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Formation of Carbon Aerogels From Glucose and as Adsorbents for Removal of Methylene Blue

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Abstract

In this communication, Carbon aerogels were prepared by hydrothermal process using glucose as raw material and the structure and morphology were characterized by XRD, SEM, and IR. Methylene blue was removed by employing the as-prepared nano materials as adsorbent. The maximum adsorption capacity determined from the Langmuir adsorption isotherm was 819.67 $mg \cdot g^{-1}$ and adsorption kinetics and adsorption isotherms were also studied.

Keywords: dyes, carbon aerogels, adsorption, methylene blue

1. Introduction

Dyes, which make the world colorful and charming, are widely used in the field of leather industry, printing industry, textiles industry, plastics, cosmetic industries and so on. However, dyes also have been bringing about a lot of environmental pollutions (Bhatnagar & Jain, 2005). Moreover, a large amount of dyes and pigments are toxic naturally and may cause serious diseases such as skin and eye irritation, allergic dermatitis, skin cancer as well as aberration (Eren & Afsin, 2009). Therefore, during the past decades, intensive attention has been paid to the removal of dyes. Chemical, physical and biological methods, which mainly including advanced oxidation, ozonation decomposition, adsorption, coagulation, flocculation, ultrafiltration, and extraction, biosorption were the most popular technologies have been developed nowadays (Ghaedi, Hassanzadeh, & NasiriKokhdan, 2011; Yao, Wang, & Qi, 2009; Abd EI-Latif, Ibrahim, & EI-Kady, 2010; Vimonses, Lei, Jin, Chow, & Saint, 2009). However, none of the above-mentioned methods were succeed in completely removing the dyes from wastewater because most of the methods often suffer from one or more boundedness. Interestingly, adsorption method is regarded as the most promising methods for removal of dyes and treatment of wastewater (Ai, Zhang, & Chen, 2011).

Carbon aerogel a novel form of cellular carbonaceous adsorbent, has been developed and has excellent adsorption properties recently. Basically, carbon aerogel, which has well-defined porous structure, high specific surface areas, is a representative cellular carbonaceous material (Moreno-Castilla & Maldonado-Hódar, 2005; Long et al., 2009). So far, there were a large number of reports on the adsorption of organic dyes (X. B. Wu, D. C. Wu, Fu, & Zeng, 2012) and inorganic (especially metal ions) based on carbon aerogel (Al-Anber & Matouq, 2008; Meena, Mishra, Rai, Rajagopal, & Nagar, 2005). Therefore, for the further application of carbon aerogel, it was meaningful to explore the adsorption properties of carbon aerogel so as to obtain adsorbent with faster adsorption rate and higher adsorption capacity.

2. Materials and Method

2.1 Synthesis of Carbon Aerogels

According to the previous reports (Fellinger, White, Titirici, & Antonietti, 2012), 1 g of H_3BO_3 was added into 15 ml deionized water and slightly heated to dissolve, then sodium hydroxide was added in portion to tune the pH at 9–10, after that 5.4 g of glucose was added to 12 ml of the as-prepared solution. After stirred violently for 0.5 h, the mixture was then shifted to a 25 mL autoclave, sealed and heated at 180 ^oC for 8 h. After cooled to ambient conditions, the mixture was washed and dried to yield the target products. The carbon aerogels were characterized before their application.

2.2 Characterization of the Carbon Aerogels

Characterization of the crystal structure and morphologies of Carbon aerogels were performed by using X-ray diffraction (XRD, Cu Kα, radiation Rigaku Ultima IV), Scanning Electron Microscope (SEM, JEOL JSM-6510LV) and Infrared Spectroscopy (IR, Thermo Scientific Nicolet 6700).

2.3 Batch Adsorption Experiments

In a thermostatic oscillator, the experiments were performed by placing an appreciate amount of carbon aerogels adsorbent in a certain volume of solution at different concentrations of methylene blue. About 4 mL of the suspension was extracted in a certain interval, and was separated by centrifugation. A UV-Vis Spectrometer was adopted to analyze the obtained supernatant in order to confirm the concentration of methylene blue. The adsorption capacity (q) of the adsorbent can be calculated by Equation (1)

$$q = \frac{(c_0 - c_e)V}{m} \tag{1}$$

In the equation, c_0 and c_e are the original and the equilibrium concentration of methylene blue ($mg \cdot L^{-1}$), respectively, and m is the mass (g) of the Carbon aerogels, and V is the total volume (L) of methylene blue solution.

