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Removal of recalcitrant organic pollutants from bio-treated coking wastewater using coal-based carbonaceous materials

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ABSTRACT

Low-cost coal-based carbonaceous material has attracted special attention for treatment of recalcitrant industrial wastewater. In this study, adsorption of recalcitrant organic pollutants from bio-treated coking wastewater using powder coke, lignite-based activated coke and tar-based activated carbon were investigated. The results showed that the adsorption followed Freundlich isotherm, indicating a heterogeneous adsorption for these substances. The activated coke exerted the best removal of COD (55%) and colority (77%) at 30 $g\cdot L^{-1}$, pH = 4 and 25ºC with contact time of 120 min, nearly 20% and 80% higher than activated carbon and powder coke at their respective optimum conditions. This is attributed to the abundant oxygen-containing functional groups in its structure in spite of the apparently lower surface area than activated carbon. The lowest adsorption demonstrated by powder coke is correlated to the smallest surface area (0.81 $m^2\cdot g^{-1}$). In addition, the adsorption behavior over time was followed the pseudo-second-order kinetic model very well. The time to reach equilibrium is short for activated carbon and intraparticle diffusion seems to be the rate controlling step. However, the adsorption on activated coke and powder coke is slower than activated carbon and the surface diffusion is more important in these processes. It is expected the study will provide a technical insight into the above said carbonaceous adsorbent and also identifying the low-cost adsorbent for bio-treated coking waste water treatment.

Keywords: Recalcitrant organic pollutants; Bio-treated coking wastewater; Adsorption; Coal-based carbonaceous materials

1. Introduction

Metallurgical coal is commonly used for producing required quality of metallurgical coke with adopted coke making technologies. During conversion of coal to coke, the large quantity of wastewater containing inorganic and organic pollutants have been accumulated from different sources like coal gas purification, by-product recovery processes, and coke quenching. In most cases, the phenol, cyanide and biological oxygen demand in wastewater can meet discharge standards after bio-treatment. However, effluents from biological wastewater treatment systems still contain a high level of recalcitrant organic pollutants (ROPs) recalcitrant to biodegradation [1]. In recent years, with the development of dry quenching technique, the effluents from biological system in coke plant loses its way as spraying water for coke quenching in coking industries. Given such a situation, bio-treated coking wastewater (BCW) has been considered as an emerging challenge to the sustainable development of coal industry [2].

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The recalcitrant organic pollutants characterized by a variety of soluble organic compounds indicated by the COD and colority in the BCW system. It mainly stems from influent organics, intermediate and final microbial by-products. Extensive effort has been devoted to enhance the removal of ROPs, such as advanced oxidation, membrane separation and adsorption, Fenton, ozone, etc. Compared to physical and chemical/electrochemical methods, membrane filtration treatment appear to be more effective in providing very good effluent quality, however the ROPs tends to become a primary barrier that hampers and deteriorate membrane performance [3]. Adsorption by carbonaceous materials, particularly activated carbon, has made significant contribution to wastewater treatment in the past few years [4]. However, the difficulty and high expense regeneration are critical issues that challenge the global wastewater treatment practice [5]. Hence, with no doubt, there is an urgent need to substantially improve the overall efficiency by adopting potential adsorbents for the ROPs treatment [6].

The industrial solid waste material is used for making cheapest adsorbent for treatment of organic and inorganic pollutant from coke making wastewater, realizing resource of solid waste and reduce the cost of coking wastewater advanced treatment. Lignite activated coke is derive from the low quality of lignite. It has attracted great attention due to its low price and high mechanical strength [7]. Powder coke is a kind of waste products in the coking process, and could also be used as the thin inhibitor for coal blending in iron ore sintering process after adsorption [8]. In such a process, ROPs can be disposed harmlessly due to the high temperature of the combustion process which makes it more economically viable and energy-efficient. The above mentioned coal-based carbonaceous materials (CCMs) are produced through pyrolysis and/or activation process. The process is similar as coke production. Thus, they would be potential adsorbents with desired and tunable physical and chemical properties.

Adsorption is limited by the potential space of a sorbent available for a given adsorbate, while adsorption affinity is dependent on the strength of attractive forces between adsorbate and adsorbent [9]. In spite of multiple studies of successful application [10], there is limited information available in public domain about the fundamental adsorption information the carbonaceous materials in the treatment of BCW. Therefore, the objective of this study is (1) to investigate the effect of dose, pH, temperature and contact time on the adsorption of recalcitrant organic pollutants from BCW by power coke, lignite activated coke and tar-based activated carbon; (2) to examine the porous structure and surface properties of the three absorbents and its relationship with the adsorption performance; (3) to study the equilibrium isotherms and sorption kinetics of the recalcitrant organic pollutants on these CCMs. The study could provide an insight on carbonaceous material as a low-cost adsorbent used to treat bio-treated coking waste water.

2. Materials and methods

2.1. Bio-treated coking wastewater samples

The BCW samples used in the experiments was collected from Hongtong coke plant located in Shanxi, China. The characteristics of recalcitrant organic pollutants in the bio-treated coking wastewater are presented in Table 1.

2.2. Coal-based carbonaceous materials

Powder coke (P-coke) was taken from Shanxi coke plants without activated by contact with the cooling gas [8]. Lignite-based activated coke (A-coke) was obtained from Xilinhaote Energy Technology Co. Tar-based activated carbon (AC) was purchased from Gongyi Tenglong Water treatment material co. The samples were washed several times with DI water until it was visibly clear to remove any fines attached to it. After that, it was dried in an oven at 105ºC for 72 h and stored in a desiccators until use. DI water was obtained from a Millipore Milli-Q system. All the other reagents were above analytical grade. The main pore characteristics of CCMs are presented in Table 2.

2.3. Optimum conditions for ROPs adsorption

Effect of dosage on COD and colority removal were conducted in 250 mL shaking flasks containing different doses of CCMs samples and 100 mL of fresh BCW. The flasks were agitated at 180 rpm in an orbital shaker.

