Effects and mechanistic aspects of absorbing organic compounds by coking coal

Kejia Ning, Junfeng Wang, Hongxiang Xu, Xianfeng Sun, Gen Huang, Guowei Liu and Lingmei Zhou

ABSTRACT

Coal is a porous medium and natural absorbent. It can be used for its original purpose after adsorbing organic compounds, its value does not reduce and the pollutants are recycled, and then through systemic circulation of coking wastewater zero emissions can be achieved. Thus, a novel method of industrial organic wastewater treatment using adsorption on coal is introduced. Coking coal was used as an adsorbent in batch adsorption experiments. The quinoline, indole, pyridine and phenol removal efficiencies of coal adsorption were investigated. In addition, several operating parameters which impact removal efficiency such as coking coal consumption, oscillation contact time, initial concentration and pH value were also investigated. The coking coal exhibited properties well-suited for organics’ adsorption. The experimental data were fitted to Langmuir and Freundlich isotherms as well as Temkin and Redlich–Peterson (R-P) models. The Freundlich isotherm model provided reasonable models of the adsorption process. Furthermore, the purification mechanism of organic compounds’ adsorption on coking coal was analysed.

Key words | adsorption, coking coal, mechanistic aspects, pH value, purification mechanism

INTRODUCTION

Coking wastewater pollution is a serious problem and difficult to treat by using traditional methods, all over the world. Coking wastewater is generated from coal coking, coal gas purification and by-product recovery processes of coking (Tong et al. 2016). It usually contains high concentrations of ammonia, sulfide, phenol, quinoline, pyridine indole and other organic compounds, most of which are refractory, toxic, mutagenic and carcinogenic (Ghose 2002; Chao et al. 2006; Lai et al. 2009; Belhachemi & Addoun 2012).

The adsorption method (Aksu & Yener 2001; Badmus & Audu 2009) is widely used in the treatment and recovery process of organic wastewater, including coking wastewater, oily wastewater and other wastewater. The adsorption method is very effective for removing water particulate matter and refractory organics. However, this method also has some disadvantages (Lee & Park 1998; Magnus et al. 2000; Mall & Srivastava 2006), the main disadvantage being that the adsorbate is always expensive. Thus, it is important to find a cheap adsorbent for the treatment of wastewater. Coal with its complex porous medium can be used as a natural adsorbent in water treatment. After adsorption, the coal can also be used for its original purpose without its value being reduced. Thus, coal as an adsorbent has been researched in some studies. Pyridine (gas) sorption isotherms for two coals give straight-line curves with non-zero intercepts (Green & Selby 1994). The reagent molecules and the functional groups on the pore surface and also the molecular orientation of the reagent to the low rank coal surface play important roles in the adsorption processes (Aktas & Woodburn 1994). The adsorption of methyl orange onto ultrafine coal powder had a good effect, and the process fits the Lagergren first-order kinetic model and the pseudo second-order kinetic model, and the adsorption is a spontaneous and exothermic process (Liu et al. 2009). However, there has been little research on organic compounds from coking wastewater adsorption on raw coal.
This research investigates the potential of adsorption for removing organic compounds in simulation coking wastewater by coking coal. The removal efficiency, operating parameters and purification mechanism were investigated.

MATERIALS AND METHODS

Adsorbates

Phenol, quinoline, pyridine and indole with purity greater than 99.5% were purchased from Shanghai Chemical Company and used as the single components (adsorbates) in this paper. According to the gas chromatography mass spectrometry (GC-MS) analysis of coking wastewater of the Linhuan coking plant, the major organic components of coking wastewater are phenol, quinoline, pyridine and indole (Caravjal-Bernal et al. 2013). The adsorbates’ concentration of the simulated coking wastewater were 25 mg·dm$^{-3}$.

