Polymer modified biomass of baker's yeast for enhancement adsorption of methylene blue, rhodamine B and basic magenta

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ABSTRACT

In this study, poly (methacrylic acid) modified biomass was prepared to improve the adsorption capacities for three dyes: methylene blue (MB), rhodamine B (RB) and basic magenta (BM). FTIR and potentiometric titration demonstrated that a large number of carboxyl groups were introduced on the biomass surface, and the concentration of the functional group was calculated to be $1.4\,\mathrm{mmol\,g^{-1}}$ by using the first and second derivative method. According to the Langmuir equation, the maximum uptake capacities (q_m) for MB, RB and BM were 869.6, 267.4 and $719.4\,\mathrm{mg\,g^{-1}}$, which were 17-, 11- and 12-fold of that obtained on the unmodified biomass, respectively. Adsorption kinetics study showed that the completion of the adsorption process needed only 70 min, which is faster than that occur with the common sorbent such as activated carbon and resin. Temperature and ionic strength experiment showed that they both had effect on the adsorption capacity of the modified biomass. Good result was obtained when the modified biomass was used to treat dye wastewater.

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1. Introduction

Dyeing industry wastewater is one of the major environmental problems. Color is one of the characteristics of an effluent, which affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action [1,2]. Even more, some of the dyes are carcinogenic and mutagenic, and they are stable to biological degradation. The majority of technologies presently employed for color removal are based on physicochemical processes such as dilution, adsorption, coagulation and flocculation, chemical precipitation, oxidation, ion-exchange, reverse osmosis and ultra filtration [3,4]. The other class of processes is based on the biodegradability of dyes. Application of biological processes to treat colored wastewater is yet to be fully established [5]. Among the treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. Common adsorbents such as activated carbon and resin are too expensive, so it is necessary to search for an alternative low-cost adsorbent [4]. Recently, more and more attention was paid on biosorbents due to the low cost. Literatures had reported that a wide variety of microorganisms, including bacteria, algae and fungi, are capable of sorbing a number of pollutants [6–8]. Baker's yeast, as a fungal biomass, is an inexpensive, readily available source of biomass. Cell wall of it contains chitin, chitosan, β-1,3-D-glucans, β-1,6-D-glucans, and mannoproteins which are abundant sources of different functional groups such as carboxyl, amine and hydroxyl. These functional groups are responsible for dyes adsorption. However, the densities of these functional groups on the biomass are generally low, and most biosorbents do not show a high sorption capacity for cationic dyes.

Since, the adsorption of dyes takes place mainly on the biomass surface, increasing the adsorption active sites on the surface would be an effective approach to enhance the adsorption capacity. It had been reported that the adsorption capacity of the biosorbent for metal ions could be improved greatly through chemical modification. Deng and Ting [9] reported that modified biomass of *Penicillium chrysogenum* with polyethylenimine (PEI) significantly improved the adsorption capacity for copper, lead and nickel. Matis et al. [10] noted that pretreatment of *P. chrysogenum* biomass with surfactants and cationic polyelectrolyte was found to improve the adsorption efficiency for As (V) anions. Klimmek et al. [11] demonstrated that the maximum adsorption capacities of the alga *Lyngbya taylorii* could be increased significantly after phosphorylation.

Poly (methacrylic acid), which is composed of a large number of carboxyl groups in a molecule, exhibits good adsorption ability for metal ions and cationic dyes. Modification of the biomass with poly (methacrylic acid) would improve the adsorption capacity of baker's yeast for the cationic dyes.

In this study, the biomass of baker's yeast was modified with poly (methacrylic acid) through a graft copolymerization reaction. The modified biomass was characterized by FTIR. Through potentiometric titration, the concentration of the functional groups

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on the modified biomass was calculated accurately by first and second derivative methods. The adsorption capacities for the common dyes: MB, RB and BM were studied. The adsorption kinetics, isotherms and temperature-dependent performance, were investigated. At last, the ability of the modified biomass to treat dye wastewater was also studied.

2. Experiments and methods

2.1. Materials

Potassium persulfate (PPS) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The three cationic dyes: MB, RB and BM were purchased from Ryond Chemical Co., Ltd., and the three dyes used without further purification. Their structures were showed in Fig. 1. These dyes, compared to other dyes, have high brilliance and color intensity, resulting in high visible color, even at a very low dye concentration. Baker's yeast was purchased from China General Microbiological Culture Center (Beijing, China) and it was dried at 60 °C for 24 h before use. Other chemicals were of reagent grade.