Effect of pH, temperature and contact time on adsorption were investigated at the same time. At the end of each adsorption, BCW samples were filtered through a 0.45 μm membrane filter prior to the analysis. If samples could not be analyzed immediately, they were preserved and placed in a refrigerator at a temperature of 4ºC. The equilibrium adsorption efficiency was calculated by Eq. (1) as follows:

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0}100 \tag{1}$$

Herein C_0 and C_e (mg·L^{-1}) are the initial and equilibrium concentration, respectively.

Table 1
The characteristics of recalcitrant organic pollutants in the bio-treated coking wastewater

Parameter	Value
pH	6.8–8.1
COD (mg·L^{-1})	100–160
BOD$_5$ (mg·L^{-1})	2.4–2.6
UV$_{254}$	1.302–1.440
Volatile Phenol (mg·L^{-1})	N.D.
Colority (°)	289–297

Table 2
The pore characteristics of the coal-based carbonaceous material

Adsorbents	BET areas (m^2·g^{-1})	Average pore size (nm)	Pore volume (cm^3·g^{-1})
P-coke	0.81	52.27	0.01
A-coke	238.05	3.82	0.21
AC	1426.63	3.34	1.19

2.4. ROPs component analysis and carbonaceous materials characterization

1. COD determination was performed using the potassium dichromate oxidation method. The colority of BCW was determined using a color meter (Chroma Tester, China). All the tests were conducted in triplicates and the data were presented with the average value.
2. UV-vis: The organic composition of BCW was characterized by Shimadzu UV-1800 visible and ultraviolet spectrophotometer scanning from 200 to 550 nm.
3. Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS): Surface morphology before and after adsorption of CCMs after coating were observed by a Quanta 200FEG environmental scanning electron microscope (FEI Company, USA). To examine the elemental dispersion on the surface of both the samples, EDS analyses were conducted using Model LEO SUPRA 50VP INCAX.
4. Fourier transform infrared (FTIR): The spectra were measured using a Perkin–Elmer SPECTRUM-2000 Meter. Each sample was powdered and mixed with anhydrous KBr (1:200 weight ratio). The mixture was pressed under vacuum to obtain the pellets. The spectra were performed between 4000 and 500 cm^{-1} (100 scans). The background spectrum of air was subtracted from the spectra of the samples.

3. Results and discussion

3.1. Optimum conditions for ROPs adsorption

3.1.1. Effect of dosage on ROPs removal

Fig. 1 shows the effect of dosage of CCM on COD and colority (ROPs removal). As demonstrated in Fig. 1a, the COD adsorption efficiency increases significantly as dosage increased initially. This is due to the number of active sites and surface areas increased, which is benefit for ROPs removal [11]. However when the dosage is further increased, the increase of adsorption efficiency is negligible, as the adsorption becomes saturated slowly. The average COD equilibrium efficiency were P-coke (40%), A-coke (55%), and AC (48%) at the dosage of 50, 30 and 30 g·L^{-1}, respectively. The variations of colority (Fig. 1b) shows the similar trend as COD, in which A-coke could remove more than 14% of organic matter with color than AC, and more than 77% than P-coke. Based on the above results, the optimum dosage was determined to be 50 g·L^{-1} for P-coke, 30 g·L^{-1} for A-coke and AC, respectively.

3.1.2. Effect of pH on ROPs removal

It could be seen from Fig. 2, the COD and colority (ROPs removal) decrease with the increase of pH value, indicating that acidic conditions was more beneficial than the corresponding alkaline conditions for ROPs adsorption. Adsorption effect is obviously better under the pH = 4 for A-coke, pH = 2 for P-coke, the neutral environment for AC (Fig. 2a). The removal rate of colority has the same trend roughly (Fig. 2b).

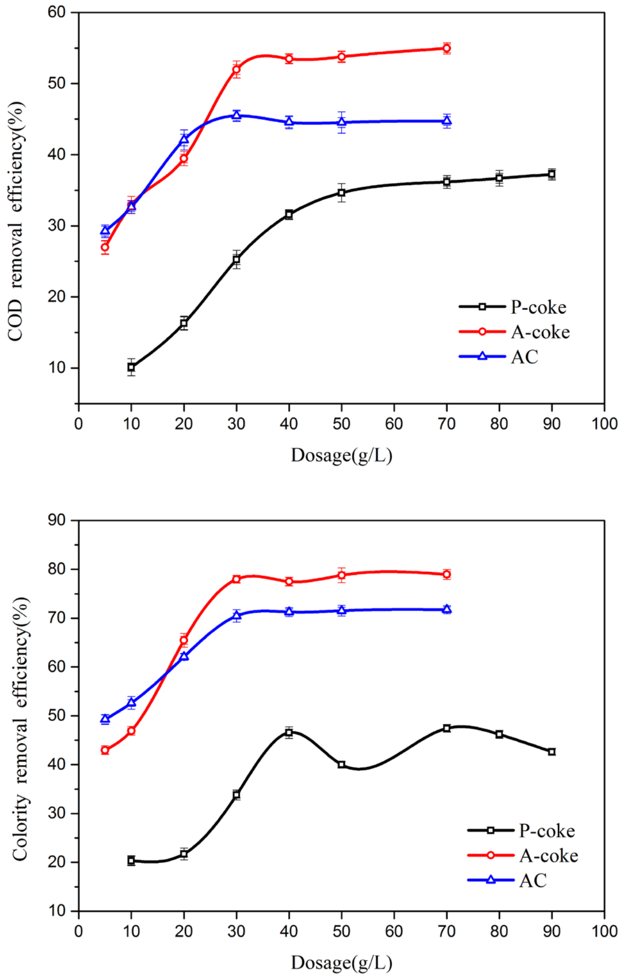

Fig. 1. The effect of dosage on COD and colority removal efficiency. (pH = 7; temperature = 25ºC; contact time = 4 h).

pH affects the adsorbate existence state and the solubility in water. The ionization of acid groups (such as carboxyl, phenolic hydroxyl) on the surface of CCMs is restrained under the acid condition. Being neutral electrically is advantageous to adsorption of nonpolar organic matter (long chain hydrocarbons, benzene series, and aromatic compounds) in BCW. Yellow of BCW is mainly caused by chromophores (containing carboxyl, olefinic bond, etc) and auxochrome (containing –NHR, –NR$_2$, –OR, –OH, etc) group. In the acidic conditions, the color could decrease due to the decomposition of chromophores and auxochrome group [11].

