Biomass-derived highly porous functional carbon fabricated by using a free-standing template for efficient removal of methylene blue

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Highly porous functional carbon material (HPFCM) was fabricated from banana peel.
A free-standing template way was used for fabrication of HPFCM.
Adsorption behavior of HPFCMs was examined by using methylene blue model dye.
The dye adsorption capacity of as-obtained HPFCM is far more than activated carbon.
The adsorption mechanism and kinetics were systematically investigated.

Highlights

ABSTRACT

Banana peel (BP), a biomass waste, was converted into a valuable highly porous functional carbon material (HPFCM) by a general chelate-assisted co-assembly process. The HPFCMs were fabricated by using Al(III)-based metal–organic framework-like as a free-standing template and commercial Pluronic F127 as a microstructure-directing agent. Several critical variables for fabrication including doses of Al(III) and F127, carbonization temperature had been optimized and the adsorption behavior of HPFCMs was examined by using methylene blue as dye model compound. The optimal adsorbent was validated as HPFCMs-5-1-800, and its equilibrium data were well fitted to the Langmuir isotherm model with a monolayer adsorption capacity of 385.12 mg g⁻¹ at ambient temperature. The surface physical properties of HPFCMs-5-1-800 were also exemplarily characterized. The findings revealed that the free-standing template is a potential route for preparation of HPFCM from waste BP.

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1. Introduction

Millions of tons of highly colored wastewater are discharged from different sources including plastic, textile, leather, cosmetics, paper-making, printing and dye manufacturing industries (Feng et al., 2012). The colored synthetic compounds of removal have been recently attracted tremendous attention due to they are hazardous to human being and environments. Various treatments for the removal of dyes have been investigated, including adsorption, chemical coagulation, photodegradation, biodegradation, active sludge, etc. (Zhuang et al., 2009). Among them, adsorption on porous carbons is one of the most efficient processes for dye removal and decoloration (Zhuang et al., 2009) because of large specific surface areas, pore volumes, chemical inertness, and good mechanical stability of carbon. Specifically, activated carbon (AC) can treat dyes in wastewater that show difficulty in biodegradation, e.g., azo dyes (Chatterjee et al., 2011). However, the practical applications of AC are restricted because of micropore sizes (Zhuang et al., 2009). Thus, the development of porous carbon materials
ions can easily bind to carboxyl and hydroxyl groups on the et al., 2012; Lv et al., 2012), which is mainly attributed to the me-
desorption of heavy metal ions from aqueous solution ( Liu had reported BP as an economical and selective sorbent for the pectins, lignins and proteins (Lv et al., 2012). Some investigations biopolymers in plant cell walls such as celluloses, hemicelluloses, To date, there is still no general and satisfactory process for the adsorbents, such as crude biomass, chemically modified biomate-
tions to dealing with. Thus the application of this method in industry is limited, and the super-high surface areas of these materials drop drastically when the processes are scaled up (Hu et al., 2012).

Carbon materials fabricated from waste biomass have shown promising applications as sorption materials, biochemicals, and others (Hu et al., 2010; He et al., 2013). Lately, various low-cost adsorbents, such as crude biomass, chemically modified biomate-
tials and some industrial wastes were desirably investigated in order to provide a competitive substitute for AC in purifying the colored wastewater (Mahmoud et al., 2012; Piccin et al., 2012). To date, there is still no general and satisfactory process for the large-scale production of valuable carbon materials from crude biomass. Banana peel (BP), a common agricultural waste, repre-
sents 40% of the total weight of fresh banana. It is composed of biopolymers in plant cell walls such as cellulosics, hemicelluloses, pectins, lignins and proteins (Lv et al., 2012). Some investigations had reported BP as an economical and selective sorbent for the adsorption of heavy metal ions from aqueous solution (Liu et al., 2012; Lv et al., 2012), which is mainly attributed to the metal ions can easily bind to carboxyl and hydroxyl groups on the surface of pores. In order to make waste BP into high-value-added product and highly porous carbon materials, the viability of BP as an efficient carbon precursor for fabrication of highly porous functional carbon materials (HPFCMs) was investigated in this work. HPFCMs were fabricated via using Al-based metal–organic framework-like (denoted as Al-based MOF-like) as a free-standing template, and Pluronic F127 (i.e., PEO–PPO–PEO) as a structure-directing agent. The significant influences of various treatment ways, structural functional and surface chemistry of the prepared adsorbent were evaluated. The adsorption equilibrium, the adsorption isotherms and kinetics for methylene blue were fur-
ther inspected.

