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REMOVAL OF QUINOLINE FROM AQUEOUS SOLUTIONS BY LIGNITE, COKING COAL AND ANTHRACITE. ADSORPTION ISOTHERMS AND THERMODYNAMICS

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Abstract: Based on the concept of circular economy, a novel method of industrial organic wastewater treatment by using adsorption on coal is introduced. Coal is used to adsorb organic pollutants from coking wastewaters. After adsorption, the coal would be used for its original purpose, its value is not reduced and the pollutant is thus recycled. Through systemic circulation of coking wastewater zero emissions can be achieved. Lignite, coking coal and anthracite were used as adsorbents in batch experiments. The quinoline removal efficiency of coal adsorption was investigated. The coking coal and anthracite exhibited properties well-suited for adsorption onto both adsorbents. The experimental data were fitted to Langmuir and Freundlich isotherms as well as Temkin, Redlich–Peterson (R-P) and Dubinin-Radushkevich (D-R) models. Both Freundlich Isotherm and D-R model provided reasonable models of the adsorption process. The thermodynamic parameters of quinoline adsorption on coking coal were calculated. The thermodynamic parameters indicated that the adsorption process is exothermic and is a physical adsorption. The $\Delta S°$ value indicated that the adsorption entropy decreased because the adsorbate molecule was under restrictions after it adsorption on the coal surface. The coal adsorption method for removing refractory organic pollutants is a great hope for achieving zero emission waste water for a coking plant.

Keywords: *quinoline adsorption; coking coal; adsorption isotherms; thermodynamics*

Introduction

Coking wastewater pollution is a serious problem all over the word. Coking wastewater is generated from coal coking, coal gas purification and by-product recovery processes of coking (Fang et al, 2012). It usually contains complex inorganic and organic pollutants, such as phenolic compounds, pyridine, indol, quinoline, ammonium, sulfate, cyanide, thiocyanate, polynuclear aromatic hydrocarbons and polycyclic

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nitrogen-containing acyclic compounds, most of which are refractory, toxic, mutagenic and carcinogenic (Ghose, 2002; Chao et al., 2006; Lai et al., 2009). The adsorption method (Aksu and Yener, 2001; Badmus and Audu, 2009) is widely used in the treatment and recovery process of organic wastewater including coking wastewater and oily wastewater. It is very effective for removing water particulate matter and refractory organics. This method has advantages and disadvantages (Lee and Park, 1998; Magnus et al., 2000; Mall and Srivastava, 2006). How to enhance advantages and avoid disadvantages was important in this research. Coal is a complex porous medium and natural adsorbent. After adsorption, the coal would be used in its original purpose and its value was not reduced.

This research investigates the potential of adsorption for removing quinoline in simulation coking wastewater by three kinds of coals. The adsorbent properties, adsorption efficiency, adsorption isotherms and thermodynamics were investigated.

Methods and materials

Adsorbate

Quinoline with purity greater than 99.5% was purchased from Shanghai Chemical Company and used as a single component (adsorbate) in this study. According to the GC-MS analysis of coking wastewater of the Linhuan coking plant, the major organic components of coking wastewater are phenol, quinoline, pyridine and indol (Fu, 2004). The quinoline concentration of the simulated coking waste water was about 25 $mg\cdot dm^{-3}$.

Adsorbents

In this research, the three adsorbents are lignite, coking coal and anthracite. Lignite was obtained from the Shenli coal mine of Shenhua Group Co., Ltd. while coking coal and anthracite were obtained from the Linhuan coal preparation plant and Chengjiao coal preparation plant of Henan Coal Chemical Industry Group Co., Ltd, respectively. Coal was crushed, ground, sieved through a 74 μm sifter, and dried at 120 °C in an oven for 2 h before to use. After drying, the adsorbent was stored in sealed glass containers.

The surface area of adsorbents was measured by surface area analyzer (BELSORP-max, BEL-JAPAN, INC). The crystalline phases present in three kinds of coal were determined via X-ray diffractometry (S8 TIGER, BRUKER AXS, German). Three kinds of coal were analyzed by the Scanning electron microscopy (SEM) (Zeiss Ultra Plus Model, Germany) to image the surface characteristic.

