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Effect of surface modification on quinoline adsorption onto coking coal

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ABSTRACT

The adsorption of quinoline from simulated wastewater by raw coking coal (RCC), HCl modified coking coal (HCC) and NaOH modified coking coal (NCC) are investigated. Effects of initial concentration, adsorbent dosage, adsorption time and temperature for quinoline adsorption on coking coal are studied in batch experiments. The adsorption efficiency for quinoline increase with increasing of adsorbent dosage and adsorption time, the optimum adsorbent dosage is 50 $g \cdot L^{-1}$, the adsorption time for quinoline adsorption on RCC, HCC and NCC is 120 mins. Kinetic experiments show that the equilibrium time for quinoline adsorption on raw and modified coking coal is 120 mins, and follow quasi-second order kinetic equation well. The adsorption isotherm data fit Freundlich models, and the adsorption capacity of quinoline on the three adsorbents increase with increasing of temperature from 288 to 313 K. HCC and NCC have a higher adsorption capacity of quinoline than RCC, because modification treatment can improve the specific surface area of RCC. Thermodynamic parameters, the Gibbs free energy change ($\Delta G°$), Enthalpy change ($\Delta H°$) and Entropy change ($\Delta S°$) are calculated and the results show that the adsorption of quinoline on three adsorbents is spontaneous and endothermic. The results illustrate that modified coking coal have high potential as low-cost adsorbent for quinoline removal.

Keywords: Coking coal; Quinoline; Surface modification; Kinetics; Thermodynamics

1. Introduction

Quinoline is usually found in wastewater from smelting [1], batteries [2], agrochemical [3] and other industrial process [4]. Excessive exposure to quinoline can cause harmful effects on human health, including dizzy, hepatic injury and cancer [5]. Therefore, many methods have been developed to remove quinoline from aqueous solution such as chemical precipitation [6], membrane separation [7], ion exchange [8] and electrochemistry removal [9]. However, the application of such treatment methods is often restricted because of economic or technical constraints. Adsorption by using low-cost materials is one of the most promising methods to remove quinoline from wastewater [10]. There are few reports on the application of raw or modified coking coal in the removal of quinoline from simulated wastewater in recent years [11–14].

It has been found in previous studies that the adsorption capacity of adsorbent is improved by modification treatment [15]. Liu [16] use HCl modified ultrafine coal powder (UCP) and carried out adsorption test of methyl orange. The test results show that the UCP adsorption capacity after HCl modification is significantly improved because the surface porosity of the modified UCP increased. Wang

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[17] use NaOH to modify coal gangue and carry out adsorption test of methylene blue. The research indicates that the removal rate of methylene blue before the modification of coal gangue is 45.45%, and the removal rate after modification is 96.87%, NaOH modification have greatly improved the adsorption capacity of coal gangue.

Considering that the adsorption capacity of raw coking coal (RCC) is improved by modification treatment [18,19], modified coking coal (MCC) is examined to be one potential low-cost adsorbent in this study. The potential of RCC and MCC remove quinoline from wastewater is evaluated through a series of batch experiments. The effects initial concentration, adsorbent dosage, adsorption and temperature on the adsorption capacity are investigated. Adsorption isotherm models and thermodynamic parameters are also studied to understand the adsorption characteristics [20]. The objective of this study is to establish a fundamental understanding of the adsorption behavior of quinoline on RCC and MCC, provide a basis for their practical application to wastewater treatment. This work is conducted in China university of mining and technology (Beijing), China.

2. Materials and methods

2.1. Material

The samples preparation experiments were carried out at room temperature (298 K) in 1000 mL beaker by mixing 100 g coking coal (Particle size - 74 μm) with 500 mL of 0.1 mol·L^{-1} HCl and NaOH solution, respectively. Using a magnetic stirrer to stir (RET basic, Shanghai Jiuran Instrument Equipment Co., Ltd.) at a speed of 300 rpm for 120 min. The test samples were filtered by Buchner Funnel (Tangshan Kaiping Shengxing Chemical Porcelain Factory). After stirring process was completed, and the PH of the samples were adjusted to 6.8 to 7.2 with deionized water, the samples were dried in a vacuum oven (Shanghai Hao Scientific Instrument Co., Ltd.) about 720 min at 378 K.

Accurately weigh 1.00 g of quinoline in a beaker using an electronic analytical balance (BSA124S, Sartorius Scientific Instruments (Beijing) Co., Ltd.), adding into a 1000 mL volumetric flask, and rinsing the beaker with deionized water for 5 times. The rinse was added to the volumetric flask, and the solution was diluted to the volumetric flask scale line with deionized water. After stirring for 6 h using a magnetic stirrer, it was sufficiently dissolved to obtain a quinoline standard solution of 1 g·L^{-1}. The standard solution was diluted to different concentration during experiment.

