

Investigation on Kinetics and Equilibrium of the Adsorption of Ammonia Nitrogen on Activated Carbon Modified By Nitric Acid

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2. Keywords

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1. Abstract

The coconut activated carbon (AC) was modified by using nitric acid as the activator. Unmodified and modified AC samples were characterized in terms of structural, morphological, surface, and chemical properties. The oxygen functional groups of surface such as hydroxyl group and carboxyl group were obviously increased after modification. Ammonia nitrogen removals from the aqueous solution were studied to determine the effect of modification on the adsorption performances in a batch adsorption system. The kinetic models of experimental data indicated that they were well described by the pseudo-first order kinetic model. The adsorption isotherm was well fitted to the Freundlich model. Thermodynamic parameters including the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated. The results showed that adsorption process of ammonia nitrogen on modified AC is mainly governed by physical adsorption that is spontaneous and exothermic.

3. Introduction

In recent years, the aquaculture industry has been developed rapidly, whereas the arising wastewater containing ammonia nitrogen has a great impact on the aquatic organisms. Excessive discharge will lead to eutrophication and reduce self-purification ability of water in the ecosystem [3, 19]. The ammonium-containing compounds or the complex organic nitrogen compounds in the water system are decomposed by the microorganism and then become ammonia nitrogen molecules or ions, which are usually presented in the form of ammonia nitrogen in water. At present, there is no effective technology for the purification of wastewater containing ammonia nitrogen, especially for the low-concentration ammonia-nitrogen wastewater. Common methods for removing ammonia nitrogen including chemical precipitation [3], ion-exchange method [23], and biological treatment process [11]. Biological treatment process has some problems such as long periodicity, large environmental impact, and incomplete removal of ammonia nitrogen. In addition, the main disadvantage of chemical precipitation method is the large amount of precipitant and the high cost of treatment method. Therefore, the developments of economical and effective ammonia nitrogen wastewater

treatment methods have become a research hotspot in the field of wastewater treatment.

The adsorption is the most economical and effective method because of its advantages of small secondary pollution, simplicity, convenient operation, and mild reaction conditions [1]. The adsorbents commonly used in sewage treatment include activated carbon (AC), diatomaceous earth, zeolite and molecular sieves [8]. In addition, it has been pointed out that the porous structure of AC and abundant surface oxygen-containing functional groups can enhance the adsorption capacity of sulfur and nitrogen compounds [2, 15]. However, the large-scale use of this method is limited due to the high production cost until the researchers used agricultural by-products such as bamboo, coconut shells and waste tea as raw materials, the cost of raw materials for preparing AC was greatly reduced [10, 29]. AC is one of the widely used industrial adsorbents and carbonaceous materials with developed internal pore structure. In industry, AC has many important applications, such as filtration and purification, supercapacitors, drug delivery, hydrogen storage, catalysts, etc [9]. In previous studies, AC was rarely used to adsorb and remove ammonia nitrogen from water. The adsorption of AC mainly relies on its

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large specific surface area, highly developed pore structure, and surface chemical functional groups located at the outer and inner surfaces, which makes the AC possessing excellent adsorption performance [18, 25]. The surface chemical properties of AC are the main factor affecting its adsorption performance in addition to the porous structure. El-Sheikh studied the activation of AC with various oxidants (nitric acid, hydrogen peroxide and ammonium persulfate) to investigate the effect of this on adsorption of metal ions in environmental water (El-Sheikh, 2008). In previous studies, nitric acid was also found to be a good surface modifier. The oxidation with nitric acid at room temperature and 120 °C increased the adsorption capacity of AC for thiophenemolecules [30]. The porous structure plays an important role in gas phase adsorption. The influence of the surface chemistry of the adsorbent is secondary. The situation in liquid phase adsorption is quite different. The effect of surface chemical properties of AC on adsorption is more significant than that of porous structure.

