an increase in pH from 1.0 to 8.0. One of the reasons for the better adsorption capacity observed at low pH (pH < 3.0) may be attributed to the electrostatic attraction between positively charged groups of the biomaterial surface and the $HCrO_4^-$ anion. Moreover, the decrease in adsorption at higher pH values may be due to the competitiveness of Cr(VI) species ($Cr_2O_7^{2-}$, CrO_4^{2-}) and OH^- ions in the bulk material.[15-16]

The result is similar to that obtained for Cr(VI) removal from aqueous solution by adsorption on treated sawdust and activated cow dung carbon.[17]
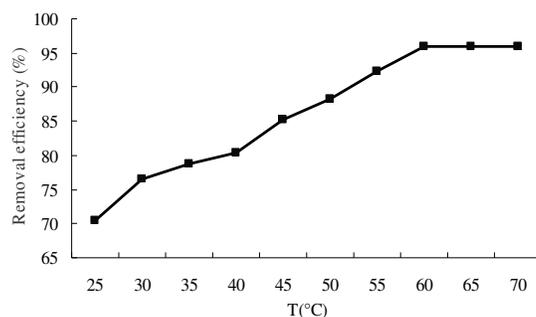
Figure 6: Effect of temperature on adsorption efficiency (adsorbent dosage = 1.0 g/L, volume of Cr(VI) solution = 100 mL, c_0 = 100 mg/L, t = 180 min, pH 2)
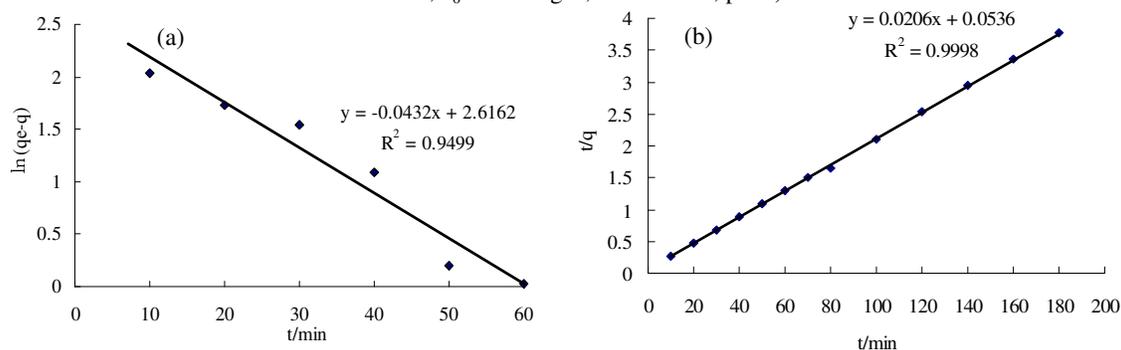

Figure 7: (a) First-order adsorption rate; (b) Second-order adsorption rate of Cr(VI) on AC

Effect of temperature

It is well known that temperature plays an important role in the adsorption process. The temperature was varied from 25 to 70 °C, at a contact time of 180 min and Cr(VI) ion concentration of 100 mg/L. It can be observed in Figure 6 that the adsorption of Cr(VI) ion at various temperature increases with the increase of temperature. As the temperature was increased from 25 to 60 °C, Cr(VI) ion removal sharply increased. As the temperature was further increased from 60 to 70 °C, Cr(VI) ion removal kept at a constant level. When the temperature was 60 °C, the removal ratio of Cr(VI) was nearly 95.9%. Results indicate that maximum adsorption for Cr(VI) was achieved at 60 °C. This could be attributed to the formation of better structured adsorbed Cr(VI) ions on the carbon surface. Meanwhile, the adsorption of Cr(VI) ion on AC particles is an exothermal process, implying a physical adsorption process when the temperature is higher than 60 °C. A similar phenomenon was found in the adsorption of Cr(VI) on sulphuric acid-treated wheat bran.[18]

Adsorption kinetic studies

The kinetics of adsorption of Cr(VI) from aqueous solution has been discussed in view of the pseudo-first-order equation and the pseudo-second-order equation.[19-20] These kinetic rate equations can be written as follows:

$$In(q_e - q) = In q_e - k_1 t \qquad (2)$$

$$\frac{t}{q} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \qquad (3)$$

where q (mg/g) is the amount of Cr(VI) adsorbed at time t (min); q_e (mg/g) is the amount of Cr(VI) adsorbed at equilibrium, k_l (1/min) is the first-order adsorption rate constant; k_2 (g mg/min) is the rate constant of second-order adsorption.

