Hexadecyl Trimethyl Ammonium Bromide-Modified Montmorillonite as a Low-Cost Sorbent for the Removal of Methyl Red from Liquid-Medium

Y. Omidi-Khaniabadi 1, B. Kamarehei 2, H. Nourmoradi 3, M. Jourvand 4, H. Basiri 4, S. Heidari 4

1 Department of Environmental Health Engineering, School of Health, Lorestan University of Medical Sciences, Khorraramabad, Iran
2 Department of Environmental Health Engineering, School of Health, Ilam University of Medical Sciences, Ilam, Iran

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A B S T R A C T

In this study, montmorillonite (MMT) modified with a cationic surfactant (Hexadecyl trimethyl ammonium bromide, (HDTMA)) was used for the removal of methyl red (MR) from aqueous solution. The effect of different parameters like surfactant loading rate, contact time, pH, adsorbent dosage and initial MR content was investigated on the sorption. The sorption capacity was increased by increasing the surfactants loading rate up to 120% cation exchange capacity (CEC) of the MMT. The optimum uptake capacity of the sorbent (84.28 mg/g) was achieved within 30 min at pH of 6. The experimental data of the sorption was well fitted by pseudo-second-order kinetic and Freundlich isotherm models. The results showed that the HDTMA-MMT can be applied as an effective and inexpensive sorbent for the removal of MR from aqueous solution.

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1. INTRODUCTION

Water pollution owing to development of industrial activities has been considered as one of the most important problems in the world, especially in developing countries [1-3]. The wastewater from many industries such as food processing, leather, paper, plastics, cosmetics, and textile are significant sources of dye stuff pollution [4-6]. Discharging dye containing wastewaters into water bodies because of their toxic properties can cause harmful outcomes on living organisms as well as human [7, 8]. Typically, industrial dyes have synthetics nature that characterized by complex aromatic molecular structures [9, 10]. The most synthetic dyestuffs are toxic, carcinogenic and mutagenic. They are also nearly stable to most of chemical and biological degradation [4, 6]. Therefore, removal of these dyes before their discharge to water bodies is necessary [11]. Methyl red or acid red 2 is a mono-azo dye, which is applied in textile industry and laboratory assay. It can cause skin and eye sensitization and pharyngeal or digestive tract irritation [12, 13]. Several physical, chemical and microbial methods such as advanced oxidation, membrane technologies, coagulation-flocculation, biological degradation, chemical oxidation, electro chemical techniques, and adsorption have been applied for the removal of the dyes from dyeing wastewaters [11, 14]. Among these methods, adsorption process is widely applied to remove organo-pollutants [11, 15]. This method is one the effective technique via high removal efficiency [16]. Activated carbon because of simplicity, high surface area and high uptake capacity has been generally investigated as sorbent to remove organic and inorganic pollutants from water. However, the main disadvantages of this sorbent are high-cost and difficulty to regeneration [17, 18]. In addition to activated carbon, application of other non-convensional sorbents include banana trunk fibers [14], durian seed [12], annona squmosa [19], galactomyces geotrichum [13], eichnoria crassipes [20], kaolin [21], feldspar [22] and tree bark powder [23] have been reported to remove MR from...
aqueous solution. Nowadays, the interests are focused on using low cost sorbents to uptake dyes from aqueous solutions. Montmorillonite is a type of clay, which has been widely employed as a cheap adsorbent. Other excellent properties of clay like eco-friendly, non-toxicity, high surface area and high sorption capacity make it as an appropriate adsorbent for organic pollutants [24-26]. The raw clay has a hydrophilic nature, thus it is needed that the surface of clay modified by organophilic substance such as surfactants. It has been proved that intercalation of cationic surfactants changes the surface properties of the clay from hydrophilic to hydrophobic [25]. In this study, montmorillonite was used as sorbent and its surface was modified by cationic surfactant (Hexadecyl trimethyl ammonium bromide) and was used to sorption of methyl red from liquid solution. The effect of various parameters include surfactant-loading rate, contact time, pH, adsorbent dosage and dye concentration were evaluated on the sorption.