AC is generally a non-polar and hydrophobic substance. Its hydrophobicity makes it able to effectively adsorb various non-polar organic substances in the aqueous solution. But it is difficult to adsorb a polar solute such as ammonia nitrogen. Depending on the nature of the reagent used in the modification, a positively or negatively charged functional site can be formed on the surface and the AC converted to be more hydrophilic or hydrophobic and acidic or basic. By oxidative modification, the functional groups on the surface of the AC are oxidized by oxidant at an appropriate temperature, which will increase the content of the oxygen-containing acidic group on the surface and enhance the polarity of the surface. This can achieve the purpose of adsorbing ammonia nitrogen. At the same time, oxidative modification can also remove a large amount of ash on AC and enhance the hydrophilic properties of the surface. In this paper, nitric acid was used to oxidize AC to improve its ability to absorb ammonia nitrogen in water. The effects of ammonia nitrogen concentration, solution pH value, and adsorption temperature on the adsorption of ammonia nitrogen were studied. Then the preliminary study on the adsorption mechanism was carried out.

4. Materials and Methods

4.1. Materials

Coconut shell AC, potassium iodide (KI) was produced by Aladdin Industrial Corporation. Nitric acids (HNO₃), ammonium chloride (NH₄Cl), potassium sodium tartrate tetrahydrate (C₄H₄O₆KNa·4H₂O), sodium hydroxide (NaOH), mercury iodide (HgI₂) were produced by Sinopharm Chemical Reagent Co., Ltd, China.

4.2. Preparation of modified AC

4g dried AC was added into 50 mL of 3 mol/L nitric acid solution. Then the mixture of AC and acid solution were heated to 80°C for 2h. Thereafter, the obtained AC was filtrated, washed, and then transferred into a flask with water. After 2 min reflux, the AC was washed again with water and washed to neutrality. Finally, the as-prepared modified AC was dried at 110°C for 12 h.

4.3. Characterization

In this experiment, a scanning electron microscope of JSM-5600LV type Japan Electron Optics Co., Ltd. was used for scanning test to observe the surface morphology. Specific surface area and the plot of the pore-diameter distribution of adsorbent were determined on Brunner-Emmet-Teller (BET) method from N₂ adsorption/desorption isotherm on a Micromeritics ASAP-2460 instrument [31]. In order to determine the functional groups on the surface of the AC before and after the modification, Fourier-Transform Infrared Spectroscopy (FTIR, Lambda Scientific 7600) was applied in the wave numbers ranging of 4000 cm⁻¹ to 400 cm⁻¹ [13]. The changes of crystalline phases of AC were characterized by X-ray diffraction (XRD, TD-3700). The ammonia nitrogen concentrations were determined by using a Nessler's reagent Spectrophotometric method. Adsorption capacity of the AC samples was determined with UV-Vis analyses (UV-3400, Shanghai Lichy Lab Instruments Co., Ltd). The analyses were performed at 420 nm for ammonia nitrogen adsorptions.

4.4. Adsorption Experiments

Ammonium chloride solution was used to simulate wastewater containing ammonia nitrogen. The 0.1 g modified AC was added into a 50 mL conical bottle and then 20 mL ammonium chloride solution with a certain concentration of ammonia nitrogen was added. After sealing, the adsorption reaction was carried out in a constant temperature water bath oscillator. After the reaction, the adsorbent and water were separated by filtration, and the ammonia nitrogen concentration in the filtrate was measured by a Nessler's reagent Spectrophotometric method [26].

The amount of adsorption can be calculated from the equation below:

$$q = \frac{c_0 - c_t}{w} \times \frac{V}{1000} \quad (1)$$

Where c_0 (mg/L) is the initial ammonia nitrogen concentration, c_t (mg/L) is the ammonia nitrogen concentration at time t (min), W (g) is the weight of the adsorbent, V (mL) is the volume of water.

5. Results and Discussion

5.1. Characterization of Original and Modified AC

(Figure 1) showed the change in surface topography of AC before and after modification with nitric acid. It can be clearly seen that the topography has not changed obviously before and after modification. However, it can be seen from the comparison of (Figure 1a and 1c) that the surface of the AC was rougher. The pores are more transparent than that before the modification. Prior to modification, some of the pores of the AC were rough or even clogged, as shown in (Figure 1a). Compared with the surface of AC in (Figure 1b and 1d), it shows that the surface of AC was corroded many defects after nitric acid modification, which made its surface rougher and conducive to the adsorption of ammonia nitrogen.

