

Adsorption Kinetics Study on Modified Carbonized Straw to High Concentration Nitrogenous Wastewater

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Abstract: This study used corn stalks as raw materials, modifying with KOH modifier under different conditions after carbonization, and making activated carbon adsorbent. High concentration nitrogenous wastewater was adsorbed by activated carbon under different conditions. Combining the modification conditions of the prepared activated carbon with the processing conditions of the adsorption experiment: the A2B2 conditional combination was modified and treated under ultrasonic conditions; the A2B1 conditional combination was modified under ultrasonic conditions and treated under oscillation conditions; The A1B1 combination conditions was modified and treated under oscillation conditions. Parallel experiments were performed in three combinations. Fitting the adsorption process data with Elovich model, double constant model, first-order kinetic model and w-m kinetic model. Among them, the adsorption mechanism of A2B1 was better with the first-order kinetics model; the adsorption mechanism of A2B2 was in accordance with the law of the double constant model. According to the analysis of adsorption thermodynamics, it was known that any combination of conditions for modification and treatment was a spontaneous endothermic process.

Keywords: straw corn; modification; high concentration nitrogenous wastewater; kinetics

1. Preface

China is a large agricultural country with developed agriculture and produces many straws. Most of the straw is not fully utilized as waste or burned in the wild. In this way, not only the straw has not been rationally utilized, but also the environmental problems caused by burning the straw are increasingly serious [1-3]. Today, the hottest haze problem, straw burning is also a major factor. Understanding the performance of straw, adjusting the energy utilization structure of straw, transforming straw into resources, and developing and utilizing rural waste straw efficiently. At the same time. At the same time, it responded to the national call for sustainable

development and placed ecological and environmental protection in the important position of development [4-6]. Wastewater from food processing plants, pharmaceutical wastewater and landfill leachate are all high concentration nitrogenous wastewater. The key to ensuring water quality and water ecological security is the efficient control of nitrogen content in water. At present, the research on the properties of activated carbon is very popular at home and abroad. Zhuangyan et al. combined carbonization of reed straw by high temperature pyrolysis with chemical activation of K₂CO₃ activator [7] to produce activated carbon, which can adsorb dye wastewater; Huang Huizhen used longan shell as raw material, modified with sulfuric acid and formaldehyde modifier to prepare activated carbon, and studied the adsorption performance of Pb(II) [8].

On the basis of the previous research [9-11], in the research of adsorption kinetics, the research on the adsorption kinetics of agricultural straws by chemical modification to prepare adsorbents is not deep enough. In this study, corn straw, which is common in agricultural production, was used as raw material. Activated carbon is made by KOH modification of straw. Activated carbon was used to treat high concentration nitrogenous wastewater. Adsorption kinetics and thermodynamics of carbonized corn straw to high concentration nitrogenous wastewater under different modification and adsorption conditions were studied.

2. Experimental Part

2.1. Materials, Reagents and Instruments

Corn stalks came from farmland in the suburbs of Chengdu, Sichuan Province.

Potassium hydroxide, hydrochloric acid, ammonium chloride, potassium iodide, mercury chloride and potassium sodium tartrate were all analytical pure. The drugs were from Chengdu Jinshan Chemical Reagent Limited company.

Electronic analytical balance: ESJ120-4, Chengdu Shengye Instrument and Meter Factory; electric heating constant temperature blast drying box: Jinghong

DHG-9140, Chengdu state-owned emerging instrument factory. Constant temperature oscillator: THZ-032, Chengdu Shengye Instrument Factory. visible spectrophotometer: V-1200, Chengdu Shengye Instrument and Meter Factory. Muffle furnace: XL high temperature oven, Beijin Tiantong technology company. Ultrasound cleaning instrument: KH-250DB. Electrothermal Digital Display Constant Temperature Water Bath, HH-2, Bangxi Instrument Technology company.

