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Shaddock peel as a novel low-cost adsorbent for removal of methylene blue from dye wastewater

Junqian Liang[a], Jinhua Wu[a,*], Ping Li[a], Xiangde Wang[a], Bo Yang[b]

[a]*The Key Laboratory of Environmental Protection and Eco-Remediation of Guangdong Regular Higher Education Institutions; The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, PR China; School of Environmental Science and Engineering, South China University of Technology, Guangzhou 510006, PR China Tel./Fax: + 86 20 39380568; email: jinhuawu@scut.edu.cn*
[b]*School of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, PR China*

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ABSTRACT

Shaddock peel was found to be a novel low-cost and locally available adsorbent for the removal of methylene blue (MB) from dye wastewater. The effects of initial pH, adsorbent diameter, dye concentration and contact time on the adsorption of MB were studied. MB could be removed effectively when initial pH ≥ 6. The adsorption data fitted very well with the Langmuir adsorption model and the maximum adsorption capacity was 305.81 mg/g at 303 K. The adsorption process followed the pseudo-second-order kinetic model. The results indicated that shaddock peel is a promising adsorbent for the removal of MB from dye wastewater.

Keywords: Adsorption; Dye wastewater; Methylene blue; Shaddock peel; Kinetics; Low-cost adsrobent

1. Introduction

Dyes are extensively used for dyeing, leather tanning, paper manufacturing and hair coloring [1]. In some developing countries, dye industry effluents were directly discharged from factories to the surface water without any treatment. Dyes in water can interfere with the growth of photoautotrophic and photoheterothophic bacteria and hinder photosynthesis in aquatic plants since they competitively adsorb and reflect the sunlight [2]. Majority of dyes are carcinogenic and mutagenic because they contain functional aromatic rings [3]. Apparently, even in low concentration and small quantities, these dye wastewater effluents deteriorate the local and even regional hydrological environment and have posed significant risk to public health. Therefore, removal of dyes is an important aspect of wastewater treatment before discharge.

It is very important that the remaining dyes in wastewater are removed efficiently to prevent them from entering the hydrological environment. Recently several methods have been developed to remove dyes from wastewaters, such as coagulation and flocculation, oxidation or ozonation, ion exchange, membrane separation, zero valent iron reduction and biodegradation [4–8]. But most of them are either costly or difficult to operate. Adsorption is another useful method because of its high efficiency in the dyes removal. Activated carbon has been widely used to remove dyes from wastewater. However, due to the relatively high operating costs, such as regeneration of the used adsorbent, has limited its application on a large scale. Discovery and development of novel low-cost adsorbents based on low cost botanic materials and agricultural wastes for dyes

*Corresponding author.

removal therefore becomes the focus in recent studies [9–14]. Although the maximum adsorption capacity of the bioadorbents may not be compared with activated carbon, they are more economic and easily accessible.

Shaddock is an important citrus cultivar in south China, covering a total area of 660 km^2 [15]. Because of its large output, nearly 270,500 t of shaddock peel has become agricultural waste annually. Landfill or biomass burning of this agricultural waste contributes to local and regional pollution. However, shaddock peel can be a novel potential adsorbent for wastewater treatment because it has a porous and spongy structure. Moreover, it is environment benign and recyclable. It can be disposed environmentally as fuel for power generation or as a fermentation substrate to produce fertilizer for eucalyptus after adsorption of dyes.

Here we report the use of shaddock peel as a novel low-cost and locally available adsorbent for dyes removal and investigated its feasibility for dye wastewater treatment. Methylene blue (MB) has been chosen as a target compound since it is a very commonly used cationic dye, which would be easily adsorbed onto a negatively charged adsorbent surface by electrostatic force. The effects of various operating parameters such as initial pH, adsorbent diameter, dye concentration and contact time on MB adsorption were studied.

2. Materials and methods

2.1. Chemicals

Shaddock peel was collected from a local market. Methylene blue (MB) was purchased from Advanced Technology Industry Ltd. (Hong Kong, PRC) and used as received. NaOH and HCl were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, PRC). All the chemicals used in the experiments were of analytical grade.

2.2. Adsorbent preparation

Shaddock peel was cut into small pieces with a crusher, and washed with distilled water several times and then soaked in distilled water for 24 h to remove impurities. It was dried in oven at 60°C. The dried slices were grounded and sieved to obtain particles with different sizes (≤0.30 mm, 0.42 mm, 0.71 mm, 1.40 mm). No other chemical or physical treatments were used before adsorption experiments.