2. Methods

2.1. Materials and chemicals

Crude BP was obtained from a local fruit market in Xi’an, China and thoroughly washed with distilled water before use. The com-
mercial triblock copolymers, Pluronic F127 (poly(ethylene oxide)-
block-poly(propylene oxide)-block-poly(ethylene oxide), PEO_{106}-
PPO_{70}-PEO_{106}, MW 12600) was purchased from Sigma–Aldrich Corp. Al(NO_3)\_3\cdot9H_2O, KOH, NaOH, KNO_3, HF, CH_3COOH, NaCl, HCl and ethanol were purchased from the Sinopharm Chemicals Co., Ltd. (Shanghai, China). Methylene blue (MB) was purchased from Shanghai Chemical Corp. MB stock solutions of 1000 mg L\(^{-1}\) was prepared and further diluted to the required concentrations for testing the adsorption capacity and investigating the adsorption process. All chemicals were of analytical grade and used without further purification. Ultrapure water (18.2 M\(\Omega\) cm) was produced by a Millipore purification system (USA) and used to prepare all aqueous solutions.

2.2. Fabrication of highly porous functional carbon materials

The fabrication process of the HPFCMs is shown in Fig. 1. Typical-
ly, about 1.6 kg BP fragments completely submerged in a certain concentration of Al(NO_3)\_3\cdot9H_2O aqueous solution (2 L) for a week at 70 °C. In this process, the –COOH and –OH on the surface of the BP pores could be coordinated easily with absorbed aluminum ions with the gradual evaporation of solvent and a type of yellow Al-based metal–organic framework-like complexes (denoted as Al-based MOF-like complexes, i.e. YACs) were obtained after drying at 70 °C. Subsequently, YACs were submerged in an ethanol solution of F127 for 24 h at 30 °C, and then held for 24 h at 120 °C for thermo-polymerization, and finally translated into deep yellow Al-based composites (denoted as DYC) with solvent evap-
oration induced self-assembly way. The DYC were carbonized at 800 °C at a heating rate of 1 °C min\(^{-1}\) for 3 h under N\(_2\) atmosphere. The resultant black monoliths were treated with 20 wt% HF for 24 h to remove the Al species, washed with deionized water and anhydrous ethanol (at least each 4 times), dried at 100 °C for 24 h and HPFCMs were obtained. The as-synthesized samples were designated “HPFCMs-a-b-c,” where “a”, “b”, and “c” indicate the mass ratio of Al-based MOF-like complexes to F127, the concentra-
tion of Al(NO_3)\_3\cdot9H_2O solution (M), and the carbonization tempera-
ture (°C), respectively. To compare the adsorptive property, other carbon materials were fabricated by direct carbonization of BP (denoted as DCBP) and chemical activation of BP using 1.0 M KOH as the activating agent under the same carbonization conditions (800 °C in \(\text{N}_2\)).

2.3. Adsorption equilibrium studies

Batch adsorption experiments were carried out in a set of 250 mL conical flasks containing 0.10 g HPFCMs-5-1-800 adsorb-
ent and 150 mL MB aqueous solutions with various initial concen-
trations (50, 100, 150, 200, 250, 300 and 350 mg L\(^{-1}\)). The flasks were agitated in a water-bath shaker at 30 °C and shaking speed of 120 rpm for 8 h. After above treatments, the samples were centrifuged to minimize interference of carbon fines with the analysis, then 1 mL of the supernatants was diluted to a suitable concentration and the absorbance of the supernatants at 665 nm (Liang et al., 2012) was measured using a double beam TU-1901 UV–visible station (Beijing Puxitong Analytical Ltd., China). Each experiment was carried out in triplicate under identical conditions and an average value was employed. The amount (\(q_e\), mg g\(^{-1}\)) of (PCMs) with higher surface areas and larger pore volumes are con-
siderably important for efficient application in dye removal. Extensive methods have been employed to fabricate various PCMs, including hard and soft templating or activation methods (Fechner et al., 2013; Lee et al., 2006). Traditional inorganic materials zeolite and silica are known templates for casting porous carbon. How-
ever, this method is costly, complicated and always involves in highly toxic substances, which hinders its application in large scale production.
MB uptake per unit mass of adsorbent and remove efficiency (RE, %) at equilibrium were calculated by:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

\[
RE(\%) = \frac{C_0 - C_e}{C_0} \times 100
\]

where \(C_0\) and \(C_e\) (mg L\(^{-1}\)) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. \(V\) (L) is the volume of the solution, and \(W\) (g) is the mass of adsorbent used.

The equilibrium data were modeled using the Langmuir, Freundlich, Temkin, Langmuir–Freundlich and Redlich–Paterson isotherm models (model equations are showed in Table S1).