Adsorbent

In this research, the adsorbent is coking coal. The coking coal was obtained from Chengjiao coal preparation plant of Henan Coal Chemical Industry Group Co., Ltd. The coal was crushed, ground, sieved through a 74 μm sifter, and dried at 100 °C in an oven for 2 h before use. After drying, the adsorbent was stored in sealed glass containers.

The constituent of coking coal was determined via X-ray fluorescence (XRF), chemical composition, scanning electron microscopy (SEM) and the special surface area of coking coal, previously published (Xu et al. 2016a).

Batch adsorption tests

The adsorption capacities of adsorbates on coking coal were investigated in batch adsorption experiments. The adsorbates were phenol, quinoline, pyridine and indole. For each experiment, different concentrations of adsorbate solution were prepared by dissolving the adsorbate material in deionized water; the concentrations were measured by UV/VIS spectroscopy (UV-4802S, Shanghai) (Lin & Dence 1992). Then, 100 cm$^3$ of each adsorbate solution was placed in a conical flask of 200 cm$^3$. Coal of different weights was respectively added to the adsorbate solutions in the conical flasks, which were then put into a thermostatic oscillator and stirred with a constant speed of 200 rpm for different times at a constant temperature. After that, samples were collected from the flasks at predetermined time intervals to analyse the residual concentration in the solution. The adsorption capacity of coal was calculated using the expression:

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

(1)

The removal efficiency of quinoline was calculated using the expression:

\[
E = \frac{C_0 - C_t}{C_0} \times 100\%
\]

(2)

where, \(Q_t\) (mg·g$^{-1}$) is the quinoline adsorption of per gram adsorbent, \(C_0\) (mg·dm$^{-3}$) is the initial quinoline concentration, \(C_t\) (mg·dm$^{-3}$) is the quinoline concentration at time \(t\), and \(M\) (g) is coal consumption. \(V\) (cm$^3$) is the quinoline solution volume.

The adsorption experiments were conducted at various time intervals to determine when adsorption equilibrium was reached and the maximum removal of organic compound was attained. After the equilibrium contact time, the samples were obtained after filtration, and then the equilibrium concentrations were measured by spectrophotometer at different wavelengths: 278 nm, 256 nm and 271 nm for quinoline, pyridine and indole, respectively. The volatile phenolic compounds of wastewater were measured by using the 4-AAP spectrophotometric method (China Environmental Science Press 2009).

The point zero of charge (PZC) and isoelectrical point (IEP) of coking coal

The determination of the pH$_{pzc}$ of the coking coal was carried out as follows (Newcombe et al. 1995; Menénéndez et al. 1995; Faria et al. 2004): 50 cm$^3$ of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask. The pH (pH$_{initial}$) was adjusted to a value between 4 and 12 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then, 0.15 g of coking coal sample was added to each Erlenmeyer flask, and then the final pH (pH$_{final}$) measured after agitation for 48 h at room temperature (around 25 °C), so \(\Delta pH = pH_{final} - pH_{initial}\). According to the relationship between \(\Delta pH\) and \(pH_{final}\) of coking coal, the pH$_{pzc}$ which is the point pH$_{initial}$ when the \(\Delta pH = 0\), was obtained.

The IEP values were determined from electrophoretic mobility measurements using a Zetasizer nano apparatus (Malvern, UK), using 0.001 M KNO$_3$ as the supporting (indifferent) electrolyte (Menénéndez et al. 1995).
RESULTS AND DISCUSSION

Effect of coking coal consumption

Experiment conditions were as follows: The adsorbate concentration of the simulated coking wastewater was 25 mg·dm\(^{-3}\), the contact time was 60 min, the adsorption shaking was done at a stable room temperature (about 25 °C), and pH values were not adjusted. The removal efficiencies and adsorption capacities of four adsorbates’ adsorption on coking coal are shown in Figure 1.