2.2. Surface modification

The modified biomass was prepared through the graft copolymerization reaction. PPS and methacrylic acid were used as an initiator and monomer, respectively. 0.45 g PPS and 1.0 g baker's yeast were added into a round bottom flask containing 50 mL water, after heating at 60 °C for 30 min under nitrogen gas atmosphere, 2 mL of methacrylic acid was added and the reaction kept under stirring for another 3 h. The obtained biomass was thoroughly rinsed with acetone to remove unreacted monomer and homopolymer. After that, it was treated with a 0.1 mol L^{-1} NaOH to convert carboxyl groups into carboxylate ions, and then rinsed with distilled water until neutral pH was obtained. The modified biomass was then freeze-dried and stored in a desiccator before use.

2.3. Potentiometric titration

Before the titration, 0.05 g of the biomass was added to conical flasks containing 20 mL of 0.01 mol L^{-1} NaCl solution, and the mixture was allowed to stand for 12 h at room temperature for stabilization. The solution was then bubbled with nitrogen gas for 2 h with vigorous mixing to remove carbon dioxide. Titration was performed using 0.0840 mol L^{-1} HCl solution. The amount of HCl consumed and the solution pH was recorded after attaining equilibrium.

2.4. Batch adsorption experiments

All sorption experiments were performed at 150 rpm on an orbital shaker with 0.05 g of the biomass in a 100 mL conical flask containing 50.00 mL of dye solutions. Batch adsorption experiments were conducted at 25 °C to examine the sorption kinetics and equilibrium, the pH of the solutions were kept at 6.5 adjusting by HCl and NaOH addition. In the sorption kinetic and pH experiments, the concentration of the three dyes was 5×10^{-3} mol L^{-1}. In the adsorption isotherm experiments, the concentration range used was $0–8 \times 10^{-3}$ mol L^{-1}. The concentration of the dyes after adsorption was determined by measuring their characteristic absorbance using UV–vis spectrometer (Purkinje General, China), and the characteristic absorbance of MB, RB, and BM are 670, 554 and 550 nm, respectively.

2.5. Treating dyeing industry wastewater

0.05 g of the modified biomass was added into 50 mL dye wastewater obtained from dyeing industry in Danjiang (Hubei, China). After adsorption for an hour, the modified biomass was separated, and the concentration of the dyes in the filtrate was analyzed by UV–vis spectrophotometer.

3. Results and discussion

3.1. Characterization of the biosorbent

The spectrum of the pristine biomass is complex due to the numerous and multifarious functional groups on the surface of the biomass. The peaks at 3344, 2929, 1654, 1532, 1238 and 1071 cm^{-1} are observed in the unmodified biomass spectrum shown in Fig. 2a. The peaks at 3344, 1071 and 1238 cm^{-1} showed the presence of hydroxyl and amide groups on the biomass surface. The peaks at 1654 and 1532 cm^{-1} were assigned to C=O and N–H stretching vibration, respectively. After modification the spectrum presented
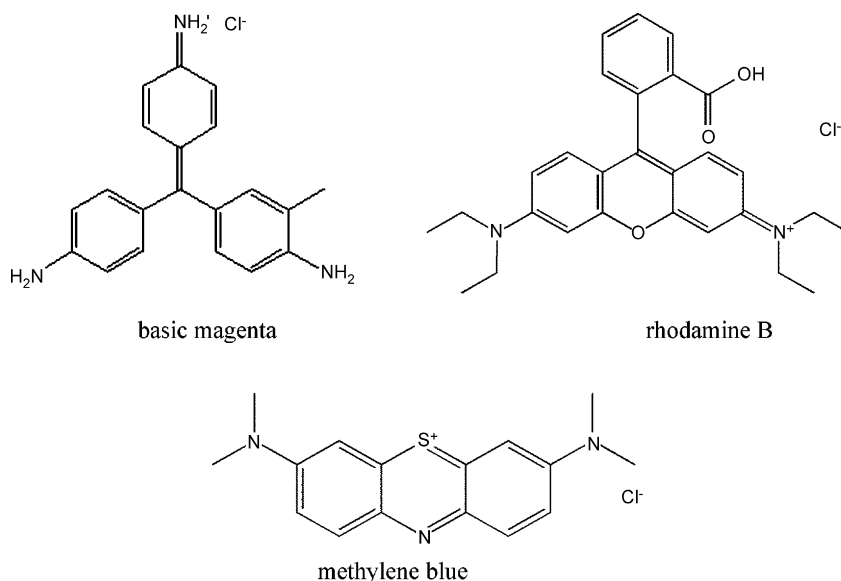