3.1.3. Effect of temperature on ROPs removal

The influence of temperature on COD and colority (ROPs removal) are not very obvious (Fig. 3), which are within a certain range without high fluctuation. The removal efficiency of the temperature at 25ºC (A-coke) and 30ºC (P-coke) were slightly higher than the other temperature.

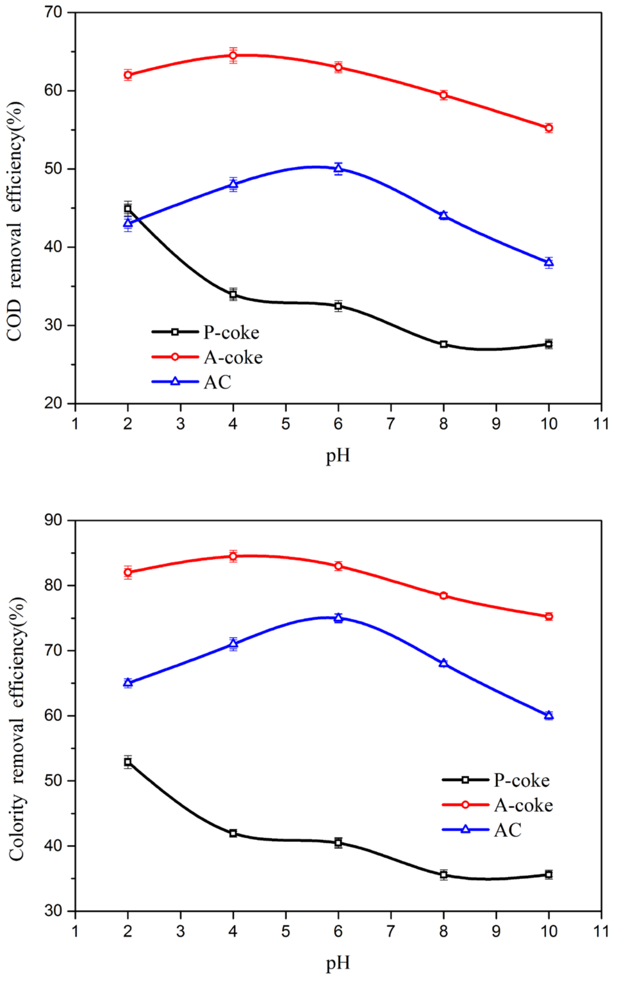

Fig. 2. The effect of pH on COD and colority removal efficiency. (dosage = 50 g·L^{-1}; temperature = 25ºC; contact time = 4 h).

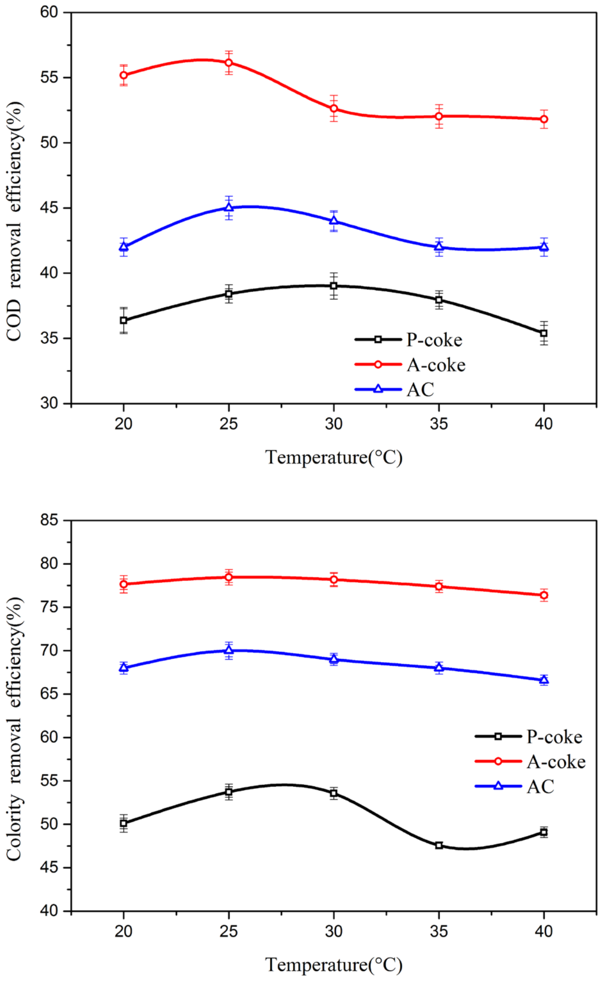

Fig. 3. The effect of temperature on COD and colority removal efficiency. (dosage = 50 g·L^{-1}; pH = 7; contact time = 4 h).

Understanding from the molecular level, the temperature is mainly influence the molecular brownian motion. Temperature increasing exacerbates the movement of CCMs and ROPs molecules, increasing the probability of their contact [12]. On the other hand, hydrolysis degree is small at a low temperature, water viscosity and shear increases, which are not conducive to the adsorption process. The natural temperature of coking wastewater from biochemical pool is around 25–30ºC, which is the most suitable temperature, so there is no need to adjust the water temperature while considering the economic costs.

3.1.4. Effect of contact time on ROPs removal

The effect of contact time on COD and colority (ROPs removal) are demonstrated in Fig.4. The adsorption equilibrium is reached within 180 min for P-coke, 120 min for A-coke and AC. Adsorbent and adsorbate need sufficient time to get in touch with each other, but the COD removal is taking more time than equilibrium time. The adsorption process got saturated with the increase of adsorption time, and the mechanical stirring rotation effect may cause molecular loss due to weak adsorption affinity in a dynamic equilibrium. The COD equilibrium removal (Fig. 4a) of P-coke, A-coke and AC after 2 h are 39, 64 and 56%, respectively. The trend of the colority removal (Fig. 4b) curve are similar as COD removal. A-coke achieved higher removal efficiency than AC and P-coke in the same time, indicating that A-coke is a more efficient adsorbent than P-coke and AC.