The pore distribution curve and the N_2 adsorption/desorption isotherm of AC that before and after the modification were shown in (Figure 2). The isotherms of AC before and after modification were typical of type I. This indicates that the pore size of AC before and after modification was mostly 2-3 nm mesoporous. The adsorption capacity was controlled by the pore volume. The adsorption curve did not change significantly before and after the modification, which means that the pore structure did not change significantly. The H4 type of hysteresis loop is the characteristic of ordered mesoporous structure, which is further confirmed by SEM images. According to the specific surface area and the average results in the (Table 1), the specific surface area of the AC was slightly reduced. The average pore diameter became large after activation by nitric acid. The reason of average pore diameter became large is that nitric acid accumulated in the voids to form strong oxidant concentrated nitric acid during the modification process. The pore walls were corroded and then burned to form new micropores. Parts of the mesopores were converted into large pores [14, 27]. The decreased specific surface area after modification could be attributed to the pore blockage and collapse of partial pore walls from the increasing oxygen functional groups on the surface.

FTIR spectra of the samples are shown in (Figure 3). The FTIR spectra of before and after modification of AC have obvious absorption peak at 3450 cm^{-1} , corresponding to the peak of hydroxyl groups from phenols, alcohols, and absorbed water [6, 12]. 2955 cm^{-1} and 2885 cm^{-1} were the vibration absorption peak of $-\text{CH}_3$, $-\text{CH}_2$, and $-\text{CH}$. The absorption peak of ester group appeared at 1620 cm^{-1} before the modification, but it disappeared after the modification. It was replaced by the stretching vibration peaks of $\text{C}=\text{C}$ in the aromatic ring at 1592 cm^{-1} and $\text{C}=\text{O}$ in carbonyl group at 1710 cm^{-1} , which were caused by the oxidation and acidity of nitric acid [28]. The vibration absorption peak of $\text{C}=\text{C}$ in the

aromatic ring skeleton were found at 1560 cm^{-1} . 1290 cm^{-1} is the vibration absorption peak of phenolic hydroxyl group [21]. The peak at 1230 cm^{-1} is the stretching vibration peak of $\text{C}-\text{O}$. After activation of nitric acid, the oxygen functional groups of surface such as hydroxyl group and carboxyl group were increased [6]. This helped to enhance the surface polarity of the AC and increase the adsorption capacity of ammonia nitrogen.

XRD spectra before and after modification was presented in (Figure 4). Peak at 2θ belonged to the larger graphite microcrystals in carbon materials. There was no other characteristic peak, which means that the amorphous structure of AC was remained.

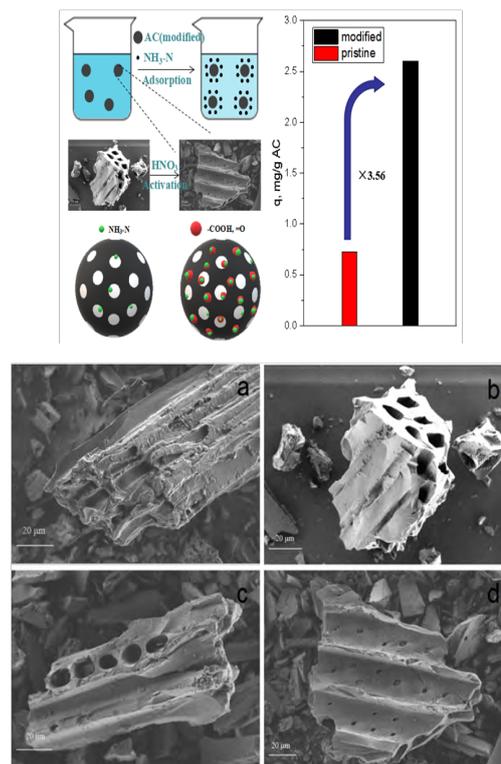


Figure 1: SEM images of AC (pristine) (a,b), AC (modified) (c,d).