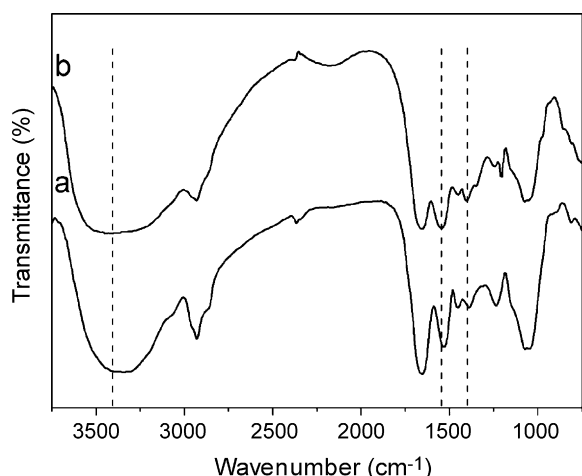**Fig. 1.** Structures of used dyes.

Fig. 2. FTIR of baker's yeast (a) the unmodified biomass and (b) modified biomass.

obvious changes. As shown in Fig. 2b, two new peaks at 1545 and 1402 cm^{-1} were observed, which was assigned to C=O asymmetric and symmetric stretching in carboxylate ions, respectively, and the peak at 3344 cm^{-1} broadened obviously. These results demonstrated that a large number of carboxyl groups were introduced on the biomass surface.

In biosorption study, titration is often used to characterize the type of functional groups and their concentrations on the biosorbents surface, which is very important in evaluating its adsorption capacity and mechanisms [12–14]. Fig. 3 shows the potentiometric titration curve of the modified and unmodified biomass. There was an obvious inflection in the curve in Fig. 3b, which was according to carboxyl groups. To evaluate the end point of the reaction and determine the concentration of the functional group on the modified biomass, first and second derivative methods were used to deal with the titration curve.

First derivative method ($\Delta \text{pH}/\Delta V - \bar{V}$)

In the first derivative method, $\bar{V}$ is the average volume (mL), $\Delta \text{pH}/\Delta V$ represent the changes of the pH value with the addition of the titrant, it could be calculated by the following equation.

$$\frac{\Delta \text{pH}}{\Delta V} = \frac{(\text{pH})_{V_2} - (\text{pH})_{V_1}}{V_2 - V_1} \tag{1}$$

First derivative method is based on the mathematical principle that an inflection of a curve corresponds to the maximum point of the first derivative curve. The inflection of a titration curve could be determined through the maximum point in the first derivative. Through the inflection, the end point and the volume of HCl consumed in the titration reaction could be determined, and the concentration of the functional group on the modified biomass could be calculated. First derivative curve of the modified and unmodified biomass is showed in Fig. 4. It could be seen that the values of $\Delta \text{pH}/\Delta V$ decreased continually with the addition of the titrant, demonstrating that the densities of the functional groups on the unmodified biomass were very low and there were no obvious inflection in the titration curve. While for the modified biomass, the values of $\Delta \text{pH}/\Delta V$ firstly increased and then decreased with the addition of the titrant, and the maximum point in the curve corresponds to the end point of the titration. The maximum point could be determined through epitaxy method. It could be seen that it was not so direct to determine the end point, and using the second derivative method may be simpler.

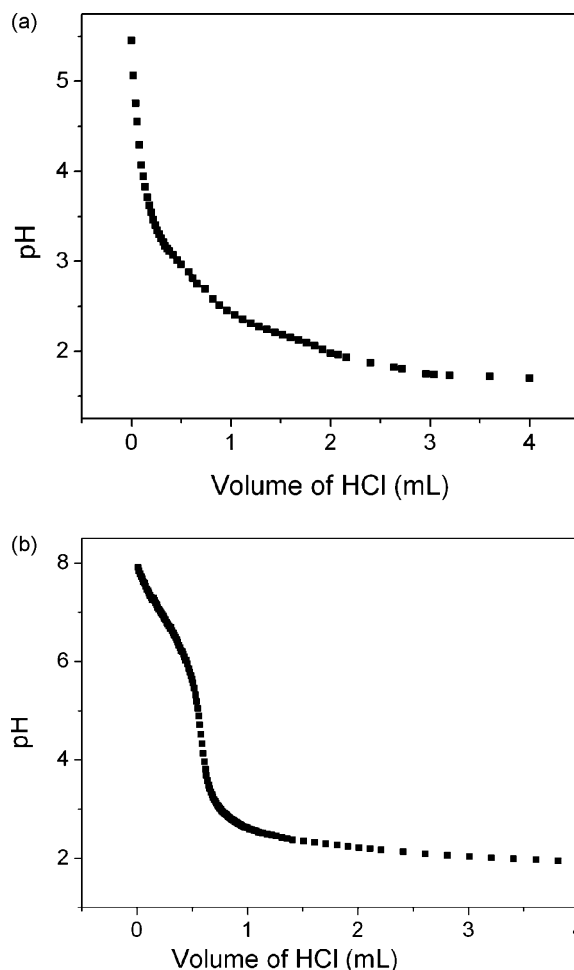Second derivative method ($\Delta^2 \text{pH}/\Delta^2 V - \bar{V}$)

Fig. 3. Potentiometric titration curve of (a) the unmodified biomass and (b) modified biomass.