The determination of the pH$_{pzc}$ of the samples was carried out as follows: (1) 25 cm^3 of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask. The pH was adjusted to a value between 2 and 12 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then, 0.5 g of each coal sample was added and the pH$_1$ measured after mixing at room temperature. (2) 0.1316 g of NaCl was added into the closed Erlenmeyer flask for adjusting the concentration to 0.1 M. Then, the pH$_2$ were measured under agitation for a while at room temperature. (3) Record the difference between pH$_1$ and pH$_2$ as ΔpH, set the ΔpH as Y axis, and the pH$_2$ as X axis, placing ΔpH with the final pH$_2$ of the solution, the pH$_{pzc}$ is the point of pH$_2$ when ΔpH = 0.

2.2. Determination of Quinoline concentration

Quinoline solution was scanned in full wavelength by UV spectrophotometer (UV-1500, Shanghai Meixi Instrument Co., Ltd.). The result shows that the wave peak was the strongest when the wavelength was 299 nm. Preparing quinoline solutions 5, 10, 20, 30, 40 and 60 mg·L^{-1},respectively. The quinoline solutions absorbance values were measured at the wavelength of 299 nm. Fitting the standard curve of quinoline solution and the result is shown as Eq. (1).

$$y = 0.0259x - 0.0046 \tag{1}$$

where x is the absorbance value of the filtrate was measured by UV spectrophotometer, quinoline solution concentration was calculated using standard curve (1).

2.3. Adsorbent dosage experiment

The adsorbent dosage experiments were carried out at room temperature (298 K) in 100 mL conical flask by mixing 0.5, 1, 1.5, 2, 2.5, 3 and 4.0 g RCC, HCC and NCC with 50 mL of 50 mg·L^{-1} quinoline solution, respectively. Using a shaking thermostat machine at a speed of 120 rpm for 120 min. The test samples were filtered by when the shaking was completed, the absorbance value of the filtrate was measured by UV spectrophotometer, quinoline solution concentration was calculated using standard curve (1). pH experiments were carried out at the same condition (except the adsorbent dosage 2.5 g, pH was set as 2, 4, 7, 10, 12).

2.4. Dynamic experiment

Batch experiment of adsorption time with RCC, HCC and NCC were performed on the same conditions compare with adsorbent dosage experiment (except for the adsorption time 5 min, 15 min, 45 min, 120 min, 270 min, 450 min and 870 min).

Quinoline adsorption process on raw and modified coking coal were fitted by Quasi-first order kinetic equation and Quasi-second order kinetic equation. The linear expressions are shown in Eqs. (2) and (3), respectively.

$$\lg\left(q_e - q_t\right) = \lg q_e - \frac{K_1}{2.303}t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e (mg·g^{-1}) is the equilibrium adsorption capacity. q_t (mg·g^{-1}) is the adsorption capacity at time t (min). K_1(min^{-1}) is the quasi-first order kinetic adsorption rate constant (min^{-1}). K_2 is the Quasi-second order kinetic adsorption rate constant, g·mg^{-1}·min^{-1}.

2.5. Thermodynamic experiment

The thermodynamic experiments were carried out at temperature 288 K, 298 K and 313 K respectively. In 100 mL conical flask by mixing 2.5 g adsorbent (RCC, HCC and

NCC) with 50 mL of quinoline solution, and quinoline concentration were 10, 15, 25, 45, 65 and 85 mg L^{-1}, respectively. Using a shaking thermostat machine at a speed of 120 rpm for 870 min. The test samples were filtered when the shaking is completed, the absorbance value of the filtrate was measured by UV spectrophotometer, quinoline solution concentration was calculated using standard curve (1).

The adsorption process on raw and modified coking coal were fitted by Langmuir, Freundlich and R-P isotherm adsorption models, respectively. The linear expressions of the Langmuir model and the Freundlich model are shown in Eqs. (4) and (5), respectively.

$$\frac{C_{eq}}{Q_{eq}} = \frac{C_{eq}}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

$$\ln Q_{eq} = \ln K_{Fr} + \left(\frac{1}{n}\right)\ln C_{eq} \tag{5}$$

The isothermal expression of Redlich-Peterson (R-P) model was expressed as.

$$Q_{eq} = \frac{K_R C_{eq}}{1 + \alpha C_{eq}^{\beta}} \tag{6}$$

where K_L is a constant related to the adsorption activation energy, $L\cdot mg^{-1}$. q_m is the single layer adsorption amount, $mg\cdot g^{-1}$. C_{eq} is the concentration of the adsorbate in solution at equilibrium, $mg\cdot L^{-1}$. K_{Fr} is the parameter for characterizing the adsorption capacity in Freundlich. $1/(n)$ is the parameter for evaluating the superiority of adsorption. K_R is a constant that maximizes the R-P model correlation coefficient R^2, $L\cdot g^{-1}$. α is the equation constant, $L\cdot g^{-1}$.

