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Preparation of activated carbon from edible fungi residue by microwave assisted K₂CO₃ activation—Application in reactive black 5 adsorption from aqueous solution

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ABSTRACT

Preparation of activated carbon from the edible fungi residue (EFR) by microwave assisted K_2CO_3 activation was studied. The optimum preparation conditions were as follows: radiation time of 16 min, K_2CO_3/EFR ratio of 0.8 and microwave power of 520 W. The iodine number, the amount of methylene blue adsorption and the yield of activated carbon prepared under optimum conditions were 732.74, 172.43 mg/g and 23.0%, respectively. The activated carbon was characterized by SEM, FT-IR, N_2 adsorption and pH_{ZPC} , and then they were used as adsorbent for removing reactive black 5 from aqueous solution. The highest removal efficiency of 100% could be achieved at the solution pH of 2.0, the adsorption efficiency descended with the increasing of pH and the optimum activated carbon dose was 8.75 g/L. The Langmuir isotherm well fit the adsorption process with the complete monolayer adsorption capacity of 19.6 mg/g and the equilibrium adsorption constant of 0.39 L/mg.

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1. Introduction

China is a major edible fungi producer in the world. According to statistics from China Edible Fungi Association (CEFA), the nationwide output of edible fungi reached 18.3 million tons in 2008, accounting for 70% of the worldwide output. Given the average biological efficiency of edible fungi is 40%, a corresponding annual production of edible fungi residues (EFRs) was 45.7 million tons. These EFRs should get safe and environment friendly treatment and disposal. Unfortunately, they were stacked or discarded in the field at random, resulting in germ's breeding, disease dissemination and threatening edible fungi production bases nearby. Therefore, how to deal with these EFRs has already become a severe problem to date.

As is well known, agro-industrial wastes (such as straw and sawdust) are commonly used as culture medium ingredients on the cultivation of edible fungi. Cellulose, hemicellulose and lignin in these ingredients were degraded at different degrees during the growth process of edible fungi. However, a considerable proportion of them still remained in the culture medium waste (i.e., EFRs). In theory, any botanic material containing cellulose, hemicellulose or lignin is possible used as a precursor of activated carbon (FitzPatrick et al., 2010). Therefore, EFRs, as a kind of second-hand residues, should also have the potential to be raw materials for preparation of activated carbon. In recent years,

preparation of activated carbon from agro-industrial residues has been intensively researched by domestic and foreign scholars. These residues included cotton stalk (Deng et al., 2009, 2010a,b), tobacco stem (Li et al., 2008), rice hull (Lv et al., 2009), bamboo (Liu et al., 2010), waste tea (Auta and Hameed, 2011; Yagmur et al., 2008), coconut shell (Yang et al., 2010), oil palm fiber (Foo and Hameed, 2011), straw (Ioannidou and Zabaniotou, 2007), durian shell (Chandra et al., 2007), wood (Wang et al., 2009) and so on. Nevertheless, preparation of activated carbon from EFRs has never been reported.

In principle, preparation methods of activated carbon can be divided into two categories: physical activation and chemical activation. Compared with physical activation, chemical activation has the following advantages: low activated temperature, simple operation, short activated time and low energy consumption (Deng et al., 2009). KOH, K₂CO₃, H₃PO₄ and ZnCl₂ are commonly used as activated reagents. Among these activated reagents, K₂CO₃ is widely used since it is nontoxic (can be used as food additives), easy to be removed by water washing and it has weak corrosion, good operating conditions. What's more, K₂CO₃ resulted in high surface area and high yield (Li et al., 2008).

Referring to heating methods for preparing activated carbon, microwave (MW) heating technology has recently gained intensive attention. The main difference between MW devices and conventional heating systems is in the way the heat is generated. In the MW device, the microwaves supply energy directly to the precursors. The microwave energy is not transferred by conduction or convection as in the conventional heating, but is readily transformed

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into heat inside the particles by dipole rotation and ionic conduction. The main advantage of using MW heating is that the treatment time as well as energy consumption can be considerably reduced. Secondly, the consumption of gases used in the treatment can also be reduced. In addition, precise control of activated temperature using MW heating ensured the high quality of the prepared activated carbon (Li et al., 2008; Yagmur et al., 2008).

