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Study on the Adsorption Characteristics of Congo Red by Sycamore Bark Activated Carbon

Li Cong[1], Lingling Feng[1], Xinlai Wei[1], Jie Jin[1,2], Ke Wu[1,2]
1.Collaborative Innovation Center for Environmental Pollution Prevention and Ecological Restoration of Anhui Province, Hefei University, Address:Hefei, Anhui 230601, China
2.Anhui Key Laboratory of Sewage Purification and Ecological Rehabilitation Materials, Address: Hefei, Anhui 230088, China

Abstract. The activated carbon was prepared from sycamore bark by activation of zinc chloride. The absorbing effect of activated carbon on Congo red wastewater is studied. The characteristics of sycamore bark activated carbon were characterized by SEM and BET. The effects of adsorbent dosage, time, and shaking speed on the adsorption properties of Congo red by sycamore bark activated carbon were studied. The isotherm, kinetics, and thermodynamics of adsorption were explored. The results revealed that the activated carbon contain a large apparent mesopores. Adsorption efficiency was increased with enhancing the adsorption dosage and time. The removal rate of Conge red reached to 98.2% under room temperature with adsorbent dosage of 3.0 g/L, adsorption time of 120 min, shaking speed of 60r/min. The adsorption of Congo red on sycamore bark activated carbon was followed Langmuir isotherm model and Lagergren pseudo-second order kinetics model. The adsorption was spontaneous, endothermic, and the entropy was increasing in the adsorption process.

Keywords: sycamore bark activated carbon, Congo red, adsorption kinetics, thermodynamics.

I. INTRODUCTION

Dye wastewater mainly comes from the production of dyes and dye intermediates industry, its deep color, complex composition, poor biodegradability and difficult degradation[1,2]. The actual use of the azo dye is the most common and the most frequently applied, approximately 50%. The precursors and intermediates of azo dyes are carcinogenic, mutagenic and toxicity[3,4,5].Congo red is a typical benzidine azo dye in dyeing and printing industry, mainly for cotton, viscose dyeing and paper industry production [2,3,4,5].Currently Congo red dye wastewater treatment methods are commonly used in adsorption, membrane separation, chemical coagulation, oxidation, biological method [6,7,8].Adsorption method is an effective means of dyeing wastewater treatment, because of its convenient operation, simple process, low cost and good treatment effect have attracted much attention [9,10,11,12].

The preparation of new activated carbon adsorbent with biomass waste as raw material has become a hotspot in recent years[13,14,15,16,17]. Sycamore tree is a common ornamental tree species and garden green road, each year a large number of sycamore bark by the sanitation sector landfill or burning treatment, caused by a huge waste of resources, the combustion of harmful gases can also cause a certain degree of atmospheric pollution. At present, there are few reports on the preparation of activated carbon adsorption materials from the sycamore bark. Sycamore bark raw materials are rich in sources, renewable, inexpensive and environmentally friendly, as a raw material for the preparation of activated carbon adsorbent for the treatment of dye wastewater can reduce pollution and waste utilization, which provides a reference for the treatment of dye wastewater by other activated carbon adsorption. In this study, sycamore bark as raw materials, sycamore bark activated carbon was prepared with zinc chloride, adsorption of Congo red from wastewater, the adsorption properties and mechanism of activated carbon from the sycamorebark to Congo red were studied by means of structural characterization, adsorption conditions and adsorption model.

II. EXPERIMENT

Materials and Reagents

Sycamore bark from the suburbs of Hefei City, wash drying, crushing and sieving standby. The reagents used are $ZnCl_2$,NaOH, HCl and Congo red and soon. The reagents used in the experiment are all analytically pure. Deionized water is used in the experiment.

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Experimental equipment and analytical instruments

FW100 universal grinder, OTF-1200X tube furnace, CP214 analytical balance, UV6000 ultraviolet visible spectrophotometer, DKZ-2thermostat, NAVO2200 nitrogen adsorption specific surface area determinator, SU8000 scanning electron microscope.

