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## PRETREATMENT OF COKING WASTEWATER BY AN ADSORPTION PROCESS USING FINE COKING COAL

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**Abstract:** A new technique for pretreatment of coking wastewater is introduced based on the concept of circular economy. Coal is fed into a coking system after adsorption. This study validates the feasibility of using coking coal to adsorb organic pollutants in coking wastewater. The sorption kinetics and equilibrium sorption isotherms of coking coal for removal of chemical oxygen demand (COD) and phenol from coking wastewater was also discussed in this paper. Gas chromatograph/mass spectroscopy (GC/MS) was used to detect changes in the quality of coking wastewater. The results showed that when coking coal dosage was 120 g/dm<sup>3</sup>, 65% of COD and 34% of phenol in waste water can be removed after 40 min of agitation. The surface functional groups of coking coal before and after adsorption were observed with a Fourier transform infrared spectrometer. The kinetics of COD and phenol adsorption from coking wastewater by coking coal fitted the pseudo second-order model. The adsorption process of coking coal can be classified into two categories, namely, rapid and slow. The Freundlich isotherm provided a better fit with all adsorption isotherms than the Langmuir isotherm. Coking coal could be a suitable low-cost adsorbent for recalcitrant organic pollutants.

**Keywords:** coking coal, coking wastewater, adsorption, COD, phenol

### Introduction

Coking wastewater is a type of highly concentrated organic wastewater generated from a process of making coke, purifying coal gas and recovering coke products (Wu and Zhu, 2012). Coking wastewater is a kind of intractable wastewater which is composed of complex inorganic and organic contaminants such as ammonia, cyanide, sulfate, phenolic compounds, polycyclic aromatic hydrocarbons and polycyclic nitrogen (Zhou, 2010; Burmistrz and Burmistrz, 2013; Burmistrz et al., 2014). The high concentration of chemical oxygen demand (COD) and phenol in coking

wastewater causes significant harm to water and soil (Sun et al., 2008). Thus, coking wastewater must be treated appropriately prior to discharge.

Current treatment methods for coking wastewater generally adopt pretreatment–biological treatment–advanced treatment. Different biodegradation techniques have been proposed for treatment of coking wastewater including anaerobic-anoxic-oxic membrane bioreactor, sequential bath reactor, activated sludge and moving bed biofilm reactors (Staib and Lant, 2006; Maranon et al., 2007; Zhao et al., 2009). Nevertheless, coexistence of toxic compounds in coking wastewater can cause inhibitory effects on the biodegradation process. Hence, it is very important to choose appropriate methods for coking wastewater pretreatment to improve the treatment efficiency of biological processes. As a consequence, multiple pretreatment processes have been studied such as catalytic oxidation treatment (Oulego et al., 2014), flocculation treatment (Pi et al., 2009), Fenton oxidation process (Lai and Zhao, 2012; Zhu, 2012) and others. Although these methods work on coking wastewater, the complexity of operation and high energy consumption make them impractical to be applied at an industrial scale.

Adsorption is an effective technique for removal of organic pollutants from coking wastewater (Vazquez et al., 2007; Burmistrz et al., 2014). Adsorbents are the key part of this technique. In the past years, some conventional adsorbents (e.g., activated carbon, zeolite, resins, silica gels, coke dust, lignite, and bottom ash) were usually applied to adsorb pollutions. Nowadays, their shortcomings of low adsorption capacity and high regeneration energy consumption requirements, however, restrict their extensive applications.

In this study a new technique for coking wastewater treatment is introduced in which coal was utilized to adsorb organic pollutants in coking wastewater based on a treatment proprietary process disclosed previously (Wang et al., 2014). In this process (Fig. 1), coal is fed into the coking system and wastewater is poured into biological treatment after adsorption. The process facilitates coking coal recycling. This paper focuses on the feasibility of using coking coal to adsorb organic pollutants from coking wastewater.

