



Desorption behavior of methylene blue on pyromellitic dianhydride modified biosorbent by a novel eluent: Acid TiO₂ hydrosol

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ABSTRACT

In this study, waste beer yeast powder was modified by pyromellitic dianhydride to improve its adsorption capacities for cationic dye: methylene blue (MB). According to the Langmuir equation, the maximum uptake capacities (q_m) of the modified biomass for MB was 830.8 mg g⁻¹, which was about five times than that obtained on the unmodified biomass. Adsorption mechanism was investigated by FTIR. Desorption kinetics of methylene blue in six solvents: HCl (0.1 mol L⁻¹), ethanol, mixtures of HCl (0.1 mol L⁻¹) and ethanol with different volume ratio and a self-clean eluent: acid TiO₂ were studied in details. Results showed that desorption kinetics curve fit the two-step kinetic model, and methylene blue release process was distinctly divided into two steps: rapid and slow desorption steps. 52.2% of the methylene blue could be desorbed into TiO₂ hydrosol after 30 h desorption at the first desorption cycle, and the desorbed dye in TiO₂ hydrosol could be degrade completely under sunlight irradiation. After three desorption-photodegradation cycles, 80.0% of the absorbed dyes could be desorbed from the surface of the modified biomass. Although there was much work to do, the self-clean eluent: TiO₂ hydrosol had great potential in practical use.

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1. Introduction

Many industries, such as paper, plastics, food, cosmetics, textile, etc., use dyes in order to color their products. The presence of these dyes in water, even at very low concentrations, is highly visible and undesirable. The sorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters [1,2]. The most widely used and effective method in industry is activated carbon, although running costs are expensive [3]. In recent years, more and more attention was paid on biosorbents due to the low cost and ready availability [4–7]. Waste beer yeast is an industry by-product, which is available in large quantities at no cost and can form a good basis for the development of adsorbent materials. However, the native biomass of yeast had low adsorption capacity for either metal ions or cationic dyes [8–10]. It had been reported that the adsorption capacity of the biosorbent for metal ions could be improved greatly after surface modification [11–13]. In our previous study, poly(amic acid) and poly(methacrylic acid) modified biomass were prepared to enhance the adsorption capacity of the biomass for cationic dyes [14,15]. The amount of dyes adsorbed on the biomass improved significantly after polymers modification. In order to lower the cost of

the biosorption process, the dyes loaded biosorbents should be regenerated.

Dilute HCl or HNO₃ solution was often used as eluent to regenerate the biosorbents [16,17]. Vijayaraghavan et al. had reported that more than 99% of methylene blue could be desorbed from *Corynebacterium glutamicum* by using HCl (0.1 mol L⁻¹) as eluent [17]. In this study, besides the common solvents such as HCl and mixtures of HCl and ethanol, a new self-clean eluent—acid TiO₂ hydrosol with nanoparticles (pH 1) were investigated as eluent in details. The acid TiO₂ hydrosol with high photocatalytic activity could degrade dyes completely under sunlight irradiation. Photodegradation under visible light irradiation followed the sensitized photocatalysis mechanism [18,19]. The process involves the excitation of the dye molecules with visible light and the subsequent electron injection or electron transfer from excited dye molecules to the conduction band (CB) of semiconductor TiO₂. Electrons on the CB were then trapped by oxygen molecule and formed active radicals such as O^{2•-} and •OH. These radicals broke down the dyes to smaller fragments that eventually decomposed into simple inorganic minerals. Acid TiO₂ hydrosol could be used as a self-clean eluent.

In this study, pyromellitic dianhydride (Fig. 1) modified waste beer yeast powder was prepared. After modification, large amount of carboxyl groups were introduced on the surface of the biosorbent, which could improve the adsorption capacity of the biosorbent for cationic dyes. Methylene blue (MB) was selected as

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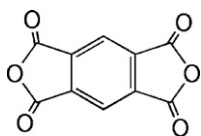


Fig. 1. Molecular structure of pyromellitic dianhydride.

a model compound in order to evaluate the capacity of the modified biosorbent. Adsorption performances of the modified biomass for MB including sorption kinetics, isotherms, pH experiment and mechanism were investigated in details. Moreover, desorption kinetics of methylene blue in different eluent, especially in acid TiO_2 hydrosol, were studied. Two-step kinetic model was used to fit the data to investigate the desorption mechanism. As a self-clean eluent, degradation rate of methylene blue in TiO_2 hydrosol under sunlight irradiation were also studied.

