Kinetic Study of COD in Coking Wastewater on Lignite Activated Carbon
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Keyword: Lignite activated carbon, COD, Adsorption, Kinetics.

Abstract. The adsorption kinetics and adsorption mechanism of the activated carbon on COD were studied. The reaction kinetics of lignite activated carbon at different temperatures is verified by pseudo first order reaction and pseudo second-order reaction model, and the rate constants of these dynamics models are fitted. The results showed that the adsorption can be expressed by the pseudo-second-order model, the equilibrium adsorption is 50.8mg/g at 98K temperature, the adsorption process is the exothermic process. Finally, the activation energy of the adsorption process is calculated as 5.76kJ/mol, and the adsorption process is physical adsorption.

Introduction
Coking wastewater is produced from coal coke, gas purification and coking product recovery. Because of its complex and changeable components, it is a typical industrial waste water containing refractory organic pollutants.[1] According to the statistical results of biochemical treatment of coking wastewater in metallurgical enterprises, coking wastewater has higher removal rate of volatile phenol and cyanide, while the removal rate of COD is generally less than 80%, which basically can't meet the national industrial wastewater discharge standard. In order to explore new ways of coking wastewater treatment, lignite activated carbon was directly treated to treat coking wastewater. The kinetics and adsorption mechanism of activated carbon for coking wastewater COD adsorption were mainly studied. The kinetic model is used to fit the experimental data, and the adsorption mechanism of the adsorbent is discussed.

The Experimental Part
The Experimental Materials
The wastewater samples: Wastewater from a gasification plant. The appearance of the water sample is dark brown, and the water quality is complex. The COD value is 3900~4300mg/L and the pH value is 7.5~8.5.

The adsorbents: the lignite activated carbon, the particle size is less than 1.6mm.

The Experimental Instrument
The THZ-100 type rocking bed; the COD digestion tube and the COD digestion reactor.

The Determination of COD
The content of COD is determined by potassium dichromate reflux method, the principle is that the known potassium dichromate solution is added to the water sample of the wastewater. In acidic conditions, using silver as catalyst, water by boiling reflux, using ferroin as an indicator, titration of the non reductive potassium dichromate with ammonium ferrous sulfate, the amount of the consumed ammonium ferrous sulfate is converted into the mass of the oxygen consumption.

The specific experimental steps: take 2ml water sample into HACH tube, add 1ml 0.25mol/l potassium dichromate solution and 3ml sulfuric acid and silver sulfate solution, heat and digest for 2 hours, then cool to room temperature and move into 150mL cone bottle. The HACH tube is washed with deionized water, and together into a cone bottle, a drop of ferritil is added as an indicator and titrated with ammonium ferrous sulfate.
The main solutions:
(1) 0.035mol/l ammonium ferrous sulfate solution; (2) 0.25mol/l potassium dichromate solution;
(3) Sulphuric acid silver sulfate solution; (4) Ferroin indicator solution.

Adsorption Test of COD by Activated Carbon of Lignite

Lignite activated carbon is used to adsorb COD in the coking wastewater solution, the concentration of COD solution before and after adsorption is calibrated at different oscillation time and different temperature, adsorption capacity of activated carbon to COD is calculated; the linear equation of the adsorption kinetics is fitted and the activation energy of the adsorption is calculated.

The specific steps as follows: (1) Lignite activated carbon 10g is weighed and placed in 250 mL conical bottle; (2) Take 150 mL coking wastewater solution, its COD concentration is 4195.2mg/L, put it in a conical bottle; (3) the conical flask is placed in the THZ-100 table, the table setting temperature was 25 degrees, 35 degrees and 45 C, its speed is 240 r/min; (4) Setting the oscillation time were 5min, 15 min, 30 min, 60 min, 180 min, 360 min, after the concussion time is completed, the conical bottle filtration is filtered in turn, the original 10mL filtrate was abandoned. The COD equilibrium concentration (Ce) in each conical bottle was measured by sampling. (5) According to the COD concentration before and after adsorption, calculate the adsorption capacity of activated carbon.

Results and Discussion

The Changes in the Amount of Adsorption with Time

The formula for calculating the amount of adsorption is:

\[ q_t = \frac{V(C_0 - C_t)}{M} \]  \ \ (1)

Formula: \( q_t \) is adsorbent, mg/g; \( V \) is solution volume, L; \( M \) as adsorbent dosage, C; \( C_0 \) is initial concentration of solution, mg/L; \( C_t \) is COD concentration in adsorption equilibrium, mg/L.

