Removal of methylene blue from aqueous solutions using modified clay

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Abstract

Introduction: Discharging of industrial colored wastewaters especially into aqueous environments can cause adverse effects on aquatic life due to their toxic natures. In this study, montmorillonite modified by hexadecyltrimethyl ammonium bromide (HDTMA-Mt) was used for the adsorption of methylene blue (MB).

Materials and Methods: The influence of surfactant loading rate, contact time, pH, adsorbent dosage, adsorbate concentration and ion strength in batch system was evaluated. HDTMA-Mt was also characterized by using Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

Results: Fitting the experimental data to different kinetics and isotherm models including pseudo-first order kinetic, pseudo-second order kinetic, Langmuir and Freundlich isotherms showed that the experimental data is well descripted by pseudo-second order kinetic (R^2=1) and Freundlich (R^2>99) models. The optimum contact time for the sorption was achieved at 60 min and changing in pH values had insignificant effects on the sorption.

Conclusion: The findings of the present study indicated that HDTMA-Mt can be successfully applied for the removal of MB from aqueous solutions. The modified Mt, due to high accessibility, low cost and non-toxicity, can be considered to replace with other high cost adsorbents.

Keywords: Modified Clay, Methylene Blue, Adsorption, Aqueous Solution

Introduction

Water pollution due to industrials development is considered as worldwide problem especially in developing countries. Discharging industrial colored wastewaters into aquatic bodies can cause adverse effects on aquatic life due to their toxic properties (1-3). Dyes usually have synthetic natures which are characterized by aromatic molecular structures. This characteristic provides physicochemical, thermal and biological resistants (4, 5). They may carcinogenic, mutagenic and teratogenic. Dyes can be classified into anionic and cationic or non-ionic dye (4, 6). Methylene blue or basic blue 9 is a cationic dye that is applied for dying fabric in textile industries (7). Methylene blue (MB) has been used as a model for the removal of organic dyes from colored solutions. It can cause some advertise effects in animal and also humans (8). Physical, Chemical and Biological methods have been developed for the adsorption of MB. A variety of other methods such as ozonation, coagulation, chemical oxidation, electrochemical, membrane processes and adsorption technique has been used to remove for this dye (1, 8, 9).

Adsorption process has been widely used to the treatment of industrial dye wastewaters (10, 11). This technique is one of the best treatment alternatives for the removal of organic pollutants including dyes from the water and wastewater because it is possible to recover of the adsorbate and adsorbent (12, 13). Activated carbon is the most frequently applied for this purpose because having simple procedure and high adsorption capacity, but it is quite expensive. So, its high-cost trend to limit its use (14). Several low-cost adsorbents including Moroccan clay (9), Rice Husk(15), chitosan/bentonite (14), sawdust (16), flay ash (17), Iranian milk vetch activated carbon (7) and red mud (17) have been conducted to removal of dyes from aqueous solutions. Montmorillonite clay has been widely used as an adsorbent to remove of organic pollutants (12). The characteristics such as low-cost, high surface area, high adsorption capacity, ecosystem friendly and non-toxicity (8, 12) have been caused that montmorillonite is considered as a good adsorbent for organic dyes. Because of the hydrophilic nature of raw clay, this sorbent is not efficient for the removal of organic pollutants. In order to overcome this problem, surfaces of clay can be modified by an organophilic matter such as surfactants (18). In this study, montmorillonite clay was modified by hexadecyltrimethyl ammonium bromide, as a cationic surfactant, and applied for the removal of MB from synthetic wastewater. Also, the effects of surfactant loading rate, contact time, pH, adsorbent dosage, dye concentration and solution ion strength were evaluated on the sorption.

Materials and methods

MB dye, H_2SO_4 ،NaCl and $CaCl_2$ were purchased from Merck Co (Germany). The chemical structure and general properties of the dye are shown in figure 1 and table 1, respectively. The montmorillonite (Mt) was purchased from Laviosa Co (Italy). The cation exchange capacity (CEC) of Mt was found to be 108 meq per 100 g of the adsorbent (12). Hexadecyltrimethyl ammonium bromide (HDTMA) was purchased from Aldrich CO (USA).The solution pH was adjusted by adding 0.1 N H_2SO_4 and NaOH through a pH meter (50-pp-sartorious model). Other chemical used were of analytical grade. The stock solution of MB (1000 mg/L) was prepared by dissolving 1g of MB in 1 liter deionized water and the working solutions were made by dilution of the stock solution.