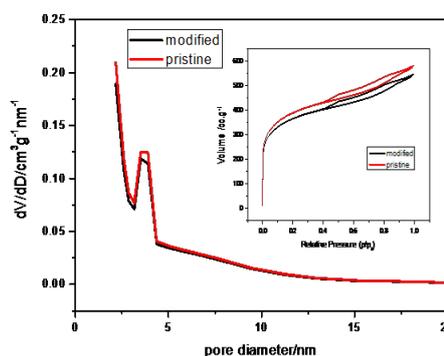


Figure 2: N_2 adsorption-desorption isotherm curves and the corresponding pore-size of AC (pristine and modified).

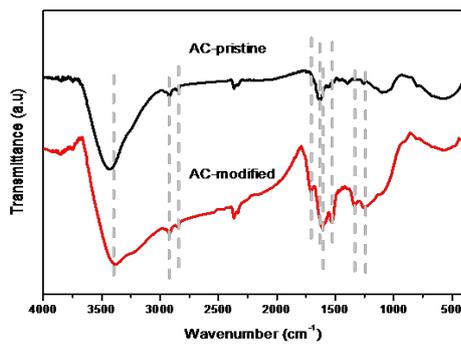


Figure 3: FTIR spectra of AC (pristine and modified).

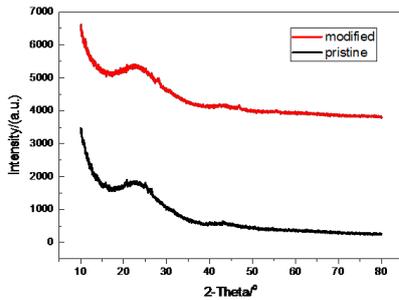


Figure 4: XRD spectra of AC (pristine and modified)

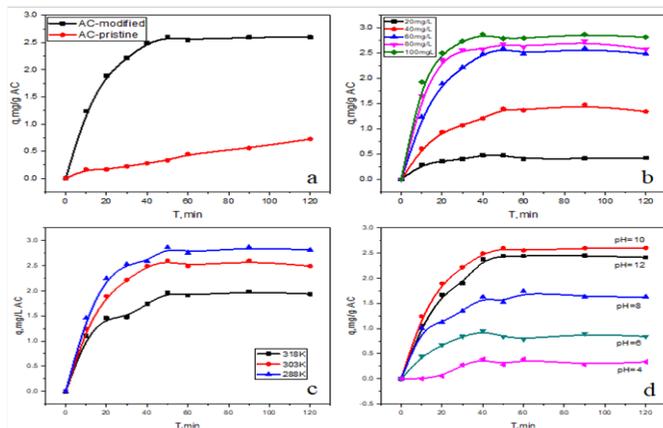


Figure 5: Ammonia nitrogen absorption performances of different AC samples(a) and effects of concentration on adsorbate(b), adsorption temperature(c), water pH(d).

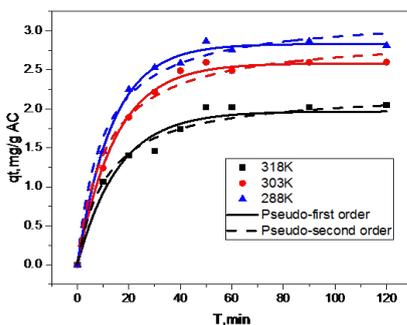


Figure 6: Pseudo-first order and pseudo-second order kinetics for the adsorption of NH4+ onto AC (modified).