### 2.4. Adsorption kinetic

In the current study, three widely used kinetic models, pseudo-first-order, pseudo-second-order kinetic models (Fan et al., 2011) and Elovich kinetic model (McIntock, 1967), are selected to characterize the adsorption process of HPFCMs under seven different initial dye concentrations. The concentrations of MB were measured at different time intervals and the amount of adsorption at time \(t\), \(q_t\) (mg g\(^{-1}\)), was calculated by:

\[
q_t = \frac{(C_0 - C_t)V}{W}
\]

where \(C_t\) (mg L\(^{-1}\)) is the liquid-phase concentration of dye at time \(t\). The pseudo-first-order and pseudo-second-order kinetic model equations are expressed as:

\[
\ln\left(\frac{q_e}{q_t - q_e}\right) = -\frac{k_1}{2.303}t
\]

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2q_e^2}
\]

where \(k_1\) (min\(^{-1}\)) and \(k_2\) (g mg\(^{-1}\)min\(^{-1}\)) are the adsorption rate constants of pseudo-first-order equation and pseudo-second-order equation, respectively. The Elovich kinetic equation is expressed as:

\[
q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t
\]

where \(a\) (mg g\(^{-1}\)min\(^{-1}\)) is the initial sorption rate and \(b\) (g mg\(^{-1}\)) is related to the extent of surface coverage and activation energy for chemisorption. The value of \((1/b)\) is indicative of the available number of sites for adsorption while \((1/b) \ln (ab)\) is the adsorption quantity when \(ln t = 0\).

The suitability of the kinetic model to describe the adsorption process was further validated by the normalized standard deviation (Krishnan et al., 2011; Foo and Hameed, 2012), \(\Delta q(\%)\):

\[
\Delta q = 100\sqrt{\frac{\sum (q_{exp} - q_{cal})^2}{n-1}}
\]

where \(n\) is the number of data points, \(q_{exp}\) (mg g\(^{-1}\)) and \(q_{cal}\) (mg g\(^{-1}\)) are the experimental and calculated adsorption capacity, respectively.

In addition, the intraparticle diffusion kinetic model based on the theory proposed by Weber and Morris was tested by using the following equation (Foo and Hameed, 2012):

\[
q_t = k_p t^{1/2} + C
\]

where \(k_p\) (mg g\(^{-1}\)min\(^{0.5}\)) and \(C\) are the diffusion rate constant and the thickness of the boundary layer, respectively.

To distinguish between the pore and film diffusion step involved in the adsorption process, the kinetic data were further analyzed using the Boyd model (Boyd et al., 1947):

\[
B_t = -0.4997 - \ln \left(1 - \frac{q_t}{q_e}\right)
\]

### 2.5. Adsorption thermodynamic

The thermodynamic parameters of enthalpy change (\(\Delta H\)), Gibbs free energy change (\(\Delta G\)), entropy change (\(\Delta S\)) and activation energy (\(E_a\)) were computed following the equations:

\[
\ln K_L = \frac{\Delta S}{R} \frac{\Delta H}{RT}
\]

\[
\Delta G = -RT \ln K_L
\]

\[
K_L = A \cdot \exp \left(\frac{-E_a}{RT}\right)
\]

where \(R\) (8.314 J mol\(^{-1}\)K\(^{-1}\)) is the universal gas constant, \(T\) (K) is the absolute solution temperature, \(K_L\) (L mg\(^{-1}\)) is the Langmuir isotherm constant at various temperatures and \(A\) is the Arrhenius constant.
2.6. Desorption and regeneration experiments

The hydrochloric acid aqueous solution (0.01 M), acetic acid aqueous solution (0.01 M), sodium chloride aqueous solution (0.01 M) and deionized water were used for the desorption study. The desorption percentage (%) was applied to evaluate the desorption efficiency and it was defined as the percentage of desorption amounts (mg) versus the original without desorption.

The regeneration research for adsorbent was performed. Typically, 0.05 g of HPFCMs-5-1-800 adsorbent was added to 50 mL of dye solution with a concentration of 400 mg L$^{-1}$, and the mixture was carefully stirred at ambient temperature for 8 h. After centrifugal separation, the MB-adsorbed HPFCMs-5-1-800 adsorbent was added to 10 mL of ethanol and stirred for 20 min for desorption. This desorption process was carried out at least three times. The adsorbent was collected and reused to investigate the recycle rate.

