ADSORPTION OF Cr(VI) FROM AQUEOUS SOLUTION USING CARBON-MICROSILICA COMPOSITE ADSORBENT

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ABSTRACT

In this work, Microsilica, one kind of industry solid waste material, was utilized firstly to prepare a carbon-Microsilica composite adsorbent from a partial carbonization, mixture and sulfoxidation process and was proposed for the removal of Cr(VI) from solutions. The surface chemistry characteristics of the prepared adsorbent were analysis by XPS and FT-IR. The characterization results indicated that an abundant of oxygen functional groups, such as hydroxyl, carboxyl and sulfonic groups, were introduced into the surface of the prepared composite adsorbent. Meanwhile, the adsorption characteristics of Cr(VI) onto the adsorbent in aqueous solutions was studied as a function of solution pH, ionic strength, contact time, and temperature. The results showed that Cr(VI) adsorption onto the adsorbent is strongly dependent on pH and, to a lesser extent, ionic strength. Kinetics data were found to follow the pseudo-second-order kinetic model while the adsorption data corresponded to L-shape adsorption isotherm which corresponds to the classification of Giles. Activation thermodynamic parameters, such as activation enthalpy (ΔH^*), activation entropy (ΔS^*), activation Gibbs free energy (ΔG^*) and activation energy (E_a), have been evaluated and the possible adsorption mechanism also was suggested.

Keywords: Microsilica, Adsorption, Cr(VI), Isotherm, Kinetics

1. INTRODUCTION

Nowadays, heavy metals are among the most important pollutants in source and treated water and becoming a severe public health problem. Chromium, a toxic heavy metal ion, is found in wastewater of various industries, such as paint and pigment manufacturing, stainless steel production, corrosion control, leather tanning, chrome plating and wood preservation [1]. Chromium exists almost exclusively in the Cr(III) oxidation state or in the Cr(VI) oxidation state, however, Cr(VI) is 500 times more toxic than the trivalent form [2]. Thus, the presence of Cr(VI) ions in the environment is posing serious problems and causing great public concern [3]. According to USEPA, the permissible level of Cr(VI) in drinking water should be less than 100 $\mu\text{g/L}$ [4].

Many physical-chemical methods, included reduction [5], ion exchange [6], precipitation [7] and membrane separation [8], have been proposed for Cr(VI) removal from industrial effluent. However, these methods are often inefficient and/or cost disadvantageous when they are used to remove heavy metal ions from solution [9]. Adsorption methods were found to be more effective and attractive due to its lower costs and the higher efficiency of heavy metal ions removal from wastewater [10]. Carbonaceous adsorbents, such as active carbon, are the most widely used adsorbent to remove heavy metal ions from wastewater. In recent years, the production of carbonaceous adsorbent from a range of low-cost precursors, mainly industrial or agricultural by-products, has received increasing attention [11,12].

Microsilica is a by-product of the production silicon metal or ferrosilicon alloys with a particle size ranging from ca. 100–500nm [13]. The dominant constituent of Microsilica is amorphous silicon dioxide. At present, Microsilica is mainly used as an additive in Portland cement concretes and fireproof material to improve material properties due to extremely high surface area and amorphous nature [14,15]. But the applied study of Microsilica for metal ion removal had not been reported in the literatures. In this work, Microsilica was utilized firstly to prepare a carbon-Microsilica composite adsorbent and was proposed for the removal of Cr(VI) from solutions. Its feasibility for Cr(VI) removal was assessed by studying the effect of solution pH, ionic strength, contact time, and temperature. In addition, the adsorption kinetic, isotherm and activation thermodynamics were investigated. The possible adsorption mechanism of the adsorption process also was suggested.

2. MATERIALS AND METHODS

2.1. Materials

Microsilica ($\text{SiO}_2 > 68\%$) was provided by Jiuquan Iron & Steel Group Co., Ltd. Sucrose of chemical purity was purchased from Shanghai Experiment Reagent Co., Ltd. Sulfuric acid (AR) was used as carburetant. Other chemicals used were analytical reagent (AR).