3.2. ROPs component analysis and carbonaceous materials characterization

3.2.1. UV-vis analysis

The UV spectrum of BCW and treated BCW are shown in Fig. 5. According to the spectral peak position and peak shape feature of ultraviolet-visible, the characteristics of molecular structure in adsorbate can be judged. Aromatic chromophores and humic substances generally show strong absorbance particularly in the UV region from 200 to 500 nm. The UV absorptivity at 220–250 nm showed strong absorption of the components with conjugated double bonds (conjugated dienes, unsaturated aldehyde,

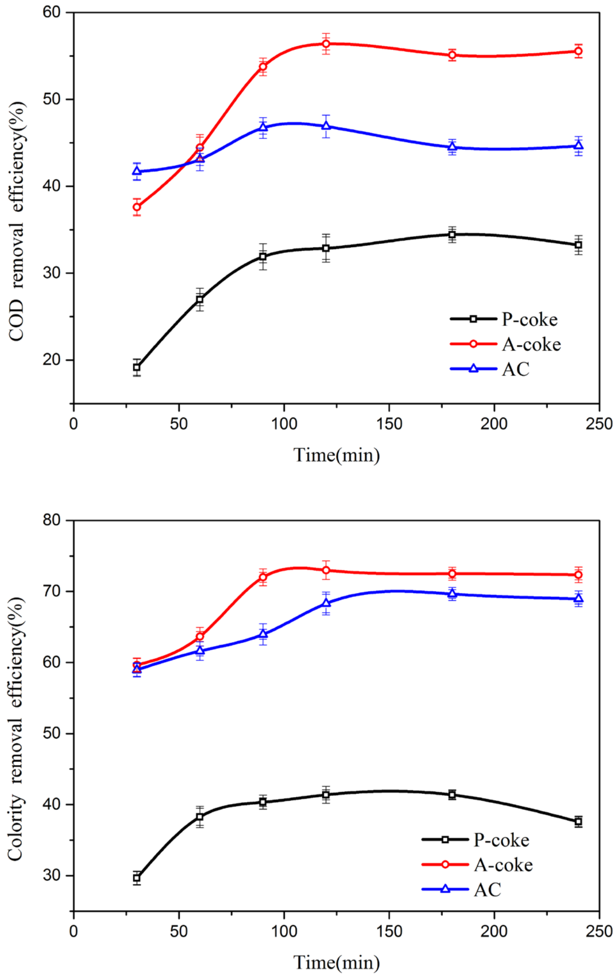

Fig. 4. The effect of contact time on COD and colority removal efficiency. (dosage = 50 g·L^{-1}; pH = 7; temperature = 25°C).

unsaturated ketones) [13]. The UV absorptivity at 254 nm is called specific UV aromaticity (UV_{254}), and it is strongly correlated with DOM's aromaticity [14]. It is commonly used to determine the relative abundance of aromatic C=C content, because π–π* transitions in substituted benzenes or polyphenols occur in this wavelength region [15]. The UV absorptivity at 400–800 nm showed strong absorption of the components with chromophores and auxochrome.

A clear decrease of absorbance implies a decrease of the ROPs from BCW, and the order of descending degree is A-coke > AC > P-coke. To be specific, the peak at 200–270 nm is caused by the E2 and B band of monocyclic aromatic, polycyclic aromatic and heterocyclic compounds, namely heterocyclic compounds was removed largely by adsorption using A-coke and AC. The absorption peak at 254 nm exhibits larger decrease compared with the BCW, demonstrating a decrease of aromaticity caused by the adsorption using CCMs. It shows a local absorption minimum at 260 nm for A-coke and AC, indicating that A-coke and AC could replace hydrocarbons effectively and reduce the content of alcohols, ketones and esters in the wastewater significantly. In addition, absorbing light in the visible region (400–800 nm) indicates that there are colored matter within BCW and have removed significantly by CCMs, especially A-coke and AC. In this regard, it can be concluded that A-coke has the better adsorption performance than AC and P-coke for ROPs removal from BCW.

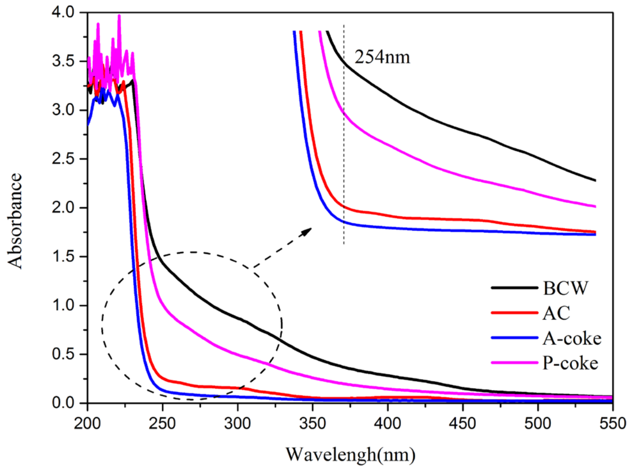

Fig. 5. UV–vis spectra of wastewater samples before and after adsorption.

3.2.2. SEM-EDS analysis

Fig. 6 illustrates the SEM photographs of CCMs before and after adsorption. CCMs have distinct morphology, showing different spaces for adsorption. The surface of all CCMs has a plenty of ravines structure and void space before adsorption. In contrast, CCMs after adsorption presents a relatively smooth surface, compact structure, no obvious pore structure, indicating these voids were covered by the adsorbate. It also can be seen that AC and A-coke have more pore structure than P-coke. The different types of pore structure provide active sites and also perform as a material transport channel, which has certain influence on adsorption performance of ROPs [16]. The inner cavities would also be inaccessible for ROPs molecules because these cavities would be blocked by impurities. Interstitial spaces and grooves, surrounded by the external surface of CCMs, are the pores that are possibly available for adsorption.

