Dye removal of activated carbons prepared from NaOH-pretreated rice husks by low-temperature solution-processed carbonization and H\textsubscript{3}PO\textsubscript{4} activation

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Highlights

- Preparation of activated carbons by coupling of H\textsubscript{2}SO\textsubscript{4}-assisted carbonization and H\textsubscript{3}PO\textsubscript{4} activation.
- Optimization of preparative conditions and systematic analysis of surface functional groups.
- Relationship of dye removal of activated carbons on processing conditions.

Abstract

A coupling of low-temperature sulfuric acid-assisted carbonization and H\textsubscript{3}PO\textsubscript{4} activation was employed to convert NaOH-pretreated rice husks into activated carbons with extremely high surface area (2028 m\textsuperscript{2} g\textsuperscript{-1}) and integrated characteristics. The influences of the activation temperature and impregnation ratio on the surface area, pore volume of activated carbons were thoroughly investigated. The morphology and surface chemistry of activated carbons were characterized using N\textsubscript{2} sorption, FTIR, XPS, SEM, TEM, etc. The adsorption capacity of resulting carbons obtained under optimum preparation conditions was systematically evaluated using methylene blue under various simulated conditions. The adsorption process can be well described by both Langmuir isotherm model and the pseudo-second order kinetics models; and the maximum monolayer capacity of methylene blue was ca. 578 mg g\textsuperscript{-1}.

1. Introduction

Nowadays, energy shortage, environmental crisis, and developing customer demands have driven people to find facile route to produce carbonaceous materials that can be widely applied in various fields (Wang et al., 2010). Activated carbons, a kind of amorphous carbonaceous material with high porosity and surface area, have been applied in various industries for several decades owing to its wonderful structures and easy availability. Specifically, due to its high adsorption capacity towards pollutants such as methylene blue (Ka-Lok and Ng, 2012; Liu et al., 2012; Yogesh and Uma, 2010), phenolic compound, metallic ions (Liu and Zhang, 2011) and some volatile organic compounds (Foster et al., 1992), activated carbons have been extensively studied for the water treatment, air purification (Ka-Lok and Ng, 2012), solvent recovery and gas separation and so on (Bagheri and Abedi, 2009).

Recently, much attention has been paid to the efficient utilization of biomass to produce carbonaceous materials from the viewpoint of economic, environmental and societal issues. In China, a large of population consumes rice; China and India account for more than half of world rice production (Yogesh and Uma, 2010). Therefore, the production of a greater quantity of paddies results in the production of a larger of amount of rice husk. Rice husks are commonly used as a low-value energy resource, burned in the field or discarded, which are detrimental to the environment (Lin et al., 2013). Considering that rice husks, mainly composed of organic hemicellulose, cellulose, lignin and inorganic silicon dioxide (Wang et al., 2010), have great potentiality to be utilized to prepare task-specific products, such as silica-based and carbonaceous materials (Lin et al., 2012).

Indeed, rice husk-derived carbonaceous materials have received great attention due to the easy-to-handle conversion of organic components into carbonaceous substances under varied processing conditions (Kennedy et al., 2004; Yogesh and Uma, 2010). However, contrary to conventional carbonization process achieved by high-temperature heating treatment in inert atmosphere, hydrothermal carbonization or solution-processed carbonization is more...
favorable to tailor the surface chemistry of resultant products (Román et al., 2013). More interestingly, during solution-processed carbonization, if sulfuric acid were present, not only can temperature be significantly lowered in contrast to hydrothermal carbonization process (usually higher than 180 °C), but also carbohydrate components of rice husks can be broken up into small molecules and dissolved in the water, following a complex cascade of dehydration, decarboxylation, aldol-reactions, cycloditions, and condensations, finally leading to a carbon rich solid product (Wang et al., 2010). Simultaneously, this process is energetically favorable and is exothermic, which can contribute to a part of the energy needed to complete the carbonization process. This carbonization process presents superior characteristics that make it a promising route toward efficient carbonization of biomass substances under milder conditions. Consequently, the possibility of using a low-temperature solution-processed chars as precursors for activated carbons can offer a versatile way to produce potential materials with favorable surface chemistry.