3. Results and Discussions

3.1 Crystal Structure of Carbon Aerogels

The carbon aerogels were characterized by XRD, IR, and SEM. The XRD pattern of the carbon aerogels was exhibited in Figure 1a), as can be seen clearly that only in the vicinity of 24° has a wide peak, which is due to the reaction of carbon through an amorphous carbon, and the crystallinity is low, the peak bit wider. Figure 1b) demonstrates the infrared spectrum, the peak at 3400 cm^{-1} corresponds to the absorption of -OH, and the peak at 1030 cm^{-1} corresponds to the absorption of C-OH, the two peaks clearly indicate that a large amount of carbon-OH exist in the spherical surface. The peak at 1620 cm^{-1} can be ascribed to the conjugated olefin skeleton caused by vibration, while the peak at 1700 cm^{-1} are induced by the C=O stretching vibration. A great number of hydrophilic functional groups -OH and C=O exist in the carbon surface of the ball, which obviously improve its dispersibility in aqueous solution. The SEM image of the dispersive nanosphere was shown in Figure 2, and the average diameter is approximately 200–300 nm.

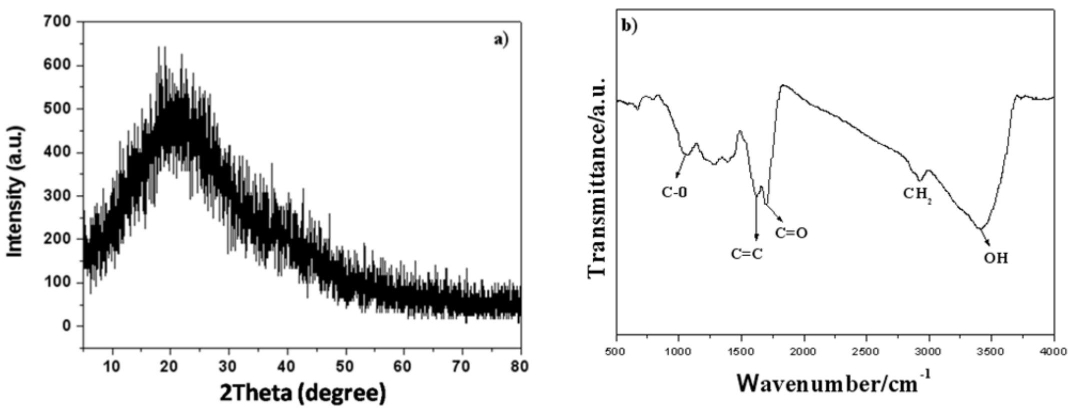

Figure 1. XRD pattern (a) and IR spectrogram (b) of Carbon aerogels

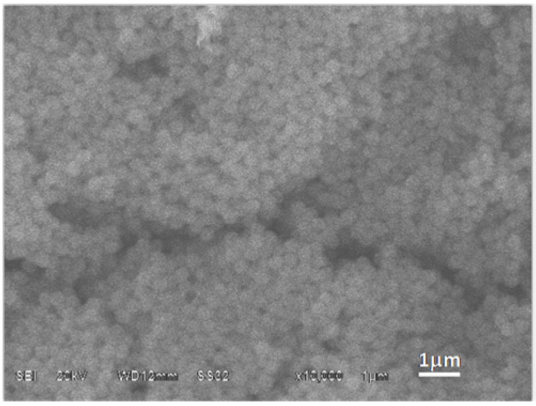

Figure 2. SEM of Carbon aerogels

3.2 Effect of Contact Time

In each batch experiment, 50 mL of initial MB aqueous solution with the concentration of 100 mg·L^{-1} and 15 mg carbon aerogels were put in a beaker flask. The mixture solution was agitated in a thermostatic oscillator under ambient conditions. The samples were extracted at certain intervals and centrifuged. UV-Vis Spectrometer was adopted to determine the concentration of MB left in the supernatant solution at 664 nm. Figure 3 demonstrates that adsorption capacity of MB was affected markedly by contact time by using the carbon aerogels as adsorbent. It was obvious that the adsorption capacities increase rapidly in the first 10 min and then slow increase and reach equilibrium after 30 min.