As shown in Figure 1, with the increase of coking coal consumption, the four adsorbents’ removal efficiencies increased and adsorption capacities decreased. In the case of the same coking coal consumption of the adsorption experiment, the removal rate of the four organic adsorbents is in the order: quinoline > indole > pyridine > phenol.

The total surface area of adsorbent increased with the increase of coal consumption, so the total adsorption capacity increased which resulted in improved organic removal efficiency. With the increase of coking coal consumption, the frequency of effective collision between the organic molecular and adsorption site on unit coking coal surface declined, so the unit adsorption capacity also decreased. Due to the total number of effective collisions for adsorption increasing with the increase of coal consumption, the total adsorption capacity improved, thus the organic removal efficiency improved with the increase of coal consumption. The optimum coking coal consumption determined by test was 3.0 g.

Effect of oscillation contact time

Experiment conditions: The adsorbate concentration of the simulated coking wastewater was 25 mg·dm\(^{-3}\), the coking coal consumption was 2.0 g, the adsorption shaking was at stable room temperature (about 25 °C), and pH values were not adjusted. The removal efficiencies and adsorption capacities of the four adsorbates’ adsorption on coking coal are shown in Figure 2.

Adsorption is a process of molecular motion and adhesion onto the solid surface. The process is not finished until the organic molecules in coking wastewater move to the surface and into the internal pores. Therefore, the adsorption time is a key factor in the adsorption because the process takes some time to complete.

As shown in Figure 2, both the organic removal efficiency and adsorption capacity increased with the increase in adsorption time. At the beginning, the adsorption rate of the organic removal efficiency increased rapidly, then increased slowly and tended to be constant after more than 60 min. The shortest time to reach adsorption equilibrium...
was for quinoline and indole, then pyridine adsorption, and phenol adsorption was last. The optimum adsorption time determined by test was 30–50 min.

There are many blank adsorption points on the coal surface when the coal is just starting to contact with the organic compounds in the coking wastewater at that time, and the adsorption rate was much higher than the desorption rate, therefore the adsorption curve slope was large at the beginning. With increasing adsorption time, more and more organic molecules were adsorbed on the coal surface, thus the organic removal efficiency increased. After an oscillation contact time of more than 60 min, the adsorption point and functional group were almost occupied by organic molecules, and the adsorption rate was equal to the desorption rate, and therefore the organic removal efficiency tended to be constant after that time.

**Effect of initial concentration**

The experiment conditions were as follows: the oscillation contact time was 60 min, the coking coal consumption was 0.8 mg coal·(1.0 mg adsorbate)⁻¹, the adsorption shaking was at stable room temperature (about 25 °C), and pH values were not adjusted. The removal efficiencies and adsorption capacities of the four adsorbates’ adsorption on coking coal are shown in Figure 3.

As shown in Figure 3, both the organic removal efficiency and adsorption capacity increased with the initial concentration. At the beginning, the adsorption rate of the organic removal efficiency increased rapidly, then increased slowly and tended to be constant after more than 40 mg·L⁻¹ of initial concentration.

The adsorption power mainly comes from the concentration difference between the concentration of organic matter in the solution and the concentration of organic matter in the coal surface during the process of adsorption. The greater the concentration difference, the higher the adsorption power and the adsorption rate. When the initial organic concentration is low, the probability of the effective collision between organic molecules and the effective adsorption sites on the coking coal surface is small, so the organic removal efficiency is slow. While the initial organic concentration increased, the probability of the effective collision improved continuously, so both the adsorption capacity and the removal efficiency increased continuously (Luna et al. 2011).

**Isothermal equilibrium modelling**

Experiments were carried out with a solution volume of 100 cm³ and with different organic compound concentrations, coal consumption was 2.0 g, adsorption...
temperature was 25 °C, and the adsorption time was 4 h. Isotherm constants were obtained by using linear regression analysis to the linear forms of the isotherm expressions of the organic compound adsorption experiments for pyridine, quinoline, indole and phenol. The results of the isotherm constants and the correlation coefficients are shown in Table 1. The curves of the calculated equilibrium amount of adsorbate on the adsorbent surface ($Q_{eq}$) versus the amount in solution ($C_{eq}$) used by the various models and the obtained constants are shown in Figure 4.

