Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.1001444

57 (2016) 5193–5199
March

Taylor & Francis
Taylor & Francis Group

Removal of cationic dyes from aqueous solutions by a low-cost biosorbent: longan shell

Shengfang Li[a,b,*], Min Tao[b]

[a]*School of Chemistry and Chemical Engineering, Hubei Polytechnic University, Huangshi 435003, P.R. China, Tel./Fax: +86 714 6367957; email: lishengf_@163.com*
[b]*Hubei Key Laboratory of Mine Environmental Pollution Control and Remediation, Hubei Polytechnic University, Huangshi 435003, P.R. China*

Received 6 October 2014; Accepted 17 December 2014

ABSTRACT

Longan shell was investigated as a low-cost biosorbent for fast removal of two cationic dyes such as basic magenta (BM) and methylene blue (MB) from aqueous solution. Various factors affecting the biosorption, like initial pH of solution, biosorbent dosage, particle size, contact time and dye concentration were studied. When the initial pH of solution increased from 2.2 to 5.5, the uptake of cationic dyes at equilibration time (q_e) also increased. For BM and MB, q_e decreased from 33.45, 38.32 to 3.22, 4.63 mg/g with the increase of longan shell dosage. Additionally, q_e slightly increased with a decrease of longan shell particle size from 40–60 mesh to 80–100 mesh (i.e. for BM, q_e increased from 29.61 to 33.45 mg/g; and for MB, q_e increased from 32.83 to 38.45 mg/g, respectively). It was found that the biosorption process followed the pseudo-second-order kinetics and the biosorption isotherm agreed with Langmuir model. The results indicated that powdered longan shell was a promising biosorbent for rapid removal of cationic dyes from aqueous solution.

Keywords: Biosorption; Longan shell; Cationic dye; Kinetics; Isotherm

1. Introduction

Nowadays, environmental contaminations from dyes have gained much attention because they can cause negative ecotoxicological effects and bioaccumulation in life [1]. Many dyes are very toxic and have adverse effects on public health when they are discharged into water. Cationic dyes (e.g. basic magenta (BM) and methylene blue (MB)) can easily interact with negatively charged cell membrane surface, and can enter into cells and concentrate in the cytoplasm. Furthermore, they cannot be easily removed by conventional wastewater treatment processes due to their complex structure and synthetic origins [2–4]. Therefore, the removal of dyes is still a huge challenge today.

Adsorption is one of the conventional methods for the removal of dyes from aqueous solution. However, the high costs have prevented the application of common adsorbent i.e. activated carbon for dyes removal from aqueous solution. Recently, several agricultural waste materials such as wheat shell, palm shell, cashew shell, peanut shell, hazelnut shell, seashell, bottom ash, eggshell, and hen feather have been evaluated as biosorbents for the removal of dyes from

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*Corresponding author.

aqueous solution due to their low cost and good biosorption performance [5–18].

Longan shells are typical by-products in the food industry, which exist in a large quantity in many warm regions in the world [19,20]. Unfortunately, a number of longan shells are wasted without any reasonable reuse every year. Few researchers focus on using the longan shell as an adsorbent for the removal of contaminations from aqueous solutions. So far, only one report has showed that longan shell could be used as a biosorbent for selective removal of lead and mercury ions from aqueous solutions [21]. In this study, the feasibility of using the natural longan shell as a biosorbent for the removal of cationic dyes was investigated. The biosorption kinetic data, equilibrium isotherms, and thermodynamic parameters were also evaluated.

2. Experimental

2.1. Preparation of biosorbent

Longan shells were obtained from a local supermarket in Huangshi, China. The longan shells were washed with distilled water to remove the surface impurities and then dried in an air oven at 50℃ for three days. Later, the dried longan shells were grounded in a blender and sieved to obtain a suitable particle size.

2.2. Adsorbates

The cationic dyes used in the adsorption experiments were BM [molecular formula, $C_{20}H_{20}ClN_3$; molecular weight, 337.85] and MB [molecular formula, $C_{16}H_{18}N_3SCl$; molecular weight, 319.86].