Table 1. Effect of adsorption time on adsorption of COD by activated carbon.

| t/min | 5    | 15   | 30   | 60   | 180  | 360  |
|-------|------|------|------|------|------|------|
| C/mg·L⁻¹ | 2497.7 | 1849 | 1531 | 931  | 877.6 | 807.4 |
| q/mg·g⁻¹   | 2497.7 | 34.351 | 39.964 | 48.964 | 49.764 | 50.818 |

Effect of adsorption time on the adsorption of COD on activated carbon is shown in Table 1, the relation curve between adsorption capacity and adsorption time is shown in Figure 1. It is known from Figure 1: Within the first 60 min, the adsorption capacity of lignite activated carbon to COD increased with the increase of the oscillating adsorption time. When the adsorption time was more than 60min, the amount of adsorption was no longer significantly changed.

![Figure 1. The relationship between adsorption and adsorption time.](image)
Study on Adsorption Kinetics

Study on Diffusion Mechanism. In theory, the whole process of solid adsorption can be divided into three stages. The first stage is the phase of membrane diffusion, which is also called membrane diffusion stage; the second stage is the phase of particle diffusion, and the third stage is the adsorption stage. In general, the diffusion of solid adsorption process is controlled by second stages. The internal particle diffusion can be reflected by the empirical formula proposed by Weber-Morris\(^2\).

\[
q_t = k_{id} \cdot t^{1/2} + C
\]  \hspace{1cm} (2)

In the formula, \(k_{id}\) is the diffusion rate constant in the particle, mg/(g·min\(^{1/2}\)); \(q_t\) is the adsorption amount at \(t\) time, mg/g; \(C\) is a constant.

If a straight line is obtained by \(q_t\) to \(t^{1/2}\), it shows that the adsorption process is controlled by the diffusion in the particles. In the first 60 minutes of the beginning of the adsorption, the relationship between \(q_t\) and \(t^{1/2}\) is shown in Figure 2, based on the experimental data, using \(q_t\) for the mapping of \(t^{1/2}\).

![Figure 2. The relationship between \(q_t\) and \(t^{1/2}\) adsorbed by lignite activated carbon (COD).](image)

It is known from Figure 2 that: the equation of \(q_t\) and \(t^{1/2}\) relation curve is very good. It shows that the adsorption process of lignite activated carbon to COD is mainly controlled by the internal diffusion of particles. According to the slope of the straight line, the diffusion rate constant \(k_{id}\) in the adsorbed particles is 4.1811 mg/(g·min\(^{1/2}\)).

Fitting of Adsorption Rate Equation. The Lagerグれ's first order adsorption rate equation and the two stage adsorption rate equation are two kinds of widely used adsorption kinetic rate equations\(^3\). In order to study the adsorption kinetics of COD with lignite active carbon, the above two kinetic models were selected to fit the adsorption of COD on the activated carbon of lignite.

(1) Pseudo first order adsorption model
It adopts the first order dynamic equation of Lagerグれ\(^4\).

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  \hspace{1cm} (3)

In the formula: \(q_t\) is the amount of adsorption at \(t\) time, mg/g; \(q_e\) is the amount of adsorption in the equilibrium state mg/g; \(k_1\) is a pseudo first order adsorption rate constant, min\(^{-1}\).

According to the above model, the experimental data are fitted with the least square method, a curve is drawn with \(t\) as a horizontal coordinate and \(\ln(q_e - q_t)\) as a longitudinal coordinate. The result is shown in Figure 3.
It is known from Figure 3 that: the linear fitting equation for the first order adsorption rate equation of Lagergren is $Y = -0.0074x + 1.2169$, $R^2 = 0.7717$, and the linear correlation coefficient $R$ is relatively small, it shows that the adsorption process is not well fitted to the Lagergren first order adsorption rate equation.

(2) Pseudo two order adsorption model

The rate control step of pseudo two level kinetic model is chemical reaction, chemisorption of electronic share or electron gain. Based on this, the pseudo two order kinetics equation \[5\] is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}$$  \hspace{1cm} (4)

In the formula: $k_2$ is pseudo two adsorption rate constant, g·mg$^{-1}$·min$^{-1}$.

According to the above model, the experimental data are fitted with the least square method, a curve is drawn with $t$ as a horizontal coordinate and $\ln(q_e - q_t)$ as a longitudinal coordinate. The result is shown in Figure 4.