Batch adsorption studies

The adsorption isotherms of quinoline on three kinds of coal were investigated in batch sorption equilibrium experiments. For each experiment, fresh quinoline solutions were prepared by dissolving the quinoline material in deionized water and measuring the concentration by UV/VIS spectroscopy (UV-4802S, Shanghai) (Lin and Dence, 1992). The adsorbents were added to the quinoline solutions in 200 cm^3 sample conical flasks mounted on a shaker. The flasks were agitated at a constant speed of 200 rpm for different timings at constant temperature. Samples were collected from the flasks at predetermined time intervals for analyzing the residual concentration in the solution. The adsorption capacity of coal was calculated using the expression,

$$Q_\mathrm{t} = \frac{(C_0 - C_\mathrm{t})\mathrm{V}}{M}. \tag{1}$$

The removal efficiency of quinoline was calculated using the expression,

$$E = \frac{C_0 - C_\mathrm{t}}{C_0} \tag{2}$$

where, Q_t ($mg \cdot g^{-1}$) is the quinoline removed at time t by a unit mass of the adsorbent, C_0 ($mg \cdot dm^{-3}$) is the initial quinoline concentration, C_t ($mg \cdot dm^{-3}$) is the quinoline concentration at time t, and M (g) is coal consumption. V (cm^{-3}) is the quinoline solutions volume. The adsorption experiments, which were conducted at various time intervals and temperatures (283 K, 298 K and 313 K) to determine when the adsorption equilibrium was reached and the maximum removal of naphthalene was attained. After the equilibrium contact time, the samples were filtered and the equilibrium concentrations ascertained by spectrophotometer at the respective standard curve equations, which is 278 nm for quinoline.

Adsorption models

Both the capacity of the adsorbent and driving force of adsorption is useful for the design of a sorption treatment plant (Ho and McKay, 1999; Zhang et al., 2010). Isotherm models describe the equilibrium relationship of the adsorbate in the solid and liquid phases of the system.

The Langmuir isotherm

The Langmuir isotherm (Langmuir, 1916; Ruthven, 1984) is most widely applied sorption isotherm in the pollutant adsorption field. The Langmuir isotherm expression is given as:

$$Q_\mathrm{eq} = \frac{q_\mathrm{m} K_\mathrm{L} C_\mathrm{eq}}{1 + K_\mathrm{L} C_\mathrm{eq}} \tag{3}$$

The linear form of the Langmuir isotherm is:

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

where, Q_eq ($mg \cdot g^{-1}$) is the equilibrium amount of adsorbate on the solid surface; C_eq ($mg \cdot dm^{-3}$) the equilibrium amount of adsorbate in solution; K_L($dm^3 \cdot mg^{-1}$) is related to the energy of adsorption and the affinity between adsorbate and adsorbent. q_m (mg·g^{-1}) is monolayer adsorption capacity (Andersson et al., 2011).

The Freundlich isotherm

The Freundlich isotherm expression is given as (Cicek et al., 2007; Sahu et al 2008):

$$Q_{\mathrm{eq}} = K_{\mathrm{Fr}} {C_{\mathrm{eq}}}^{1/n}. \tag{5}$$

The linear form of the Freundlich isotherm is:

$$\ln Q_{\mathrm{eq}} = \ln K_{\mathrm{Fr}} + \left(\frac{1}{\mathrm{n}}\right) \ln C_{\mathrm{eq}} \tag{6}$$

where, K_{Fr} represents the adsorption capacity. $1/n$ is adsorption index, $1/n > 2$ indicates an unfavorable adsorption process. $0.1 < 1/n < 0.5$ indicates a favorable adsorption process.

The Temkin model

The Temkin model expression is given as (Basar 2006; Gunay et al., 2007):

$$Q_{\mathrm{eq}} = \left(\frac{RT}{b_{\mathrm{T}}}\right) \ln(K_{\mathrm{T}} C_{\mathrm{eq}}) \cdot \tag{7}$$

The linear form of the Temkin model is:

$$Q_{eq} = \left(\frac{RT}{b_T}\right) lnC_{eq} + \frac{RTlnK_t}{b_T} \cdot \tag{8}$$

The K_t expression is

$$K_{\mathrm{T}} = \exp(\frac{\text{intercept}}{\text{slope}}) \tag{9}$$

where K_{T} (dm^3·g^{-1}) is the equilibrium binding constant and b_{T} (J·mol^{-1}) is related to the heat of adsorption.