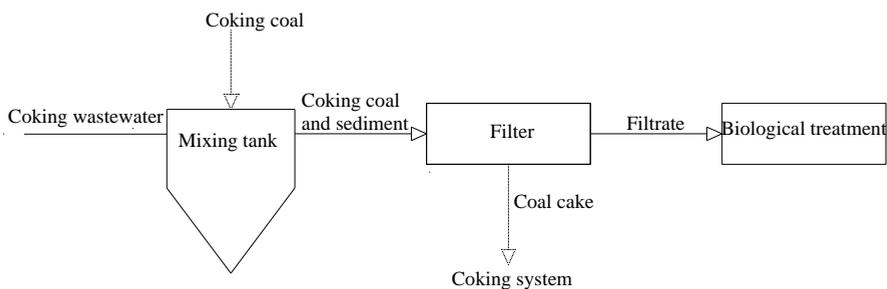


Fig. 1. Schematic of plant for coking wastewater treatment

## Materials and methods

### Coking wastewater and coal

The coking wastewater used in the experiments was obtained from Huayu Coke Plant, China. It was treated by ammonia distillation. The wastewater (pH value of 9.56) was deep brown in color and emitted a foul odor. Table 1 shows the analytical results of the coking wastewater sample.

Table 1. Water quality of coking wastewater

Parameter	Value
Color	Deep brown
pH	9.56
COD (g/dm <sup>3</sup> )	7.600
Phenol (mg/dm <sup>3</sup> )	418.35
Ammonia (mg/dm <sup>3</sup> )	118.50

Coking coal was also obtained from the Huayu Coke Plant, China. The particle size ranged from 0.5 to 30 mm. The samples were ground and screened to produce different particle sizes, such as +0.5, 0.5–0.25, 0.25–0.125, 0.125–0.074 and –0.074 mm. The mineral components, functional groups of the coal surface were analyzed with an X ray diffractometer (D8 ADVANCE, Bruker, Germany), a Fourier transform infrared spectrometer (VERTEX 80/80v, Bruker, Germany), respectively.

Through the XRD analysis, coking coal was mainly composed of amorphous coal with some minerals including quartz, kaolinite, illite and pyrite. Coal composition has an important role in adsorption although minerals also have some adsorption capacity, they can be ignored because of their low contents.

### Experimental methods

Different quantities of coking coal with a specific size were added into a 250 cm<sup>3</sup> triangular flask and 100 cm<sup>3</sup> coking wastewater was then added. H<sub>2</sub>SO<sub>4</sub> (1:10) was utilized to adjust the pH value. All the experiments were conducted in a water bath shaker for different adsorption times at 25 °C. After adsorption, the water samples were centrifuged at 3000 rpm for 10 min. The supernate was analyzed for chemical oxygen demand (COD), ammonia, and phenol removal.

An orthogonal test was implemented to examine the effect of particle size (A), coal dosage (B), coking wastewater pH value (C) and adsorption time (D) (Table 2). The experiment was designed according to the L<sub>25</sub> (5<sup>6</sup>) table (Table 3). The optimum experimental condition was determined based on the removal rate of COD, ammonia, and phenol.

Table 2. Factors and levels of orthogonal experiment

Level	Factors			
	A particle (mm)	B dosage (g)	C pH	D adsorption time (min)
1	A <sub>1</sub> = -0.074	B <sub>1</sub> = 8	C <sub>1</sub> = 2	D <sub>1</sub> = 10
2	A <sub>2</sub> = 0.074-0.125	B <sub>2</sub> = 10	C <sub>2</sub> = 4	D <sub>2</sub> = 20
3	A <sub>3</sub> = 0.125-0.25	B <sub>3</sub> = 12	C <sub>3</sub> = 5	D <sub>3</sub> = 40
4	A <sub>4</sub> = 0.25-0.5	B <sub>4</sub> = 15	C <sub>4</sub> = 6	D <sub>4</sub> = 100
5	A <sub>5</sub> = +0.5	B <sub>5</sub> = 20	C <sub>5</sub> = 7	D <sub>5</sub> = 150