The chemical composition have been examined by energy dispersive X-ray (EDS) (Fig. 7). It shows that the surface of CCMs is mainly composed of graphitized carbon and a certain amount of heteroatoms (oxygen, nitrogen, and sulfur) bonded to the edges of the carbon layers. In the meantime, it demonstrates distinct surface chemistry in terms of element C, O, N and S content. AC and P-coke are dominated by graphitized C (76.5, 74.2%) and have a low O content (16.2, 17.4%). As for A-coke, carbon contents (60.7%) is decreased whereas oxygen content (32.1%) is increased. The O compounds normally refer to oxygen-containing functional group, which have a favorable influence on the adsorption of organic matter. It also be demonstrated in this study that A-coke has a large number of active S points on surface, which could also interact with adsorbate through chemical bonds. It should be noted that the surface chemis-

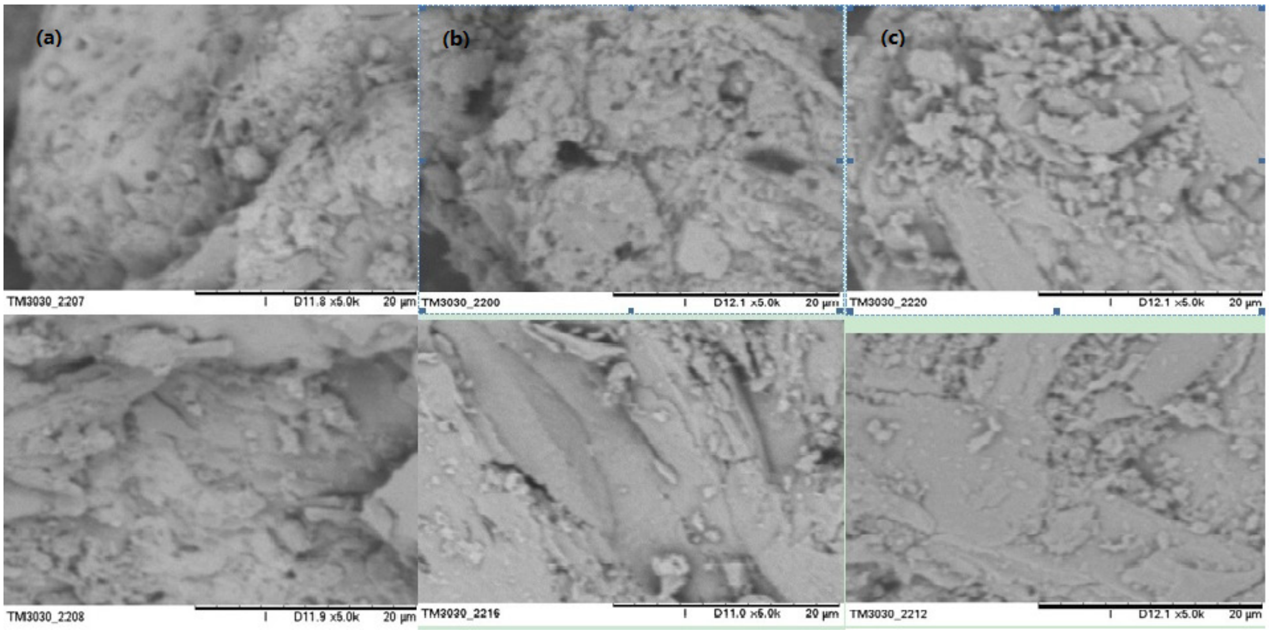

Fig. 6. SEM pictures of CCMs before and after adsorption. (a) P-coke; (b) A-coke; (c) AC.