2.7. Characterizations

Nitrogen adsorption–desorption isotherms were measured at 77 K using a volumetric adsorption analyzer (Micromeritics ASAP 2020). Prior to analysis, the sample was automatically and manually degassed for 12 and 4 h under vacuum at 523 K, respectively. The sample was then transferred to the analysis system where it was cooled in liquid nitrogen. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation using adsorption data in a relative pressure range from 0.05 to 0.3; the total pore volume was evaluated by converting the adsorption volume of nitrogen at relative pressure 0.976 to equivalent liquid volume of the adsorbate. Pore size distributions were determined from the adsorption branches of the isotherms using nonlocal density functional theory (NLDFT) model. The Fourier transform infrared spectroscopy (FTIR) spectra were measured by a Bruker Tensor 27 spectrometer with the KBr pellet technique ranging from 400 to 4000 cm$^{-1}$. Scanning electron microscopy (SEM) images were obtained on a FEI Quanta 200 scanning electron microscope at an accelerating voltage of 20 kV. A thin gold film was sputtered on the samples before SEM measurements. The elemental composition of the optimal HPFCM was determined from energy dispersive X-ray (EDX) analysis attached with SEM. Transmission electron microscopic (TEM) images were conducted on a JEOL JEM-2100 microscope operated at 200 kV. Samples were first dispersed in ethanol and then collected using carbon-film-covered copper grids for analysis. Elemental analyses (C, H, N) were done on an Elementar Vario EL III microanalyzer.

2.8. Surface acidity/basicity and zeta potential measurement

The surface acidity was estimated by mixing 0.20 g of HPFCMs-5-1-800 with 25 mL of 0.05 M NaOH solution in a closed flask, and agitating for 48 h at room temperature. The suspension was decanted, and the remaining NaOH was titrated with 0.05 M HCl. The surface basicity was measured by titration with 0.05 M NaOH after incubation 0.20 g of sorbent with 0.05 M HCl.

The point of zero charge (pH$_{pzc}$) was measured according to the reference (Foo and Hameed, 2012). Briefly, the HPFCMs-5-1-800 (0.15 g) was added into the 50 mL 0.1 M KNO$_3$ solution by adjusting the pH values between 2 and 12 with 1 M HCl or 1 M NaOH, and the final pH was measured after 48 h under agitation in triplicate. The difference between the initial (pH$_0$) and final pH (pH$_f$) values ($\Delta$pH = pH$_f$ – pH$_0$) was plotted against the pH$_0$. The pH$_{pzc}$ was obtained from the point of intersection of the resulting curve with abscissa ($\Delta$pH = 0).

3. Results and discussion

3.1. Optimization of fabrication conditions and environmental effects on adsorption

3.1.1. Effect of various treatment ways for BP on adsorption

The treatment ways for BP is a crucial factor for the achievement of the highest adsorption capacity, reducing the cost of sample preparation. The BP was modified via different methods, whereas adsorption experimental conditions were held constant in set of experiments. As shown in Fig. 2, the means of various disposing resulted in a completely different products, especially the BP with F127 and aluminium nitrate co-processing appeared a highest adsorption capacity and remove efficiency of MB. This possibly ascribed to the synergistic effect of self-assembly process of F127 and Al-based MOF-like precursor, which makes the as-obtained HPFCM have more developed three-dimensional porous network and more functional groups, thereby strongly adsorption capacity of MB.

3.1.2. Effect of concentration of aluminum nitrate solution on adsorption

Concentration of metal ions is an important parameter to obtain high quality Al-based MOF-like composite and further used for achieving highly porous carbon. As shown in Fig. 3a, with the concentrations (from 0 to 1.0 M) of aluminum nitrate gradually increased, the adsorptive capacities and remove efficiencies of MB showed regular enhancement from 136 to 265 mg g$^{-1}$ and 45.33% to 83.33%, respectively. Beyond this value, further increase in concentrations presented a gradual decrease of adsorptive capacity and remove efficiency of MB. It could be mainly attributed to the dispersed Al species were aggregated to form larger Al$_2$O$_3$ matrix and further led to the porous collapse of carbon after carbonization and 20 wt% HF treatment.

3.1.3. Effect of impregnation mass ratio of Al-based MOF-like to F127 on adsorption

It can be seen from Fig. 3b that the different impregnation mass ratios of Al-based MOF-like to F127 markedly affected the adsorptive performance of HPFCM. The adsorptive capacities and remove
efficiencies of MB initially increased and then declined with increasing mass ratios of Al-based MOF-like to F127. It could be attributed to the superfluous F127 (<5.0) interacted with Al-based MOF-like precursor induced overloaded combustion/decomposition of biopolymer during carbonization process leaving a low purity carbon. As the mass ratio was further increased, the adsorptive capacity and remove efficiency became more and more poor because of the optimal synergistic effect of Al-based MOF-like and F127 was not achieved, which resulted in the pore structure was not adequately tuned or expanded under the condition of lower content of F127 (>5.0). Notably, the optimal impregnation mass ratio of Al-based MOF-like composite to F127 was verified as 5.0.