Table 3. L<sub>25</sub>(5<sup>6</sup>) orthogonal array

Exp.	A	B	C	D	E	F	G
	Particle Size (mm)	Dosage (g)	pH	Adsorption Time (min)	The removal rate of ammonium (%)	The removal rate of Phenol (%)	The removal rate of COD (%)
1	A <sub>1</sub>	B <sub>1</sub>	C <sub>1</sub>	D <sub>1</sub>	8.48	23.59	47.37
2	A <sub>1</sub>	B <sub>2</sub>	C <sub>2</sub>	D <sub>2</sub>	14.14	33.58	73.68
3	A <sub>1</sub>	B <sub>3</sub>	C <sub>3</sub>	D <sub>3</sub>	6.50	39.02	78.43
4	A <sub>1</sub>	B <sub>4</sub>	C <sub>4</sub>	D <sub>4</sub>	14.89	28.46	51.47
5	A <sub>1</sub>	B <sub>5</sub>	C <sub>5</sub>	D <sub>5</sub>	9.79	31.65	56.86
6	A <sub>2</sub>	B <sub>1</sub>	C <sub>2</sub>	D <sub>3</sub>	4.04	15.43	78.43
7	A <sub>2</sub>	B <sub>2</sub>	C <sub>3</sub>	D <sub>4</sub>	11.46	16.33	52.07
8	A <sub>2</sub>	B <sub>3</sub>	C <sub>4</sub>	D <sub>5</sub>	10.23	23.39	56.86
9	A <sub>2</sub>	B <sub>4</sub>	C <sub>5</sub>	D <sub>1</sub>	5.80	26.54	51.84
10	A <sub>2</sub>	B <sub>5</sub>	C <sub>1</sub>	D <sub>2</sub>	3.86	28.21	63.16
11	A <sub>3</sub>	B <sub>1</sub>	C <sub>3</sub>	D <sub>5</sub>	6.28	13.61	62.25
12	A <sub>3</sub>	B <sub>2</sub>	C <sub>4</sub>	D <sub>1</sub>	6.68	26.95	47.37
13	A <sub>3</sub>	B <sub>3</sub>	C <sub>5</sub>	D <sub>2</sub>	15.37	23.59	57.89
14	A <sub>3</sub>	B <sub>4</sub>	C <sub>1</sub>	D <sub>3</sub>	4.57	24.06	69.43
15	A <sub>3</sub>	B <sub>5</sub>	C <sub>2</sub>	D <sub>4</sub>	15.33	26.76	67.64
16	A <sub>4</sub>	B <sub>1</sub>	C <sub>4</sub>	D <sub>2</sub>	20.29	9.98	60.16
17	A <sub>4</sub>	B <sub>2</sub>	C <sub>5</sub>	D <sub>3</sub>	5.27	8.17	46.07
18	A <sub>4</sub>	B <sub>3</sub>	C <sub>1</sub>	D <sub>4</sub>	6.28	10.89	69.43
19	A <sub>4</sub>	B <sub>4</sub>	C <sub>2</sub>	D <sub>5</sub>	8.04	10.80	66.43
20	A <sub>4</sub>	B <sub>5</sub>	C <sub>3</sub>	D <sub>1</sub>	5.53	13.61	63.16
21	A <sub>5</sub>	B <sub>1</sub>	C <sub>5</sub>	D <sub>4</sub>	11.73	8.17	68.04
22	A <sub>5</sub>	B <sub>2</sub>	C <sub>1</sub>	D <sub>5</sub>	9.27	17.24	62.25
23	A <sub>5</sub>	B <sub>3</sub>	C <sub>2</sub>	D <sub>1</sub>	4.57	15.43	67.68
24	A <sub>5</sub>	B <sub>4</sub>	C <sub>3</sub>	D <sub>2</sub>	10.32	16.54	52.63
25	A <sub>5</sub>	B <sub>5</sub>	C <sub>4</sub>	D <sub>3</sub>	3.95	11.80	40.68

Table 3 provides a description of the  $L_{25}$  orthogonal array involving four factors ( $A$ – $D$ ), each at five levels. The first column in this array contains the number of experiments; factors  $A$ – $D$  are arbitrarily assigned to columns 2–5, respectively. The table suggests that 25 trials of experiments are required, with the level of each factor for each trial run indicated in the array. Elements  $A_i$ ,  $B_i$ ,  $C_i$ , and  $D_i$  for  $i = 1, 2, \dots, 5$  represent the level of each factor. The vertical column represents the experimental factors to be studied using the array. Each column contains five assignments at each level (1, 2, 3, 4, or 5) for the corresponding factors. The last three columns are the experiment results under a corresponding combination of the factor levels. Parameters can be set easily by allocating variable levels to the individual columns. Thus, parameter setting is implemented by merely selecting an orthogonal array; this process is highly convenient (Chen et al, 2007).