The adsorption free energy was calculated by the following Eq. (7).

$$\Delta G^\circ = -RT\ln K_0 \tag{7}$$

The relationship between the adsorption standard Gibbs free energy ΔG° and the adsorption standard enthalpy change ΔH° and the adsorption standard entropy change ΔS° is as follows.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

Simultaneous Eqs. (7) and (8).

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

where R is the ideal gas constant (8.314 $J\cdot mol^{-1}\cdot K^{-1}$). T is the absolute temperature of adsorption, K. K_0 is obtained from K_{Fr} in the Freundlich model. ΔG° is calculated using the K_{Fr} value of the Freundlich model.

3. Results and discussion

3.1. Proximate analysis

Proximate analysis of different coal samples according to GB/T212-2008 standard, the results are shown in Table 1.

Table 1
Proximate analysis of raw and modified coking coal

Proximate analysis/%				
Adsorbent	M_{ad}	A_{ad}	V_{daf}	FC_d
RCC	1.28	6.70	28.61	63.42
HCC	0.83	3.33	31.67	64.17
NCC	1.09	2.97	33.12	62.82

Note: ad—air dried basis; d—dry basis; daf—dry ash free basis; M—moisture; A—ash; V—volatile matter; FC—fixed carbon.

Table 2
Specific surface area and average pore size of raw and modified coking coal

Adsorbents	Specific surface area/ $m^2\cdot g^{-1}$	Average pore size/nm
RCC	2.998	12.212
HCC	3.169	10.157
NCC	3.042	22.795

It can be seen from Table 1, the original ash of RCC is 6.70%, which belongs to low ash coal. The volatile matter is 28.61% and belongs to medium volatile coking coal. The moisture content is low and the mass fraction is 1.28% only because the test samples have been naturally dried for a long time. There are something dissolved during the modification process because of the ash of HCC and NCC are lower than raw coking coal [21].

3.2. Specific surface area

The specific surface areas and adsorption average pore sizes on three adsorbents are measured by static nitrogen adsorption meter (JW-BK122W, Beijing Jingwei Gaobo Science and Technology Co., Ltd.), and the results are shown in Table 2.

It can be seen from Table 2, the specific surface area of HCC and NCC are increased and the pore sizes of HCC is reduced. Due to some minerals in coking coal is dissolved by HCl, new small pore channels on coking coal surface are created. The decrease of pore volume caused by shrinkage is more than newly generated pore volume, the specific surface area increase of the newly generated channel is more than decrement of specific surface area caused by shrinkage, so the specific surface areas of coking coal after modification are increased, but the pore volume and the pore diameter are smaller than RCC. NCC expose more internal structure, the specific surface areas of the material are increased, the oxygen-containing functional groups on the surface are reduced, and the hydrophobicity are increased, so the adsorption capacity of NCC is improved than RCC. The results of this study are similar with the study of Toprak [22].

3.3. Mineral composition analysis

The crystallization characteristics of three adsorbents are studied by X-ray diffraction, and the results are shown in Fig. 1.

It can be seen from Fig. 1, the characteristic diffraction peaks of raw and modified coking coal are located at 12.41°, 21.5°, 24.9°, 29.3°, 35.6°, 38.5° and 62.5°, respectively. The peak intensity and area of NCC which locate at 21.5°, 24.9°, 35.6°, 38.5° and 62.5° are increased (except for 12.41°), and the number of hydroxyl groups in the coal is increased by NaOH modified. The peak at 29.3° is decreased which the corresponding phase is phosphate. It is concluded that modifier is reacted with phosphate, and resulted phosphate dissolved during the modification process. As the pores are created, the specific surface areas are increased, this conclusion is consistent with the pore size analysis of the material. HCC peaks which locate at 12.41°, 35.6°, 38.5° and 62.5° do not change significantly [13].

Variation of three adsorbents interlamellar spacing are shown in Table 3.