It is known from Figure 4 that: the fitting equation of the adsorption process to the linear equation of two stage linear rate is $Y = 0.0193x + 0.1205$; $R^2 = 0.9998$. The linear correlation coefficient $R$ is close to 1, it shows that the adsorption process is good for the linear equation of two order linear equation, and it also shows that the adsorption process belongs to the two stage adsorption. According to the slope value of the linear equation, the equilibrium adsorption capacity $q_e$ is 51.8mg/g, the actual adsorption amount is 50.8mg/L, there is little difference from the calculated value of the theory, it is also indicated that the adsorption of COD by activated carbon is two class adsorption; According to its slope numerical calculation, the rate constant of the two stage rate at 298 K temperature is 0.0031g/(mg·min).

In the same way, the pseudo first and pseudo two parameters of activated carbon adsorbed on COD at different temperatures are shown in Table 2.
Table 2. Pseudo first order and quasi two class parameters of COD adsorbed by activated carbon at different temperatures.

| T/K  | Actual adsorption capacity (mg/g) | First order parameter | Two order parameters |
|------|----------------------------------|-----------------------|----------------------|
|      |                                  | First order reaction constant (g/(mg·min)) | correlation coefficient ($R^2$) | Theoretical adsorption capacity (mg/g) | Two order reaction constant (g/(mg·min)) | correlation coefficient ($R^2$) | Theoretical adsorption capacity (mg/g) |
| 298  | 50.8                             | 0.0074                 | 0.7717               | 3.38 | 0.0031 | 0.9998 | 51.80 |
| 308  | 47.92                            | 0.0155                 | 0.8061               | 5.21 | 0.0057 | 1.0000 | 48.23 |
| 318  | 45.48                            | 0.0343                 | 0.8687               | 32.40 | 0.0124 | 0.9998 | 46.35 |

It is known from table 2: at three different temperatures, the Q value obtained by the Lagrange pseudo two stage dynamic model is close to the experimental measured value, it is shown that the adsorption equilibrium of COD by activated carbon is in good agreement with the pseudo two stage kinetic model. But the q values obtained by the Lagrange pseudo first order kinetic model are not consistent with the experimental measured values. Although the first order kinetic model is widely used in various adsorption processes, but it also has limitations [6]; in addition, the adsorption rate constant increases with the increase of the adsorption temperature, but the equilibrium adsorption capacity ($q_e$) decreases with the increase of temperature, it is indicated that the adsorption of COD on the activated carbon of lignite is an exothermic process.

**Adsorption Activation State Function.** The activation energy is the energy needed for the reaction. The size of the activation energy affects the reaction rate. The larger the activation energy indicates the higher the energy required, the reaction is difficult to carry on, the reaction rate is slower.

The pseudo two reaction rate constant $K$ can be expressed as follows by the Arrhenius equation [7]:

$$k_2 = k_0 \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (5)

In the formula, $k_2$ is the rate constant of the adsorption reaction, g·mg$^{-1}$·min$^{-1}$; $k_0$ is the frequency factor; $E_a$ is the activation energy, kJ/mol; $R$ is the gas constant, 8.314J/(mol·K); $T$ is the absolute temperature, K. To take the logarithm of both sides of equation (5), the following formula can be obtained.

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT}$$ \hspace{1cm} (6)

A straight line $\ln k_2=0.6931/T-6.4975$ (R2=0.9951) can be obtained by linear regression of 103/T and $\ln k_2$, so the activation energy of the absorption reaction by the slope is 5.76 kJ/mol. Generally speaking, the $E_a$ value of physical adsorption is generally 5~405.76kJ/mol [8], but the $E_a$ value of the activation energy required by chemical adsorption is generally greater than 83.72 kJ/mol [9]. It can be seen that the COD in the coking wastewater of lignite activated carbon belongs to the physical adsorption, and the adsorption activation energy is small, and the adsorption is easy to be carried out.

**Conclusion**

1. The adsorption process of COD in coking wastewater by lignite activated carbon was mainly controlled by the diffusion of particles, and the rate constant of particle diffusion rate was 4.1811 mg/(g·min$^{1/2}$).

2. The adsorption of COD in coking wastewater by lignite activated carbon is well fit for the second-order rate equation. The adsorption rate at three different temperatures are solved that (298 K) is 0.0031g/mg (min), (308K) is 0.0057g/(mg, min) and (318 K) is 0.0124 g/(mg, min). Moreover, as the adsorption temperature increases, the equilibrium adsorption ($q_e$) decreases gradually, indicating that the adsorption process is exothermic reaction.
According to the empirical formula of Arrhenius, the adsorption of COD in coking wastewater by lignite activated carbon was 5.76kJ/mol, and the reaction is physical adsorption; and the activation energy is small, the adsorption is easy to carry on.

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