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Adsorption of malachite green on micro- and mesoporous rice husk-based active carbon

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Abstract

The adsorption of malachite green (MG) from aqueous medium by rice husk-based porous carbons (RHCs) were studied. The extent of adsorption was studied as a function of pH, contact time, contact temperature, adsorbate concentration, ion strength and adsorbent with different pore structural. The comparison of adsorption of MG on oxidized carbons and their heat-treated derivatives were studied. The results obtained under various experimental conditions were found to follow the Freundlich adsorption isotherm. The adsorption capacity of carbons activated by NaOH-activation was larger than that of carbons activated by KOH-activation, the adsorption of MG on oxidized carbons was decreased and was enhanced after heat-treatment.

Keywords: Rice husk; Carbon; Adsorption; Malachite green

1. Introduction

As a kind of adsorption material activated carbons can be widely used as industrial adsorbents for separation, purification, and recovery processes due to their highly porous texture and large adsorption capacity [1–3]. They are also used as catalytic supports, chromatography columns and electrode materials for batteries and capacitors [4–9]. Malachite green has found extensive use all over the world in the fish farming industry as a fungicide, ectoparasiticide and disinfectant [10]. This dye has also been used extensively for dyeing silk, wool, jute, leather and cotton [11]. It has been shown recently that such a substance is linked to an increased risk of cancer. MG is highly cytotoxic to mammalian cells and also acts as a liver tumor-enhancing agent [12]. Activated carbon filtration has been extensively used in portable water treatment for the removal of MG [13]. The use of activated carbon for removal of MG 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 works [14,15], rice husks was used as the precursor material by chemical activation with KOH and NaOH in lower temperature. Previous research has demonstrated the ability of

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activated carbon in hexavalent chromium adsorption [16]. In the present work, RHC with good adsorption capacity was prepared from rice husks by KOH-activation [14] and NaOH-activation. Although the correlation of their structures to the adsorption behavior is considerably understood, the porous structure and adsorption behavior of these activated carbons varied widely from one type of carbon to another. Microporous carbons are used for gas or vapor adsorption, whereas organic molecules are removed from aqueous solution using mesoporous carbons. In contrast, the adsorption of ionic species from solution on activated carbon is usually dominated by the surface functional groups [17].The aim of this work is to evaluate the feasibility of using RHC for the removal of larger organic molecule from aqueous solution. The influence of experimental conditions such as contact time, contact temperature, adsorbate concentration and adsorbent with different pore structure will be studied. The effect of ion strength and the comparison of adsorption of MG on oxidized carbons treated by HCl, H_2O_2 and HNO_3 and adsorption of MG on their heat-treated derivatives were first introduced.

2. Experimental

The activated carbon used in this study was prepared by ourselves [14,15]. They were active carbon powders. The activated carbons were prepared by sealed dry distillation and activation from rice husk. 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 0.3–1.0 h to dehydrate the combination, thereafter the temperature was raised to a higher temperature to activate the combination; finally, the activated product was ground, washed with water and dried at 120 °C to form the porous carbon. Details of the apparatus and experimental methods have been given elsewhere [14]. The main physicochemical characteristics of the carbon were summarized in Table 1. The pore structures of active carbon were investigated by using a computer controlled automated porosimeter (Micromeritics ASAP 2010,single port). Nitrogen was used as the cold bath (77 K) and BET equation was used to calculate the specific surface area. The BJH [18] method was used to calculate the mesopore distribution.

Surface chemistry of activated carbons can be changed by HNO_3 and H_2O_2 treatments [19]. The activated carbon used in this study was washed with distilled water to remove water soluble materials present in the carbon prior to the adsorption study. Then the carbon was treated by HCl and 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 it was dried at 120 °C. Heat treatment derivatives were heated at 10 °C min^{-1} under flowing nitrogen to the desired temperature

Table 1
A summary of the porous structural of all active carbons studied in the paper

Samples	Activation condition	BET. (m^2/g)	Pore vol. (cc/g)	M. vol (cc/g)	S. mi. (m^2/g)	Av. size (A)
N1	750 °C30 min	1886	0.98	0.32	721	20.00
N2	750 °C60 min	1987	1.32	0.39	785	23.47
N3	750 °C90 min	2721	1.88	0.46	1044	25.79
K1	650 °C120 min	1392	0.70	0.44	955	20.20
K2	700 °C60 min	1759	0.79	0.78	1735	17.89
K3	750 °C60 min	1930	0.97	0.50	1090	20.02

Samples N1, N2 and N3 were prepared by NaOH-activation, a ratio of NaOH/C is 3/1; precalcination temperature was 400 °C, and 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, and precalcination time was 25 min for K1, K3 and 40 min for K2.