It can be seen from Table 3 that diffraction peak has no change in the interlamellar spacing at kaolinite after modified, but the interlamellar spacing at hydrogen vanadium phosphate hydrate increased. Crystal impurities is dissolved by adsorbents, the pore of HCC and NCC are increased during the modified process, so the adsorption capacity of the modified coking coal is improved [23].

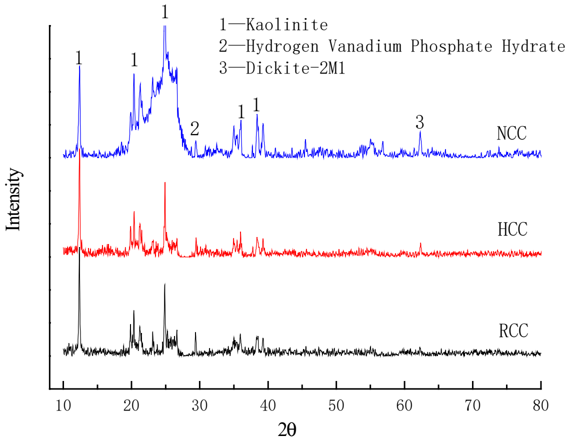


Fig. 1. XRD spectra of raw and modified coking coal.

Table 3

Changes in the interlamellar spacing of raw and modified coking coal

Mineral	2θ/°	Interlamellar spacing/nm		
		RCC	HCC	NCC
Kaolinite	12.41	7.15	7.15	7.13
	21.5	4.13	4.13	4.12
	24.9	3.62	4.07	3.56
	35.6	2.52	2.82	2.53
	38.5	2.34	2.34	2.34
Hydrogen vanadium Phosphate hydrate	29.3	3.04	3.34	3.32
Dickite-2M1	62.5	1.62	1.48	1.51

3.4. Effect of adsorbents dosage on quinoline adsorption

The effect of adsorbents dosage on quinoline removal rates for quinoline adsorption onto raw and modified coking coal are shown in Fig. 2.

Fig. 2 illustrates the adsorption capacity of HCC and NCC are better than RCC. Quinoline removal rates are increased with the increasing of adsorbent dosage, and it is increased rapidly when the dosage is less than 50 g·L^{-1}. When adsorbent dosage is 50 g·L^{-1}, the quinoline removal rates are 90.61% and 90.15% for HCC and NCC, respectively. The quinoline removal rates tend to slowly when the dosage is more than 50 g·L^{-1}. The experiment result shows that the adsorption capacity of coking coal is positively correlated with the specific surface area and total pore volume. The total specific surface area provide by adsorbent have increased with the adsorbent dosage increment, quinoline removal rates will improve as the total adsorbable capacity increased. Quinoline removal rates are decreased with increasing of adsorbent dosage, because there are not enough adsorbents to provide adsorption site, so high probability of collision is good for the quinoline adsorption on the adsorbent. The adsorbent exhibitor a high adsorption capacity when adsorbent dosage is 50 g·L^{-1}. The optimum dosage of three adsorbents determined is 50 g·L^{-1} based on the quinoline removal rates and the test cost.

3.5. Effect of quinoline initial concentration on quinoline adsorption

The plot of quinoline initial concentration vs. quinoline removal rates for quinoline adsorption onto raw and modified coking coal are shown in Fig. 3.

It can be seen from Fig. 3, quinoline removal rates on HCC and NCC are better than RCC. With the increase of quinoline initial concentration, the quinoline removal rates are decreased gradually. When the concentration is less than 50 mg·L^{-1}, difference between HCC and NCC are not very obviously. As the concentration is 50 mg·L^{-1}, quinoline removal rates of RCC, HCC and NCC are 91.00%, 96.17% and 95.94%, respectively. Quinoline removal rates are greatly reduced when concentration is more than 50 mg·L^{-1}, because the adsorbent surface cannot carry an excessive amount of quinoline molecules when adsorbent have a limited number

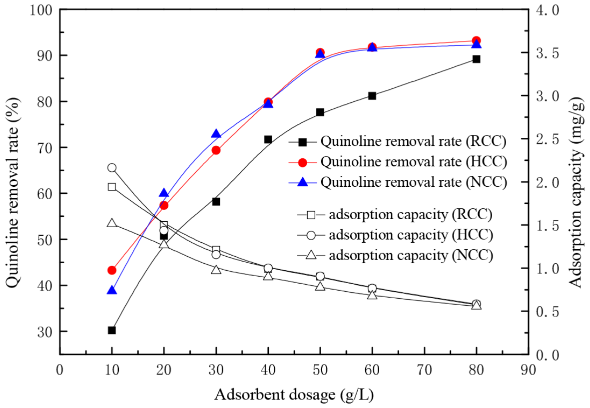


Fig. 2. Effect of adsorbents dosage on quinoline removal rate.

