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RESEARCH ARTICLE

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Kinetics of adsorption of di-*n*-butyl phthalate (DBP) by four different granule-activated carbons

Abstract The kinetics of the adsorption of an endocrine disruptor, di-*n*-butyl phthalate (DBP), by four different granulated-activated carbons (GACs) is presented in this paper. Results showed that adsorption of DBP by the four GACs followed first-order kinetics and the adsorption constant of the four GAC was found to follow the order: nut shell > coconut shell > Coaly carbon 1.0 > Coaly carbon 1.5. Batch adsorption studies were also conducted to investigate the effect of pH on the adsorption process. The optimum pH for the removal of DBP from aqueous solutions under the experimental conditions used in this work was found to be 5.0. The characterization of the carbon surfaces was conducted by using scanning electron microscopy (SEM). Furthermore, results from infrared spectroscopic (IR) studies showed that physical adsorption plays an important role in the adsorption of DBP by the four selected GACs.

Keywords activated carbon, adsorptive kinetics, scanning electron microscopy (SEM), pore size, infrared spectroscopy

1 Introduction

Phthalates is a group of organic compounds widely used as plasticizers to improve the flexibility and durability of polyvinyl chloride-based plastics. They are also used as additives in the fabrication of multilayer ceramic capacitors, paper, cosmetics, coatings, inks and paints [1,2]. Since phthalates are not chemically bound to the host polymers, they may leach from the host and eventually migrate into the environment. In addition, several industrial plants produce large amounts of wastewater containing high concentrations of phthalates which may have negative effects on the water environment. Many studies have shown that phthalates may have endocrine disrupting effects on aquatic species by altering the action of endogenous steroid hormones and may cause reproductive tract malformations [3,4]. The di-*n*-butyl phthalate (DBP), diethylhexyl phthalate (DEHP) and dimethyl phthalate (DMP) were also classified as priority controlling contaminants by the Environmental Monitoring Station and Environmental Protection Agency (EPA) in China. It is on this basis that DBP was selected to be the adsorbate of interest in the present research. Finally due to its various harmful effects, its removal from wastewater is of paramount importance to avoid any potential threat on the ecology of aqueous systems.

Phthalates can be removed from aqueous solutions by adsorption onto various adsorbents. Adhoum et al. [5] reported the removal of phthalate on modified activated carbon in powder form while Herbert and Zeng [6] studied the adsorption of phthalates by activated sludge and its biopolymers. Due to the low solubility and highly hydrophobic nature of phthalates, activated carbon was considered to be a potentially effective adsorbent for the removal of phthalates from wastewater.

The type of adsorbing species is important in understanding the adsorption of ionizable compounds such as phthalic acid on GACs and is mainly dependent on the pH of the solution containing the adsorbate (ref?). The pH of the solution determines not only the predominant species in the solution but also the net charge on the carbon. This aspect has been studied by Ayranci and Bayram [7] on adsorption of phthalic acid and its esters onto activated carbon-cloth.

The aim of the present work is to compare the removal efficiency of the four GACs and study the adsorption kinetics of a typical endocrine disruptor, di-*n*-butyl phthalate (DBP), by four selected GACs, and finally to propose a suitable kinetic and isotherm model.

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2 Materials and methods

2.1 Materials

Some performance parameters of the four different GACs are shown in Table 1.

Table 1 Performance parameters of the four different GACs

type of carbon	producing area	iodine number /mg·g^{-1}	phenol value /mg·g^{-1}	methylene blue value /mg·g^{-1}	surface area /m^2·g^{-1}
coaly1.0	Taiyuan	658.39	112.84	162.8	596.2
coaly1.5	Maoming	689.62	188.94	116.7	427.4
nut shell	Guangzhou	1062	207.86	246.9	903.7
coconut shell	Guangzhou	913	194.52	182.4	667.6

The methylene blue value, phenol value and iodine number of carbons were measured according to the China National Standards (CNS) GB7702.7-87 and the surface area was measured by the liquor adsorption method.