2.2. Preparation of the adsorbent

The carbon-Microsilica composite was prepared according to the process below. Briefly, 2g of sucrose was dissolved in 1 mL H_2O , after which 4 mL 98%

H_2SO_4 was added dropwise at ambient temperature to obtain carbon precursor, and then 5 g Microsilica was immediately added in this precursor, and stirred to a mash, which was then maintained in a thermostatic drying oven at 150°C for 1h. After which it was transferred to a vacuum drying oven, and heated at 220°C for 5h at 0.06MPa. Finally, the sample was directly cooled to ambient temperature under vacuum. A black carbon-covered Microsilica composite adsorbent powder then was obtained. The pH of the prepared composite adsorbent is about 5.0–6.0. BET surface area and total pore volume determined by Surface area and porosimetry analyzer (Tristar 3000, Micromeritics Ltd., USA) in 77 K are 51 m^2/g and 0.04 cm^3/g , respectively. The waste gas generated during the preparation process was adsorbed by KOH solution.

2.3. Surface chemistry determination

X-ray photoelectron spectra (XPS, Escalab210, Vg Scientific Ltd., UK) and Fourier transform infrared spectroscopy (FT-IR, Nexus 670, Thermo-Nicolet, USA) were utilized for surface chemistry determination.

2.4. Adsorption of Cr(VI)

A stock solution of Cr(VI) was prepared (2000 mg/L) by dissolving required amount of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 50 to 300 mg/L. Batch adsorption experiments were performed by contacting 0.2 g of the adsorbent samples with 70 mL of the aqueous solution of different initial concentration. The experiments were performed in a shaking thermostatic gas bath at controlled temperatures for a period of 72h at 160 rpm using 100 mL Erlenmeyer flasks. The suspensions were then filtered off, and the residual Cr(VI) in the filtrate was measured spectrophotometrically using 1,5 diphenylcarbazide method at 540 nm (Perkin Elmer UV-vis spectrophotometer Lambda 25) [16]. The Cr(VI) concentration retained in the adsorbent phase was calculated according to

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (1)$$

where c_0 and c_e are the initial and equilibrium concentrations (mg/L) of Cr(VI) solution, respectively; V is the volume (L); and W is the weight (g) of the adsorbent.

In order to study the effect of pH on the adsorption of Cr(VI) onto the adsorbent, before mixing with adsorbent, initial pH of each solution was adjusted to an appropriate value by adding 0.1 mol/L HCl or/and NaOH solutions.

The effect of ionic strength on the adsorption was investigated at 0–4.0 mol/L NaCl salt concentrations at 25°C, natural solution pH, 160 rpm and constant initial Cr(VI) concentration.

Adsorption kinetics were studied with an initial Cr(VI) concentration of 100 mg/L at natural solution pH, an initial volume of 70 mL, and a sample weight of 0.2 g. A series of replicates samples were prepared, and the samples were removed at different time for the analysis of Cr(VI) concentration.

Adsorption isotherms were performed at different initial Cr(VI) concentrations. For each solution, 0.2 g of adsorbent was added and the samples were shaken for 72h.

3. RESULTS AND DISCUSSIONS

3.1. Surface chemistry characteristics of the prepared adsorbent

XPS and FT-IR spectrum were employed to determine the surface elemental composition and function groups of the prepared adsorbent.

Fig.1. The XPS survey spectra of the prepared adsorbent (a: XPS survey spectra; b: The high-resolution XPS S2p spectra).

Fig.2. The high-resolution XPS C1s spectra of the prepared adsorbent.

XPS survey spectra, as is shown in Fig. 1a, indicates that carbon, oxygen, silica and sulfur element are main elements on the prepared adsorbent surface, thereinto, carbon and oxygen elements are dominant superficial elements. The atomic ratio of O/C reaches 2.3:1, which implies that there are abundant oxygen functional groups on the prepared adsorbent surface. The content of silica element on the prepared adsorbent surface only is 8.65%, and is much lower than that of Microsilica, that result illuminates that most of the prepared adsorbent surface is coated by carbon particles. The XPS survey spectra of the prepared adsorbent also exhibits a single S2p peak attributable to SO₃H groups at 168 eV (see Fig. 1b) [17]. The high-resolution XPS C1s spectrum of the adsorbent (Fig. 2) shows several relatively well-resolved peaks corresponding to carbon atoms in different chemical environments. So, it was resolved into four individual component peaks representing graphitic carbon (C-C, B.E.=284.5eV, 26.84%), hydroxyl/ether groups (C-O, B.E.= 285.8eV, 38.81%), carbonyl groups (C=O, B.E.=287.2eV, 5.97%) and carboxyl groups (COOH, B.E.=288.7eV, 28.38%) [18,19]. The characterization results of XPS indicated that hydroxyl groups, carboxylic groups and sulfonic groups are the main oxygen groups on the surface of the prepared adsorbent.

