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Use of rice husk-based porous carbon for adsorption of Rhodamine B from aqueous solutions

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Abstract

This paper complements the previous one (adsorption of Malachite Green). Adsorption of Rhodamine B (RB) by rice husk-based porous carbons (RHCs) and commercial carbons from aqueous medium have been studied. Three samples of carbons prepared by NaOH activation, three samples prepared by KOH activation and two samples of commercial carbons have been used. The adsorption isotherms have been determined after modifying the carbon N3 surfaces by oxidation with nitric acid and hydrogen peroxide and after degassing at 800 °C. Three samples of N series have larger capacity for removing RB from solution compared to that of the tested commercial carbons, and the capacity of commercial carbons for RB is larger than K series. The adsorption capacity of RB on oxidation carbons is increased and the adsorption capacities on carbons with heat treatment are larger than that on oxidation. The adsorption mechanisms have been proposed through studying the effect of adsorption conditions. They are complicated and appear attributable to various factors, including pore size distribution and chemical interactions between the RB and the surface functional groups on the carbon surfaces.

Keywords: Rice husk; Carbon; Adsorption; Rhodamine B

1. Introduction

Many industries often use dyes and pigments such as Malachite Green and Rhodamine B extensively for dyeing silk, wool, jute, leather and cotton [1]. Malachite Green has been shown recently to be linked to an increased risk of cancer; it is highly cytotoxic to mammalian cells and also acts as a liver tumor-enhancing agent [2]. The adsorption of Malachite Green has been studied in a previous work [3]. Although RB is inert and non-toxic at the concentration discharged into the receiving water, they impart color undesirable to the water user. Color removal from textile effluents is a major environmental problem because of the difficulty in treating such streams by conventional physicochemical and biological treatment methods. Liquid-phase adsorption has been shown to be an effective way for removing dyes [4]. As a kind of adsorption material, activated carbons can be widely used as industrial adsorbents for this purpose [5–7]. The use of activated carbon for removal of dyes present in low concentration in aqueous solution is of considerable importance due to their well-developed porous structure comprised of hydrophobic graphene layers and hydrophilic surface functional groups. In our previous studies [8,9], rice husks were used as the precursor material by chemical activation with KOH and NaOH at lower temperatures. Previous research has demonstrated the ability of activated carbon for hexavalent chromium adsorption and Malachite Green adsorption [3,10]. However, the possibility of using RHCs for adsorption of RB with

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a bigger molecular size and then compare RHCs with commercial grade carbons has not been studied before. Thus the present work was undertaken, to provide an understanding of the influence of pore size and surface chemistry on the adsorption on RHCs. This was achieved by studying the adsorption of RB on the RHCs with different pore size and commercial carbons, and the comparison of adsorption of RB on oxidized carbons treated by HCl, H_2O_2 and HNO_3 and their heat-treated derivatives. The influence of experimental conditions such as pH, ionic strength and contact temperature has also been studied.

2. Experimental

The RHCs were prepared by sealed dry distillation and activation from rice husk [8,9]. They were active carbon powders. Firstly, the rice husk was washed and dried; secondly, the drying rice husk was carbonized at 450 °C in the presence of nitrogen; then the carbonized product was heated in the presence of a substantial weight of potassium hydroxide or sodium hydroxide at 400 °C for 0.3 to 1.0 h to dehydrate the combination. Thereafter the temperature was raised to activate the combination; finally, the activated product was ground, washed with water and dried at 120 °C to form the porous carbon. Commercial grade porous carbons were derived from wood by $ZnCl_2$–H_2O activation at 800–850 °C. The main physicochemical characteristics of the carbons are summarized in Table 1. The specific surface area and the pore diameter of the samples were measured by N_2 adsorption isotherm using an ASAP 2010 Micromeritics instrument and by the Brunauer–Emmett–Teller (BET) method. Micropore volumes were calculated with Dubinin–Raduskevich equation and mesopore volumes were calculated with the Barrett–Joyner–Hanlenda (BJH) method (ASTM D4641-94). The average pore diameter was estimated from the surface area and total pore volume.

