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Enhanced adsorption of anionic dyes from aqueous solution by gemini cationic surfactant-modified diatomite

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ABSTRACT

In this article, gemini cationic surfactant (1,4-butyl-bis (dimethyldodecylammonium bromide))-modified diatomite (GSMD) was prepared originally. Unmodified diatomite (UD) and GSMD were characterized by Fourier transform infrared (FTIR) spectroscopy, thermal analysis (TG) and specific surface area analysis. The adsorptions of anionic dyes methyl orange (MO), Suparalan Red GWN (SR) and Ramazol Blue RGB (RB) from aqueous solution onto UD and GSMD were carried out. The effects of pH, adsorption time, and initial concentration of dyes were also investigated. The results showed that GSMD had much higher adsorption capacity for anionic dye than UD in a broad pH range. The experimental maximum adsorption capacity of GSMD for MO, SR and RB was 9.4, 31.0, and 43.9 mg/g at pH 6.0 and about 13, 13 and 4.5 times of that of UD respectively. Adsorption isotherms showed that the adsorption of three dyes on GSMD followed Langmuir isotherm better than Freundlich isotherm. The effect of the amount of surfactant on adsorption capacity of GSMD and surfactant DTAB modified diatomite (DTAB-D) for MO was also compared, and the mechanism of enhanced dye adsorption capacity on GSMD was proposed.

Keywords: Gemini cationic surfactant; Modified diatomite; Adsorption; Anionic dye

1. Introduction

Industrial wastewater containing dyes, which are widely used in paper, textile, and leather industries, cause serious pollution of the environment. Azo dyes that are widely used organic dyes make up 60–70% of all textile dyes [1]. Some of them can degrade to produce carcinogenic aromatic amines. Some can also cause tumor and allergy [2,3]. Discharging even a small amount of these dyes into water can affect aquatic life and food webs. In addition, water-soluble organic dyes give water an undesirable color, resulting in a aesthetic contamination even at very low concentrations. Various physical, chemical and biological treatment techniques can be employed to remove dyes from wastewater. But some dyes may degrade to produce suspected carcinogens and toxic products, and water-soluble dyes can also adsorb/reflect sunlight, which can inhibit the growth of bacteria to sufficient levels to biologically degrade impurities [4,5]. Consequently, such as common coagulation processes and biological methods have not been very successful. However, adsorption

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method has been proven to be successful and convenient [6–8]. Adsorption with activated carbon appears to be best for the elimination of this dye. But this adsorbent is expensive and difficult to regenerate after use. So there is growing interest in using low cost, commercially available materials for the adsorption of dyes, such as peat [9], saw dust [10], sepiolite [11,12], clay and modified clay [1,2,13,14], and diatomite [3,15–18].

Diatomite, available in abundance in various locations around the world, has cylindraceous porous texture and has received attention for its unique physical and chemical properties, such as high permeability, high porosity (35–65%), small particle size, large surface area, low thermal conductivity, and chemical inertness [19–21]. Diatomite can react with many polar organic compounds because of silanol groups that spread over the matrix of silica [22]. It has been commonly used in water purification, filtration of commercial fluids, separation of various oils and chemicals, and adsorption of heavy metal ions [23,24] and dyes. Diatomite can be modified to improve its adsorption properties by different methods like heat treatment [21], acid treatment [25], microemulsion modification [26,27], manganese oxides modification [28,29], iron-oxide coating [30], polyethyleneimine modification [31]. Several literatures were concerned with the adsorption of dye from aqueous solution using diatomite or modified diatomite. As we know, natural diatomite exhibits a negative charge in a wide range of pH value, which allows it to adsorb positively charged dyes but inducing a low adsorption capacity for anionic dyes [16,19]. However, many water-soluble dyes (such as reactive dye, acid dye, direct dye etc.) that are widely used in industries are anionic dyes [32]. Al-Ghouti showed that microemulsion modification [26] and manganese oxides modification [28] can improve the adsorption capacity of diatomite for reactive dyes. Zhan [33] showed that magnesium hydroxide-modified diatomite was an effective adsorbent for removing acid dyes from aqueous solution. In addition, Sprynskyya [15] reported that the diatomite modified by hexadecyltrimethylammonium bromide had over 20 times higher adsorption capacity for uranium ions than unmodified diatomite. Several literatures concerning with usual cationic surfactant-modified montmorillonite [14] or bentonite [34,35] indicated that cationic surfactant modification could improve the adsorption capacity of these adsorbents. Considering that gemini surfactants (they are made up of two hydrophobic tails and two hydrophilic headgroups connected by a spacer of various kinds) as a new generation of surfactants are superior to the corresponding conventional surfactants in a number of aspects [36]. So the aim of our study is to improve the adsorption capacity of diatomite for anionic dyes by gemini cationic surfactant modification.