2. Materials and methods

2.1. Materials

Pyromellitic dianhydride (PMDA) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). MB was used without further purification. Beer yeast was collected from the beer plant and washed with distilled water for three times, and then dried at 60°C for 24 h. The dried biomass was ground with a mill to pass through a 140-mesh sieve for the following biosorption experiments.

2.2. Surface modification

0.3 g of PMDA and 0.5 g of the yeast powder were added into a round-bottomed flask containing 30 mL of N,N-dimethylacetamide. After stirring at 50°C for 4 h, the biomass was centrifuged and washed in order with NaOH (0.1 mol L^{-1}) and distilled water, and then it was oven dried at 60°C for 24 h and stored in a desiccator before use.

2.3. Batch adsorption experiments

The adsorption experiments were performed at room temperature and 125 rpm on an orbital shaker. 0.01 g of the biosorbent was added into a 100 mL conical flask containing 20 mL dye solution. The solution pH was kept at 6.0 in both the kinetic and equilibrium experiment. In the kinetic experiments, 0.01 g of the biosorbent was added into 50 mL methylene blue solutions ($4 \times 10^{-4}\text{ mol L}^{-1}$). In the pH experiment, the concentration of MB used was $1.0 \times 10^{-3}\text{ mol L}^{-1}$. After the completion of the adsorption, the biosorbent was centrifuged and collected for the regeneration experiment, and the concentration of the dye in the filtrate was determined by measuring their characteristic absorbance.

2.4. Preparation of acid TiO_2 hydrosol

TiO_2 hydrosol was prepared according to [20,21] with some modification: 1 mL tetrabutyl titanate was dissolved in 25 mL absolute ethanol, and the solution was added dropwise into 50 mL doubly distilled water under a vigorous stir. After that, the suspension was kept stirring under 70°C for about 45 min to ensure complete hydrolysis, then 100 mL $0.1\text{ mol L}^{-1}\text{ HNO}_3$ was added, and the mixture was ultrasonic at 70°C for 4 h. Transparent hydrosol was obtained, and the pH value of the hydrosol was about 1. The size of the hydrosol particle was about 10 nm. It was very easy to separate the biosorbent from TiO_2 hydrosol.

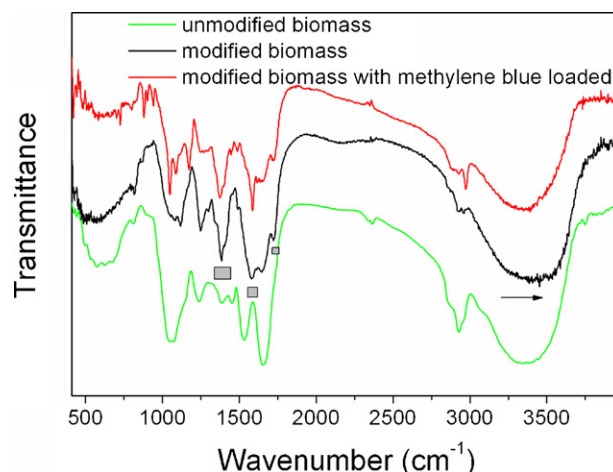


Fig. 2. FTIR spectra of modified, unmodified biomass and modified biomass with methylene blue loaded.