Coking wastewater ( $100 \text{ cm}^3$ ) was placed in a  $250 \text{ cm}^3$  triangular flask. The experiments were conducted at the optimum experimental conditions at different adsorption times of 10, 20, 30, 40, 60, and 90 min in a water bath shaker at  $25^\circ\text{C}$ . After adsorption, the water samples were centrifuged at 3000 rpm for 10 min. The supernate was then further analyzed.

Coking wastewater ( $100 \text{ cm}^3$ ) was poured into a  $250 \text{ cm}^3$  triangular flask with different initial concentrations ranging from 3.040 to  $6.840 \text{ g/dm}^3$ . The experiments were conducted at the optimum experimental conditions in a water bath shaker with a temperature of  $25^\circ\text{C}$ . Post adsorption water samples were centrifuged at 3000 rpm for 10 min and the supernate was then further analyzed.

The COD, ammonia, and phenol contents of the wastewater samples were determined by potassium dichromate oxidation, salicylic acid spectrophotometry, and 4-AAP spectrophotometric method, respectively followed by the relevant standards (National Environment Bureau Water and Wastewater Monitoring Analysis Committee, 2002).

## Results and discussion

### Orthogonal experiment results

One assumption in the experiments was that any two factors do not interact with each other. The superiority and the degree of the influence (sensitivity) of each design factor  $R$  (Eq. 1) can easily be determined according to Table 4. The sensitivity of factor  $C$  was highest, and factors  $A$ ,  $B$ , and  $D$  had a less significant influence, because  $R_C$  was significantly larger than  $R_A$ ,  $R_B$ , and  $R_D$ . The best combination of each factor level for COD removal was when  $K$  (Eq. 2) has the largest value, namely,  $A_1$ ,  $B_3$ ,  $C_2$ , and  $D_3$ .

The five ordered degree values, with the  $E$  (removal rate of COD) of each factor in the same level ( $i$ ), were added. The corresponding average value  $K_i$  and range  $R$  were calculated as follows:

$$R = k_{\max} - k_{\min} \tag{1}$$

$$K_i = \frac{\Sigma E}{5} \tag{2}$$

where  $R$  reflects the effect of the factors on the removal rate of COD. A factor with high  $R$  suggests a strong effect on the removal rate of COD. In Eq. 2  $K_i$  represents the effect of level  $i$  of each factor on the removal rate of COD. A high  $K_i$  value suggests good removal rate.  $K_{\max}$  is the highest value among  $K_i$  values of each factor, whereas  $K_{\min}$  is the minimum value.

Table 4. Analysis of COD removal rate

	The removal rate of COD/%			
	Particle size/mm	dosage/g	pH	Adsorption time/min
	A	B	C	D
$\bar{K}_1$	<b>61.56</b>	63.25	62.33	55.48
$\bar{K}_2$	60.47	56.29	<b>70.77</b>	61.50
$\bar{K}_3$	60.92	<b>66.06</b>	61.71	<b>62.61</b>
$\bar{K}_4$	61.05	58.36	51.31	61.73
$\bar{K}_5$	58.26	58.30	56.14	60.93
R	3.31	9.77	19.46	7.12
$S_i$	33.14	328.01	1069.03	161.49

Table 5 shows that the sensitivity of factor  $A$  was the highest followed by  $D$ ,  $C$ ,  $B$ , and had weaker influence because  $R_A$  was significantly larger than  $R_B$ ,  $R_C$ , and  $R_D$ . The best combination for phenol removal was thus  $A_1$ ,  $B_3$ ,  $C_1$ , and  $D_2$ .