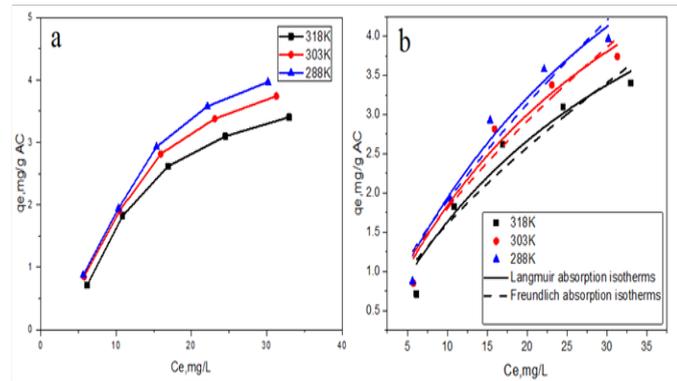


Figure 7: Langmuir and Freundlich adsorption isotherms for the removal of NH4+-N.

Table 1: Surface area and pore volume data of the samples

Sample	S _{BET} (m ² /g)	S _{mic} (m ² /g)	V _{total} (cm ³ /g)	V _{mic} (cm ³ /g)	Average pore diameter (nm)
AC (pristine)	1424	1111	0.8985	0.5014	4.0258
AC (modified)	1337	1166	0.8443	0.5191	4.0744

Table 2: Kinetic parameters of ammonia nitrogen adsorption by two models.

T/K	Pseudo-first order			Pseudo-second order		
	K ₁ /(min ⁻¹)	q _e /(mg·g ⁻¹)	R ²	K ₂ /[g·(mg·min ⁻¹)]	q _e /(mg·g ⁻¹)	R ²
288	0.0744	2.83	0.996	0.0325	3.21	0.985
303	0.0673	2.58	0.995	0.031	2.94	0.977
318	0.0631	1.97	0.9663	0.0397	2.23	0.964

Table 3: Parameters of Langmuir and Freundlich adsorption isotherm.

T/K	Langmuir			Freundlich		
	Q ⁰ /(mg·g ⁻¹)	K _L /(L·mg ⁻¹)	R ²	K _F /(mg·g ⁻¹ ·(L·mg ⁻¹))	n	R ²
288	9.49	0.0256	0.966	0.3647	1.38	0.942
303	8.21	0.0288	0.966	0.3576	1.441	0.977
318	7.28	0.0289	0.95	0.3305	1.458	0.964

Table 4: Thermodynamic parameters for adsorption of ammonia nitrogen.

ΔH ⁰ (kJ·mol ⁻¹)	ΔS ⁰ (kJ·mol ⁻¹ ·K ⁻¹)	ΔG(kJ·mol ⁻¹)		
		288K	303K	318K
-2.255	-0.4238	-0.873	-0.856	-0.791

5.2. Removal Performance of Ammonia Nitrogen

Experiments were performed to study the effect of different adsorption condition on ammonia nitrogen removal by AC. As can be seen from Fig. 5a, the adsorption capacity of AC modified by nitric acid for ammonia nitrogen has been greatly improved. When the initial concentration of ammonia nitrogen and pH was 60 mg/L and 10 mg/L, respectively, the adsorption capacity of the unmodified AC for 2 h was 0.73 mg/g. However, the equilibrium adsorption capacity of the modified AC reached 2.60 mg/g in the same condition which was 3.56 times than that of unmodified AC. It is clear that the presence of oxygen functional group on the AC plays a crucial role in the adsorption of ammonia nitrogen. Although the modification of nitric acid had a descend trend in the specific surface area and pore volume of AC, resulting in the significantly improved adsorption amount of ammo-

nia nitrogen (356.16%).

As shown in **Fig. 5b**, under different initial concentration of ammonia nitrogen, the adsorption equilibrium was reached at 40 min after the start of adsorption in each case. As the concentration of ammonia nitrogen increased, the equilibrium adsorption capacity of AC also increased. When the concentration of ammonia nitrogen was below 60 mg/L, the equilibrium adsorption capacity increased rapidly with the increase of the concentration of ammonia nitrogen. However, when the concentration of ammonia nitrogen was more than 60 mg/L, the equilibrium adsorption amount has changed a little. This is because that the adsorption capacity of AC is close to saturation, hence it is hard to increase even if the concentration of adsorbate increased.