In the second derivative method, $\Delta^2 \text{pH}/\Delta^2 V$ is calculated by the following equation.

$$\frac{\Delta^2 \text{pH}}{\Delta^2 V} = \frac{(\Delta \text{pH}/\Delta V)_{V_2} - (\Delta \text{pH}/\Delta V)_{V_1}}{V_2 - V_1} \tag{2}$$

Second derivative method is based on that the maximum point in the first derivative curve is the zero point in the second derivative curve, and the end point corresponds to the point that $\Delta^2 \text{pH}/\Delta^2 V = 0$. It could directly show the end point. Second derivative curve of the modified biomass is showed in Fig. 5. It could be observed that the volume of HCl consumed is 0.835 mL. The number of the functional groups per gram of biomass could be calculated through the equation below:

$$[\text{functional groups}]_{\text{total}} = \frac{V_{\text{HCl}} \times C_{\text{HCl}}}{M} \tag{3}$$

where M (g) is the mass of the modified biomass. The concentration of the functional group was calculated to be 1.4 mmol g^{-1}.

The pK_a value of the functional groups could also be evaluated through the second derivative curve. The equilibrium constant K_a is defined as follows:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \tag{4}$$

where A$^-$ is the functional group. When the concentration of A$^-$ is equal to the concentration of HA, the value of pK_a is equal to the value of pH. According to the titration curve, the pH value of
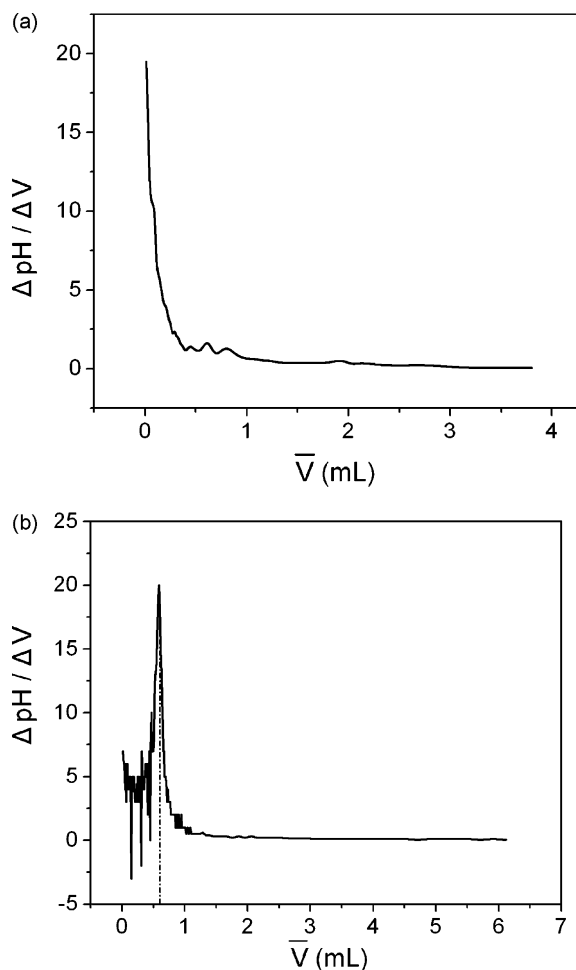
(a)

(b)

Fig. 4. First derivative curve of (a) the unmodified biomass and (b) modified biomass.

the solution is 6.2 when the volume of titrant is 0.835 mL/2. The calculate pK_a for the main functional groups is 6.2.

