ADSORPTION PERFORMANCE OF SILVER-LOADED ACTIVATED CARBON FIBERS

by

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Silver-loaded activated carbon fiber is prepared, and its adsorption performance is studied experimentally using five methylene blue solutions with different concentrations under three different temperature conditions. The adsorption tests show that fibers adsorption increase as the increase of temperature, and there is an optimal value for solution concentration, beyond which its adsorption will decrease. Fibers isothermal adsorption to methylene blue is different from those by the monolayer adsorption by Langmuir model and the multilayer adsorption by Freundlich model. Through the analysis of thermodynamic parameters, Gibbs free energy, standard entropy, and standard enthalpy, it is found that the fibers adsorption to methylene blue is an exothermic process of physical adsorption.

Key words: *adsorption, methylene blue, Langmuir model, thermodynamics*

Introduction

As one of main industrial pollutions, dye waste water has characteristics of complicated composition, high content of organic substance, stable chemical properties, deep chromaticity, strong toxicity, and difficult biological degradation, which have posed hazard to the water supplies and has received more and more attention [1, 2]. Methylene blue (MB) is a typical water-soluble cationic dye, which has been widely applied in textile dyeing and printing industry [3]. The MB is used as an indicator for evaluating the adsorption performance of liquid absorbent [4].

At present, there are many methods to treat the waste water of dyeing and printing, such as biological method [5], electrochemical method [6], and adsorption method [7], among which the adsorption method has been frequently used to remove the water refractory pollutants with its advantages of handy operation, obvious effect, wide range of application, and low price [8, 9]. According to some reports, the adsorption of activated carbon fibers is particularly suitable for the treatment of printing and dyeing wastewater and phenolic wastewater [10, 11]. Researchers have carried out a lot of studies for the adsorption performance of activated carbon fibers to MB. Di *et al.* [12] studied the adsorption performance of meso-porous carbon fibers to MB. They found that the adsorbing mechanism was in line with the Langmuir isotherm model. Liao [13] indicated that the adsorbing mechanism of rice husk based activated carbon fibers to MB was in accordance with the Langmuir model, which was a spontaneous exothermic reaction. Ma and Zhan [14] studied the adsorption performance of activated

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carbon fibers to MB in water. The result demonstrated that the reaction was an exothermic process, which complied with the isothermal models of Langmuir and Freundlich with correlation coefficient higher than 0.99.

Silver-loaded activated carbon fiber (hereinafter referred to as Ag/ACF) is a kind of new activated carbon fibers, which has characteristics of a large specific surface area, more pores, and also has some chemical properties of nanosilver particles [15, 16], thus it can be used as a multi-effect adsorbent. Therefore, the study on the adsorption performance of Ag/ACF materials is very necessary. This paper prepares the silver-loaded activated carbon fibers by means of silver precursor as the adsorbent to adsorb the MB in water, and analyzes the adsorbing performance of isothermal curves and thermodynamics.

Experiment

Dipping the viscose fiber after pretreatment in the nanosilver complexation solution with the concentration of 40 ppm, heating up to 90 °C for 10 min, after dehydrating and drying, we obtained nanosilver loaded viscose fibers. Then the fibers were put into the aqueous solution of ammonium dihydrogen phosphate with a concentration of 40 g/L for 16 hours. Under nitrogen atmosphere, the materials were carbonized at a heating rate of 5 °C per minute till 800 °C for 30 mintes, then the materials were activated at temperature of 900 °C by the overheating steam with a pressure of 0.6 MPa for 10 minutes. Finally the Ag/ACF were prepared for later use.

Determination of adsorption isotherm

The MB solution with concentrations of 50, 100, 150, 200, and 250 mg/L were prepared, respectively. Under different temperature circumstances of 303, 313, and 323 K, five portions of 20 mL MB solution with different concentrations were taken, added with 10 mg Ag/ACF, respectively, and oscillated at a speed of 130 rpm at a constant temperature for some time. Later, filter was done after they exhibited the adsorption equilibrium. Then the absorbance of the solution was tested at the maximum absorption wavelength 665 nm by ultraviolet-visible spectrophotometer. According to the standard curve, the equilibrium adsorption concentration, C_e, was calculated and incorporated into the formula

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

where q_e is the equilibrium adsorption quantity, C_0 – the initial concentration of the solution, C_e – the equilibrium concentration of the solution, m – the mass of adsorbent, and V – the volume of solution.