Moreover, in contrast to physical activation, chemical activation achieved using activating agents is a double-step, controllable and effective method for activated carbons with developed porosity (Nakagawa et al., 2007). Among those chemical activation processes, activation with phosphoric acid is a well-established method for the preparation of activated carbons (Yagmur, 2012). Additionally, the presence of H3PO4 in the interior of the precursor can restrict the formation of tar species and inhibit the shrinkage of the precursor particle by occupying certain substantial volumes, especially when cellulosic and lignocellulosic substances were used as carbonaceous precursors (Gupta et al., 2013). More favorably, after activation phosphoric acid can be easily washed away with water, and have rich in containing phosphorus groups on the surface of activated carbons (Kennedy et al., 2004).

Therefore, in continuation of previous work on utilizing rice husks, i.e. dispersed SiO2 microspheres and high-performance activated carbons have been successfully prepared from inorganic and organic components (Lin et al., 2012, 2013), respectively, this work is a step forward to prepare porous carbons from NaOH-pretreated rice husks by coupling of low-temperature solution-processed carbonization and H3PO4 activation. The processing conditions have been optimized by varying phosphoric acid concentration and activation temperature, based on systematic characterization of N2 sorption technique. The correlation of textural properties and surface chemistry of resultant carbons with adsorption affinity with cationic methylene blue molecules was examined under various testing conditions; the adsorption isotherms, kinetics, and thermodynamics of the model compound over resulting carbons were also discussed.

2. Experimental

2.1. Materials

Rice husk was provided by a rice mill near Dalian, China, in the autumn of 2012. Previous to carbonization process, rice husk was washed thoroughly with distilled water to remove adhering soil, dust and parts of metal impurities. After drying at 105 °C overnight, these precursors were finely ground into 60 mesh. All chemical reagents were analytically reagent from Tianjin Kermel Co. Ltd. Methylene blue (C16H18ClN2S2H2O) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Distilled water was employed throughout the experimental process.

2.2. Preparation of activated carbon

Rice husk was washed thoroughly with distilled water to remove adhering soil, dust and parts of metal impurities. Subsequently, rice husks and 2 mol L−1 NaOH were mixed at a ratio of 1:7 (w/v) in a 500 mL three-neck round-bottom flask equipped with a thermometer and heated to 100 °C for 4 h. Solid Rhs residue was separated from the liquid by filtration, washed to neutrality with distilled water and dried at 120 °C overnight. After that, 5.0 g of the precursors in 24 mL distilled water was acidified with 26 mL sulfuric acid (approximately 60% wt). The suspension was stirred at room temperature for 10 min, then transferred into a 120 mL sealed Teflon-lined stainless steel autoclave for carbonization at 90 °C for 6 h. The black product was collected by filtration, washed to neutrality with distilled water and dried at 120 °C for 12 h; the rice husk char obtained at this stage was defined as SPC (solution-processed char).

In a typical activation process, 0.5 g of SPC impregnated with 1.2 mL phosphoric acid (the weight ratio of phosphoric acid to SPC was 4:1) was placed in a quartz boat and heated from room temperature to 500 °C with a heating rate of 10 °C/min under nitrogen atmosphere in a horizontal pyrolysis reactor. Being activated at 500 °C for 1 h and naturally cooled to room temperature, the activated product (designated as ASPC) was washed to neutral with water and dried at 120 °C for 24 h, ready for adsorption test.

