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Adsorption of dyes using magnesium hydroxide-modified diatomite

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ABSTRACT

Diatomite and $Mg(OH)_2$-modified diatomite (MMD) were employed as adsorbents for the removal of one cationic dye, Methylene Blue (MB), and two anionic dyes, Ramazol Golden Yellow (RGY) and Telon Blue (TB), from aqueous solution. Physical characteristics of the adsorbents were investigated using scanning electron microscope (SEM), energy dispersive X-rays (EDX), pH value of isoelectric point of zeta potential (pH_{IEP}) and Fourier transform infrared (FTIR) analyses. The $Mg(OH)_2$ content of MMD was found to be 13.45%, and three isoelectric points were observed around pH 2.0, 8.5 and 11.5 for MMD. The adsorption performance of dyes onto diatomite and MMD was studied using spectrophotometric analysis. It showed that the modification of diatomite enhanced removal of the anionic dyes from aqueous solution. The adsorption data were fitted to the Langmuir, Freundlich and Redlich-Peterson models. The results indicated that the Redlich-Peterson model was the best one in simulation of the adsorption isotherms, suggesting some heterogeneity in the surface or pores of the adsorbents. The adsorption of dyes onto diatomite and MMD may be attributed to electrostatic interaction, hydrogen bonding interaction, n-π interaction and Van Der Waals interaction.

Keywords: Adsorption; Diatomite; Textile dye; Magnesium hydroxide

1. Introduction

It is known that textile-processing wastewaters which contain dyes are generally high in biological oxygen demand (BOD) and chemical oxygen demand (COD). The removal of dyes is one of the main problems associated with the treatment of textile wastewater. As dyes are designed to be chemically stable, they are highly persistent in natural environments. The discharge of dyes may therefore present an eco-toxic hazard and introduce the potential danger of bioaccumulation that may eventually affect human by transport through the food chain. Various physical, chemical and biological treatment techniques can be employed to remove the hazardous dyes from wastewater. However, due to the nonbiodegradable nature of most of the dyes, chemical and biological technologies do not show great effectiveness and economic advantage, while adsorption method has been proven to be successful and convenient. Activated carbon is the most popular adsorbent with high adsorption capacity, but it is expensive and desorption of the dye molecules is not easily achieved [1]. Therefore, various low-cost adsorbents were studied for dyes removal from wastewater, e.g. fly ash [2], sepiolite [3], bentonite [4], wheat straw [5], peanut hull [6], clay [7] or diatomite [8].

As a siliceous rock made up largely from diatoms, diatomite has a unique combination of physical and

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chemical properties, which make it applicable for the removal of heavy metals and organic pollutants, and as a filtration medium in a number of industrial uses [9]. In recent years, many studies [10–17] have been conducted with diatomite to adsorb some dyes present in wastewater. However, an application of diatomite on the wastewater treatment depends mightily on its origin, and the removal of textile dyes from aqueous solution using $Mg(OH)_2$-modified diatomite (MMD) remains unexplored.

It has been reported that the precipitate of $Mg(OH)_2$ acts through an adsorptive coagulating mechanism in the removal of pollutant [18]. Hence we modified the diatomite by *in situ* precipitation of $Mg(OH)_2$ for the adsorption of dyes from textile wastewater. After investigating the physical characteristics of the diatomite and MMD, we studied their adsorption performance using three commercially available dyes and proposed the probable adsorption mechanism.

2. Experimental

2.1. Materials

Raw diatomite was obtained from Zhejiang Province in China. Magnesium chloride and sodium hydroxide were mainly used in the modification of diatomite by *in situ* precipitation. Ten grams of the diatomite with 5 mmol/g diatomite of $MgCl_2$ were well dispersed in 100 mL water. NaOH solution (2 mol/L) was dropped into the mixed suspension to give a molar ratio OH/Mg of about 1.5 with agitation of the suspension during titration of the reagent. Finally, the sample was filtrated, dried and milled.

Three dyes were used in this study. Methylene Blue (MB) is a typical basic (cationic) dye with CI. No. 52015. Telon Blue A2R (TB) and Ramazol Golden Yellow RGB (RGY) are commercial anionic dyes, supplied by Dystar Company, Germany. The molecular structure diagrams and formulae of TB and RGY were not provided for commercial reasons. TB is an acid dye, while RGY represents example of reactive dye, which is characterized by the presence of nitrogen–nitrogen bonds.

2.2. Characterization of adsorbents

The energy dispersive X-rays (EDX) system was used for the chemical elemental analysis of the adsorbents. Scanning electron microscope (SEM) micrographs were obtained using model SIRION-100 microscope (Fei Company, Holland). The isoelectric points (IEP) of adsorbent were determined by an electro-acoustic technique with a ZetaProbe Analyzer™ (Colloidal Dynamic Inc., USA) at room temperature. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 560ESP spectrometer.

