

# Removal of dyes from aqueous solutions using activated carbon prepared from rice husk residue

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## ABSTRACT

The treatment of dye wastewater by activated carbon (AC) prepared from rice husk residue wastes was studied. Batch adsorption studies were conducted to investigate the effects of contact time, initial concentration (50–450 mg/L), pH (3–11) and temperature (30–70 °C) on the removal of methylene blue (MB), neutral red, and methyl orange. Kinetic investigation revealed that the adsorption of dyes followed pseudo-second-order kinetics. The results suggested that AC was effective to remove dyes, especially MB, from aqueous solutions. Desorption studies found that chemisorption by the adsorbent might be the major mode of dye removal. Fourier transform infrared results suggested that dye molecules were likely to combine with the O–H and P=OOH groups of AC.

**Key words** | activated carbon, adsorption, dye removal, rice husk residue

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## INTRODUCTION

In recent years, people have become increasingly sensitive to wastewater treatment, because of environmental or public health concerns. Dyes are one kind of organic compounds which are visible, and can be carcinogens and toxic to aquatic life in water (Li *et al.* 2011). Various treatment methods have been proposed for the removal of dyes from aqueous solutions, such as biological treatment, coagulation, floatation, oxidation and adsorption (Mane *et al.* 2007). However, adsorption is considered superior compared with other traditional treatment methods due to its easy availability, simplicity of design, high efficiency, ease of operation and ability to treat dyes in more concentrated forms (Tan *et al.* 2008). Activated carbon (AC) is one of the most effective and commonly used adsorbents for the treatment of dye wastewater because of its large specific surface areas, pore volumes, chemical inertness, and good mechanical stability (Liu *et al.* 2014). However, commercially available AC is still expensive for many countries due to the use of relatively expensive starting materials, and the high costs hamper their application in most cases (Li *et al.* 2011). With the growing emphasis on environmental protection, it is important to discover cheap and efficient methods for wastewater treatment.

Rice is regarded as one of the most important agricultural crops in Asia, and the annual quantity of rice husk is very large as a by-product from rice mills. The method of manufacturing bio-oil from rice husk was studied (Alvarez

*et al.* 2014), but in the converting process, a large amount of solid residue, named rice husk residue (RHR), was generated. The utilization of abundant RHR to produce AC is of great significance, not only to avoid the environmental pollution created from combustion, but also to produce useful materials for the wastewater treatment (Zhang *et al.* 2015).

The concentration of dyes in the textile industry is typically in the range of 10–200 mg/L (Moussavi & Mahmoudi 2009). Some others also reported that the concentration of Serilene Black SBN and Foron Red S-WF of a dyehouse in Istanbul is 500 mg/L and 30 mg/L, respectively (Arslan 2001). And the concentration of Procion Deep Red H-EXL gran and Procion Yellow H-EXL gran in a textile dyeing company of Erfoc-Acabamentos Têxteis S.A. (Famalicão, Portugal) is 6 mg/L and 40 mg/L, respectively (Domic *et al.* 2015). Methylene blue (MB), a water-soluble cationic dye, is widely used in industrial practices such as textile and printing. Neutral red (NR), a water-soluble cationic dye, is commonly used for nuclear counterstaining in biological research. Methyl orange (MO), an anionic dye belonging to the azo group of dyes, has been widely used in textile, printing, paper, pharmaceutical and food industries. MB, NR and MO were selected as model compounds in order to evaluate the capacity of AC.

The aim of the present work was to take advantage of RHR to prepare AC for the removal of three kinds of dyes from water. The influences of contact time, initial

concentration, solution pH and temperature on the adsorption capacities were examined. The results were valuable for further application of AC in dye removal.