2.3. Characterization

Nitrogen adsorption–desorption experiments were performed by Quantachrome Autosorb NOVA2200e analyzer at 77 K. Specific surface area was calculated by BET method, the total pore volume was determined by nitrogen adsorption at p/p0 = 0.995, and pore size distribution was determined from the adsorption branch with Barrett–Joyner–Halenda (BJH) theory. The morphology of ASPC was determined by scanning electron microscopy (SEM, JSM-6460LV, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2000EX, JEOL, Japan). Fourier transform infrared (FT-IR) spectra were recorded in the region of 4000–400 cm−1 employing the KBr pellet method (Perkin Elmer, USA). X-ray photoelectron spectroscopy (XPS) were performed using a Thermo Scientific Escalab 250 (Thermo VG, USA) instrument equipped with AlKα radiation (hv = 1486.6 eV), and binding energies for the high-resolution spectra were calibrated by setting C1s at 284.8 eV.

2.4. Adsorption

2.4.1. Adsorption equilibrium

Adsorption experiments were conducted by agitating 10 mg of ASPC in 30 mL of methylene blue solution of desired concentrations (70–351 mg L−1) in 250 mL conical flasks at 20, 25 and 30 °C under pH ~10 to reach equilibrium. The residual concentration of methylene blue was analyzed using a double beam UV–Vis spectrophotometer at 664 nm (UV-1600PC, Shanghai Mapada Instruments, China). Langmuir and Freundlich adsorption isotherms were employed to study the adsorption capacity of the adsorbent. The MB equilibrium adsorption uptake in the solid phase, qe (mg g−1), was calculated using the following relationships.

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

(1)

C0 and Ce (mg L−1) are the liquid-phase concentrations of MB at initial and equilibrium conditions, respectively. V (L) is the volume of the solution, and W (g) is the mass of adsorbent used. Each experiment was carried out in minimum triplicate, and the average values were presented as final adsorption results.
2.4.2. Effect of solution pH

The effect of solution pH on methylene blue adsorption was examined by varying pH from 2 to 10 while maintaining the initial methylene blue concentration at 417 and 234 mg L⁻¹, the ASPC dosage of 10 mg and the adsorption temperature at 20 °C. In each adsorption test, the pH level of the methylene blue solution was adjusted with 0.1 M HCl acid and 0.1 M NaOH solution. The pH was determined using a pH meter (pHS-2F, LEICI Instruments, China).

Generally, the contact time needed to reach adsorption equilibrium is necessary to study the adsorption kinetics and adsorption equilibrium. Adsorption kinetic provides a crucial insight into the controlling mechanism of an adsorption process which in turn affects the residence time of adsorbates at solid–liquid interface. Accordingly, the effect of contact time on methylene blue adsorption was determined by varying adsorption time from 1 min to 300 min while fixing the pH at about 7, the adsorption temperature at 20 °C, and the initial methylene blue concentration at 47 and 234 mg L⁻¹.

3. Results and discussion

3.1. Optimization of preparation conditions

Among various parameters for chemical activation process, activation temperature and dosage of activating agent are the most important factors towards the porosity development of activated carbons (Sun and Paul, 2011). Considering this, the effect of activation temperature and impregnation amount of H₃PO₄ upon the porosity of resultant carbons was firstly established.

Fig. 1 shows nitrogen adsorption–desorption isotherms and pore size distributions of the samples prepared with varied impregnation ratio of H₃PO₄. Clearly, as demonstrated by Fig. 1, the variation of textural properties of resulting activated carbons is dependent on the dosage of H₃PO₄, and the impregnation ratio of 4:1 can be considered as a suitable point. On the other hand, the isotherm of SPC is of type I, as the adsorption and desorption branch remains nearly horizontal and parallel through the range of relative pressures, which is characteristic of non-porous solids or large macropores (Liu et al., 2012), indicating the activation procedure is indispensable for the development of porosity. Meanwhile, the hysteresis effect and the slope of the plateau increased to yield type IV isotherms with significant increase in nitrogen uptake through the entire pressure range, indicating the presence of mesopores along with the increase of H₃PO₄ amount (Zhang et al., 2012); an increase in the activating agent promoted the contact area between SPC and activating agent, and therefore increasing the surface area of carbon. When the impregnation ratio exceeded 4:1, however, the surface area decreased; this indicates that the textural characteristics of products prepared from using NaOH-pretreated rice husks char are sensitive to the impregnation ratio.