Fig.3. The FT-IR spectra of the prepared adsorbent.

Fig. 3 shows the FT-IR spectrum of the prepared adsorbent. The presence of oxygen groups is also evidenced by the bands at 3000–3700cm⁻¹ (a wide band attributed to O-H stretching vibrations in hydroxyl or carboxyl groups) and 1720cm⁻¹ (C=O vibrations corresponding to carbonyl, quinone, ester or carboxyl) [20,21]. Moreover, The sulfonic group is evidenced by the bands at 1368cm⁻¹ (O=S=O stretching in SO₃H) [22].

3.2. Effect of pH

The pH of solution has been identified as the most important variable governing metal adsorption. The effect of pH on the adsorption of Cr(VI) was studied over a pH range of 2.0–8.0 at 25°C. The procedure outlined in the experimental section was followed with 0.2 g of adsorbent and 70 mL of 100 mg/L Cr(VI) solution at a desired pH. As shown in Fig. 4, it is apparent that the adsorption amount of Cr(VI) on the adsorbent decreased with increasing pH especially in the earlier stages. This variation in the amount of adsorption clearly indicated the pH of the system is very effective on the adsorption capacity of Cr(VI) onto the adsorbent.

Fig. 4. Effect of pH on the adsorption of Cr(VI) onto the prepared adsorbent .

The main factors influencing the pH on the adsorption process are Cr(VI) species and surface functional groups on the adsorbents. In aqueous solutions, Cr(VI) is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. In acidic medium, HCrO₄⁻ is the predominant form of Cr(VI), as pH increasing, HCrO₄⁻ constantly converts to CrO₄²⁻ and Cr₂O₇²⁻ [23]. This trend would weaken the ability of Cr(VI) forming H-bond with oxygen groups. On the other hand, the dissociation degree of carboxyl groups and sulfonic groups would increase with increasing pH, which would enhance the repulsion between adsorbent and HCrO₄⁻.

3.3. Effect of ionic strength

The effect of the ionic strength on the adsorption of Cr(VI) onto the adsorbent is shown in Fig. 5, these data have been obtained over an ionic strength range of 0–4.0mol/L NaCl salt concentrations at 25°C. As shown in Fig. 5, while the NaCl concentrations increased from 0 to 0.3 mol/L, the adsorption amount of Cr(VI) decreased from 12.5 to 8.7 mg/g. And then, the

adsorption amount of Cr(VI) increased with NaCl concentrations increasing. When the NaCl concentrations reached 4.0 mol/L, the adsorption amount of Cr(VI) reached 13.6 mg/g. The result indicated that the adsorbent performed a considerable adsorption amount of Cr(VI) even at strong ionic strength.

Fig. 5. Effect of ionic strength on the adsorption of Cr(VI) onto the prepared adsorbent.

The decrease of adsorption amount with increasing of ionic strength can be explained by considering the surface charge on the prepared adsorbent. Due to salt effect, increasing ionic strength would result in constant dissociation of sulfonic groups, which would lead to increasing of negative charge on the surface of the adsorbent. Increasing negative charge can effectively enhance the repulsion between adsorbent and HCrO_4^- , which disadvantageous the adsorption of Cr(VI). When $c_{\text{NaCl}} > 0.3 \text{ mol/L}$, all sulfonic groups had dissociated, increasing of ionic strength would not induce increasing of negative charge again, but would compress the double layer, neutralize negative charges on surface of the adsorbent, and thus weaken the repulsion between adsorbent and adsorbate ions [24], which favored the adsorption of Cr(VI) onto the adsorbent.

3.4. Adsorption isotherms and adsorption mechanism

The adsorption isotherm is important in the study and design of adsorption systems. The adsorption isotherm were determined by allowing a Cr(VI) solution of different initial concentration to be mixed with accurately weighed amount of adsorbent at 25 °C.