The Redlich–Peterson model

The Redlich–Peterson (R-P) model expression is given as (Redlich and Peterson, 1959; Jossens et al., 1978) :

$$Q_{\mathrm{eq}} = \frac{K_{\mathrm{R}} C_{\mathrm{eq}}}{1+\alpha {C_{\mathrm{eq}}}^{\beta}} \cdot \tag{10}$$

The linear form of the Redlich-Peterson model is:

$$\ln \left| \frac{K_{\mathrm{R}} C_{\mathrm{eq}}}{Q_{\mathrm{eq}}} - 1 \right| = \beta \ln C_{\mathrm{eq}} + \ln|\alpha| \tag{11}$$

where K_R(dm^3·g^{-1}) is constant that is varied to maximize the linear correlation coefficient R^2, α is a constant and β is a constant in the range of 0~1.

The Dubinin-Radushkevich model

The Dubinin-Radushkevich (D-R) model expression is given as (Jossens et al., 1978):

$$Q_{\mathrm{eq}} = Q_{\mathrm{m}} \exp(-K_{\mathrm{DR}}\varepsilon^2) \cdot \tag{12}$$

The linear form of the D-R model is:

$$\ln Q_{\mathrm{eq}} = -K_{\mathrm{DR}}\varepsilon^2 + \ln Q_{\mathrm{m}} \tag{13}$$

$$\varepsilon = RT\ln(1 + \frac{1}{C_{\mathrm{eq}}}) \tag{14}$$

where K_{DR} (mol·kJ^{-1})^2 is related to the energy of sorption E; T (K) is absolute temperature; Q_{m}(mg·g^{-1}) is the largest adsorbed amount at saturation.

The mean energy of sorption E expression is:

$$E = {}^{1}\!/_{(2K_{\mathrm{DR}})^{1/2}} \cdot \tag{15}$$

Adsorption thermodynamics

The transformation of adsorbate from solution to the surface of adsorbent affects the thermodynamic properties of the system (Kaya et al., 2013). The free energy change of the adsorption process, $\Delta G°$, can be calculated by:

$$\Delta G° = -RT\ln k_0 \tag{16}$$

The relationship between the standard Gibbs free energy of adsorption ΔG° (kJ·mol^{-1}), the standard enthalpy change $\Delta H°$ (kJ·mol^{-1}) and the standard entropy change $\Delta S°$ (J·mol^{-1}·K^{-1}) is given as:

$$\Delta G° = \Delta H° - T\Delta S°. \tag{17}$$

Combining Eqs. 16 and 17 yields:

$$ln k_0 = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{18}$$

where R (8.314 J·K^{-1}·mol^{-1}) is ideal gas constant, T (K) is absolute temperature and K_0 is partition coefficient.

Different adsorption models have different K_0 values, so the $\Delta G°$ value is also different. lnK_0 can be obtained from the intercept of the straight line plots of $\ln(\frac{Q_{\mathrm{eq}}}{C_{\mathrm{eq}}})$ versus Q_{eq} (Khan and Singh, 1987). This method (Shu and Jia, 2005; Chandra et al.,

2007) was used to calculate the $\Delta G°$ value in this research. The straight line plots of $\ln K_0$ against $1/T$ were tested to obtain $\Delta H°$ and $\Delta S°$, while $\Delta G°$ was obtained from Eq. 17.

Results and discussions

Chemical composition of lignite, coking coal and anthracite

The XRD of lignite, coking coal and anthracite are shown in Fig. 1–3.