2.3. Measurements

Fourier transform infrared spectroscopy (FTIR) was carried out to identify the functional groups involved in biosorption of cationic dyes; the analysis was carried in 500–4,000 cm^{-1} range on a Bruker Tensor 2 FTIR spectrometer using KBr pellet method. The concentration of cationic dyes in solution was determined by a Shimadzu 1650PC UV–visible spectrophotometer. The pH of the solution was measured with a pH meter (Shanghai, China).

2.4. Batch biosorption experiments

Batch biosorption experiments were carried out at 25℃, in magnetically stirred (160 rpm) cylindrical glass vessels in batch conditions. The stoichiometric quantity of longan shell powder was added in 50 mL of 60–120 mg/L dye solution. The uptake of cationic dyes was analyzed using a 1650PC UV–visible spectrophotometer. All the experiments were conducted in triplicate, and the average results are reported in this paper.

3. Result and discussion

3.1. FTIR analysis

In order to delineate the functional groups and adsorption bands present in the longan shell structure, which are responsible for cationic dyes biosorption, FTIR spectra of the longan shell before and after biosorption of cationic dyes were monitored in the range of 500–4,000 cm^{-1} (Fig. 1). The broad band at 3,442 cm^{-1} could be assigned to –OH stretching vibrations and the broad band at 2,921 cm^{-1} was due to C–H stretching of CH_2 groups. The bands near 1,732 cm^{-1} indicated fingerprint region of C=O, C–O, and O–H groups that existed as functional groups on longan shell. The bands at 1,618, 758, and 1,314 cm^{-1} are assigned to C=C/C–H bonds in phenylene and CH_2 groups. The peaks at 1,089 and 1,022 cm^{-1} indicated the existence of C–N from amine. Comparing the FTIR of longan shell before and after adsorption of cationic dyes, a minor shift and intensity change of the −OH group band were observed after the dyes were adsorbed on longan shell. In addition, the band at 1,732 cm^{-1} due to C=O, C–O–, and –OH groups became stronger after adsorbing cationic dyes. This could be attributed to the interaction between the functional groups (–C=O, –C–O–, and –OH groups) on the surface of longan shell and cationic dye molecules [8].

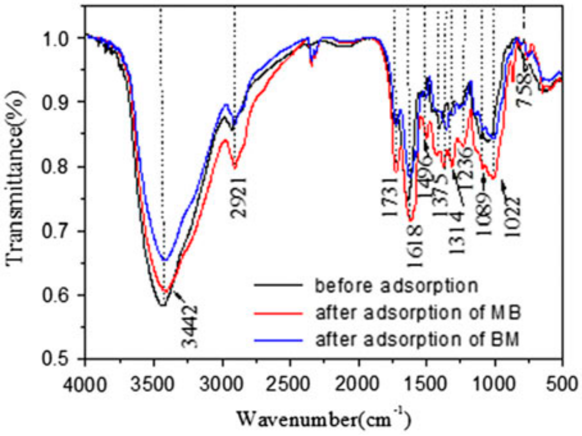

Fig. 1. FTIR spectra of longan shell before and after biosorption of dyes.

3.2. Effect of initial pH of solution

The pH value of solution can affect the surface charges of the adsorbents as well as the degree of ionization of different contaminations. The change of pH has an important effect on the adsorptive process through dissociation of functional groups on the surface active sites of adsorbent [22]. Fig. 2 shows the effect of initial pH of solution on the uptake of BM and MB with 100 mg/L initial dye concentration at 25℃, respectively. As seen in Fig. 2, q_e increased significantly with an increase in pH values from 2.2 to 5.5. For BM and MB, the value of q_e increased from 3.03 to 26.62 mg/g, and 4.15 to 30.72 mg/g, respectively. When the pH value was above six, the biosorption of longan shell almost reached equilibrium. This may be attributed that longan shell can be protonated or deprotonated to produce different surface charges in different pH solution. The point of zero charge of biosorbent was a very important characteristic that determined the pH, at which the surface has net electrical neutrality. Therefore, the point of zero charge value of longan shell was tested and found to be 5.5. The surface charges of chestnut shell were positively charged when pH < 5.5 (the point of zero charge value of longan shell). Thus, there was a competition between H_3O^+ ions and protonated dye ions for the biosorption sites, which caused a decrease in the amount of dye adsorbed. However, the charge on the surface of longan shell was negatively charged when pH > 5.5 (the point of zero charge value of longan shell). The electrostatic force of attraction between longan shell and cationic dye molecules made cationic dyes uptake low. Similar result was reported in other biosorption process [23].