Surface chemistry of activated carbons can be changed by HNO_3 and H_2O_2 treatments [11]. The activated carbons used in this study were treated by HCl and then they were washed with distilled water to remove water-soluble materials present in the carbon prior to the adsorption study. The carbon N3 was modified by oxidation using HNO_3 and H_2O_2 in order to introduce various oxygen functional groups on the carbon surface. The procedure was as follows. RHCs were refluxed in 4 M solutions for 48 h, and were washed with distilled water until H^+ was removed, then dried at 120 °C. Heat treatment derivatives were heated at 10 °C min^{-1} under flowing nitrogen to the desired temperature (800 °C) and held for 1 h at the maximum temperature, then they were cooled to ambient temperature under flowing nitrogen.

The adsorbate RB was estimated by standard spectrophotometric method at $\lambda = 630$ nm. Active carbon and RB stock solution were shook in a thermostatic water bath cum shaker. pH was adjusted using HCl and NaOH, and all pH measurements were carried out using a digital pH meter. The mixture was filtered with filter paper and the residual RB concentration in the filtrate was determined spectrophotometrically using a model 722 UV–VIS spectrophotometer (Shanghai Third Component Factory) in matched quartz cells. All chemicals used were of AR/GR grade.

3. Results and discussion

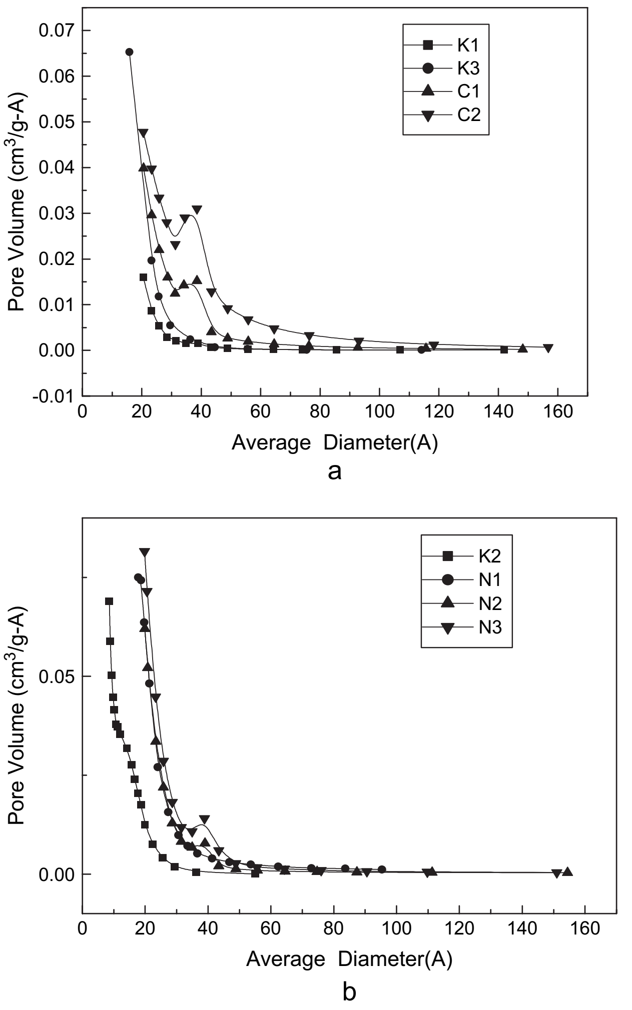
3.1. Characteristics of porous carbons

A summary of the porous structure of all porous carbons studied in the paper is shown in Table 1. Fig. 1a and b show their pore size distributions. Porous carbons with different porosity were prepared by varying the activation conditions. It can be seen that both the surface area and pore size varied widely. The maximum values approach 2800 m^2 g^{-1}, as is shown in Table 1.