(800 °C) and held for 1 h at the maximum temperature, then they were cool to ambient temperature under flowing nitrogen.

The adsorbate MG was estimated by standard spectrophotometric method at $\lambda = 520$ nm. Active carbon and MG stock solution were shaking in a thermostatic water bath cum shaker. pH was adjusted using HCl and all pH measurements were carried out using a digital pH meter. The mixture was filtered with filter paper and the residual MG concentration in the filtrate was determined spectrophotometrically using a model 722 UV–vis spectro-

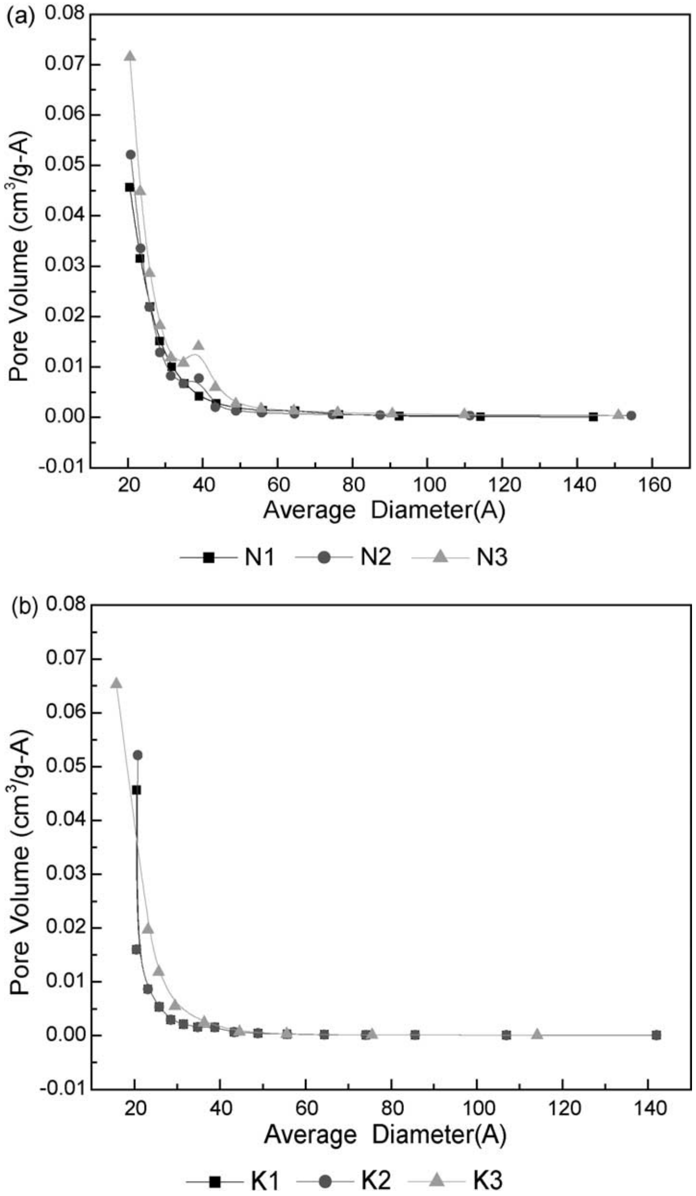

Fig. 1. Adsorption isotherm of the active carbons studied in the paper (a) the series of NaOH-activation RHCs (b) the series of KOH-activation RHCs.

photometer (Shanghai Third Component Factory) in a matched quartz cells. All chemicals used are 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 and Fig. 1 shows 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, as is shown in Table 1. Micropore was also developed by KOH activation with longer pre-calcination time, as reflected in Table 1 and Fig. 1b. The micropore surface area and micropore volume approach 1759 m^2/g and 0.78 cm^3/g, respectively. Previous works have demonstrated that NaOH-activation is very like the activation with KOH. But the outer activation is stronger [15], for the boiling point of sodium is 883 °C higher than potassium 758 °C. So the potassium can enter into the interior of carbon structure and make the activation freely. Porous carbons prepared by KOH have a well developed microporosity and lower pore size, and larger pore will be gained by NaOH-activation.