As shown in Fig. 2, with the H₃PO₄ impregnation ratio of 4, the samples activated at 400, 500, 600 and 700 °C display a significant variation in nitrogen uptake in the initial pressure range, indicating the formation of micropores during the activation process. At the same time, apparent hysteresis loops are observable for all samples, which can be possibly caused by capillary condensation in the larger pores of obtained activated carbons. These observations imply that the samples prepared by different activation temperatures possess both micro-porosity and meso-porosity (Liou and Wu, 2009).

Besides, when activated at 500 °C, the sample possesses the largest adsorption capacity, clearly indicating that the pore volume increases the most under this activation condition. Comparatively, as the activation temperature is lower than 500 °C, the rice husk chars are only partially carbonized (Liou and Wu, 2009), leading to undeveloped porosity and thus lowered surface area; similarly, however, when the activation temperature is higher than 500 °C, violent gasification reactions may cause part of the micropore structure to be destroyed by collapsing or combining together (Román et al., 2013), resulting in the reduction of micro-porosity and accordingly the increase of mesopore volume. These results are similar to the observations of other researchers (Guo and David, 2007) who reported that the surface area of carbon obtained from H₃PO₄ activation of rice husk reached its maximum at a carbonization temperature of 500 °C.

Accordingly, Table 1 and Fig. 51 (electronic Supplementary materials) illustrate the dependence of specific surface area and
pore volume of ASPC on the impregnation ratio and activation temperature. As the impregnation ratio increases from 2 to 5, the microporous volume increases in initial, reaching their maximum value when the impregnation ratio is 4:1 and then decreases. In addition, the maxima of S_{mic}, external surface area, average pore diameter and mesoporous volume are found at optimization impregnation ratio is 4:1. Mesopore volume was calculated by subtracting the total volume obtained at a relative pressure of 0.995 from the micropore volume obtained from t-plot.

Meanwhile, Figs. 1 and 2 also show the pore size distributions of SPC and ASPC samples. The pore size distribution is dependent on the ratio of impregnation activating agent and the heat treatment temperature (Kennedy et al., 2004). The average pore diameter increased with increasing impregnation up to 5 and decreased with increasing activation temperature up to 700 °C. As previously reported for the activation process of other lignocellulosic precursors (Benadjemia et al., 2011) the reaction of H₃PO₄ with the internal cellulose structure is assumed to induce a depolymerization, which lead to an enhancement of the pore volume and thus a global volume expansion. In that regard, as the amount of H₃PO₄ acid used for activation increases, the volume filled by it and the various associated polyphosphates are also enhanced, resulting in a larger pore volume and pore size, favoring the formation of mesopores (Benadjemia et al., 2011). The marginal increase in pore diameter at 700 °C can be attributed to certain unorganized carbons or residual tar materials being expelled by the opening of closed pores (Román et al., 2013) and existing pores widening into larger pores of small magnitude through gasification of carbons in the pore walls having labile carbon structures (Román et al., 2013). The decrease in the average pore diameter with activation temperature is due to the suppression of the pore widening of stable carbon structures (Kennedy et al., 2004) preformed during the carbonization process. In a word, the optimized ASPC sample which possesses the highest microporosity and mesoporosity content might be a promising adsorbent for the organic pollutants of middle molecular size (~2 nm) (Benadjemia et al., 2011).

3.2. Porous structure and surface chemistry

Representative SEM and TEM images of SPC and ASPC are shown in Fig. S2. For SPC, there is no obvious evidence of pore formation in the rice husk where only carbonization of the raw material took place without creating full pores; SPC could retain the original morphology of rice husk, mainly because of the extended crystalline cellulose as scaffold (Zhang et al., 2012). Furthermore, irregular nanoparticles and interconnected porous network highlighted by external macropores are visible on the SPC surface (Fig. S2(c)). By contrast, Fig. S2(b) indicates the formation of pores for the sample ASPC due to chemical activation. It is supposed that the opening of the pores in the surface of ASPC be due to the extraction of some component; porous structures in microporous and mesoporous regime are present throughout the image (Foo and Hameed, 2012).