In present work, activated carbon was prepared from EFRs by microwave assisted K_2CO_3 activation. Effects of the radiation time, impregnation ratio of K_2CO_3 to EFR, radiation power on the adsorption capacity and yield of the activated carbon (denoted as EFR-AC) were researched to determine the optimum preparation conditions. At the same time, the surface area, pore structure and chemical functional groups of EFRs and EFR-AC were characterized by scanning electron microscopy (SEM), nitrogen adsorption isotherm and Fourier transformed infra-red spectrum (FT-IR), laying a solid theoretical basis for the preparation technology. In addition, application of EFR-AC in adsorption of reactive black 5 from aqueous solution was studied. This work realized a win–wins goal, i.e., the elimination of pollution derived from EFRs, the reduction of production cost of activated carbon and pollution control by use of EFR-AC, and therefore opened up a promising way for the resource utilization of EFRs.

2. Methods

2.1. Materials

EFRs were collected from a local edible fungi production base in Ya'an city, Sichuan Province, China. It was washed with distilled water to remove dust, and then naturally air-dried. Prior to the experiments, the raw material was crushed and sieved to 550–830 μ m. The proximate analysis results of the air-dried EFRs were as follows: moisture 6.02%, volatile 68.55%, fixed carbon 11.86%, ash 13.57%. The contents of cellulose and lignin in the air-dried EFRs were 7.12% and 20.69%, respectively. The chemical element analysis results were as follows: C 38.74%, H 5.78%, N 1.36% and S < 0.5%. K_2CO_3 with analytical grade was used as activating reagent. High purity nitrogen (99.99%) was used to provide the inert atmosphere. The microwave heating system is the same as that described elsewhere (Li et al., 2008).

2.2. Preparation of activated carbon

In every batch of experiment, 10.0 g EFR was added into different concentrations of K2CO3 solutions, which were prepared by adding 6, 8, 10, 12, 14 and 16 g solid K₂CO₃ into 50 mL distilled water, respectively. After mixing, the slurry was placed in a constant temperature unit for 20 h of impregnation at 293 K, and then dried at 393 K overnight. The dried material was transferred into a quartz tube fixed in the chamber of the microwave oven, nitrogen gas at a pre-set flow rate was used to purge any air in the chamber before the start of the MW heating process and it continued to flow through the chamber during the subsequent process. The MW activation experiments were carried out at different power levels (360, 400, 440, 520 and 560 W) or at different radiation time levels (10, 12, 14, 16, 18 min). After activation, the cooled samples were washed with 50% (V/V) HCl and distilled water in turn until pH of the filtrate was nearly 7.0, then dried at 393 K for 2 h to obtain EFR-AC finally. The yield (Y) was calculated by equation:

$$Y = M_0/M \times 100\% \tag{1}$$

where M is the weight of the activated carbon and M_0 is the weight of the naturally air-dried EFRs.

2.3. Characterization of activated carbon

Adsorptive capacity of EFR-AC was measured by using iodine and methylene blue (MB) as adsorbates. Iodine and MB were considered as probe molecules for assessing the adsorption capacity of adsorbent for solutes of molecular sizes <1.0 and >1.5 nm, respectively (Deng et al., 2010a). The iodine number was determined at 298 K based on the Standard Test Method (GB/T12496.8-1999, testing standard of activated carbon in China). The adsorption capacity of MB was determined according to GB/T12496.10-1999. The concentration of MB was determined using a double beam UV-vis spectrophotometer (Hitachi Co, Japan) at 665 nm.

The surface physical morphology of EFR and EFR-AC was identified by using SEM technique. A S-4800 (Hitachi Co., Japan) with a 10 kV accelerating voltage was used to characterize the morphology of EFR-AC which was dried overnight at approximately 378 K under vacuum before SEM analysis. The N₂ adsorptiondesorption isotherms were measured with an accelerated surface area and porosimetry system (Autosorb 1, Quatachrome) in order to determine the surface areas and pore volumes. Prior to the measurements, the samples were outgassed at 423 K under nitrogen flow for 4 h. The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature (77 K) and was measured over a relative pressure (P/P_0) range from approximately 10^{-6} to 1. The BET surface area was calculated using the BET (Brunauer, Emmett and Teller) equation from the selected N₂ adsorption data within the range of relative pressure, P/P_0 , from 0.1 to 0.3 (Gregg and Sing, 1982). The external surface area, micropore volume and micropore area were calculated by t-plot method. The total pore volume was estimated by converting the amount of N₂ gas adsorbed (expressed in mL/g STP) at a relative pressure of 0.99 to liquid volume of the nitrogen adsorbate (Guo and Lua, 2000). The mesopore volume was estimated by subtracting the micropore volume from the total volume. The pore size distribution in the micropore range was obtained using the Horvath-Kawazoe (HK) method (Ustinov and Do. 2002). Meanwhile, the whole pore size distribution was computed by the DFT method by minimizing the grand potential as a function of the fluid density profile (Ismadji and Bhatia, 2001; Kowalczyk et al., 2003; McCallum et al., 1999; Valladares et al., 1998).