3.2. Effect of contact time

A plot of adsorption capacity vs adsorption time (min) was show in Fig. 2, indicating the process to be uniform with time. Equilibrium is achieved in about 90 min at 25 °C with an adsorbent dose of 0.8g/l and an adsorbate concentration of 1.2 mmol/l; thereafter it remains almost unchanged with respect to time. The equilibrium time is as same as the adsorption of hexavalent chromium from aqueous medium by RHCs [16].

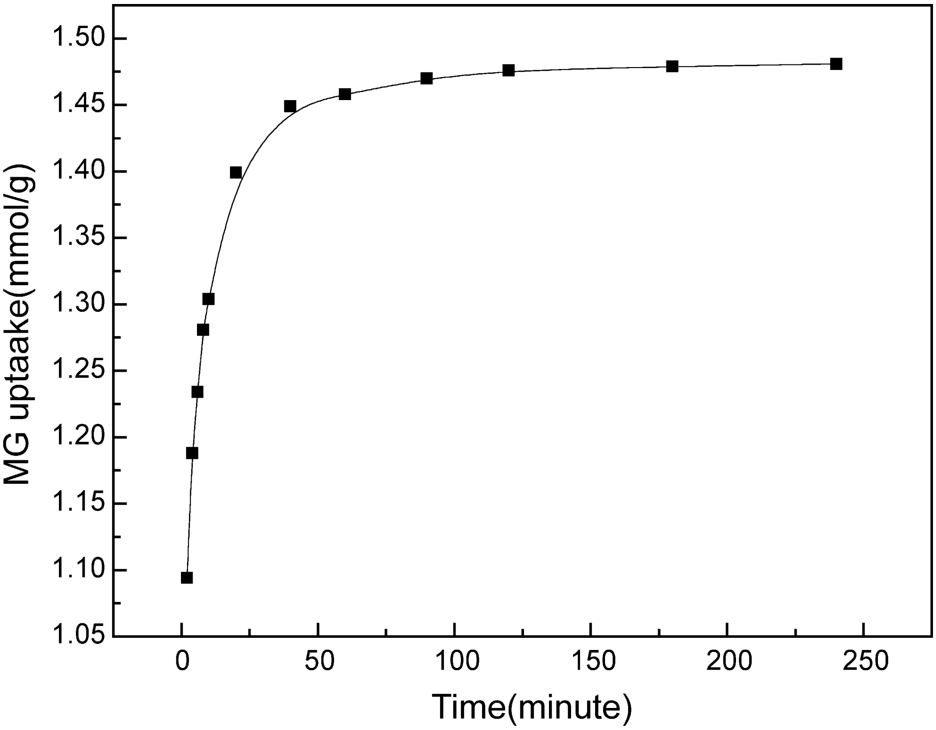

Fig. 2. Adsorption of MG on RHC as a function of contact time. Conditions: (MG: 1.2 mmol/l; RHC:0.8 g/l; temperature: 25 °C; pH: 6.59).

3.3. Effect of temperature

Temperature has great effect on the adsorption process. The plot of adsorption capacity as a function of temperature (Fig. 3) shows an increasing amount of adsorbed MG in temperature from 20 to 80 °C but not apparently, which indicate the chemisorption to take place. But the adsorption capacity does not largely depend on temperature. For the chemical interaction of carbon surface groups and the sorbate ions does not like the hexavalent chromium which is dependent on the redox between the sorbent surface groups and sorbate. The adsorption increased with temperature may be due to the increase of the intraparticle diffusion rate of sorbate ions into the pores at higher temperature as diffusion is an endothermic process [20].

3.4. Effect of pH

pH is one of the most important parameters controlling the adsorption process [16,21]. Fig. 4 shows that the RHC is active in higher pH range, but the difference between lower pH and higher pH is less than that of Cr (VI) species on the RHC [19]. The adsorption was increased with pH which may be due to the increase of the negative charge on the carbon surface; thus the electrostatic force of attraction between the carbon surface and the MG ions were increased.