Table 5. Analysis of phenol removal rate

	The removal rate of phenol/%			
	Particle size/mm	dosage/g	pH	Adsorption time/min
	A	B	C	D
$\bar{K}_1$	<b>31.26</b>	14.16	<b>20.80</b>	21.22
$\bar{K}_2$	21.98	20.45	20.40	<b>22.38</b>
$\bar{K}_3$	22.99	<b>22.46</b>	19.82	19.70
$\bar{K}_4$	10.69	21.28	20.12	18.12
$\bar{K}_5$	13.84	22.41	19.62	19.34
R	20.57	8.31	1.17	4.26
$S_i$	1321.14	238.71	4.34	55.52

Table 6 shows that the sensitivity of factor  $D$  was the highest.  $A$ ,  $B$ , and  $C$  had a weaker influence because  $R_D$  was significantly larger than  $R_A$ ,  $R_B$ , and  $R_C$ . So the best combination for ammonia removal was  $A_1$ ,  $B_1$ ,  $C_4$ , and  $D_2$ .

Table 6. Analysis of ammonia removal rate

	The removal rate of ammonia/%			
	Particle size/mm A	dosage/g B	pH C	Adsorption time/min D
$\bar{K}_1$	<b>10.76</b>	<b>10.16</b>	6.49	6.21
$\bar{K}_2$	7.08	9.36	9.22	<b>12.80</b>
$\bar{K}_3$	9.65	8.59	8.02	4.87
$\bar{K}_4$	9.08	8.72	<b>11.21</b>	11.94
$\bar{K}_5$	7.97	7.69	9.59	8.72
R	3.68	2.47	4.72	7.93
$S_i$	41.19	17.00	62.43	239.69

The result of orthogonal experiment revealed that the optimum conditions for COD, ammonia, and phenol removal were different. Because phenol and ammonia are relatively simple compounds, they are more easily to be removed during the downstream treatment processes (Burmistrz et al., 2014; Gu et al., 2014). Furthermore, phenol as an organic compound, is part of COD. And the biodegradation inhibitors (PAHs and oil substances) assessed by means of COD (Burmistrz et al., 2014). Removal of those components provides better conditions for the microorganisms in the activated sludge and intensified biodegradation, nitrification and denitrification process. So the optimum adsorption condition for coking coal pretreatment was determined as  $A_1$ ,  $B_3$ ,  $C_2$ , and  $D_3$ .

### Optimum experimental conditions

Figure 2 shows that the removal rate of COD reached 65% after adsorption. The pH value of water sample was 6.99, which was beneficial for degradation in the following biological treatment. Thus, adsorption with coking coal is an efficient method to treat coking wastewater.

Figure 3 presents the gas chromatograms of coking wastewater before and after adsorption. Numerous aromatic compounds were detected in the water sample, among which the content of phenol was the highest. Only four types of organic compounds were detected in the absorbed water sample, including phenol, 2-methylphenol, 4-methylphenol and aniline. Many organic compounds, particularly large molecular organic components, were not found in the post treatment sample indicating that most organic compounds, particularly those with complicated structures, can be removed by

using coking coal as the absorbent. Large molecular organic components usually possess a challenge for biodegradation. Thus, the absorbed coking wastewater is beneficial for the following biological degradation treatment, making it easier for the sewage treatment plant to meets the emission standards.

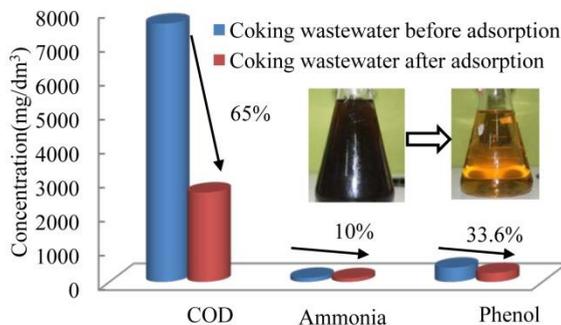


Fig. 2. Water quality of coking wastewater before and after adsorption gas chromatograph/mass spectroscopy analysis