Due to the GAC's complicated structure originating from its somewhat unknown proprietary preparation procedure, a deionization cleaning procedure was applied to avoid desorption of ions during the adsorption studies. The GACs were cleaned with deionized water, boiled for 1 h, and were kept in a desiccator at 110°C for 24 h [8].

2.2 Methods

2.2.1 Solid phase extraction (SPE)

The C18 column was activated by flushing with methanol for 2 min followed by washing with 5 mL of deionized water. Solid phase extraction of 50 mL of the extraction solution, controlled at an extraction speed of 2 mL·min^{-1}, was then carried out. The DBP adsorbed at the C18 column was removed by flushing with ethyl acetate at a speed of 2 mL·min^{-1}.

2.2.2 High-performance liquid chromatography (HPLC)

For the HPLC analysis, a C18 column was used. The mobile phase was methanol-water (85:15) at a constant flow rate of 1.0 mL·min^{-1}. The UV detection wavelength used was 254 nm.

2.2.3 Determination of adsorption isotherms

The adsorption isotherms were determined on the basis of batch analysis. GACs of varying masses were allowed to equilibrate with 150 mL solution of DBP at 35°C. The equilibration was allowed to develop in 250 mL Erlenmeyer flasks kept in a SHZ-82 shaking bath. The equilibrium concentration was measured using HPLC. The amount of adsorbate adsorbed at equilibrium per unit mass of GAC, q_e, was calculated using

$$q_e = \frac{V(C_0 - C_e)}{m}$$

where V is the volume of the adsorbate solution in L, C_0 and C_e the initial and equilibrium concentrations in mol·L^{-1}, respectively, and m is the mass of carbon used in gram.

3 Results and discussion

3.1 Adsorption isotherm and equilibrium

Equilibrium relationships between adsorbent and adsorbate can be described by an adsorption isotherm. Usually, it is the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. The distribution of DBP between the adsorbent and solution at equilibrium is important in establishing the adsorption capacity of the adsorbent for DBP. The adsorption capacity of activated carbon for a pollutant is usually determined by the establishment of an adsorption isotherm. Figure 1 shows a plot of DBP loading on the different adsorbents against the equilibrium concentration in the liquid phase at 35°C.