2.2. Preparation of Modified Corn Straw Activated Carbon

In this experiment, corn straw was directly used as raw material to prepare activated carbon. Chemical activation method was used to activate the straw, and the activator was potassium hydroxide. Corn straw was soaked in tap water for 24 hours with distilled water, and then washed repeatedly with tap water until the impurities produced by soaking were removed. Then, it was dried in an electrothermal constant temperature blast drying chamber at 100 °C and cut into about 5 cm long strips. The dried raw materials were coated with tin foil paper and carbonized in an electric furnace for 40 minutes. After

cooling to room temperature, they were grinded and sifted (40-60 mesh). The carbonized straw was mixed with KOH of 3 mol/L in a 100 mL plugged conical bottle at the mass ratio of 1:3. The cap was capped immediately and treated under ultrasonic conditions (temperature: 15 C). Time: 30 minutes. After treating under the ultrasonic conditions, filtering and obtaining solid modified carbonized straw. Washing with 1 mol/L dilute hydrochloric acid solution, then rinsing repeatedly with distilled water to neutral, then drying to constant weight. Fine activated carbon was screened after grinding in a mortar.

2.3. Adsorption Experiment of Nitrogenous Wastewater

2.3.1. Standard curve of ammonia nitrogen

The absorbance of different concentrations ammonia nitrogen solutions was measured by visible spectrophotometer of V-1200 at 420 nm and the results are shown in Table 1. The absorbance of Table 1 was taken as ordinate and the concentration was taken as the abscissa, and the standard curve of Ammonia Nitrogen was drawn as shown in Fig. 1.

Table 1. The absorbance value of different concentrations of Ammonia Nitrogen

Test tube number	0	1	2	3	4	5	6	7
Concentration (mg/L)	0	0.0001	0.0002	0.0004	0.0008	0.0012	0.0016	0.0020
Absorbance	0.011	0.029	0.046	0.084	0.16	0.23	0.308	0.378

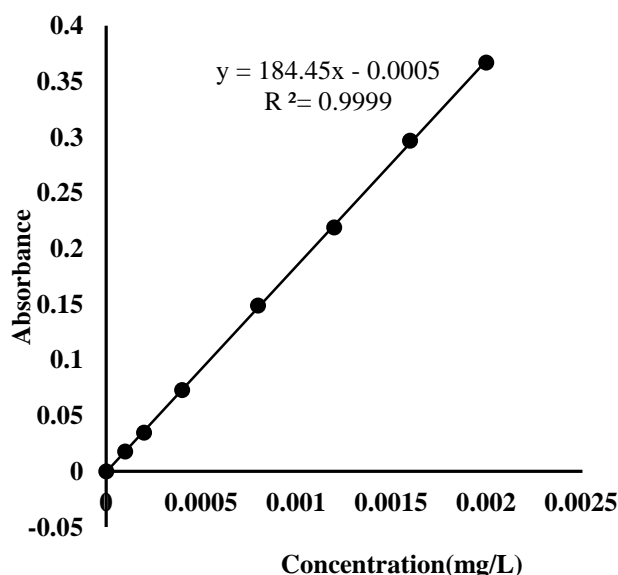


Figure 1. Standard curve of Ammonia Nitrogen.

2.3.2. Calculation of adsorption capacity of activated carbon

The condition for the activated carbon modification in

the oscillator was A1; the condition for the activated carbon modification in the ultrasonic was A2. The treatment under the conditions of the oscillator was set to

condition B1, the conditions of B1 were temperature 25 °C, pH 7, and the oscillation speed was 150 r/min; the treatment under the condition of ultrasonic cleaner was set to condition B2, and the condition of B2 was temperature 10 °C and pH 7. Adding 0.5g of activated carbon to 10ml of different initial ammonia nitrogen concentration solution, the static adsorption experiments were carried out separately, the A2B2 conditional combination was modified and treated under ultrasonic conditions; the A2B1 conditional combination was modified under ultrasonic conditions and treated under oscillation conditions; The A1B1 combination conditions was modified and treated under oscillation conditions (the conditional combination of modified under ultrasonic conditions and treated under oscillation conditions has been studied in the early stage, and the experimental conditions are different, and there is no more comparison). Adsorbing for a certain period of time, extracting, filtrating, determining ammonia nitrogen by Nessler spectrophotometry, and according to the formula (1) Calculating the amount of adsorption (q_t).

$$q_t = \frac{V_1(C_0 - C_e)}{W} \quad (1)$$

where q_t is the amount of nitrogen adsorbed by modified activated carbon (mg/kg); V_1 is the volume of liquid in the conical flask (10 ml); C_0 is the initial nitrogen concentration (mg/L); C_e is the equilibrium concentration of nitrogen (mg/L); W is the carbon weight (0.5 g).