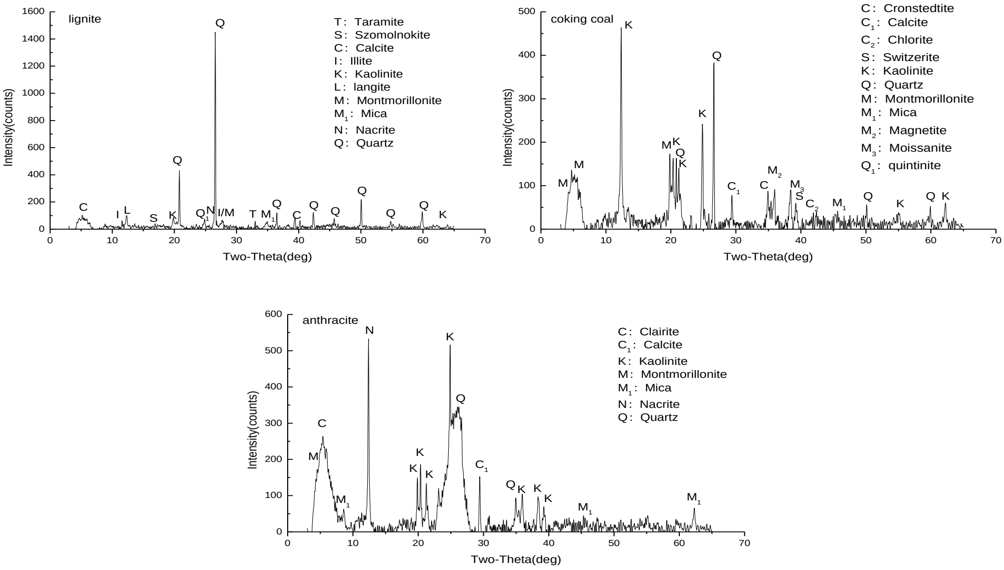

Fig. 1. X-ray Diffraction Patterns of lignite, coking coal and anthracite

Basing on the analysis, the three kinds of coal contain gangue minerals and have similar mineral compositions. The anthracite has lower content of gangue minerals than others. Based on the analysis of mineral composition content, the coal composition plays a leading role in the adsorption test. The clay minerals content also has a certain adsorption effect, but the effect is small because the content is small. The gangue minerals have a little influence on coal adsorption.

SEM analysis of adsorbents

The SEM photographs obtained for lignite, coking coal and anthracite are illustrated in Fig. 2. The three kinds of coal all have rough surfaces and pores, and they are similar. Thus, all of them may be used as an adsorbent.

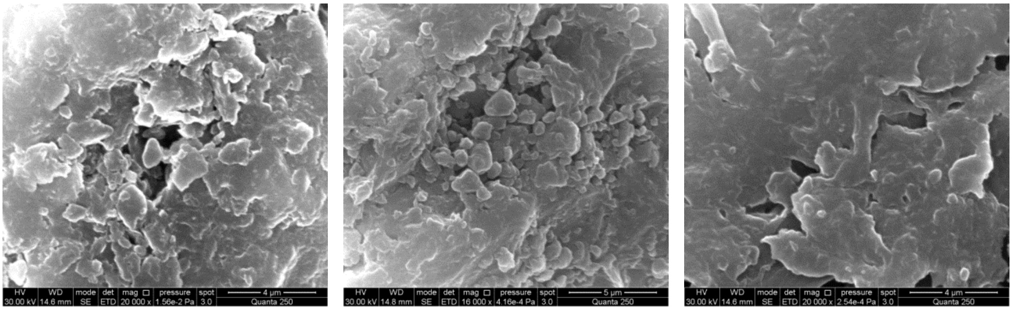

Fig. 2. SEM images of lignite (left), coking coal (middle) and anthracite (right)

The specific surface area

As shown in Table 1, the specific surface area of the lignite, coking coal and anthracite were 6.0876 $m^2 \cdot g^{-1}$, 5.7864 $m^2 \cdot g^{-1}$ and 6.1479 $m^2 \cdot g^{-1}$, respectively.

Table 1. Special surface area of lignite, coking coal and anthracite

Method	Specific surface area ($m^2 \cdot g^{-1}$)		
	Lignite	Coking coal	Anthracite
BET method	6.0876	5.7864	6.1479

The effect of adsorption time on quinoline removal efficiencies

Experimental conditions of the adsorption tests were: solution volume 100 cm^3, quinoline concentration of solution 25 $mg \cdot dm^{-3}$, coal consumption 2.0 g, adsorption temperature 25 ℃. The effect of coal consumption on quinoline removal efficiencies is shown in Fig. 3.