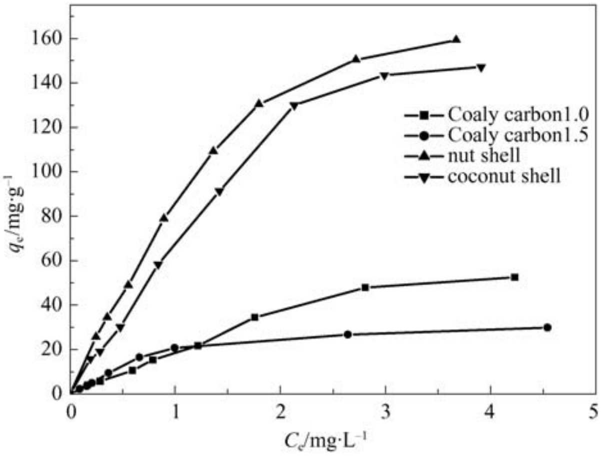
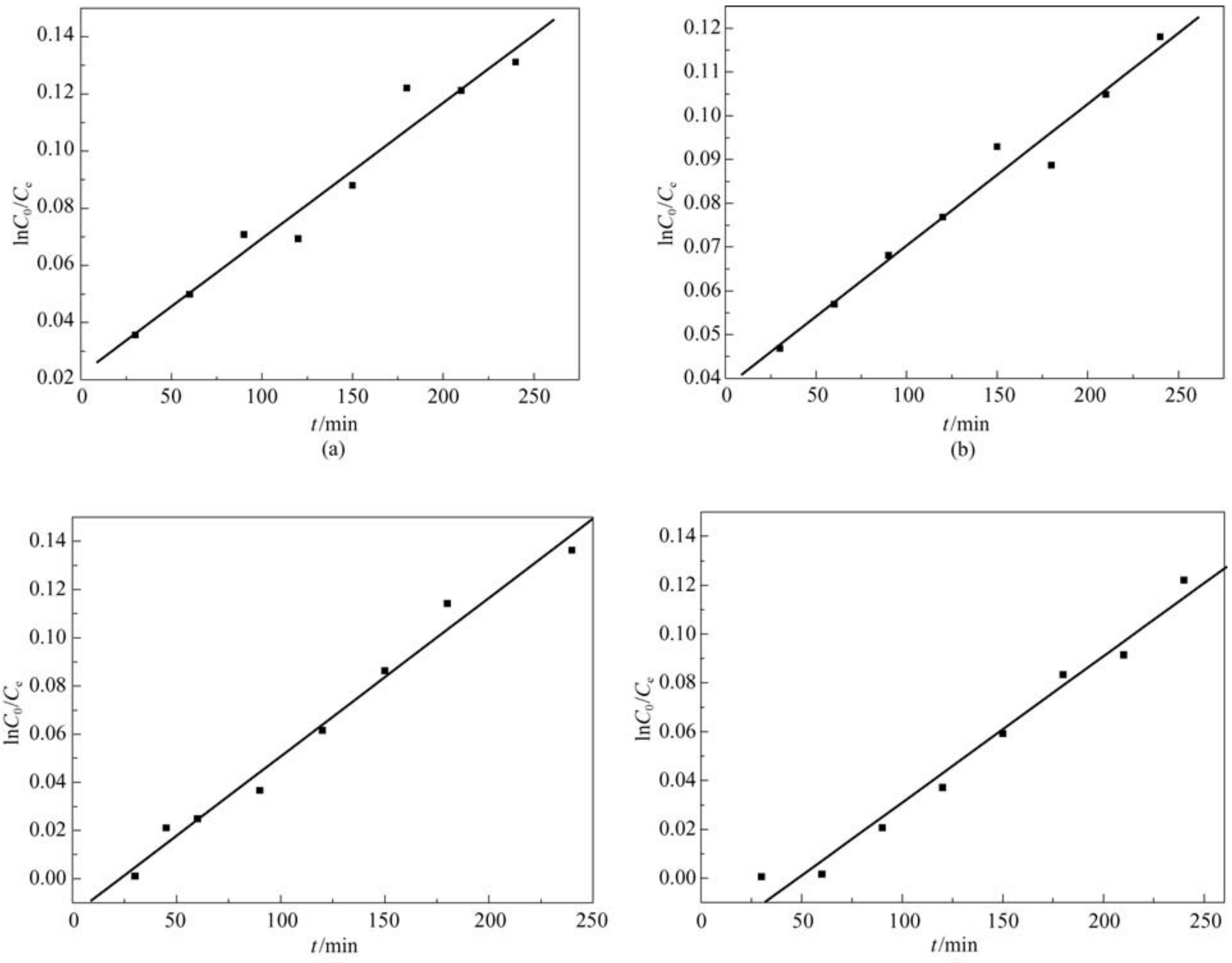


Fig. 1 The adsorption isotherms of selected GACs at 35°C

From Fig. 1, it can be observed that DBP adsorption on all activated carbons follows a similar trend. The percentage of DBP adsorbed on activated carbons was found to increase with time until equilibrium was reached. The saturation adsorption capabilities of Coaly carbon1.0, Coaly carbon1.5, nut shell carbon, coconut shell carbon were found to be 52.52 mg·g^{-1}, 29.9 mg·g^{-1}, 159.2 mg·g^{-1} and 147.2 mg·g^{-1} , respectively, at 35°C.



(a)
(b)
(c)
(d)

Fig. 2 Adsorption kinetics analysis
(a) coaly carbon 1.0, (b) coaly carbon 1.5, (c) nut shell carbon (d) coconut shell cartion

The methylene blue value, phenol value and iodine number of the four GACs studied were found to follow the same order. The nut shell carbon was found to be most effective in terms of its adsorption capacity which may be due to its more compact pore structure. The overall adsorption capacity and saturation adsorption efficiency of both coaly carbons were found to be comparatively low.