Experimental methods

Preparation of sycamore bark activated carbon

Following the method employed in the literature [18,19], take 25 g sycamore bark powder in beaker, adding 50% $ZnCl_2$ solution for 100 mL after mixing evenly impregnated with 12 h, drying at 70℃ for 12 h, stiring irregularly. After drying the sycamore bark and zinc chloride mixture in the quartz boat, then put in a tube furnace. Activation for 50 min under the condition of heating rate of 10r/min, nitrogen atmosphere and temperature of 500℃. The sample to be removed after cooling, successively washed with 3% hydrochloric acid, pure water, 0.5% of NaOH solution each for 30min. Waterwashing to neutral, then filtering and drying to obtain the sycamore bark active carbon samples.

Adsorption experiment

Take a certain amount of sycamore bark activated carbon adsorbent in 250 mL Erlenmeyer flask, adding 100 mL concentration of 100 mg/L Congo red solution, packed in sealed bottles in the constant temperature bath, adsorption in a certain time and temperature, the filtered solution was measured by UV VIS spectrophotometer at 497 nm. The removal rate of Et (%) and adsorption capacity Qt (mg/g) were calculated.

$$E_t = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

$$Q_t = (C_0 - C_t)V/W \quad (2)$$

In the formula, C_0 is the initial concentration of Congo red (mg/L),C_t is the residual concentration of Congo red adsorption (mg/L) after t time, W is the quality of sycamore bark activated carbon (g), Q_t is the adsorption amount of t time (mg/g), V is the solution volume (L).

Isothermal adsorption experiment

Preparation of different initial concentrations (150~350 mg/L) of the Congo red solution of 100 mL, adding 0.3 g of sycamore bark activated carbon, oscillation adsorption for 4h respectively at 293, 303 and 313 K in constant temperature water bath, filtered, the residual red Congo concentration was measured.

Kinetics of adsorption experiments

In a series of 250mL conical flask were added to a concentration of 100 mg/L Congo red solution 100 mL and 0.3 g of sycamore bark activated carbon, at different temperatures (283, 293 and 303 K) in the constant temperature water bath, with 60r/min oscillating adsorption for a certain period of time, filtered, the residual red Congo concentration was measured.

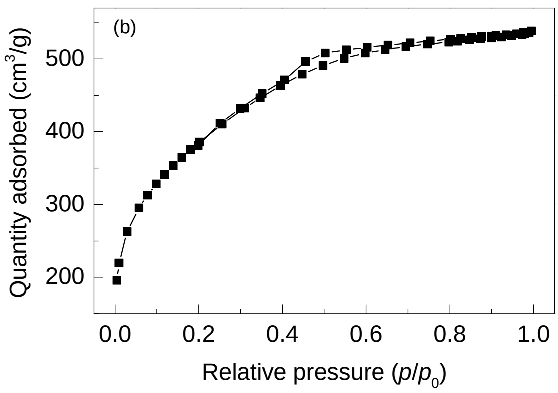
III. RESULTS AND DISCUSSIONS

The characterization of sycamore bark activated carbon

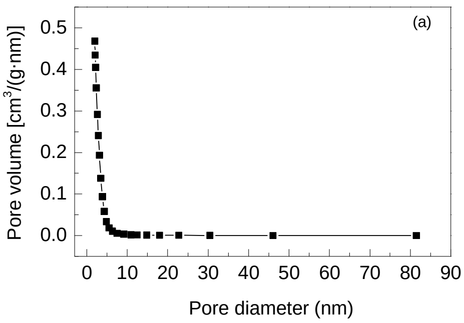
The adsorption generally occurred in the surface of adsorbent, the specific surface area and pore structure of adsorbent are one of the important factors affecting the adsorption performance [20].The pore structure of activated carbon was characterized by nitrogen adsorption, the nitrogen adsorption desorption isotherms under 77K are shown in Figure 1(a).It can be seen from the figure that the nitrogen adsorption isotherms belong to the I type in the IUPC classification [19]. At the beginning of adsorption , nitrogen adsorption reached 200 cm3/g, the results indicated that the activated carbon had a certain pore diameter less than 1 nm[21].In the relative pressure near 0.1, adsorption isotherms rise rapidly, the relative pressure is greater than 0.3, the adsorption isotherm increased slowly, showed that a large number of porous structure exist in activated carbon. The adsorption desorption isotherms have fine desorption hysteresis loop, may be due to nitrogen in the capillary condensation in the hole, the results showed that the activated carbon has a certain number and shape of mesopores.