2.3. Adsorption experiment

One g MB was dissolved in 1 l distilled water and then diluted to give dye solutions with appropriate concentrations. The natural pH of dye solutions was about 7.8.

The adsorption experiments were conducted in 250 ml flasks containing 100 ml of different concentrations of dye solutions. 0.2 g of shaddock peel (diameter 0.42 mm) was added to the dye solution, and agitated in an isothermal shaker (293 K) at 120 rpm. The reaction was monitored by periodically taking a sample of 3 ml via a straw. The sample was filtered through 0.45 μm PTFE membrane and the concentration of MB was determined by absorbance measurement using a spectrophotometer. Each experiment was run in triplicate, and average value was shown in this study.

2.4. Analytical methods

Shaddock peel samples used in BET surface area, FTIR spectra and zeta potential analysis were crydesiccated to remove the moistures before and after adsorption. The BET surface area was obtained at 77 K in an ASAP 2020 surface area analyzer (Micromeritics Co., USA). The FTIR spectra were obtained using a Nicolet 6700 FTIR spectrophotometer (Thermo Fisher Scientific Co., USA). Zeta potentials were measured by a JS94H micro electrophoresis (Zhengdong Co., China). The absorbance of the filtrate was measured by a 2450 UV-VIS spectrophotometer (Shimadzu Co., Japan) at 644 nm. The equilibrium adsorption capacity (q_e) was calculated from the equation:

$$q_e = (C_0 - C_e)V/1000m \tag{1}$$

where C_0 and C_e (mg/l) were dye concentrations in the initial solution and at equilibrium, respectively. V was the solution volume (ml) and m (g) was the dosage of the adsorbent.

3. Results and discussion

3.1. Characterization of shaddock peel

The FTIR spectra of shaddock peel before and after adsorption were performed to compare the functional groups IR wavenumber changes. As shown in Fig. 1, the peak corresponding to the bonded hydroxyl groups (-OH) shifted from 3392 cm^{-1} to 3394 cm^{-1} after adsorption. A new peak detected at 1540 cm^{-1} was attributed to the secondary amine group [16]. The peak corresponding to the C=O stretching band of carbonyl group shifted from 1244 cm^{-1} to 1250 cm^{-1} [17]. A new peak at 887 cm^{-1} was assigned to the C=C band of MB [18]. The aldehyde groups (-CHO) shifted from 761 cm^{-1} to 759 cm^{-1} after adsorption. The FTIR results showed that there were interactions between the MB secondary amine groups and shaddock peel's hydroxyl groups, aldehyde groups, carboxyl groups.

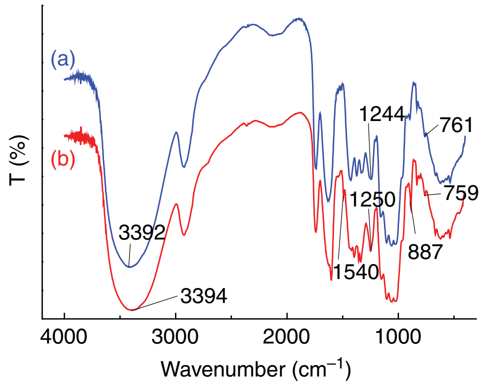

Fig. 1. FTIR of shaddock peel: (a) before adsorption and (b) after adsorption.

3.2. Effect of initial pH on MB adsorption

The effect of initial dye solution pH on MB adsorption was carried out in a pH range from 2 to12. The effect of initial pH on dye uptake and zeta potential is represented in Fig. 2. The q_e was 1.25 mg/g at the initial pH 2, it increased dramatically by 27.8 folds to 35.97 mg/g when initial pH increased to 6 and remained nearly constant over a range of initial pH from 6 to 12. This can be explained by the electrostatic interaction that exists between MB and the negatively charged surface of shaddock peel. The smallest adsorption at the initial pH 2 was because there is positive charge (3.68 mV) on adsorbent surface and excess of H^+ ions competed with the dye cations for adsorption sites. At higher pH, H^+ concentration decreased, the negatively charged sites on adsorbent increased. It enhanced the electrostatic interaction and increased shaddock peel's adsorption. Similar trends were observed for the adsorption of MB onto yellow passion fruit peel [19] and kohlrabi peel [20]. The optimum pH for the adsorption of MB was found to be ≥6.