2. EXPERIMENTAL

2. 1. Materials Methyl red dye was purchased from Alvan Sabet Co, Iran. The clay, montmorillonite and Hexadecyl trimethyl ammonium bromide were obtained from Laviosa Co, Italy, and Aldrich CO, USA, respectively. H2SO4 and NaOH were achieved from Merck Co, Germany. The chemical structure and other properties of MR are presented in Table 1. On the basis of the Sear's method, the cationic exchange capacity (CEC) of MMT was 108 meq/100 g [24]. The solution pH was adjusted via a digital pH-meter (50-pp-sartorius model) by adding 0.1 N H2SO4 or NaOH solution. Other chemical used in present study were of analytical grade. The stock solution of MR (1000 mg/L) was made by dissolving 1 g MR in one liter deionized water.

2. 2. Characterization and Analysis The morphology of the modified MMT was specified by a scanning electron microscope (SEM, Jeol Model Jsm-T330). The FTIR spectral analysis (JASCO, FT/IR-6300 Japan) of the sorbent before and after modification was recorded in the region of 400-4000 cm\(^{-1}\). The characterization of the clay was also determined by X-ray diffractometer (Bruker, D8 ADVANCE, Germany) using Ni filtered Cu Ka radiation (1.5406\(\text{Å}\)). The concentration of MR dye in the solution was determined by an UV–Vis spectrophotometer (PG Instrument Limited Model) at the maximum visible absorbance wavelength of 515 nm.

2. 3. Purification of MMT Clay For the purification of the clay, 30 g of MMT was poured in 1 L deionized water. The suspension was mixed by a rotary shaker (250 rpm for 24 h) at room temperature (25 °C) and then centrifuged (4000 rpm for 20 min). Because of higher density, the black impurities of the clay include iron oxide and quartz was precipitated at the bottom of the centrifuge tube and the lighter clay was placed at the upper region of the tube. The higher pure MMT was separated from the impurities, then dried at 105 °C for 24 h and sieved to particle sizes less than 125 μm [24]. In order to attain HDTMA-MMT in the ranges of 20-150% times of the clay CEC, HDTMA-MMT suspensions were separately prepared into various conical flasks using mixing 5 g the high purity clay with desired amounts of the cationic surfactant in 100 mL diluted water. A stirrer (250 rpm for 24 h) at room temperature agitated the suspensions. The HDTMA-MMT were centrifuged (4000 rpm for 20 min), washed with distilled water (four times), dried (60 °C for 24 h) and then passed through an ASTM sieve of 120-mesh (125 μm).

2. 4. Batch Adsorption Experiments Batch sorption method was used to investigate the influence of different factors such as surfactant loading rates (20-150% CEC of the clay), contact time (0-60 min), pH (2-12), HDTMA-MMT dosage (0.5-5 g/L) and dye concentration (50-400 mg/L) on the removal of MR dye from aqueous solutions. All the sorption experiments were conducted by an orbital shaker (150 rpm) at room temperature (25 °C). After the mixing period, the suspensions were centrifuged (3500 rpm for 20 min) and MR concentration in the clear supernatant was calculated by UV-Visible spectrophotometer.

<p>| TABLE 1. General properties of MR dye |</p>
<table>
<thead>
<tr>
<th>Scientific name</th>
<th>General name</th>
<th>Chemical formula</th>
<th>Chemical structure</th>
<th>Ionization</th>
<th>MW (g/mol)</th>
<th>λmax(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Red</td>
<td>Acid red 2</td>
<td>C6H4N2O</td>
<td>Acetic</td>
<td>Acidic</td>
<td>269.3</td>
<td>515</td>
</tr>
</tbody>
</table>
The experiments were carried out in duplicates and the average values were applied. The adsorption capacity for MR was estimated by the following equation:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where, \( q_e \) (mg/g) is sorption capacity of HDTMA-MMT, \( C_0 \) and \( C_e \) (mg/L) are the primary and the equilibrium MR contents, respectively. M (g) is the mass of the sorbent and V (L) is the volume of the solution [27].

3. RESULTS AND DISCUSSION

3.1. Characterization of Sorbent

3.1.1. SEM Image

The SEM studies provide useful information regarding the surface morphology of the adsorbent structure. The SEM image of the HDTMA-MMT is illustrated in Figure 1. As seen, the HDTMA-MMT had a homogenous and smooth surface and the surfactant particles are seen upon it.