2.3.3. Adsorption kinetic model

In fact, the adsorption of solution was a complicated process. Therefore, in order to design an efficient adsorption system, the analysis of adsorption kinetics and mass transfer process was very important. The kinetic study was helpful to study the adsorption mechanism. The adsorption process can be further analyzed and described by fitting the kinetic model and data. The adsorption mechanism under different conditions was studied by using W-M equation, first-order kinetic equation, Elovich equation and double-normal equation [12,13].

W-M equation: $q_t = a + bt^{1/n}$ (2)

First-order kinetic equation: $\ln q_t = a + bt$ (3)

Elovich equation: $q_t = a + b \ln t$ (4)

Double constant equation: $\ln q_t = a + b \ln t$ (5)

where q_t is the amount of nitrogen adsorbed by modified activated carbon (mg/kg); t is the adsorption time (min); a, b are model parameters.

2.3.4. Thermodynamic parameter analysis of adsorption activation state

To determine if the process was spontaneous and it was an endothermic or exothermic reaction, adsorption thermodynamic experiments were carried out at different temperatures. According to the formula, the thermodynamic parameters of the adsorption process were calculated, Gibbs free energy ΔG_0 , standard

adsorption enthalpy change ΔH_0 and standard adsorption entropy change ΔS_0 [14-16].

$$\Delta G = -R \ln K_c \quad (6)$$

$$\ln K_c = -\frac{\Delta H_0}{RT} + C \quad (7)$$

$$\Delta S_0 = \frac{\Delta H_0 - \Delta G_0}{T} \quad (8)$$

where R is the ideal gas molar constant (8.314 J mol⁻¹ K⁻¹); K_c is an equilibrium constant ($K_c = qe/ce$, mL/g); R is the thermodynamic temperature; K linearly fits $\ln K_c$ to $1/(RT)$.

3. Results and Discussion

3.1. Kinetic Adsorption State

The surface area, pore volume and micropore ratio of modified activated carbon increased. Different modification conditions have different effects. The mechanical action of ultrasonic waves by ultrasonic cavitation increases the pore space of the activated carbon, and the specific surface area increases to increase the chance of exposure to ammonia nitrogen. Oscillation was a physical process that allows a sufficient mixing of the solution and the adsorbent. It can also effectively increase the contact area. The adsorption kinetics data under different modified adsorption conditions are shown in the following figure.

As shown in the Fig. 2, the adsorption amount increases correspondingly with the increase of the initial ammonia nitrogen concentration under the A1B1 condition. At the beginning, there was a slow adsorption process. With the increase of time, the dispersibility of adsorbent and ammonia nitrogen molecule increases, with the increase of time, the dispersibility of the adsorbent and ammonia nitrogen molecules was improved and the mixing was more uniform, and the adsorption rate was significantly accelerated. The balance was reached at 120 min and maintained for a while. A relative saturation phase was reached among the pores, the pore volume and the filling of the ammonia nitrogen molecules. With the increase of oscillation time, the initial equilibrium stage was broken, and later fluctuations occurred. It is preliminarily concluded that the cause of the above phenomenon was related to activated carbon particles. It was concluded that the initial adsorption was due to the particle pores among the external activated carbons; the late adsorption was related to the internal order of the activated carbon.

As shown in the Fig. 3, under the condition of A2B1, the adsorbent was well mixed with the ammonia nitrogen molecule at different initial concentrations, and the pore volume was continuously filled with ammonia nitrogen, and the adsorption capacity also increases. Before 90 minutes, it showed a slow adsorption state, and the adsorption capacity increased slowly. When it reached 120 minutes, the adsorption rate decreased significantly and gradually became saturated. Compared with the oscillator modification treatment, the adsorption amount reduced. The preliminary analysis was as follow, because

the sonication of the sonic modification changed the internal structure of the carbon, and the long-term oscillation changed the saturation of the activated carbon, its adsorption effect was affected.