As shown in the (**Figure 5d**), the amount of ammonia nitrogen adsorption increased gradually with the increase of pH when in a certain range of pH from 4 to 10. This was due to the existence of a large amount of H^+ in the solution under acidic conditions, which would compete with ammonia nitrogen on the surface of AC. Consequently, the adsorbed amount of ammonia nitrogen was very low in low pH. With the increase of pH, the concentration of H^+ decreased and the amount of ammonia nitrogen adsorption increased. At pH=10, the adsorption capacity reached the maximum. When pH=12, most of the OH^- will combine with NH_4^+ to form $NH_3 \cdot H_2O$, which will reduce the concentration of NH_4^+ and affect the adsorption effect.

Modified AC was used to adsorb ammonia nitrogen in water at different temperatures. The adsorption results are shown in **Fig. 5c**. The volume of water sample, concentration of ammonia nitrogen, and the dosage of AC was 20 mL, 60 mg/L, and 0.1 g, respectively. The adsorption was carried out in a constant temperature water bath oscillator. The results showed that the adsorption capacity decreased with the increase of temperature, and the adsorption capacity was the highest at 288K, reaching 2.70 mg / g.

5.3 Mechanism of Ammonia Nitrogen Removal

5.3.1 Adsorption Kinetics: In order to study and express the adsorption mechanism of ammonia nitrogen on the modified AC, the adsorption kinetic equation models of pseudo-first order and pseudo-second order kinetic equations were used to describe and study the relationship between adsorbate concentration and adsorption rate. The Pseudo-first order equation is [17]:

$$q_t = q_e (1 - e^{-K_1 t}) \quad (1)$$

The Pseudo-second order is:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (2)$$

Where q_t (mg/g) is the amount of ammonia nitrogen adsorption at time t (min), q_e (mg/g) is the adsorption amount when the adsorption equilibrium is reached, K_1 (min^{-1}) is the rate constant of the pseudo-first order kinetic equation, K_2 ($\text{g} \cdot (\text{mg}/\text{min})^{-1}$) is the standard rate constant for pseudo-second order kinetic equation. K_1 is proportional to the rate of adsorption and K_2 is inversely proportional.

The variation of the adsorption capacity of modified AC on ammonia nitrogen with time was shown in the (**Figure 6**). At temperatures of 15°C, 30°C and 45°C, the amount of adsorption increased with time and decreased with increasing temperature. In the initial stage of adsorption (40 min), the adsorption rate was high and the adsorption amount raised rapidly. As the reaction progressed, the adsorption rate decreased, but the speed of adsorption capacity increased slowly and reached equilibrium at 60 min. The kinetic rate constants and correlation coefficients R^2 of ammonia nitrogen adsorption on modified AC at different temperatures were shown in (**Table 2**). It can be found from the (**Table 2**) that the correlation coefficient of the pseudo-first order model is higher, and the calculated $q_{e(\text{cal.})}$ (2.83 mg/g) value of the adsorption amount is more consistent with the experimental $q_{e(\text{exp.})}$ value (2.81 mg/g) [24]. All these data indicated that the process of adsorbing ammonia nitrogen by modified AC is in line with the pseudo-first order kinetic model. The adsorption process was a physical adsorption and controlled by the diffusion step.

The adsorption equilibrium concentration and the equilibrium adsorption capacity at different initial concentration of ammonia nitrogen were measured at 288K, 303K and 318K, respectively, and then the data was used to fit the adsorption isotherm. As shown in the (**Figure 7a**), when the initial concentration of ammonia nitrogen was higher, the value of corresponding equilibrium adsorption amount was also larger. Temperature also has great effect on the equilibrium adsorption amount. The equilibrium adsorption amount of AC for ammonia nitrogen decreased as the increase of temperature, because the adsorption process is exothermic. The isothermal adsorption curves were fitted with the Langmuir and Freundlich equations, respectively, and their parameters were calculated and then listed in (**Table 3**).

Langmuir isotherm adsorption equation is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

In the formula, q_e (mg/g) is the amount of adsorption at equilibrium, C_e (mg/L) is the concentration of the solution at the equilibrium, q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the constant of the Langmuir isotherm adsorption equation. This equation describes the formation of a single layer of uniform adsorption of adsorbate on the surface of the adsorbent. This equation describes the formation of a single layer of uni-

form adsorption on the surface of the adsorbent.