According to the BET formula, the total specific surface area of sycamore bark activated carbon was 1393 m2/g. BJH method was used to calculate the pore size distribution, the results are shown in Figure 1(b). From the map it can be seen that the most hole diameter below 10 nm. The pore diameter of 2~5 nm is the main hole. The pore volume is 0.623 m3/g by BJH method, among which the micropores are 7.2% and the mesopores are 91.6%. It can be seen that the distribution of activated carbon pore diameter is concentrated in the mesopore.

The morphology and structure of activated carbon were studied by scanning electron microscope, The results as shown in Figure 2.It can be seen that sycamore bark activated carbon in various shapes and sizes, uneven surface, structure of fluffy, sporadic bumps, irregular porous structure faults.



(a)



(b)

Fig.1. Nitrogen adsorption–desorption isotherms and pore distribution of sycamore bark activated carbon

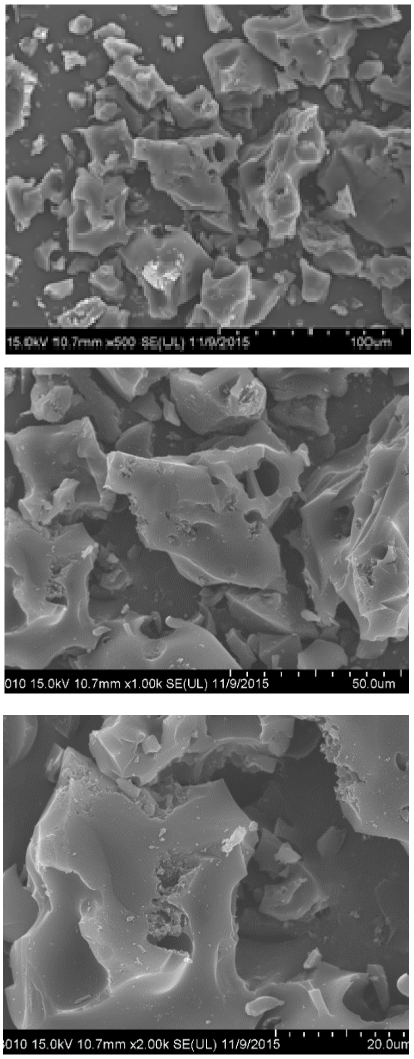


Fig.2. SEM images of sycamore bark activated carbon

Effect of dosage on the removal rate of Congo red.

Take 100 mg/L Congo red solution of 100 mL, plus different doses of the sycamore bark activated carbon, Adsorption of 180 min at room temperature and 60 r/min, figure 3 is different dosage effect of the sycamore bark activated carbon on the removal of Congo red in water. From the map it can be seen that the dosage of 1, 2, 2.5 g/L，The removal rate of Congo red was 49.5%, 85.1%, 94.1%respectively, the removal rate of sycamore barkactive carbon with dosage increasing，This may be due to the increase in the total amount of adsorbent, the adsorption of the total surface area and functional groups increased, the removal rate of Congo red increased.

When the dosage was 3 g/L, the removal rate of Congo red was up to 98.6%, and the removal rate was not increased. The results showed that the solution of Congo red was completely removed by adsorption.

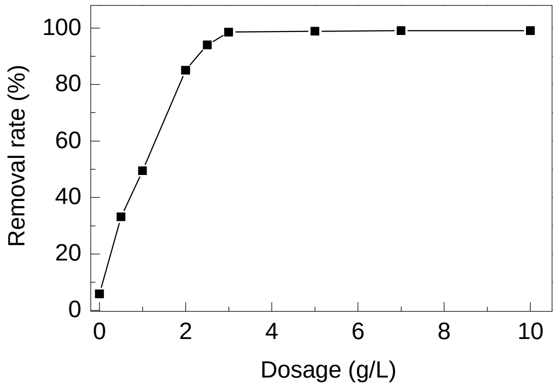


Fig.3. Effect of amount of adsorbent on removal of congo red

Effect of adsorption time on removal rate of Congo red

Take 100 mg/L Congo red solution of 100 mL, adding 3 g/L of sycamore bark activated carbon, adsorption of certain time at room temperature and 60 r/min, the removal effect of Congo red is shown in Figure 4.