As shown in the Fig. 4, under the condition of A2B2, the whole adsorption state tends to increase, and the ultrasonic condition treatment increases the pore volume, pore volume and surface area. Under the ultrasonic condition, the pores were gradually filled and gradually saturated, so the treatment adsorption rate first increases and then decreases.

The three conditions were compared together, and the adsorption state under A2B2 conditions was significantly different from the other. The preliminary inference is that the effect of ultrasound on adsorption performance is determined by the instantaneous released and transmission of energy from cavitation bubbles produced by cavitation. The frequency and radiation of ultrasonic field desorbed more adsorbates, broke the original phase equilibrium and led to the increasing trend of adsorptive capacity, thus affecting the adsorption system of activated carbon and changing its optimal adsorption concentration [17]. It can be demonstrated by single factor experiment in the early stage. In the initial stage of adsorption under three different conditions, the adsorption law of q_t increased rapidly with the prolongation of adsorption time. The reason was that in the initial stage of adsorption, there was a large concentration difference between adsorbent and solution. At the same time, the adsorbent surface was not covered completely and the coverage ratio was small, which led to the rapid increase of q_t and the rapid reversal of q_t . At last, it tended to be balanced [18].

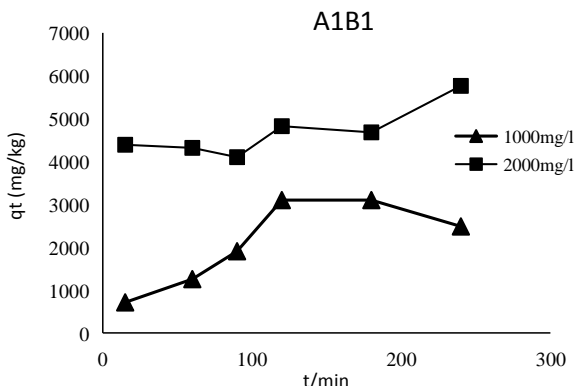


Figure 2. Adsorption Kinetics of Activated Carbon at Different Initial Concentrations of Ammonia Nitrogen at Different Time under A1B1 Condition.

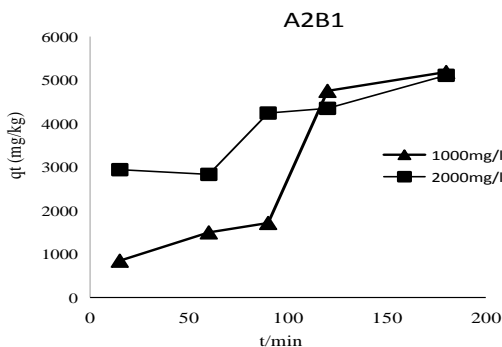


Figure 3. Adsorption Kinetics of Activated Carbon at Different Initial Concentrations of Ammonia Nitrogen at Different Time under A2B1 Condition.

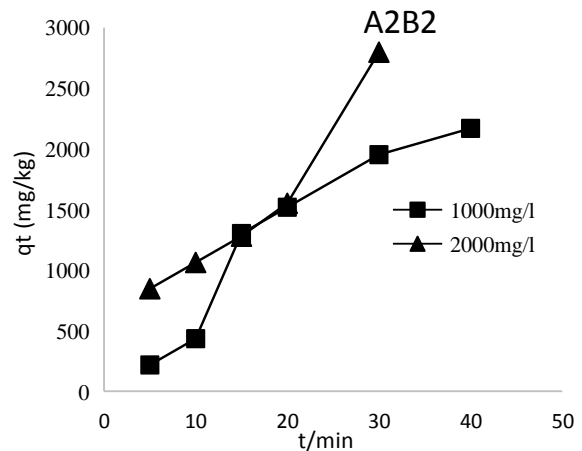


Figure 4. Adsorption kinetics of activated carbon at different initial concentration of ammonia nitrogen at different time under A2B2 condition.