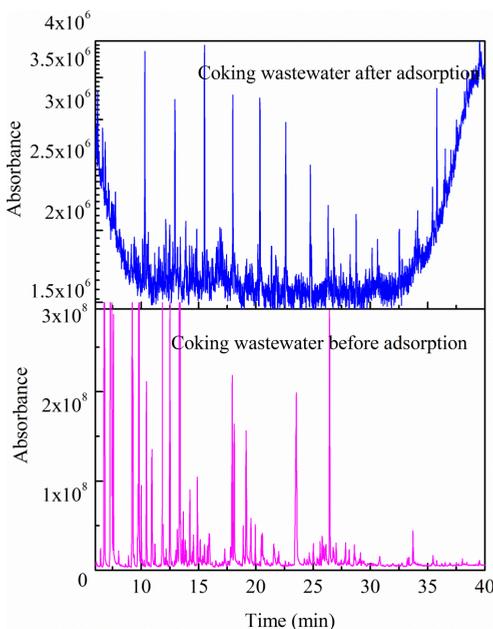


Fig. 3. Gas chromatograms of coking wastewater before and after adsorption

Figure 4 and infrared spectroscopic analysis (Liu et al,1999) reveal that the major functional groups of coking coal are  $-OH$ ,  $C=O$ ,  $-CH$ ,  $-CH_2$ , and  $CH_3$ . Table 7 shows the adsorption peak of this pattern. As shown in Fig. 4 the location of peaks before and after adsorption was similar. The absorbance by coking coal after adsorption was

higher than that of using raw coal. The surface of coking coal did not exhibit a new adsorption peak but did show fluctuations in the original position after adsorption. Therefore, this adsorption may mainly be a physical process.

Coking and caking capacities are extremely important indicators for the coking material. However, these indicators are not related to the content of coal surface functional groups (Zhang, 2009). Thus, the use of coking coal for coking after adsorption have no effect on the quality of coke and other products (data not shown).

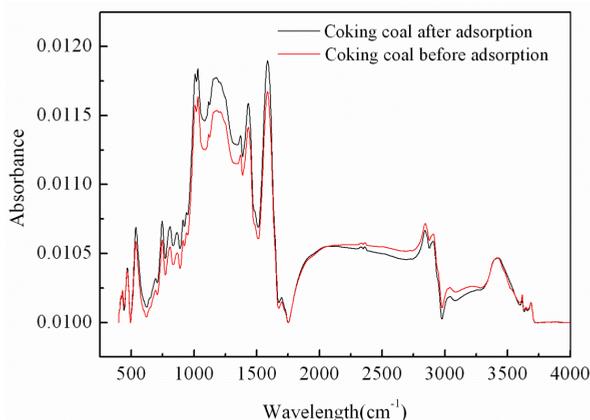


Fig. 4. FTIR analysis patterns of coking coal before and after adsorption

Table 7. Functional groups of every adsorption peak

Wavelength (cm <sup>-1</sup> )	Functional group
>4000	—
3800~3600	free hydroxyl
3500~3400	hydroxyl of intramolecular association
2920	-CH <sub>3</sub>
2910~2850	-CH <sub>3</sub>
2760~2300	-OH
1600	C=O; C=C
1450	-CH <sub>2</sub> 、-CH <sub>3</sub>
1380	-CH <sub>3</sub>
1300~1100	C-O
860~700	CH
540	-S-S-
475	-S-H
420	FeS <sub>2</sub>

### Sorption kinetics

Pseudo first-order (Eq. 3, Fig. 5) and second-order (Eq. 5, Fig. 6) models were employed to examine the mechanism of COD and phenol adsorption by coking coal. The adsorption mechanism of ammonia was not detected because of the low removal rate.

The pseudo first-order model can be expressed as (Lagergren, 1898):

$$\frac{dp_t}{dt} = k_1 (q_1 - q_t) \quad (3)$$

where  $q_1$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of COD and phenol adsorbed at equilibrium,  $q_t$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of COD adsorbed at time  $t$  (min), and  $k_1$  ( $\text{min}^{-1}$ ) is the equilibrium rate constant of pseudo first-order sorption. The integrated form of the pseudo first-order model is:

$$\log(q_1 - q_t) = \log q_1 - \frac{k_1 t}{2.303} \quad (4)$$

The straight line plots of  $\log(q_1 - q_t)$  against  $t$  were tested to obtain the parameters of  $k_1$  and  $q_1$ .

