Enhanced Removal of Methylene Blue from Aqueous Solution by Pummelo Peel Pretreated with Sodium Hydroxide

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In the present study, pummelo peel pretreated with sodium hydroxide is used for adsorption of methylene blue (MB). In order to investigate the effects of pretreatment on the cationic dye adsorption, the kinetics and capacities of raw pummelo peel (RPP) and sodium hydroxide treated pummelo peel (TPP) to remove MB from aqueous solutions were compared. The effects of various experimental parameters (*e.g.,* initial pH, dye concentration, contact time) were also studied. According to the maximum adsorption capacity (q_m) obtained, adsorption capability of pummelo peel is significantly increased after sodium hydroxide treatment. Both adsorption isotherms of RPP and sodium hydroxide TPP fitted the Langmuir model well, but not the Freundlich model. The processes of uptake followed pseudo-first order rate kinetics. The results in this study indicated that sodium hydroxide TPP is a promising adsorbent for removing MB from aqueous solution.

Key words —— methylene blue, pretreatment, pummelo peel, adsorption, sodium hydroxide, wastewater

INTRODUCTION

Dyes are used widely in many modern industries, such as food, paper, rubber, plastics, cosmetics and textile, in order to color their products.[1)] Many developing countries discharge the effluent to surface water without any treatment because of technological and economical limitations.[2)] Because most of the dyes are stable to light and oxidizing agents, the elimination of color from dye-bearing wastewaters is one of the major environmental problems. Adsorption is one of the most economical and efficient treatment techniques for the elimination of dyes. Many studies on low cost, non-conventional adsorbents have been carried out. Crini[3)] has recently reviewed non-conventional adsorbents for the removal of dyes. Most of them are cellulose-based and can be used without any previous thermal or chemical treatment, such as wood sawdust, wheat straw, orange peel, banana pitch, peanut hull, rice husk, water hyacinth roots, guava seeds, *etc.*

The pummelo is a native of southeastern Asia. The main areas of production are southern China, southern Japan, Thailand, Vietnam, Malaysia, Indonesia, U.S.A. (California and Florida), the Caribbean islands and Africa.[4)] It is the largest of all *Citrus* fruits and contains a thick, spongy peel. Pummelo peel was used as an adsorbent for removal of basic dye (basic blue 3) from aqueous solution and found to be an attractive candidate.[5)]

Methylene blue (MB) is a cationic dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools, *etc.* Though MB is not strongly hazardous, it can cause some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans.[6)] MB is generally used to test the adsorption capacity of various adsorbents, and it also permits a quantitative comparison between the adsorption capacities of various adsorbents.[7)]

The object of the present work was to explore the adsorption capability of the NaOH treated pummelo peel (TPP) as an adsorbent for removal of the basic dye MB from aqueous solution. Meanwhile, the equilibrium and kinetic data of the adsorption were also provided. To illuminate the adsorption efficiency of TPP, the adsorption data of TPP were then compared with those of the raw pummelo peel (RPP).

MATERIALS AND METHODS

Chemicals and Materials —— The pummelo peel used in this study was obtained from a local fruit

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market of Nanjing in China. The collected biomaterial was rinsed with distilled water, cut into small pieces and then dried in an oven at 60°C for 48 hr. Dry biomass was crushed into granules, sieved to different particle sizes, and then 60–100 mesh particles of RPP were preserved in desiccators for further use. Pretreatment of pummelo peel was according to Xuan *et al.*[8] Briefly, ten gram of RPP was added to 0.1 M NaOH solution. The solution was stirred at room temperature for 1 hr, and then vacuum filtered. The sample was kept for dry in an oven at 55°C for 24 hr after washed with distilled water to neutral pH, hereafter the treated pummelo peel was abbreviated as TPP.