2.3. Adsorption studies

Batch adsorption experiments were carried out. A known amount of adsorbent (0.5 g) was added into 50 mL of dye (MB, TB or RGY) solution with initial concentration of 50 mg/L, and the aqueous solution was shaken at 130 rpm in a shaker for 5 h at 25 °C. Then the solution was centrifuged at 2000 rpm in a centrifugal machine for the separation of adsorbent from the aqueous solution. Each experiment was at least duplicated under the conditions. The visible spectra of dye solutions were measured spectrophotometrically by using ET99731 Visible spectrophotometer (Tintometer GmbH, Germany).

It was found that the adsorption equilibrium can be established in 70 h. The adsorbent concentration selected in this work was typically 1 g/L and the pH value was around 7. Thus, the adsorption isotherm study was performed in a set of 100 mL flask, where 0.05 g of modified diatomite and 50 mL of dyes with different initial concentration were added. The solution with diatomite was shaken at 130 r/min in a shaker for 72 h to reach the equilibrium at 25 °C. The flasks were then taken from the shaker, and the equilibrium concentration of the dye was measured by the spectrophotometer at the wavelength of maximum absorbance of the dye. The amount of dye uptake by the adsorbent, q_e (mg/g), was obtained as follows:

$$q_e = \frac{C_o - C_e}{m_s}, \tag{1}$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations, respectively, of the dye in the solution, and m_s (g/L) is the concentration of the adsorbent.

3. Results and discussion

3.1. Characteristics of adsorbents

The applicability of diatomite for the wastewater treatment may depend on its physical characteristic. The diatomite used in this study is in the form of cylindraceous particle with bulk density of 616 g/L and median particle diameter of 10.25μm (Laser particle size). The major oxide analysis by X-ray diffraction (XRD) and EDX techniques shows that the diatomite mainly consists of SiO_2 (67.3%), Al_2O_3 (15.4%), Fe_2O_3 (7.07%) and K_2O (3.97%).

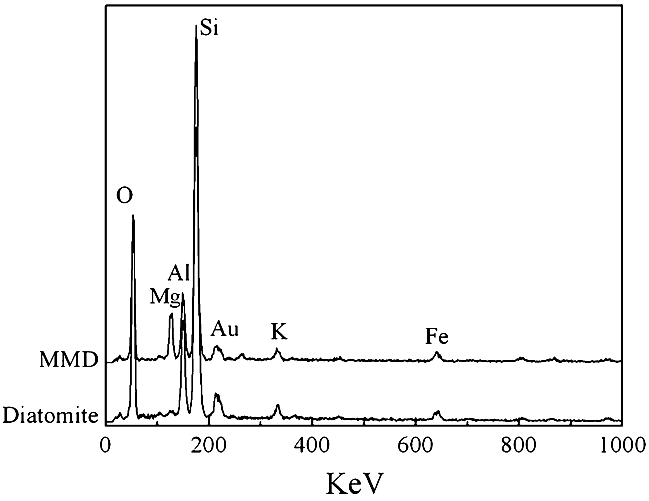

Fig. 1. EDX patterns of diatomite and MMD.

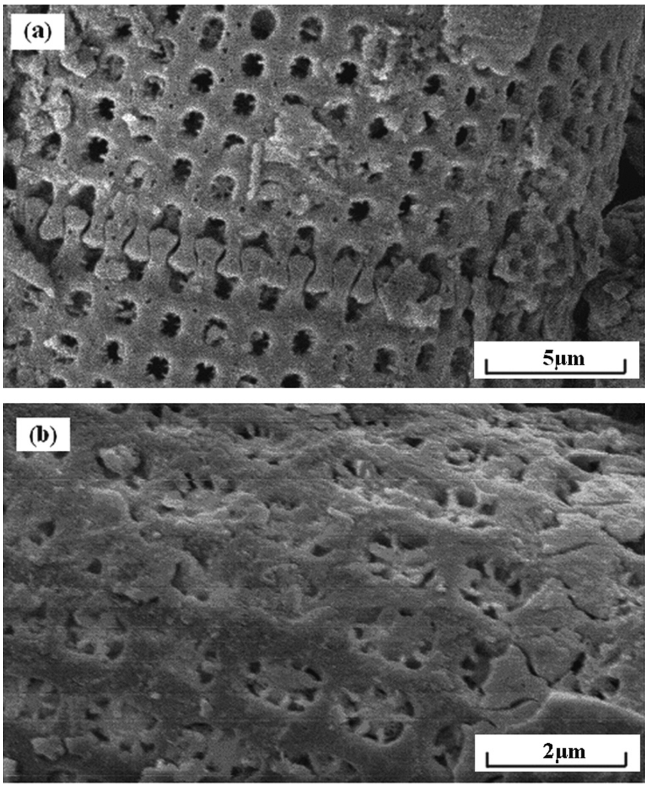

Fig. 2. SEM photographs of (a) diatomite and (b) MMD.