In this work, gemini cationic surfactant-modified diatomite was prepared originally and used to adsorb anionic dyes. To our knowledge, so far there are no reports on the adsorption of dye by gemini surfactant-modified clay or diatomite. We expect that cationic gemini surfactant modification could improve the adsorption capacity of diatomite for anionic dyes. To further study the mechanism of enhanced adsorption of dyes by gemini cationic surfactant-modified diatomite, methyl orange (MO) dye adsorption on mono cationic surfactant-modified diatomite was also compared.

2. Materials and methods

2.1. Materials

MO dye, from Tianjing Chemical Reagent Research Institute, was selected as a base model anionic dye. Acid dye Supralan Red GWN (SR) and reactive dye Ramazol Blue RGB (RB) are commercial dyes, supplied by Dystar Company, Germany. The chemical structures of SR and RB were not provided for commercial reasons. Diatomite was calcined diatomite and obtained from Xilong Chemical Co. Shantou, China. The diatomite was sieved to 106∼250 μm (100∼140 mesh) particles size for further experiments. The cationic surfactant, dodecyltrimethylamonium bromide (DTAB, G.R.), was purchased from Sinopharm chemical reagent Co. Ltd., China and used as received. The gemini cationic surfactant 4-butyl-bis (dimethyldodecylammonium bromide) was synthesized according to the method reported in the literature [37]. 1,4-Dibromo butane (20 mmol) and an excess of N,N-dimethyldodecylamine (44 mmol) were added into isopropyl alcohol solvent. The mixture reacted at 80℃ for 48 h. Then, the solvent was removed in a rotary evaporator under reduced pressure, and raw solid product obtained was recrystallized three times from ethyl acetate. The structure of gemini cationic surfactant was checked by ^{1}H NMR spectra. Other chemicals used were of analytical reagent grade. Water used in this work was deionized water.

2.2. Modification of diatomite

The modification procedure was as following: 30.00 g of diatomite was added into 300 mL of surfactant solution with an accurate concentration. The mixture was stirred mechanically at 25℃ for 6 h and was statically placed overnight. The modified diatomite was separated from the mixture by filtration, subsequently washed four times with deionized water, then dried at 80℃ for 5 h and conserved in a desiccator. The accurate concentration of gemini surfactant was 1.00, 2.00, and 4.00 mmol/L respectively. So the modified diatomite with different amounts of gemini surfactants (denoted as GSMD) was prepared. And cationic surfactant DTAB, which has one quaternary ammonium cation and same length of hydrophobic tail to that of the gemini surfactant, was also used to modify diatomite according to the above-mentioned procedure for comparing (denoted as DTAB-D).

2.3. Characterization

The surface area of the adsorbents was obtained from the N_2/77 K adsorption isotherms by applying the BET method using a Surface Area and Pore Size Analyzer ST-2000 (Beijing Puqi Institute of analysis instrument, China). And samples were outgassed with H_2 for 2 h at 105℃ prior to the adsorption measurement. Infrared spectra of UD and GSMD were obtained using a Fourier transform infrared (FTIR) spectrometer (TENSOR 27, Bruker Corp., Germany) to determine the structural groups of the diatomite. The morphology of the adsorbents was examined by scanning electron microscopy (JEOL JSM-6,480). Thermogravimetric analyses were carried out using a NETZSCH STA 449F3 instrument thermal analyzer, operating at a ramp of 10.0 K/min from 40℃ to 700℃ in a high-purity flow nitrogen atmosphere (100.0 mL/min).

2.4. Adsorption experiments

Dye solutions with various pH and concentration were prepared ahead. A fixed amount of the adsorbent (0.300 g) was added to 50.0 mL of dye solution of the required concentration at desired pH. And the mixture was agitated mechanically for a predetermined time at 25℃. The supernatant solution was then centrifuged at 3,000 rpm for 3 min, and the final concentration of the dye was measured by spectrophotometry. Dye removal percentage was then calculated as following:

$$\text{Dye removal } (\%) = \frac{(c_\mathrm{i} - c_\mathrm{e})}{c_\mathrm{i}} \times 100\% \tag{1}$$

The amount of dye adsorbed at the adsorption equilibrium (q_e) was calculated using the following relationship:

$$q_\mathrm{e} = \frac{(c_\mathrm{i} - c_\mathrm{e}) \times V}{m} \tag{2}$$

where c_i is the initial concentration of the dye solution (mg/L), c_e is the concentration of the dye solution at the adsorption equilibrium (mg/L), V is the volume of the dye solution (mL), and m is the mass of the diatomite (mg).