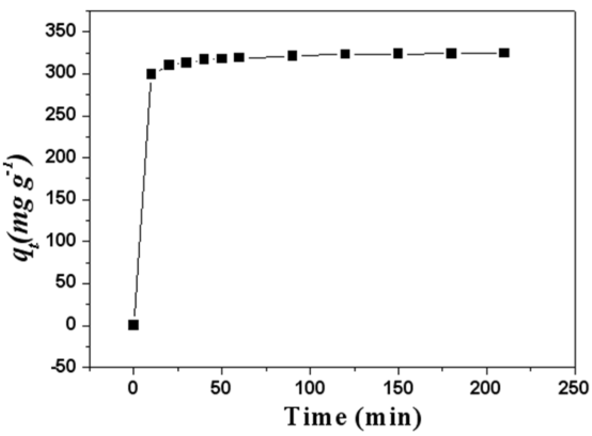

Figure 3. Effect of the contact time on adsorption

3.3 Adsorption Kinetics

To explore the intrinsic mechanism of the adsorption process, experimental data are analyzed by employing the pseudo-first-order and pseudo-second-order (Figure 4).

The pseudo-first-order equation can be given by (Khataee, Vafaei, & Jannatkhah, 2013)

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

In the equation, q_e and q_t stand for the amounts of MB adsorbed (mg·g^{-1}) at equilibrium and time t (min), respectively, k_1 stands for the rate constant of pseudo-first-order (min^{-1}). Values of k_1 can be calculated from the plots of $\log(q_e - q_t)$ versus t for Equation (2).

The pseudo-second-order equation can be given by Equation (3) (Cherifi, Bentahar, & Salah, 2013).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

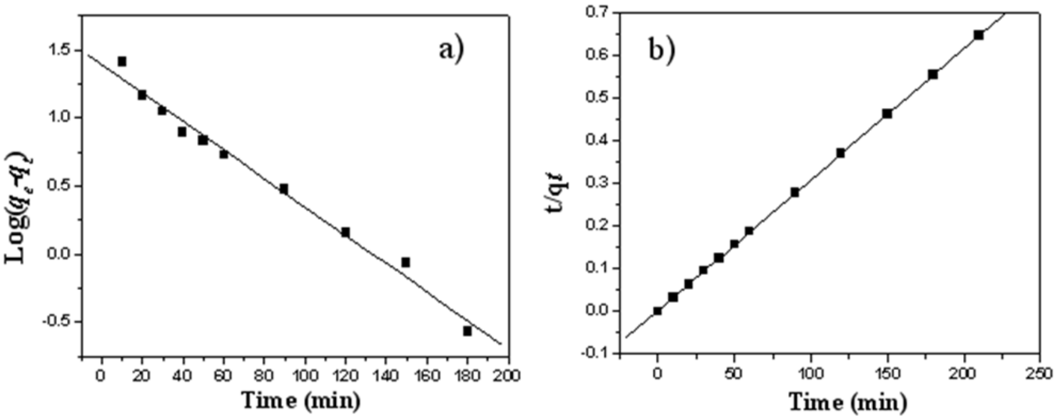

Figure 4. Adsorption kinetics: a) pseudo-first-order plot; b) pseudo-second-order plot

In the Equation (3), k_2 stands for the pseudo-second-order rate constant (mg·g^{-1}·min). The values of $1/q_e$ and $1/k_2q_e^2$ are yielded by the slope and intercept of the linear plots of t/q_t against t for Equation (3).

By linear regression for the two models, the kinetic constants were obtained, which are summarized in Table 1. Obviously, with regard to the pseudo-first-order model, the correlation coefficients (R^2) are relatively low, and the calculated q_e values ($q_{e,cal}$) does not accord with the experimental data ($q_{e,exp}$), indicating that the MB adsorption on the Carbon aerogels does not fit to the pseudo-first-order model. Usually, this model does not fit well to the whole range of contact time in many cases. The pseudo-first-order equation is applicable only to the initial stage of the adsorption processes. In contrast, as far as the pseudo-second-order model is concerned, the $q_{e,cal}$ values conform very well to the experimental results, indicating there are a good linear relation with R^2 above 0.999. Therefore, the conclusion can be drawn that the adsorption process follows the pseudo-second-order model.