The EDX patterns of diatomite and MMD are presented in Fig. 1. Two samples show similar EDX patterns and their major elements are found to be silicon and oxygen, while the MMD sample presents a stronger intensity in the magnesium peak, suggesting the formation of $Mg(OH)_2$ in diatomite after the modification. The results indicate that the content of $Mg(OH)_2$ precipitation in MMD is about 13.45%. Fig. 2 displays the SEM photographs of unmodified diatomite and MMD. Fig. 2(a) clearly reveals the cylindraceous figure and the porous texture of diatomite, while Fig. 2(b) shows that the modification of diatomite by *in situ* precipitation of $Mg(OH)_2$ leads to incorporation of precipitate within the pores.

There is a correlation between dyes exchange capacity and the surface charge carried by the adsorbent. A convenient index of the propensity of a surface to become either positively or negatively charged can be characterized by the pH value of zero point of charge (pH_{zpc}) or the pH value of isoelectric point of zeta potential (pH_{IEP}). Fig. 3 shows the zeta potential of diatomite, $Mg(OH)_2$ and MMD as a function of pH. The intersection of the curve with x-axis at zeta potential equaling zero gives the pH_{IEP}. As seen that the pH_{IEP} of diatomite is about 1.88, and the pH_{IEP} of $Mg(OH)_2$ can be estimated as 12.1, which is in agreement with the value (12.0) reported by Parks [19]. While the MMD shows three charge reversals (CR) with varying pH. These CRs give three IEPs between 1.88 and 12.1 for MMD. The first charge reversal (CR_1) around pH 2.0 reflects the IEP of diatomite as the $Mg(OH)_2$ precipitate formation can not occur on the surface at low pH. The second charge reversal (CR_2) around pH 8.5 reveals the beginning of $Mg(OH)_2$ depositing on diatomite. The third charge reversal (CR_3) around pH 11.5 reflects the IEP of $Mg(OH)_2$. The pH value of CR_3 would equal to the pH_{IEP} of $Mg(OH)_2$ if the diatomite surface is completely covered by the $Mg(OH)_2$. It can be seen that the value (pH 11.5) is lower than the pH_{IEP} value of $Mg(OH)_2$ (pH 12.1). This suggests that the

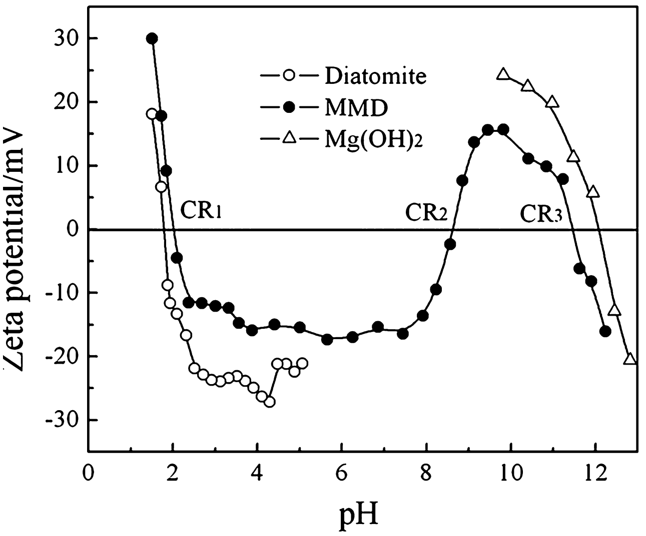

Fig. 3. Zeta potential and pH_{IEP} of diatomite, $Mg(OH)_2$ and MMD.