Results and discussion

Analysis of adsorption isotherm

An exact description of the adsorption performance requires a mathematical model. Zhang *et al.* [17] suggested a fuzzy model, and obtained an analytical solution by the variational iteration method. This paper focuses on experimental study. Figure 1 shows the isothermal curves of Ag/ACF adsorbing MB under three different temperature circumstances.

As shown in fig. 1, the adsorption performance improved with the rising temperature and was strikingly superior when the temperature arrived at 323 K compared with that at 303 and 313 K. This phenomenon suggests that Ag/ACF at a low temperature, the activity of silver nanoparticles could not be excited, because the silver mainly covered the surface of fibers and thus hindered the adsorption of MB onto activated carbon fibers. When temperature rising, smaller silver nanoparticles were activated first, which increased the adsorption quantity. When the temperature climbed further, bigger silver nanoparticles were also activated, which promote the occurrence of adsorption. In another word, the activation of silver nanoparticles obviously stimulated the adsorption performance of Ag/ACF. Moreover, it can be seen from the isothermal curves that, as the initial concentration of MB solution thickened, each adsorption performance displayed a tendency of firstly increase and then decrease. It demonstrates that the increase in concentration would help improve the adsorption performance, and too much increase would also inhibit the adsorption.

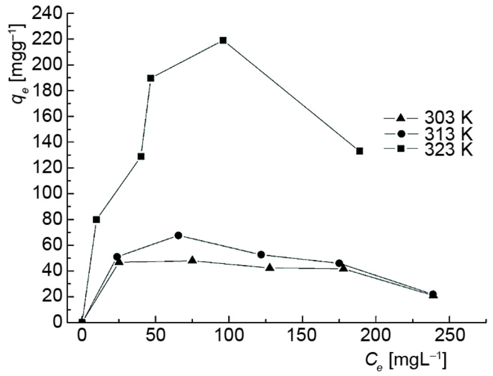

Figure 1. Adsorption isotherm of Ag/ACF to MB

When exploring the mechanism of adsorption process of activated carbon, Langmuir and Freundlich models which describe the solid-liquid isothermal curves are frequently used. Fitting the experimental data with Langmuir adsorption isotherm, eq. (2), and Freundlich adsorption isotherm, eq. (3), respectively, the results are gained and shown in figs. 2 and 3.

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{C_\mathrm{e}}{q_\mathrm{m}} + \frac{1}{k_l q_\mathrm{m}} \tag{2}$$

$$\ln q_\mathrm{e} = \ln K_\mathrm{F} + \frac{1}{n}\ln C_\mathrm{e} \tag{3}$$

where q_m is the saturated adsorption quantity of monolayers, k_l – the Langmuir equilibrium constant, K_F – the Freundlich equilibrium constant, and n – the constant related to the adsorption capacity.

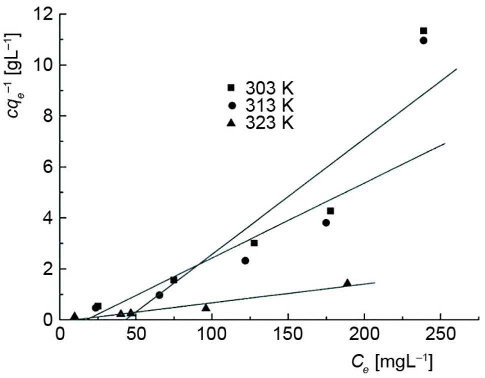

Figure 2. The fitting of Langmuir adsorption isotherm curves of MB onto Ag/ACF

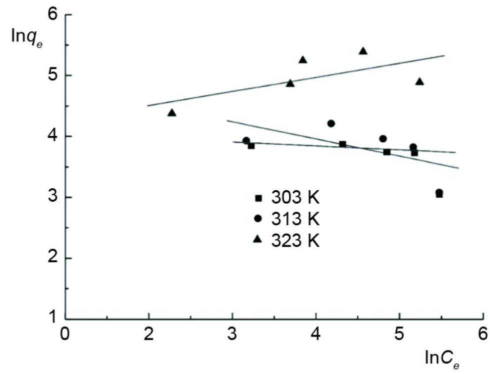

Figure 3. The fitting of Freundlich adsorption isotherm curves of MB onto Ag/ACF

The fitting equation deriving from figs. 2 and 3 is shown in tab. 1.