## METHODS

### Materials

RHR was produced from rice husk in a fluidized bed reactor, where rice husk was exposed to 475 °C for less than 2 s to get bio-oil for the purpose of energy material (Lu *et al.* 2008). Sodium hydroxide (NaOH) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%) were of analytical grade and applied without further purification. N<sub>2</sub> was of chemical grade (at a purity of 99.9%). The three kinds of dyes used in the present study, MB (C<sub>16</sub>H<sub>18</sub>ClN<sub>5</sub>S), NR (C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>HCl), and MO (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub>SNa), were of analytical reagent grade. Deionized water was employed throughout all the treatment and adsorption processes.

### Preparation of AC

The preparation of AC was reported in our previous work (Li *et al.* 2015). RHR (40–80 mesh) was washed with deionized water to remove the impurities, and then dried in an oven at 100 °C for 24 h. 30 g of dried RHR was put into a flask, and 200 mL of 3 mol/L NaOH solution was added into the reactor, then the temperature was increased to 105 °C and kept for 5 h. The suspension was filtrated, and the base treated solid residue (abbreviated as BTRHR) was washed with deionized water and then dried for use in the preparation of AC. Two grams of BTRHR was impregnated with 15 mL H<sub>3</sub>PO<sub>4</sub> aqueous solution at BTRHR/H<sub>3</sub>PO<sub>4</sub> ratio of 1:2. The mixture was put into an oven at 100 °C for one night to remove the excess water, and then used for activation, where it was heated from room temperature at 5 °C/min up to 500 °C for 1 h under N<sub>2</sub> flow of 60 mL/min in a horizontal cylindrical furnace. After activation process, the mixture was washed with deionized water until neutral and dried, ready for adsorption test.

### Characterization

The specific surface area and pore size of AC samples were measured at –196 °C by means of a standard Brunauer-Emmett-Teller (BET) N<sub>2</sub> adsorption procedure (Micromeritics TriStar 3020).

According to Boehm titration method, carboxylic, lactic, phenolic and carbonyl groups could be differentiated by neutralization with the solution of NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH and C<sub>2</sub>H<sub>5</sub>ONa. First, 0.1 g of AC was impregnated in the aqueous solutions for 24 h. Then the variation of concentration was tested and calculated to get the information of the amount of groups.

The morphology of AC was examined using a JEM-100CX transmission electron microscope (TEM) (JEOL, Japan) at an accelerating voltage of 80 kV.

Samples were analyzed by Fourier transform infrared (FT-IR) spectroscopy on a Nicolet Nexus 670 instrument (Thermo Nicolet, USA) in order to identify the surface functional groups of AC before and after dye adsorption. The spectra were recorded in the region of 4,000–400 cm<sup>-1</sup> employing the KBr pellet method.

### Adsorption experiments

In order to make a comparison of the adsorption capacity of RHR, BTRHR and AC, dyes were adsorbed at the initial concentration of 150 mg/L in the neutral solutions. The ambient temperature of 30 °C may be the best choice in view of obtaining an energy-saving treatment process in further studies.

The effect of pH on dye adsorption was examined with fixed initial dye concentration and adsorption temperature. The initial pH value of the solution was adjusted by 0.1 mol/L NaOH and 0.1 mol/L HCl, and it was determined by a pH meter. To study the effect of temperature on dye adsorption characteristics, AC was put into contact with dye solutions at 30, 40, 50, 60 and 70 °C. The effect of initial concentration on the sorption characteristics was investigated at 30 °C.

Stock solution (1,000 mg/L) of dyes was prepared by dissolving an accurately weighed quantity of dye in deionized water. The experimental solution (100 mL) was prepared by diluting the stock solution with deionized water to the required concentration. The concentration of MB, NR and MO was determined using a U-4100 Ultraviolet visible and near infrared spectrometer (Hitachi, Japan) at 663 nm, 530 nm and 465 nm, respectively. All the adsorption experiments were carried out in a 250 mL stoppered conical flask and 30 mg of AC was added. The removal rate and the amounts of dyes adsorbed at time *t* (*q<sub>t</sub>*, mg/g) and at equilibrium *q<sub>e</sub>* (mg/g) were calculated using the following equations:

$$\text{Removal rate (\%)} = \frac{100(C_0 - C_t)}{C_0} \quad (1)$$

$$q_t = \frac{m(C_0 - C_t)}{V} \quad (2)$$

$$q_e = \frac{m(C_0 - C_e)}{V} \quad (3)$$

where  $C_0$ ,  $C_t$  and  $C_e$  (mg/L) were the initial, time  $t$  and equilibrium concentrations of dyes, respectively.