2.5. Desorption kinetics experiments

Different solvents (TiO_2 hydrosol, ethanol, $0.1\text{ mol L}^{-1}\text{ HCl}$, mixtures of ethanol and $0.1\text{ mol L}^{-1}\text{ HCl}$ with different volume ratio) were tested for desorption of MB from dye loaded biosorbent. The dye loaded biosorbent was prepared by exposing the dried modified biomass to MB solution (1 mmol L^{-1}) for 10 h on a rotary shaker, then the biomass covered with MB was taken out by centrifugation, and dried at 60°C for 24 h before use. The amount of MB absorbed calculated to be 740 mg g^{-1} . Dye desorption was studied by shaking 10 mg of MB loaded biomass in 550 mL of different desorbing agents. At different desorption time, the concentration of MB in liquid phase was measured by UV-spectrum.

2.6. Photodegradation of methylene blue by TiO_2 hydrosol

After the completion of the desorption experiment, TiO_2 hydrosol containing methylene blue was irradiated directly under sunlight, and it was sampled at interval times to determine the photodegradation rate of the dyes by measuring their characteristic absorbance.

3. Results and discussion

3.1. Characterization of the biosorbent

Fig. 2 shows FTIR spectrum of the pristine biomass. The amide I band was primarily a $\text{C}=\text{O}$ stretching mode and was centered at 1657 cm^{-1} ; the amide II band was a combination of N–H bending and C–N stretching and was centered near 1547 cm^{-1} ; the more complex amide III band was located near 1242 cm^{-1} . Two peaks at 3344, 1071 demonstrated the presence of hydroxyl groups on the biomass surface. After modification, the spectrum showed obvious changes. Two new peaks at 1578 and 1384 cm^{-1} were observed, which was assigned to $\text{C}=\text{O}$ asymmetric and symmetric stretching in carboxylate ions. These results demonstrated that PMDA were grafted on the biomass surface, and great amount of carboxyl groups were introduced.

3.2. Effect of pH on adsorption

Fig. 3 shows the effect of pH on MB adsorption on the unmodified and modified biomass. It could be seen that the uptake of MB increased with increasing pH from 2 to 6 until equilibrium obtained.

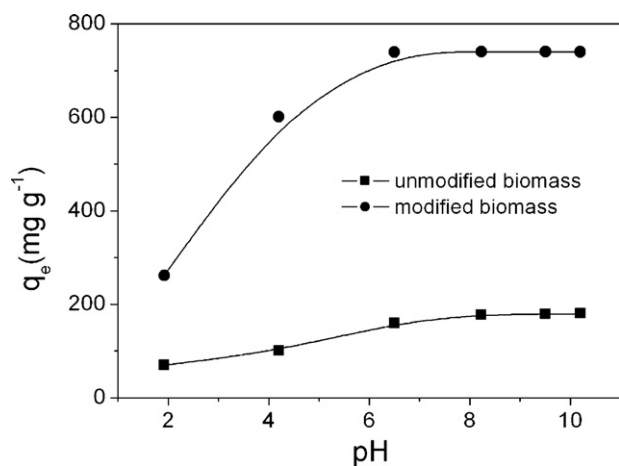


Fig. 3. Effect of pH on methylene blue adsorption on the modified and unmodified biomass.

It had been reported that the biosorbent interact with the cationic dyes mainly through electrostatic, hydrogen bonding and van der Waals interactions [22]. At low solution pH, the high concentration of H⁺ ions promoted the protonation of the functional groups, and thus the sorbents became more positively charged, which inhibits the sorption of the cationic dyes on it. On the other hand, excess H⁺ ions would compete with cationic dye molecules for the sorption sites. So the adsorption capacity of the biosorbents decreased greatly at low solution pH. When the solution pH increased, the number of positively charged available sites decreased, meanwhile the number of the negatively charged sites increased. The surface of sorbents became more negatively charged, which improved the interaction between the sorbents and the cationic dye molecules. Therefore, the adsorption capacity of the sorbents increased at higher pH value.