Table 1. Kinetic parameters for adsorption of MB onto the Carbon aerogel

	Kinetic parameters	MB
Pseudo-first-order	$q_{e,exp}$ (mg·g^{-1})	324.56
	$q_{e,cal}$ (mg·g^{-1})	24.59
	k_1	0.024
	R_1^2	0.987 18
Pseudo-second-order	$q_{e,cal}$ (mg·g^{-1})	325.73
	k_2	0.003 27
	R_2^2	0.999 98

3.4 Effect of Temperature and Adsorption Isotherms

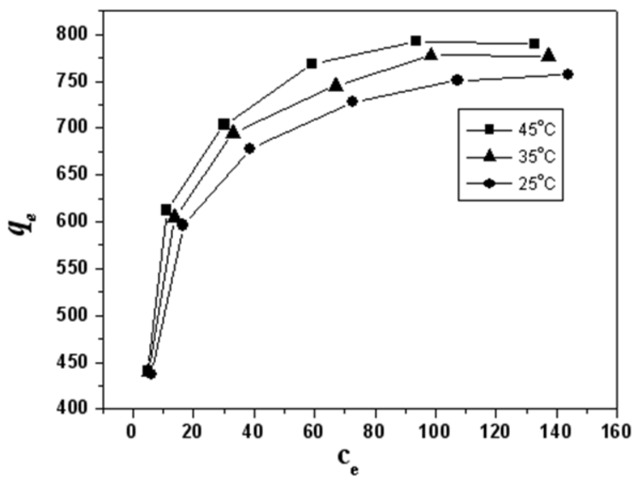

Figure 5. Effect of temperature on the adsorption of MB

To investigate the temperature effect on the adsorption, adsorption experiments were carried out at three different temperatures (25, 35, and 45 °C) with distinct original concentrations (from 150 to 400 mg·L^{-1}). Figure 5 demonstrated the experimental results. From the results, we can see clearly that the MB adsorption capacities increase when the temperature increase, indicating that the adsorption process is endothermic naturally.

The specific relationship between the adsorption capacity of adsorbent and the concentration of adsorbate can be clearly described by adsorption isotherms. Therefore, it is crucial to design and determine an adsorption system. Usually, Langmuir and Freundlich isotherms equations are often applied to analyze the experimental results. Generally, the Langmuir isotherm is suitable to a process that adsorption surface is homogeneous and all the adsorption sites have equal adsorbate affinity.

The Langmuir isotherm equation can be exhibited by the following equation (Langmuir, 1918):

$$\frac{c_e}{q_e} = \frac{1}{b q_m} + \frac{c_e}{q_m} \tag{4}$$

In the equation, q_m stands for the maximum capacity (mg·g^{-1}) and b is a constant with respect to the energy of adsorption (L·mg^{-1}). Figure 6a) shows the Langmuir plot according to Equation (4).

R_L, a dimensionless constant, can express the essential characteristics of the Langmuir isotherm and parameter is given by the following equation (Weber & Chakravorti, 1974).

$$R_L = 1/(1 + bc_0) \tag{5}$$

In the equation, c_0 (mg·L^{-1}) stands for the original MB concentration. The adsorption is favorable if the value of R_L locates between 0 and 1.

By comparison, the Freundlich isotherm model assumes heterogeneity of adsorption surfaces, and adsorption capacity is related to the equilibrium concentration of MB. The Freundlich isotherm equation is presented as follows (Freundlich, 1906).

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \tag{6}$$

where K_f stands for indicator of the adsorption capacity and $1/n$ is the adsorption intensity.

For comparison, the Freundlich plot is also presented in Figure 6b) according to Equation (6).