3.2 Adsorption kinetics

The rate constant of adsorption was determined from the first-order rate equation [9]:

$$\ln C_0/C_e = -kt$$

C_0 and C_e are the initial and equilibrium concentrations in mg/L, respectively, and k is the rate constant of adsorption (min^{-1}). Figure 2 shows a plot of $\ln C_0/C_e$ against t at 35°C. The values of k can be calculated from it and inserted in Table 2.

According to Fig. 2, the linear plots of $\ln C_0/C_e$ versus t show good agreement for the DBP using the four different GACs. The correlation coefficients for the first-order kinetic model are greater than 0.95. These indicate that the adsorption system belongs to the first-order kinetic model. The adsorption rate constant of the four GACs followed the order: nut shell > coconut shell > coaly carbon1.0 > coaly carbon 1.5. The adsorption rate of nut shell activated carbon is much higher that than that of the other carbons.

3.3 Effect of pH on DBP adsorption onto GAC

The effect of pH on the removal of DBP by the four different GACs is shown in Fig. 3. Here, all the other

Table 2 Adsorption kinetics parameters

type of carbons	kinetics equations	R	$k/10^{-4}$
coaly1.0	$\ln C_0/C_e = -0.022 + 4.754 \times 10^{-4} t$	0.9777	4.754
coaly1.5	$\ln C_0/C_e = -0.038 + 3.235 \times 10^{-4} t$	0.9868	3.235
nut shell	$\ln C_0/C_e = -0.0149 + 6.570 \times 10^{-4} t$	0.9912	6.570
coconut shell	$\ln C_0/C_e = -0.0288 + 5.986 \times 10^{-4} t$	0.9885	5.986

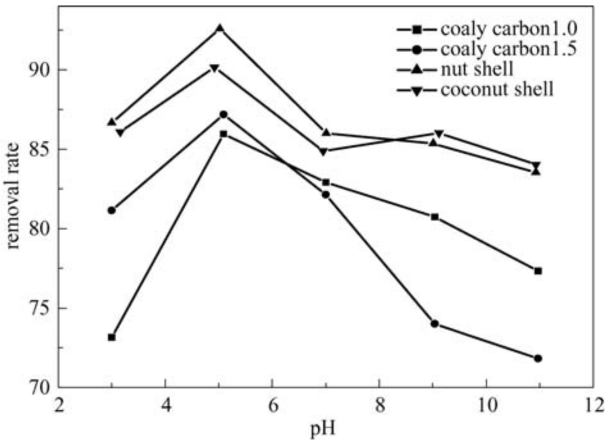


Fig. 3 The effect of pH

parameters like initial concentration (2 mg·L^{-1}), aqueous volume (450 mL), carbon dosage (0.20 g) and agitation time (12 h) were kept constant.