3.1.4. Effect of carbonization temperature on adsorption
Carbonization temperature not only influenced the carbon textures but also affected the adsorption properties of MB. As shown
in Fig. 3c, the adsorption uptake of MB was only 198.3 mg g⁻¹ under the carbonization temperature level of 400 °C, which is mainly due to the pore structure was not adequately formed. Enhancing carbonization temperature from 500 to 800 °C showed a drastic increase in adsorption capacity, possibly ascribed to the high temperature promote the expansion of carbon networks. However, the adsorption capacity and remove efficiency decreased progressively at higher carbonization temperature levels of 900 and 1000 °C. This fact most likely ascribed to the sintering effect, which largely destroyed the pore walls between adjacent pores (Hu et al., 2012). Furthermore, over-temperature might produce local heating, leading to break down the active groups and collapse of the carbon framework and further resulting in reduced accessibility of carbon active sites. Thus, the optimal carbonization temperature was inferred as 800 °C.

3.1.5. Effect of initial solution pH and contact temperature on adsorption

Solution pH affects adsorption by regulating the adsorbents surface charge as well as degree of ionization of adsorbates present in the solution (Foo and Hameed, 2012). It is clear from Fig. 3d, that the adsorption capacity and remove efficiency of MB gradually enhanced from 74.0 mg g⁻¹ (16.4%) to 444.6 mg g⁻¹ (98.8%) with increasing solution pH values from 2 to 12. The protonation of MB and H₂O⁻ ions competing with dye cations for adsorption sites lead to lower adsorption at strong acidity. While the number of negatively charged sites increase and the formation of an electric double layer change the polarity of adsorbents in the basic medium, which favors the adsorption of MB cations. This fact could be further described by the pHZPC. The adsorbents with positive surface reacted as the solution pH < pHZPC (5.8, Fig. S1) and with negative surface reacted as the solution pH > pHZPC. The negative charge density of adsorbent surface enhanced with pH further increased, consequently the dye uptake capacity raised.

The temperature is a driving force for the adsorption process. Higher temperature is benefit to thermal and mass transfer and the optimal contact temperature was found to be over 60 °C (Fig. 3e). In view of achieving a low-cost, environmentally friendly and energy-saving wastewater treatment process, the ambient temperature condition is still eagerly welcomed.

3.1.6. Effects of initial concentration and contact time on adsorption

To investigate the effects of initial dye concentration and contact time on the adsorption process, seven initial MB concentrations were selected and sampled at different time intervals. The result showed that the adsorption process increased sharply at the initial stage (Fig. 3f), indicating the availability of readily accessible sites. Higher qₑ values were observed in higher initial dye concentration (350 mg L⁻¹), which might be attribute to that dye concentration provided an important driving force to overcome the mass transfer resistance between HPFCMs-5-1-800 and aqueous solutions.

In addition, it was obviously different time to attain the equilibrium for different initial dye concentrations. Higher initial dye concentration meant longer time to reach equilibrium (Fig. 3f). Owning to the sorption sites on the surface of HPFCMs-5-1-800 were not sufficient to attach most of the MB molecules in solutions and part of the unattached molecules needed to penetrate the boundary layer on the surface and entered into the HPFCMs-5-1-800 particles through intraparticle diffusion (i.e., rate-limiting step) at higher initial dye concentrations. This result was similar to many reported studies (Feng et al., 2012; Mahmoud et al., 2012; Somasekhar Reddy et al., 2012).

3.2. Adsorption isotherm

Adsorption isotherm was usually applied to describe the interaction between the adsorbates and the carbonaceous adsorbent. The correlation of equilibrium data is essential for practical design and operation of adsorption systems. In current study, a comparison of linear and non-linear Langmuir, Freundlich, Temkin, Langmuir–Freundlich and Redlich–Peterson isotherm models were fitted to analyze the equilibrium data. The Langmuir constants varied for different forms of linear Langmuir equations (Table S2 and Fig. S2), indicating the mathematical complexities associated with linear method in estimating the isotherm parameters. However, nonlinear method by maximizing the respective coefficient of determination between experimental data and the isotherms could avoid such drawbacks of linearization. Compared with linear and non-linear Langmuir isotherm models, the determined correlation coefficient of Freundlich model was less satisfactory (R² = 0.826) (Table S2 and Fig. S3). In addition, the Langmuir–Freundlich constant (n = 0.996) and Redlich–Peterson constant (g = 0.998) obtained respectively are close to 1 (Table S2), further indicating the closeness of the model to the Langmuir isotherm (Manos and Kanatzidis, 2012). Thus, the Freundlich isotherm model did not fit well with the experimental data suggesting its inapplicability to describe these isotherm data. Generally, the Freundlich isotherm model assumes a multilayer adsorption that occurs on a heterogeneous surface, and the heat of adsorption is not uniform between the molecules that adsorbs onto the adsorbent surface. Obviously, the adsorption takes place on homogenous adsorption sites, with each molecule possessing constant enthalpies and sorption activation energy. The Langmuir parameters can be used to predict affinity between the adsorbate and the adsorbent using the dimensionless separation factor (Rₛ), given by Eq. (13):