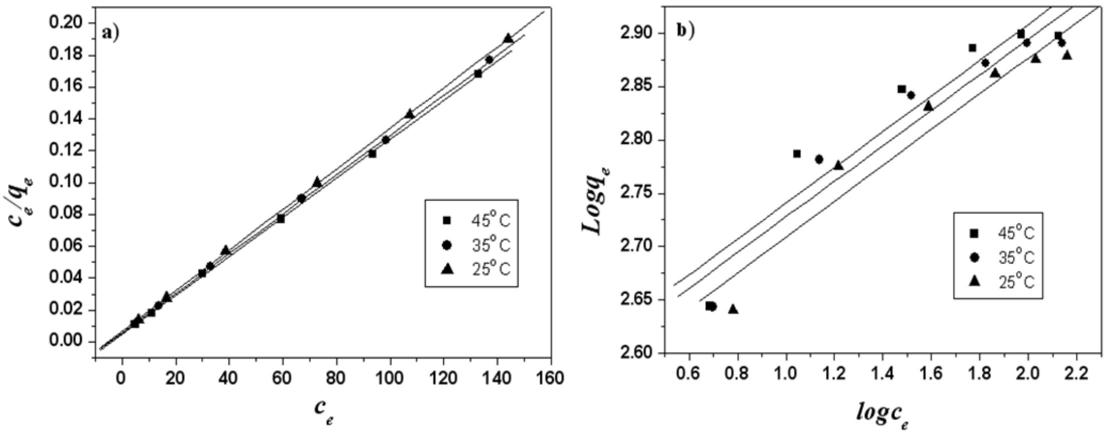

Figure 6. Langmuir (a) and (b) Freundlich isotherm plots at different temperatures

As are demonstrate in Table 2, the Langmuir model shows the high regression correlation coefficient, which indicates that the Langmuir model is more suitable than Freundlich model for depicting the adsorption equilibrium of MB by the Carbon aerogels. The maximum adsorption amount is 819.67 mg·g^{-1} determined from the Langmuir isotherm.

Table 2. Adsorption isotherms constants for the adsorption of MB on Carbon aerogel

		Langmuir				Freundlich		
	Temp.	q_m	b	R_1^2	R_L	k_F	n	R_2^2
	298	787.40	0.1865	0.9951	0.0133	347.31	5.949	0.9242
MB	308	806.45	0.2160	0.9998	0.0115	363.89	5.990	0.9213
	318	819.67	0.2455	0.9999	0.0102	374.30	5.964	0.8919

The thermodynamic parameters including the standard free energy (ΔG^o, kJ·mol^{-1}), enthalpy (ΔH^o, kJ·mol^{-1}) and entropy (ΔS^o, J·mol^{-1}·K^{-1}) for the process of MB adsorption on the Carbon aerogels were calculated using the equations as follows (Gupta, Ali, & Saini, 2007).

$$\Delta G^\circ = -RT\ln(b) \tag{7}$$

$$\Delta H^\circ = R\frac{T_2 T_1}{(T_2 - T_1)}\ln(\frac{b_2}{b_1}) \tag{8}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{9}$$

In the equations, T stands for absolute temperature (K), R stands for the gas constant (8.314 J·mol^{-1}·K^{-1}), and b stands for Langmuir constant at a specific temperature studied here. Table 3 exhibited the results calculated by the above equations. From the results, a conclusion can be drawn that the MB adsorption on the Carbon aerogels is endothermic and entropy production, which indicates that the adsorption process is a spontaneous process and can occur at any given temperature.

Table 3. Thermodynamic parameters at different temperatures

	Thermodynamic parameters		
Temp.(K)	ΔG^o(kJ·mol^{-1})	ΔH^o(kJ·mol^{-1})	ΔS^o(J·mol^{-1}·K^{-1})
298	−30.08	10.82	137.21
308	−31.47		137.30
318	−32.85		137.33

In conclusion, Carbon aerogels were prepared by hydrothermal process using glucose as raw material and the structure and morphology were characterized by XRD, SEM, and IR. Methylene blue was removed by employing the as-prepared nanomaterials as adsorbent. The maximum adsorption property is 819.67 $mg \cdot g^{-1}$ determined from the Langmuir isotherm and the adsorption kinetics and adsorption isotherms were also studied. The excellent adsorption property indicates the huge potential application of the Carbon aerogels for removal of dyes from wastewater.

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