The influence of pH on dyes removal was studied by adjusting dye solutions to different pH values (2.0, 4.0, 6.0, 8.0, and 10.0) by adding a small amount of 1.0 mol/L HCl solution or 1.0 mol/L NaOH solution using pHs-25 pH meter (Shanghai Precision & Scientific Instrument Co. Ltd., Shanghai, China). The absorbance of the dye solution was measured at $\lambda_{\max}$. The $\lambda_{\max}$ of SR and RB dye are 518 nm and 604 nm respectively. There is a hypsochromic shift for MO when the pH of dye solution increased from 2.0 to 6.0. The $\lambda_{\max}$ of MO dye are 508 nm, 470 nm and 465 nm when pH values are 2.0, 4.0 and 6.0 (or 8.0 and 10.0).

Effects of adsorption time were conducted by that 1.800 g adsorbent was mixed with 300.0 mL of dye solution (pH 6.0) at 25℃. At different time intervals (2, 5, 10, 15, 25, 35, 60, 120, 180 and 240 min), the samples of 4 mL were taken from the solution and the concentration was analyzed.

Effects of concentration of dyes were carried out by adding 0.300 g of the adsorbent to 50.0 mL of dye solution of varying concentrations (10–100 mg/L for MO, 20–250 mg/L for SR, 20–400 mg/L for RB) at pH 6.0 for equilibrium time.

To further explain the mechanism of enhanced adsorption capacity of GSMD, the effect of the amount of surfactant on maximum adsorption capacities of GSMD and DTAB-D for MO dye at pH 6.0 was investigated at 25℃.

3. Results and discussion

3.1. Characterization of adsorbents

3.1.1. Specific surface area

Surface areas were investigated using BET analysis. The surface area values are found to be 14.75 and 9.03 m^2/g for UD and GSMD (4.00 mmol/L surfactant solution modified), respectively. The higher surface area of UD is due to the enhanced adsorption of N_2 in the wider micropores and mesopores. The lower surface area of GSMD is probably due to the diatomite surface partly occupied by surfactants.

3.1.2. Fourier transform infrared spectroscopy

The IR spectra of UD and GSMD are shown in Fig. 1. The UD is characterized by the bands: the broad band in the 3,440 cm^{-1} region is ascribed to

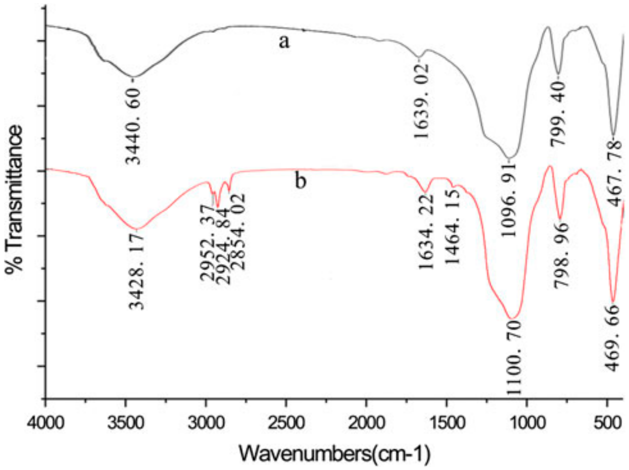

Fig. 1. FTIR spectra of (a) UD and (b) GSMD.

O–H stretching vibration, while O–H bending vibration band occurs at 1,639 cm^{-1}, Si–O stretching vibration band is observed at 1,096 cm^{-1} [38,39], bands in the 400–800 cm^{-1} region may attribute to Si–O and Al–O bending vibration [24]. From Fig. 1, it can be concluded that GSMD not only has characteristic diatomite bands, but also has characteristic alkyl bands. Bands at 2,952, 2,924 and 2,854 cm^{-1} are ascribed to the C–H stretching vibration of the CH_3 and CH_2 groups of the alkyl chain of quaternary ammonium molecules, while band 1,464 cm^{-1} is due to C–H bending vibration of the alkyl chain. Due to these changes in the IR spectra, it is thought that the surfactant modification of diatomite has been achieved.