Table 1. Fitting results of Langmuir and Freundlich isothermal equation

Temperature [K]	Langmuir model		Freundlich model	
	Isothermal equation	R^2	Isothermal equation	R^2
303	$C_e/q_e = 0.0263C_e - 0.4208$	0.8983	$\ln q_e = 0.2518\ln C_e + 4.8095$	0.4274
313	$C_e/q_e = 0.0453C_e - 1.9585$	0.8286	$\ln q_e = 0.2813\ln C_e + 5.0851$	0.3618
323	$C_e/q_e = 0.0072C_e - 0.0422$	0.9373	$\ln q_e = 0.4271\ln C_e + 4.0436$	0.4271

It is demonstrated in tab. 1 that the correlation coefficient R^2 under the Langmuir model was among 0.8286 to 0.9373, and among 0.3618 to 0.4274 under the Freundlich model, which indicated that the isothermal adsorption of MB onto Ag/ACF is different from mono-layer adsorption under the Langmuir model and the multi-layer adsorption under the Freundlich model. The results come from several possible reasons. Firstly, the surface of the activated carbon fibers is loaded with silver nanoparticles, which makes a difference to the distribution and energy of the adsorption sits. Secondly, the chemical activity of silver nanoparticles varies under different circumstances. Thirdly, when adsorbed by activated carbon fibers, the MB is also adsorbed by silver nanoparticles.

Analysis of adsorption thermodynamic performance

The change of gibbs free energy (ΔG^0) in the process of adsorption can be estimated by:

$$\Delta G^0 = -\mathrm{R}T \ln K_c \tag{4}$$

where K_c is the adsorption equilibrium constant, can be shown by:

$$K_c = \frac{q_\mathrm{e}}{C_\mathrm{e}} \tag{5}$$

By the Van 't Hoff equation (6), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) are gained:

$$\ln K_c = \frac{\Delta S^0}{\mathrm{R}} + \frac{\Delta H^o}{\mathrm{R}T} \tag{6}$$

The MB with an initial concentration of 200 mg/L was chosen for experiment to calculate the adsorption thermodynamic parameters of Ag/ACF. Based on eqs. (4) and (5), K_c and ΔG^0 were calculated, respectively. Then the linear fitting was done between $\ln K_c$ and $1/T$ on the basis of eq. (6). Finally, standard enthalpy, ΔH^0, and standard entropy, ΔS^0 were gained by fitting equation. The results are shown in tab. 2.

Table 2. Thermodynamic parameters for adsorption of methylene blue by Ag/ACF

Temperature [K]	ΔG^0 [kJmol^{-1}]	ΔH^0 [kJmol^{-1}]	ΔS^0 [Jmol^{-1}K^{-1}]
303	3.39	–87.88	276.47
313	2.88		
323	–2.24		

As shown in tab. 2 for temperatures 303 K and 313 K, ΔG^0 value is positive, but for temperature 323 K, ΔG^0 value is negative. The negative value of ΔG^0 suggests that the adsorption of MB onto Ag/ACF is a spontaneous process, that is to say, when at a lower temperature, nanosilver loading can inhibit the spontaneous adsorption of MB onto Ag/ACF. Literature has shown that when the ΔG^0 was less than 40 kJ/mol, it was a process of physical adsorption, otherwise, it was a process of chemical adsorption [7]. Calculating the absolute value of free energy ΔG^0 with three different temperature conditions, it is found that they were all between 2.24 and 3.39 kJ/mol, less than 40 kJ/mol, which proved that the adsorption of MB onto Ag/ACF was a physical process. Adsorption enthalpy $\Delta H^0 < 0$ showed that heat was released in the process of adsorption and adsorption entropy $\Delta S^0 > 0$ suggested that the spontaneity of adsorption intensified with the ring temperature.

Conclusion

As to the adsorption of MB onto Ag/ACF, the performance was enhanced with the rising temperature. When at 323 K, the adsorption quantity was obviously higher than that at 303 and 313 K. With the increasing concentration, the adsorption quantity increased first and reduced later. Because of the silver nanoparticles loaded, the adsorption of MB onto Ag/ACF differed from the mono-layer adsorption under Langmuir model and the multi-layer adsorption under Freundlich model. Through analysis done on the adsorption thermodynamic parameters, it is found that when the temperature was at 303 and 313 K, ΔG^0 value was positive, while the temperature was at 323 K, ΔG^0 value was negative. Adsorption entropy $\Delta S^0 > 0$, adsorption enthalpy $\Delta H^0 < 0$, and the absolute value of ΔG^0 was less than 40 kJ/mol, it is suggested that the adsorption was a physical exothermic process, and it can occur spontaneously at higher temperature, getting intense with the rise of temperature.

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