A comparison of the correlation coefficients in Table 1 shows that the Redlich–Peterson (R-P) model is more fit for the four adsorbates’ adsorption on coking coal than other models; $R^2$ for pyridine, quinoline, indol and phenol is 0.9945, 0.9999, 0.9999 and 0.9962, respectively. The R-P model constants results showed that $\beta < 1$ and $|\alpha|C_{eq}^\beta > 1$.

Table 1 | Constants and correlation coefficients obtained for the Langmuir, Freundlich, Temkin and R-P isotherm models of four adsorbates’ adsorption onto coking coal

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>Redlich–Peterson (R-P) model</th>
<th>Temkin model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$/dm$^3$·mg$^{-1}$</td>
<td>$q_m$/mg·g$^{-1}$</td>
<td>$R^2$</td>
<td>$K_{Fr}$/mg·g$^{-1}$</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.1272</td>
<td>1.73</td>
<td>0.14</td>
<td>0.9126</td>
</tr>
<tr>
<td>Quinoline</td>
<td>0.4612</td>
<td>3.09</td>
<td>0.04</td>
<td>0.8282</td>
</tr>
<tr>
<td>Indol</td>
<td>0.0729</td>
<td>8.26</td>
<td>0.22</td>
<td>0.9633</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.0234</td>
<td>2.62</td>
<td>0.30</td>
<td>0.9142</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$K_R$/dm$^3$·g$^{-1}$</th>
<th>$\omega$/dm$^2$·mg$^{-1}$</th>
<th>$\beta$</th>
<th>$R^2$</th>
<th>$K_T$/dm$^3$·g$^{-1}$</th>
<th>$b_T$/kJ·mol$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>1.8938</td>
<td>6.675</td>
<td>0.493</td>
<td>0.9945</td>
<td>0.7329</td>
<td>8.03</td>
<td>0.8730</td>
</tr>
<tr>
<td>Quinoline</td>
<td>-1.2197</td>
<td>-2.500</td>
<td>0.220</td>
<td>0.9999</td>
<td>2.2199</td>
<td>4.92</td>
<td>0.8205</td>
</tr>
<tr>
<td>Indol</td>
<td>0.6643</td>
<td>0.195</td>
<td>0.569</td>
<td>0.9999</td>
<td>0.9747</td>
<td>3.28</td>
<td>0.8843</td>
</tr>
<tr>
<td>Phenol</td>
<td>-0.8863</td>
<td>-1.956</td>
<td>0.481</td>
<td>0.9962</td>
<td>-0.7951</td>
<td>5.74</td>
<td>0.8872</td>
</tr>
</tbody>
</table>

$R^2$ is the calculation for $C_0 = 50$ mg·dm$^{-3}$. 

Figure 3 | The influence of initial concentration on removal efficiencies and adsorption capacities.

Figure 4 | The calculated equilibrium amount of adsorbate on the adsorbent surface ($Q_{eq}$) versus the amount in solution ($C_{eq}$) used by the various models and the obtained constants.
thus the four adsorbates’ adsorption on coking coal belongs to the Freundlich isotherm. The four adsorbates’ adsorption on coking coal also fit to the Freundlich isotherm basis for the correlation coefficients results. The $R_L$ values from the Langmuir equation were all between 0 and 1, indicating a favourable sorption process. This was supported by the $1/n$ values less than 1 obtained for the Freundlich model.

According to the constant $K_F$, the order of the adsorption rate is: quinoline > indole > pyridine > phenol. As shown in Figure 4, it can also be seen that the Freundlich and R-P models showed a better fit to the experimental data than the others, and the R-P model is best.