Table 1
Summary of porous structure of all porous carbons

Sample	Activation condition	BET. (m^2 g^{-1})	Pore vol. (cc g^{-1})	M. vol. (cc g^{-1})	S. mi. (m^2 g^{-1})	Av. size (Å)
N1	750 °C, 30 min	1886	0.98	0.32	721	20.00
N2	750 °C, 60 min	1987	1.32	0.39	785	23.47
N3	750 °C, 90 min	2721	1.88	0.46	1044	25.79
K1	650 °C, 120 min	1392	0.70	0.44	955	20.20
K2	700 °C, 60 min	1759	0.79	0.78	1735	17.89
K3	750 °C, 60 min	1930	0.97	0.50	1090	20.02
C1		1579	0.95	0.19	451	24.16
C2		1750	1.42	0.07	198	32.50

Samples N1, N2 and N3 were prepared by NaOH activation, a ratio of NaOH/C is 3:1; precalcination temperature was 400 °C; precalcination time was 25 min. K1, K2 and K3 were prepared by KOH activation, a ratio of KOH/C is 4:1; precalcination temperature was 400 °C; precalcination time was 25 min for K1, K3 and 40 min for K2. C1 and C2 were commercial grade carbons derived from wood by $ZnCl_2$ and H_2O activation; activation temperature 750–850 °C.



a

b

Fig. 1. Pore size distribution of porous carbons determined by using ASAP 2010 Micromeritics (a: the series of NaOH activation RHCs; b: the series of KOH activation RHCs).

The micropores are also developed by KOH activation with longer precalcination time, as reflected in Table 1 and Fig. 1b. The micropore surface area and volume approach 1759 m^2 g^{-1} and 0.78 cm^3 g^{-1}, respectively. Previous studies have demonstrated that porous carbons prepared by KOH have a well developed microporosity and lower pore size, and larger pore will be gained by NaOH activation [9]. Commercial grade porous carbons were derived from wood. The average pore size is larger than K series, and the BET surface area is similar to K series. The activation mechanism for the preparation was reported in the literature [12,13].

3.2. Effect of temperature

Temperature has a great effect on the adsorption process. The plot of adsorption capacity as a function of temperature (Fig. 2) shows an increasing amount of adsorbed RB in temperature from 30 to 80 °C and it indicates that adsorption capacity depends on temperature significantly, which is different to that for Malachite Green. The adsorption capacity for Malachite Green largely does not depend on temperature [3]. The molecular size of RB (L: 1.8 nm; B: 0.7 nm) is larger than that of MG (0.8 nm), as is shown in Fig. 3. The average pore size of the carbon is near to 2 nm. Therefore, after the pore has adsorbed RB molecules at the opening, it will hinder the subsequent entrance of RB molecules. The intraparticle diffusion rate of sorbate ions into the pores will be intensified as temperature increases, as diffusion is an endothermic process [14]. So the adsorption increases with temperature.

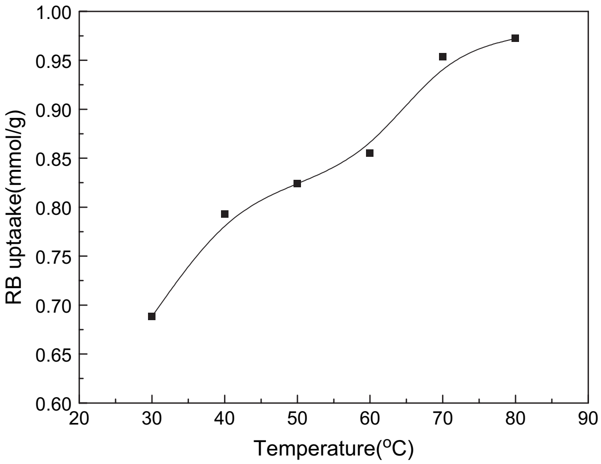
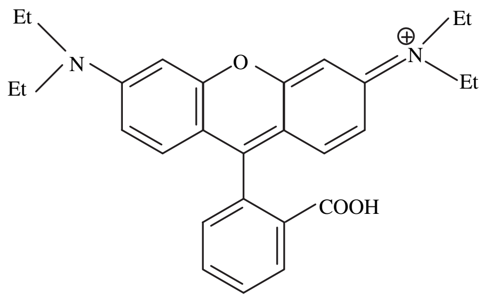
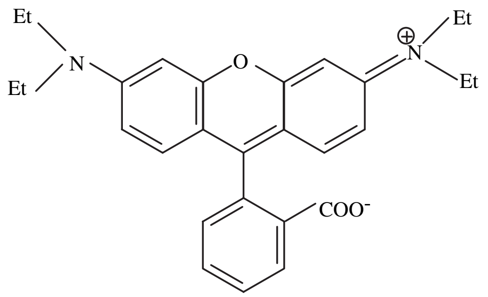


Fig. 2. Adsorption of RB on RHC as a function of temperature. Conditions: pH 3.42; contact time 2 h; RHC 0.8 g/L; [RB] 1.2 mmol/L.



