

AN ADSORPTION ISOTHERM MODEL FOR ADSORPTION PERFORMANCE OF SILVER-LOADED ACTIVATED CARBON

by

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The adsorption mechanism of methylene blue onto silver-loaded activated carbon fiber is different from those by Langmuir and Freundlich models. In this paper, an adsorption isotherm model is established with two parameters to describe nanosilver impact and load amount of silver nanoparticles, respectively, on adsorbability. In the process, the absorbance value of equilibrium solution was measured by spectrophotometry, and thus equilibrium concentrations and equilibrium adsorption quantity were calculated. The model was determined according to the fitting curve and comparison was made between the theoretical prediction and experimental data, showing relative good consistence.

Key words: *activated carbon fiber, adsorption isotherm model, methylene blue, Langmuir*

Introduction

Methylene blue (MB) is a representative compound of water-soluble azo dyes, the wastewater involving this kind of dye has a lot of problems: a large amount of emissions, high chromaticity, and difficulty in bio-degradation. Therefore, how to effectively control the water pollution has become a key problem for clean environment [1-4]. Adsorption method is a common way to remove the refractory pollutants in water [5, 6]. Nanosilver loaded activated carbon fiber (Ag/ACF) is a new composite material of silver and carbon, not only having high specific surface area and abundant pores, also having the unique physical and chemical properties of silver nanoparticles [7, 8], which can be used as a multi-effect adsorbent. Therefore, the theoretical and experimental research of the adsorption performance of Ag/ACF materials is very important.

Commonly used models for the description of adsorption performance of porous materials are Langmuir and Freundlich models. Langmuir adsorption isotherm model is a hypothesis when the adsorption value arrives at the maximum and the corresponding adsorbate molecule arrives at a state of monolayer saturation. It is thought there is only one adsorption site with fixed energy and adsorption, having no interaction between adsorbed molecules. The model is applicable to monolayer adsorption on the surface of the smooth homogeneous [9]. The Freundlich isothermal adsorption equation is an empirical formula, suitable for uneven adsorbent surface [10, 11]. However, our previous research indicated that the isothermal ad-

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sorption of MB onto Ag/ACF is different from mono-layer adsorption under the Langmuir model and the multi-layer adsorption under the Freundlich model.

Based on the ideal theory Langmuir model, nanosilver impact factor, α , and load amount of silver nanoparticles, E , as two parameters were introduced, and the theoretical model of adsorption performance of MB onto Ag/ACF was established. It is hoped that the model would serve as a reference for the quantitative research on adsorption performance of Ag/ACF.

Establishment of adsorption isothermal model of Ag/ACF adsorbing MB

It is assumed that the Ag/ACF adsorbing MB is monolayer adsorption [12], silver nanoparticles evenly distributed on the surface of fiber with each adsorption site having same adsorption capacity to the MB and the adsorbed MB having no interaction against each other. According to the Langmuir adsorption isotherm equations:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_1 q_m} \quad (1)$$

where C_e [mgL^{-1}] is the equilibrium concentrations of the solution, q_e [mgg^{-1}] – the equilibrium adsorption quantity, q_m [mgg^{-1}] – the adsorption quantity of saturated monolayers, and K_1 [Lmg^{-1}] – equilibrium constant of Langmuir.

The Ag/ACF was regarded as a whole adsorbent, and on a certain temperature condition, when the adsorption of MB onto Ag/ACF achieved balance, the equilibrium concentration of the solution was C_b , the equilibrium adsorption capacity of the fiber was Q_b . Based on the Langmuir model, the isotherm adsorption equation for Ag/ACF could be obtained:

$$\frac{C_b}{Q_b} = A + \frac{1}{K_1 q_m} \quad (2)$$

where A is the monolayer saturate adsorption of Ag/ACF under the circumstances of the equilibrium concentration.

The A stands for the saturated adsorption of Ag/ACF mono-molecular layers under the circumstances of the equilibrium concentration. According to the characteristics of the Ag/ACF materials, the establishment of the equation must consider the following points: 1 – with the rising temperature, the activity of silver nanoparticles would be enhanced, which would improve the monolayer saturate adsorption of fibers, 2 – the loaded silver nanoparticles would change the specific surface area of activated carbon fibers, which in turn would change the distribution of adsorption site and therefore affect the adsorption performance, and 3 – the load amount of silver nanoparticles would make a difference to the particle size and distribution of silver nanoparticles, which would also affect the specific surface area of fibers.

Firstly, considering the influential factor of temperature to the activity of silver nanoparticles, which would change the adsorption performance of mono-molecular layers, an impact factor α [gL^{-1}] was introduced. It suggests the influence of fiber consumption by silver nanoparticles for Ag/ACF adsorbing MB on a certain temperature condition. When the value is positive, the loaded silver would promote the adsorption performance of fibers, when the value is negative, the result goes to the opposite way. It is specified:

$$\alpha = \frac{C_x}{q_m} \quad (3)$$

where C_x is the concentration of methylene solution in the monolayer adsorption.

The B is the adsorption ability of adsorption sits on fiber surfaces, which shows:

$$B = \frac{C_b}{q_m} + \alpha \quad (4)$$

Secondly, the loaded silver nanoparticles would change the specific surface area of fibers. Assuming that each adsorption sit is a regular plane, the change in the specific surface area would lead to corresponding change in adsorption sits in squares. Hence, B^2 represents the change:

$$B^2 = \left(\frac{C_b}{q_m} + \alpha \right)^2 \quad (5)$$

The load amount and the specific surface area of nanosilver is relevant to its activity. Therefore, when Ag/ACF is in a constant manner, the monolayer saturate adsorption equation A can be displayed:

$$A = K_1 E B^2 \quad (6)$$

where K_1 [Lmg^{-1}] is the equilibrium constant and E [mgg^{-1}] – the amount of silver nanoparticles loaded on per gram fiber.