The functional groups on the surface of EFR and EFR-AC were identified by using FT-IR technique. Analytical pure KBr presented as single crystal fragments was ground into 200-mesh powders in the agate mortar and then stored in a desiccator for future use. About 2 mg of dried 200-mesh EFR or EFR-AC sample was mixed with 200 mg of KBr powders and then the mixture was carefully ground and well mixed. Subsequently, the mixture was dried in an infrared dryer for at least 20 min to eliminate the moisture absorption by KBr. Thereafter, the dried mixture was compressed into wafer. Blank experiment with only the KBr powders was carried out following the same procedures. FT-IR spectra were recorded by AVATAR 360 (Thermo Nicolet Co., USA) FT-IR spectrophotometer.

The zero surface charge characteristic of EFR-AC was determined by using the solid addition method (Kumar et al., 2008). The experiments were conducted in a series of 50-mL glass-stoppered flasks. Each flask was filled with 20 mL of different initial pH KNO $_3$ solutions and 0.20 g of EFR-AC. The pH values of the KNO $_3$ solutions were adjusted between 2 and 12 by adding either 0.1 M HCl or 0.1 M NaOH. The suspensions were then sealed and shaken for 36 h at 160 rpm. The final pH values of the supernatant liquid were recorded. The difference between the initial pH (pH $_0$) and final pH (pH $_f$) values (pH = pH $_0$ -pH $_f$) was plotted against the pH $_0$. The point of intersection of the resulting curve with abscissa, where pH was zero, gave the pH $_{PZC}$.

2.4. Adsorption of reactive black 5

A commercial textile MB was purchased from Tian jin Chemicals & Reagent Corp., China. Reactive black 5 was dissolved in double distilled water to prepare the stock solution (200 mg/L). And the pH of the working solutions was adjusted to desired values with 0.1 M HCl or 0.1 M NaOH. Experimental solutions of other desired initial concentrations (80, 100, 120, 140, 160, 180 mg/L) were obtained by successive dilution. Twenty-five milliliters of reactive black 5 solution and 0.175 g EFR-AC were added into a 50 mL glass-stoppered flask on a mechanical shaker (160 rpm) at 298 K for 2 h. Then the absorbance of supernatant solution was measured at 597 nm to determine the residual concentration (Chang et al., 2010). Blank runs with only the adsorbent in 25 mL of double distilled water and 25 mL of dye solution without any adsorbent, were conducted simultaneously at similar conditions.

3. Results and discussion

The experiments were repeated for three times to confirm the repeatability of the experiments and the authenticity of the generated data. Each experimental point is the average of three independent runs and all the results were reproducible with ±4% error limit.

3.1. Preparation of EFR-AC

3.1.1. Effects of microwave radiation time on the adsorption capacity and yield of EFR-AC

Effects of microwave radiation time on adsorption capacity and the yield of EFR-AC were evaluated under the experimental conditions of microwave power 520 W and K₂CO₃/EFR ratio 1.0. The results were shown in Fig. 1(a). It showed that accompanying the increase of MW radiation time from 10 to 16 min, the iodine number of EFR-AC was increased from 509.87 to 654.83 mg/g and the amount of MB adsorption of EFR-AC was increased from 102.79 to 169.54 mg/g. However, when the MW radiation time was prolonged from 16 to 18 min, the iodine number and the amount of MB adsorption of EFR-AC decreased to 567.79 and 118.12 mg/g, respectively. As regards the yield of EFR-AC, it was always gradually decreasing with the prolongation of MW radiation time. This process could be explained as follow: the activation degree was much more dependent on the MW radiation time. With the extending of MW radiation time, much more active sites and pores were formed on the surface of EFR-AC samples. Therefore, the adsorption capacity of EFR-AC would be improved with the prolongation of MW radiation time within low level range. However, once MW radiation time was beyond a certain value, the pores of carbon would be burnt off by MW heating, which would lessen the iodine number, the amount of MB adsorption and the yield of activated carbon (Deng et al., 2009; Li et al., 2008). Taking the adsorption capacity and the yield of EFR-AC into combined considerations, MW radiation time of 16 min was favorable.