As shown in Fig. 3, both the organic removal efficiency and adsorption capacity increased with the increasing adsorption time. At the beginning, the adsorption rate of the organic removal efficiency increased rapidly, and tended to be constant after 60 min. The shortest time for reaching adsorption equilibrium was in the case of anthracite, followed by lignite, and finally coking coal. The optimum adsorption time determined by test was 30~60 min.

The coal surface did not adsorb the organic material when the coal was just at the beginning of contact with the organic in the aqueous phase, probably because it was not fully wetted. Initially there were many sorptive sites without an adsorbant on coal surface, so the adsorption rate was higher than the desorption rate. The organic removal efficiency increased with the increasing time. The adsorption rate equalled the desorption rate when the adsorption point and the functional group were almost occupied by the organic molecule after 60 min. So, the organic removal efficiency tends to be constant after that.

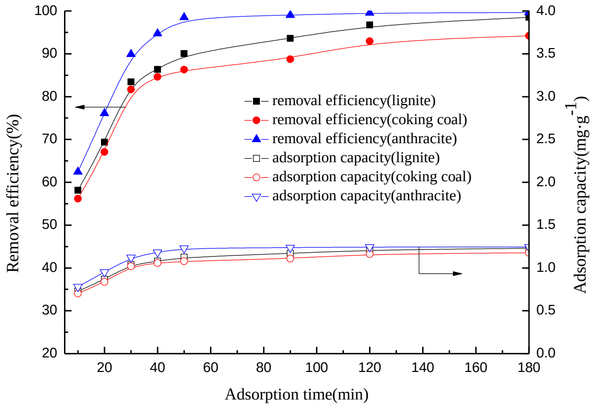

Fig. 3. The effect of adsorption time on quinolone removal efficiency

Isothermal experimental results and equilibrium modeling

Experiments were carried out for a solution volume of 100 cm^3, with a quinoline concentration, coal consumption 2.0 g, adsorption temperature 25 ℃ and adsorption time 4 h. The results of quinoline adsorption in isothermal experiments are shown in Table 2.

Table 2. The results of quinoline adsorption isothermal experiment

Absorbent	Initial concentration / mg·dm^{-3}	5	10	20	30	50
Lignite	Equilibrium concentration / mg·dm^{-3}	0.06	0.28	1.09	1.95	4.40
	Removal efficiency / %	98.71	97.21	94.53	93.49	91.20
	Equilibrium absorption capacity / mg·g^{-1}	0.25	0.49	0.95	1.40	2.28
Coking coal	Equilibrium concentration / mg·dm^{-3}	0.11	0.41	1.27	2.25	4.66
	Removal efficiency / %	97.85	95.92	93.67	92.49	90.69
	Equilibrium absorption capacity / mg·g^{-1}	0.24	0.48	0.94	1.39	2.27
Anthracite	Equilibrium concentration / mg dm^{-3}	0.06	0.19	0.88	1.70	3.37
	Removal efficiency / %	98.71	98.07	95.60	94.35	93.26
	Equilibrium absorption capacity / mg·g^{-1}	0.25	0.49	0.96	1.42	2.33

The isotherm constants were obtained by using a linear regression analysis of the quinoline adsorption isotherm. The isotherm constants and the correlation coefficients are shown in Table 3.

The curves of the calculated equilibrium amount of adsorbate on the adsorbent surface (Q_{eq}) versus the amount in solution (C_{eq}) which were used in the various models and the obtained constants are shown in Fig. 4.