Based on eqs. (2), (3), (5), and (6), the adsorption isothermal equation of Ag/ACF adsorbing MB is established:

$$\frac{C_b}{Q_b} = K_1 E \left(\frac{C_b}{q_m} + \frac{C_x}{q_m} \right)^2 + \frac{1}{K_1 q_m} \quad (7)$$

Adsorption model parameters

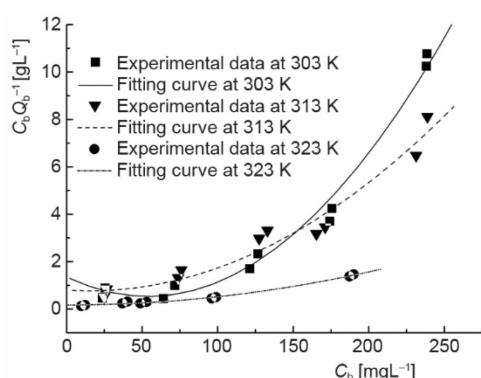
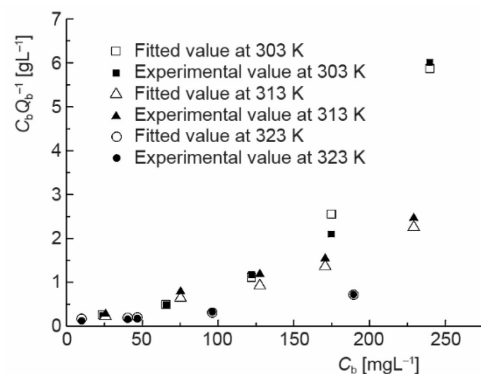
In order to calculate the adsorption model parameters of MB onto Ag/ACF, selection was made to the Ag/ACF which had a silver loaded amount of 20000 ppm and was subjected to wash and dry. The MB solution with concentrations of 50, 100, 150, 200, and 250 mg/L were prepared. Under different circumstances with a temperature 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 with a constant temperature for some time. Later, the absorbance of the solution was tested at the maximum absorbing wavelength 665 nm by spectrophotometer. According to the standard curve, the value of C_b was calculated and incorporated into the formula $Q_b = (C_0 - C_b)V/m$ to calculate Q_b .

Fitting was done among different values of C_b and C_b/Q_b with three different temperature. Fitting curves are shown in fig. 1.

Based on the fitting curves, model parameters and adsorption isotherm equation are shown in tab. 1.

Table 1. Fitting results of adsorption isothermal equation

Temperature [K]	Isothermal equation	K_1 [Lmg ⁻¹]	α [gL ⁻¹]	q_m [mgg ⁻¹]	R^2
303	$C_b/Q_b = 0.0003(C_e - 57.5)^2 + 0.485$	0.0399	-1.11	51.68	0.9775
313	$C_b/Q_b = 0.0001(C_e - 47.5)^2 + 0.602$	0.0328	-0.59	81.08	0.9735
323	$C_b/Q_b = 0.00003(C_e + 1.67)^2 + 0.164$	0.0382	0.01	159.62	0.9885

**Figure 1. Fitting curve at 303, 313, and 323 K****Figure 2. Comparison between fitted value and experimental value of MB adsorption onto Ag/ACF at 303, 313, and 323 K**

Model test

In order to verify the accuracy of the model, similar tests were conducted. Under different temperature circumstances 303, 313, and 323 K, selection was made to Ag/ACF which had a silver loading of 10000 ppm. Methylene solution with concentrations of 50, 100, 150, 200, and 250 mg/L were prepared. Materials were tested after they exhibited the adsorption equilibrium and filtered. Then they were measured three times at the maximum absorbing wavelength 665 nm by ultraviolet-visible spectrophotometer and average value was gained. According to the standard curve, the value of C_b was calculated and incorporated into the formula $Q_b = (C_0 - C_b)V/m$ to calculate C_b/Q_b of Ag/ACF to MB on different temperature conditions. Finally, the results were compared with that of the model, which is shown in fig. 2.

Figure 2 demonstrates that with different temperature conditions, the results measuring the adsorption performance of Ag/ACF to MB are basically consistent with those of the model. It is indicated that the adsorption isothermal model can be proposed as a theoretical formula, providing theoretical guidance for the preparation of Ag/ACF adsorbent.

Conclusions

The study mainly focused on the relevance between the characteristics of Ag/ACF and their adsorption performance. Based on the Langmuir model, two influential parameters of nanosilver impact factor, α , and load amount of silver nanoparticles, E , were considered to establish the adsorption isotherm equation of MB onto Ag/ACF. Experiments were conducted to see the values of C_b and C_b/Q_b with different temperature conditions and concentrations. Different values were fitted by the proposed equation and values of K_1 , α , and q_m were thus calculated. Comparison of the results calculated by the model and the results from the experiment was made. The final result showed that they were basically same and verified the relia-

bility of model which could be used as a theoretical formula for the calculating the adsorption performance of Ag/ACF to MB. A more exact model with fuzzy conditions [13] will be discussed in a forthcoming paper.

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