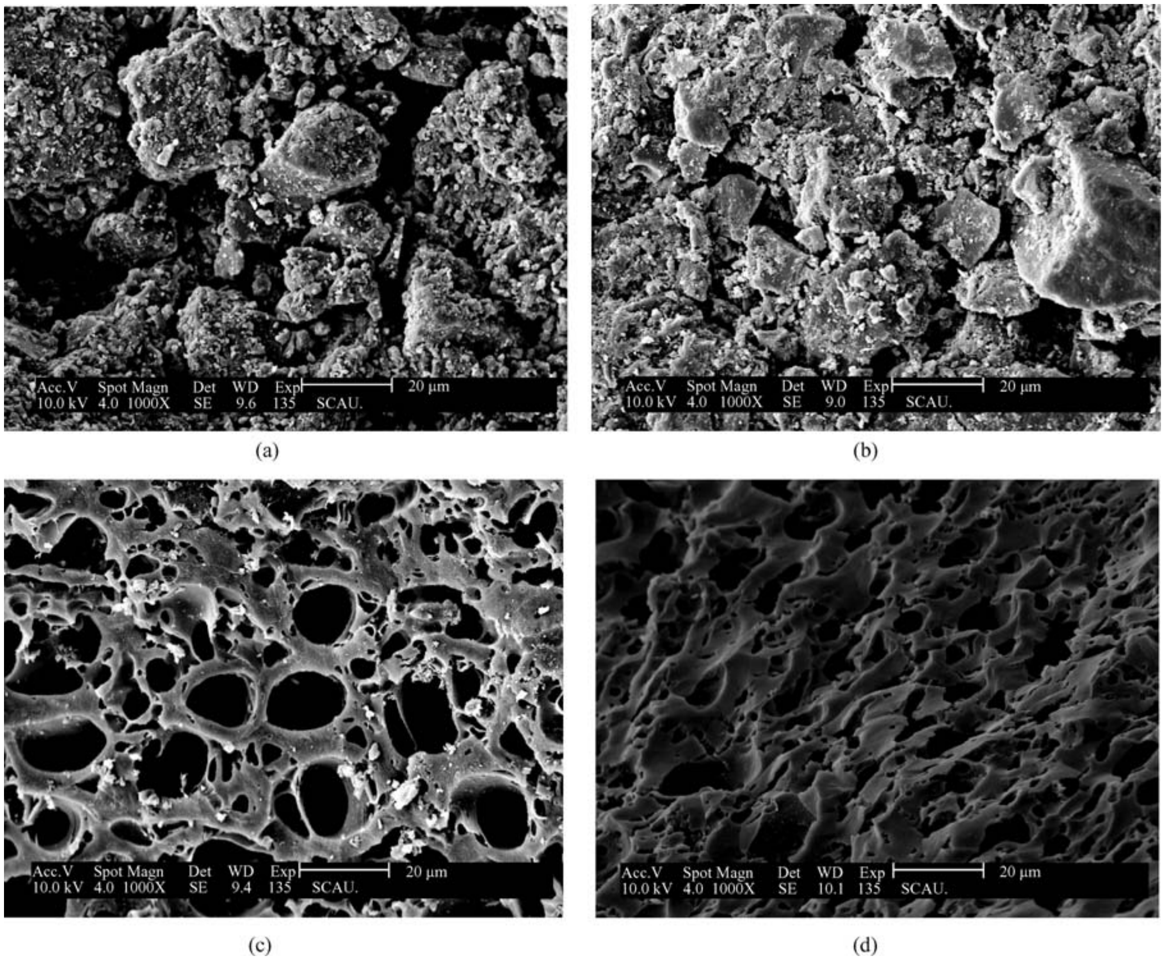
It can be found from Fig. 3 that as the solution pH increases, the removal rate increases first and then decreases. The removal rate reaches a peak when pH is 5. At higher pH, the change of removal rate of nut shell carbon and coconut shell was slight but the change of removal rate of coaly carbon1.0 and coaly carbon1.5 were significantly high with increase in pH.

The pH of the solution may influence the extent of adsorption in that it governs the degree of ionization of the acidic and basic compounds [10]. The initial pH value may enhance or depress the removal depending on the change of the charge of the adsorbent surface with the change of pH.

The hydrolysis of DBP at pH $\leqslant 7$ is:

When pH > 7, the hydrolysis reaction:

When pH of solution is less than or equal to 7, the activated carbon adsorbent surface has more positively charged sites and DBP hydrolyzes into phthalate. The carbonyl of phthalate has nucleophilicity and can easily bond with H$^+$ to a carry positive charge. Therefore, electrostatic repulsion causes a decrease in removal rate. When the pH of the solution is greater than 7, DBP hydrolyzes into phthalate anions. Similarly, removal rate decreases because of electrostatic repulsion. With increase in pH, the removal rate decreases.