3.1.2. FTIR Analysis

The FTIR spectra of Raw-MMt and HDTMA-MMt are indicated in Figure 2 (a). As can be seen, both Raw-MMt and HDTMA-MMt had regular properties of montmorillonite peaks. The characteristic bands at 3627 cm\(^{-1}\) and large band at 3436 cm\(^{-1}\) were associated \(-\)OH and H\(_2\)O stretching vibration, respectively [24]. Intensity decrease at the band of 1635 cm\(^{-1}\) in HDTMA-MMt illustrated that water content was decreased owing to the substitution of hydrate cations by the surfactant. This process showed that properties of the adsorbent surface were altered from hydrophilic to hydrophobic by the modification via HDTMA. The IR bands at 1036 cm\(^{-1}\), 525 cm\(^{-1}\) and 468 cm\(^{-1}\) were associated to stretching vibration of Si-O groups, Al-O-Si, and Si-O-Si, respectively [28]. The new peak at the modified adsorbent in 2922 cm\(^{-1}\) can be in relation to modification of MMT by HDTMA surfactant. The IR board band at the range of 2800-3000 cm\(^{-1}\) in the HDTMA-MMt was assigned to stretching vibration the carbon-hydrogen (C-H) groups, which can has an important role in the sorption of pollutants [7].

3.1.3. XRD Analysis

The X-ray diffraction (XRD) patterns of Raw-MMt and HDTMA-MMt are presented in Figure 2(b). The results illustrated that the modification of Raw-MMt by HDTMA surfactant has caused the basic changes in the MMT.

The XRD basal spacing in Raw-MMt was 12.10 Å. This increment in the basal spacing of HDTMA-MMT showed that the surfactant intercalated in the interlayer space of the modified MMT [24].

3.2. Effect of Surfactant Loading Rate

Figure 3 illustrates the effect of surfactant loading rates (20 up to 150% CEC of the clay) on the uptake capacity of MR (100 mg/L) at initial pH. As seen, the uptake capacity of HDTMA-MMt for MR was increased via increasing the surfactant loaded onto the modified MMT up to 120% CEC of the clay. This result was in consist with results from study of Jourvand et al. in removal of methylene blue by HDTMA-MMt from aqueous solution [7]. The surfactant modification of MMT
changed the properties of adsorbent from hydrophilic to organophilic [24]. At surfactant loading rates beyond 120% CEC of the clay, the sorption capacity of the sorbent was decreased from 74.26 to 69.78 mg/g. This result can be due to the complete occupation the internal layers of the clay that caused to lower diffusion of the dye to these areas. Thus, HDTMA-MMT surfactant loading rates of 120% CEC of the clay was selected and all the experiments were conducted by this value surfactant loading rate.

where; qe (mg/g) and qi (mg/g) are the amounts of MR dye adsorbed onto the HDTMA-MMT at the equilibrium and at time (min), respectively. Moreover, K1 (1/min) is the rate constant of the pseudo-first-order kinetic. K1 and qe were determined from linear plotting ln(qe - qi) against time (min) that was obtained from the slope and intercept of the plot, respectively [25, 29].

The pseudo-second-order kinetic model can be illustrated by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}$$

where; K2 (g/mg.min) is the rate constant of the pseudo-second-order kinetic model. K2 and qe can be achieved from the cut-off and slope of t/qe versus t (min), respectively. Table 2 and Figure 4(b) show the kinetic models parameters of the MR sorption by HDTMA-MMT and the pseudo-second-order kinetic, respectively [25, 29]. As can be seen in Table 2, the highest value of correlation coefficient (R²) was corresponded to the pseudo-second-order kinetic model. Thus, this kinetic model was well fitted by experimental data from MR sorption onto HDTMA-MMT. Santhi et al. concluded that experimental data of the MR sorption by activated carbon prepared from annon a squamosa seed was fitted via pseudo-second-order kinetic model [19].

![Figure 3](image)

**Figure 3.** Effect of surfactant loading rate on the clay to sorption of MR dye (initial dye concentration=100 mg/L, contact time=24 h, HDTMA-MMT=1 g/L, and initial pH=7).

3.3. Effect of Contact Time

The effect of different contact times (0-60 min) on the sorption of MR was investigated and the results are presented in Figure 4(a). As seen, the rapid uptake of MR was occurred in the beginning the sorption process and the sorption rate was nearly constant after 30 min. The equilibrium sorption capacity (80.72 mg/g) was achieved at contact time of 30 min. The fast sorption of MR at the initial stage of the sorption can be owing to higher availability of large numbers of vacant sites on the adsorbent surface that readily filled by MR dye.

Ahmed et al. reported that the contact time reached to equilibrium at a contact time of 6 hours for removal of MR dye using modified durian seed [12]. In other study by Haris et al., the equilibrium time of the removal MR by banana trunk fibers was observed at contact time of 45 min [14]. Comparing our contact time results with other abovementioned studies showed that HDTMA-MMT had a higher tendency to MR dye.