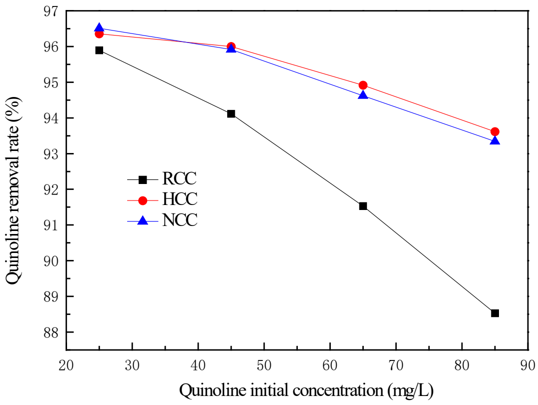


Fig. 3. Plot of quinoline initial concentration vs. quinoline removal rates for quinoline adsorption onto raw and modified coking coal.

of adsorption sites, so quinoline removal rates are decreased with the increasing of quinoline concentration.

3.6. Effect of pH on auinoline adsorption

The effect of pH on quinoline removal rates and adsorption capacities for quinoline adsorption onto raw and modified coking coal are shown in Fig. 4.

As seen from Fig. 4, quinoline removal rates and adsorption capacities for quinoline adsorption onto raw and modified coking coal increase first and then decrease with the increase of pH value. Under the condition of acid modification, the adsorption rates of organic matter increase with the increase of pH value. When the pH is 6.7–7.2, the removal rates of quinoline is the highest. The removal rates of organic matter decrease rapidly with the increase of pH when the pH exceeds 10. The optimum pH is pH = 7. The pH_{pzc} of coal samples are shown in Fig. 5.

Coking coal are materials with amphoteric character, thus, depending on the pH of the solution, their surface might be positively or negatively charged. At pH > pH_{pzc} the coal surface becomes negatively charged favouring the adsorption of cationic species. On the other hand, adsorption of anionic species will be favoured at pH < pH_{pzc}. As seen from Fig. 5, the pH_{pzc} for RCC, HCC and NCC are between pH = 6 and pH = 7. In the present work, the results show that when the initial pH of quinoline solutions was lower than pH_{pzc}, enhance the pH is good for adsorption. When the initial pH of quinoline solutions was bigger than pH_{pzc}, enhance the pH become useless for adsorption [24].

3.7. Dynamics study

The effect of adsorption time on quinoline removal rates and adsorption capacities for quinoline adsorption onto raw and modified coking coal is shown in Fig. 6.

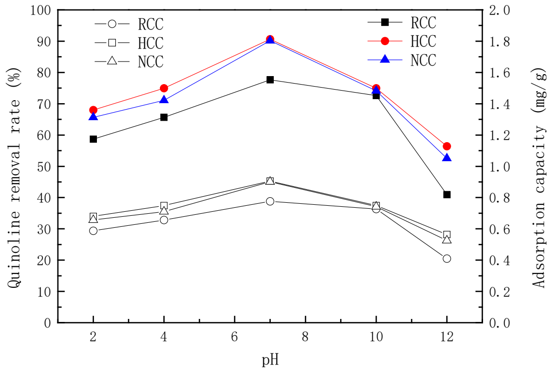


Fig. 4. Effect of pH on quinoline removal rates and adsorption capacities.

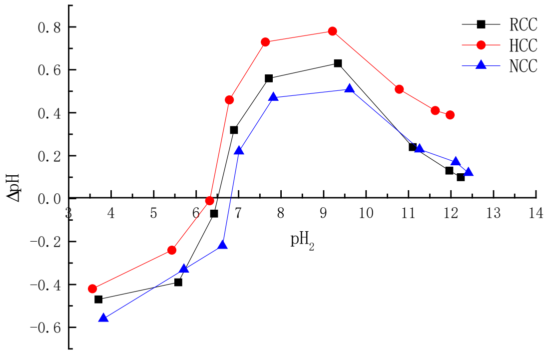


Fig. 5. The relationship between ΔpH and final pH_2 of RCC, HCC and NCC.