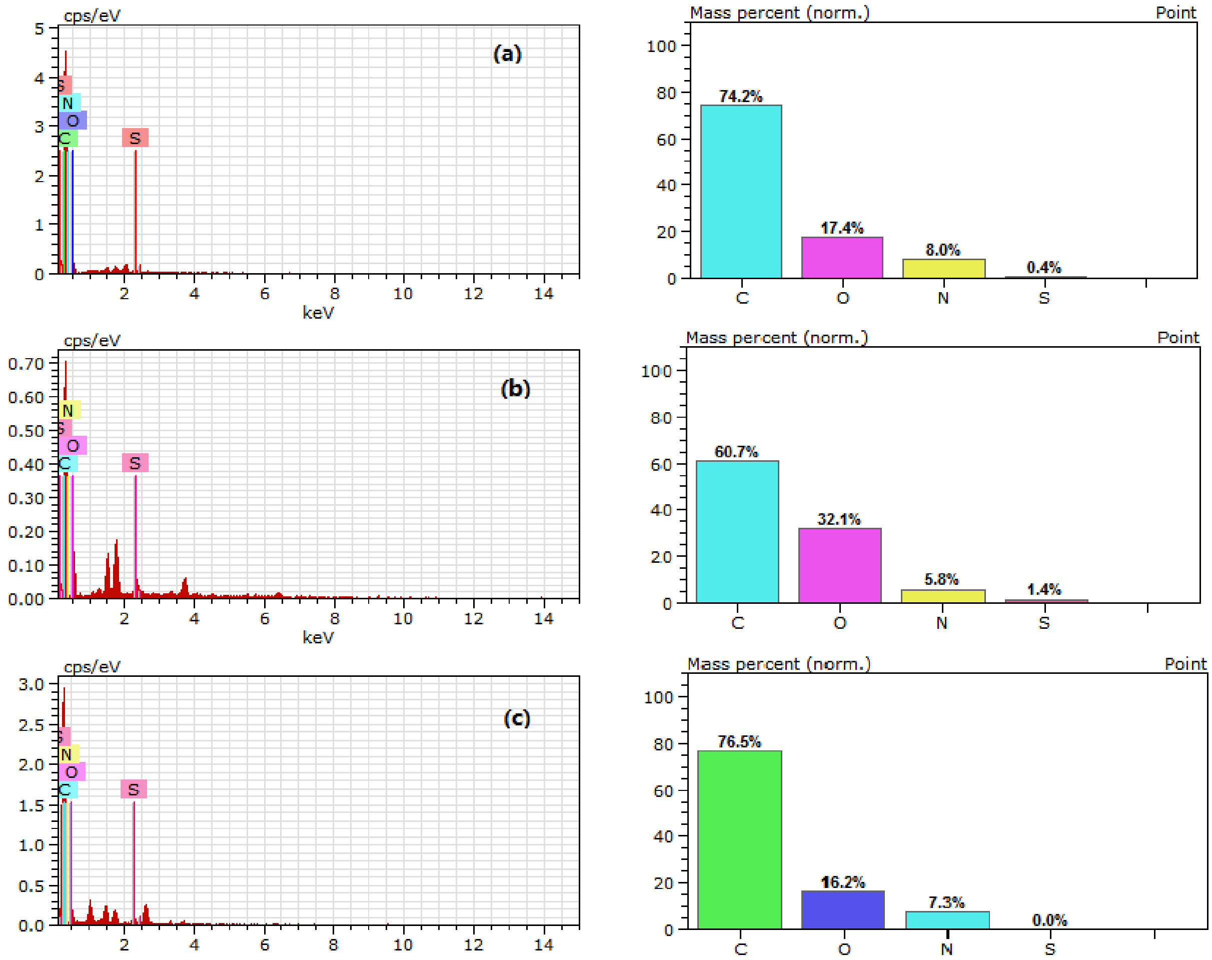

Fig. 7. EDS spectrum and mass percent of CCMs. (a) P-coke; (b) A-coke; (c) AC.

try of CCMs could have a significant effect on the uptake of ROPs [17]. Consequently, it seem to suggest that the more challenging ROPs adsorption performance demonstrated by A-coke was due to its specific surface chemistry.

3.2.3. FTIR analysis

FTIR spectroscopy (Fig. 8) provides valuable information on the structural and functional properties of CCMs. Differences in the relative intensity of some specific absorption bands are observed among CCMs. Infrared spectra of P-coke is very smooth with unconspicuous peak, indicating that the surface of P-coke has seldom functional groups. Compared to the spectrum of P-coke, more peaks appear on the spectra of A-coke and AC. Major spectra bands are assigned as follows: The band of P-coke at 635 cm^{-1} (symmetrical stretching of C–C–C(O)), 1460 cm^{-1} (stretch of C=O in ethers) [18]. A-coke displays a relatively higher IR absorption intensity and a broader peak width at 1090 cm^{-1} (C–O–C or C–O stretching) [19], 1160 cm^{-1} (COH stretch indicating carbohydrates), and 1442 cm^{-1} (symmetrical stretching of COO, OH deformation, and C–O stretching) [20]. The band of AC at 3400 cm^{-1} (O–H stretching vibrations of alcohol, phenol, water, N–H stretching vibrations of –NH and $–NH_2$) [19], 2966 cm^{-1} (C–H stretching vibrations of $–CH_2$ and $–CH_3$) , 1600 cm^{-1} (Stretch of C=O in cyclic amides), 1160 cm^{-1} (C-OH stretch indicating carbohydrates) [21]. Based on the above results, the higher adsorption efficiency of A-coke is likely due to the rise of the relatively content of C=O, C–O, COO– stretching groups and the decline of the relatively content of O–H stretching vibrations of alcohol, phenol, water, namely basicity increasement. These results again confirm our previous SEM-EDS observations that the O/C and (O + N)/C increase of A-coke reflects the presence of nonpolar surface functional groups and increase of hydrophobicity, which can be demonstrated by the preference adsorption of hydrocarbon.

Correspondingly, ROPs is mainly composed of hydrophobic material, such as polycyclic aromatic hydrocarbons, heterocyclic compounds and chroma. Therefore, hydrophobic interaction was employed to interpret the adsorption of ROPs by CCMs. However, hydrophobic interaction alone is not enough to interpret the observed adsorption, acid oxygen-containing functional groups of CCMs can also form hydrogen bonds with water molecules. Hydrogen-bonding interaction would be stronger than that between functional groups of CCMs and ROPs, which results in the competitive sorption of water with ROPs. As a result, basic functional groups of A-coke can avoid the formation of H-bonds with water molecules, which can consequently make more hydrophobic to strengthen the adsorption of ROPs through the competition of water molecules [9]. In this regard, A-coke as discussed may offer the most feasible option toward ROPs treatment.

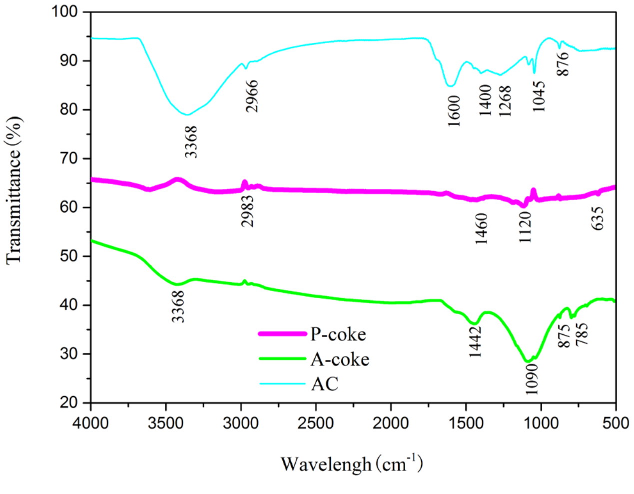

Fig. 8. FTIR spectras of CCMs.