(a) (b)

(c) (d)

Fig. 4 Scanning Electron Microscopy(SEM) of four GACs
(a) coaly carbon 1.0, (b) coaly carbon 1.5, (c) nut shell carbon, (d) coconut shell carbon

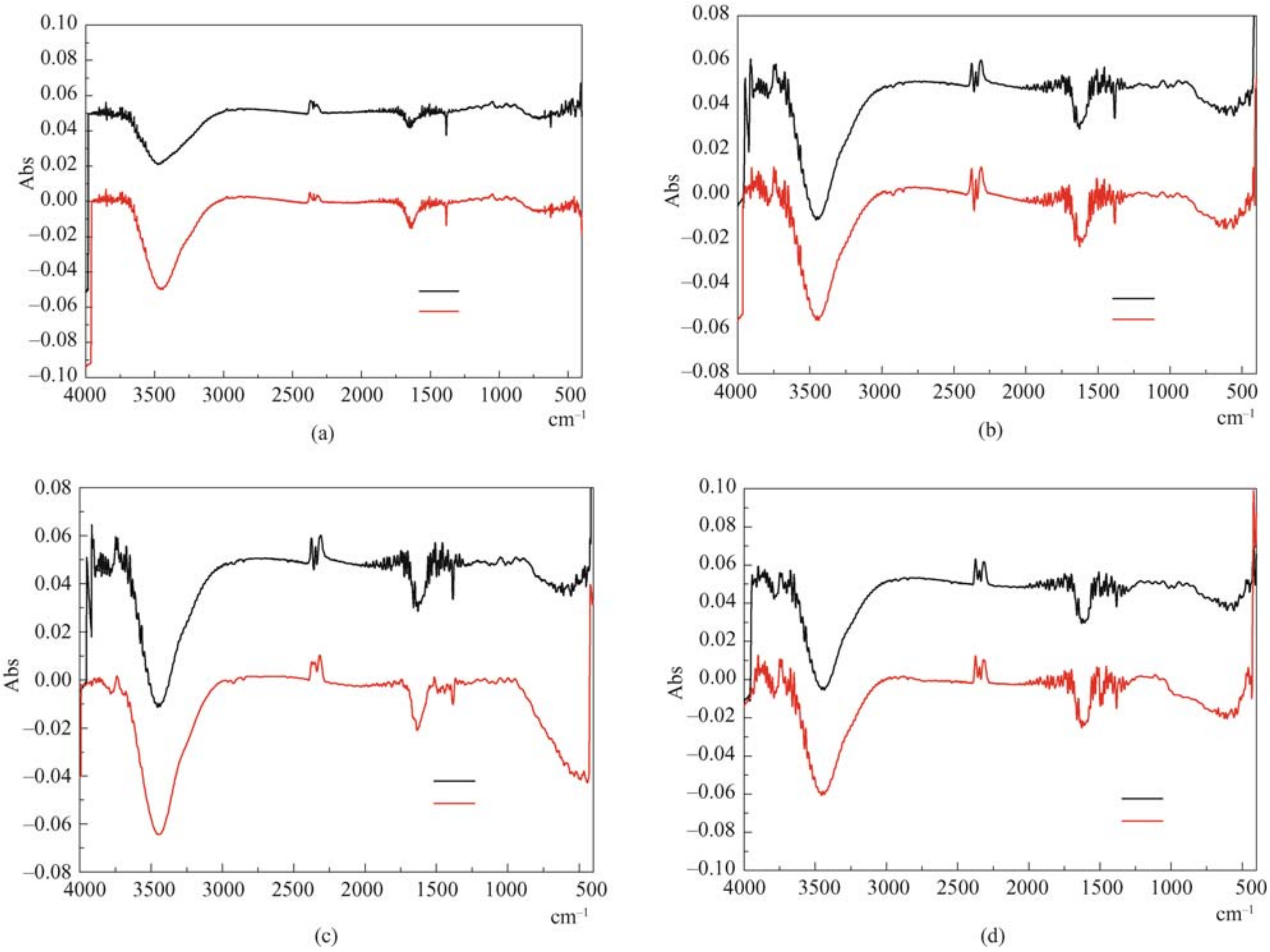
3.4 SEM analysis

Four GCAs were examined through SEM to investigate the character of the surface. Activated carbons can be divided into three kinds [11] based on pore width: micropore ($pw < 2$ nm), transition pore ($2 \text{ nm} < pw < 50$ nm) and macropore ($pw > 50$ nm). In the process of adsorption, absorbate can enter the inner part of the activated carbon through macropores and midpores, and then diffuse to the micropores.