Freundlich isotherm adsorption equation is:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where q_e (mg/g) is the adsorption amount at equilibrium, K_F is the Freundlich adsorption constant and usually the higher K_F value indicates that the adsorption reaction is easier to proceed, C_e (mg/L) is the solution concentration at the equilibrium of adsorption, n is a dimensionless parameter, which is related to the driving force of adsorption and the energy of adsorption potential, respectively [10]. This equation describes the irregular multilayer adsorption of adsorbate on the surface of adsorbents [4].

It can be seen from the data in (Figure 7b) and (Table 3) that the Langmuir and Freundlich models can well simulate the adsorption process of adsorption of ammonia nitrogen by AC. (Table 3) showed that the Langmuir isotherms have higher correlation coefficients. However, the calculated theoretical saturated adsorption amount is quite different from the actual experimental value, which indicates that Langmuir isotherm was not suitable to describe the process of adsorbing ammonia nitrogen by modified AC very well. The adsorption process does not belong to monolayer adsorption. (Table 3) showed that the correlation coefficients of the Freundlich isotherm fitting results are all greater than 0.94, which can also well describe the adsorption of ammonia nitrogen on AC. Moreover, the value of n in Freundlich equation was greater than 1 and increased with the increase of temperature, indicating that the AC modified by nitric acid was easy to adsorb ammonia nitrogen, and the adsorption process was an exothermic reaction.

The formulas for calculating the thermodynamic parameters of adsorption are as follows [3]:

$$\Delta G = \Delta H^0 - T\Delta S^0 \quad (5)$$

$$\ln K_F = \Delta S/R - \Delta H/R \quad (6)$$

Where ΔH is the enthalpy change, ΔG is Gibbs free energy change, ΔH^0 (kJ·mol⁻¹) is standard enthalpy, ΔS^0 (kJ·mol⁻¹·K⁻¹) is standard entropy, K_F is the Freundlich adsorption constant, T (K) is the absolute temperature, R is the gas constant.

The negative value of ΔH indicates that the adsorption process of ammonia nitrogen is exothermic reaction, which is consistent with the previous discussion on the effect of temperature on the adsorption capacity [22]. Because of $\Delta H^0 < 20$ kJ/mol, the adsorption process has also been proved to be physical adsorption, which is consistent with the results of adsorption kinetics. The negative value of ΔG indicates that the entire reaction process was spontaneous. In addition, the value of ΔG increased with the increase of temperature, which also indicates that the reaction process is physical adsorption [24].

6. Conclusion

According to the results of this study, the nitric acid modified AC can effectively remove ammonia nitrogen from water. The adsorbent was characterized by SEM, FTIR, BET and XRD. The results showed that the specific surface area of the modified AC decreased. The content of acidic oxygen functional groups on the surface increased greatly. The effects of initial concentration of ammonia nitrogen, pH, adsorption temperature, and adsorption time on ammonia nitrogen removal were studied. When the pH, temperature, and the concentration of ammonia nitrogen was 10.0, 288K, and 60mg/L, respectively, the equilibrium adsorption reached 2.70 mg/g. The kinetics and thermodynamics of ammonia nitrogen adsorption under different conditions were also studied. The results of data fitting showed that the pseudo-first order kinetics was more consistent with the adsorption process, and the adsorption process was mainly controlled by diffusion process. The results of the Langmuir and Freundlich adsorption isotherms show that the adsorption process is exothermic, and the process was governed by physical adsorption.

7. Highlights

- Modified AC using nitric acid has been made for economical and effective ammonia nitrogen wastewater treatment.
- The adsorption capacity of modified AC to ammonia nitrogen improved by 3.56 times.
- Abundant surface oxygen-containing functional groups on modified AC can enhance its adsorption capacity of ammonia nitrogen.
- Adsorption process of ammonia nitrogen on modified AC is spontaneous and exothermic.

8. Acknowledgements

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