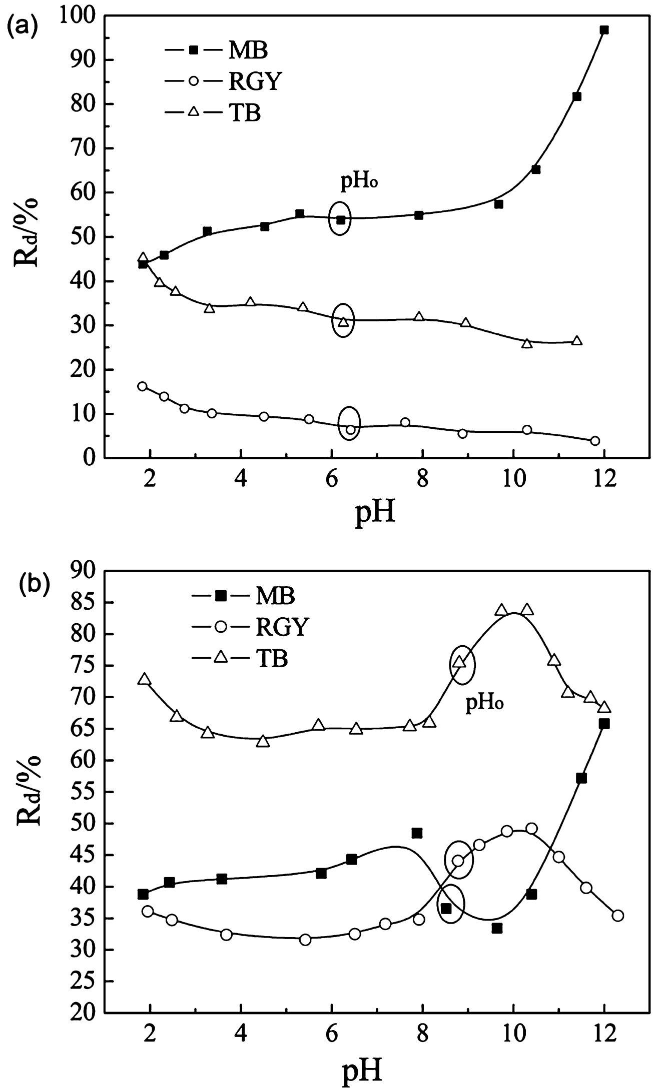

Fig. 4. pH dependency of dyes removal of (a) diatomite and (b) MMD.

MMD still exhibits the properties of diatomite, which can be confirmed by the SEM photograph in Fig. 2(b).

3.2. Adsorption of dyes

In the dyes adsorption process, there are various influencing factors, such as contact time, adsorbate concentration, adsorbent concentration, pH value and temperature. We optimized these factors by a preliminary investigation and undertook the adsorption experiments under the same conditions.

The pH of the dye solution is an important factor in the adsorption process. The dependencies of the dye adsorption on pH are shown in Fig. 4 (pH_o denotes the original pH of the adsorbate–adsorbent system). As can be seen from Fig. 4(a), the dye removal (R_d %) of MB (cationic dye) onto diatomite increased with pH. The reason is that above the pH_{zpc} of the adsorbent the negative charge on its surface increases, which favours the adsorption of cationic dye. On the other hand, the adsorption of anionic dyes (TB and RGY) decreased with increasing pH for the same reason. The pH dependencies of three dyes onto MMD are more complicated. As shown in Fig. 4(b), the variation trends of adsorption are similar with diatomite, before the formation of magnesium hydroxide precipitate. With the pH value increasing from 9 to 12, the colour removal shows the corresponding variation to the pH_{zpc} variation of MMD (Fig. 3), owing to the formation of precipitate.

The visible spectra of the initial dye solutions and the solutions after dye adsorption onto the adsorbent were recorded (Fig. 5). It can be seen that the wavelengths of maximum absorption (λ_{max}) of MB, RGY and TB solutions are 664, 410 and 590 nm, respectively. No significant spectral shift or development of a new peak was noted. This indicates that the dyes are not transformed or degraded by the adsorbents, and the colour removal occurs by adsorption only. Therefore, the dyes concentration could be determined by the spectrophotometer corresponding to these λ_{max} values in the adsorption study. Moreover, it is observed that RGY and TB solutions after adsorbed by MMD have lower absorbance than that adsorbed by the diatomite. This indicates that the modification of diatomite can enhance the adsorption capacity of the anionic dyes. And the adsorption capacity, i.e., the maximum adsorption amount, of the adsorbents can be obtained in the study of adsorption isotherm.

The adsorption isotherm is important in the design of adsorption system. It indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model which can be used for design purposes [20]. Many isotherm equations have been reported and three well-known isotherms, the Langmuir, Freundlich and Redlich-Peterson isotherms, were selected in this article. The Langmuir isotherm has been successful in application to lots of sorption processes, which assumes that adsorption takes place at specific homogeneous sites in the adsorbent. It can be expressed as follows:

$$q_e = \frac{QbC_e}{1 + bC_e}, \tag{2}$$

where Q (mg/g) is the adsorption capacity corresponding to form a complete monolayer, and b (L/mg) is the Langmuir constant.