3.2. Kinetic Model Fitting

Based on the changes of adsorption capacity at different initial concentrations and different times, we fitted the four models under the conditions of A1B1, A2B1 and A2B2, including w-m model, first-order kinetic model, Elovich model and double constant model. The fitting parameters of the four models were shown in Table 2. According to the combination of graph and table, the double constant model R2 with a concentration of 1000 mg/L under A1B1 condition was relatively large at 0.862, while the double constant model with 2000 mg/L had the worst fitting effect. Among them, the first-order kinetic model was fitted. The correlation coefficient of the fitting at different initial concentrations was approximated but the value was greater than 0.5 and less than 0.8. It was not easy to fit. The adsorption law of A1B1 condition needed further investigation.

Four models were used to fit the data under A2B1 condition. The correlation coefficients of the first-order kinetic model were greater than 0.8 under different initial concentration, and the average value of R2 was 0.8555. The fitting effect was good. The average value of R2 fitted by the W-M model was 0.8, and the effect was basically significant. The elovich model had the worst fit. It was preliminarily concluded that under the A2B1 condition, the whole adsorption process was caused by a variety of adsorption mechanisms (external liquid membrane diffusion, surface adsorption and intraparticle diffusion). In addition, it was preliminarily concluded that the data error caused by the excessive initial concentration was one of the reasons why the better fitting effect was not obtained.

Under the A2B2 condition, both the double constant model and the W-M model R2 were greater than 0.92, which were significantly correlated. According to the correlation coefficient R2, the double constant model was superior to the W-M model and superior to the elovich model, and the double constant model was optimal. The double constant and the W-M mean equation fit were

significantly and strongly correlated. The adsorption process could generally be divided into three stages: the first stage was the diffusion of ammonia nitrogen through the liquid membrane to the outer surface of the adsorbent material, also known as the membrane diffusion process; the second stage was the entrance of ammonia nitrogen through the outer surface of the material into the interior of the material, also known as the internal diffusion process; the third stage was that ammonia nitrogen was adsorbed onto the active sites on the inner and outer surfaces of the activated carbon. The double constant model can be used to illustrate the heterogeneous diffusion process under A2B2 conditions and reflect the more complex dynamic process; in the short period of the initial phase, the direction of motion diffusion is undirected and random, and the change in particle position does not affect the concentration of the adsorbate. The W-M model could be interpreted as follows, the diffusion resistance of the liquid film was so small that it could be ignored. It could be seen from the table that there were constant b in all W-M models of this experiment, and the W-M equation did not pass through the origin. It could be speculated that intraparticle

diffusion was not the only step to control the adsorption process. The adsorption process was controlled by other adsorptions, and may also involve thickness and boundary layer. [19]

Under three combinations, four models are fitted separately. Activated carbon modified under ultrasound condition had better fitting effect with various models. The results showed that the specific surface area of activated carbon was gradually increased and the dispersing effect in the pore of activated carbon was improved in the process of ultrasonic treatment and modification. The movement of ammonia nitrogen from the surface to the inside of the channel was smoother and can be better fitted with various dynamic models. Compared with A1B1, A2B2 treated completely under ultrasonic conditions indicates the mechanical stress of cavitation of ultrasonic wave modification and sonication, which had the effect of increasing the pore volume of the surface area. It was beneficial to the diffusion and movement of ammonia nitrogen molecules to better contact with active sites, obtaining better fitting effect [20].

Table 2. Dynamic parameters of w-m model, first-order kinetic model, Elovich model, and double constant model