Cationic form



Zwitterionic form

Fig. 3. Molecular forms of RB.

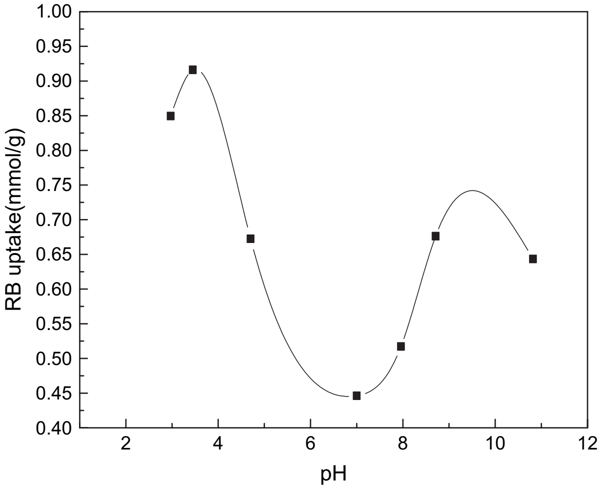


Fig. 4. Adsorption of RB on RHC as a function of pH. Conditions: contact time 2 h; RHC 0.8 g/L; [RB] 1. 2 mmol/L; temperature 25 °C.

3.3. Effect of pH

pH is one of the most important parameters controlling the adsorption process [15]. The effect of pH of the solution on the adsorption of RB ions on sample N3 was determined. The result is shown in Fig. 4. The pH of the solution was controlled by the addition of HCl or NaOH. The uptake of RB ions at pH 7 was the minimum, and a maximum in uptake was obtained at pH 3.45. However, when the pH of the solution was increased (more than pH 7), the uptake of RB ions was increased.

It appears that a change in pH of the solution results in the formation of different ionic species, and different carbon surface charge. At pH values lower than 4, the RB ions is cationic and monomeric molecular form [16]. Thus RB ions can enter into the pore structure. At a pH value higher than 4, the zwitterionic form of RB in water may increase the aggregation of RB to form a bigger molecular form (dimer) and become unable to enter into the pore. Ghanadzadeh et al. [17] have studied the aggregation of RB in the microporous solid hosts. Lopez Arbeloa and Ruiz Ojeda [18] determined the equilibrium constant for the dimer⇔monomer transition of RB in aqueous solution. The greater aggregation of the zwitterionic form is due to the attractive electrostatic interactions between the carboxyl and xanthene groups of the monomers [19]. At a pH value higher than 8, the preponderance of OH^- generates a competition between $-N^+$ and $-COO^-$ and it will decrease the aggregation of RB, which causes an increase in the adsorption of RB ions on the carbon surface. The effect of the charge on the carbon surface and the electrostatic force of attraction and repulsion between the carbon surface and the RB ions cannot explain the result.

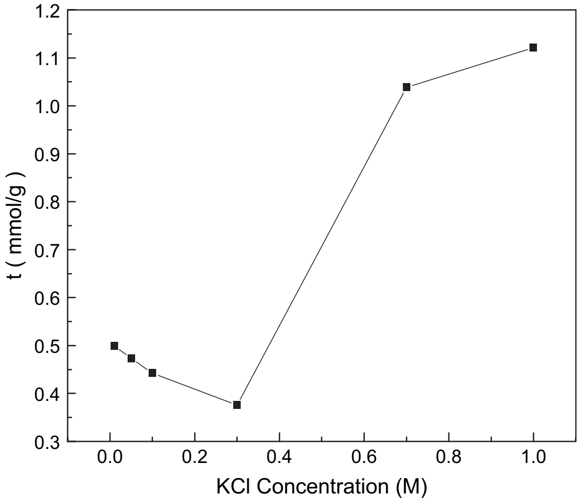


Fig. 5. Adsorption of RB on RHC as a function of KCl. Conditions: contact time 2 h; RHC 0.8 g/L; [RB] 1.2 mmol/L; temperature 25 °C.