MB (basic blue 9) was purchased from Sanaisi reagent Ltd. (Shanghai, China) and used without further purification. It has molecular formula $C_{16}H_{24}ClN_3O_3S$ (mol. wt. 373.9 g/mol) with Colour Index Number 52015. The structure of MB is shown as follows (Fig. 1).

The wavelength of maximum absorption (λ_{max}) of this dye is 663 nm. The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 1000 mg/l. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

Adsorption Procedure of TPP and RPP —— Adsorption experiments were carried out in a rotary shaker at 150 rpm and 30°C using 100 ml flasks containing 40 ml of different concentrations and initial pH values of dye solutions. The initial pH values of the solutions were previously adjusted with 0.1 M HNO_3 or NaOH. Different doses of adsorbent were added to each flask and then the flasks were sealed to prevent change in volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were taken out from the flasks and the MB solutions were separated from the adsorbent by filtration with a 200 mesh stainless steel sieve and then centrifuged (BECKMAN J2-MC, Los Angeles, California, U.S.A.). Dye concentrations in the supernatant solutions were estimated by measuring the absorbance at the maximum wavelength 663 nm using a spectrophotometer (VIS-7220, Beijing, China). The amount of dyes sorbed by the biomaterial was calculated using the following equation:

$$q = (C_0 - C_e)\, V/W$$

where q (mg/g) is the amount of dye sorbed by biomass, C_0 and C_e (mg/l) are the initial and equilibrium liquid-phase concentrations of the dye, respectively. V (l), the initial volume of dye solution, and W (g), the weight of the pummelo peel.

The experiments were conducted in triplicate and the negative controls (with no adsorbent) were simultaneously carried out to ensure that adsorption was by pummelo peel and not by the container.

IR Spectra Study —— The IR spectra of RPP and TPP were performed on a Fourier transform infrared spectrometer (VECTOR 22, Bruker, Karlsruhe, Germany) to elucidate the functional groups presenting in pummelo peel before and after treatment.

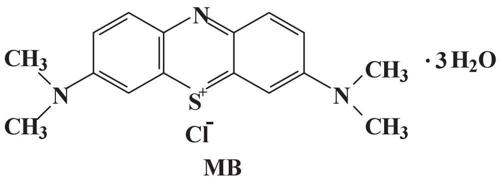

Fig. 1. Chemical structure of MB

RESULTS AND DISCUSSION

Analysis of IR Spectra before and after NaOH Pretreatment

The IR spectra of RPP and TPP are shown in Fig. 2. Comparing with the IR spectrum of RPP, it could be seen that there is a much weaker characteristic stretching vibration absorption band of C = O at 1741.4 cm^{-1} and a stronger stretching vibration absorption band of carboxyl group at 1627.8 cm^{-1}

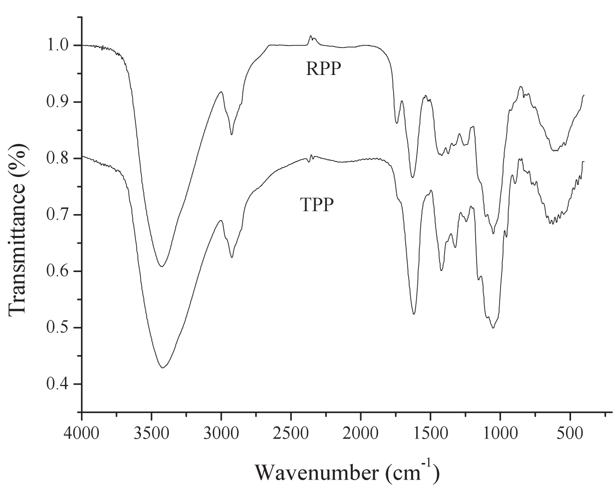

Fig. 2. IR spectra of RPP and NaOH TPP

in IR spectrum of TPP. One of the reasons for this might be the following. After pretreatment, the glycosyl radical which contains aldehyde group located at the end of cellulose may be removed and molecular rearrangement occurs. This could make carboxyl group to form at the end of cellulose and thereby is beneficial to adsorption of the cationic dye MB.