3.1.2. Effects of K_2CO_3/EFR ratios on the adsorption capacity and yield of EFR-AC

Effects of K₂CO₃/EFR ratios on the adsorption capacity and yield of EFR-AC were researched under the experimental conditions of MW power 520 W and MW radiation time 16 min. The results were shown in Fig. 1(b). With the increasing of K₂CO₃/EFR ratio from 0.6 to 0.8, the iodine number and the amount of MB adsorption of EFR-AC increased and reached peak values (i.e., 514.68 and 103.45 mg/g, respectively) at K₂CO₃/EFR ratio of 0.8. Thereafter, both the two indexes declined with further increase in K₂CO₃/EFR ratios. This could be explained as follow: decomposition of K₂CO₃ under MW heating produced K₂O and CO₂, giving rise to the formation of carbon pores. Meanwhile, K₂CO₃ and K₂O were reduced by carbons to form K and

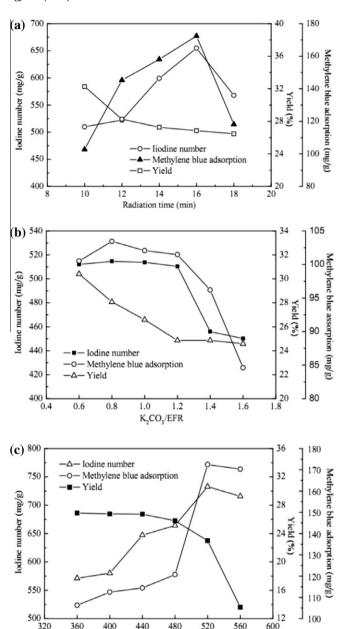


Fig. 1. (a) Effect of radiation time on yield and adsorption capacity of EFR-AC (MW radiation power = 520 W, $K_2\text{CO}_3/\text{EFR}$ ratio = 1); (b) effect of $K_2\text{CO}_3/\text{EFR}$ ratio on yield and adsorption capacity of EFR-AC (MW radiation power = 520 W, radiation time = 16 min); (c) effect of MW radiation power on yield and adsorption capacity of EFR-AC (MW radiation time = 16 min, $K_2\text{CO}_3/\text{EFR}$ ratio = 1).

Radiation power (W)

 CO_2 and therefore more pores were formed. Furthermore, when activation temperature reached the boiling point of potassium (1035 K), potassium would diffuse into the layer of carbons, also causing the formation of pores of activated carbons (Deng et al., 2010a; Li et al., 2008). With increasing of the K_2CO_3 /EFR ratio within low level range, more pores would be produced. However, once the ratio exceeded a certain value, the pores would be widened and burnt off (Li et al., 2008). As a whole, the adsorption capacity of activated carbons would increase to a certain value and then decrease with the increasing of K_2CO_3 /EFR ratios.

3.1.3. Effects of MW radiation power on the adsorption capacity and yield of EFR-AC $\,$

Under the preparation conditions of MW radiation time 9 min and K₂CO₃/EFR ratio 0.8, effects of MW radiation power on the

adsorption capacity and yield of activated carbon were studied. Fig. 1(c) showed that while increasing MW radiation power from 360 to 520 W. the iodine number of EFR-AC was increased from 571.37 to 732.74 mg/g and the amount of MB adsorption of EFR-AC was increased from 106.27 to 172.43 mg/g. When the MW radiation power was further increased from 520 to 560 W, the iodine number and the amount of MB adsorption of EFR-AC decreased. In terms of the yield, it decreased slightly with the increasing of MW radiation power from 360 to 480 W, and it decreased sharply when MW radiation power exceeded 520 W. The possible reason was that the higher energy was offered to the samples by increasing the power level, the more active sites and pores on them. When MW power reached a certain level, superfluous energy would burn a small quantity of carbon off and destroy the structure of pores (Deng et al., 2010a). Therefore, taking the adsorption capacity and the yield of EFR-AC into comprehensive considerations. MW radiation power level of 520 W was preferred.