3.3. Adsorption isotherm experiments

Fig. 4 shows the adsorption isotherm and removal rate of methylene blue on the modified biomass. It was found that the amount of MB absorbed increased with the increase of their initial concentration until maximum values were obtained, while the removal rate of MB in the solution decreased with the increasing dye concentration. It could be seen that 0.01 g of the modified biomass could remove MB completely from 20 mL of dye solution when its concen-

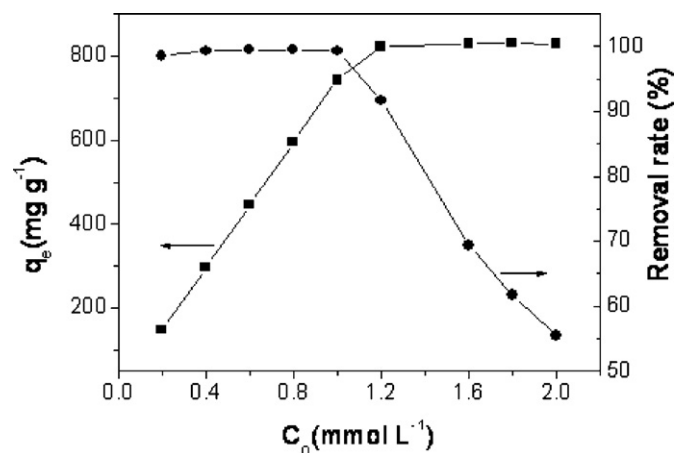


Fig. 4. Adsorption isotherms and removal rate of methylene blue on the modified biomass.

tration was less than 1 mmol L⁻¹, demonstrating that the modified biomass could be used to deal with high concentration wastewater. According to Langmuir equation, the maximum uptake capacities (q_m) of the modified biomass for MB was 830.8 mg g⁻¹, while that of the unmodified biomass is 180.2 mg g⁻¹. The increases were about five times. This increase was due to the introduction of carboxyl groups on the modified biomass surface.

Table 1 shows adsorption capacities of MB on different sorbents. Although a direct comparison between the examined modified biomass with those obtained in literatures was difficult, the modified biomass used in the present study showed reasonably good adsorption capacity for MB.

3.4. Adsorption kinetics

Fig. 5 shows the adsorption kinetics of methylene blue on the modified and unmodified biomass. It was observed that q_t increased rapidly during the adsorption starting step and then followed by a slowly increase in the following adsorption. According to the computer simulation, the adsorption kinetics tended to follow the two-step kinetic rate equation in the following form [33,34]:

$$q_t = q_0 + q_{t,1}(1 - e^{-k_1 t}) + q_{t,2}(1 - e^{-k_2 t}) \quad (1)$$

where q_t was the amount of dye adsorbed at time t expressed in milligrams per gram of biosorbent (mg g⁻¹); q_0 is the amount of

Table 1
Comparison of the adsorption capacity for methylene blue by the application of several adsorbents.

Adsorbent	PH	Adsorption capacity (mg g ⁻¹)	Reference
Oil palm shell	6.5	243.9	[23]
Untreated wood shaving	–	20.9	[24]
HCl-treated wood shaving	–	14.6	[24]
Na ₂ CO ₃ treated wood shaving	–	68.8	[24]
Na ₂ HPO ₄ treated wood shaving	–	34.0	[24]
Raw biomass	6	117.4	[17]
Succinated biomass	6	147.5	[17]
SPC-100	6	295.6	[17]
SPS-200	6	493.6	[17]
<i>Luffa cylindrica</i> fibers	2.5	122.0	[25]
Activated carbon	–	435.0	[26]
Jute fiber carbon	4.0	225.6	[27]
Teak wood bark	6.5	915.0	[28]
Dead macro-fungi	6.0	232.7	[29]
Peat	–	324.0	[30]
Dehydrated peanut hull	3.5	108.0	[31]
Spent activated clay	5.5	127.5	[32]
Unmodified biomass	6.0	180.4	This work
Modified biomass of baker's yeast	6.0	840.0	This work