Effect of Initial pH on Dye Uptake

Effects of pH on adsorption of basic dye MB have been reported by many researchers, and the results showed that pH of solution could significantly influence adsorption process.[9] To study the influence of pH on the adsorption capacity of RPP and TPP, the experiments were performed at 300 mg/l initial dye concentration with 2 g/l adsorbent at 30°C for 6 hr equilibrium time. The range of pH chosen was from 3 to 10. As elucidated in Fig. 3, for both materials, the ratios of dye sorbed increased as initial pH increased from 3 to 5, and then the dye removal ratios were not significantly changed ($p > 0.05$) beyond pH 6. Therefore, the pH 8 was chosen for the following experiments. Furthermore, compared with RPP, TPP also displayed higher adsorption capabilities at all selected pH.

Adsorption Kinetics

RPP and TPP both showed a rapid adsorption rate and promising removal efficiency to MB (Fig. 4). The equilibriums were almost achieved in 30 min. After 3 hr adsorption, removal efficiencies of RPP and TPP reached 90.2% and 99.1%, respectively. It suggests the possibility of monolayer coverage of MB on the outer surface of the adsorbent, because the curves of removal versus time are single, smooth and continuous leading to saturation.[10)]

The kinetic data were treated with the following Lagergren's pseudo-first order rate equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (1)$$

where q_e and q_t (mg/g) refer to the amount of dye sorbed at equilibrium and time t (min), respectively, and k_1 is the rate constant.

The plot of the linearised form of the pseudo-first order curve is shown in Fig. 5. The adsorption data of TPP are well represented by Lagergren's model of Eq. (1) for the earlier period of adsorption

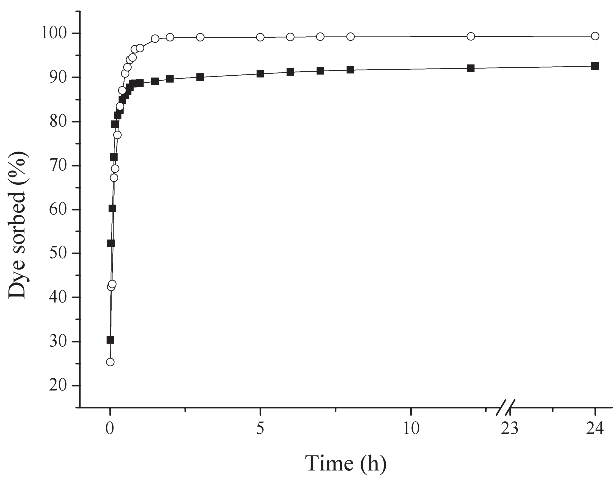

Fig. 4. Adsorption kinetics of MB on RPP (-■-) and NaOH TPP (-○-) (dye concentration: 300 mg/l; adsorbent dose: 2 g/l; temperature: 30°C)

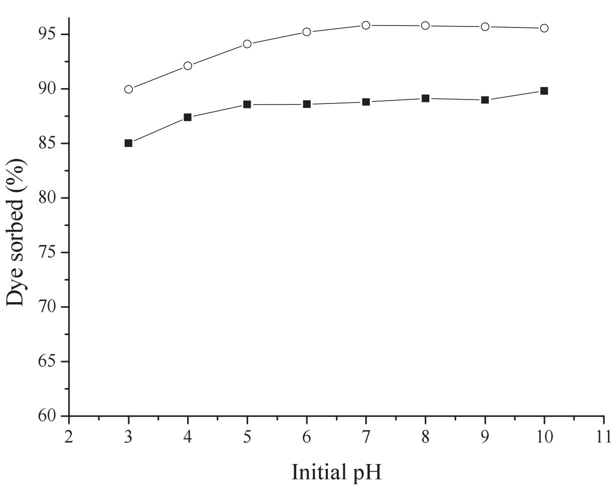

Fig. 3. Effect of initial pH on MB adsorption by RPP (-■-) and NaOH TPP (-○-) (dye concentration: 300 mg/l; adsorbent dose: 2 g/l)