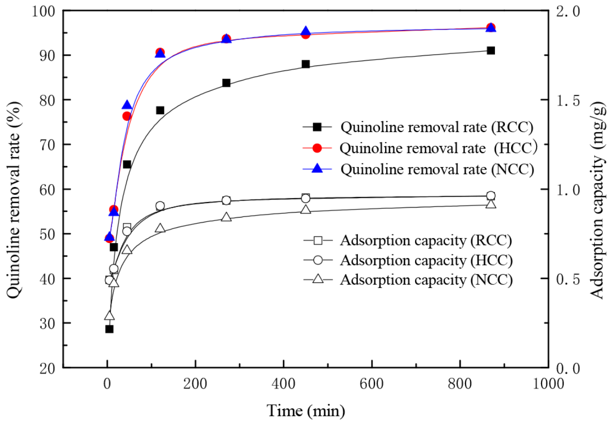


Fig. 6. Effect of adsorption time on quinoline removal rates and adsorption capacities.

Quinoline removal rates and adsorption capacity will increase with the increasing of adsorption time in Fig. 6. The removal rates increased rapidly at the initial stage of the reaction, it has exceeded 90% when the adsorption time reached 200 mins and tended to be slow after 200 mins. It indicates that the adsorption capacity for three adsorbents are HCC > NCC > RCC. The adsorption process on raw and modified coking coal is fitted by Quasi-first order kinetic equation and Quasi-second order kinetic equation, respectively. The plot of $\log(q_e - q_t)$vs. t is shown in Fig. 7, and the plot of t/q_t vs. t is shown in Fig. 8.

The values of q_e, K_1 and K_2 are calculated according to the intercept and slope of the curve fitted in Fig. 8, the calculation results are shown in Table 4. It can be seen from Table 4, the correlation coefficient R^2 of the quasi-first order kinetic model is lower than quasi-second order kinetic model, and the calculated value $q_{e(calc)}$ is much lower than the experimental value $q_{e(exp)}$, indicating that quasi-first order kinetic rate equation is not fitted the quinoline adsorption. The correlation coefficient R^2 of the quasi-second order kinetic rate equation is higher than quasi-first order kinetic model, and the calculated value $q_{e(calc)}$ is close to the experimental value $q_{e(exp)}$, it indicates that the quinoline adsorption on raw and modified coking coal conforms to the quasi-second kinetic rate model. It can also be seen from Table 4, both k_1 and k_2 increased with the increase of temperature, that is high temperature is good for adsorption process.

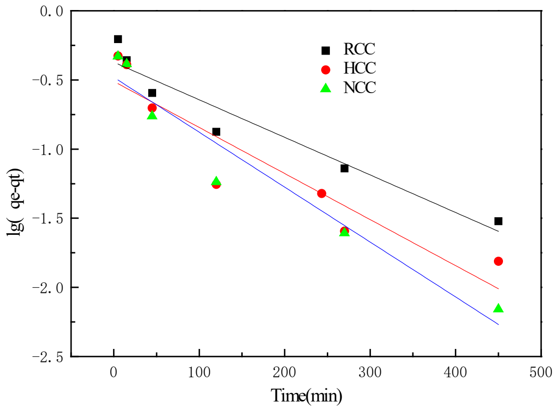


Fig. 7. Fitting curve of quasi-first order kinetic model for quinoline adsorption on raw and modified coking coal.

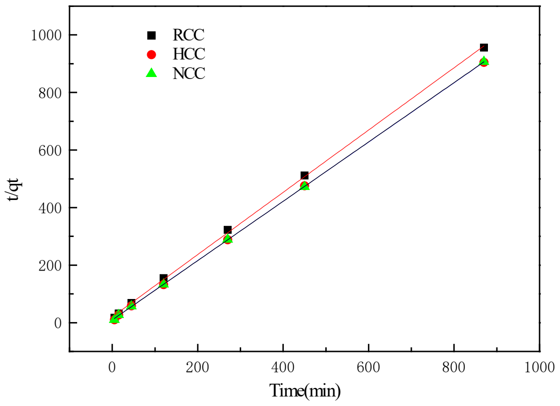


Fig. 8. Fitting curve of quasi-second order kinetic model for quinoline adsorption on raw and modified coking coal.

3.8. Thermodynamics study

Quinoline adsorption isotherms on raw and modified coking coal with different temperature are shown in Fig. 9.

As seen from Fig. 9, quinoline equilibrium adsorption capacity on raw and modified coking coal increase with temperature and quinoline equilibrium concentration in the solution, equilibrium adsorption concentration value is decreased with the increase of temperature. The removal rates of quinoline increase with the increase of temperature, it indicates that high temperature is good for adsorption process.

Langmuir, Freundlich and R-P isotherm equations are used for fitting the adsorption of solid-liquid systems in this paper, and the fitting constants and correlation coefficient values are shown in Table 5.