The pseudo-first-order kinetic model was expressed by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where  $q_e$  and  $q_t$  were the amount of dye adsorbed (mg/g) at equilibrium and after time  $t$  (min), respectively, and  $k_1$  (1/min) was the equilibrium rate constant of pseudo-first-order sorption. The slope and intercept of the plot of  $\ln(q_e - q_t)$  versus  $t$  were used to determine the rate constant,  $k_1$ . Another kinetic model was the pseudo-second-order model, which was represented by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where  $k_2$  (g/mg·min) referred to the equilibrium rate constant of pseudo-second-order adsorption. The slope and intercept of the plot of  $t/q_t$  versus  $t$  were used to calculate the rate constant,  $k_2$ .

An intraparticle diffusion model was tested to identify the diffusion mechanism. It was expressed by:

$$q_t = k_3 t^{1/2} + C \quad (6)$$

where  $k_3$  (mg/g·min<sup>1/2</sup>) was the intraparticle diffusion rate constant and  $C$  (mg/g) was the intercept.

In order to investigate the interaction between the adsorbate and the adsorbent, two classical equilibrium models were tested. The Langmuir model was developed to represent monolayer sorption on a set of distinct localized sorption sites. The Langmuir model can be expressed by the linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (7)$$

where  $C_e$  (mg/L),  $K_L$  (L/mg) and  $q_m$  (mg/g) referred to the equilibrium dye concentration in solution, the Langmuir

constant and the monolayer capacity of the adsorbent, respectively. The Freundlich model dealt with physicochemical sorption on heterogeneous surfaces. Equation (8) represents the linearized form of the Freundlich equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

where  $K_F$  (mg/g (mg/L<sup>3</sup>)<sup>n</sup>) is the Freundlich constant and  $n$  is the heterogeneity factor.

## Desorption experiments

Before the desorption experiments, the amount of dye adsorbed to a known amount of AC was measured. This was done by adding 0.06 g of AC to 100 mL of dye solution with a concentration of 1,000 mg/L, and then stirring for 300 min at ambient temperature. The amount of dye adsorbed was calculated by measuring the concentration of dye solution before and after adsorption. After filtration, AC was dried for further experiments. A known amount of AC with adsorbed dye was added into 50 mL of deionized water with different pH (2–12) and stood at ambient temperature for 24 h. Then the concentration of the solutions was measured at 663 nm, 530 nm and 465 nm for MB, NR and MO, respectively, to calculate the amount of dyes desorbed.

## RESULTS AND DISCUSSION

### Characterization results

The characterization results of BET, TEM and Boehm titration are displayed in the Supplementary Material (available with the online version of this paper).

### The adsorption capacity of RHR, BTRHR and AC

Figure S3 (available with the online version of this paper) presents the adsorption capacity of RHR, BTRHR and AC for the removal of dyes. The data were obtained under the following experimental conditions: the adsorption temperature, 30 °C; the initial concentrations of dyes, 150 mg/L in the neutral aqueous solutions. The removal rate of the three dyes on RHR, BTRHR and AC was below 10%, 9.4–25.2%, and 56.6–80.2%, respectively. The different removal rates of the dyes on the samples could be attributed to the difference of the surface area and functional groups. Similar results were reported by Liu *et al.* (2011). In total,

the base-leaching of RHR improved the adsorption capacity slightly. However, the activation of BTRHR enhanced the adsorption a lot, indicating better adsorption capacity.