As is shown in Fig. 4, there are remarkable differences in the character of surface pore among the four different activated carbons due to textural differences. The surface structure of Coaly carbon1.0 (a) and Coaly carbon1.5 (b) is similar with compact texture and nonregular pore structure. The aperture of nut shell carbon (c) and coconut shell carbon (d) is even and the pores were abundant. Most of them are round shaped and a few of them were elliptic. Micropores existed among the pores and the diameter of the micropores was around 5–15 μm. In comparison to coconut shell carbon, the aperture of nut shell carbon is small and the surface area is large so the saturate adsorption capacity is a little higher. At the same time, there is a large amount of micropores and macropores on the surface of nut shell carbon and coconut shell carbon and the specific surface area is large. In addition to the agglomeration of capillaries, the absorption capacity is greatly enhanced. Therefore, the saturate adsorption of nut shell carbon and coconut shell carbon is much greater compared to that of Coaly carbon1.0 and Coaly carbon1.5.

3.5 The IR spectrum analysis

The IR spectrum is useful in studying reaction mechanisms on solid surfaces. The IR spectra of four GACs before and after adsorption are shown in Fig. 5. Chemical adsorption and physical adsorption can be determined via the variation of the IR spectrum of activated carbons before and after adsorption. The occurrence of new adsorption band indicates the presence of chemical adsorption, while the displacement or variation of intensity of characteristic absorption band indicates that only physical adsorption occurs.



(a) (b) (c) (d)

Fig. 5 IR spectra of four GACs
(a) coaly carton 1.0, (b) coaly carbon 1.5, (c) nut shell carbon, (d) coconut shell carbon

Figures 5 shows that the adsorption peaks of four GAC are in the same place. The presence of a hexagon O–H stretching vibration peak was indicated by a wide band at 3488 cm^{-1} and the peak at 1550 cm^{-1} was assigned to the –OH group which indicated that functional groups on the surface of four different activated carbons were the same. No new characteristic adsorption band occurred and only minor variations in the intensity of characteristic absorption bands were observed indicating that the adsorption was mainly physical adsorption via weak van der Waals' forces. Chemical adsorption mainly based on catalytic oxidation did not exist.

4 Conclusions

(1) The saturation adsorption capability of Coaly carbon1.0, Coaly carbon1.5, nut shell carbon, coconut shell carbon were 52.52 $\mathrm{mg \cdot g^{-1}}$, 29.9 $\mathrm{mg \cdot g^{-1}}$, 159.2 $\mathrm{mg \cdot g^{-1}}$ and 147.2 $\mathrm{mg \cdot g^{-1}}$ at 35°C.

(2) Linear plots of $\ln C_0/C_e$ versus t showed good agreement for the DBP using the four different GACs. The correlation coefficients for the first-order kinetic model are greater than 0.95 indicating that the adsorption system belongs to the first-order kinetic model. The adsorption rate constant of the four GACs was in the order: nut shell > coconut shell > coaly carbon1.0 > coaly carbon1.5.

(3) SEM of the four GACs showed that the surface structure of Coaly carbon1.0 and Coaly carbon1.5 was similar with compact texture and nonregular pore structure. The aperture of nut shell carbon and coconut shell carbon was even and the pores were abundant. In comparison to coconut shell carbon, the aperture of nut shell carbon was small and the surface area was large.

(4) The IR spectra showed that functional groups on the surface of four different activated carbons were the same. No new characteristic adsorption bands occurred indicating that the adsorption was physical rather than chemical.

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