3.1.4. Optimum experimental conditions to prepare the EFR-AC

From the discussions presented above, the optimum conditions to prepare the EFR-AC were as follows: the MW radiation time of 16 min, the K₂CO₃/EFR ratio of 0.8 and the MW power of 520 W. The iodine number, the amount of MB adsorption and the yield of the EFR-AC prepared under optimum conditions were 732.74, 172.43 mg/g and 23.0%, respectively. Though the iodine number and the amount of MB adsorption of the EFR-AC were somewhat less than that of the activated carbon prepared from cotton stalks, for which the iodine number and amount of MB adsorption were 972.92 and 193.50 mg/g, respectively (Deng et al., 2009), the amount of MB adsorption of EFR-AC was more than that of activated carbon prepared from peanut hulls (103.2 mg/g) (Girgis et al., 2002). Given the particularity of the EFR, the adsorption capacity of EFR-AC was acceptable and even satisfactory. The activated carbon prepared under optimum conditions was used in the characterization analysis and adsorption experiments.

3.2. Characterization of EFR-AC

3.2.1. SEM analysis of EFR and EFR-AC

SEM photographs of EFR and EFR-AC prepared under the optimum condition were presented in the Supplementary material. It can be seen from the micrographs that the external surface of the EFR-AC was full of pores compared with EFR. These pores formed during the activation process and accounted for the good adsorption capacity of EFR-AC.

3.2.2. Specific surface area and pore structural characterization analysis of EFR-AC

The N_2 adsorption and desorption isotherms obtained for the EFR-AC sample prepared under the optimum condition were shown in Fig. 2, it was found that the isotherm was more of type I character as defined by Union of Pure and Applied Chemistry (IU-PAC) classification, as reflected by its initial adsorption and flatter plateau region at higher relative pressure. After a sharp increase up to 0.1 of relative pressure, the isotherm showed a slow increment in the further adsorption at higher pressure. This suggested that the EFR-AC was characteristic of a narrow micropore size distribution. However, isotherms also displayed a hysteresis loop, indicating the presence of mesopores. The textural characteristics of EFR-AC could be further analyzed from nitrogen adsorption isotherm, and the results were presented in Table 1.

Pore size distribution (PSD) is a very important property of adsorbents because the difference in the pore size affects the adsorption capacity for molecules of different sizes and shapes, and also this is one of the criteria by which carbon adsorbents are

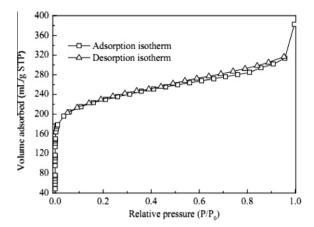


Fig. 2. Adsorption and desorption isotherms of EFR-AC prepared under optimum conditions

Table 1Textural characteristics of EFR-AC prepared under the optimum conditions.

Typical properties	
BET surface area (m ² /g)	683.76
External surface area (m ² /g)	227.50
Micropore surface area (m ² /g)	456.26
Total pore volume (mL/g)	0.591
Micropore volume (mL/g)	0.257
Mesopore volume (mL/g)	0.334
Average pore diameter (nm)	3.46

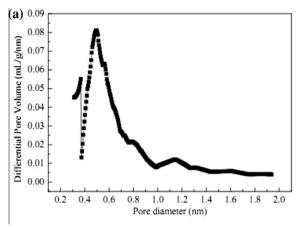
selected for a particular application. According to the classification adopted by IUPAC, adsorbent pores are classified into three groups: micropores (size < 2 nm), mesopores (2–50 nm), and macropores (>50 nm). Micropores can be further divided into ultramicropores (width less than 0.7 nm) and supermicropores (width from 0.7 to 2 nm).

The micropore size distribution for the activated carbon according to the HK method was shown in Fig. 3(a), in which micropores less than 2.0 nm were presented. The micropore size distribution is directly related to the adsorption capacity of activated carbon for small pollutant molecules. Fig. 3(a) exhibited a narrow micropore distribution occurred at range of 0.40-0.80 nm and showed that the vast majority of micropores were ultramicropores. From an adsorption free energy standpoint, compounds are preferentially adsorbed into pores that are similar in size to the adsorbate because of the greater number of contact points between the molecule and the adsorbent (Pelekani and Snoeyink, 1999). The estimated diameter of iodine molecule is 0.516 nm (Reid et al., 1987) and the size of MB molecule is $1.43 \times 0.61 \times 0.40 \text{ nm}^3$ (Pelekani and Snoeyink, 2000). Therefore, such micropores with size of 0.4-0.8 nm were partly accessible for iodine molecules, but were not accessible for MB molecules.