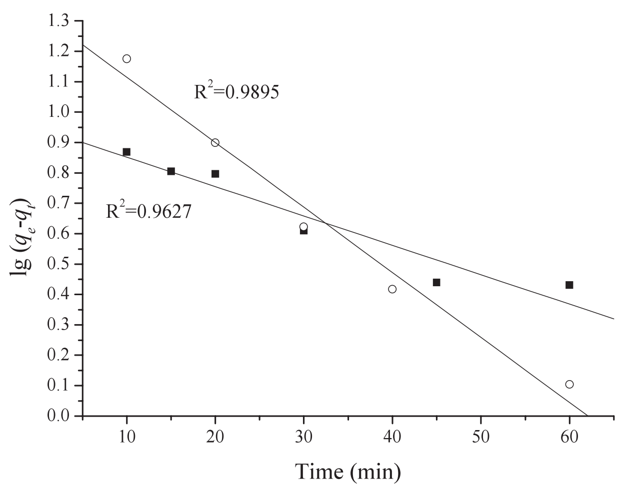

Fig. 5. Pseudo-first order kinetics for adsorption of MB on RPP (■) and NaOH TPP (○) (dye concentration: 300 mg/l; adsorbent dose: 2 g/l; temperature: 30°C)

(5–60 min), while the coefficient of the adsorption of RPP is somewhat lower. It appears appropriate to use Lagergren's model for the kinetics of MB adsorption on TPP.

Intraparticle Diffusion Study

The intra-particle diffusion model was applied to describe the dye adsorption. Assuming that the rate is controlled by pore and intra-particle diffusion, the amount adsorbed (q_t) is proportional to the square root of time ($t^{1/2}$).

$$q_t = k_{id}t^{1/2} \tag{2}$$

where q_t is the amount of dye sorbed (mg/g) at time t (min). k_{id} values were obtained from the slopes of the linear plots of q_t versus $t^{1/2}$.

The plot of q_t versus $t^{1/2}$ may present multi linearity,[11] which indicates that two or more steps occur in the adsorption processes. Figure 6 shows the plot of q_t versus $t^{1/2}$ about adsorption of the MB on RPP and TPP in first 50 min. The k_{id} value was increased from 3.37 to 5.58 mg/g min$^{1/2}$ due to NaOH pretreatment.

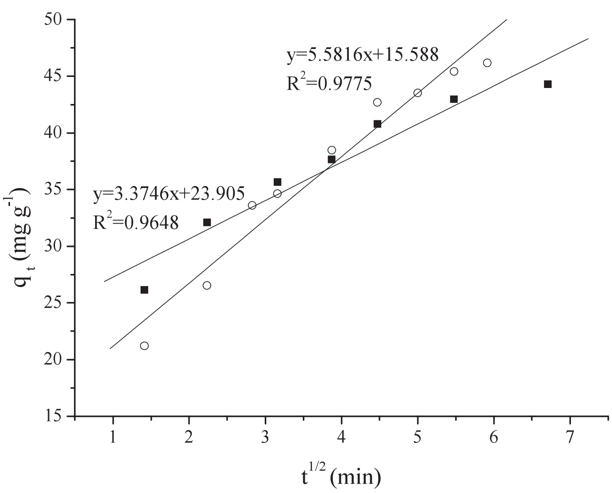

Fig. 6. Amount of dye sorbed versus $t^{1/2}$ for intraparticle transport of MB by RPP (■) and NaOH TPP (○)

Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose.

The Langmuir and Freundlich are the most frequently employed models to describe the experimental data of adsorption isotherms.[12] In this work, both models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration.