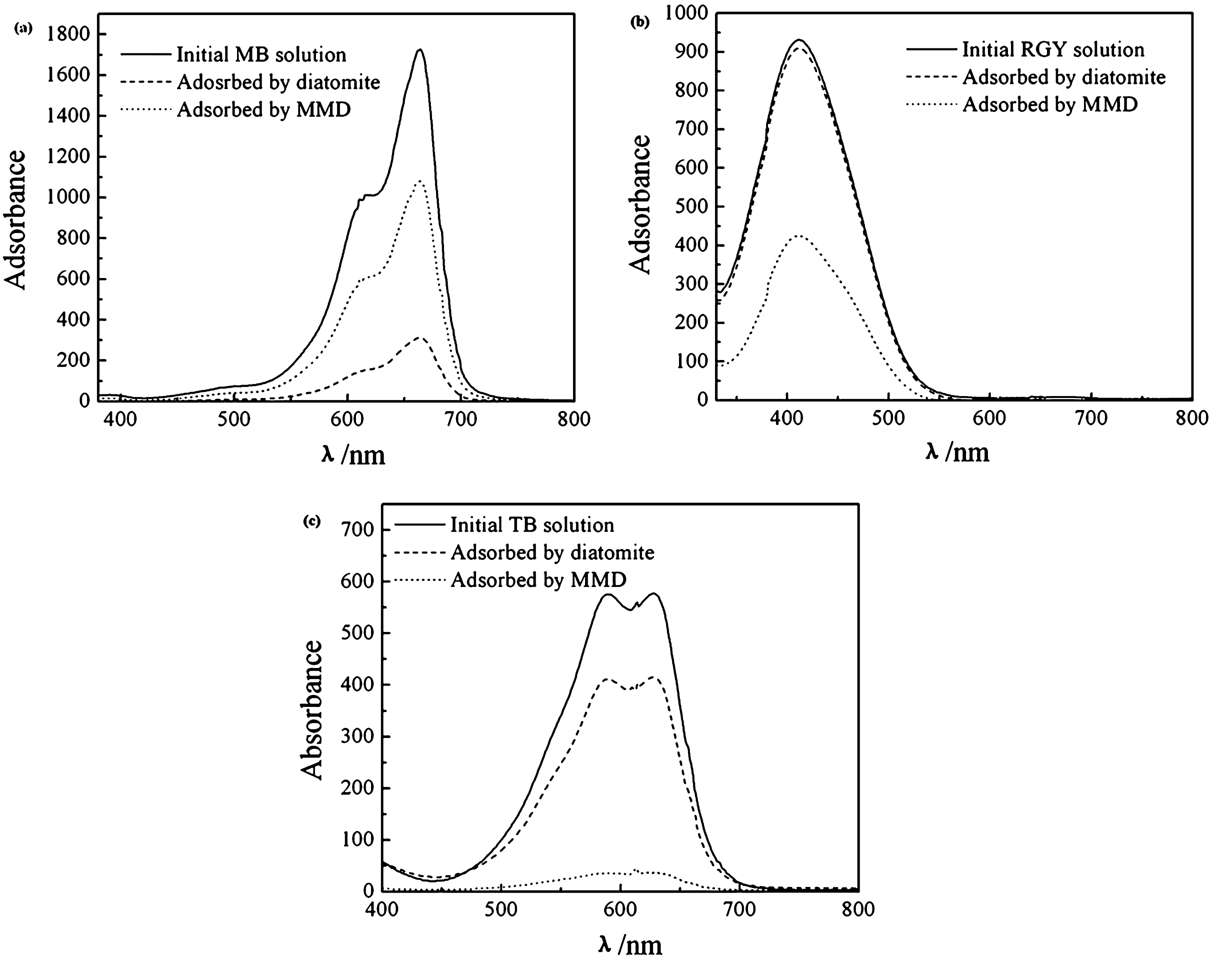

Fig. 5. Visible spectra of (a) MB, (b) RGY and (c) TB solutions before and after absorbed by diatomite and MMD.

The Freundlich isotherm, which is empirical for heterogeneous surface energy, is in the form

$$q_e = K_f C_e^{1/n}, \tag{3}$$

where K_f (mg/g) is the extent of the adsorption and n is the degree of nonlinearity between the dye concentration and the adsorption.

The Redlich-Peterson isotherm combines the Langmuir and Freundlich isotherms, and its adsorption mechanism does not obey ideal monolayer adsorption, but an impure one. The Redlich-Peterson equation is expressed as follows:

$$q_e = \frac{KC_e}{1 + \alpha C_e^{\beta}}, \tag{4}$$

where K (L/g) and α (L/mg) are the Redlich-Peterson constants and β is the exponent.

The dependencies of the adsorbed amounts of dyes on their equilibrium concentrations are shown in Fig. 6. It shows that the uptakes increase with increasing the solution concentration to reach the adsorption capacity. Fig. 6 also displays a comparison of adsorption isotherms for curve fitting of the experimental data with above three isotherm models. Parameters of the models determined from the nonlinear regression are listed in Table 1 for all the examined dyes and adsorbents. The Freundlich exponent $1/n$ gives information about surface heterogeneity and surface affinity for the solute. For a favourable adsorption, $0 < 1/n < 1$ [21]. The exponent $1/n$ between 0.062 and 0.461 in Table 1 indicates a high affinity of two adsorbents for three dyes. The high correlation coefficients (R^2) of Redlich-Peterson model indicate that the Redlich-Peterson model is the best one in simulating the equilibrium isotherms of dyes adsorbed onto diatomite and MMD. This suggests that some heterogeneous pores or surface of the adsorbents will play an active role in dye