The whole pore size distribution was calculated by the DFT method and was shown in Fig. 3(b). The pore size distribution curve suggested a predominant micropore owing to the sharp increase of pore size distribution curve to pore diameter less than 2 nm, in good agreement with the HK results. As could be seen in Fig. 3(b), besides micropores, a reasonable quantity of mesopores in the range 2–5 nm formed in EFR-AC. Calculating from the data in Table 1, the micropore volume was around 43.5% of the total pore volume.

3.2.3. Function groups analysis of EFR and EFR-AC

The FT-IR spectra of EFR and EFR-AC were presented in the Supplementary material. It was observed that the absorbance bands had peaks at 3415.9, 2916.3, 2358.9, 2341.5, 1653.0 and



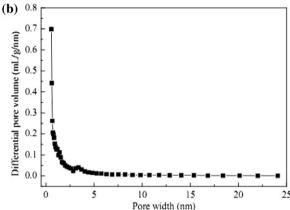


Fig. 3. (a) Micropore size distribution of EFR-AC prepared under optimum conditions by HK method; (b) pore size distribution of EFR-AC prepared under optimum conditions by DFT method.

1041.5 cm⁻¹. Most of these bands have been reported by other researchers for different carbon materials. The band at around 3415.9 cm⁻¹ could be assigned to the -OH stretching vibration mode of hydroxyl functional groups (Aguilar et al., 2003). The band located at about 2916.3 cm⁻¹ was attributed to the C-H symmetric and asymmetric vibration (Yang et al., 2010). The bands 2358.9 cm⁻¹ and 2341.5 cm⁻¹ were attributed to the C≡C stretching (Boonamnuayvitaya et al., 2005). The peak at 1653.0 cm⁻¹ may be ascribed to C=O stretching vibration of lignin-related conjugated carbonyl, and the peak at 1041.5 cm⁻¹ may be ascribed to C—O stretching vibration related with cellulose and hemicellulose. Compared the FT-IR spectra of EFR with that of EFR-AC, the characteristic peaks at 3415.9, 2916.3, 1653.0 and 1041.5 cm⁻¹ in the former no longer appeared in the latter, the peaks at 2358.9 and 2341.5 cm⁻¹ were weakened and the peaks at 1558.4 and $1220.9~\text{cm}^{-1}$ may be assigned to C=C and C-OH stretching vibration mode of phenolic hydroxyl groups. In general, function groups on the surface of EFR changed evidently during the process of MW assisted K₂CO₃ activation.

3.2.4. Zero point charge analysis of EFR-AC

The pH_{ZPC} , defined as the pH at which the adsorbent surface has net electrical neutrality, is a very important surface characteristic of an adsorbent. The pH_{ZPC} of EFR-AC was found to be as 5.23.

3.3. Adsorption of reactive black 5

3.3.1. Effect of EFR-AC dose on adsorption of reactive black 5

Under the preparation conditions of pH 7.0, C₀ 200 mg/L, and contact time 2 h, the effect of EFR-AC dose on the removal efficiency of reactive black 5 was indicated in Fig. 4(a). It was apparent

that the removal efficiency of reactive black 5 was increased rapidly with the increasing of EFR-AC dose from 2.5 to 8.75 g/L. The reason lay in that the number of available adsorption sites was increased by increasing the adsorbent dose (Garg et al., 2003). However, when EFR-AC dose further increased from 8.75 to 12.5 g/L, the removal efficiency of reactive black 5 did not increase any more. This phenomenon could be explained by the mutual screen among activated carbon particles for high addition amount (Zhang et al., 2007). In the case of large EFR-AC dose, some adsorption sites on activated carbon particles contacted with each other and became not available for the adsorption of reactive black 5 in the solution, which was described as mutual screen.