3.1.3. Scanning electron microscopy

The electron micrographs clearly reveal the surface texture and morphologies of UD and GSMD (Fig. 2).It is evident from the micrographs that UD has many clean large pores of around 200–500 nm and micropores. And there are also small broken particles of other kinds of diatoms. Fig. 2(b) shows that the surface of diatomite was covered by gemini cationic surfactant and the surfactants along the edge of large pores exhibit a tendency to form floccule.

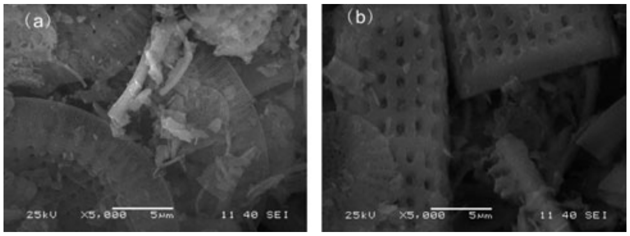

Fig. 2. SEM images of (a) UD and (b) GSMD.

3.1.4. Thermogravimetric analysis

Fig. 3 shows the TG curves of UD and GSMD (4.00 mmol/L surfactant solution modified). UD undergoes two main steps decomposition process from 40 to 700℃. The first decomposition step, between 40 and 100℃, is related to the loss of physisorbed water. The second main step, which appears between 100 and 350℃, is due to the structural water loss [40].

As for GSMD, it shows two-step decomposition process. The first weight loss of GSMD occurs between 40 and 100℃, which associates with the loss of physisorbed water. In this step, GSMD has a little higher mass loss than UD, implying more physisorbed water in GSMD. In the temperature range from 100 to 700℃, more weight loss of GSMD indicates that there is not only structural water loss but also the decomposition of surfactants modified on the diatomite surface. From Fig. 3, only one main mass loss for GSMD during this region demonstrates that there is one molecular environment of the surfactants in the GSMD and that gemini surfactants are almost modified on the external surface [41,42]. This is probably because the molecular size of 1,4-butyl-bis (dimethyldodecylammonium bromide) is too large to enter into inside small pore. On the other hand, the surfactant contents of modified diatomite can be estimated by the weight loss difference of unmodified and modified diatomite, which is about 0.65% (g/g) for GSMB. To order to obtain efficient and low-cost adsorbent, surfactant solutions with low concentration

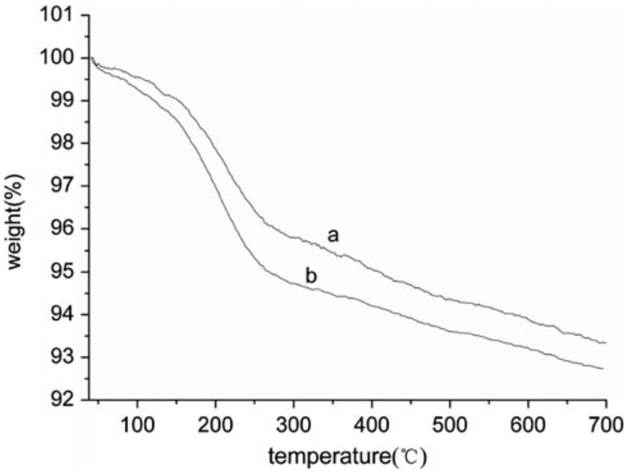

Fig. 3. TG curves of (a) UD and (b) GSMD.

were used for modification, which induced relatively low surfactant contents in diatomite.

3.2. *Effect of pH value on adsorption*

The hydroxyl groups on the surface of the diatomite can gain or lose a proton, resulting in different surface charge with changing pH. At low pH, surface sites are protonated and the surface becomes positively charged. At high pH, the deprotonation of hydroxyl groups takes place, and the surface becomes anionic [31]. The effect of solution pH on the adsorption of MO, SR and RB onto UD and GSMD (4.00 mmol/L surfactant solution modified) was studied. The experimental data were analyzed by plotting the percentage dye removal against pH of the dye solution and the results are illustrated in Fig. 4. The pH was measured before and after the adsorption process and the difference between the two measurements values of pH was less than 0.2 for all samples.