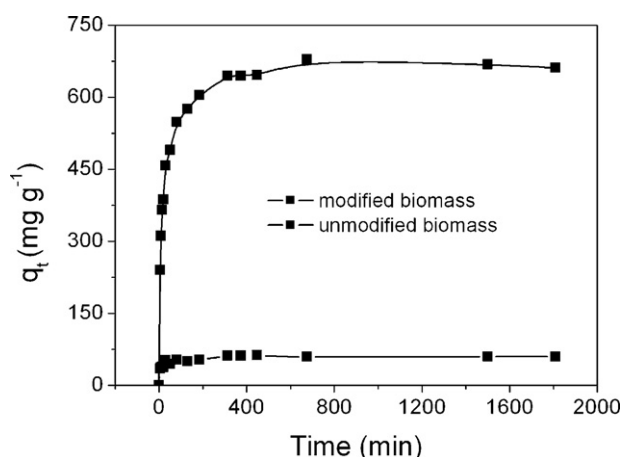


Fig. 5. Adsorption kinetics of methylene blue on the modified and unmodified biomass.

dye adsorbed at time $t=0$, which is equal to 0; k_1 and k_2 are the kinetic rate constants associated with different kinetic steps; and $q_{t,1}$ and $q_{t,2}$ are their pre-exponential amplitude terms, which can indicate the adsorption amount at different kinetic steps. Define q_e as:

$$q_e = q_0 + q_{t,1} + q_{t,2} \quad (2)$$

which represents the amount of dye adsorbed at equilibrium, the following expression, namely two-step kinetic rate equation, is obtained:

$$q_t = q_e - q_{t,1}e^{-k_1t} - q_{t,2}e^{-k_2t} \quad (3)$$

Adsorption rate constants values by fitting with two-step kinetic rate equation are listed in Table 2. The values of q_e , $q_{t,1}$, and $q_{t,2}$ of the modified and unmodified biomass showed that the modified biomass had high adsorption capacity for methylene blue, and the adsorption process on the biosorbents were controlled by both rapid and slow desorption kinetics.

3.5. Adsorption mechanism

Fig. 2 and Fig. 6 show FTIR spectrum of the modified biomass before and after MB adsorption. After MB loaded, New peaks at 879, 902, 941 and 1172 cm^{-1} , which was due to MB molecule, were present. Moreover, it could be seen that the peak of C=O symmetric and asymmetric stretching in carboxyl group shifted from 1578 and 1384 cm^{-1} to 1586 and 1373 cm^{-1} , respectively, and the peak at 3408 cm^{-1} (O–H) shifted significantly to 3391 cm^{-1} . These changes demonstrated that carboxyl and hydroxyl groups were both involved in the adsorption of MB. The adsorption of

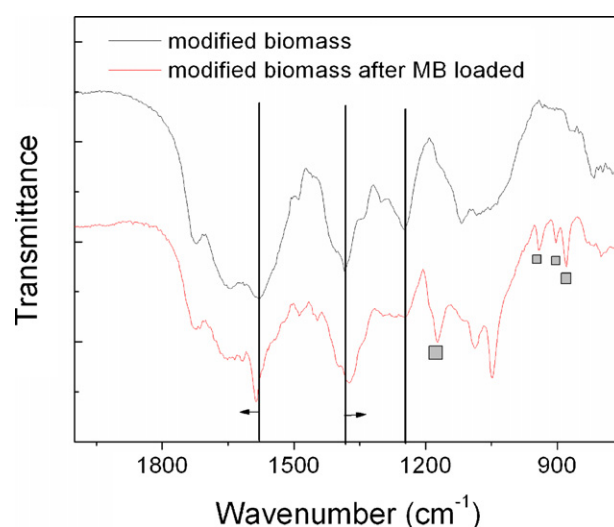


Fig. 6. FTIR spectrum of the modified biomass before and after MB loaded.

MB on the modified biomass may be attributed to (1) electrostatic interaction between the dye molecules and carboxylate ions on the biomass surface, (2) weak physical forces such as hydrogen bonding between nitrogen atom of MB and hydroxyl groups on the biomass surface, and (3) 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 [22]. A schematic diagram of dye molecule adsorbed on the biomass surface is presented in Fig. 7.