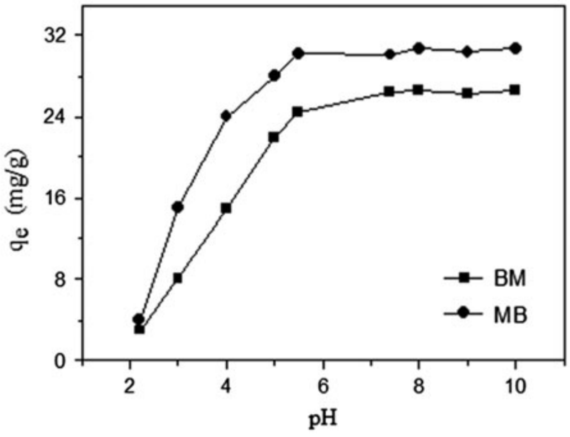

Fig. 2. Effect of initial pH of solution on dyes biosorption (dye concentration: 100 mg/L, biosorbent dosage: 5 g/L, contact time: 160 min, and temperature: 25℃).

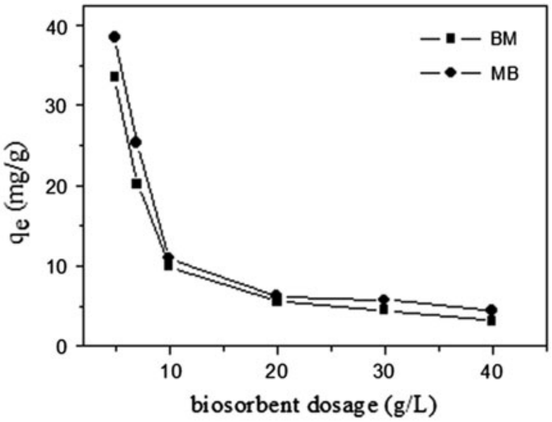

Fig. 3. Effect of biosorbent dosage on biosorption of BM and MB (dye concentration: 120 mg/L, pH 8.0, contact time: 160 min, temperature: 25℃).

3.3. Effect of biosorbent dosage

To investigate the effect of longan shell dosage on the biosorption, biosorption experiments were carried out with a different longan shell amount. As shown in Fig. 3, for BM and MB, q_e decreased from 33.45, 38.32 to 3.22, and 4.63 mg/g, indicating a lower utilization of the adsorption capacity of the longan shell. Similar result was reported [23].

3.4. Effect of biosorbent particle size

The effect of particle size of longan shell on biosorption of BM and MB is shown in Fig. 4. It indicated that q_e slightly increased (i.e. for BM, q_e increased from 29.61 to 33.45 mg/g; and for MB, q_e increased from 32.83 to 38.45 mg/g, respectively) with a decrease of longan

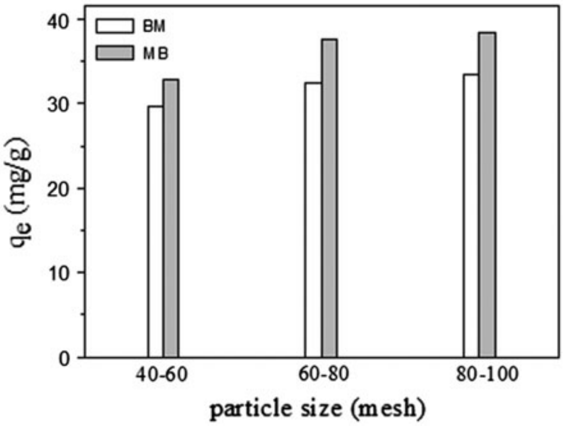

Fig. 4. Effect of particle size on biosorption of BM and MB (dye concentration: 120 mg/L, pH 8.0, biosorbent dosage: 5 g/L, contact time: 160 min, and temperature: 25℃).