The point zero of charge (PZC) and iso-electrical point (IEP)

The point zero of charge

The relationship between ΔpH and pH$_{\text{final}}$ of coking coal is shown in Figure 5. It can be seen that the coking coal pH$_{\text{PZC}}$ of PZC is 6.50. This means that the coking coal surface charge is negative because the coking coal surface contains acidic oxygen functional groups such as hydroxyl, carboxyl and carbonyl containing acid. The more oxygen groups on the coal surface, the stronger coal surface electronegativity and the smaller pH$_{\text{PZC}}$.
The iso-electrical point

The relationship between pH and ζ potential of coking coal is shown in Figure 6. It can be seen that the pH_{IEP} of coking coal was 3.95. The ζ potential of coking coal increased with the increase of pH value, and the ζ potential of coking coal changed from positive to negative. The ζ potential of coking coal is negative when the pH value of solution is higher than pH_{IEP}. This illustrated that the charge of coking coal surface is negative, and counter-ions in the Stern electric double layer are positively charged ions. The H^+ concentration in both the Stern and diffusion layer declined with the decrease of H^+ concentration in solution. The electric double layer became thicker, which makes the ζ potential gradually decrease and the absolute value increase. Therefore, the optimum pH value for the adsorption experiment should be a value between the pH_{IEP} and 7 when the electrical property of the adsorbate molecular is positive, and also the optimum pH value for the adsorption experiment should be a value between 0 and the pH_{IEP} when the electrical property of the adsorbate molecular is negative (Menénéndez et al. 1995).
Effect of pH value

The experiment conditions were as follows: The adsorbates’ concentration of the simulated coking wastewater was 25 mg·dm$^{-3}$, the oscillation contact time was 60 min, the coking coal consumption was 2.0 g, the adsorption shaking was at stable room temperature (about 25°C), and the pH was adjusted to a value between 1 and 11 by adding HCl 0.1 M or NaOH 0.1 M solutions. The removal efficiencies and adsorption capacities of the four adsorbates’ adsorption on coking coal are shown in Figure 7.

As shown in Figure 7, with increasing pH value, the adsorption capacities and the removal efficiencies of the three organics, quinoline, indole and pyridine decreased; phenol removal efficiency increased at first and then decreased. The maximum phenol removal efficiency is located at around a pH value of 4.0.

Phenol is weakly acidic, and its adsorption on coking coal is related to the degree of dissociation in water; the greater the degree of dissociation, the smaller the adsorption capacity. Due to this, phenol exists in the neutral molecular form C$_6$H$_5$OH and the dissociation degree of phenol in acidic medium is small, so the phenol adsorption capacity on coking coal was high during pH value of 0 to 4.7. The pKa value of phenol is 9.89 (Dean 1990), so when the pH value was >9.89, phenol takes the form of anion C$_6$H$_5$O$^-$$^-$$^-$. The phenol adsorption capacity on coking coal decreased with the increase of pH value. The carboxyl groups on the coking coal surface are the phenol adsorption site; they can form the $\pi$-$\pi$ electron donor-acceptor, but the phenol adsorption capacity on coking coal is small when the pH value is low and because of that H$^+$ reacts with carboxyl groups first. Due to the combined effects of these two reasons, the phenol removal efficiency varied less during low pH values. Experimental results demonstrate that phenol adsorption on the coking coal, mainly by the uncharged molecular form, and the phenol adsorption capacity on the coking coal can be improved by reducing the number of acid groups of the coal surface and adjusting the pH value of the solution.

Quinoline, indole and pyridine are alkaline, but the coking coal surface charge is negative when the pH value is higher than the pHIEP, so it benefits adsorption. With the increase of pH value, the chemical adsorption disappeared and because of that the acidic oxygen functional groups on the surface of coal were neutralized by hydroxyl ions. In addition, according to my previous research (Xu et al. 2016b), the specific surface area of coking coal reduced with the increase of pH value of solution, and the adsorption process is mainly physical adsorption. Thus the adsorption capacities and the removal efficiencies of the three organics,
quinoline, indole and pyridine, decreased with the increase of pH value of the solution.