3.3.2. Effect of solution pH on adsorption of reactive black 5

Solution pH is an important parameter for the adsorption process. The effect of initial solution pH on the percentage removal of reactive black 5 was studied by varying the initial solution pH under the conditions of C₀ 200 mg/L, contact time 2 h and EFR-AC dose 8.75 g/L. The results were shown in Fig. 4(b). The amount of reactive black 5 adsorption was found to increase with the decreasing of pH values and reach a peak at pH 2.0. This can be explained in terms of pH_{PZC} . At $pH < pH_{PZC}$, the EFR-AC surface was positively charged and the electrostatic attraction between negative adsorbate ions and adsorbent particles helped to increase the adsorption capacity of reactive black 5. The lower the pH of the solution was, the higher the removal efficiency was. At pH > pH_{PZC}, the adsorbent surface was negatively charged, the electrostatic repulsive force between the negative adsorbate ions and the negative adsorbent particles would decrease adsorption capacity of reactive black 5.

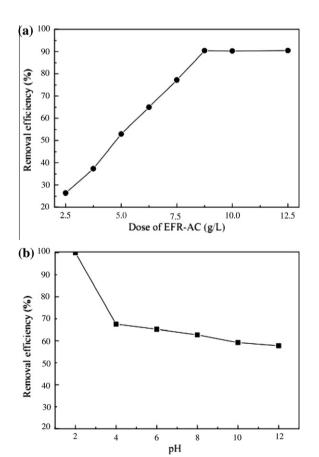


Fig. 4. (a) Effect of EFR-AC dose on the adsorption of reactive black 5; (b) effect of solution pH on the adsorption of reactive black 5.

Table 2Isotherm model constants and correlation coefficients for adsorption of reactive black 5.

Isotherm	Parameters	
Langmuir	$q_{ m m}$ (mg/g)	19.6
	$K_{\rm L}$ (L/mg)	0.39
	R^2	0.9941
	$R_{ m L}$	0.03
Freundlich	$K_{\rm F}$ (mg/g)	11.8
	n	8.77
	R^2	0.4235

3.3.3. Equilibrium isotherms

The thermodynamic assumptions of adsorption isotherms and their estimated parameters provide the insight for both the properties of the surface and the mechanism of adsorption. In this study, Langmuir isotherm and Freundlich isotherm were used for describing the results. The Langmuir isotherm is derived on the assumption of monolayer adsorption on a homogenous surface. It is expressed by following equation (Langmuir, 1916):

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{C_{\rm e}}{q_{\rm m}} + \frac{1}{q_{\rm m}K_{\rm L}} \tag{2}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate (mg/g), q_m is q_e for complete monolayer adsorption capacity (mg/g), and K_L is the equilibrium adsorption constant (L/mg).

The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L (Hall et al., 1966):

$$R_{\rm L} = \frac{1}{1 + K_{\rm L}C_0} \tag{3}$$

where K_L is the Langmuir constant and C_0 is the lowest initial adsorbate concentration (mg/L).

The Freundlich isotherm is suitable for non-ideal adsorption on heterogeneous surfaces. The heterogeneity is caused by the presence of different functional groups on the surface, and several adsorbent–adsorbate interactions. The Freundlich isotherm is expressed by the following empirical equation (Freundlich, 1906):

$$\ln q_{\rm e} = \frac{1}{n} \ln C_{\rm e} + \ln K_{\rm F} \tag{4}$$

where K_F (mg/g) is the Freundlich adsorption constant and 1/n is a measure of the adsorption intensity.

The fitting results, i.e. isotherm parameters and the coefficient of determination, R^2 , were shown in Table 2. The value of R_L for adsorption of reactive black 5 indicated that the adsorption behavior of activated carbon was favorable for the dye ($R_L < 1$) (Hall et al., 1966).

According to a linear regression method, the Freundlich isotherm was poorly suitability to the adsorption of EFR-AC in comparison to the Langmuir isotherm. The validity of the Langmuir model suggested the adsorption of reactive black 5 molecules was due to their monolayer coverage onto the surface of EFR-AC and the adsorption of each molecule has equal activation energy. The similar behavior was observed by other researchers (Deng et al., 2009; Hameed et al., 2008).

4. Conclusion

Preparation of activated carbon from edible fungi by microwave assisted K_2CO_3 activation was proved to be feasible. The iodine number and the amount of methylene blue adsorption methylene blue (MB) of the EFR-AC prepared under optimum conditions

were acceptable and even satisfactory. The external surface of EFR-AC was full of pores compared with EFR, the micropore volume was around 43.5% of the total pore volume and the vast majority of micropores were ultramicropores. EFR-AC could effectively adsorb reactive black 5 from aqueous solutions and low pH was favorable to the adsorption process, which was well fitted to Langmuir isotherm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2012.02.054.

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