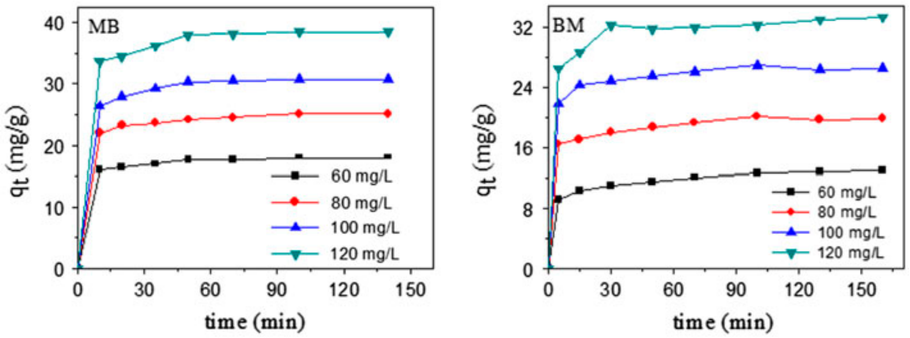

Fig. 5. The biosorption kinetics of BM and MB onto longan shell with different initial dye concentrations (60, 80, 100, and 120 mg/L, respectively).

shell particle size from 40–60 mesh to 80–100 mesh. The amount of BM and MB absorbed on the longan shell particle in 80–100 mesh was the highest among the three sizes of particles (40–60, 60–80, and 80–100 mesh). So, the particle size of longan shell in 80–100 mesh was chosen in all biosorption experiments.

3.5. Effect of contact time and biosorption kinetics

Fig. 5 shows the biosorption kinetics of BM and MB onto longan shell. As shown in Fig. 5, the biosorption rates for BM and MB were very fast. It took only 10–30 min to reach biosorption equilibrium. The pseudo-first-order and pseudo-second-order models were used to evaluate the kinetic experiment data [24,25]. They are given as Eqs. (1) and (2), respectively,

$$\ln\,(q_e - q_t) = \ln\, q_e - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{2}$$

where q_e is equilibrium adsorption amount (mg/g), and k_1 is the pseudo-first-order rate constant (min^{-1}). q_t is the amount of adsorption dye (mg/g) at time t (min), and k_2 is the pseudo-second-order rate constant (g/mg/min). The constants were determined experimentally by plotting ln ($q_e - q_t$) vs. time and t/q_t vs. time in Figs. 6 and 7. The results are listed in Table 1.

As seen in Table 1, for BM and MB, the theoretical values ($q_{e,cal}$) estimated from the pseudo-first-order kinetic model were much lower than those experimental values ($q_{e,exp}$), and the correlation coefficients (R^2) were also found to be lower. However, the theoretical values ($q_{e,cal}$) estimated from the pseudo-second-order kinetic model were very close to those experimental values ($q_{e,exp}$), and the correlation coefficients (R^2) were higher. These results suggested that the biosorption of cationic dyes on longan shell did not follow the pseudo-first-order model, but followed pseudo-second-order kinetic model. The rate-limiting step of BM and MB onto longan shell may be chemical sorption or chemosorption [26].

3.6. Effect of initial dye concentration and biosorption isotherms

The influence of dye concentration on biosorption of BM and MB was estimated. For BM, when the dye concentration was increased from 60 to 120 mg/L, q_e increased from 13.09 to 33.45 mg/g; while for MB, q_e increased from 17.88 to 38.45 mg/g. Langmuir, Freundlich, and Temkin equations were employed to study the biosorption isotherms of BM and MB, respectively. The Langmuir isotherm considers the adsorbent surface as homogeneous with identical sites in terms of energy. Langmuir isotherm model [27,28] is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{3}$$

where q_e is equilibrium adsorption amount, C_e (mg/L) is the equilibrium concentration of dyes, b is a constant of adsorption equilibrium (L/mg), and Q_0 is the saturated monolayer adsorption capacity (mg/g). $R_L = 1/(1+ bC_0)$, the value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich model [29] based on adsorption on a heterogeneous surface is given by the following equation:

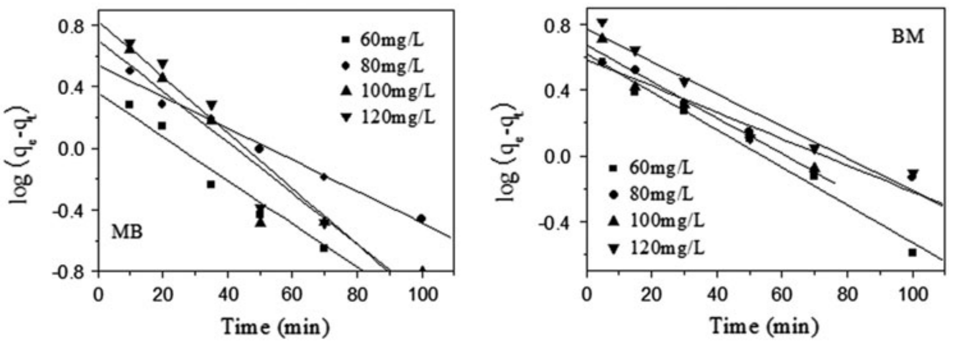

Fig. 6. Pseudo-first-order kinetics plots for biosorption of BM and MB on longan shell.

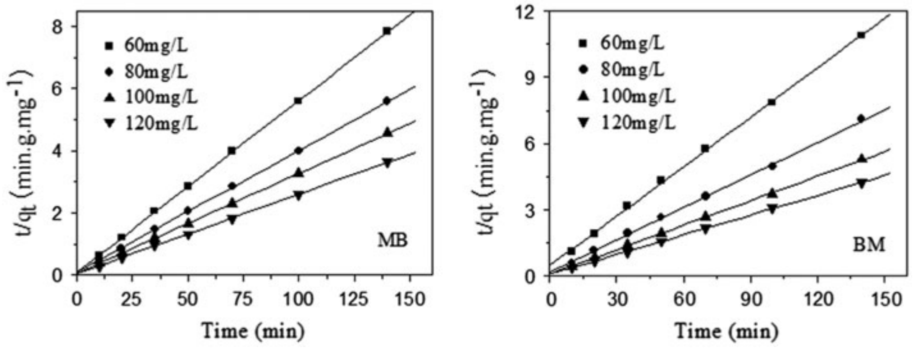

Fig. 7. Pseudo-second-order kinetics plots for biosorption of BM and MB on longan shell.

Table 1
Kinetic parameters for biosorption of BM and MB on longan shell

		Pseudo-first-order kinetics			Pseudo-second-order kinetics		
Dye	C_0[a] (mg/L)	q_e[b] (mg/g)	k_1[c] (min^{-1})	R^2[d]	q_e (mg/g)	k_2[e] (g/mg/min)	R^2
BM	60	3.31	0.0424	0.989	13.39	0.01426	0.998
	80	3.87	0.0567	0.967	20.28	0.01882	0.999
	100	4.54	0.0509	0.968	26.95	0.02099	0.997
	120	9.14	0.0797	0.994	33.67	0.01275	0.996
MB	60	5.13	0.1370	0.961	18.15	0.03060	0.999
	80	3.38	0.0629	0.957	25.51	0.01750	0.998
	100	6.86	0.0606	0.998	31.25	0.01583	0.999
	120	6.65	0.0569	0.956	39.22	0.01171	0.999

[a] Initial dye concentration.

[b] Adsorption capacity at equilibrium.

[c] Rate constant of pseudo first-order adsorption.

[d] Correlation coefficient.

[e] Rate constant of pseudo second-order adsorption.

$$\text{In } q_e = \text{In } K_F + \frac{1}{n} \text{In } C_e \tag{4}$$

where K_F and n are Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively.

The Temkin isotherm model [30] assumes that the heat of adsorption of all molecules decreases linearly with coverage due to adsorbent/adsorbate interactions.