3.3. Equilibrium isotherms and adsorption kinetics

3.3.1. Equilibrium isotherms

The adsorption isotherm can be used to determine the minimum adsorbent usage and the solid–liquid interface concentration relationship in a kinetic model based on pore. In order to establish the most appropriate correlation for the equilibrium isotherm curves, two equilibrium isotherms were analyzed: Langmuir and Freundlich. At constant temperature, COD adsorbed onto CCMs will be in equilibrium with COD in bulk solution. The saturated monolayer isotherm can be represented as Langmuir isotherm, was based on the theory that the adsorption takes place at homogeneous sites with uniform energy levels [22]. This model assumes that the adsorbate covers on the surface equally and the adsorbate molecules are non-interacting [23]. The Langmuir adsorption model can be described by the Eq. (2) as follows:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{2}$$

where C_e (mg·L^{-1}) is the equilibrium concentration; q_e (mg·g^{-1}) is the equilibrium amount of COD adsorbed; q_m (mg·g^{-1}) is q_e for a complete monolayer, Ka (L·mg^{-1}) is the sorption equilibrium constant. The Langmuir isotherm can be linearized into the form as follows by the Eq. (3):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m C_e} \tag{3}$$

The empirical Freundlich isotherm, based on adsorption on heterogeneous surface, can be derived of assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites and is the following Eq. (4):

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F and $1/n$ are the Freundlich constants characteristics and the heterogeneity factor of the system, indicating the sorption capacity and sorption intensity, respectively. This model is only valid in a narrow range of concentrations. Eq. (5) can be linearized in logarithmic form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

The Langmuir and Freundlich isotherm equations were used to fit the experimental results (Fig. 9), the determination coefficients and the constants obtained for the models are summarized in Table 3. Coefficient of determination (R^2) was used to evaluate the goodness of fitting, the correlation coefficients for Freundlich were higher than those for Langmuir isotherms. This shows that there are multilayer adsorption in adsorption process of ROPs on CCMs besides monolayer adsorption. The main reason is that CCMs are micro- and mesoporous carbon materials, which promoted surface adsorption and pore adsorption in the adsorption process. The relative value depends on the organic molecular diameter and pore size distribution of CCMs.

The different equation parameters often provide insight into the adsorption mechanism, the surface properties and affinity of the adsorbent. When the constant n is ranged between 1 and 10, the adsorption can be considered favorable and the adsorbent surface as heterogeneous [22]. The strong nonlinearity is mainly attributed to the adsorption in hydrophobic pores and the heterogeneous distribution of adsorption sites on CCMs.

3.3.2. Adsorption kinetics

The adsorption of ROPs on CCMs reached equilibrium within 4 h (Fig. 10a). In order to evaluate the adsorption kinetics mechanisms, the experimental data were fitted by the pseudo-first-order [Eq. (6)] and pseudo-second-order [Eq. (7)] kinetic models, as well as the diffusion-based Weber–Morris models by linear regression [24].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where q_e (mg·g^{-1}) and q_t (mg·g^{-1}) are the amounts of adsorbate adsorbed on adsorbents at equilibrium and time t, respectively. k_1 (min^{-1}) and k_2 (g·(mg·h)$^{-1}$) are the equilibrium rate constants of the pseudo first- and second-order models.

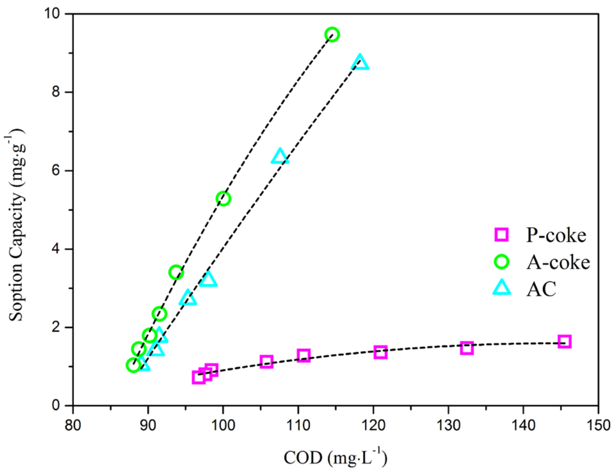

Fig. 9. Equilibrium adsorption isotherms of BCW by P-coke, A-coke and AC.

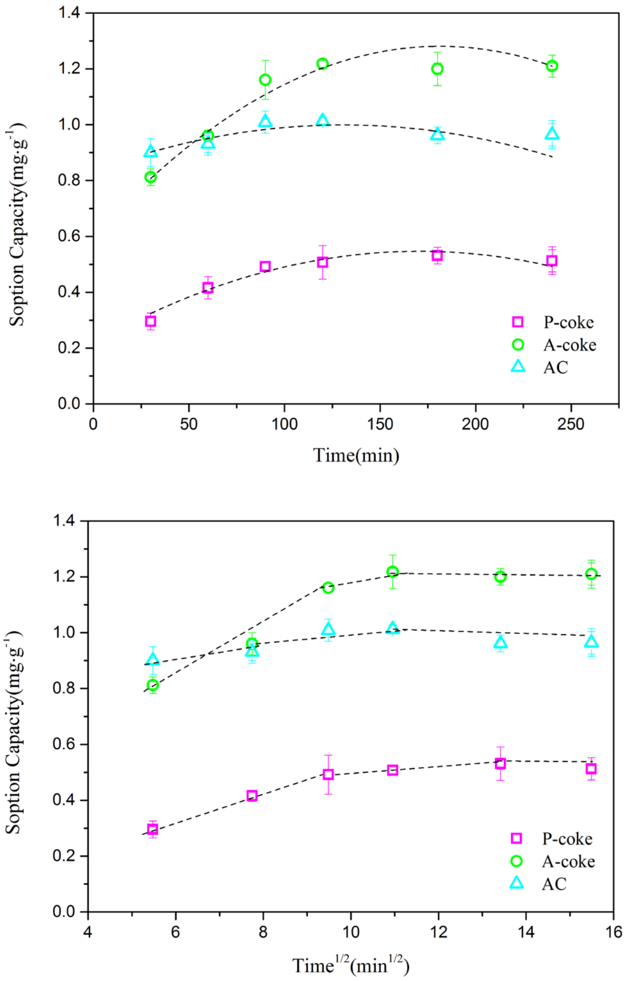

Fig. 10. The adsorption kinetics fitting: (a) Pseudo-second-order kinetic models, (b) Intraparticle diffusion equation.