### Effect of initial solution pH

The MB removal rate was high in the initial concentration of 150 mg/L; therefore, the effect of pH on adsorption behavior of MB on AC was studied at 250 mg/L by varying the pH of the dye solution from 3 to 11. The removal rate of MB increased with increasing pH, as shown in Figure S4(a) (Figure S4 is available with the online version of this paper). It was noteworthy that, with pH gradually increasing from 3 to 9, the removal rate of MB on AC showed only a slight increase. Nevertheless, the removal rate was remarkably increased when the solution pH was increased from 9 to 11. The presence of excess  $H^+$  ions competed with dye cations for adsorption sites, leading to lower adsorption. With the increase of pH, the number of negatively charged sites increased and the formation of an electric double layer changed the polarity of adsorbents, which favored the adsorption of MB cations (Liu *et al.* 2014). The reason for the similar adsorption from pH 3 to 9 might be attributed to the lower impact of competitive force on the removal rate of MB in acidic solution. When the solution pH was 9, the negatively charged carbon surface groups were still inadequate to have electrostatic interaction with MB, leading to similar results with  $pH \leq 9$ . The remarkable increase from pH 9 to 11 could be attributed to the significant effect of electrostatic interaction. This observation was similar to previously reported results (El Qada *et al.* 2008).

Since NR precipitated under basic conditions, the range of pH was set from 3 to 7 to study the effect of initial solution pH on the removal rate of NR at 150 mg/L. The results are displayed in Figure S4(b). AC could remove 50.8–56.6% of NR at a pH range from pH 3 to 7. The difference in removal rate was not significant in acidic solution. This could be due to the irregularity of material present in the surface of AC, which may contain a large number of active sites, such as carboxyl and hydroxyl groups, and the solute (NR ions) uptake may be related to the active sites (Chen *et al.* 2011). The initial solution pH of 7 would be the best choice for the adsorption of NR.

Figure S4(c) shows the variation in the removal of MO at various solution initial pHs (3–11) at 150 mg/L. It was evident that the maximum removal of MO was at pH 3. With increase in pH from 3 to 9, the removal rate gradually decreased from 63.8 to 57.9%. However, from 9 to 11, the removal rate markedly decreased from 57.9 to 47.3%. MO

had two chemical structures, whose chromophores were anthraquinone or azo bond depending on the pH of the solution, as shown in Figure S5 (available with the online version of this paper). The tendency of the removal rate could be attributed to the abundance of  $H^+$  ions on the surfaces of AC attracting the anionic MO molecules, which enhanced the ability of adsorption for MO onto AC. In contrast,  $OH^-$  ions caused repulsion between the negatively charged surface and the dye molecules (Chen *et al.* 2010). It could be observed that the removal rate was reduced by a different magnitude in acidic and basic solution. This phenomenon might be due to the extent of the influence of attraction and repulsion forces.

Hence, pH 11, 7 and 3 were considered appropriate conditions in further studies for the removal of MB, NR and MO, respectively.

### Effect of temperature

Figure S6(a) shows the effect of temperature on the adsorption of MB at 250 mg/L (Figure S6 is available with the online version of this paper). The adsorption studies were performed at 30, 40, 50, 60 and 70 °C to evaluate the influence of temperature. It can be seen from Figure S6(a) that temperature had a significant effect on the equilibrium time required. Rapid uptake and quick establishment of equilibrium were seen at 50, 60 and 70 °C. At lower temperature, longer equilibrium time was required. At 30 and 40 °C, the adsorption was almost close to equilibrium within 280 min, but the removal amount at 40 °C was larger than at 30 °C. The initial increase of removal rate of MB was due to the amount of available adsorption sites on AC. As the sites became progressively covered, the rate of adsorption decreased (Li *et al.* 2011). Increasing the temperature was known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, due to the decrease in the viscosity of the solution. In addition, the enhancement of removal rate might be due to the chemical interaction between adsorbates and adsorbent, and the creation of some new adsorption sites at higher temperature (Tan *et al.* 2008).