\[
R_s = \frac{1}{1 + b\frac{C_0}{C}}
\]

where Rₛ is the dimensionless separation factor, C₀ is the initial concentration of the adsorbate (mg L⁻¹), and b is the Langmuir constant (L mg⁻¹). The Rₛ can be used to verify if the adsorption in the system studied is unfavorable (Rₛ > 1), linear (Rₛ = 1), favorable (0 < Rₛ < 1), or irreversible (Rₛ = 0) (Vargas et al., 2011). In the concentration range studied (50–350 mg L⁻¹), the values between 2.48 × 10⁻² and 3.62 × 10⁻³ indicating favorable adsorption in this system. The values of Rₛ decreased with an increase in the initial concentration, declaring that the adsorption is more favorable at high concentrations (Fig. S4). It can be concluded that the HPFCMs-5-1-800 have a maximum monolayer adsorption capacity of 385.12 mg g⁻¹, which is far more than the DCBP (98 mg g⁻¹), commercial activated carbon (9.8–238 mg g⁻¹) (Bestani et al., 2008; Manos and Kanatzidis, 2007; Basava Rao and Mohan Rao, 2006) and other low-cost biosorbents (Table S3). The higher dye adsorption capacity could be attributed to the presence of more functional groups (e.g., –COOH) on the surface and developed 3D porous frameworks of HPFCMs-5-1-800. Thus, it is noteworthy that considerable changes in the surface and structure properties of as-made carbon material were achieved by the free-standing template way.

3.3. Kinetics of the adsorption process

3.3.1. Kinetics modeling

Three pseudo kinetic models corresponding to the regression curves (Fig. 4) and relevant parameters were fitted and calculated, respectively. As a result, the regression correlation coefficients of pseudo-second-order kinetic model (R² > 0.99) were significantly higher than that of the pseudo-first-order kinetic model (R² < 0.96) for all MB concentrations, and with the lowest
normalized standard deviation ($\Delta q$), which ranged between 0.53% and 5.16% (Table S4 and Fig. 4). Notably, the adsorption of MB onto HPFCMs-5-1-800 obeyed pseudo-second-order kinetic model very well. It meant that chemisorption was the rate controlling step over the whole range of adsorption. It can also be found that the $q_{e,calc}$ values increased with the increasing of initial dye concentrations and were very close to the experimental $q_e$ values; but the rate constants ($k_2$ values) decreased with the increasing of initial concentrations. This mainly ascribed to that the competition for the surface sorption sites would be high at higher MB concentrations, which would consequently lead to a comparatively low rate constant (Feng et al., 2012). Moreover, the Elovich kinetic model fitted the experimental data well (Table S4 and Fig. 4), and further validated that the rate-limiting step was very close to chemisorption, which involved valency forces through electrons sharing between the hydrophilic edges sites of HPFCMs-5-1-800 and dye cations.

### 3.3.2. Diffusion model

For a solid–liquid adsorption system, the solute transfer is usually characterized by boundary layer diffusion, intraparticle diffusion or both, and the controlling step of the adsorption could be intraparticle and/or external diffusion process (Dawood and Sen, 2012). To understand the adsorption mechanism involved in the adsorption of MB onto HPFCMs-5-1-800, the kinetic data were analyzed by intraparticle diffusion model and Boyd’s model.

The result showed that the adsorption process could be divided into three steps (Fig. 5). The first region within the first 15–60 min was the instantaneous adsorption or external surface adsorption, representing the mass transfer of adsorbate molecules from the bulk solution to the adsorbent surface. Because of the existence of some functional groups on the external surface of HPFCMs-5-1-800 (especially $\mbox{--COO}^-$ groups confirmed by FTIR in Fig. S5), the rapid attachment was probably due to the strong electrostatic attraction between MB$^+$ and $\mbox{--COO}^-$. Thereafter, the second step within about 120 min could be attributed to the intraparticle diffusion process, which was the rate limiting step. Though the sorption sites were not sufficient to attach most of the MB molecules after the first rapid stage, the concentration gradient between the solution and the solid inner surface (i.e., pores or caves) was still enough to drive the adsorption. The third step was the equilibrium stage.