Fig. 4 shows that the percentage removal of these dyes on UD decrease with increase in solution pH, and the maximum removal rate is achieved at pH 2.0. This is attributed to that anionic dye molecules are easy to be adsorbed on positively diatomite surfaces at low pH. While at higher pH, the surface becomes negatively charged, and electrostatic repulsions cause decrease in dyes adsorption, and the adsorption is mainly induced by intermolecular force between diatomite surface and dye molecular [19]. The percentage removal of the MO on GSMD is 94.9% at pH 2.0, and remains nearly 100% in the pH range from 4.0 to 8.0, and slightly decreases at pH 10.0 (99.3%). The percentage removal of the SR and RB on GSMD decrease from 99.2 to 90.0% and from 85.4 to 73.5%, respectively. Although the specific surface of GSMD is smaller than that of UD, it is clear that modification with a small dosage of gemini cationic surfactant can notably enhance the adsorption capacity of diatomite for MO, SR, and RB dyes in pH from 2.0 to 10.0. And the effect of the pH on the adsorption capacity of GSMD for dyes is weaker than that of UD. The difference is attributed to different acting forces between dyes and modified diatomite. The mechanism of enhanced adsorption capacity of GSMD for these dyes will be further explained in section 3.5.

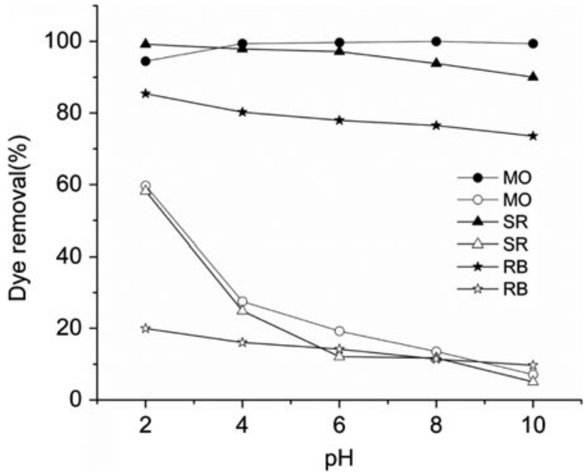

Fig. 4. Effect of pH on removal of dyes by GSMD (solid) and UD (open). Initial MO concentration 20.0 mg/L, initial SR and RB dye concentration 100.0 mg/L, adsorption time 120 min, temperature of solution 25℃.

3.3. *Effect of adsorption time on adsorption*

Fig. 5 shows the effect of adsorption time on the adsorption capacity of UD and GSMD (4.00 mmol/L surfactant solution modified) for dyes at pH 6.0. The adsorptions are rapid in the initial stage of contact time and gradually decrease until equilibrium. The rapid adsorption observed during the first 5 min is probably due to the abundant active sites on the adsorbents surface. The adsorption of MO and SR on UD and GSMD all can reach equilibrium at about 2 h under our experimental conditions. The equilibrium time required for the adsorption of RB on UD and GSMD is almost 3 h. Therefore, 3-h equilibrium adsorption was used in the subsequent adsorption isotherms experiment.

3.4. *Adsorption isotherms*

Fig. 6 shows the plot of adsorption isotherm, adsorption capacity vs. the equilibrium dye concentration

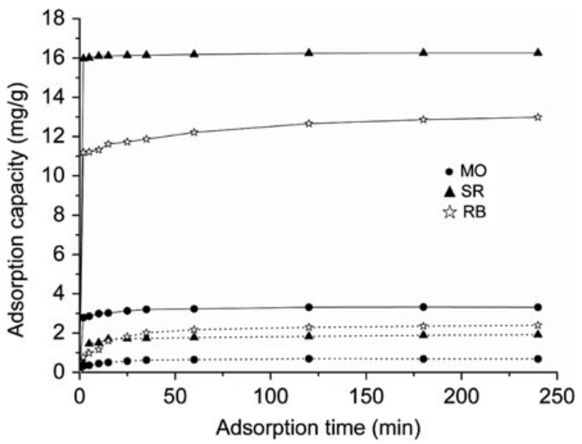

Fig. 5. Effects of adsorption time on dyes adsorption capacity of GSMD (–) and UD (…). Initial MO concentration, 20.0 mg/L; initial SR and RB dye concentration: 100.0 mg/L; temperature of solution, 25℃, pH 6.0.

for the adsorption of dyes onto UD and GSMD (4.00 mmol/L surfactant solution modified) at pH 6.0. The experimental maximum adsorption capacity of GSMD for MO is 9.4 mg/g and about 13 times of that of UD (0.72 mg/g). The adsorption capacity of GSMD for SR is 31.0 mg/g and also about 13 times of that of UD (around 2.37 mg/g), while the adsorption capacity of GSMD for RB can reach 43.9 mg/g. It can be also seen in Fig. 6 that the adsorption isotherm of RB on UD is a curve of S type approximately, and the sorption tends to be saturated at 9.7 mg/g.