The correlation coefficient R^2 of the thermodynamic parameters are shown in Table 5, it can be seen that the correlation coefficient R^2 of R-P model are 0.996, 0.997 and 0.992, respectively. The adsorption process can be approximated as Freundlich equation model after calculation $|\alpha| C_{eq}^{\beta} > 1$. It is concluded that quinoline adsorption on raw and modified coking coal is easy to happen because the values of $1/n$ is in the range of 0.1 to 1.0.

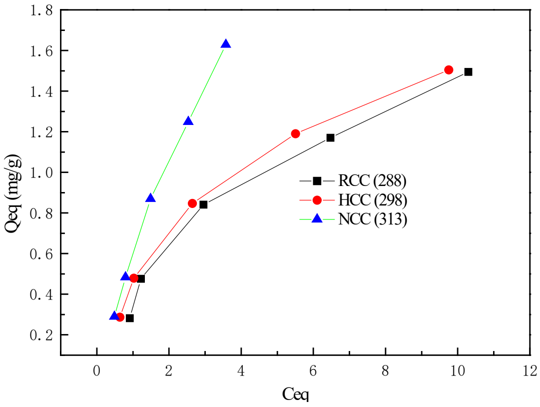
3.9. Calculation of thermodynamic parameters

The plot of ln K_{Fr} vs. 1000/T for quinoline adsorption on raw and modified coking coal is shown in Fig. 10.

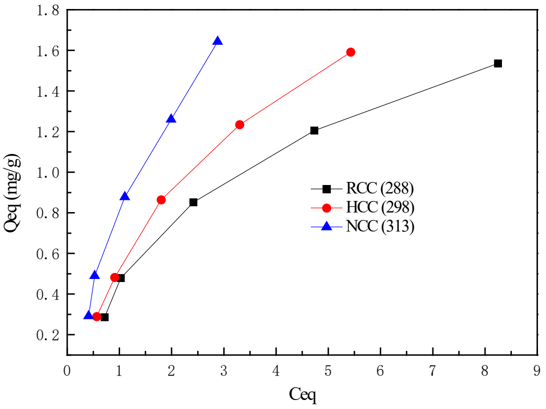
$\Delta H°$ and $\Delta S°$ can be obtained according to the slope and intercept of the curve in Fig. 10. The thermodynamic function value of the quinoline adsorption on raw the modified coking coal are calculated according to Eq. (8). The results are shown in Table 6.

Table 4
Fitting constants and correlation coefficient values of quasi-first order and quasi-second order kinetic models

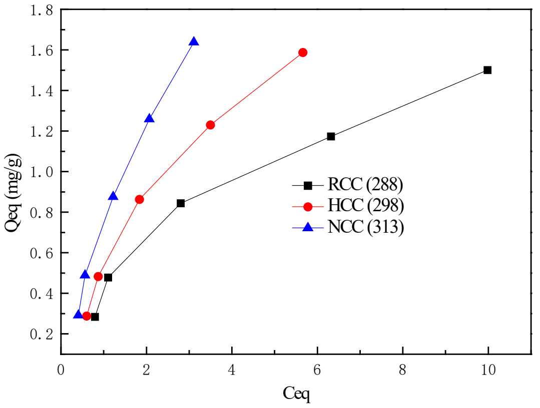
T/K	Adsorbent	$q_{e(exp)}$/mg·g^{-1}	Quasi-first order kinetics			Quasi-second order kinetics		
			$K_1 10^2$ /min^{-1}	$q_{e(calc)}$/mg·g^{-1}	R^2	$K_2 10^2$ /min^{-1}	$q_{e(calc)}$/mg·g^{-1}	R^2
288	RCC	0.90	0.57	0.46	0.8914	3.60	0.92	0.9995
	HCC	0.94	0.83	0.42	0.8963	5.92	0.95	0.9999
	NCC	0.94	0.52	0.46	0.8184	4.46	0.95	0.9996
298	RCC	0.91	0.63	0.42	0.9155	5.79	0.92	0.9996
	HCC	0.96	0.77	0.31	0.8345	10.74	0.97	0.9999
	NCC	0.96	0.91	0.33	0.9248	11.43	0.97	0.9999
313	RCC	0.92	0.72	0.30	0.8914	10.77	0.93	0.9999
	HCC	0.98	0.82	0.26	0.8963	13.80	0.98	0.9999
	NCC	0.97	0.83	0.25	0.8184	15.14	0.98	0.9999



(a) Adsorbate, quinoline. Adsorbent, RCC



(b) Adsorbate, quinoline. Adsorbent, HCC



(c) Adsorbate, quinoline. Adsorbent, NCC

Fig. 9. Adsorption of quinoline isotherms.