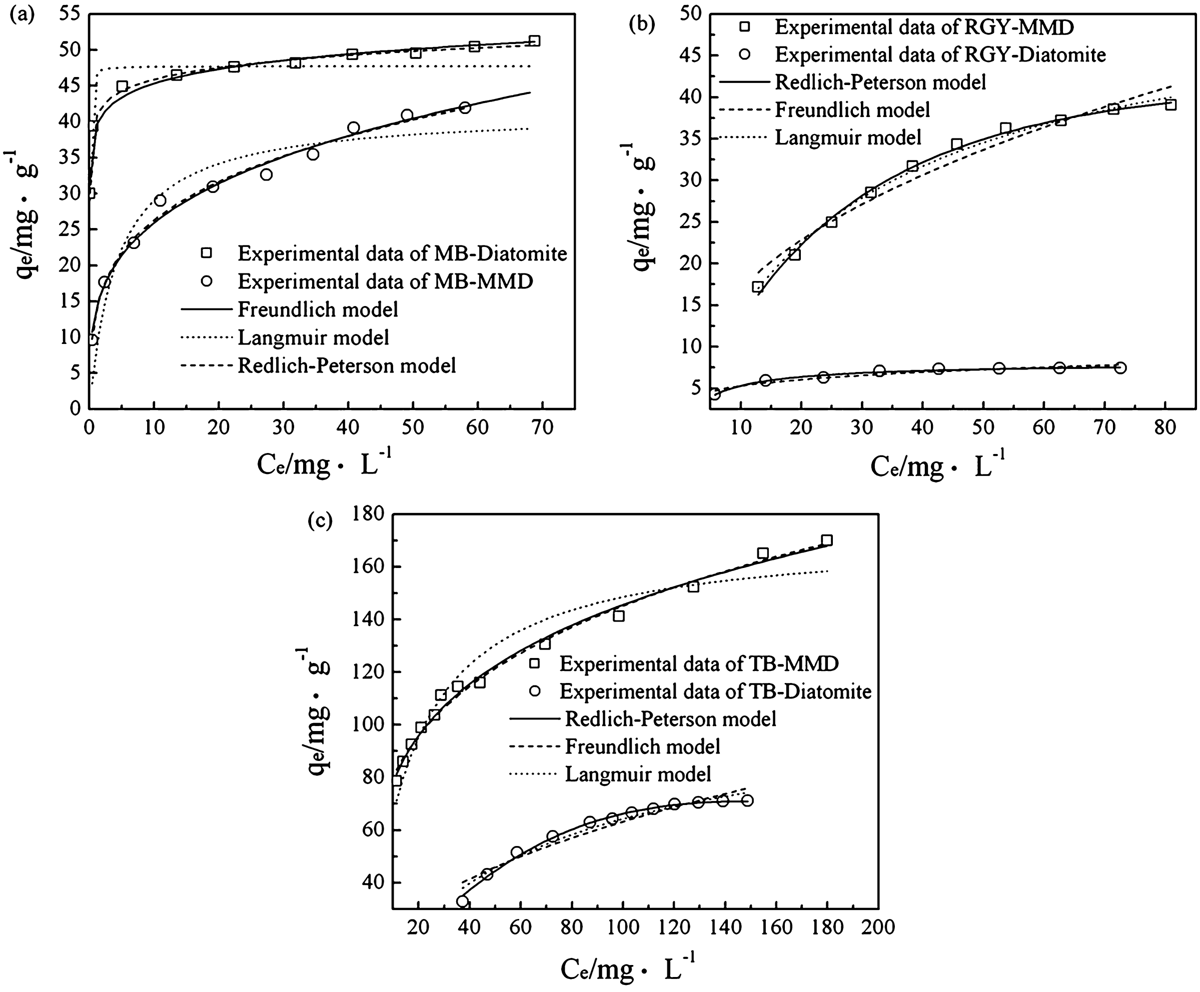

Fig. 6. Adsorption isotherms of (a) MB, (b) RGY and (c) TB onto diatomite and MMD.

adsorption. Moreover, the theoretical monolayer saturation capacity (Q) presented in Table 1 shows that the equilibrium adsorptions are quite different from the dye-adsorbent systems.

From Fig. 6 and the capacity Q, it is clear that the anionic dyes (TB and RGY) exhibit much higher adsorption for MMD, while the adsorption capacity is smaller in the case of cationic dye (MB). This may be attributed to the positive electrostatic adsorptive charge on MMD surface. As the molar ratio OH/Mg = 1.5 has been chosen to precipitate the $Mg(OH)_2$ in diatomite, there will be a deficiency of OH^-, which promotes the formation of polymeric complexes of the forms $(Mg_x(OH)_y)^+$, e.g., $Mg(OH)^+$, $Mg_2(OH)_3{}^+$, etc.,

Table 1
Comparison of the model parameters of dyes adsorption onto the adsorbents