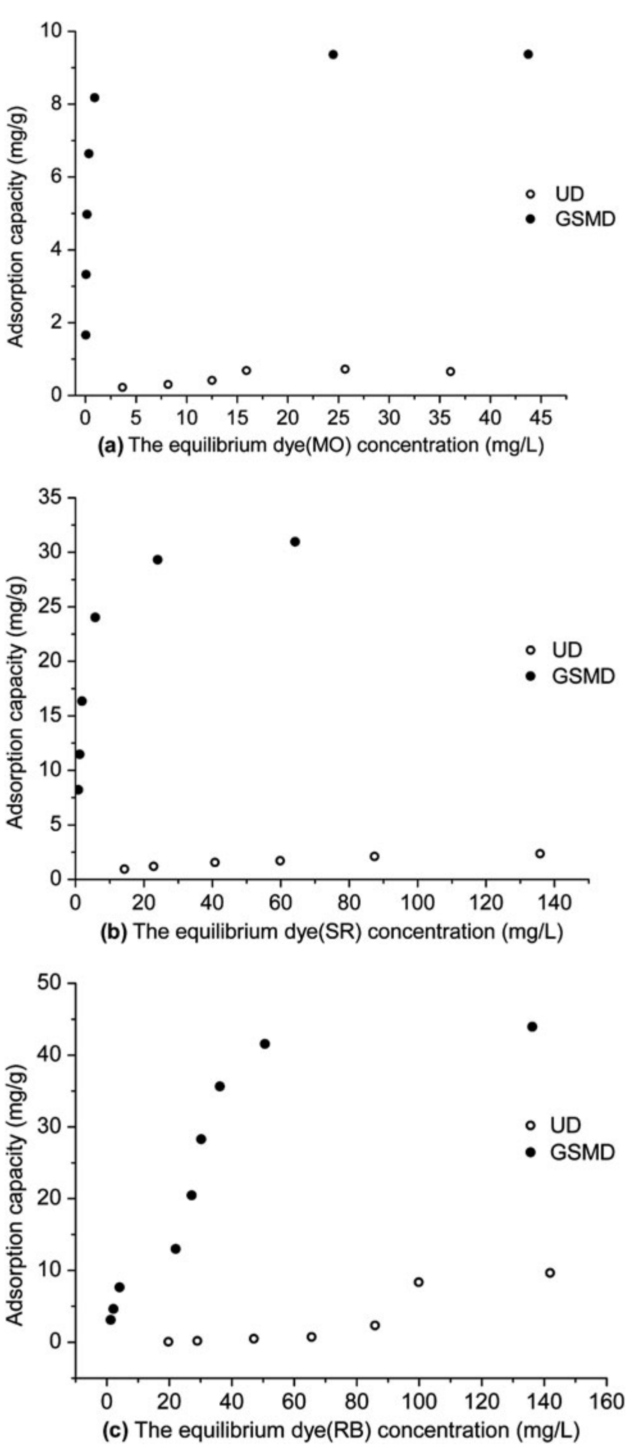

Fig. 6. Plots of adsorption isotherm for the adsorption of dyes on UD and GSMD.

Equilibrium isotherms are very important in designing adsorption systems. The Langmuir and Freundlich [34,37] are the most frequently employed models, which are represented by the following equations, respectively:

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max} c_e} + \frac{1}{q_{\max}} \tag{3}$$

$$q_e = K_f c_e^{1/n} \tag{4}$$

where q_e is the amount of MO dye adsorbed onto adsorbents at equilibrium (mg/g^{-1}), $q_{\max}$ is the theoretical maximum monolayer capacity (mg/g^{-1}), K_L is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption, c_e is the equilibrium solution concentration (mg/L^{-1}), K_f is the Freundlich constant of the relative adsorption capacity of the adsorbent and $1/n$ is the adsorption intensity.

Two adsorption isotherms were constructed by plotting the $1/q_e$ vs. $1/c_e$, lgq_e vs. lgc_e using experimental data, respectively. Langmuir constants and Freundlich constants as well as the corresponding correlation coefficient values are presented in Table 1.

As shown in Table 1, the higher values of the correlation coefficient from Langmuir expression indicate that the adsorptions of three dyes onto GSMD are in good agreement with the Langmuir isotherm rather than the Freundlich isotherm. From Table 1, it can be seen that $q_{\max}$ of GSMD obtained from the Langmuir isotherm is approximate to the experimental data for MO and SR, while the $q_{\max}$ of GSMD obtained from the Langmuir isotherm for RB is lower than the experimental data. In addition, model constants suggested that experimental data of RB on UD are poor fit to the Langmuir isotherm. Freundlich constant K_f values of three GSMD/dye systems are much higher than that of UD/dye systems, indicating the high adsorption capacity of GSMD. The magnitude of the exponent 1/n indicates the favorability of adsorption. It is generally stated that the values of $1/n$ in the range 0.1–1 represent good adsorption. In this work, the exponents of three GSMD/dye systems are $0.1 < 1/n < 1$ and lower than UD/dye systems, indicating more favourable adsorption.