The pseudo second-order model can be expressed as (Ho and McKay, 1999):

$$\frac{dp_t}{dt} = k_2 (q_2 - q_t)^2 \quad (5)$$

where  $q_2$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of COD and phenol adsorbed at equilibrium,  $k_2$  ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ) is the equilibrium rate constant of pseudo second-order sorption. The integrated form of the pseudo second-order model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (6)$$

Initial sorption rate  $h$  ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ ) can be calculated by:

$$h = k_2 q_2^2 \quad (7)$$

The straight line plots of  $t/q_t$  against  $t$  were tested to obtain the parameters of  $k_2$ ,  $h$ , and  $q_2$ .

The kinetic adsorption data on the adsorption of COD and phenol by coking coal were analyzed with the first-order and second-order models. The fitting results shown in Table 8 present better compliance with the pseudo second-order model. The regression coefficients for the linear plots are high (Table 8) and equal to 0.9993 and 0.998.

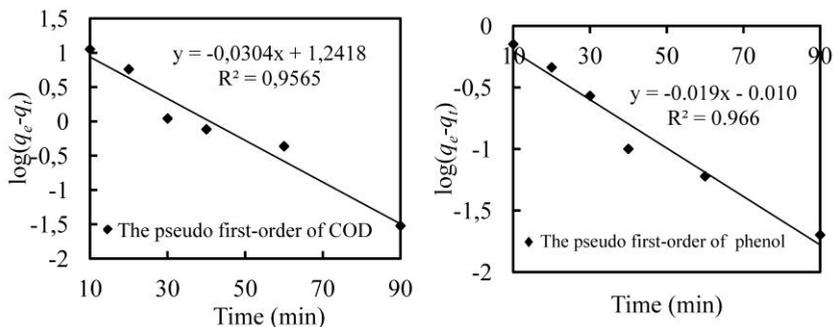


Fig. 5. The pseudo first-order of COD (left) and phenol (right)

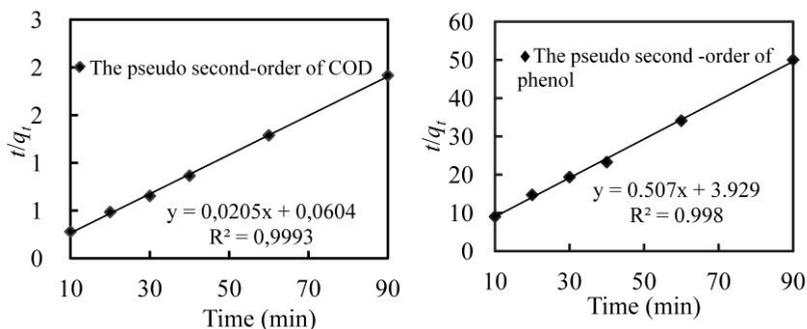


Fig. 6. The pseudo second-order of COD (left) and phenol (right)

Table 8. Kinetics parameters for adsorption of COD and phenol onto coking coal

Components	$q_e^{exp}$ ( $mg \cdot g^{-1}$ )	Pseudo-first order model			Pseudo-second order model		
		$q_e$ ( $mg \cdot g^{-1}$ )	$k_1$ ( $min^{-1}$ )	$R_1^2$	$q_e$ ( $mg \cdot g^{-1}$ )	$k_2$ ( $g \cdot mg^{-1} \cdot min^{-1}$ )	$R_2^2$
COD	47.03	17.45	0.013	0.9565	48.78	0.006958	0.9993
phenol	1.82	0.98	0.0086	0.9664	1.97	0.06552	0.9985

Figure 7 presents the kinetic curves of coking coal. It shows that the sorption capacity increased rapidly in the first 10 min before slowing down till it reached equilibrium at 40 min. Hu et al. (2008) reported that active carbon adsorbed coking wastewater can be divided into two phases, one involving a rapid adsorption process, and the second being a slow adsorption process. Figure 4 indicates that the adsorption of coking coal in the present study can also be divided into two processes, namely, rapid and slow process, respectively.