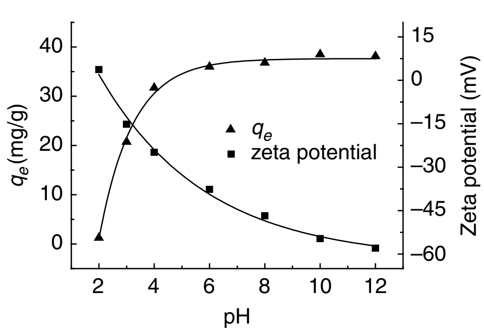

Fig. 2. Effect of initial pH on dye uptake and zeta potential (adsorbent dosage: 2 g/l; dye concentration: 100 mg/l; temperature: 293 K; contact time: 180 min).

3.3. Effect of adsorbent diameter on MB adsorption

Shaddock peels with different diameters (<0.30 mm, 0.42 mm, 0.71 mm, 1.40 mm) were studied to estimate particle size effect. The effect of adsorbent diameter on dye uptake and surface area is illustrated in Fig. 3. The q_e increased from 35.09 mg/g to 36.55 mg/g when adsorbent diameter decreased from 1.40 mm to 0.30 mm. The adsorption capacity increased slightly with a decrease of adsorbent diameter. The surface area of shaddock peel did not increase significantly when it was grounded into smaller pieces due to its spongy structure. So it is not necessary to grind the shaddock peel to very small pieces in its wastewater treatment application.

3.4. Effect of initial dye concentration and contact time on MB adsorption

The effect of initial dye concentration and contact time was studied over a range of dye concentration from 100 mg/l to 900 mg/l in 300 min. As shown in Fig. 4, the adsorption rate was extremely quick at the first 100 min and subsequently slowed down. The q_e increased from 38.73 mg/g to 247.07 mg/l when initial dye concentration increased from 100 mg/l to 900 mg/l, respectively. The adsorption equilibrium was reached in approximately 300 min over a range of initial dye concentrations from 200 mg/l to 700 mg/l. The amount adsorbed MB increased with the increase in the initial dye concentration of solution, but it needed longer time to reach adsorption equilibrium.

3.5. Adsorption isotherms

The q_e versus C_e plots at different temperature are shown in Fig. 5. Since q_e decreased with the increase of

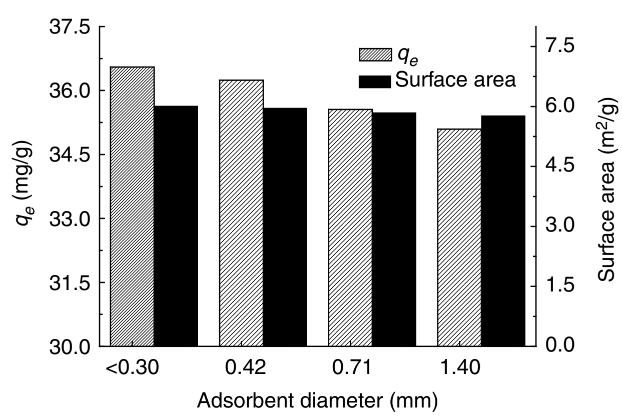

Fig. 3. Effect of adsorbent diameter on dye uptake and surface area (adsorbent dosage: 2 g/l; initial pH value: 7.8; dye concentration: 100 mg/l; temperature: 293 K; contact time: 180 min).

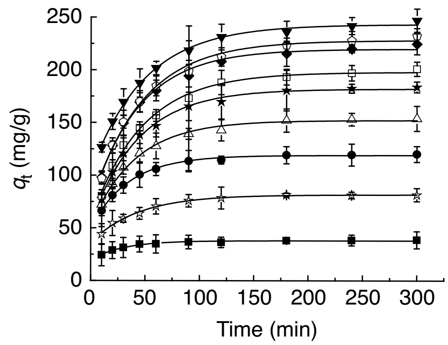

Fig. 4. Effect of initial dye concentration and contact time (adsorbent dosage: 2 g/l; initial pH value: 7.8; temperature: 293 K; contact time: 300 min). ■100 mg/l ☆200 mg/l •300 mg/l Δ400 mg/l ★500 mg/l □600 mg/l ◆700 mg/l ○800 mg/l ▼900 mg/l.

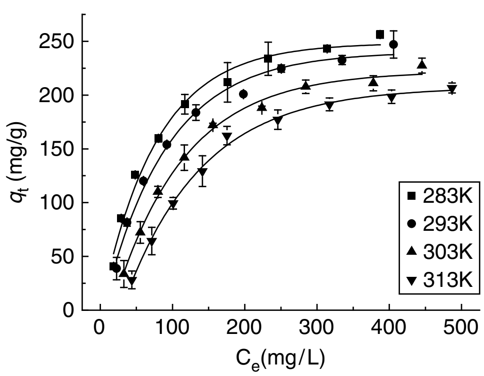

Fig. 5. Adsorption isotherms (adsorbent dosage: 2 g/l; initial pH value: 7.8; contact time: 500 min).

temperature, it implied that the adsorption process was an exothermic reaction.