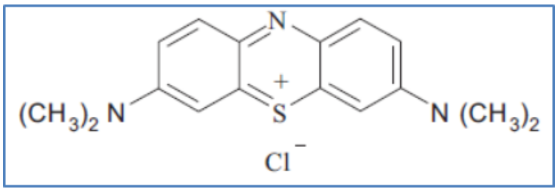

Figure 1. Chemical structure of methylene blue.

Table 1. General characteristics of the methylene blue.

Characteristic	MB
Scientific name	Methylene blue
Chemical formula	$C_{16}H_{18}N_3ClS$
Molecular weight (g/mol)	319.85
λ_{max} (nm)	665
Nature	Cationic

Characterization and analysis: The morphology of HDTMA-Mt was characterized by a scanning electron microscope (SEM, Jeol Model Jsm-T330). FTIR spectral analysis (JASCO, FT/IR-6300 Japan) was also recorded in the region of 400-4000 cm^{-1}. The concentration of MB in the solution was measured by an UV–vis spectrophotometer (PG Instrument Limited

Model) at the maximum visible absorbance at a wavelength of 665 nm.

Purification of Mt clay: For the purification of the clay, 30 g of it was dissolved in 1 L deionized water. The solution was agitated by a stirrer (250 rpm) for 24 h at room temperature and then centrifuged (4000 rpm for 20 min). Due to higher density, the impurities were precipitated at the bottom of the centrifuge tube. The higher purity Mt was then dried at 105 °C for 24 h, and then sieved to less than 125 µm sizes (12).

Preparation of the HDTMA-Mt: In order to achieve HDTMA modified montmorillonite in rates of 0.2-2.0 times of clay CEC, the HDTMA-Mt was prepared by mixing 5 g the high purity clay (in before stage) with amounts of 0.393, 0.984, 1.37, 2.36, 2.95 and 3.93 g of the surfactant and was then separately dissolved in 100 mL deionized water. The suspension was agitated by a stirrer (250 rpm for 24 h) at room temperature. The HDTMA-Mt was centrifuged, washed, dried (60 °C) and then passed through a 125 µm sieve.

Batch adsorption experiments: Batch adsorption experiments were carried out to determine the influence of parameters including surfactant loading rates (20%-200% CEC of the clay), contact time (0-150 min), pH (4-12), HDTMA-Mt dosage (1-20 g/L), adsorbate concentration (20-200 mg/L) and ion strength (20-100 mg/L Ca^{2+} ions) on the removal of MB from aqueous solutions. All of the adsorption experiments were conducted at room temperature and agitated in 250 rpm.

After the mixing time, the suspension was centrifuged (3500 rpm for 20 min) and the clear supernatant was analyzed by UV-visible spectrophotometer. The experiments were conducted in triplicates and the average values were considered. The adsorption capacity (mg/g) of MB was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

Where q_e is the adsorption capacity of MB (mg/g), C_0 and C_e are the initial and equilibrium dye concentration (mg/L), V is the volume of the solution (l) and M is the mass of adsorbent (g) (9).

Results

Characterization of HDTMA-Mt: The results from this study are presented in figures 2-7. Scan electron microscopy (SEM) morphology of HDTMA-Mt is shown in figure 2(a). Also, the FTIR spectrum of the sorbent is presented in figure 2(b).