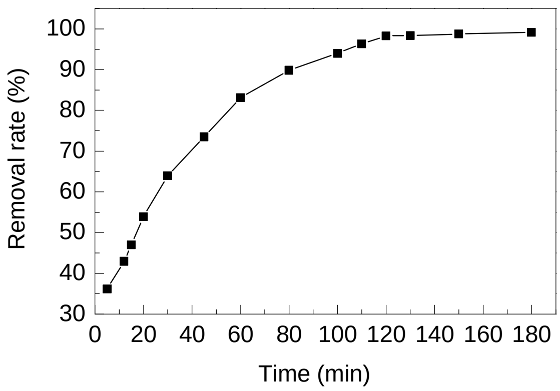


Fig.4. Effect of adsorption time on removal of Congo red

It can be seen from the figure that the first 40 min adsorption is very fast, belonging to the rapid adsorption phase, may the sycamore bark activated carbon adsorbent surface contains a large number of active sites. It can quickly adsorb Congo red in water, and the concentration of Congo red is higher at the beginning of adsorption, also increased the adsorption mass transfer force， Congo red removal rate increasing rapidly. With the increase of adsorption time, a large number of Congored was adsorbed on the surface ofadsorbent, active sites can be provided decrease gradually, at the same time, Congo red solution concentration decreased, the mass transfer driving force is reduced, the adsorption rate decreased, removal rate tends to be slow, enter the slow adsorption stage. After 120 min of adsorption adsorption gradually reached equilibrium, the removal rate tended to be stable. The equilibrium time of adsorption is 120 min.

Effect of oscillation intensity on removal rate of Congo red

Take 100 mg/L Congo red solution of 100 mL, adding 3 g/L of sycamore bark activated carbon, adsorption of 60 and 120 min at room temperature under different oscillation intensities. The effect of oscillation intensity on the removal rate of Congo red is shown in Figure 5. From the map it can be seen that as the oscillation intensity increases, the removal rate of Congo red rise. The adsorption time is 120 min, the oscillation intensity 60 r/min removal rate reached 98.4%, continue to increase the intensity of oscillation, the removal rate of Congo red remains unchanged, at this time may have reached the adsorption equilibrium. Under the same oscillation intensity, the removal efficiency of Congo red at adsorption of 60 min was significantly less than 120 min.

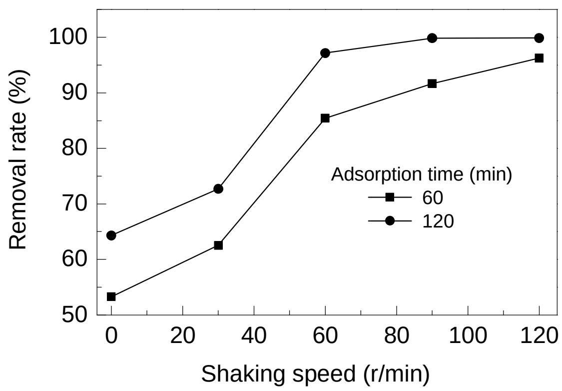


Fig.5. Effect of shaking speed on the removal of Congo red

Analysis of isothermal adsorption model

The most commonly used two adsorption isotherm models are Langmuir isotherm equation and Freundlich isotherm adsorption equation [22,23].