The Temkin isotherm is given by the following equation:

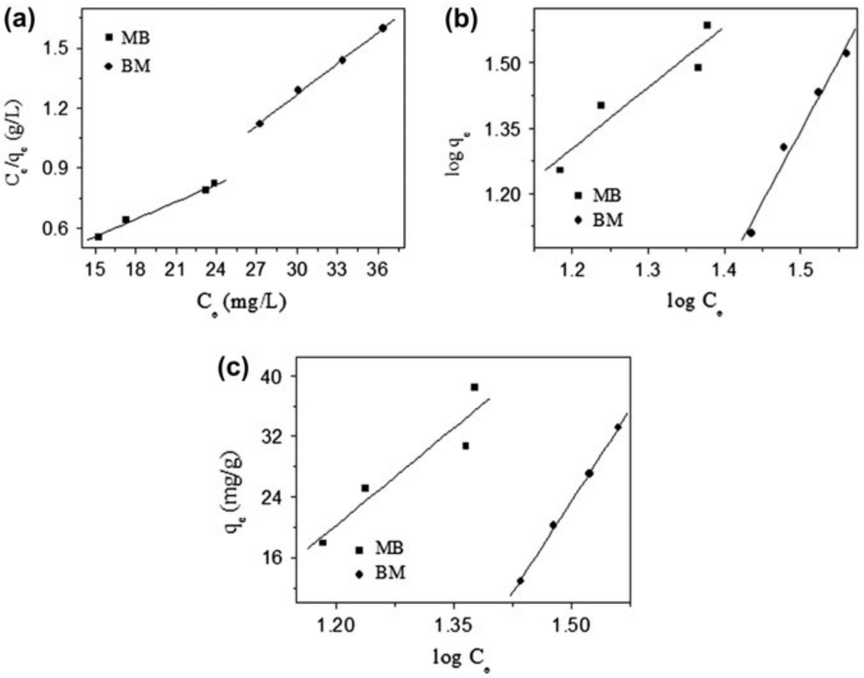

Fig. 8. Langmuir (a), Freundlich (b), and Temkin (c) biosorption isotherms of BM and MB on longan shell.

Table 2
Langmuir, Freundlich, and Temkin isotherm parameters for the biosorption of BM and MB on longan shell

	Langmuir			Freundlich			Temkin		
Dye	Q_0 (mg/g)	R_L (L/mg)	R^2	K_F	n	R^2	A	B	R^2
BM	33.32	0.032	0.998	0.304	0.31	0.976	0.04	69.79	0.999
MB	37.21	0.056	0.996	0.424	0.72	0.896	0.12	37.13	0.881

$$q_e = B \log k_t + B \log C_e \tag{5}$$

where $B = RT/b$, represents heat of adsorption. T is the absolute solution temperature in Kelvin. R is the universal gas constant. $1/b$ indicates the adsorption potential of the adsorbent, while k_t is the equilibrium binding constant corresponding to the maximum binding energy.

The Langmuir, Freundlich, and Temkin isotherms obtained from the equilibrium adsorption data of this study are shown graphically in Fig. 8 and the isotherm parameters are listed in Table 2.

As shown in Fig. 8, all the plots showed a straight line, indicating the adsorption of BM and MB on longan shell followed the three isotherms well. Comparing the coefficient (R^2) for three isotherms, it was found that the Langmuir isotherm fitted more precisely ($R^2 = 0.998$ and 0.996, respectively) than Freundlich isotherm ($R^2 = 0.976$ and 0.896, respectively) and Temkin isotherm ($R^2 = 0.999$ and 0.881, respectively). Langmuir-type biosorption isotherm was suitable for equilibrium studies, thus, indicating the formation of monolayer coverage of BM and MB on the surface of longan shell.

4. Conclusion

This study highlighted the ability of longan shell for the removal of cationic dyes from aqueous solutions. In the batch biosorption experiments, biosorption was found to depend on initial pH of solution, biosorbent dosage, particle size, contact time, and dye concentration. The biosorption process followed pseudo-second-order kinetics and fitted Langmuir adsorption isotherm well. Low cost and rapid adsorptive ability of longan shell would offer a promising technique for cationic dyes removal from wastewater.

Acknowledgments

The project sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry; Hubei provincial Science & Technology Department (2013CFB040); Hubei Provincial Department of Education (D20123001); Hubei Polytechnic University (13xjz01A; 2012101), China.

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