The effect of temperature on adsorption of NR and MO was tested at 150 mg/L. From Figure S6(b) and S6(c), it was noted that the removal rate of NR and MO increased more rapidly over the range from 40 to 60 °C than over the range of 30 to 40 °C or 60 to 70 °C. As a whole, the adsorption rates increased markedly at first, followed by a longer period of slower uptake. The initial rapid adsorption could be attributed to the availability of the positively charged surface of AC,

and the slow rate of dye adsorption was probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent (Chen *et al.* 2010). It is known that changing the temperature would change the equilibrium capacity of the adsorbent for adsorbate, leading to the rise of removal rate with the increase of temperature. The reason might be that the physical bonding between dye molecules and the active sites of the adsorbent weakened as temperature increased, whereas the solubility of dyes increased, thus enhancing the interaction forces between the solute and the solvent (Chen *et al.* 2010). The removal rate, which rose with a different magnitude with the increase of temperature, might be related to the character of dye molecules and the force between the functional groups present on the AC surface.

Three dyes inclined to be adsorbed at higher temperature, indicating that the adsorption of these dyes on AC was endothermic in nature (de Oliveira Brito *et al.* 2010). In total, the enhancement in the removal rate might be due to (a) an increased number of active sites on the sorbent surface, (b) a reduction of boundary layer thickness surrounding the sorbent and (c) a greater dissociability of functional groups present on the AC surface able to link dyes (Daneshvar *et al.* 2012). A similar increase in adsorption capacity with temperature was reported elsewhere (Liu *et al.* 2014).

### Effect of initial concentration and adsorption kinetics

Figure S8 (available with the online version of this paper) shows the effect of initial concentration on the adsorption of dyes. When the initial concentration increased from 50 to 450 mg/L, the removal rate of MB adsorbed decreased from 100 to 59.7%. The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of MB between the aqueous and solid phases. The increase of initial concentration enhanced the interaction between MB and AC. The percent color removal decreased with increasing dye concentrations because of nearly complete coverage of the binding sites at high dye concentrations (Dincer *et al.* 2007). This result was in agreement with another study (Hameed 2009).

The effect of initial concentration (50–250 mg/L) of NR adsorption is displayed in Figure S8(b). The removal rate decreased from 100 to 30.9% with the increase of initial concentration. As to MO, the removal rate of MO adsorbed decreased from 100 to 41.2% with the increase of initial concentration from 50 to 250 mg/L according to Figure S8(c). The mechanism of NR and MO adsorption was in accordance with MB adsorption. A similar result was achieved in another study (Ghaedi *et al.* 2014).

Under comparable conditions, the adsorption capacity of dyes, MB, NR and MO onto AC increased in the order of MB > NR > MO. Such variation was attributed to different molecular size and morphological and/or chemical structure of the three dyes.

The results of MB (250 mg/L), NR (150 mg/L) and MO (150 mg/L) adsorption were fitted by pseudo-first-order kinetic and pseudo-second-order kinetic models, as shown in Figure S9 (available with the online version of this paper). The corresponding kinetic parameters are shown in Table S4 (available with the online version of this paper). The correlation coefficient ( $R^2$ ) for the pseudo-second-order adsorption model was higher than for the pseudo-first-order adsorption model. It suggested that the pseudo-second-order adsorption mechanism was predominant, and that the overall rate of the dye adsorption process appeared to be controlled by the chemisorption process.

The kinetic parameters of intraparticle diffusion are displayed in Table S4. The C value of Equation (6) represented the boundary layer effect. If the plot of  $q_t$  versus  $t^{1/2}$  satisfied a linear relationship with the experimental data, then the sorption process was found to be controlled by intraparticle diffusion only. However, if the data exhibited multi-linear plots, then two or more steps influenced the sorption process. As shown in Figure S9(c), the data exhibited two linear plots, implying that the process was not exclusively controlled by intraparticle diffusion (Gundogdu *et al.* 2012).  $C_1$  and  $C_2$  were the intercept of the two lines at different  $t^{1/2}$ , indicating the boundary layer effect. The adsorption of dyes might be controlled by external mass transfer followed by intraparticle diffusion mass transfer. Similar results of adsorption kinetics had already been reported for dye adsorption onto different materials (Luo *et al.* 2010; Cazetta *et al.* 2011).