The FT-IR spectra for SPC and ASPC products are displayed in Fig. S3. Noting that, SPC shows more absorption bands in comparison with activated carbon of ASPC. The wide bands at 3419 and 3406 cm⁻¹, visible for both SPC and ASPC, respectively, can be attributable to the –OH stretching vibrations of hydroxyl groups and/or carboxyl groups (Román et al., 2013), indicating that these products should be hydrophilic and slightly acidic in nature. It is distinct that SPC shows bands corresponding to the stretching vibrations of aliphatic C–H (2924 and 2835 cm⁻¹), which is totally absent in ASPC. A pronounced band at 1606 cm⁻¹ due to the aromatic ring stretching mode is observed over SPC (Sych et al., 2012), indicating the existence of single or multiple aromatic rings in the structure of SPC. Besides, another several distinct peaks at 1707, 1204 and 1026 cm⁻¹, due to the C=O absorption from carboxyl and/or carboxyl groups, aromatic skeletal and C–O stretching vibrations from carboxylic, alcohols, phenols, ethers and esters (Sych et al., 2012), respectively, are also present in SPC.

It is evidenced by the FT-IR profile of ASPC that, in contrast to SPC, the formation of structures containing multiple carbon–carbon bonds as well as the presence of P–O=C groups has been achieved during H₃PO₄ activation. Clearly, a broad peak around 2019 cm⁻¹ can be due to the carbon–oxygen and ketene groups; the band near 1615 cm⁻¹ is from aromatic stretching vibrations (C=C) (Kennedy et al., 2004); the bands at 1185 and 1072 cm⁻¹ can be attributed to C–O single bond, such as in ethers, esters or lactones, carboxylic groups, etc. Moreover, the peak at 1185 cm⁻¹ can be assigned to the stretching mode of hydrogen-bonded P=O derived from phosphoric acid activation (Guo and David, 2007). Simultaneously, the peak at 1072 cm⁻¹ can be ascribed to the ionized linkage P—O in acid phosphate esters and to symmetrical vibration in a chain of P—O—P (polyphosphate) (Benadjemia et al., 2011).

Besides, XPS was further used to characterize functional groups of both samples. The C 1s, core level spectra obtained for SPC and ASPC, together with the peak-fitting of its envelope, are deposited in Fig. 3a and b. The spectrum of ASPC was resolved into four individual component peaks, namely, (1) aliphatic or aromatic carbon group (CHₓ, C–C=C; BE = 284.6 eV); (2) sp³ hybridized carbon atoms (BE = 285.6 eV); (3) carbonyl groups (C=O; BE = 287.6 eV); (4) carboxylic groups, esters or lactones (COOR; BE = 290.7 eV) (Xiao et al., 2012; Sevilla et al., 2011). On the other hand, Fig. 3c shows that the O 1s region in the XPS spectrum of ASPC exhibits two deconvoluted peaks at 533.1 and 531.7 eV, representing C–O stretching vibrations of alcohols, ethers and/or carboxyl groups (Román et al., 2013) and existing pores widening into larger pores of small magnitude through gasification of carbons in the pore walls having labile carbon structures (Román et al., 2013). The decrease in the average pore diameter with activation temperature is due to the suppression of the pore widening of stable carbon structures (Kennedy et al., 2004) preformed during the carbonization process. In a word, the optimized ASPC sample which possesses the highest microporosity and mesoporosity content might be a promising adsorbent for the organic pollutants of middle molecular size (~2 nm) (Benadjemia et al., 2011).