Table 3. Constants and correlation coefficients obtained for the Langmuir, Freundlich, Temkin, R-P and D-R isotherm models of quinolone adsorption onto lignite, coking coal and anthracite

Adsorbent	Langmuir Isotherm				Freundlich Isotherm		
	K_L/dm^3·mg^{-1}	q_m/mg·g^{-1}	$R_L{}^a$	R^2	K_{Fr}/mg·g^{-1}(mg·dm^{-3})	1/n	R^2
Lignite	0.5829	2.99	0.03	0.8871	0.95	0.586	0.9949
Coking coal	0.4612	3.09	0.04	0.8282	0.86	0.589	0.9943
Anthracite	0.8535	2.86	0.02	0.8247	1.12	0.544	0.8269
	Redlich –Peterson (R-P) Model				Temkin Model		
	K_R/dm^3·g^{-1}	α/dm^3·mg^{-1}	β	R^2	K_T/dm^3·g^{-1}	b_T/KJ·mol^{-1}	R^2
Lignite	–6.381	–7.875	0.354	0.9986	2.34	4.82	0.87118
Coking coal	–1.220	–2.500	0.220	0.9999	2.22	4.92	0.82048
Anthracite	–1.658	–2.590	0.229	0.9964	2.84	5.19	0.8269
	Dubinin–Radushkevich (D–R) Model						
	K_D/(mol·kJ^{-1})^2		E/ KJ·mol^{-1}	R^2			
Lignite	–0.039		3.60	0.7363			
Coking coal	–0.056		3.00	0.7254			
Anthracite	–0.040		3.52	0.8234			

$R_L{}^a$ is calculated for $C_0 = 50$ mg·dm^{-3}

A comparison of the correlation coefficients in Table 3 showed that the Redlich-Peterson model fits better quinoline adsorption on lignite, coking coal and anthracite than other models and R^2 for the three types of coals are 0.9986, 0.9999 and 0.9964, respectively. The R-P model constants results showed that the $\beta < 1$ and $|\alpha|C_{eq}{}^{\beta} > 1$, so the quinoline adsorption on lignite, coking coal and anthracite fits well the isotherm. The quinoline adsorptions on three coals also fit the Freundlich isotherm. The R_L values from the Langmuir equation were all between 0 and 1, indicating a favorable sorption process. This was supported by the 1/n values less than 1 obtained for the Freundlich model.

The Langmuir values of q_m, signifying adsorption capacity, were 2.99, 3.09 and 2.86 mg·g^{-1} for quinoline adsorption on lignite, coking coal and anthracite, respectively. According to the constant K_{Fr}, the order of rate of adsorption are anthracite ＞ lignite ＞ coking coal. Due to E in the range of 1.0~8.0 kJ·mol^{-1}, the adsorption process seems to be physical (Zhang et al., 2010).

As shown in Fig. 4, the Langmuir, Freundlich, Temkin and R-P models provide better correlations than the D-R model. The Freundlich and R-P model showed the best fit of the experimental data.