Dye–adsorbent	Langmuir model			Freundlich model			Redlich-Peterson model			
	Q/mg g^{-1}	b/L mg^{-1}	R^2	K_f/mg g^{-1}	1/n	R^2	K/L mg^{-1}	α/L mg^{-1}	β	R^2
MB–diatomite	47.7	52.1	0.7824	39.3	0.062	0.9811	8154	200	0.949	0.9969
MB–MMD	41.5	0.233	0.9048	13.7	0.276	0.9875	138	9.26	0.744	0.9890
RGY–diatomite	8.06	0.192	0.9841	3.36	0.198	0.9159	1.58	0.200	0.995	0.9841
RGY–MMD	53.7	0.036	0.9931	6.42	0.424	0.9631	1.57	0.011	1.21	0.9961
TB-diatomite	109.0	0.014	0.9671	7.57	0.461	0.9262	1.02	0.0001	1.87	0.9941
TB–MMD	173.9	0.0618	0.9387	41.96	0.271	0.9865	76.8	1.50	0.768	0.9916

which are positively charged and can be attracted, by electric forces, from the negative dye molecule [22]. Moreover, The precipitated $Mg(OH)_2$ on diatomite acts by an adsorptive coagulative mechanism. Its structure which provides a large adsorptive surface area and its positive electrostatic adsorptive charge enables it to act as a powerful and efficient coagulant also on stable organic colloids and give high degrees of clarification. Therefore, modification of diatomite by $Mg(OH)_2$ greatly enhanced the removal of anionic dyes from aqueous solution.

3.3. Mechanisms of the adsorption

Diatomite is regarded as a mineral of organic origin, where the silica of fossilised diatom skeleton resembles opal or hydrous silica in composition ($SiO_2{\cdot}H_2O$). The surface contains silanol groups that spread over the matrix of silica. The silanol group is an active one which tends to react with many polar organic compounds and various functional groups [23]. The FTIR spectra (Fig. 7) were recorded to investigate the possible interactions between the dye molecules and the active groups present in the adsorbent surface. The strong bands at the region 3200–3700 cm^{-1} are characteristic of N–H and O–H stretching vibrations. It can be seen that the peaks at 3430 cm^{-1} slightly shift and the bands are distorted when the dyes adsorbing onto the adsorbents. This may suggest the interactions between the dye molecules and the silanol groups, and can be interpreted as adsorption on the neutral sites [24]. The distinct peaks at 2700–3000 cm^{-1} can be attributed to the groups of organic dyes, such as $–CH_3$ and $–CH_2–$. The bands at 1700–2000 cm^{-1} can also be attributed to the groups of dyes, such as aromatic rings and C–N groups. The peaks near 1645 cm^{-1} may reflect the water molecule, C=O group or the Mg-OH stretching vibration. The region under 1600 cm^{-1} is the fingerprint region of infrared spectrum, which contains a very complicated series of absorptions. The bands at 1000–1200 cm^{-1} are due to the siloxane (–Si-O-Si–) group or the C–O bond, and after the adsorption of dyes the peaks also slightly shift, which reflects the interactions with the dye molecules.

Zeta potential analysis (Fig. 3) suggests the complexity of the functional groups, which makes the dye adsorption much more complicated. Surface adsorption is generally assisted through ionic, chemical, and physical interactions. The schematic diagrams of the functional groups and possible interactions between the groups and the dye molecules are presented in Fig. 8. It shows that diatomite and MMD surfaces are mainly terminated by OH groups or oxygen bridges.