3.3. Adsorption studies

3.3.1. Effect of pH on adsorption capacity

Fig. 4 shows the dependence of the uptake amount of methylene blue on the solution pH over optimally prepared ASPC at

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Impregnation ratio</th>
<th>S_{mic} (m² g⁻¹)</th>
<th>S_{meso} (m² g⁻¹)</th>
<th>S_{ext} (m² g⁻¹)</th>
<th>V_{mic} (cm³ g⁻¹)</th>
<th>V_{meso} (cm³ g⁻¹)</th>
<th>V_{total} (cm³ g⁻¹)</th>
<th>D_{meso} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>2:1</td>
<td>1572</td>
<td>1309</td>
<td>203</td>
<td>0.673</td>
<td>0.250</td>
<td>0.923</td>
<td>2.352</td>
</tr>
<tr>
<td>500</td>
<td>3:1</td>
<td>1724</td>
<td>1416</td>
<td>309</td>
<td>0.696</td>
<td>0.388</td>
<td>1.084</td>
<td>2.516</td>
</tr>
<tr>
<td>400</td>
<td>4:1</td>
<td>1345</td>
<td>1005</td>
<td>340</td>
<td>0.496</td>
<td>0.435</td>
<td>0.931</td>
<td>2.768</td>
</tr>
<tr>
<td>500</td>
<td>4:1</td>
<td>2028</td>
<td>1595</td>
<td>434</td>
<td>0.787</td>
<td>0.554</td>
<td>1.341</td>
<td>2.644</td>
</tr>
<tr>
<td>600</td>
<td>4:1</td>
<td>1692</td>
<td>1444</td>
<td>247</td>
<td>0.717</td>
<td>0.310</td>
<td>1.027</td>
<td>2.428</td>
</tr>
<tr>
<td>700</td>
<td>4:1</td>
<td>1783</td>
<td>1519</td>
<td>263</td>
<td>0.753</td>
<td>0.331</td>
<td>1.086</td>
<td>2.436</td>
</tr>
<tr>
<td>500</td>
<td>5:1</td>
<td>1948</td>
<td>1508</td>
<td>438</td>
<td>0.731</td>
<td>0.559</td>
<td>1.290</td>
<td>2.652</td>
</tr>
</tbody>
</table>
20 °C, while keeping the initial methylene blue concentration at 141, 187, 234 mg/L. It is remarkable that, with pH gradually increasing from 2 to 10, the uptake amount of methylene blue onto ASPC significantly increased, for which can be interpreted as the enhanced electrostatic interaction between cationic methylene blue molecules and negatively charged carbon substrate modified with phosphate species (Benadjemia et al., 2011). As the electrostatic attraction between the cationic dye and activated carbon is strengthened along with pH increasing, the highest adsorption amount can be gained around pH ~10 under testing conditions. Conversely, lower adsorption capacity at lower pH is mainly due to the protonation of MB in acidic medium and the presence of excess H⁺ ions that can compete with the cationic dye molecules for adsorption sites (Foo and Hameed, 2011).

3.3.2. Contact time and adsorption kinetics

Fig. 5a shows the effect of equilibrium time on the adsorption of methylene blue onto ASPC with different initial concentrations of 47 and 234 mg L⁻¹. For different concentrations of methylene blue, it is apparent that adsorption is very fast at the beginning, whereas the time required to reaching equilibrium increases with increasing concentration. Combining both adsorption processes achieved in low and high methylene blue concentrations, an agitation period of 1.5 h can be considered as a suitable time interval for adsorption equilibrium. Additionally, it should be noted that, beyond agitation period of 2.5 h, both curves exhibit a flat plateau, clearly indicative of a monolayer adsorption process of methylene blue molecules onto ASPC powders. Correspondingly, the adsorption kinetics of methylene blue on ASPC was further investigated by three different models, the pseudo first-order, pseudo second-order, and intra-particle diffusion.
The linear pseudo-first-order model of Lageren is given as follows (Lagergren, 1898):

$$\log\left(\frac{q_e}{C_0} - \frac{q_t}{C_0}\right) = \log\left(\frac{q_e}{C_0}\right) - k_1 \cdot \frac{t}{2.303}$$  \hspace{1cm} (2)

where $q_e$ and $q_t$ are the amounts of methylene blue absorbed onto the adsorbent (mg g$^{-1}$) at equilibrium and at $t$, respectively; and $k_1$ is the rate constant of first-order adsorption (min$^{-1}$). By contrast, the pseudo-second-order kinetic model is based on the experimental information of solid-phase sorption and can be expressed as follows (Ho and McKay, 1998):

$$t \cdot \frac{q_t}{C_0} = \frac{k_2}{k_3} q_e^2 + \frac{t}{q_e}$$  \hspace{1cm} (3)

where $k_2$ is the rate constant of second-order adsorption (g mg$^{-1}$ min$^{-1}$).