3.5. Effect of ion strength on the adsorption of MG on RHCs

The effects of KCl on the adsorption of MG on RHCs with HCl, H_2O_2 and HNO_3 treatment are shown in Fig. 5. The data were obtained at 25 °C and a pH of 6.59. Fig. 5 shows the effect of KCl on MG adsorption on RHC with a solution concentration of 1.2 mmol/l. And Fig. 6 shows the adsorpion isotherm of MG at two salt concentrations. In a low solution concentration KCl had little influence on capacity, as shown in Fig. 5. It can be concluded that the available adsorption

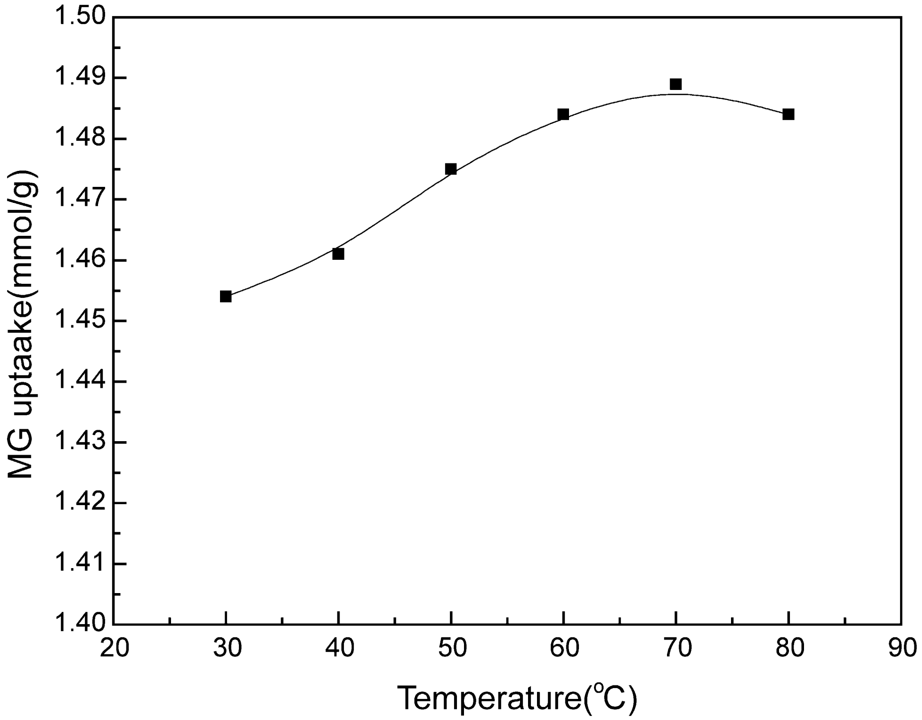

Fig. 3. Adsorption of MG on RHC as a function of temperature. Conditions: (pH: 6.59; contact time: 2 h; RHC: 0.8g/l; MG: 1.2 mmol/l).

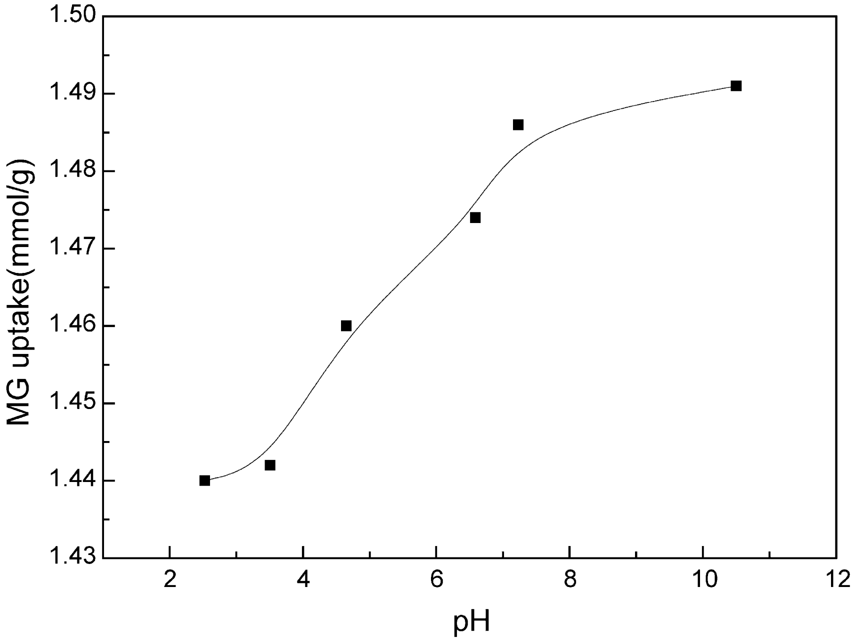

Fig. 4. Adsorption of MG on RHC as a function of pH. Conditions: (contact time: 2 h; RHC: 0.8g/l; MG: 1.2 mmol/l; temperature: 25 °C).