In general, unmodified diatomite showed very low adsorption capacity for three anionic dyes. This is in

Table 1
Langmuir and Freundlich isotherms constants for the adsorption of dyes onto GSMD and UD.

Sample	Langmuir			Freundlich		
	K_L	q_{max}	R^2	K_f	$1/n$	R^2
MO						
UD	0.082	0.92	0.9122	0.109	0.556	0.8689
GSMD	8.837	9.20	0.9986	5.78	0.189	0.7265
SR						
UD	0.039	2.58	0.9853	0.33	0.406	0.9913
GSMD	0.447	33.23	0.9966	11.40	0.283	0.8668
RB						
UD	−0.011	−0.24	0.9114	1.81E−05	2.681	0.9589
GSMD	0.086	32.26	0.9799	3.01	0.603	0.9407

accordance with the results obtained in adsorption experiments of similar reactive dyes SB and EBR [3], RGY [16]. Gemini surfactant modification can improve 13, 13 and 4.5 times of adsorption capacities of diatomite, respectively in this study and more effective than microemulsion modification [26] (about 1.5 times). The maximum adsorption capacity of GSMD is lower compared with manganese oxides modified diatomite [28] (228 mg/g for RY) and magnesium hydroxide-modified diatomite [33] (173.9 mg/g for TB and 398.6 mg/g for TR). We think that the different structure of dye and low surface area of calcined diatomite may cause larger difference of adsorption capacity. The previous study [18] has shown that calcined diatomite gave much lower adsorbing capacity for basic and reactive dyes from aqueous solution. So we predicted that there would be higher adsorption capacity if using modified raw diatomite.

3.5. The mechanism of enhanced adsorption capacity of GSMD for dyes

To further explain the mechanism of enhanced adsorption capacity of GSMD, effect of the amount of surfactant on MO adsorption capacity of GSMD and DTAB-D at pH 6.0 was compared.

Fig. 7 shows that the experimental maximum adsorption capacities of GSMD and DTAB-D increase with increase in the concentration of surfactant used in the modification process. Obviously the amount of surfactant modified onto diatomite will increase with increase in the concentration of surfactant used in the modification process. So the amount of quaternary ammonium cation on diatomite surface increases, which results in increasing of electrostatic attractions between MO dye and adsorbent. In addition, the adsorption capacity of GSMD for MO is about 2.8, 2.85 and 5.6 times that of DTAB-D, respectively, in the concentration of surfactant used in modification range from 1.0 to 4.0 mmol/L. It is obvious that the gap of

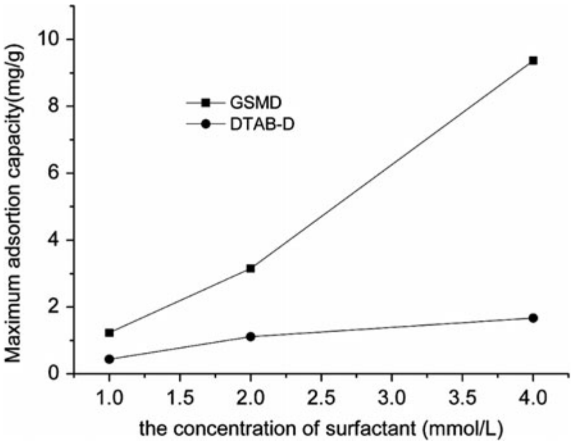

Fig. 7. Effect of the amounts of surfactant on MO adsorption capacity of GSMD and DTAB-D.

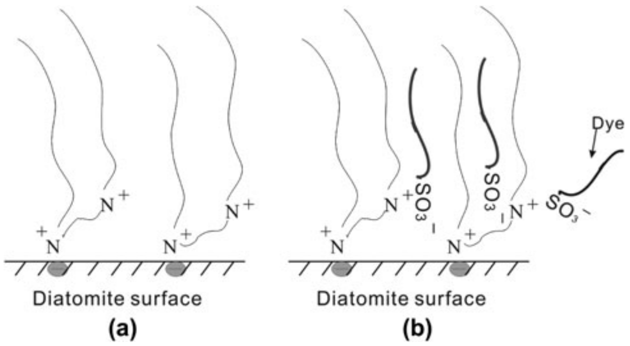

Fig. 8. The conformations of gemini surfactant on diatomite (a) and the adsorption model of dyes on GSMD (b).