In Figure 7(a) and (b), the fitting plots using the pseudo-first-order equation and the pseudo-second-order equation are shown. A comparison of the data obtained by the two models is given in Table 1. The coefficient of determination (R^2) for the formula showed that the pseudo-second-order equation was more

suitable for the experimental data. The data showed that a good agreement between the experimental and the calculated q_e values was observed by using the pseudo-second-order equation. The obtained results suggested that the pseudo-second-order model provides the best correlation of the data, based on the assumption that the rate-limiting step may be caused by chemical sorption or chemisorptions involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate.[21]

Adsorption isotherms

The Langmuir and Freundlich models were the most common models to describe the adsorption isotherms.[22-27] The Langmuir adsorption isotherm is given by the following equation:[28]

$$\frac{c_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{c_e}{q_m}$$

(4)

where q_m (mg/g) is the amount of adsorption

corresponding to complete monolayer coverage and b (1/mg) is the Langmuir constant related to the energy or net enthalpy of adsorption. The linear plots of C_e/q_e *versus* C_e are shown in Figure 8(a). R_L shows the adsorption capacity ($R_L = 1/(1+K_Lq_m)$). When $0 < R_L < 1$, it has a fine adsorption.

The Freundlich adsorption isotherm is given by the following equation:[29]

$$q_e = K_f C_e^{1/n}$$

(5)

where K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity in Figure 8(b). Usually, for a good adsorbent, $1 < n < 10$. The above relation is presented in Table 2.

As can be seen from Figure 8(a), the value of the coefficient of determination (R^2) is 0.9881, and it was higher for the Langmuir isotherm than for the Freundlich isotherm, which is 0.9643. The result shows that the adsorption isotherm of Cr(VI) exhibited Langmuir behavior.

Table 1
Parameters of adsorption rate of Cr(VI)

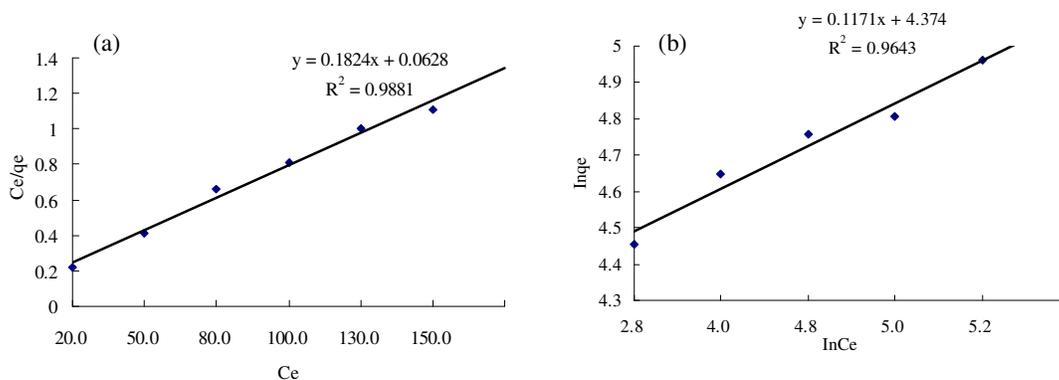| AC-KOH	Pseudo-first-order equation	Pseudo-second-order equation
q_e/mg/g	13.68	48.54
K_1/min^{-1}	0.0432	0.0079
R^2	0.9499	0.9998

Figure 8: (a) Langmuir adsorption isotherm; (b) Freundlich adsorption isotherm

Table 2
Adsorption isotherm constants for Cr(VI) by AC

AC-KOH	Langmuir				Freundlich		
	q_m	K_L	R_L	R^2	1/n	K_F	R^2
	5.48	2.9	0.059	0.9881	0.1171	79.36	0.9643

CONCLUSION

The study indicates that mushroom medium can be developed into an effective adsorbent for the removal of Cr(VI) from aqueous solutions. The experimental results show that a dosage of AC of 0.1 g, reaction time of 3 h, temperature of 60 °C and pH 2 are the optimum conditions for Cr(VI) removal. With an increase of the initial concentration of the chromium solution, the Cr(VI) removal rate reduced. In addition, the adsorption behaviour of Cr(VI) by AC is more in line with the Langmuir model. Considering the dynamics equation of Lagergren primary and secondary data on the rate of adsorption, the adsorption behavior of AC for Cr(VI) followed the law of secondary dynamics.

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