Fig. 6. Adsorption isotherm plots for the adsorption of Cr(VI) onto the prepared adsorbent.

The obtained experimental equilibrium data for the adsorption of Cr(VI) onto the adsorbent at the different Cr(VI) equilibrium concentration are presented in Fig. 6. It is apparent that this adsorption isotherm belongs to subgroup 3 of L-shape isotherm which corresponds to the classification of Giles [25]. This type isotherm indicate that the second layer can form readily [25]. As present, an abound of oxygen functional groups, such as hydroxyl,

carboxyl and sulfonic groups were introduced into the surface of the prepared sorbent. these oxygen groups can form H-bond with HCrO_4^- radical at acid aqueous solution and remove Cr(VI) from the aqueous solution. When all of the available monolayer sites are occupied, the HCrO_4^- radical in solution also could be adsorbed by H-bond between the HCrO_4^- radical in solution and the HCrO_4^- radical adsorbed on the adsorbent. The potential adsorption mechanism is suggested in Fig. 7.

Fig. 7. Possible adsorption mechanism of the adsorption of Cr(VI) onto the prepared adsorbent.

3.5. Adsorption kinetics

In order to investigate the controlling mechanism of adsorption processes, the pseudo-first- order [26], and pseudo-second-order equations [27], are applied to model the kinetics of Cr(VI) adsorption onto the adsorption.

(1) Pseudo-first-order model

A pseudo first-order equation can be expressed in a linear form as

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} (t) \quad (2)$$

The non-linear form of the model can be expressed as

$$q_t = q_e - \frac{q_e}{k_1} e^{-\frac{t}{2.303}} \quad (3)$$

where q_t is the adsorption amount of Cr(VI) (mg/g) at time t (min), q_e is the adsorption amount of Cr(VI) at equilibrium (mg/g), and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}).

(2) Pseudo-second-order model

The adsorption kinetics may also be described by a pseudo-second-order kinetics model. The linear form of the model is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (4)$$

The model also can be expressed in a non-linear form:

$$q_t = \frac{q_e}{\frac{1}{k_2 q_e} + 1} \quad (5)$$

where k_2 is the pseudo-second-order rate constant of adsorption.

The adsorption kinetics studies were conducted using an initial Cr(VI) concentrations of 100 mg/L at nature solution pH. Kinetics parameters at different temperatures of the two models obtained by using non-linear regression are listed in Table 1. Both the two kinetics models at three different temperatures are illustrated in Fig. 8 and Fig. 9, respectively. It was found that the fitting to the pseudo-second-order mode gave the higher values of correlation coefficients than those for the pseudo-first-order kinetic model at the temperatures investigated. The above results showed that the pseudo-second-order model fits better the experimental data than the pseudo-first-order model at the temperatures investigated.

Fig. 8. Kinetics of the adsorption of Cr(VI) onto the adsorbent according to the non-linear pseudo-first-order kinetic equation.

Fig. 9. Kinetics of the adsorption of Cr(VI) onto the adsorbent according to the non-linear pseudo-second-order kinetic equation.

Table 1: Parameters of two kinetic models for the adsorption of Cr(VI) onto the prepared adsorbent.

Temperature (K)	Pseudo-first-order			Pseudo-second-order		
	q_e (mg/g)	k_1 (min ⁻¹)	R ²	q_e (mg/g)	k_2 (m ³ /mg·min)	R ²
298	18.90	6.18×10^{-3}	0.810	21.82	1.53×10^{-4}	0.971
308	23.70	5.48×10^{-3}	0.833	26.10	1.807×10^{-4}	0.967
318	25.75	6.01×10^{-3}	0.859	28.14	1.990×10^{-4}	0.971

3.6 Activation thermodynamics parameters

According to the results of the kinetic study the pseudo-second-order model was found to be the best model to describe the experimental kinetic data for the adsorption of Cr(VI) onto the adsorbent. The second-order rate constants listed in Tables 1 are used to estimate the activation energy of Cr(VI) adsorption onto the adsorbent using Arrhenius equation:

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \quad (6)$$

where E_a is the activation energy (J/mol), k_2 is the rate constant of adsorption, k_0 is Arrhenius factor, which is the temperature independent factor, R is the gas constant (J/K·mol), and T is the solution temperature (K). Accordingly, the activation energy of the adsorption was calculated using Eq. (6). The value of E_a was obtained from the slope of the plot of $\ln k_2$ versus $1/T$ (Figure is not shown) and recorded in Table 2 [28]. Since the values of the activation energy are lower than 40 kJ/mol, this indicates that the adsorption has a potential barrier corresponding to a physisorption [28].