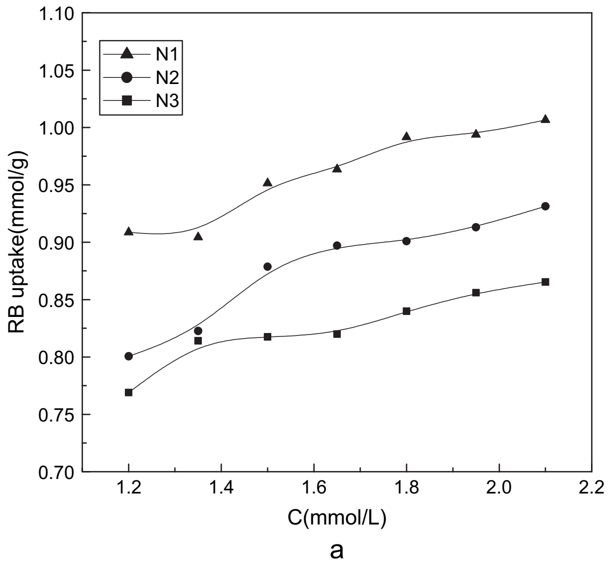
3.4. Effect of ion strength on the adsorption of RB on RHCs

The effects of KCl on the adsorption of RB on sample N3 is shown in Fig. 5. In a low solution concentration KCl had little influence on the capacity. Larger uptake of RB will be obtained at higher ionic strength. The addition of KCl causes a partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl^- anion. The Cl^- ion can also enhance the adsorption capacity by pairing with the RB ions, hence, reducing the repulsion between adjacent RB molecules adsorbed on the surface. This enables the carbon to adsorb more of the positive RB ions.

3.5. Adsorption capacity of adsorbent prepared in different conditions

The adsorption properties depend on the active site where the adsorbate molecules are adsorbed. Therefore, a large specific surface is needed to obtain a large amount of adsorbed RB. Fig. 6a and b show adsorption isotherms of RB on RHCs and commercial carbons. The adsorption capacity is increased with BET surface area and pore volume. The RHCs with NaOH activation have a larger surface area, ensuring that they have a larger amount of adsorbed RB, as was seen from Table 1 and Fig. 6. But the uptake of RB is smaller in the case of N3 compared with N1 and N2. This cannot be explained on the basis of surface area and pore size, which has a larger BET surface area.

Fig. 6a and b provide a comparison of adsorptive capabilities for RHCs relative to commercial activated carbons for RB adsorption. These figures show that the



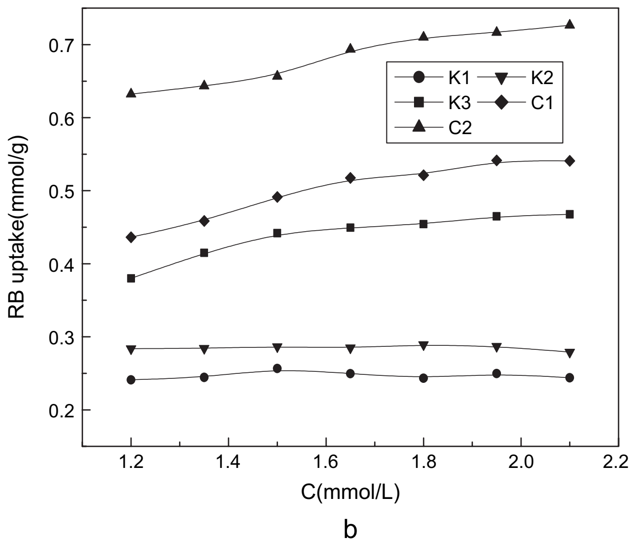


Fig. 6. Adsorption isotherms of RB on RHCs (a: RHCs with NaOH activation; b: RHCs with KOH activation).

tested commercial carbons have much lower performance compared to the carbon N series.