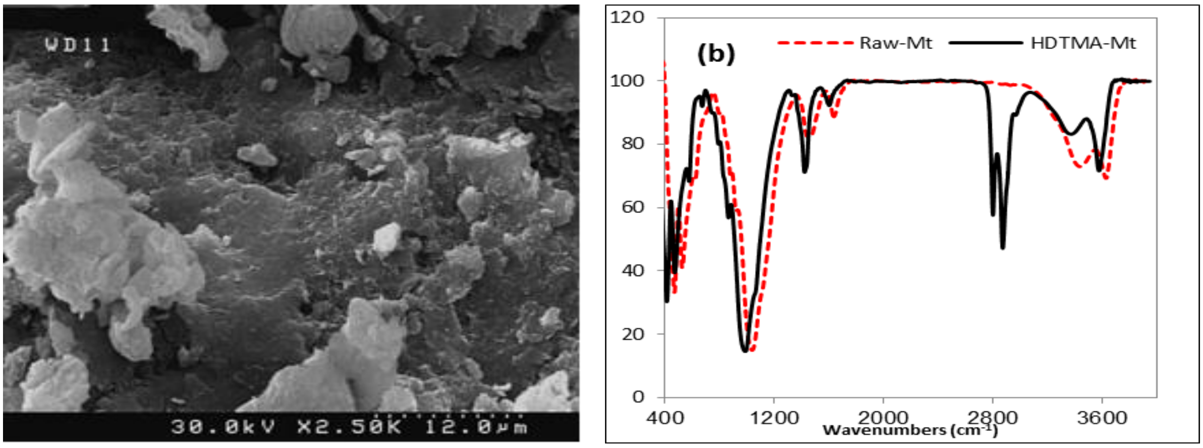

Figure 2. The characteristics of the hexadecyltrimethyl ammonium bromide (HDTMA-Mt). (a) Scanning electron microscopy and (b) Fourier transform infrared spectroscopy.

Effect of the surfactant loading rate: The adsorption of MB by HDTMA-Mt with various lading amounts of the surfactant is illustrated in figure 3. The surfactant loading rates were at amounts of 20% CEC, 50% CEC, 70% CEC, 120% CEC, 150% CEC and 200% CEC of the clay at initial concentration of 20 mg/L MB for 24 h in initial pH. As seen, the adsorption capacity was rapidly increased from 20% to 70% CEC of the clay and then decreased to 200% the CEC.

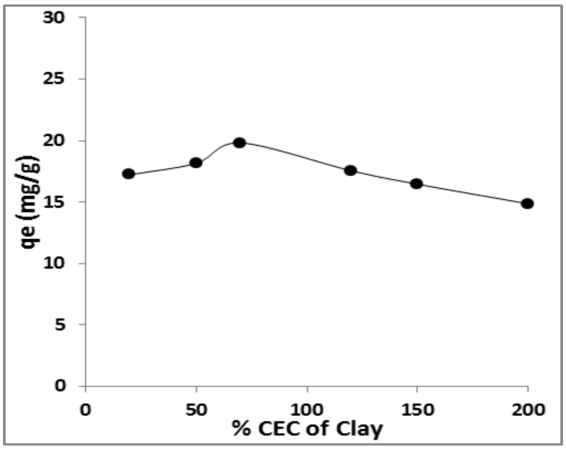

Figure 3. The effect of different surfactant loading rates on the MB adsorption (MB concentration= 20 mg/L, contact time=24 h, initial pH=7, and adsorbent dosage 1 g/L).

Effect of contact time: The effect of different contact time on the adsorption capacity of MB is illustrated in figure 4. As it is obvious, it appears that a fast initial adsorption was occurred and the equilibrium reached in less than 60 min.

Kinetics study: The pseudo-first order kinetic model can be expressed by the following equation (14, 19, 20).

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \qquad (2)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of MB adsorbed on the HDTMA-Mt at the equilibrium and at any time t (min), respectively. K_1 (1/h) is the rate constant of the pseudo-first order kinetic. K_1 and q_e were determined from linear plots of $\ln(q_e - q_t)$ against t, which were obtained from the slope and intercept, respectively. The values of q_e calculated, K_1 and correlation coefficient (R^2) are listed in Table 2.

The experiment data was also fitted by pseudo-first order kinetic. This adsorption model can be presented by the following equation(14, 21):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where q_e and q_t are similar defines as the pseudo-first order kinetic. K_2 (g/mg. min) is the rate constant of the pseudo-first order kinetic. K_2 and q_e can be obtained from the intercept and slope of ${}^{t}/_{q_t}$ versus t in Eq. 3, respectively. The values of K_2, q experimental and calculated and correlation coefficient are also presented in Table 1.