Another aim of this paper is to consider the effect of solution temperature on the transport/kinetic process of Cr(VI) adsorption. Therefore, the activation thermodynamic parameters of the adsorption such as activation enthalpy (ΔH^*) and activation entropy (ΔS^*) were determined using the Eyring equation [29,30]:

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h_p}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (7)$$

Table 2 : Activation thermodynamic parameters of the adsorption of Cr(VI) onto the prepared adsorbent.

T(K)	Activation thermodynamics parameters			
	ΔG^* (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol·K)	E_a (kJ/mol)
298	94.79	7.82	-291.60	10.46
308	97.63			
318	100.55			

where k_B is the Boltzmann constant (1.3807×10^{-23} J/K) and h_p is the Planck constant (6.6261×10^{-34} J·s). The value of ΔH^* and ΔS^* were obtained from the slope of the plot of $\ln(k_2/T)$ versus $1/T$ (Figure is not shown).

The value of ΔG^* is given by following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (8)$$

The values of these parameters were recorded in Table 2. The value of ΔH^* (7.82 kJ/mol) indicated that the adsorption is physical in nature involving weak forces of attraction and is also endothermic. At the same time, the low value of ΔH^* implied that there was loose bonding between the adsorbate molecules and the adsorbent surface [31]. The negative activation entropy change (ΔS^*) value corresponds to a decrease in the degree of freedom of the adsorbed species [29]. The positive ΔG^* values indicate that the instability activation complex of the adsorption reaction increases with increasing temperature.

3.7 Comparison with other adsorbents

The adsorption capacity of the prepared adsorbent for Cr(VI) have been compared with active carbon and other industry wasters reported in the literatures and the values of adsorption capacities are presented in Table 3. As shown in Tables 3, the BET surface area of the prepared adsorbent is far lower than that of active carbon, but the Cr(VI) adsorptive capacity still can reach about 60.8% of the capacity of active carbon and more than that of other industry wasters. This result indicated that oxygen functional groups on the prepared adsorbent surface play an imported role in the adsorption process of Cr(VI) (As shown in Fig. 7).

Table 3: Comparison of adsorption capacities of chromium with various adsorbents.

Adsorbents	Surface area (m ² /g)	Adsorption capacity (mg/g)	Initial Cr(VI) concentration (mg/L)	pH	Reference
Activate carbon	1286	31.1	100	6.0	[32]
Carbon slurr		15.24	100	2.0	[33]
Fly ash	62	0.258			[34]
Pomace	1	10.34	100		[35]
Wood sawdust	3	4.87	150	2.0	[36]
Sugarcane bagasse		13.40	500	2.0	[37]
Carbon-Microsilica	51	18.9	100	5.0-6.0	This paper

4. CONCLUSION

A novel carbon-Microsilica composite adsorbent was prepared using Microsilica as raw material. The results of surface chemistry determination indicated that there are an abundance of oxygen groups, such as hydroxy groups, carboxyl groups and sulfonic groups, were introduced into the surface of the prepared adsorbent. These oxygen groups are potential adsorption sites for Cr(VI) ions, which could form H-bond with Cr(VI) excited by HCrO_4^- form in acid solution. The apparent effect of solution pH and ionic strength on the adsorption also supported the H-bond adsorption mechanism. The adsorption equilibrium date of the adsorption was found to correspond to subgroup 3 of L-shape isotherm, which type isotherm indicates the second layer can form readily. Kinetics date of the adsorption was found to follow the pseudo-second-

order kinetic model. The positive ΔH^* value indicated that the adsorption process are endothermic in nature, while the positive ΔG^* values indicate that the instability activation complex of the adsorption reaction increases with increasing temperature.

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