Conditional combination	concentration mg/L	W-M model		first-order kinetic model		Elovich model		double constant model	
		$q_t = a + bt^{1/2}$ equation	R ²	$\ln q_t = a + bt$ equation	R ²	$q_t = a + blnt$ equation	R ²	$\ln q_t = a + blnt$ equation	R ²
A1B1	1000	$q_t = 105.04t^{1/2} + 3610.8$	0.540	$\ln q_t = 0.0056t + 6.8619$	0.634	$q_t = 855.3 \ln t - 1723$	0.7424	$\ln q_t = 0.5445 \ln t + 5.0962$	0.862
	2000	$q_t = 198.75t^{1/2} + 72.519$	0.7006	$\ln q_t = 0.0012t + 8.3027$	0.6760	$q_t = 361.95 \ln t + 3063.7$	0.3669	$\ln q_t = 0.0734 \ln t + 8.1173$	0.365
A2B1	1000	$q_t = 495.71t^{1/2} - 1710.4$	0.780	$\ln q_t = 0.0038t + 7.8873$	0.825	$q_t = 1713.7 \ln t - 4496$	0.6608	$\ln q_t = 0.7394 \ln t + 4.5561$	0.8123
	2000	$q_t = 246.24t^{1/2} + 1654.1$	0.810	$\ln q_t = 0.0118t + 6.6019$	0.886	$q_t = 855.05 \ln t + 254.18$	0.6926	$\ln q_t = 0.2254 \ln t + 7.2812$	0.6842
A2B2	1000	$q_t = 47t^{1/2} - 1147.8$	0.9041	$\ln q_t = 0.0253t + 6.3959$	0.988	$q_t = 1021.9 \ln t - 1580$	0.9503	$\ln q_t = 1.1808 \ln t + 3.5802$	0.9248
	2000	$q_t = 513.93t^{1/2} - 922.71$	0.944	$\ln q_t = 0.0613t + 5.6413$	0.7411	$q_t = 1282.7 \ln t - 2824.8$	0.842	$\ln q_t = 0.8036 \ln t + 4.5156$	0.9416

3.3. Analysis of Thermodynamic Parameters of Adsorption Activation State

and the corresponding values were calculated as shown in the table:

It could be obtained from the thermodynamic formula,

Table 3. Thermodynamic parameters of adsorption of ammonia nitrogen by activated carbon

Condition	T/K	nk _c	ΔG ₀ /(KJ.mol ⁻¹)	ΔH ₀ /(KJ.mol ⁻¹)	ΔS ₀ /(J.mol ⁻¹)
A1B1	293	1.331	-3.243	13.832	58.275
	298	1.131	-2.802		9.402
	303	1.522	-3.834		12.653
A2B1	293	1.142	-2.783	9.659	42.464
	298	1.176	-2.915		9.781
	303	1.514	-3.814		12.587
A2B2	290	1.561	-3.7630	57.980	212.905
	293	1.796	-4.376		14.934
	298	2.236	-5.539		18.587

As shown in the Table 3. The free energy ΔG₀ of the modified carbon adsorption ammonia nitrogen was less than zero, indicating that the process was spontaneous; the enthalpy change ΔH₀ is greater than zero, indicating

that the adsorption was an endothermic process. According to the literature, when ΔH < 20 KJ/mol, the adsorption process was physical adsorption. The ΔH₀ of A1B1 was 13.832 KJ/mol, and the ΔH₀ of A2B1 was

9.659 KJ/mol, which was less than 20 KJ/mol, indicating that the two adsorptions were mainly physical adsorption. Without the strong force of chemical bonds, it was preliminarily concluded that the main forces involved were weak forces such as hydrogen bonding, van der Waals forces and dipole bond forces [21,22]; The ΔH_0 of A2B2 was 57.980 KJ/mol, which was greater than 20 KJ/mol, It was indicated that the adsorption process was not based on physical adsorption, and there was a force involved in the chemical bond, Preliminary inference was that the relative change is due to the addition of ultrasound. Their ΔS_0 was greater than 0, indicating that the solid-liquid interface of the three adsorption processes increases disorderly.

4. Conclusions

Compared with the oscillator, the external energy provided by ultrasonic wave was different, which made the adsorption mechanism of activated carbon change. The process of the modification under ultrasonic condition and adsorption under oscillation condition was better with the first-order kinetics model; the adsorption process of modified and adsorbed under the ultrasonic condition was in accordance with the law of the double constant model, and the dynamics of modified and adsorbed under the oscillating condition needs further study.

Modified and treated under ultrasonic conditions, modified and treated under oscillating conditions, modified under ultrasonic conditions and treated under oscillating conditions, three experiments above were spontaneous endothermic processes.

The adsorption process of modification under ultrasonic conditions and adsorption under ultrasonic conditions was not only based on physical adsorption, but also has chemical bond changes in the adsorption process; The adsorption process of modification under ultrasonic conditions and adsorption under the oscillating condition was mainly physical adsorption; The adsorption process of modification and adsorption under the oscillating condition was mainly physical adsorption.

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