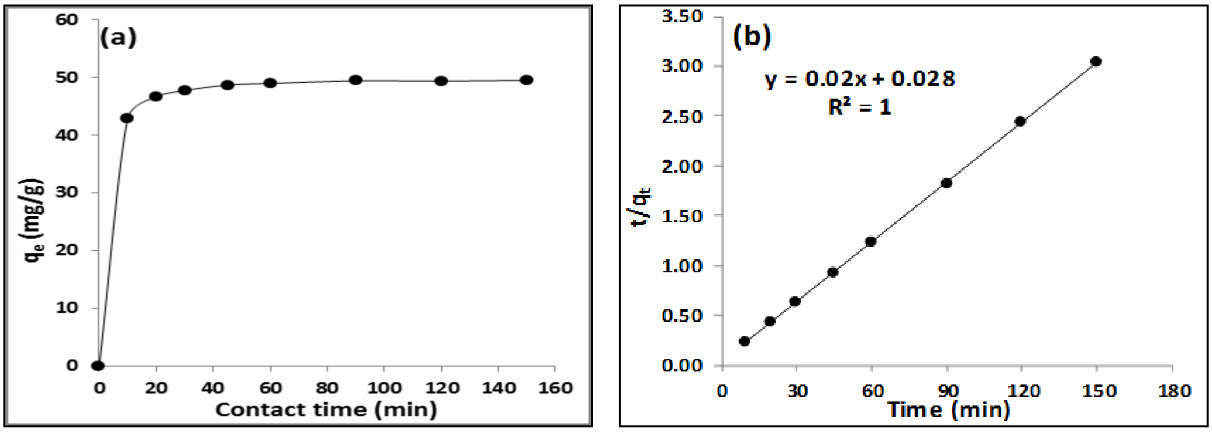

Figure 4. (a) Effect of contact time on the MB adsorption (MB concentration=50 mg/L, initial pH=7, and adsorbent dosage=1 g/L) and (b) pseudo-second order kinetic model.

Table 2. Parameters of pseudo-first order and pseudo-second order obtained from this study.

Adsorbent	Pseudo first-order			Pseudo second-order			
	$q_{e,experimental}$ (mg/g)	K_1 (1/h)	R^2	$q_{e,experimental}$ (mg/g)	K_2 (g/mg.min)	$q_{e,calculated}$ (mg/g)	R^2
MB	44.64	0.065	0.97	44.64	0.0224	50	1

Effects of solution pH and adsorbent dosage: The influence of solution pH in range of 4-12 on the adsorption of MB by HDTMA-Mt is shown in Fig 5 (a). Also, the effect of adsorbent dosage from (1 to 20 g/L) on the sorption of MB is illustrated in Figure 5(b).

As shown, the adsorption capacity of MB via HDTMA-Mt was gradually decreased with increasing in adsorbent dosage. With increasing the adsorbent dosage from 1 g/L up to 20 g/L, the adsorption capacity was reduced from 49.73 mg/g to 2.48 mg/g for HDTMA-Mt.