3.2. Adsorption kinetics experiments

The mechanism for the sorption of the three dyes on the biomass may be assumed to involve the following sequential steps [15,16]:
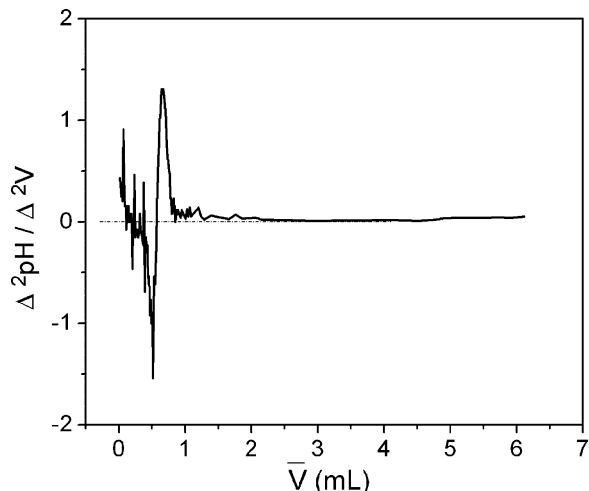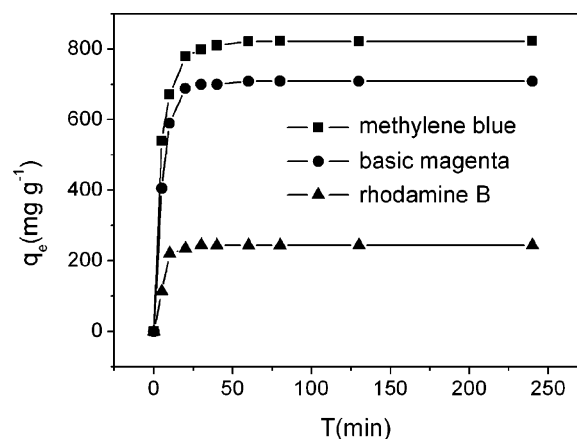

Fig. 5. Second derivative curve of the modified biomass.

Fig. 6. Adsorption kinetics of basic magenta, rhodamine B and methylene blue on the modified biomass.

1. Migration of dyes from bulk of the solution to the boundary layer of the biosorbent.
2. Diffusion of dyes through the boundary layer to the surface of the sorbent.
3. Intraparticle diffusion of dyes into the interior pores of the sorbent particle.
4. Sorption of dyes at an active site on the exterior or interior surface of biosorbent.

Fig. 6 illustrates the sorption kinetics curves of the three dyes. The removal rates were all very rapid during the initial stages of the sorption process. After a very rapid sorption, uptake rates slowly declined with lapse of time and reached equilibrium values at about 70 min for all three dyes. The three phases of the dyes sorption could be attributed to boundary layer diffusion sorption, intraparticle diffusion sorption and sorption equilibrium, respectively. The high initial uptake rate and the short adsorption equilibrium time demonstrated that the surfaces of the modified biomass had a high density of active sites for dyes adsorption. Compared to most of the biosorbents and porous adsorbents such as activated carbon and resin, the adsorption kinetics of the modified biomass was faster [17]. Hence, a practical advantage of using the modified biomass as an adsorbent would be in its ability to remove more dyes in a much shorter adsorption time. On the other hand, it could be seen that the adsorption rate followed the order: MB > BM > RB. Higher molecular weight, larger ionic size and the presence of carboxylic group were the probable reasons for the lower sorption of RB.

3.3. Adsorption isotherm experiments

Studies on the adsorption isotherm are a prerequisite to understand the adsorbate–adsorbent interaction and to optimize the use of the adsorbent. Fig. 7 shows the adsorption isotherms of BM, RB and MB on the modified and unmodified biomass. It was observed that the amount of the adsorbed dyes increased with increase in equilibrium concentration and ultimately attained a saturated value. The adsorption data for the modified and unmodified biomass were analyzed using Langmuir and Freundlich adsorption isotherms. The Langmuir equation is based on the assumption that maximum sorption corresponds to saturated monolayer of sorbate molecule on the sorbent surface, that the energy of sorption is constant and that there is no transmigration of sorbate in the plane of the surface [18,19]. The linear Langmuir equation was shown as follows:

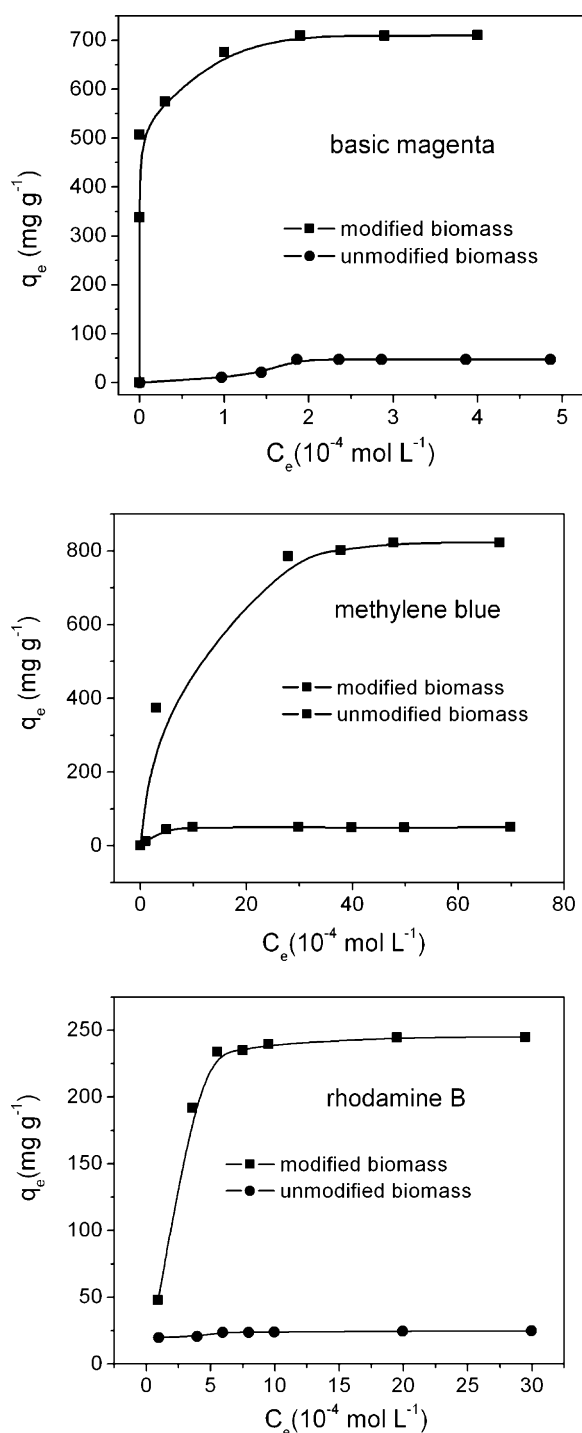$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

(5)

Fig. 7. Adsorption isotherms of basic magenta, rhodamine B and methylene blue on the modified and unmodified biomass.

where q_m is the maximum amount of adsorption (mg g^{-1}), b is the adsorption equilibrium constant (L mg^{-1}) and C_e is the equilibrium concentration of substrates in the solution (mg L^{-1}).

The Freundlich equation is an empirical model can be linearized in logarithmic form as follows [20]:

$$\ln q_e = \ln a + \frac{1}{n} \ln C_e \qquad (6)$$

where a (mg mol$^{-1/n}$ L$^{1/n}$ g^{-1}) is a constant representing the adsorption capacity, and n is a constant depicting the adsorption intensity. The Langmuir and Freundlich adsorption constants evaluated from

the isotherms with the correlation coefficients are listed in Table 1. As it can be seen that the Langmuir isotherm gave better fits than the Freundlich isotherm, illustrating that the adsorption on the modified and unmodified biomass was monolayer adsorption. According to the Langmuir equation, the maximum uptake capacities (q_m) of the modified biomass for MB, RB and BM were 869.6, 267.4 and 719.4 mg g^{-1}, while that of the unmodified biomass were 51.5, 25.2 and 59.8 mg g^{-1}. The increases were about 17, 11 and 12 times for MB, RB, and BM, respectively.

Cell walls of fungal biomass including that of baker's yeast contain chitin, chitosan, β-1,3-D-glucans, β-1,6-D-glucans, and mannoproteins [21]. The complexity of the microbial structure makes the biosorption process much more complicated. For the nonliving biomass, adsorption occurred mainly on the cell surface. Surface adsorption is generally assisted through ionic, chemical, and physical interaction. The adsorption of cationic dyes on the biosorbents may be attributed to (1) electrostatic interaction between the dye molecules and the electron rich sites (active sites) on the cell surface, and (2) weak physical forces such as hydrogen bonding and van der Waals interactions between the hydrophobic parts of the dye molecules (e.g., the aromatic rings) and the polysaccharides of the biomass as proposed by Blackburn [21,22]. For the unmodified biomass, the adsorption occurred mainly through hydrogen bonding between the hydroxyl groups of the polysaccharides and the electronegative groups in the dyes, and some electrostatic interactions between the negatively charged groups of cell surface and the cationic dye molecules. After modification, large amount of carboxylate ions were introduced. The added carboxylate ions provide more electron rich sites to interact with the dye molecules through electrostatic interaction, so, the adsorption capacity of the modified biomass for three dyes increased significantly.

Dyes adsorption had been studied by various investigators, using a variety of different adsorbents. The respective adsorption efficiencies of different biomass are presented in Table 2 for comparison with the studied modified baker's yeast. Although a direct comparison between the examined modified biomass with those obtained in literatures was difficult, due to the varying experimental conditions employed in those studies, the modified biomass used in the present study showed reasonably high adsorption capacity for the three dyes, as compared with other adsorbents.