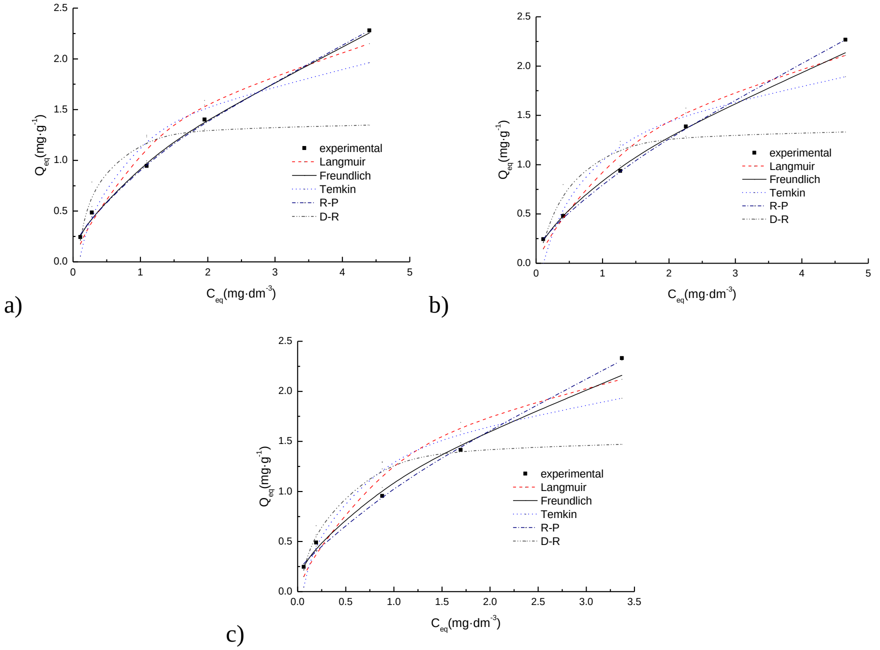

Fig. 4. Equilibrium amount of quinoline adsorbed on the adsorbent surface (Q_{eq}) at increasing equilibrium quinoline concentrations (C_{eq}) expressed by the Langmuir, Freundlich, Temkin, R-P and D-R isotherm models
(a) adsorbent: lignite (b) adsorbent: coking coal (c) adsorbent: anthracite

Thermodynamics

According to experimental data, the relationship graph of $\ln\left(\frac{Q_{\mathrm{eq}}}{C_{\mathrm{eq}}}\right) - Q_{\mathrm{eq}}$ was obtained. It is shown in Fig. 5.

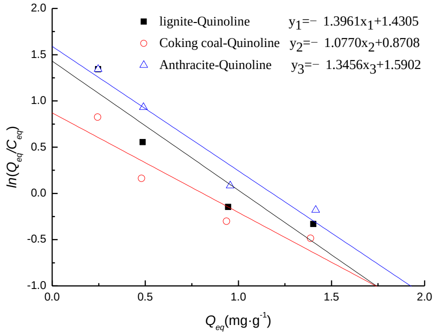

Fig. 5. Plot *of* $\ln(\frac{Q_{eq}}{C_{eq}})$ versus Q_{eq} for quinoline adsorption on lignite, coking coal and anthracite

Different K_0 can affect the calculated value of thermodynamical function (Khan and Singh, 1987). Except the lnK_0 which was calculated by the line of $\ln\left(\frac{Q_{eq}}{C_{eq}}\right) - Q_{\mathrm{eq}}$, the constant K_{L} of Langmuir isotherm and K_{Fr} of Freundlich isotherm also can be used to calculate the $\Delta G°$ value.

Table 4. Values of lnK_0 and $\Delta G°$ of adsorption on different coals

Adsorbent	T / K	$\ln\left(\frac{Q_{\mathrm{eq}}}{C_{\mathrm{eq}}}\right) - Q_{\mathrm{eq}}$ line		Langmuir isotherm		Freundlich isotherm	
		lnK_0	$\Delta G°$ / kJ·mol^{-1}	lnK_L	$\Delta G°$ / kJ·mol^{-1}	lnK_{Fr}	$\Delta G°$ / kJ·mol^{-1}
Lignite	298.15	1.4305	–2.35	–0.54	1.34	–0.06	0.14
Coking coal	298.15	0.8708	–1.43	–0.77	1.92	–0.15	0.37
Anthracite	298.15	1.5902	–2.62	–0.16	0.39	0.11	–0.27

As shown in the Table 4, the process of quinoline adsorption on three coals is spontaneous and physical because the $\Delta G°$ values were below zero, and their absolute values are in the range of 0~20 kJ·mol^{-1} (Sahu et al., 2008). For comparison, K_L and K_{Fr}, which were obtained respectively from the Langmuir model and Freundlich models, can be used to calculate $\Delta G°$ values. The $\Delta G°$ values of quinoline adsorption on lignite, coking coal and anthracite which were calculated using the equilibrium constants of the Langmuir expression where K_{L} were 1.34 kJ·mol^{-1}, 1.29 kJ·mol^{-1} and 0.39 kJ·mol^{-1}, respectively. It can be seen that the two $\Delta G°$ values, which were obtained using the equilibrium constants of the Langmuir and Freundlich expressions, were different from those obtained by the straight line plots of $\ln(\frac{Q_{\mathrm{eq}}}{C_{\mathrm{eq}}})$ versus Q_{eq}. Consequently, the $\Delta G°$ values need to be obtained by the same procedure when