3.6. Desorption kinetics

To understand the nature of adsorbate desorption from adsorbent, it is necessary to study the desorption kinetic of the adsorbed dye from the modified biomass. As illustrated in Fig. 3, low adsorption for methylene blue was observed at a low solution pH, which implies that adsorbed dye can be desorbed easily from the surface of the biosorbent in an acid medium. On the other hand, it is easier for the MB to dissolve in ethanol than in distilled water. MB loaded modified biomass was treated with HCl (0.1 mol L⁻¹), ethanol, the mixtures of HCl (0.1 mol L⁻¹) and ethanol, and acid TiO₂ hydrosol (pH 1). Desorption kinetic curves of MB in different eluents are shown in Fig. 8. It could be seen that the amount of MB desorbed from the biomass increased rapidly and then slowly until equilibrium obtained, and it could be represented by the two-step kinetic rate equation in the following form [33,34]:

$$q_d = q_{d,0} + q_{d,1}(1 - e^{-k_{d,1}t}) + q_{d,2}(1 - e^{-k_{d,2}t}) \quad (4)$$

Table 2

Kinetic parameters obtained from the two-step kinetic model for adsorption and desorption of methylene blue on the modified biomass.

Biomass	q_e (mg g ⁻¹)	Removal rate (%)	$q_{t,1}$ (mg g ⁻¹)	k_1 (min ⁻¹)	$q_{t,2}$ (mg g ⁻¹)	$k_{d,2}$ (min ⁻¹)	r_d^2
<i>Adsorption kinetics</i>							
Modified biomass	646.0	86.4	334.2 ± 26.6	0.19 ± 0.03	306.6 ± 22.3	0.013 ± 0.002	0.995
Unmodified biomass	60.6	8.1	25.1 ± 3.1	8.33 ± 0.00	35.5 ± 5	0.011 ± 0.004	0.953
Solvents	q'_e (mg g ⁻¹)	Desorption rate (%)	$q_{d,1}$ (mg g ⁻¹)	$k_{d,1}$ (min ⁻¹)	$q_{d,2}$ (mg g ⁻¹)	$k_{d,2}$ (min ⁻¹)	r_d^2
<i>Desorption kinetics</i>							
0.1 M HCl	373.6	50.5	195.3 ± 12.8	0.069 ± 0.01	178.3 ± 10.2	0.002 ± 0.0003	0.997
TiO ₂ hydrosol	386.1	52.2	247.1 ± 24.5	0.14 ± 0.07	139.0 ± 21.6	0.004 ± 0.001	0.997
HCl:ethanol (1:4)	617.4	83.4	308.8 ± 16.6	6.33 ± 0.00	308.6 ± 13.3	0.019 ± 0.001	0.998
HCl:ethanol (3:2)	701.3	94.7	392.4 ± 24.9	10.50 ± 0.00	308.9 ± 18.1	0.013 ± 0.003	0.997
HCl:ethanol (4:1)	403.4	54.5	234.6 ± 13.0	3.29 ± 0.00	168.8 ± 10.5	0.004 ± 0.0005	0.998
Ethanol	320.4	43.3	60.3 ± 18.7	0.02 ± 0.01	260.1 ± 45.9	0.0007 ± 0.0005	0.999

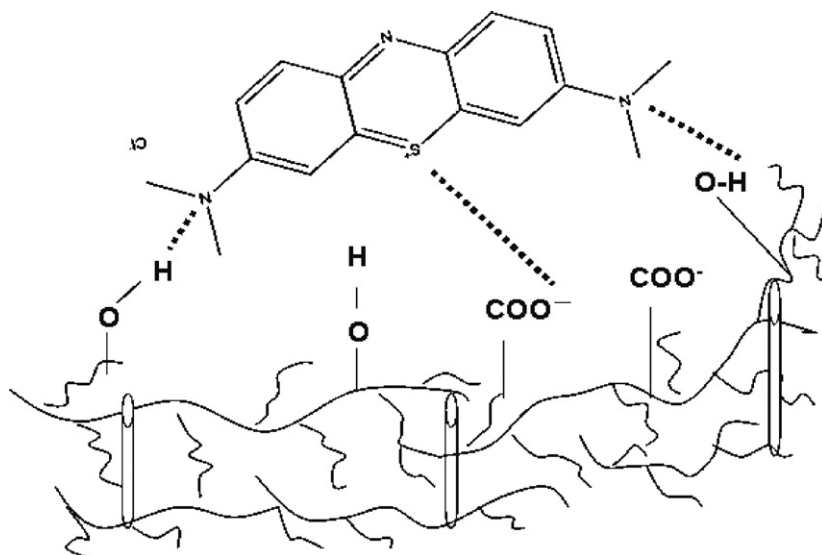


Fig. 7. Schematic diagram of dye-biomass interactions on the modified biomass surface.