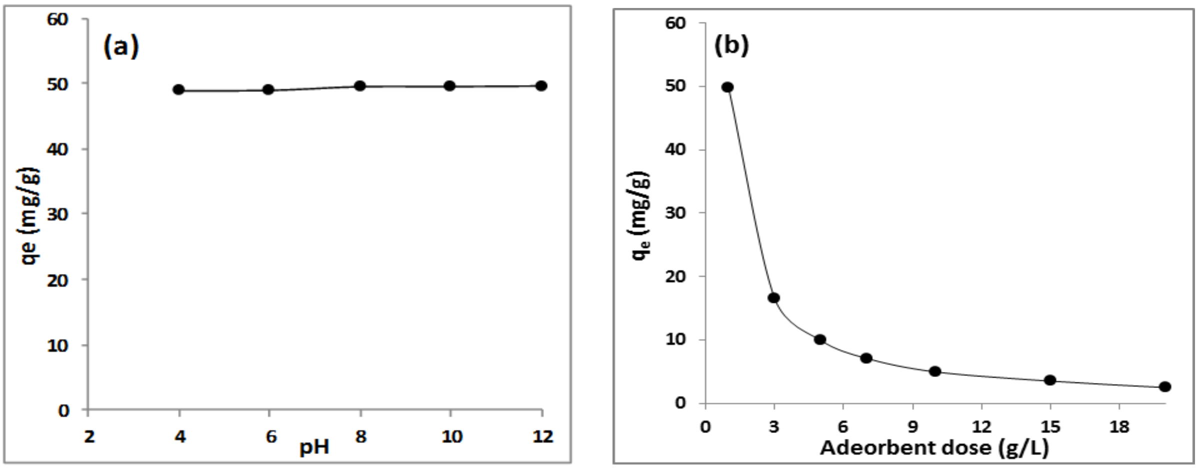

Figure 5. (a) Effect of solution pH on the MB adsorption (MB concentration=50 mg/L, contact time=60 min, initial pH=7, and adsorbent dosage=1 g/L) and (b) Effect of adsorbent dosage on the MB adsorption (MB concentration=50 mg/L, contact time=60 min, and initial pH=7).

Effect of MB concentration: The effect of initial MB concentration in range of 20-200 mg/L was investigated on the sorption with HDTMA-Mt in initial pH, adsorbent dosage of 1 g/L and contact time of 60 min at room temperature (25 ^{0}C), Figure 6 (a). As can be seen, by increasing the initial MB concentration from 20 to 200 mg/L, the uptake amount of MB onto the sorbent was remarkably increased.

Isotherm study: The results for the MB concentration on the adsorption process were used to study adsorption isotherm. The Langmuir isotherm is linearized by the Eq (4):

$$\frac{C_e}{q_e} = \left(\frac{1}{bQ_m}\right) + \frac{C_e}{Q_m} \qquad (4)$$

Where; C_e (mg/L) and q_e (mg/g) are the initial adsorbate concentration and the adsorption capacity of the adsorbent in the equilibrium time, respectively.

Values of the maximum adsorption capacity, b and correlation coefficient are listed in Table 2.

This isotherm can be linearized and showed that by Eq 5:

$$ln q_e = ln K_f + \left(\frac{1}{n}\right) ln C_e \qquad (5)$$

Where K_f (l/g) and n are the Freundlich constants and illustrate the capacity and intensity of the adsorption process, respectively.

Values of K_f, n and correlation coefficient (R^2) are presented in Table 3.

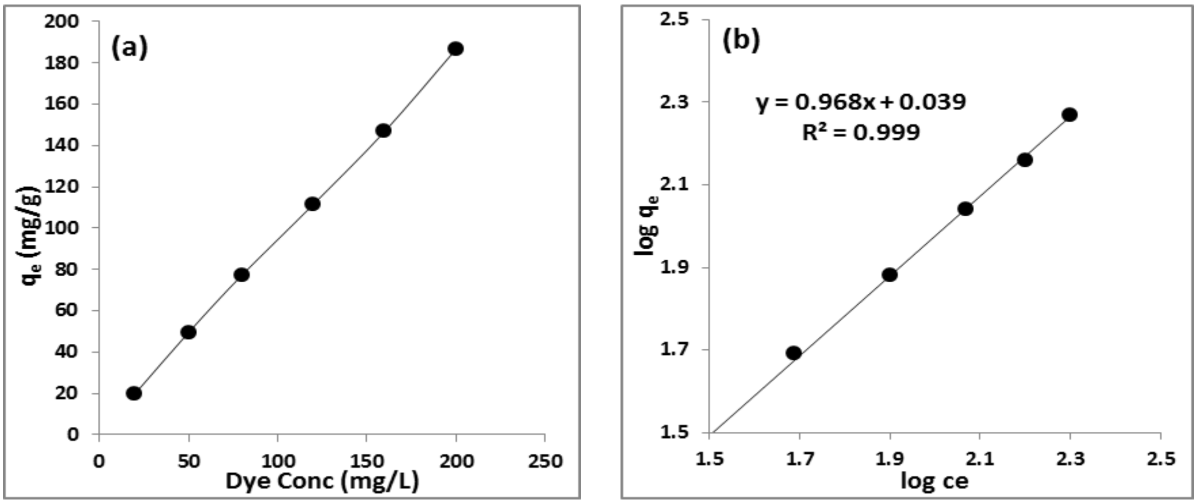

Figure 6. (a) Effect of MB concentration on the MB adsorption (contact time=60 min, initial pH=7, and adsorbent dosage=1 g/L) and (b) Freundlich isotherm model.