Calculated using experimental data, Fig. 5b and c illustrate the graphs of $\ln(q_e - q_t)$ versus $t$ for the first-order kinetic model and the graphs of $t/q_t$ versus $t$ for the second-order kinetic model, and corresponding constants obtained from two different methylene blue concentrations are given in Table 2. As can be seen from Table 2, as far as $r^2$ values are considered for two different methylene blue concentrations, the pseudo second-order kinetic model correlates the time-dependent function of equilibrium slightly better than the pseudo first-order kinetic model; therefore, a good compatibility of testing systems reaching equilibrium with the pseudo second-order kinetic model can be established.

Besides, to clarify the adsorption mechanism and elucidate rate-determining step(s) towards simulated adsorption, the intra-particle diffusion model, listed as below, was applied to correlate the equilibrium data (Weber and Morris, 1963),

$$q_t = k_{id} t^{1/2} + C$$ \hspace{1cm} (4)

where $k_{id}$ (mg g$^{-1}$ min$^{-1/2}$) is the intra-particle diffusion rate constant and $C$ (mg g$^{-1}$) is a constant characterizing boundary layer thickness. Both $k_{id}$ and $C$ can be determined from the slope and intercept of a plot drawn between $q_t$ and $t^{1/2}$. Accordingly, as shown in Fig. 5d, the graphs of $q_t$ versus $t^{1/2}$ plotted for intra-particle diffusion suggest that a two-step adsorption process essentially appeared under testing systems. Within the first minute, a very fast adsorption took place in the film layer on ASPC surface; after that, intra-particle diffusion of methylene blue molecules toward the pores in inner surface of ASPC started, through which the migration of adsorbate molecules toward the sites where actual adsorption took place is common for porous adsorbents (Auta and Hameed, 2011); this step is usually thought to be a rate-determining or -limiting step under aqueous conditions. However, since none of C constants obtained for intra-particle diffusion approached zero (Table 2), it emerges that the adsorption process is not exclusively controlled by intra-particle diffusion (Gundogdu et al., 2012).
3.3.3. Adsorption isotherms

In this study, two widely used isotherm models, Langmuir model and Freundlich model were employed to describe the adsorption process. Langmuir isotherm model suggests that adsorption occurs on homogeneous sites within an adsorbent, assuming that each molecule possesses constant enthalpies and sorption activation energy; and this model can be expressed by following equation (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} + \frac{C_e}{K_L q_{max}}$$  \hspace{1cm} (5)

where $q_e$ is the amount of adsorbate adsorbed by absorbent at equilibrium (mg g$^{-1}$), $q_{max}$ is the maximum single layer adsorption capacity (mg g$^{-1}$), $C_e$ is the amount of adsorbate remaining in the solution at equilibrium (mg g$^{-1}$), and $K_L$ is a constant related to free energy or adsorption enthalpy (L mg$^{-1}$). Another important parameter of the Langmuir isotherm model is the term “$R_L$” which is a non-dimensional constant and called as separation factor or equilibrium parameter, and it is represented by the following equation (Hall et al., 1966):

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} (6)

where $K_L$ is the Langmuir constant and $C_0$ is the initial adsorbate concentration (mg L$^{-1}$). The $R_L$ parameter gives important signs on the possibility of the adsorption process that might be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linearity of adsorption ($R_L = 1$) or unfavorable ($R_L > 1$).