where $k_{d,1}$ and $k_{d,2}$ are the desorption rate constants associated with different kinetic steps; q_d is the amount of dye desorbed at time t present per gram of the modified biomass (mg g^{-1}); $q_{d,0}$ is the amount of dye desorbed at time $t=0$, $q_{d,0}=0$; and the pre-exponential amplitude terms $q_{d,1}$ and $q_{d,2}$ can indicate the desorption amount at different kinetic steps. At $t=\infty$, $q_d = q_{d,0} + q_{d,1} + q_{d,2} = q'_e \leq q_e$, in which q'_e represents the desorbed amount at desorption equilibrium. And at $t=0$, desorption does not start so that $q_d = q_{d,0} = 0$. Theoretically, as time extends limitlessly, desorption process could proceed completely and $q_d = q'_e$. But actually the complete desorption cannot take place and $q'_e < q_e$. Therefore, Eq. (4) can be rearranged to the following form:

$$q_d = q'_e - q_{d,1}e^{-k_{d,1}t} - q_{d,2}e^{-k_{d,2}t} \quad (5)$$

Desorption rate constants were estimated by fitting the corresponding experimental data by using Eq. (5) and listed in Table 2. It could be seen that the r_d^2 values in all the cases were more than 0.99, demonstrating desorption kinetics curve fit the two-step kinetic model and methylene blue release process was distinctly divided into two steps. Desorption rates and $k_{d,1}$ both followed an order as: HCl:ethanol (3:2) > HCl:ethanol (1:4) > HCl:ethanol (4:1) \approx acid hydrosol \approx 0.1 M HCl > ethanol, and 94.7% of the absorbed methylene blue could be desorbed by using

0.1 M HCl and ethanol mixtures (3:2) as eluent. From the values of $q_{d,1}$ and $q_{d,2}$, it could be seen that the desorption process in 0.1 mol L⁻¹ HCl, acid hydrosol and the mixtures of HCl (0.1 mol L⁻¹) and ethanol solutions were all controlled by both rapid and slow desorption kinetics, while it was controlled mostly by slow desorption kinetics in ethanol medium. After 30 h, desorption equilibrium could be obtained for all the eluents.

Good results were obtained by using the mixtures of ethanol and HCl (0.1 mol L⁻¹) as solvents, but the large volume of the concentrated eluent of dye without treatment would bring secondary pollution to the environment. From experimental results, it appears that this process could be interesting for full scale application but before doing so a detailed technico-economical analysis should be performed. The acidity of it made it could be used as eluent for cationic dye desorption, and the desorbed dye in TiO₂ hydrosol could be photodegraded under sunlight irradiation. Desorption process by TiO₂ hydrosol would not bring secondary pollution to the environment. Most importantly, it could be used repeatedly without losing its photocatalytic activity, which could minimize the volume of eluent needed. Fig. 9 shows the UV absorption spectra of TiO₂ hydrosol at different desorption times. The desorption rate of methylene blue by using TiO₂ hydrosol as eluent was 52.2% at the first desorption cycle, which value was very close to that obtained on 0.1 mol L⁻¹ HCl. Fig. 10 shows the UV-vis absorption