Langmuir and Freundlich models were used to simulate the adsorption process. The linearized form of the Langmuir equation is as follows:

$$C_e/q_e = 1/q_{\max}K_L + C_e/q_{\max} \quad (2)$$

where $q_{\max}$ and K_L can be calculated from the slope and intercept of plots C_e/q_e versus C_e. The linearized form of the Freundlich equation is as follows:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (3)$$

where K_F and n are the Freundlich constants. The values of K_F and n can be calculated from the slope and intercept of the ln q_e versus ln C_e plots.

Table 1 lists the comparison of the Langmuir and Freundlich adsorption models. In term of the linear regression coefficients, the adsorption process showed a better fit with the Langmuir model than the Freundlich model. For the Langmuir model, the $q_{\max}$ values were bigger than 300 mg/g at all of the experimental temperatures. These values were very close to the results reported for the adsorption of MB on spent tea leaves, rattan sawdust-based activated carbon, coconut shell carbon and rice husk carbon [21–23]. The corresponding $q_{\max}$ values for the aforementioned materials at 30°C were 300.052 mg/g, 294.12 mg/g, 277.9 mg/g and 343.5 mg/g, respectively. The $q_{\max}$ values (Table 1) decreased with temperature was likely due to the adsorption process was an exothermic reaction and lower temperature was favorable for the adsorption of MB onto the adsorbent.

3.6. Adsorption kinetics

Two kinetic models (pseudo-first-order and pseudo-second-order) were applied to investigate the adsorption process. Pseudo-first-order kinetic is as follows:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (4)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}), which can be determined experimentally from slope and intercept of plots $\log(q_e\text{-}q_t)$ versus t. The pseudo-second-order kinetic equation is as follows:

$$q_t/t = 1/k_2 q_e^2 + t/q_t \quad (5)$$

Table 1
Comparison of Langmuir and Freundlich model constants and correlation coefficients

T (K)	Langmuir				Freundlich		
	$q_{\max}$ (mg/g)	K_L (l/mg)	b (l/mmol)	R_L^2	n	K_F	R_F^2
283	309.60	0.0146	5.45	0.9993	2.07	16.80	0.9577
293	307.69	0.0100	3.75	0.9956	1.84	11.10	0.9506
303	305.81	0.0067	2.52	0.9824	1.66	6.84	0.9455
313	302.12	0.0050	1.87	0.9783	1.57	4.87	0.9525

Table 2
Comparison of adsorption rate constants, calculated and experimental q_e values obtained at different temperature between pseudo-first-order and pseudo-second-order kinetics (adsorbent dosage: 2 g/l; initial pH value: 7.8; dye concentration: 300 mg/l; contact time: 500 min)

Temperature (K)	q_e (mg/g) (experimental)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		q_e (mg/g) (calculated)	k_1	R_1^2	q_e (mg/g) (calculated)	k_2	R_2^2
283	125.85	56.47	0.0141	0.9734	131.19	0.00005	0.9998
293	120.11	50.00	0.0185	0.9828	124.55	0.00006	0.9999
303	110.45	33.90	0.0194	0.9711	113.12	0.00009	0.9999
313	99.47	43.81	0.0481	0.9506	104.29	0.00010	0.9995

where k_2 (g/(mg min)) is the rate constant of second-order adsorption. q_e and k_2 can be determined from slope and intercept of plots t/q_t versus t.

The values of adsorption rate constants and q_e (calculated and experimental) at different temperatures are shown in Table 2. The correlation coefficients of pseudo-first-order kinetic were found to be above 0.9488, but the calculated q_e did not match the experimental data. In contrast, the correlation coefficients of pseudo-second-order kinetic were above 0.999, and the calculated q_e was similar to the experimental data. It suggested that the adsorption process followed the pseudo-second-order kinetic model.

4. Conclusions

This study showed that shaddock peel, which is an agricultural waste material and locally available in large quantity, is an effective adsorbent to remove MB from aqueous solution. The optimum pH for MB adsorption was ≥6. The particle size had very little effect on MB adsorption. The adsorption equilibrium was reached in approximately 300 min over a range of initial MB concentrations from 200 mg/l to 700 mg/l. The adsorption process followed the Langmuir adsorption model and pseudo-second-order kinetic model. The maximum equilibrium adsorption capacity was 305.81 mg/g at 303 K.

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