3.4. Effect of temperature on the adsorption

The equilibrium uptakes as a function of temperature are given in Table 3 for the studied dyes. In this experiment, the concentration of the three dyes were 1×10^{-3} mol L^{-1}, and the solution pH was kept at 6.5. For MB, the equilibrium uptakes decreased with increasing temperature up to 35 °C. The decrease of the uptakes with further increase in temperature means that methylene blue biosorption process is exothermic. While for BM and RB, the uptakes increased with an increase in temperature. Temperature could affect desorption step and consequently the reversibility of the adsorption equilibrium. In general, an increase in temperature is followed by an increase in the diffusivity of the ion, and consequently an increase in the adsorption rate if diffusion is the rate controlling step [49]. So, BM and RB sorption may be controlled diffusion, the adsorption capacity increased with the increasing temperature. From the temperature experiment, it could be concluded that MB inclined to be adsorbed at lower temperature, while BM and RB inclined to be adsorbed at higher temperature.

3.5. Effect of ionic strength on the adsorption

Wastewater from textile-manufacturing or dye-producing industries contains various types of suspended and dissolved com-

Table 1
The constants of Langmuir and Freundlich isotherms for basic magenta, rhodamine B and methylene blue adsorption.

Sorbent	Dyes	Langmuir			Freundlich		
		q_m (mg g^{-1})	b (L mol^{-1})	R^2	a (mg mol$^{-1/n}$ L$^{1/n}$ g^{-1})	n	R^2
Unmodified	BM	59.8	59.0	0.963	28.3	2.4	0.824
biomass	MB	51.5	35.8	0.999	17.9	3.4	0.828
	RB	25.2	48.7	0.999	19.8	13.6	0.924
Modified	BM	719.4	181.8	0.999	388.8	2.3	0.936
biomass	MB	869.6	123.2	0.991	49.1	1.3	0.976
	RB	267.4	133.9	0.992	74.4	2.2	0.846

Table 2
Comparison of the adsorption capacity for basic magenta, rhodamine B and methylene blue by the application of several adsorbents.

Adsorbent	pH	Adsorption capacity (mg g^{-1})	Reference
For methylene blue			
Oil palm shell	6.5	243.9	[23]
Luffa cylindrica fibers	2.5	122.0	[24]
Pyrophyllite	–	70.4	[25]
Activated carbon	–	435.0	[25]
Oil palm shell activated carbon	6.5	303.0	[26]
Jute fiber-based	4.0	225.6	[27]
Oil palm fiber-based	6.5	277.8	[28]
Filtrasorb F300	–	240.0	[29]
Guava leaf powder	7.5	295.0	[30]
Teak wood bark	6.5	915.0	[31]
Activated carbon	–	435.0	[32]
Dead macro-fungi	6.0	232.7	[4]
Peat	–	324.0	[33]
Dehydrated peanut hull	3.5	108.0	[34]
Spent activated clay	5.5	127.5	[35]
Modified biomass of baker's yeast	6.5	869.6	This work
For rhodamine B			
Treated parthenium biomass	7.0	59.2	[36]
Surfactant-modified coconut coir pith	9.2	14.9	[37]
Modified parthenium biomass	7.0	18.5	[38]
Activated carbons	–	400.0	[39]
Poly(glutamic acid)	5.25	390.2	[40]
Zeolite	–	37.8	[41]
Unburned carbon	–	46.5	[42]
Fly ash	–	4.5	[43]
Industrial solid waste	5.7	16.1	[44]
Porous carbon	–	479.0	[45]
Carbonaceous adsorbent	–	82.8	[46]
Coir pith	–	2.6	[47]
Modified biomass of baker's yeast	6.5	267.4	This work
For basic magenta			
Modified peat–resin particle	–	400.0	[48]
Modified biomass of baker's yeast	6.5	719.4	This work

pounds apart from the dyes. Cations such as Na$^+$, K$^+$, Cu^{2+} and Ca^{2+} are the most common metal ions present in the wastewater. The presences of ions lead to high ionic strength, which may significantly affect the performance of the biosorption process. Fig. 8 presents the effect of ionic strength on the uptake of RB. It was observed that the adsorption capacity decreased with the increase in ionic strength, and similar results happed to other two dyes. As the concentration of K$^+$ and Ca^{2+} ions changed from 0.01 to 0.08 mol L^{-1}, the capacity decreased to 76.1 and 55.4 mg g^{-1}, respectively. These results showed ionic strength had an adverse effect on the dyes adsorption, which may be induced by the com-

Table 3
Effects of temperature on the adsorption capacity.