Table 3
Isotherm parameters for adsorption by different dosage of CCMs

Effluent sample	Organic	Langmuir			Freundlich		
		q_m (mg·g^{-1})	K_a(L·mg^{-1})	R^2	K_F (mg/g) (L/mg) 1/n	n	R^2
P-coke	COD	1.2009	0.0051	0.7973	0.000212	1.8154	0.8420
A-coke	COD	0.5022	0.0042	0.8100	3.05E+12	6.4911	0.9783
AC	COD	0.4932	0.0042	0.5819	2.85E+14	6.9982	0.9388

To identify the key process controlling the rate of ROPs adsorption on CCMs, intraparticle diffusion [25] was determined by Eq. (8).

$$q_t = k_3 t^{0.5} \tag{8}$$

where k_3 (mg/(g·min$^{0.5}$)) is the intraparticle diffusion rate constant.

The pseudo-second-order kinetic model fitted the adsorption data better than pseudo-first-order model owing to higher R^2 values. And the calculated values q_e of sorption capacity of CCMs agreed very well with the experimental data ($q_{e\,exp}$), suggesting that the pseudo-second-order kinetic model is more appropriate for describing the adsorption process of COD on CCMs. From the rate constant k_2 of the Lagergren second-order dynamic model, adsorption rate of ROPs on AC is higher than A-Coke and P-Coke, the most direct reason is the size of the specific surface area. Adsorption rate of CCMs decreases over time, indicating ROPs adsorption on CCMs gradually saturated [6]. Pseudo second-order model constants and correlation coefficients are listed in Table 4.

According to the Lagergren second-order dynamic model, the adsorption of ROPs on CCMs primarily consisted of the following three processes [26] namely: transport of ROPs molecular from the liquid phase to the ROPs-CCMs interface; transport of ROPs molecular from ROPs-CCMs interface to the surface of CCMs; and transport of ROPs molecular from the surface of CCMs to inside the pore of CCMs through either pore diffusion or surface diffusion. Transport of ROPs molecules from the liquid phase to the ROPs-CCMs interface is not rate-limited because the adsorption occurred during rigorous shaking conditions in a shaker. Therefore two remaining steps are responsible for the overall rate of adsorption [27].

To reveal the relative contribution of surface diffusion and intraparticle diffusion to the kinetic process, the adsorption kinetics is further fitted using Weber–Morris model (Fig. 10b). Intraparticle diffusion is assumed to be the sole rate-controlling step if the regression of q_e vs. $t^{1/2}$ is linear and the plot passes through origin [28]. In this study, q_e is linearly correlated with $t^{1/2}$ with positive intercepts, suggesting that intraparticle diffusion is not the rate controlling step for the adsorption. The constants C ≠ 0 in Table 5 can also demonstrate that intraparticle diffusion in the process of ROPs adsorption on CCMs played a contribution, but not the rate control steps. The multi-linearity relationship indicates there were three stages occur in adsorption. The first stage was start 1–2 h, most ROPs were absorbed, this is mainly due to the instantaneous external mass transfer and the surface adsorption between CCMs and ROPs. The second stage mainly occurred between 2–3 h, this was a routine ROPs diffusion from outer boundary layer to inside porous, the diffusion rate of the process was obviously lower than that of surface diffusion. The third stage was attributed to the final equilibrium stage. The above discussion shows that the time to reach equilibrium is apparently longer for A-coke and P-coke than AC. The surface absorption for AC was not the rate controlling step and the intraparticle diffusion effect was predominated especially in later stage. The difference in absorption rate of these CCMs is attributed to the different structure presented in section 3.2. Due to the highly developed pore structure in AC, the ROPs were quickly transported into macro- and mesopores, and then slowly to micro-pores. In contrast, the P-coke shows much less pores in its structure, leading to the slow adsorption and low adsorption capacity. Activated coke has a less developed pore structure than activated carbon, resulting in a slow initial absorption rate than activated carbon. However, since the abundant oxygen-containing functional groups present, activated coke demonstrated an apparently higher absorption capacity in the long run. This study showed that surface chemical property was the key for the adsorption of ROPs by these carbonaceous absorbents. Given its pros and cons, a detail analysis of adsorbent and adsorbate should be further conducted in a more holistic manner, and high efficient adsorbents based on coal based carbonaceous materials need to be designed according to the above results for significantly improving the adsorption potential in further study.

Table 4
Pseudo second-order model constants and correlation coefficients for adsorption

Effluent sample	Organic	$q_{e\,exp}$ (mg·g^{-1})	q_e (mg·g^{-1})	K_2 (g·mg^{-1}·min^{-1})	R^2
P-Coke	COD	1.30	1.4946	0.1089	0.9895
A-Coke	COD	4.29	5.0869	3.0824	0.9777
AC	COD	3.49	3.5148	22.5194	0.9999

4. Conclusions

The adsorption of recalcitrant organic pollutants from bio-treated coking wastewater by three coal-based carbonaceous adsorbents was studied. The adsorption of these substances could be expressed by Freundlich isotherm and the removal efficiency at optimal conditions was in the order of Activated coke > Activated carbon > Powder coke. Activated coke shows about 20% higher adsorption efficiency

Table 5
Intra-particle diffusion model constants and correlation coefficients for adsorption

Effluent sample	Organic	K_1 (mg·g^{-1}min$^{1/2}$)	K_2 (mg·g^{-1}min$^{1/2}$)	C_1	C_2	R$_1^2$	R$_2^2$
P-Coke	COD	0.14525	0.01823	0.1496	1.0253	0.9395	0.9817
A-Coke	COD	0.30605	0.07283	0.5273	3.1519	0.8135	0.9721
AC	COD	0.02758	0.00899	0.1818	3.3527	0.9578	0.9277

than activated carbon in spite of its less porous structure and much lower surface area due to the abundant basic oxygen-containing groups, resulting in a higher hydrophobicity and attractive affinity. The lowest adsorption efficiency of the powder coke was due to its much lower surface area and negligible oxygen-containing functional groups. In addition, ROPs adsorption behavior over time by these CCMs was investigated and the kinetics was fitted with the pseudo-second-order model very well. This study showed that surface chemical property was the key for the adsorption of ROPs by these carbonaceous absorbents. It is suggested that the lignite activated coke can be a potential low-cost coal-based carbonaceous adsorbent for ROPs removal from bio-treated coking wastewaters.

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