Purification mechanism of organic adsorption on coking coal

The difference between physical and chemical adsorption is the property of force. The main force of physical adsorption is physical force including van der Waals force and hydrogen bonding; van der Waals' includes dispersion force, induced force and dipole force which do not have direction and saturation. The dispersion forces are mainly between non-polar and low-polar molecules. If there is an electron exchange, transfer or the forming of a covalent bond between the adsorbate molecular and the adsorbent surface, the adsorption belongs to chemical adsorption.

According to the XRF results, the constituents of coking coal are shown in Table 2. Based on the analysis, three kinds of coal contain small gangue minerals and have the same mineral composition. Anthracite has a lower content of gangue minerals than the others. Based on the analysis of mineral composition content, coal composition plays a leading role in the adsorption test. Clay mineral content also has a certain adsorption effect, but the effect is small because that content is low. The gangue minerals have a little influence on coal adsorption.

According to the chemical composition of coking coal previously published (Xu et al. 2016b) and the XRF results, the coking coal surface contains oxygen functional groups and calcium, silicon, iron, magnesium, and other oxides. These oxygen functional groups and oxides can change the charge of the coking coal surface via contact with water. Below, M denotes silicon, calcium, iron, and others. The chemical interactions of oxides can be summarized by the following equilibria:

\begin{align}
H_2O & \rightleftharpoons H^+ + OH^- \\
M + OH^- & \rightleftharpoons MOH \\
M - OH + H^+ & \rightleftharpoons M - OH_2 \\
MOH + OH^- & \rightleftharpoons M - O^+ + H_2O
\end{align}

Co represents coking coal. The chemical interaction of oxygen functional groups is shown as follows:

\begin{align}
Co - OH & \rightleftharpoons Co - O^- + H^+ \\
Or + H^+ & \rightleftharpoons OrH^+ \\
Or + Co & \rightleftharpoons Or - Co \\
OrH^+ + Co - O^- & \rightleftharpoons OrH^+ - Co - O^- \\
OrH^+ + M^+ - Co & \rightleftharpoons OrH^+ - Co + M^+ \\
H^+ + OrH^+ - Co & \rightleftharpoons H^+ - Co + OrH^+ \\
H^+ + Co & \rightleftharpoons H^+ - Co \\
Or - H^+ + Co & \rightleftharpoons OrH^+ - Co \\
Or - H^+ + Co - M - O^- & \rightleftharpoons OrH^+ - O^- - M^- - Co \\
Co - C = O + OrH^+ & \rightarrow Co - C - O - H - Or
\end{align}

The solubility of quinoline, indole and pyridine is low, and the lower the solubility and the better hydrophobicity of the molecule, makes the molecular adsorption on the coal surface easier. Three kinds of organic compounds have similar properties, and all of them are alkalenescent. Take the example of pyridine (Py). The molar fraction of PyH+ is less than 5 mol% when the pH value is higher than 6.5. Pyridine first adsorbs on the positive charge surface at this point because the electronegativity of Py is higher than the carbon atom. At pH value higher than 5.25 (the pKa of pyridine is 5.25) (Dean 1990), both π-π dispersion interactions and electrostatic interactions become

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
Name & Na_2O & TiO_2 & K_2O & S & MgO & Fe_2O_3 & CaO & Al_2O_3 & SiO_2 \\
\hline
Content (%) & 0.566 & 0.763 & 1.820 & 2.554 & 2.690 & 5.010 & 6.324 & 18.260 & 50.390 \\
\hline
\end{tabular}
important and the Py molecule is adsorbed onto coking coal via Equations (9) and (10). When the pH value is lower than 5.25, the Py is converted to PyH\(^+\) through protonation via the reaction of Equation (8). The pyridine first adsorbs on the negative charge surface at this point. According to Figure 7, the optimum pH value of pyridine (Py and PyH\(^+\)) adsorption on coking coal is 4 because of the adsorption methods, including physical (Equation (14)) and chemical (Equation (11)) adsorption. When the pH value is higher than 7, the adsorption mode is mainly physical adsorption, and the adsorption is mainly based on Equation (9), so the adsorption effect is poor because there is only one adsorption form at high pH value.