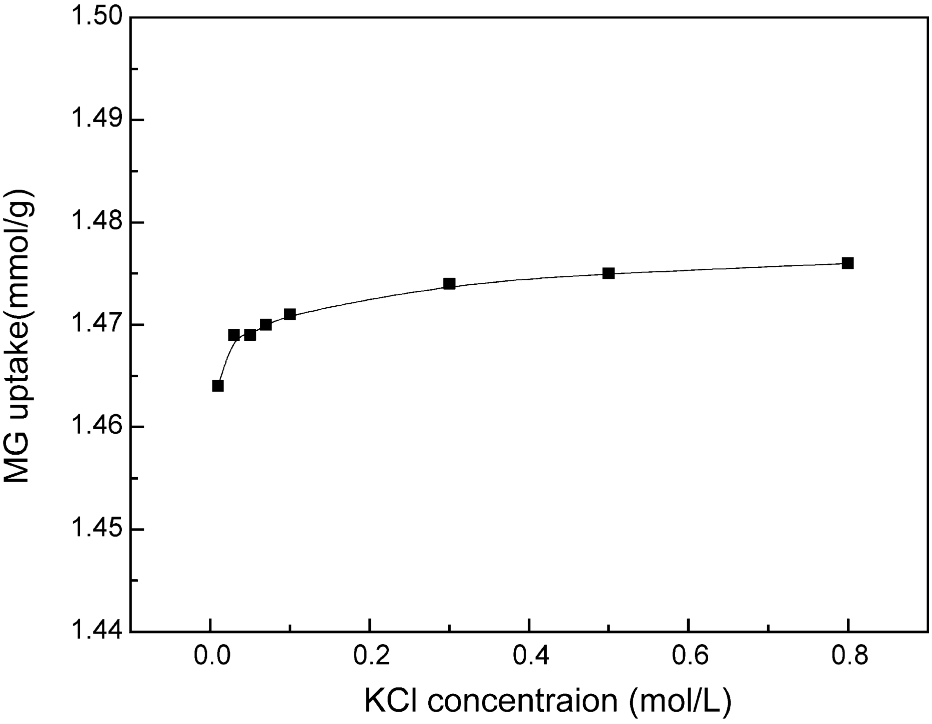

Fig. 5. Adsorption of MG on RHC as a function of KCl. Conditions: (contact time: 2 h; RHC: 0.8g/l; MG: 1.2 mmol/l; temperature: 25 °C).

sites are enough for MG at a relatively low solution concentration. In contrast, with increasing equilibrium solution concentration, adsorption occurs on progressively less accessible sites. A stronger effect is observed in higher concentration, as shown in Fig. 6. The capacity observed at higher salt concentration (0.3M) for MG is higher than lower concentration (0.01M). 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 MG ions, hence, reducing the repulsion between adjacent MG molecules adsorbed on the surface. This enables the carbon to adsorb more of the positive MG ions, Since the repulsive forces between the surface and MG and repulsive force among positve MG ions are reduced. Similar explanations have been given by other researchers for other organic materials [22–24].

3.6. Adsorption capacity of adsorbent prepared in different conditions

Fig. 7 shows adsorption isotherms of MG on RHCs. Based on the data shown in Table 1 and Fig. 7, the different adsorption capacities of RHC were seen. The adsorption capacity was increased with BET surface area and pore volume, which were enhanced by KOH-activation. While the same result will not be gained for NaOH-activation. The potassium can enter the interior of carbon structure and make the activation freely, and micropore was produced. The micropore surface area and micropore volume of carbon K2 approach 1759 m^2/g and 0.78 cm^3/g, respectively. And no mesopore was seen from Table 2 and Fig. 1. Which confirm that micropore was produced by KOH-acitivation. MG has bigger molecules than many inorganic ions. Small pores are not fully accessible to MG molecular in the liquid phase. So the K series with lower pore size have lower capacity