Langmuir Model：

$$C_e/Q_e = C_e/Q_{max} + 1/Q_{max}K_L \quad (3)$$

Freundlich Model：

$$\ln Q_e = \ln C_e/n + \ln K_f \quad (4)$$

In the formula, C_e is the adsorption equilibrium concentration (mg/L) of Congo red solution, Q_{max} is the maximum adsorption capacity(mg/g), Q_e is the equilibrium adsorption capacity(mg/g), K_L is the Langmuir equilibrium constant，N is a dimensionless factor related to adsorption strength, K_f is the Freundlich adsorption equilibrium constant.

Langmuir adsorption isotherm equation and Freundlich adsorption isotherm equation were fitted to sycamore bark of activated carbon on Congo red，the results are shown in Figure 6 and table 1.

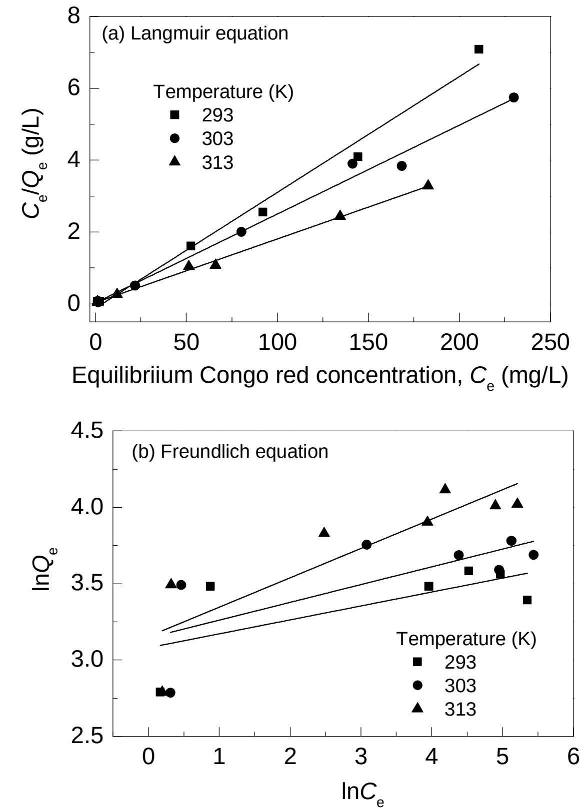


Fig.6. Adsorption of Congo red with sycamore bark activated by Langmuir and Freundlich isotherm equation

As can be seen from Figure 6 and table 1, the adsorption of Congo red by the sycamore barkactivated carbon at different temperatures is in accordance with the Langmuir equation. The correlation coefficients R2were greater than 0.983, The linear fitting is better. When the temperature rises from 293 K to 313 K, the maximum adsorption capacity Q_{max} of sycamore bark activated carbon of Congo red rose from 34.30 mg/g to 56.43 mg/g，the results showed that the increase of temperature was favorable to the adsorption of Congo red by the sycamore barkactivated carbon. The adsorption is an endothermic process.

Table 1
Isotherm model parameters of Congo red adsorption on sycamore bark activated carbon

Temperature(K)	Langmuir equation			Freundlich equation		
	K_L(L/mg)	Q_{max}(mg/g)	R_L^2	K_f(mg/g)	n^{-1}	R_F^2
293	0.986	34.30	0.983	21.56	0.097	0.53
303	0.871	40.44	0.990	23.21	0.116	0.54
313	0.499	56.43	0.997	23.42	0.192	0.76

The Freundlich model coefficients n^{-1} <0.5, showed that the adsorption ofsycamore barkactivated carbon of Congo red is easy adsorption process[4], Sycamore barkactivated carbon has good adsorption properties and can be used as adsorbents for removal of Congo red.

Analysis of the adsorption kinetics model

The adsorption kinetics can be used to describe the adsorption rate of solid adsorbents，revealing the adsorption mechanism，the relationship between the structure of the adsorbent and the adsorption performance can also be analyzed based on the kinetic model and the adsorption process [24,25,26].

The adsorption kinetics process was simulated by Lagergren pseudo first order kinetics model and pseudo two order kinetics model[27].

Lagergren pseudo first order kinetic model:

$$\ln(Q_e - Q_t) = \ln Q_e - K_{1t} \quad (5)$$

Quasi two level kinetic model of Lagergren:

$$t/Q_t = 1/(K_2 Q_e{}^2) + t/Q_e \quad (6)$$

In the formula, K_1 is the first order rate constant(min^{-1}) , K_2 is a quasi two order rate constant[g/(mg·min)].