The chemical interactions of phenol (Be-OH) can be summarized by the following equilibria:

\[
\begin{align*}
\text{Be} - \text{OH} & \rightleftharpoons \text{Be} - \text{O}^- + \text{H}^+ \quad (17) \\
\text{Be} - \text{OH} + \text{Co} & \rightleftharpoons \text{BeOH} - \text{Co} \quad (18) \\
\text{Be} - \text{O}^- + \text{Co} - \text{O}^- & \rightleftharpoons \text{O}^- - \text{Be} - \text{Co} - \text{O}^- \quad (19)
\end{align*}
\]

First, the higher the solubility, the better the hydrophilicity of the molecule, so molecular adsorption is difficult on the coal surface because the solubility of the phenol is high. Second, phenol is weakly acidic, the phenol of ionization coefficient Ka = 1.1 \times 10^{-10}, pKa = 9.96 (Dean 1990). When the pH value was less than 9.96, the phenol was mainly C\(_6\)H\(_5\)OH via reaction Equation (18). The adsorption mode is mainly physical adsorption at this point, and the adsorption capacity is proportional to the specific surface area of the adsorbent. When the pH value was higher than 9.96, the phenol exits as C\(_6\)H\(_5\) after ionization via Equation (17), and Co\(^-\) was formed after electrolysis of oxygen containing functional groups on the coking coal surface. Due to both the coking coal surface charge and phenol ion being the same electrical property, the adsorption effect becomes worse. The greater the degree of dissociation, the smaller the adsorption amount on the surface of the adsorbent particles, and the same with the experimental results as shown in Figure 7.

Thus, the adsorption of macromolecular organic compounds on the coal surface is mainly physical adsorption; the physical adsorption mechanism is mainly of three kinds, as follows:

1. Adsorption by electrostatic interactions: The counter ion on the coal surface may be exchanged by organic ions of the same charge, which is ion exchange adsorption, such as in Equation (11). The organic ions can be adsorbed on the coal surface of different charges, which is ion pairing adsorption, such as in Equation (10).

2. Adsorption by van der Waals forces: The adsorption of the coal surface with organic molecules may be caused by van der Waals forces, such as in Equations (9) and (18). The characteristic of this adsorption is that the adsorption capacity is proportional to the molecular weight of the organic matter.

3. Adsorption by hydrogen bond: The adsorption caused by hydrogen bonds which are formed between the functional group on the coal surface and the organic molecules; its adsorption mechanism is shown in Figure 8.

**CONCLUSIONS**

The adsorption ability of coking coal adsorbed organic matter has been investigated, and several operating parameters which impact the removal efficiency were investigated and the best operation conditions were determined. The organic removal efficiency increased with the increase of coking coal consumption, and the order of removal efficiency is: quinoline > indole > pyridine > phenol. The optimum adsorption time...
determined by test is 30–60 min. With increasing pH value, the removal efficiencies of the three organics, quinoline, indole and pyridine, decreased. Phenol removal efficiency increased at first and then decreased. The maximum phenol removal efficiency is located at around a pH value of 4.0. The adsorption of macromolecular organic compounds on the coal surface is mainly physical adsorption, and the physical adsorption mechanism is mainly of three kinds: adsorption by electrostatic interactions, van der Waals forces, and by hydrogen bond. In the future, coking coal can be used in the treatment of wastewater as an inexpensive adsorbent to achieve ‘wastewater zero emissions’.

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