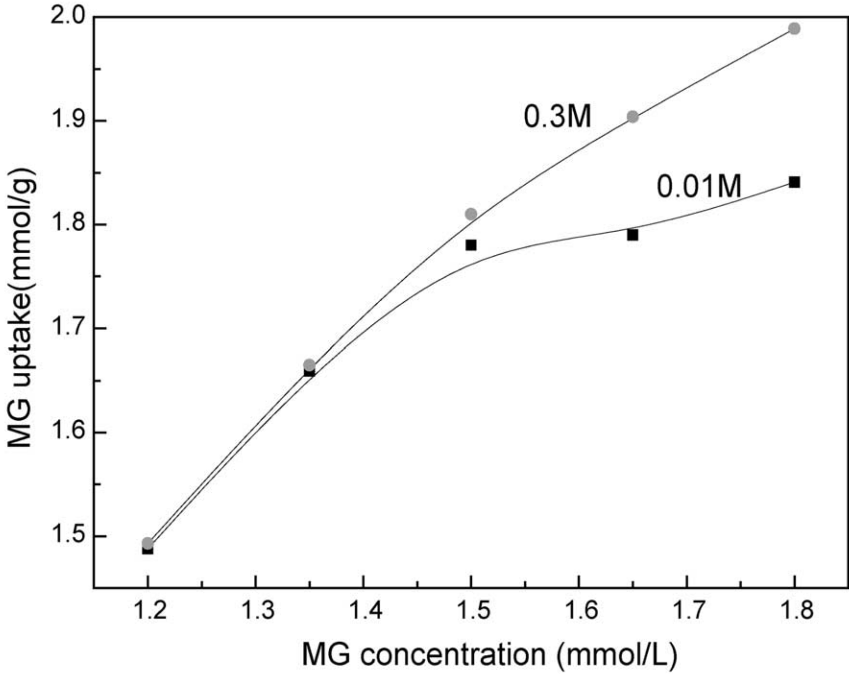

Fig. 6. Adsorption isotherm of MG on RHC as a function of KCl. Conditions: (contact time: 2 h; RHC: 0.8g/l; KCl: 0.3,0.01 mol/l; temperature: 25 °C).

than the N series, though they have similar surface area, as we can see from Table 1 and Fig. 7. The pore size may the main reason for the difference of the K and N series. But we may see that N1 has the largest adsorption capacity among all the carbons, although it has not got the biggest surface area and pore volume. The reason can not 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, etc. So other measures must be taken for further research.