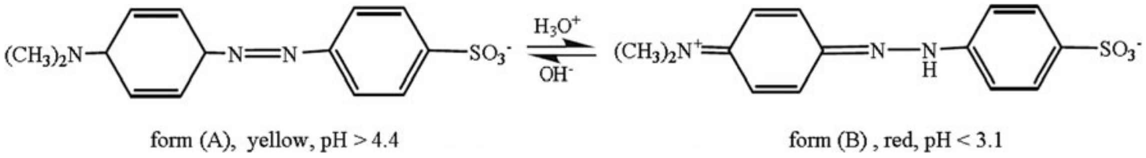

Fig. 9. The structural form of MO in aqueous solution.

adsorption capacity between GSMD and DTAB-D is growing. These may be explained by the conformation of gemini surfactant in GSMD. Previous research [43,44] demonstrated that the gemini surfactants with a short spacer were adsorbed by only one polar headgroup on silica surface. But according to our experimental facts, we conjecture that the two quaternary ammonium cations of most gemini surfactants are fixed on diatomite surface at low concentration modification. While at higher concentration modification, owing to active sites decreasing with occupation of surfactant on the diatomite surface, more gemini surfactants adopt the conformation (see Fig. 8(a)) that one quaternary ammonium cation is not fixed on diatomite surface and is free. Mainly due to the strong electrostatic attractions between the free quaternary ammonium cation and the negatively charged group of the dye molecule, GSMD shows much higher adsorption capacity than UD, though it has a lower surface area than UD.

Furthermore, we compared the adsorption capacities of UD and GSMD for MO at pH 2 and 6, respectively (see Fig. 4). It was found that the percentage removal of MO on GSMD at pH 6 is higher than at pH 2.0. This may be explained by the forms of MO (as shown in Fig. 9) at different pH. At pH 6, there are probably hydrophobic interactions in addition to the dominated electrostatic interaction between surfactants and MO molecules (form (A)). At pH 2.0, MO transforms to the form (B), and hydrophobic interactions between surfactant tail and MO are significantly reduced by the positively charged amine groups of MO, resulting in decrease in the percentage removal of MO. This phenomenon was not observed in the adsorption of SR and RB dye because they have no structural transformation. This viewpoint may also be verified by the experimental facts of Wang et al. [14] and Alkaram et al. [34], but they did not explain the experimental phenomenon.

Therefore, a mixed adsorptive mechanism under these experimental conditions can be suggested. The higher adsorption capacity of GSMD is mainly due to the strong electrostatic attractions between the quaternary ammonium cation unfixed on diatomite surface and the negatively charged group of dye molecule. In addition, hydrophobic interactions between surfactant tails and dyes also contribute to the adsorption of dyes.

4. Conclusions

Gemini cationic surfactant 1,4-butyl-bis (dimethyldodecylammonium bromide)-modified diatomite (GSMD) was prepared originally to adsorb anionic dyes methyl orange (MO), Suparalan Red GWN (SR), and Ramazol Blue RGB (RB) from aqueous solution. The adsorptions of MO, SR and RB on UD and GSMD all can reach equilibrium at about 3 h under our experimental conditions. The results show that gemini cationic surfactant modification could greatly enhance the adsorption capacity of diatomite for anionic dyes in a broad pH range. The experimental maximum adsorption capacity of GSMD with about 0.65% gemini surfactant for MO, SR, and RB is 9.4, 31.0, and 43.9 mg/g and about 13, 13, and 4.5 times of that of UD respectively. The higher values of the correlation coefficient from adsorption isotherm expression indicate that adsorption of three dyes on GSMD follows Langmuir isotherm better than Freundlich isotherm.

A comparative study of adsorption of MO on DTAB-D and GSMD indicates that more gemini surfactants were fixed on diatomite surface by only one cationic headgroup at higher concentration, and the other cationic headgroup is free. The higher adsorption capacity of GSMD is mainly due to the strong electrostatic attractions between the free quaternary ammonium cation and the negatively charged group of dye molecule. In addition, the different adsorption capacities of GSMD for MO at pH 2 and pH 6 show that the hydrophobic interactions between surfactant tails and dyes also contribute to the adsorption of dyes.

The results presented in this study clearly reveal that the modified diatomite with a small dosage of gemini cationic surfactant may be used as an efficient adsorbent for the removal of anionic dye that are widely used.

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