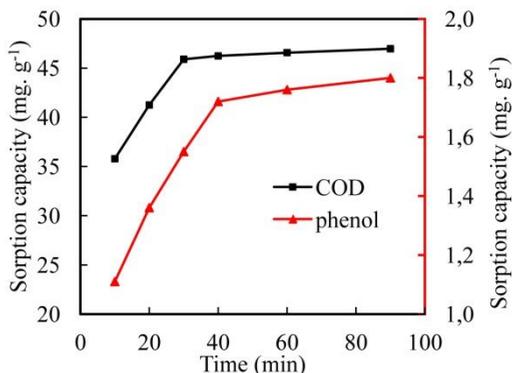


Fig. 7. Kinetic curves of COD and phenol onto coking coal

### Equilibrium isotherms

The COD and phenol adsorbed by coking coal are in equilibrium with the COD and phenol in the bulk solution under constant temperature. The saturated monolayer isotherm is represented as the Langmuir isotherm as follows (Langmuir, 1916):

$$q_e = \frac{q_m k_a C_e}{1 + K_a C_e} \tag{8}$$

where  $C_e$  (mg/dm<sup>3</sup>) is the equilibrium concentration,  $q_e$  (mg·g<sup>-1</sup>) is the equilibrium amount of COD adsorbed,  $q_m$  (mg·g<sup>-1</sup>) is  $q_e$  for a complete monolayer, and  $K_a$  (dm<sup>3</sup>·mg<sup>-1</sup>) is the sorption equilibrium constant. The Langmuir isotherm can be linearized into (Kinniburgh, 1986):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \tag{9}$$

The empirical Freundlich isotherm (Freundlich, 1906) can be derived based on adsorption on the heterogeneous surface by assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites

$$q_e = K_F C_e^{\frac{1}{n}} \tag{10}$$

where  $K_F$  and  $1/n$  are the Freundlich constant characteristics of the system and indicate the sorption capacity and sorption intensity, respectively. The formula can be linearized in logarithmic form as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{11}$$

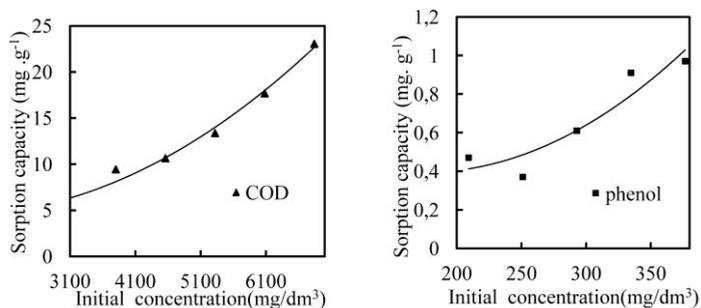


Fig. 8. Isotherm curves of COD (right) and phenol (left) onto coking coal

Table 9. Isotherm parameters for adsorption of COD and phenol onto coking coal

Adsorption isotherm	COD			Phenol		
Langmuir	$q_{m1}$	$K_{a1}$	$R_1^2$	$q_{m1}$	$K_{a2}$	$R_2^2$
	-92.59	$2.6 \times 10^{-5}$	0.8265	2.556	0.0017	0.618
Freundlich	$K_{F1}$	$n_1$	$R_3^2$	$K_{F1}$	$n_1$	$R_4^2$
	0.0187	0.889	0.8713	234.96	1.416	0.63

Figure 8 shows the isotherm curves of COD and phenol adsorbed by coking coal at different initial concentrations. The equilibrium sorption capacity increased with an increasing initial concentration. Different isotherms were utilized to fit the experimental results as shown in Table 9. The correlation coefficients for the Freundlich isotherm are higher than those for the Langmuir isotherm. However, all the values of  $R^2$  are smaller than 0.99 probably because of the complexity of coking wastewater composition. Therefore, the adsorption type of coking wastewater adsorbed by coking coal could be a combination of physical and chemical adsorption.

## Conclusion

Coking coal is a kind of material suited for adsorbing organic compounds in coking wastewater. When the dosage of coking coal was  $120 \text{ g/dm}^3$ , pH value of coking wastewater was 4,65% of chemical oxygen demand (COD) and 34% of phenol could be removed after 40 min agitation. Gas chromatograph/mass spectroscopy (GC/MS) results showed that most large molecular organic components could be adsorbed by coking coal. The kinetics of COD and phenol adsorption from coking wastewater by coking coal fitted the pseudo second-order model. The Freundlich isotherm provided a better fit with all adsorption isotherms than the Langmuir isotherm.

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