It can be seen from Table 6, ΔG° are negative at three different temperatures. It indicates the quinoline adsorption on both raw and modified coking coal are spontaneous process. ΔG° had decreased as the increase of temperature, and the degree of spontaneousness is increased, that temperature increase is good for the adsorption process. ΔH° are positive at three different temperatures, it indicates that

Table 5
Fitting constants and correlation coefficients in isothermal adsorption model

Name	T/K	Langmuir isothermal adsorption equation			
		K_L/L·mg^{-1}	q_m/mg·g^{-1}		R^2
RCC	298	0.22	2.20		0.9644
HCC		0.18	3.29		0.9610
NCC		0.17	3.29		0.8988
Name	T/K	Freundlich isothermal adsorption equation			
		K_{Fr}/mg·mg^{-1} (mg·L^{-1})	1/n		R^2
RCC	298	0.38	0.67		0.9401
HCC		0.48	0.80		0.9794
NCC		0.45	0.80		0.9657
Name	T/K	R-P model			
		K_R/L·g^{-1}	α/L·mg^{-1}	β	R^2
RCC	298	0.65	0.45	0.86	0.9964
HCC		0.59	0.13	1.22	0.9973
NCC		0.61	0.18	1.10	0.9927

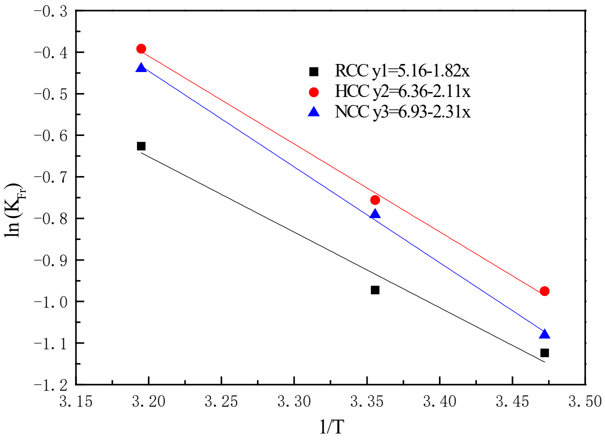


Fig. 10. Plot of ln k_{Fr} vs. 1000/T for quinoline adsorption onto raw and modified coking coal.

Table 6
Thermodynamic function values ln K_{Fr}, ΔH°, ΔS° and ΔG°

Adsorbent	T(K)	ln K_{Fr}	ΔH°/ KJ·mol^{-1}	ΔS°/ J·mol^{-1}·K^{-1}	ΔG°/ KJ·mol^{-1}
RCC	288	−1.12	15.10	53.71	−0.37
	298	−0.97			−0.91
	313	−0.63			−1.71
HCC	288	−0.98	17.58	63.66	−0.75
	298	−0.76			−1.39
	313	−0.39			−2.35
NCC	288	−1.08	19.17	68.44	−0.54
	298	−0.79			−1.23
	313	−0.44			−2.25

quinoline adsorption on raw and modified coking coal is an endothermic process, and high temperature is good for the adsorption process. The adsorption enthalpy change $\Delta H°<20$ KJ·mol^{-1}, it shows that the adsorption process is mainly physical adsorption [25]. Quinoline adsorption on coking coal is mainly controlled by van der waals force, and the adsorption reaction is a process of entropy increase as $\Delta S° > 0$, the system have a certain degree of turbulence with the disorder of solid-liquid interface increased.

4.Conclusion

The equilibrium time for quinoline adsorption on raw and modified coking coal is 2 h, the equilibrium adsorption capacity of three adsorbents are increased as the increase of temperature. The optimum adsorbents dosage is 50 mg·L^{-1}, and the optimum pH is pH = 7. The values of specific surface area for RCC, HCC and NCC are 2.998, 3.169 and 3.042 m^2·g^{-1}, respectively. The specific surface area of coking coal is increased, the pore volume and the pore diameter become smaller after HCl and NaOH modification. Quinoline adsorption onto raw and modified coking coal obeys the Quasi-second order kinetics rate model and the Freundlich isotherm adsorption model. Compared with raw coking coal (91.00%), HCl and NaOH modified coking coal can make the quinoline removal rates increased about 5%, and the adsorption capacities of HCC (96.17%) is better than NCC (95.94%). The quinoline adsorption process is a process of physical adsorption, endothermic, spontaneous, and entropy increased.

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