The C value of Eq. (8) represents the boundary layer effect. Higher C values indicate greater contributions of the surface sorption in the rate-controlling step. The C values were increased with the increase of initial dye concentrations (Table S5), demonstrating bigger boundary layer thickness at higher initial dye concentrations. Likewise, the $k_{pi}$ values were increased with the increasing dye concentrations, meaning the adsorption driving force stronger and consequently an enhanced MB diffusion rate. According to the intraparticle diffusion model, if intraparticle diffusion occurs, the $q_t$ versus $t^{0.5}$ will be linear, and if intraparticle diffusion is the sole rate limiting step, the regression curve will pass through the origin. It can be seen from Fig. 5a, the curves for all seven initial dye concentrations, if extended, did not pass through the origin. It meant some other mechanisms along with intraparticle diffusion were involved in the process (Feng et al., 2012). According to the Boyd’s model, if the plot $B_t$ versus $t$ passes through the origin, pore diffusion is the rate-limiting step. Conversely, the adsorption process is film diffusion controlled. As shown in Fig. 5b, the plots were linear only at the initial period and did not pass through the origin. It meant the rate-limiting mechanism was external mass transfer and then intraparticle diffusion. Thus it was ascertained that the adsorption of MB onto HPFCMs-5-1-800 was mainly governed by film diffusion controlled mechanism (Foo and Hameed, 2012).

To further visually observe the rate of adsorption MB, two initial MB concentrations (25 and 60 mg L$^{-1}$) were selected and tested at identical conditions (Fig. S6). The result obviously showed that the HPFCMs-5-1-800 had a very fast adsorption rate for MB.
3.4. Adsorption thermodynamic

Thermodynamics parameters such as enthalpy change ($\Delta H$), Gibbs free energy change ($\Delta G$) and entropy change ($\Delta S$) provide an insight into the mechanism and adsorption behavior of an isolated system. In this study, the $\Delta H$ value was calculated as 2.95 kJ mol$^{-1}$ (Fig. S7), revealing endothermic nature of the adsorption process. Thus increasing temperature would be conducive to the reinforcement of dye uptake due to enhancing of adsorptive forces between the active sites and the dye species, and between the adjacent dye molecules on the adsorbed phase. Negative $\Delta G$ ($0.118, -0.356, -0.831$ and $-1.305$ kJ mol$^{-1}$ at 303, 313, 323 and 333 K, respectively) at high temperature revealed spontaneous nature of adsorption. Meanwhile, positive $\Delta S$ (47.38 J mol$^{-1}$ K$^{-1}$) illustrated the affinity of HPFCMs-5-1-800 and increasing randomness at the solid-solution interface during fixation of MB onto the active sites of HPFCMs-5-1-800. In general, the adsorption process is classified to be film-diffusion controlled as $E_a$ below 16 kJ mol$^{-1}$, particle-diffusion controlled as $E_a$ between 16–40 kJ mol$^{-1}$, and chemical-reaction controlled as $E_a$ over 40 kJ mol$^{-1}$ (Boyd and Soldano, 1953). The $E_a$ value of 2.09 kJ mol$^{-1}$ determined in this work further validated that the adsorption of the anionic dyes was a film-diffusion-controlled process, which is consistent with the Boyd model mechanism.

3.5. Desorption and regeneration studies

Desorption study is usually applied to further elucidate the adsorption mechanism and to recover the depleted adsorbent (Feng et al., 2012). If the attached dye molecule could be desorbed by deionized water, the adsorption should be usually dominated by weak bonds; otherwise, if it could be desorbed by acid, the adsorption should be dominated by ion exchange (Chen et al., 2011). Compared with the other three solvents, the hydrochloric acid solution (0.01 M) was the most efficient strippant for adsorbed MB on HPFCMs-5-1-800 (ca. 75%, Fig. S8a). It implies that ion change was the dominating mechanism in the adsorption process. The regeneration study demonstrated that the dye removal efficiency of ca. 64.4% could be retained after seven adsorption-desorption cycles (Fig. S8b and c).

3.6. Textural and surface characterization

The detailed morphology and microstructure of the DCBP and HPFCMs-5-1-800 were characterized by SEM and TEM analyses. The surface of DCBP almost had no any porous structure (Fig. S9a), while HPFCMs-5-1-800 exhibited a well pronounced porosity, with a series of irregular cavities distributed around the surface (Fig. S9b). The TEM image showed that the DCBP material was thin planar 2D structure (Fig. S9c). However, lots of distinctly 3D porous textures were observed of HPFCMs-5-1-800 after the chemical treatment using 20 wt% HF (Fig. S9d), which could provide a fast mass transfer pathway through the mesostructure.