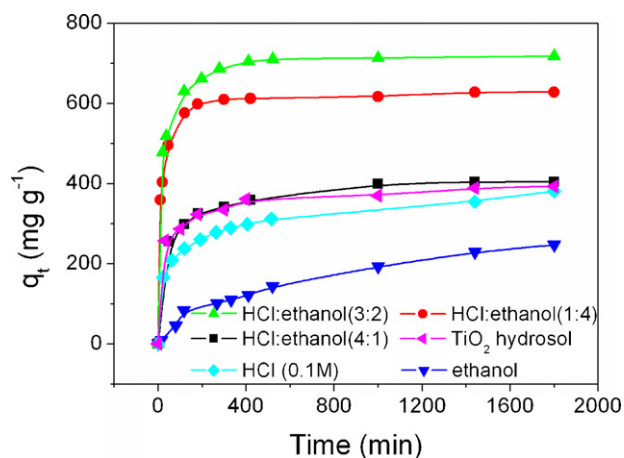


Fig. 8. Desorption kinetics curve of methylene blue from the modified biomass in different eluent.

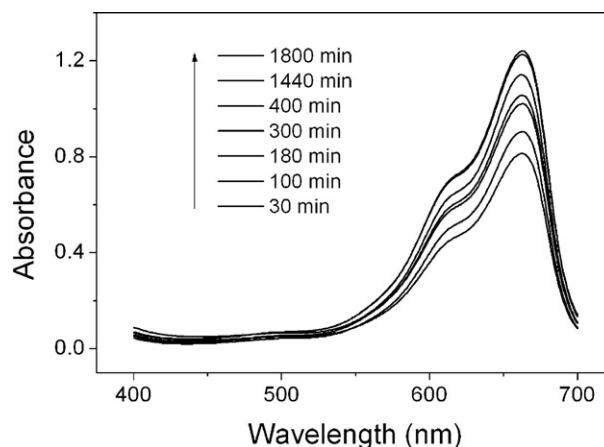


Fig. 9. UV-vis absorption spectra of TiO₂ hydrosol at different desorption times.

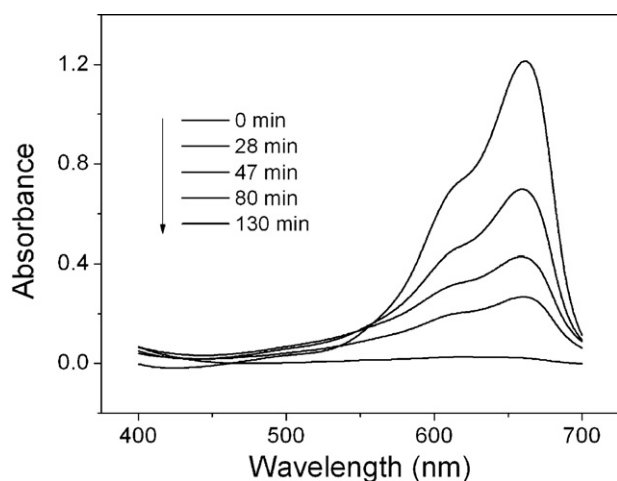


Fig. 10. UV-vis absorption spectra of TiO_2 hydrosol at different irradiation times.

spectra of TiO_2 hydrosol at different irradiation times. It could be seen that methylene blue was gradually degraded under sunlight irradiation, and the time needed for degradation was 130 min.

After the first desorption-photodegradation cycle, only 52.2% of methylene blue was desorbed from the biosorbent. In order to improve the desorption rate, the mixture of TiO_2 hydrosol and the modified biomass with undesorbed methylene blue was put on the shaker again for next desorption-photodegradation cycle. After three cycles, 80.0% of the loaded methylene blue could be desorbed from the surface of the modified biomass, and the regenerated biomass could be used in the next sorption process. Using TiO_2 hydrosol as eluent could economize great volume of solvents, and moreover, it would not bring secondary pollution to environment.

4. Conclusions

PMDA modified biomass was prepared through a simple way. Experiment results showed that the adsorption capacity of the modified biomass for methylene blue showed a significant increase compared with the unmodified biomass due to the presence of a large number of carboxyl groups. Good result was obtained by using a new self-clean eluent: TiO_2 hydrosol to regenerate the biosorbent. Acid TiO_2 hydrosol would be a potential alternative to conventional eluent to regenerate the sorbents with cationic dye loaded.

Acknowledgements

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