As another typical simulation model for adsorption under aqueous conditions, Freundlich isotherm can be expressed as follows (Freundlich, 1906):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (7)

where $K_f$ (mg g$^{-1}$) is the Freundlich adsorption constant, and $1/n$ is a measurement of the adsorption intensity that determines
whether the adsorption intensity and type of isotherm is favorable (0.1 < 1/n < 0.5) or unfavorable (1/n > 2).

A linearized plot of $C_r$ versus $q_e$ is widely used to correlate the derivation of various isotherms, and therefore providing reasonable interpretation for experimental data. As shown in Fig. 6a, the residual equilibrium concentration of methylene blue in solution increases with increasing initial solution concentrations, whereas the amount of methylene blue adsorbed ($q_e$) does not change significantly. This indicates that the adsorption of methylene blue onto ASPC cannot proceed beyond monolayer adsorption, which is in agreement with the Langmuir model. Meanwhile, equilibrium isotherm constants and correlation coefficients obtained from linear fits of Langmuir and Freundlich isotherms are given in Table 3; and Fig. 6b and c are the linearized Langmuir and Freundlich graphs, respectively. Taking account of the correlation coefficients ($r^2$) of both models, the related coefficient $r^2$ of Langmuir equations is significantly higher than that of Freundlich equations, further confirming the occurrence of monolayer adsorption of methylene blue molecules onto the internal and external surfaces of ASPCs. By the courtesy of Langmuir isotherm model, the maximum adsorption capacity ($q_{max}$) of methylene blue on ASPC, was calculated to be 578 mg g$^{-1}$ at 30 °C.

Furthermore, $R_s$ is usually employed to determine the conformance of adsorption to a selected adsorbate–adsorbent system (Gundogdu et al., 2012). As shown by the $R_s$ - $C_0$ graph in Fig. 6d, all $R_s$ values are below 1, demonstrating that methylene blue adsorption onto ASPC with phosphate groups is favorable. In the view of these results, the binding sites were homogeneously distributed over the external and pore surfaces of ASPC during activation process (Unur, 2013).

3.3.4. Effect of temperature

In addition, Fig. 6a also demonstrates the dependence of methylene blue adsorption on testing temperatures. Possibly, the rate of molecular diffusion increases and the viscosity of solution decreases with increasing temperature (Liao et al., 2013), facilitating methylene blue molecules diffuse across the external boundary layer into the internal pores of ASPC. Furthermore, in terms of a dimensionless equilibrium parameter $R_s$ derived from the experiments were all less than unity, indicating that the adsorption processes were favorable. With increased temperature, the $K_L$ values accordingly increased, clearly demonstrating that the adsorption process was endothermic. Similarly, the $K_f$ values also increased with increased temperature, further confirming the endothermic feature of the studied adsorption processes. As illustrated by the adsorption experiments conducted at different temperatures (Table 3), higher temperatures contributed to a relatively higher saturated adsorption capacity, which was also induced by the strong interactions between adsorbent and adsorbate (Lin et al., 2013).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$q_{max}$ (mg g$^{-1}$)</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_L$ (L mg$^{-1}$)</td>
<td>$n$</td>
</tr>
<tr>
<td>20</td>
<td>543.5</td>
<td>0.5974</td>
<td>0.9901</td>
</tr>
<tr>
<td>25</td>
<td>552.5</td>
<td>0.6754</td>
<td>0.9931</td>
</tr>
<tr>
<td>30</td>
<td>578.1</td>
<td>0.6758</td>
<td>0.9895</td>
</tr>
</tbody>
</table>

4. Conclusions

Activated carbons with developed porosity and excellent methylene blue adsorption performance have been prepared from the residue of NaOH-pretreated rice husks through coupling of H$_2$SO$_4$-assisted carbonization and H$_2$PO$_4$ activation. Kinetic and isotherm model analyses the adsorption of methylene blue on ASPCs revealed that the experimental data well fitted for the pseudo-second order model and Langmuir isotherm; and the adsorption process was endothermic. The present study indicates that ASPC is an efficient and environmental friendly that may be as a promising bio-adsorbent to remove the dye from industrial wastewater.

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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.2013.07.002.

References