The Langmuir and Freundlich isotherms of MB adsorption are shown in Fig. 7. They reveals that, over the range of MB concentrations studied, all experimental data of RPP and TPP were fitted well by the Langmuir isotherms with the regression coefficients (R^2) 0.9970 and 0.9999, respectively. On the contrary, the data did not fit the Freundlich model.

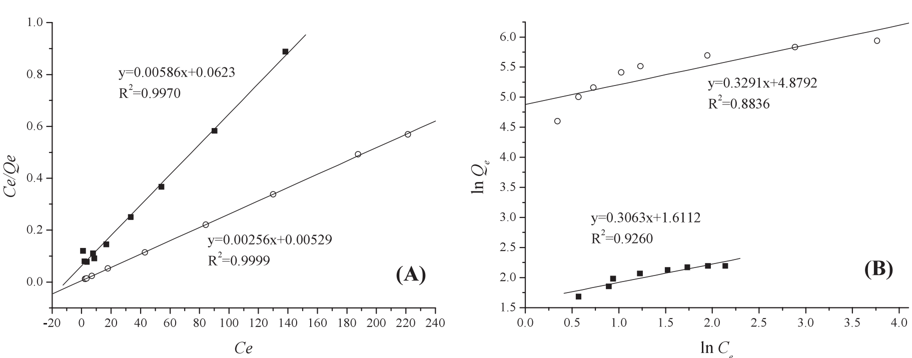

Fig. 7. Comparison of linearised Langmuir isotherms (A) and Freundlich isotherms (B) for MB adsorption by RPP (■) and NaOH TPP (○) at 30°C

Table 1. The Values of Parameters and Correlation Coefficients of Langmuir and Freundlich Equations

Dye	Langmuir isotherm			Freundlich isotherm		
	q_m(mg/g)	K_a	R^2	$1/n$	K_F	R^2
RPP	170.6	0.094	0.9970	0.3063	5.009	0.9260
TPP	390.6	0.484	0.9999	0.3291	131.53	0.8836$^{a)}$

a) $R^2 = 0.8836 \ll 1$, the Freundlich model was not fitted.

The relative adsorption parameters of MB on RPP and TPP are summarized in Table 1. As in the observation, maximum adsorption capacity (q_m) of the pummelo peel alters from 170.6 mg/l to 390.6 mg/l after treatment with NaOH, with increasing of 129.4%. It indicates that TPP possesses promising potential as an adsorbent for MB. The TPP had a much higher removal capability to MB. The reason is likely to be the availability of cellulose and hemicellulose for binding with the dye molecules due to the removal of lignin and natural pigments. At the same time, the surface area available for adsorption may be increased.

According to the report of Hameed *et al.*,[5] the q_{m} of RPP for basic blue 3 is 344.83 mg/l. In our work, MB (basic blue 9) was chosen to test adsorption capability of RPP and TPP. The results suggest that TPP has a better adsorption capability to this dye than RPP.

The NaOH pretreatment presents different effects on various biomaterials. Robinson *et al.* reported that pretreatment with 0.25 M NaOH could produce an increase in the amount of dyes on wheat straw,[13] but not on corncob and barley husk. Inthorn *et al.* found that narrow-leaved cattail pretreated by 0.1 M NaOH removed basic violet 7 and Basic Red 14 efficiently.[14] In our study, the pretreatment brings a significant increase in adsorption of MB, while the mechanism remains to be elucidated in further research.

In conclusions, pummelo peel pretreated with 0.1 M NaOH has better potential than RPP as a low-cost adsorbent for removal of MB from aqueous solution.

The adsorptions are solution pH dependent and the pH range of highest removal of MB is 6.0–10.0. The pretreatment does not alter the suitable pH range of adsorption.

The adsorption data of the pretreated pummelo peel are closely fitted Langmuir model and Lagergren's pseudo-first order rate equation. The values of coefficient are higher than those of the RPP. The maximum MB uptake of the pretreated pummelo peel is 390.6 mg/g, which is 129.4% higher than RPP.

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