The uptake of RB on commercial carbons is larger than adsorption on K series. Different pore structure may be the reason. Commercial grade porous carbons were derived from wood by $ZnCl_2$–H_2O activation at 800–850 °C, with a larger mesopore volume and a larger pore size as is shown in Table 1 and Fig. 1a, whereas the K series has a lower mesopore volume and a smaller pore size. The micropore volume of carbon K2 approaches 0.78 $cm^3\ g^{-1}$. No mesopore was seen in Table 1 and Fig. 1b. The RB is a moderately sized molecule (1.8 nm), larger than that of the MG molecule (0.8 nm). Small pores are not fully accessible to RB molecules in the liquid phase, and the sample K series mainly have micropores smaller than 2 nm. Therefore, after the micropore walls have adsorbed MG molecules, the diameter of the pore is reduced, which hinders the subsequent entrance of RB molecules. To ensure that the adsorption process occurs, a larger pore diameter and volume are needed. So commercial carbons with large pore diameter have a larger adsorption capacity for RB than the carbon K series.

Sample N1 has the largest adsorption capacity among all the carbons although it does not have the biggest surface area, average pore diameter and pore volume. A similar result was obtained with the adsorption of MG. The reason cannot be explained through the data of the experiment. The adsorption is dependent on many factors such as surface chemistry, surface charge, pore structure and concentration of charged and uncharged functional groups. Therefore other measures must be taken for further research.

3.6. Adsorption on oxidized carbons and their heat-treated derivatives

The samples treated with HNO_3, H_2O_2 and HCl have larger capacities compared to the samples without any treatment, as is shown in Fig. 7. The largest capacities will be obtained on their heat-treated derivatives. The result is different from the adsorption of MG [3]. The treatments with HNO_3 and H_2O_2 produce three types of surface oxides: acidic, basic, and neutral [20–22]. Fixation of the acidic groups on the surface of the activated carbon make it more hydrophilic and decrease its pH of the point of zero charge [20]. No oxygen surface functional groups are formed on carbons when it is treated with HCl, and the treatment has little effect on the surface area and pore texture. Puri and Mahajan [23] have reported that the replacement of alkaline ions with

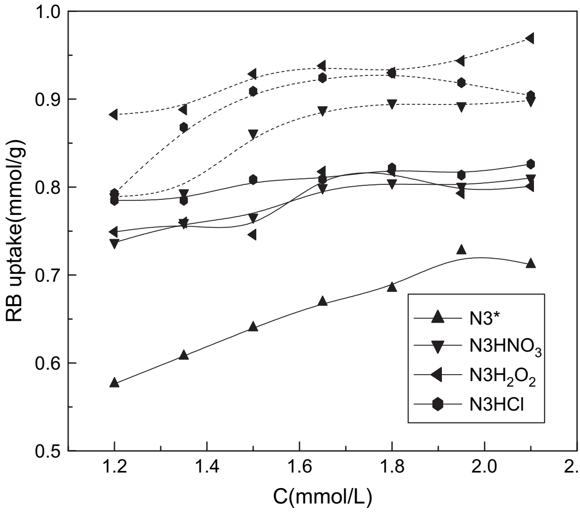


Fig. 7. Comparison of adsorption of RB on oxidized carbons and their heat-treated derivatives. N3*, without HCl treatment; The broken line is the absorption isotherm of the carbon with heat-treated.

H^+ on charcoal causes the hydrophobicity of the surface of the carbon to increase. Three agents can produce different surface properties. Higher adsorption capacity indicates two possibilities. One is that the hydrophobicity and hyrophilicty of the carbon surface have no effect on the adsorption; the other is that they are all fit for the adsorption process, as the RB ions have different functional groups. Heat treatment decreases the oxygen and hydrogen content gradually. The chemical composition and structure of the oxidized carbons heat treated at 800 °C were similar to those of the original samples, but some surface functional groups were removed.

4. Conclusion

Three series of porous carbons were studied for the adsorption of RB ions in aqueous solution. The adsorption process is complex and many factors can affect the adsorption capacity. The pore structure and surface chemistry of the carbons have the most important effect on adsorption of the large molecule RB. The adsorption capacity of RB on oxidation carbon (including HCl treatment) with heat treatment at 800 °C is the largest. Carbon N series have the largest adsorption capacity among the three series of carbons. The carbons prepared with NaOH could be used for the removal of dyes effectively.

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