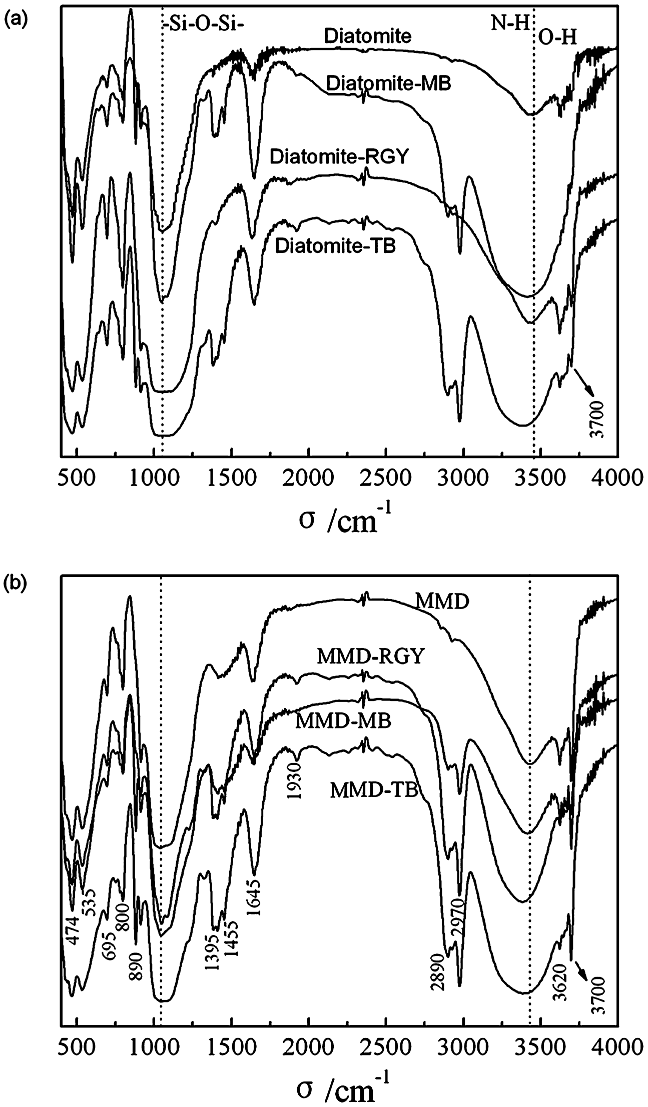

Fig. 7. Infrared spectra of (a) diatomite and (b) MMD before and after adsorbed MB, RGY and TB.

The OH groups could be divided into isolated free silanol (–Si-OH) and geminal free silanol (HO-Si-OH), and they can act as centres for adsorption by forming hydrogen bonds with the nitrogen atoms in dye molecules (Fig. 8A and B). It is observed from Fig. 3 that, at low pH (<pH_{IEP} of diatomite), the amount of positively charged surface groups, such as $–Si\text{-}OH^{+}\text{-}Si–$ (Fig. 8D) and $–Si\text{-}OH_2^{+}$ (Fig. 8E), may increase in the adsorbents; while the amount of negatively charged groups ($–Si\text{-}O^{-}$) may increase with an increase of pH. This indicates that electrostatic attractions between these charged groups and the oppositely charged dyes possibly occur in the adsorption (Fig. 8D–F and I–K). Moreover, the electron lone pairs of the oxygen atoms of siloxane group of the diatomite and MMD may form a *n*-π

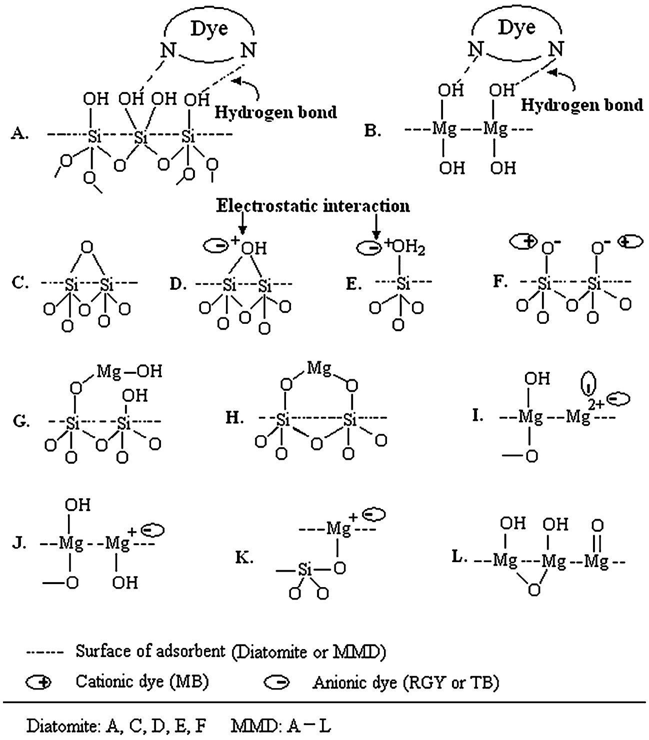

Fig. 8. Schematic presentation of surface groups of diatomite and MMD and their interactions with dye molecules.

interaction with the π system of the azo group of the dyes as proposed by Khraisheh et al. [23] and Tapia Estevez et al. [25].

In conclusion, the adsorption of dyes onto diatomite and MMD may be attributed to (1) electrostatic interaction between the dye molecules and the electron rich sites on the adsorbents surface, (2) the hydrogen bonding interaction between the nitrogen atoms in the dye molecules and the hydroxy groups on the adsorbent surface, (3) dye adsorption on the external surface by *n*-π interaction and (4) weak physical forces such as Van Der Waals interactions between the hydrophobic parts of the dye molecules (e.g., the aromatic rings) and the neutral sites on the adsorbent surface.

4. Conclusions

Diatomite and magnesium hydroxide-modified diatomite were used as adsorbents for adsorption of two types of textile dyes from wastewater. It was found that the modification of diatomite enhanced the removal of anionic dyes, RGY and TB, from aqueous solution. The nonlinear fitting of the experimental results with three isotherm models showed that the Redlich-Peterson model was best in simulation of the adsorption process, suggesting that some heterogeneity in the surface or pores of the adsorbents will play a role in dyes adsorption. The adsorption of dyes onto diatomite and MMD is possibly attributed to electrostatic interaction, hydrogen bonding interaction, *n*-π interaction between the π system of the dye and the electron lone pairs of the oxygen atom, and the weak physical force of Van Der Waals interaction.

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