Table 3. Parameters of Langmuir and Freundlich obtained from this study.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	b (l/mg)	R^2	K_f (l/g)	n	R^2
MB	1666.6	0.0006	0.92	1.281	1.032	0.99

Effect of solution ion strength: Figure 7 illustrates the influence of different concentrations of $CaCl_2$ (20-100 mg/L of Ca^{2+} ions) on the adsorption of MB through HDTMA-Mt.

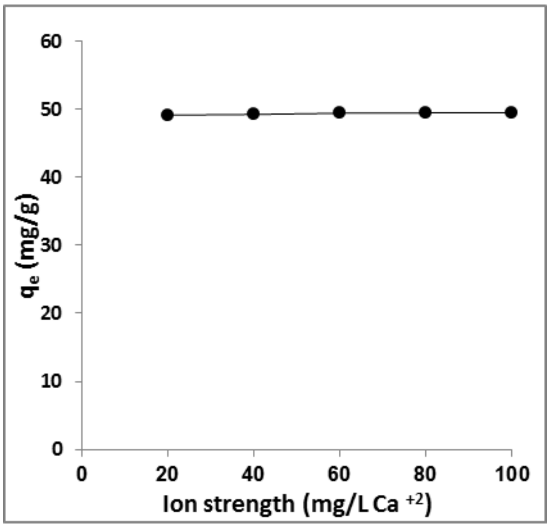

Figure 7. Effect of solution ion strength on the MB adsorption (MB concentration=50 mg/L, contact time=60 min, initial pH=7, and adsorbent dosage=1 g/L).

Discussion

SEM studies provide useful information regarding the surface morphology of the adsorbent structure.

The SEM of HDTMA-Mt showed that its surface structure is homogenous and smooth. As seen, the characteristic bands at 3627 cm^{-1} and 3627 cm^{-1} were associated with -OH and H_2O stretching vibration, respectively. The IR band of 1635 cm^{-1} was attributed to Mg and Al bound water molecules. The intensity decrease of the IR band in 1635 cm^{-1} illustrated that water content was diminished as a result of substitute of the hydrated cations with the surfactant (22, 23). This finding depicted that the surface properties of the adsorbent shifted from hydrophilic to hydrophobic by the modification with HDTMA surfactant. A band at 1036 cm^{-1} was associated with the stretching vibration of Si-O groups. Peaks at 463 cm^{-1} and 521 cm^{-1} were also assigned to Al-O-Si and Si-O-Si vibration, respectively(12). The new peak in the modified sorbent at 2922 cm^{-1} was due to the modification of Mt by HDTMA. The broad band at the region of 2800–3000 cm^{-1} was attributed to the C-H stretching vibration from the modification of Mt by HDTMA surfactant.

The higher surfactant loading rates, beyond 70% CEC of the clay, may lead to complete occupancy of the interior pores of the HDTMA-Mt that as a result of it, the penetration of MB to these points was reduced. The Mt with the surfactant loading rate of 70% CEC of the sorbent was chosen for the subsequent experiments.

The rapid adsorption MB on HDTMA-Mt at the initial contact time can be due to the availability of large numbers of the vacant sites of the adsorbent surface to the adsorbate. The contact time of 60 min was used to the rest of the experiments. Ozer et al. (2012) indicated that the adsorption capacity of MB via activated carbon in the equilibrium contact time of 120 min was 37 mg/g in an initial dye concentration of 50 mg/L (24). Kazembeigi et al. (2014) also reported that the equilibrium contact time for the sorption of MB by Modified-RH was achieved during 90 min with the sorption capacity of 9.6 mg/g in an initial concentration of 10 mg/L (15).