As can be seen from table 2, the equilibrium adsorption capacity $Q_{e,\ cal}$ calculated by the pseudo first order kinetic model is different from the measured adsorption capacity $Q_{e,exp}$. The quasi two level dynamic model of $R_2{}^2 \geq 0.987$，The calculated value of equilibrium adsorption $Q_{e,cal}$ is close to the measured adsorption capacity $Q_{e,exp,}$ showed that the adsorption data fit well with the pseudo two order kinetics model, the relevance of better.K2 increased with the increasing of temperature, showed that the increase of temperature was beneficial to the adsorption of Congo red by thesycamore bark activated carbon.

Table 2
Kinetics modeling parameters of Congo red adsorption with sycamore bark activated carbon

Temperature(k)	$Q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		K_1(min^{-1})	$Q_{e,cal}$(mg/L)	$R_1{}^2$	K_2 [g/(mg·min)]	$Q_{e,cal}$(mg/g)	$R_2{}^2$
283	21.77	0.008	24.32	0.944	0.079	22.51	0.987
293	32.9	0.024	34.31	0.947	0.095	29.97	0.988
303	33.1	0.015	40.44	0.946	0.113	35.13	0.998

Analysis of adsorption thermodynamics model

The thermodynamic properties of the adsorption process can be characterized by thermodynamic parameters, standard Gibbs free energy change (ΔG0, kJ/mol), standard reaction enthalpy change (ΔH0, kJ/mol) and standard reaction entropy [ΔS0,kJ/(mol·K)] [23]. The thermodynamic parameters of the adsorption of Congo red by the sycamore bark activated carbon can be calculated by the following equation [4,28]:

$$\Delta G_0 = \Delta H_0 - T\Delta\Delta_0 \quad (7)$$

$$\ln(Q_e/C_e) = \Delta S_0/R - \Delta H_0/RT \quad (8)$$

In the formula, T is the temperature, R is the ideal gas constant [8.314 J/(mol·K)].

The adsorption data of Congo red by the sycamore barkactivated carbon were plotted with 293, 303 and 313 Kby ln (Qe/Ce) to obtain ΔH^0 and ΔS^0, and the results are shown in Table 3. From the table we can see that sycamore bark activated carbon adsorption enthalpy of adsorption of Congo red variable Delta ΔH^0 is positive, indicated that the adsorption process is endothermic reaction, Increasing temperature is favorable to the reaction[23]. The adsorption energy free energy change ΔG^0 at different temperatures is negative, indicating that the adsorption was a spontaneous process. The ΔS^0 of adsorption process of sycamore bark activated carbon on Congo red is greater than 0, indicating that the adsorption is a entropy production process, the adsorption spontaneous is increased with temperature [28].

Table 3
Thermodynamic parameters for congo red adsorption with sycamore bark activated carbon

Temperature(K)	ΔG^0(kJ/mol)	ΔH^0(kJ/mol)	ΔS^0[kJ/(mol·K)]	R^2
293	−6.40			
303	−7.75	33.16	0.135	0.998
313	−9.10			

IV. CONCLUSION

The activated carbon from the sycamore bark was prepared by the activation of zinc chloride, the adsorption of Congo red was studied, the conclusions as following:

(1) the content of sycamore bark activated carbon is high, the shape of the pore is various, the structure of the void is developed, and the specific surface area is up to 1393 m^2/g.

(2) Increasing the amount of adsorbent can enhance the adsorption of Congo red. The adsorption reached equilibrium within 120 min. The removal rate of Congo red was up to 98.2% under the condition of room temperature, dosage of 3 g/L, adsorption time of 120 min and oscillation intensity of 60 r/min,

(3) The adsorption of Congo red on sycamore bark activated carbon was followed Langmuir isotherm model and Lagergren pseudo-second order kinetics model. The adsorption was spontaneous, endothermic, and the entropy were increasing in the adsorption process.

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