Adsorption capacity (mg g^{-1})	Temperature (°C)		
	13	25	35
Methylene blue	560.9	548.1	546.3
Basic magenta	581.0	594.0	608.1
Rhodamine B	230.1	234.5	239.0
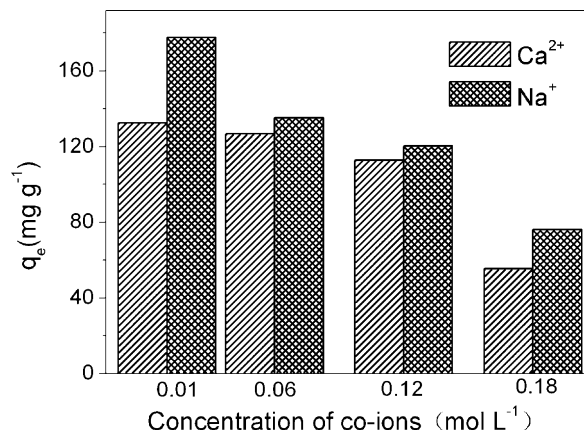
Fig. 8. Effect of ion strength on the adsorption capacity of the modified biomass.
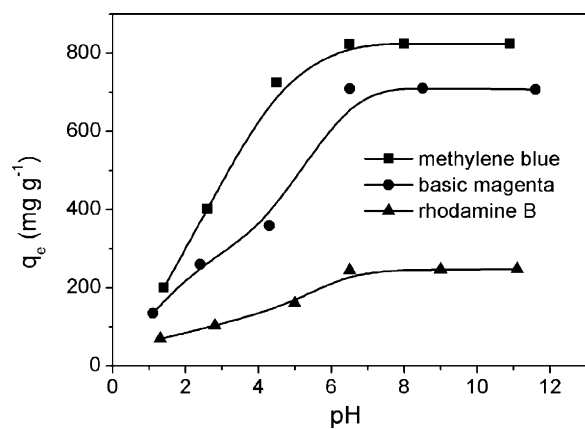
Fig. 9. Effect of pH on basic magenta, rhodamine B and methylene blue adsorption on the modified biomass.
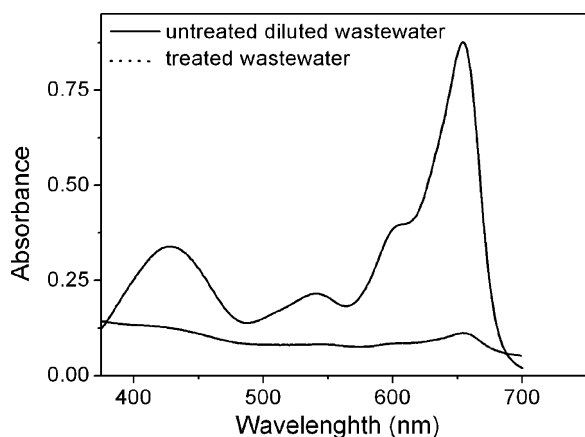

Fig. 10. UV–vis absorption spectra of the wastewater before and after treating.

petition between the cations and the dyes for the electron rich sites.

3.6. Effect of pH on the adsorption

pH is one of the parameters that significantly influenced the dye adsorption, and it would affect the interaction between sorbate. Fig. 9 shows the three dyes adsorption on the modified biomass at different initial solution pHs. It could be seen that the adsorption capacity for the three dyes increased initially with an increase in pH, after which it was approximately constant. The solution pH affected the activity of the functional groups (carboxyl groups) as well as the species of the cationic dyes. At lower pH value, the surface of the modified biomass became more positively charged, thus increasing the electrostatic repulsive force between the biosorbent and cationic dyes, and the adsorption capacity for the dyes decreased. In contrast, as the pH value increased, the biosorbent surface was more negatively changed, which promoted the uptake of dyes on the modified biomass.

3.7. Treating wastewater

The adsorption capacity of the modified biomass in treating dye wastewater was studied. The UV–vis spectrum of the diluted wastewater, whose concentration is one-tenth of that of the original dye wastewater, is shown in Fig. 10. It could be observed that the component of the wastewater is very complicated, and it may contain various types of organic compounds at the same time. After dealing with the modified biomass, the wastewater became color-

less, and the peaks of the different dyes disappeared, indicating the efficiency of the modified biomass in treating dye wastewater. These results indicate that the modified biomass would have great potential in practical applications for the removal of dyes from wastewater.

4. Conclusion

The poly (methacrylic acid) modified biomass was prepared through a simple way. The isotherm experiments showed that the adsorption capacity of the modified biomass for MB, RB and BM showed a significant increase compared with that of the pristine biomass due to the presence of a large number of carboxyl groups. Kinetics experiment illustrated that the adsorption process could be completed in 70 min. Ionic strength has an adverse effect on the adsorption capacity. The obtained biomass has great potential in practical use.

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