3.3.1. Kinetic Study

In order to reach a better perception of the sorption process, the experimental data were fitted by two kinetics models, pseudo-first-order and pseudo-second-order. The pseudo-first-order model can be shown by Equation (2):

$$\ln(q_e - q_t) = \ln q_e - k_1t$$

![Figure 4](image)

**Figure 4.** (a) Effect of contact time on the sorption of MR dye (initial dye concentration=100 mg/L, adsorbent dosage=1 g/L, and initial pH=7) and (b) Pseudo-second-order kinetic.
3.4. Effect of Solution pH

The solution pH is a significant parameter that affects on the adsorption process [17, 30]. The solution pH has a regulator influence on the ionization, dissociation, nature and surface properties of the adsorbent [1, 2]. The effect of solution pH in the range of 2-12 on the sorption of MR by HDTMA-MMT was investigated and the results are illustrated in Figure 5. As seen, the sorption capacity was increased with increasing the solution pH from 2 to 6. The maximum uptake sorption (84.28 mg/g) was obtained at pH 6. This result may be due to change in surface charge of MR dye molecules and functional groups of the HDTMA-MMT. In the study of Santhi et al., the maximum sorption capacity of the MR by activated carbon was obtained at pH 4 [19]. Abdullah and et al. observed that the efficiency removal of MR dye by sugarcane bagasse was significantly increased at pH range of 3 to 7 [31].

3.5. Effect of Adsorbent Dosage

The influence of different dosages (0.5 to 5 g/L) of HDTMA-MMT on the sorption of MR dye was investigated in an initial concentration of 100 mg/L at 25 °C and the results are shown in Figure 6. As can be seen, with increasing the sorbent dosage from 0.5 up to 5 g/L, the uptake capacity was reduced. Decreasing the sorption capacity in higher dosage of HDTMA-MMT can be because of the unavailability of the dye molecules that cannot cover all the surface active sites of the adsorbent. In other words, a large number of the active sites of the sorbent surface cannot reach to saturation state at higher dosages of HDTMA-MMT. Thus, dose of 0.5 g/L was chosen as the optimum dosage for the next stages of the experiments.

![Figure 5](image-url) Effect of pH on the sorption of MR dye (contact time=30 min, initial dye concentration=100 mg/L, and adsorbent dosage=1 g/L).

![Figure 6](image-url) Effect of adsorbent dose on the sorption (contact time=30 min, initial concentration=100 mg/L, and solution pH=6).

3.6. Effect of Initial Dye Concentration

The effect of initial MR concentrations (50 to 400 mg/L) with 0.5 g/L of the sorbent was evaluated on the sorption capacity and the findings are shown in Figure 7(a). As can be seen, the uptake capacity of the sorbent was quickly increased from 68.58 up to 688.58 mg/g via increasing MR content from 50 to 500 mg/L in the solution. This phenomenon can be caused from the increase in driving force of the dye molecules including Van der Waals's force to the vacant sites of the sorbent surface, which occurs at higher concentrations of MR [1, 2].

3.6.1. Isotherm Study

The sorption data were investigated by two isotherms, Langmuir and Freundlich models. These models are commonly used to find out sorption mechanism and also to design a sorption system [4, 32]. The Langmuir isotherm assumes that monolayer adsorption happens at binding sites via homogenous energy levels [33]. The Langmuir isotherm is explained by the following equation:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m}
\]

(4)

where, \(C_e\) (mg/L) is the equilibrium content of MR, \(q_e\) (mg/g) is the uptake capacity of HDTMA-MMT in the equilibrium time. The parameters of \(Q_m\) (maximum sorption capacity) and \(b\) (the Langmuir constant) are achieved from the slope and intercept of liner plotting \(C_e/q_e\) versus \(C_e\), respectively [11, 25]. A dimensionless constant separation factor, \(R_L\), has been used in associated to Langmuir isotherm model. This

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**TABLE 2.** Parameters of pseudo-first-order and pseudo-second-order kinetic models

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_e) calculated (mg/g)</td>
<td>(K_1) (1/min)</td>
</tr>
<tr>
<td>MR</td>
<td>1.34</td>
<td>0.010</td>
</tr>
</tbody>
</table>
parameter called also the equilibrium factor and is defined by Equation (5):

$$ R_L = \frac{1}{1+bC_0} $$

(5)

where; b and C₀ were mentioned above for Langmuir isotherm model. The amount of $R_L$ shows that the sorption process is unfavorable ($R_L > 1$), irreversible ($R_L = 0$), linear ($R_L = 1$), or favorable ($0 < R_L < 1$) [11]. In this study (Table 3), based on the value of $R_L = 0.952$, the sorption system of MR dye onto HDTMA-MMT was favorable.