Adsorption kinetic models are useful for identify the mechanism of adsorption process and removal efficiency of MB onto HDTMA-Mt. The experimental data was fitted through two kinetics models including pseudo-first order and pseudo-second order kinetic models.

The pseudo-second order kinetic model was used to descript of the adsorption process (25). As seen, the correlation coefficient (R^2) for pseudo-first order kinetic model (R^2=0.97) was less than of pseudo-second order kinetic model (R^2=1). Therefore, the adsorption process of MB did not follow pseudo-first order kinetic. The adsorption kinetics of MB on HDTMA-Mt is showed in Fig. 4 (b). Moreover, the $q_{e,\ experimental}$ obtained from experimental data was similar to $q_{e,\ calculated}$ from pseudo-second order kinetic model.

As seen, the change in solution pH values had insignificant effects on the pollutant adsorption. Nourmoradi et al. (2012) showed that the increasing in solution pH had insignificant influence on the removal of adsorbate by PEG-Mt (12, 26).

Decreasing the sorption capacity of MB in the higher dosages of HDTMA-Mt may be due to the unavailability of dye molecules that cannot cover all the active sites on the adsorbent surface. In other words, a large number of the surface active sites of the adsorbent could not reach saturation at high HDTMA-Mt dosage. Therefore, dose 1 g/L of HDTMA-Mt was selected as the optimum dosage for the next stage.

Increasing the initial MB concentration may stem from an increase in driving force of MB compounds including Vander Waal's force to the surface active sites of the adsorbent, which occurs at the higher concentrations of the adsorbate.

The adsorption isotherms are necessary and useful to describing how to pollutant molecules distribute between the fluid and solid phase when the adsorption process attains to an equilibrium state (8, 27). Langmuir and Freundlich isotherms model were used to evaluate relationship between the concentrations of MB adsorbed onto HDTMA-Mt. The Langmuir isotherm predicts the maximum uptake capacity on the homogenous surface of the adsorbent (12). Q_m (maximum adsorption capacity, mg/g) and b (the Langmuir constant, l/mg) are taken from the slope and intercept of linear plots of C_e/q_e against C_e, respectively (28). Freundlich isotherm is usually described for multilayer adsorption on a heterogeneous adsorbent surface (29).

As shown in Fig 6 (b), k_f and n were determined by the intercept and slope of linear plot of log q_e against log c_e, respectively.

Also, n value calculated by Freundlich model is 1.032. The higher n value more than 1 demonstrates that the adsorption bond between adsorbent and adsorbate is appropriately strong.

Freundlich isotherm showed higher R^2 value than Langmuir isotherm. Therefore, the adsorption of MB on the HDTMA-Mt is best-fitted with the Freundlich model. Similar isotherm results were reported for the adsorption of MB onto other adsorbents such as fly ash treated by HCl, rice husk and cetylpyridinium-modified montmorillonite (15, 30, 31).

The effect of ionic strength on the adsorption is a necessary parameter, because the dye containing effluents generally have a high salt content (32).

As seen, an increasing in the solution ion strength from 20 to 100 mg/L of Ca^{2+} ions had insignificant effect on the adsorption of MB.

This finding showed that HDTMA-Mt can be efficiently used to adsorption of MB from aqueous solutions in low to high ionic strength. Nourmoradi et al. (2014) reported that an increasing in the solution ion strength even in higher concentrations (100 mg/L of Ca^{2+} ion) resulted in negligible changes in MB removal by activated carbon modified with ZnO nanoparticles (1).

Conclusion

In this present study, montmorillonite modified with Hexadecyltrimethyl ammonium bromide (HDTMA- Mt) was used in the adsorption of methylene blue (MB) from aqueous solutions. The adsorption capacity of MB by the sorbent was increased with increasing contact time (until 60 min) and with increasing initial MB concentration. But, the solution ionic strength and pH had no significant influence on the uptake of MB. The results of the solution ionic strength and pH on the sorption showed that HDTMA-Mt had a good stability in a wide range /of solution ionic strength and pH. The adsorption of MB onto the HDTMA-Mt surface was well followed by the pseudo-second order kinetic and Freundlich isotherm models. Based on these results, HDTMA-Mt is an effective option for the removal of MB from aqueous media.

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