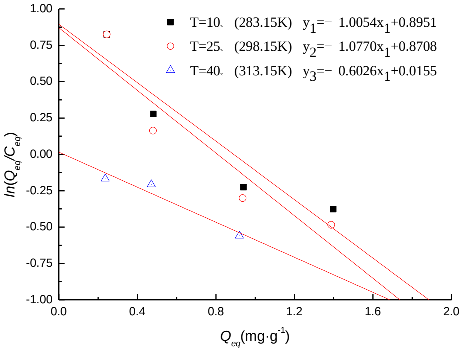

Fig. 6. Plot of $ln(\frac{Q_{eq}}{C_{eq}})$ versus Q_{eq} for quinoline adsorption on coking coal at different temperatures

comparing the results of various sorption tests. The $\Delta H°$ and $\Delta S°$ values of the process of quinoline adsorption on coking coal were calculated. Using the experimental data, the relationship lines of $ln\left(\frac{Q_{eq}}{C_{eq}}\right) - Q_{\mathrm{eq}}$ for different temperatures were obtained. It is shown in Fig. 6. The $\ln K_0$ values were used to plot of $\ln K_0$ versus $1000/T$ as is shown in Fig. 7.

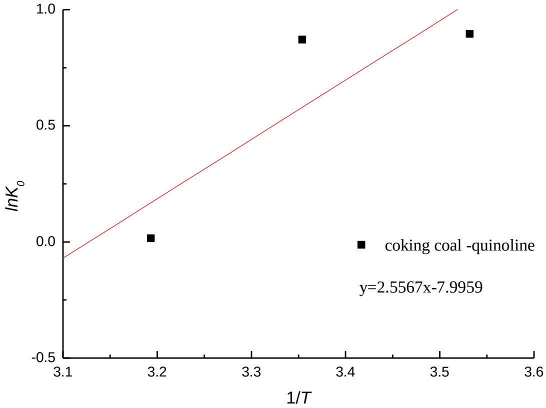

Fig. 7. Plot of lnK_0 versus $1000/T$ for quinoline adsorption on coking coal

The $\Delta H°$ and $\Delta S°$, reflecting the thermodynamics of the system for quinoline adsorption on coking coal, were determined from the slope and intercept of line in Fig. 6, respectively. The obtained values are presented in Table 5.

Table 5. Obtained values of $\ln k_0$, $\Delta H°$, $\Delta S°$ and $\Delta G°$ for quinoline adsorption on coking coal

T (K)	$\ln k_0$	$\Delta H°$/kJ·mol^{-1}	$\Delta S°$/J·mol^{-1}·K^{-1}	$\Delta G°$/kJ·mol^{-1}
283.15	0.8352	–21.27	–66.48	–1.47
298.15	0.8708			–1.43
333.15	0.0155			–0.03

As shown in Table 4, $\Delta H°= –21.27$ kJ·mol^{-1} < 0 illustrates that the adsorption process is an exothermic reaction and also points to physical adsorption. Thus, low temperature is better for this adsorption process. $\Delta S°= –66.48$ J·mol^{-1}·K^{-1} < 0 indicates that the adsorption entropy decreased because the adsorbate molecule was under restrictions after it was adsorbed on the coal surface. Adsorption process is not a separate process Even if the system entropy decreases, the total entropy, which includes the system and surrounding environment, may increase. The maximum temperature of the spontaneous adsorption process was 319.75 K, which was obtained by Eq.18 and the values from Table 5.

Conclusions

Fitting experimental data to various equilibrium models showed that the adsorption processes follow the Freundlich isotherm. The main oxygen-containing functional groups on the three kinds of coal surface are acidic. The adsorption capacity is proportional to special surface area of coal. The rate of quinoline adsorption on anthracite is largest. Both the organic removal efficiency and adsorption capacity increased, and then tend to be constant with the increase of adsorption time. The optimum adsorption time determined by test is 30~60 min. According to the result of thermodynamics, the negative value of change in Gibbs free energy ($\Delta G°$) indicates that adsorption of quinoline on coal is spontaneous, and that the $\Delta H°$ of quinoline adsorption on coking coal was 21.27 $\text{kJ}\cdot\text{mol}^{-1}$. Thus, the adsorption is exothermic and physical. The adsorption entropy decreased because the adsorbate molecule was under restrictions after it was adsorbed on the coal surface.

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