The Freundlich isotherm model can be presented by Equation (6):

$$ \ln q_e = \ln k_f + \frac{1}{n} \ln C_e $$

(6)

where, $K_f$ (L/g) and n are constants of the isotherm and they show the capacity and intensity of the sorption, respectively.

The parameter of $K_f$ is obtained from the cut-off and n is achieved from the gradient of linear plotting ln $q_e$ against ln $C_e$ [29]. Table 3 and Figure 7(b) show the parameters of Langmuir and Freundlich isotherm models and the Freundlich isotherm plot for the uptake of MR dye on the sorbent, respectively. As shown, the sorption data were well described by the Freundlich isotherm model. Ahmed et al. reported that the experimental data of MR dye onto modified durian seed were clearly fitted by Freundlich isotherm model [12].

**TABLE 3.** Parameters of Langmuir and Freundlich isotherms obtained from present study.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$ (mg/g)</td>
<td>b (l/mg)</td>
</tr>
<tr>
<td>MR</td>
<td>1428.5</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

**TABLE 4.** Comparison of maximum sorption capacity HDTMA-MMT with other sorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum adsorption capacity (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feldspar</td>
<td>0.7</td>
<td>[22]</td>
</tr>
<tr>
<td>Rice Hulls</td>
<td>3.3</td>
<td>[34]</td>
</tr>
<tr>
<td>Annona squamosa</td>
<td>40.5</td>
<td>[19]</td>
</tr>
<tr>
<td>Kaolin</td>
<td>64.1</td>
<td>[21]</td>
</tr>
<tr>
<td>Modified durian seed</td>
<td>348.6</td>
<td>[12]</td>
</tr>
<tr>
<td>Modified-BTF</td>
<td>555.6</td>
<td>[14]</td>
</tr>
<tr>
<td>HDTMA-MMT</td>
<td>1428.5</td>
<td>This study</td>
</tr>
</tbody>
</table>

**4. CONCLUSION**

In this study, Hexadecyl trimethyl ammonium bromide (as a cationic surfactant) modified montmorillonite (HDTMA-MMT) was used as a low cost adsorbent for the removal of methyl red (MR) from aqueous solutions. The effect of various parameters such as surfactant loading rate, contact time, pH, adsorbent dosage, and initial dye concentration was assessed on the sorption. The optimum contact time in the sorption process was achieved 30 min. Furthermore, the optimum pH was also obtained at pH 6. The experimental data were well fitted by pseudo-second-order kinetic and Freundlich isotherm model. The results illustrated that HDTMA-MMT as a low cost, eco-friendly, non-toxicity and high capacity sorbent towards other sorbents can be used as an effective material for the removal of MR from aqueous solution.
5. REFERENCES


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Y. Omidi-Khaniabadi, B. Kamarehei, H. Nourmoradi, M. Jourvand, H. Basiri, S. Heidari

**Department of Environmental Health Engineering, School of Health, Lorestan University of Medical Sciences, Khorramabad, Iran**

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**Hexadecyl Trimethyl Ammonium Bromide-Modified Montmorillonite as a Low-Cost Sorbent for the Removal of Methyl Red from Liquid-Medium**

**Abstract**

In this study, modified montmorillonite (MMT) (Hexadecyl Trimethyl Ammonium Bromide (HDTMA) modified Montmorillonite Mg-MMT) was used as an adsorbent for the removal of methyl red from aqueous solutions. The effects of various parameters such as surfactant loading, contact time, pH, dosage, and initial concentration of methyl red dye on the adsorption capacity were investigated. The adsorption capacity of HDTMA-MMT increased with increasing surfactant loading up to 21.0% under the exchange capacity of montmorillonite. The optimum adsorption capacity was 22.0 mg/g at 0.1 min and pH 6. The experimental data was well fitted to the pseudo-second-order kinetic and Freundlich isotherm models. The results indicated that HDTMA-MMT can be used as an effective and low-cost adsorbent for the removal of methyl red from aqueous solutions. The chemical formula of the adsorbent is HDTMA-MMT.

**Keywords:** Adsorption, Montmorillonite, Surfactant, Methyl Red.

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