Nitrogen sorption isotherms could provide qualitative information on the porous structure of carbonaceous adsorbents. As shown in Fig. 6a, the isotherm featured an intermediate between types I and II isotherms of the International Union of Pure and Applied Chemistry (IUPAC) classification, indicating the existence of...
different pore sizes from micro-to macropores. The steep increase in the adsorbed volume at low relative pressure was related with the presence of micropores, the desorption hysteresis at medium relative pressure revealed the existence of developed mesopores, and the almost vertical tails at a relative pressure near to 1.0 denoted the presence of macroporosity (Liu et al., 2008). It is clear seen from Table 1 data and Fig. 6b that the BET surface area and total pore volume of HPFCMs-5-1-800 were greatly improved compared to DCBP. The pore size distributions (Fig. 6c) ascertained by NLDFT model showed the sharpest peak occurred at pore diameters between 0.5 and 3.0 nm, with an average pore size of 3.55 nm for HPFCMs-5-1-800. This finding revealed that the vast majority of the pores fell into the range of mesopore for HPFCMs-5-1-800, while the DCBP only composed of micropores.

These obvious difference could be interpreted as multiple functional groups (i.e., –OH and –COOH, etc.) of BP could coordinate with Al ions into Al-based MOF-like composites and the composites could be used as a free-standing template for structuring HPFCMs. In addition, the strong interaction (e.g., hydrogen-bonding) between block-copolymer PEO-chains of F127 and OH-groups of Al-based MOF-like precursor made the F127 molecules readily penetrating into the Al-based MOF-like pore channels during the solvent evaporation induced self-assembly process. The resulting Al-based MOF-like-F127 could be easily transformed into carbonaceous chains with different pore structures at high temperature.

3.7. Elemental, functional, and surface chemistry

The chemical composition of DCBP and HPFCMs-5-1-800 was listed in Table 1. It can be markedly found that the contents of carbon, hydrogen, and nitrogen were significant improvements by the free-standing template way treatment. This was attributed to the partial decomposition of volatiles compounds and degradation of organic substances under the premise of Al-based MOF-like precursor interaction with F127. In addition, the energy dispersive spectrum (EDS) analysis obtained similar results (Fig. S10) as well.

The FTIR spectra of HPFCMs-5-1-800 had more peaks compared to DCBP (Fig. S5). Apart from the broad band at 3410 cm⁻¹ related to OH groups, 1630 cm⁻¹ assigned to COO⁻ anion stretching, some new peaks were found at 856, 750, and 683 cm⁻¹, which should be attributed to the out-of-plane N–H deformation vibration of the aromatic compounds (between 950 and 650 cm⁻¹) (Hao et al., 2010). It could be found that many new peaks were introduced into the FTIR spectrum of HPFCMs-5-1-800 after MB adsorption (Fig. S11). These new peaks at 1730–1800 and 1000–1589 cm⁻¹ were in accordance with the peaks of MB, which indicated that a large number of MB molecules had been adsorbed onto the surface or pore channels of HPFCMs-5-1-800. However, a few absorption bands clearly vanished at 1630, 956, 869 804 and 663 cm⁻¹. This fact most likely ascribed to complete encapsulation of the HPFCMs-5-1-800 surface with the MB molecules.

Surface acidity and basicity are important criteria describing the surface chemistry of carbon adsorbents. The results showed that HPFCMs-5-1-800 exhibited an acidic character with a surface acidity of 2.14 mmol g⁻¹ and surface basicity of 0.52 mmol g⁻¹ (Table 1). The acidic nature of HPFCMs-5-1-800 was derived primarily from carboxylic, anhydrides, lactones and phenol-containing groups. However, the surface basicity was associated with the presence of oxygen-free Lewis sites, carboxyls, pyrone and chromene type structures (Foo and Hameed, 2012).

4. Conclusion

This investigation demonstrated that the treatment of BP with a free-standing template way resulted in developed pore structures and abundant functional groups, and tremendous improvement of adsorption capacity. The maximum monolayer adsorption capacity of HPFCMs-5-1-800 was up to 385.12 mg g⁻¹ of MB. The free-standing template route would be an efficient and environmentally-friendly strategy for large-scale fabrication of HPFCMs, and maximum development and utilization of abundant biomass waste toward multi-purpose applications.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (21275098), Doctor Base Foundation of Chinese Ministry of Education (20110202110005) and the Fundamental Research Funds for the Central Universities (GK201304003).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.12.034.

References


Table 1

<table>
<thead>
<tr>
<th>Properties and element</th>
<th>DCBP</th>
<th>HPFCMs-5-1-800</th>
</tr>
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<tbody>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>99.5</td>
<td>2086</td>
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<tr>
<td>Total pore volume (cc g⁻¹)</td>
<td>0.03</td>
<td>1.65</td>
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<tr>
<td>Mesopore volume (cc g⁻¹)</td>
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<tr>
<td>Average pore size (nm)</td>
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<td>Carbon (wt%)</td>
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<tr>
<td>Nitrogen (wt%)</td>
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<tr>
<td>Hydrogen (wt%)</td>
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</tr>
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<td>Acidity (mmol g⁻¹)</td>
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<td>2.137</td>
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<td>Basicity (mmol g⁻¹)</td>
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</table>


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