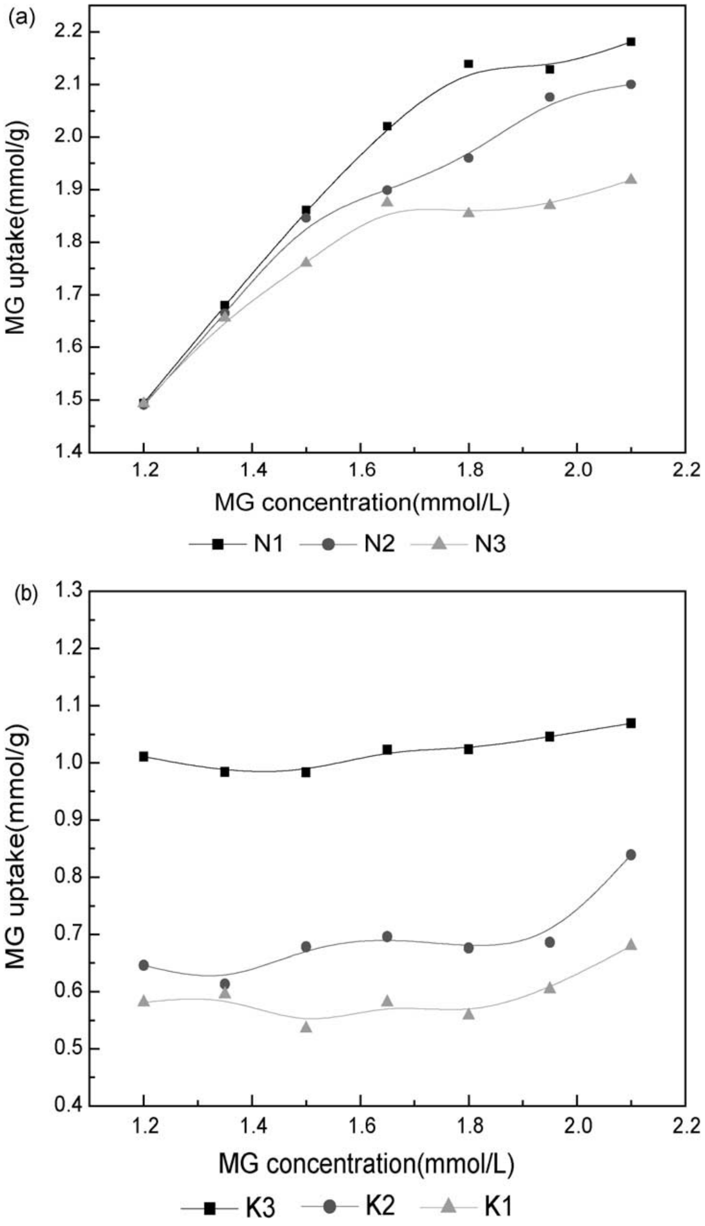

Fig. 7. Adsorption isotherms of MG on RHCs (a) RHCs with NaOH-activation, (b) RHCs with KOH-activation.

3.7. Adsorption of MG on oxidized carbons and their heat-treated derivatives

Oxygen surface functional groups are formed on activated carbons when they are treated with oxidizing agents either in the gas phase or in solution. The treatments produce three types of surface oxides: acidic, basic, and neutral [25,26]. Treatment by H_2O_2 and HNO_3 introduce predominantly acidic surface oxides, and decreases its pH of the point of zero change, and at the same time, the treatments can affect the surface area and pore texture of the activated carbons [19]. Treatment with HNO_3 causes a decrease in surface

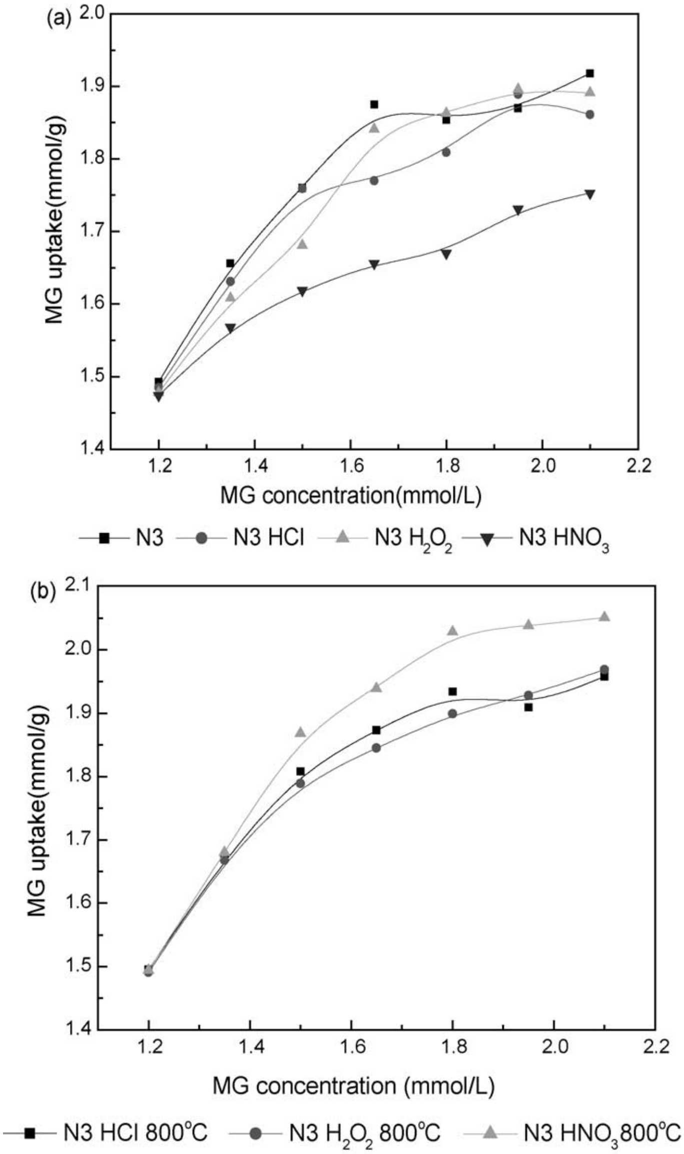

Fig. 8. Comparison of adsorption of MG on oxidized carbons and their heat-treated derivatives. (a) Oxidized carbons, (b) oxidized carbons with heat treatments.