### Desorption and FT-IR studies

Desorption studies were usually applied to elucidate the adsorption mechanism. The desorption ratio (%), which was the ratio of the weight of dyes desorbed and the weight of dyes adsorbed, was close to zero in the pH range 2.0–12.0. The desorption ratio suggested that the adsorbed dye remained almost stable on the adsorbent and chemisorption might be the major mode of dye removal by the adsorbent (Li *et al.* 2011).

The FT-IR spectra of AC before and after dye adsorption are displayed in Figure S10 (available with the online version of this paper). A wide band located around  $3,400\text{ cm}^{-1}$  of AC was attributed to  $\nu(\text{O-H})$  vibration in hydroxyl groups or

adsorbed water. The stretching absorption band of O–H seemed reduced after adsorption with dyes, probably indicating some interactions between O–H groups in AC and those of the dye functional groups. Furthermore, a band at about  $3,100\text{ cm}^{-1}$  displayed significant variation from AC after adsorption of dyes, which corresponded to the stretching vibration of H–C ( $\text{sp}^2$  hybridized) (Amela *et al.* 2012). It should be due to the adsorbed dyes on AC. The band near  $1,600\text{ cm}^{-1}$  of AC was due to aromatic ring  $\nu(\text{C}=\text{C})$  vibration (Zhang *et al.* 2011). However, two bands at  $1,600$  and  $1,500\text{ cm}^{-1}$  of MB and NR could be observed, which were assigned to aromatic skeletal vibrations. The two bands at about  $1,600$  and  $1,540\text{ cm}^{-1}$  of MO show slight variation because of the di-aromatic structure. The band around  $1,400\text{ cm}^{-1}$  of the samples could be assigned to  $\nu(\text{C}-\text{O})$  vibration in the carboxylate group and/or  $\nu(\text{C}-\text{N})$  vibration (Juan & Ke-Qiang 2009; Alencar *et al.* 2014). It should be noticed that the stretching band at around  $1,400\text{ cm}^{-1}$  considerably increased, which might be attributed to the functional groups of adsorbed dyes on AC. MB and NR showed a band at about  $1,311\text{ cm}^{-1}$ , which could be assigned to C=N central ring (Inbaraj & Chen 2011). MO showed no band near  $1,311\text{ cm}^{-1}$ , which indicated that the main structure adsorbed on AC was azo bond. The adsorption around  $1,180\text{ cm}^{-1}$  of AC was assigned to the stretching mode of hydrogen-bonded P=O, to O–C stretching vibrations in P–O–C (aromatic) linkage and to P=OOH (Puziy *et al.* 2002). The shift from  $1,180$  to  $1,124\text{ cm}^{-1}$  with MB, to  $1,134\text{ cm}^{-1}$  with NR and to  $1,164\text{ cm}^{-1}$  with MO might be due to the interaction of functional groups of dyes with P=OOH. The different capacity of AC in the adsorption of MB, NR and MO might be due to different interactions between dye molecules and AC. Similar results were observed in the removal of three acid dyes by the brown macroalga *Stoechospermum marginatum* biomass (Daneshvar *et al.* 2012).

## CONCLUSIONS

The removal of MB, NR, and MO from aqueous solutions was found to vary with pH, temperature, initial concentration and contact time. The kinetic parameters indicated that the pseudo-second-order kinetic gave much better fittings than other kinetics. AC prepared from RHR showed good adsorption performance in aqueous solutions, especially for MB adsorption. Dyes connected with AC through interactions of the functional groups with those of AC. AC might act as a promising adsorbent to remove dyes from industrial wastewater.

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