area and in the microporosity of the activated carbons and these effects are more drastic than H_2O_2 [9,27]. No oxygen surface functional groups are formed on carbons when they are treated with HCl, and the treatment has little effect on the surface area and pore texture. The difference of the treatment with three agents can explain the adsorption extent on the RHCs. For the MG is big molecularly with a molecule size of 0.8 nm. The intrinsic RHCs of the present work mainly have mesopores near 2 nm. Therefore, the adsorption properties depend on the active site where the adsorbate molecules are adsorbed. Therefore, a large specific surface area and large pore are needed to obtain a large amount of adsorbed MG. So the amount of MG adsorbed on the RHCs with HNO_3 and H_2O_2 treatment is smaller than the RHCs without treatments, as shown in Fig. 8. This indicates that introduction of oxygen functional groups in mesopores has hindered the access of MG to some of these pores or decreases the active site of the carbons. The chemical composition and structure of the oxidized carbons heat treated at 800 °C were similar to those of the original samples for the removal of some surface functional groups. So MG adsorption was decreased significantly after the carbon was oxidized with HNO_3, and dramatically enhanced after the carbon was heat treated at 800 °C.

3.8. Adsorption isotherms

The adsorption data were fitted to linearly transformed Freundlich isotherms, as shown in Fig. 9. The linearized Freundlich equation is given as:

$$\tau = KC^{1/n} \tag{1}$$

where τ is the amount of MG adsorbed per unit mass of adsorbent (mmol/g), C is the residual concentration of MG in solution (mmol/l), K is a constant which is a measure of adsorption capacity and $1/n$ is a measure of adsorption intensity. The data obtained from the experiments are fitted to Eq. (1). It must be emphasized that the Freundlich model in no way is meant to imply that the model assumptions are valid for this case. It was selected only because it provides a simple and effective representation of the trends observed.

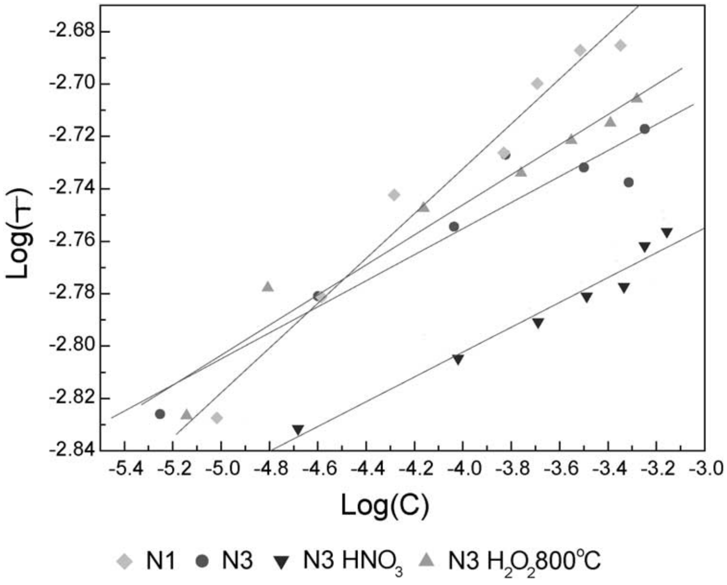

Fig. 9. Freundlich isotherm for adsorption of MG on some RHCs at 25 °C.

4. Conclusion

Two series of RHCs with different pore size distributions were prepared for the adsorption of malachite green in aqueous solution. N series RHCs have larger adsorption capacity than K series for their larger pore size. The adsorption process is complex and many factors can affect the adsorption capacity in the same adsorption conditions, such as surface chemistry, surface charge and pore structure etc. The adsorption capacity does not always increase with surface area. Carbon with HNO_3 treatments has significantly decreased the MG adsorption capacity among three agents and was dramatically enhanced after the carbon was heat treated at 800 °C.

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