Cationic Surfactant-modified Clay as an Adsorbent for the Removal of Synthetic Dyes from Aqueous Solutions

1 Introduction

Water pollution due to the discharge of different pollutants from industrial activities is considered as a major environmental issue, especially in developing countries (Alavi et al. 2016; Biglari et al. 2017; Hassani et al. 2016; Neisi et al. 2017). Synthetic dyes or pigments are one of the most important industrial pollutants. Indeed, several industries such as textile, paper, leather, plastic, carpet, cosmetics and food produce large amounts of...
dye-containing effluents (Almeida et al. 2009; Debnath et al. 2015; Ghasemi et al. 2016; Omidi-Khaniabadi et al. 2016a; Mohammadi et al. 2017b; 2017a). The untreated discharge of such effluents into water resources causes adverse impacts on aquatic lives as well as on human health (Demarchi, Campos, and Rodrigues 2013; Niri et al. 2015). Synthetic dye components can be toxic, carcinogenic and mutagenic (Cheng et al. 2015; Elmoubarki et al. 2015). Then, dye removal before being discharged into the aquatic bodies is essential (Liu et al. 2015; Omidi-Khaniabadi et al. 2017a; 2015). Synthetic dyes can be categorized into anionic, cationic and non-ionic dyes (Kazembeigi et al. 2014). Alizarin Red S (ARS) is an anionic dye synthesized by sulfurization of alizarin extracted (Jadhava, Khetre, and Bamane 2011) from the root of madder plants (Rubia tinctorum) (Rehman et al. 2011). ARS is a water soluble dye widely used as a staining agent in the textile industry (Abou-Gamra 2014; Albadarin and Mangwandi 2015).

Owing to its complex structure, namely aromatic rings that afford high optical and physico-chemical stability, it is considered to be one of the most recalcitrant and persistent pollutants (Ahmad and Kumar 2008; Fu et al. 2011). Bromocresol Green (BCG) belongs to the triphenylmethane family dyes and is also an anionic dye used as pH indicator and DNA tracer (Ghaedi et al. 2012).

Dyes block sunlight penetration in water bodies, thus, reducing the photosynthetic activities of autotrophic organisms (Albadarin et al. 2014). For this reason, their presence in water bodies is unfavorable. Several physical, chemical and microbial techniques including advanced oxidation, membrane technologies, coagulation-flocculation, biological degradation, chemical oxidation, electro-chemical and adsorption methods have been applied to remove dyes from dye-containing wastewater (Abou-Gamra 2014; Ahmad and Kumar 2008; Jadhava, Khetre, and Bamane 2011; Moussavi, Rashidi, and Khavanin 2013; Nadafi et al. 2014; Omidi-Khaniabadi et al. 2016a; Shirimardi et al. 2013). The latter techniques have been widely applied to remove organic pollutants from contaminated water (Basiri et al. 2015; Jiang et al. 2012; Tchuifon et al. 2014). Among the available adsorbents, activated carbon is largely implemented to remove organic and inorganic pollutants from wastewater because of its simplicity, high surface area and high uptake capacity (Basiri et al. 2015; Omidi-Khaniabadi et al. 2015). However, it presents the following disadvantages: high-cost and difficult regeneration (Chatterjee, Lee, and Woo 2010; Cheng et al. 2015; De Luna et al. 2013). In addition to activated carbon, the use of other non-conventional adsorbents such as olive stone (Albadarin and Mangwandi 2015), mint waste (Ahmad and Kumar 2008), nanocrystal (Jadhava, Khetre, and Bamane 2011), coconut shell, maize (Zea mays), gold nanoparticles, polypyrrole-coated magnetic nanoparticles (Gholivand et al. 2015), cynodon dactylon, cammum hydroxide-activated carbon (Ghaedi et al. 2012), Ziziphus nummularia () and granite (Kadhim 2012) have been reported for the removal of ARS and BCG from aqueous media. Today, research and commercial interests are focused on the implementation of cheap adsorbents to remove organic pollutants from wastewater. Among them clay, especially montmorillonite has been widely applied for wastewater treatment. In addition to being eco-friendly, montmorillonite is non-toxic, it has a high surface area and adsorption capacity. All these relevant properties make montmorillonite as an appropriate adsorbent for the removal of organic pollutants from aqueous solutions (Omidi-Khaniabadi et al. 2016b). Raw montmorillonite has a hydrophilic nature, thus the modification of the clay surface by organophilic substances, such as surfactants, is needed. It has been proved that the intercalation of cationic surfactants modifies the surface properties of montmorillonite from hydrophilic to hydrophobic through cation exchange (Omidi-Khaniabadi et al. 2016b; Nourmoradi et al. 2016).

In this study, the potential use of hexadecyl trimethyl ammonium bromide-modified montmorillonite as a low-cost adsorbent to remove the ARS and BCG dyes from liquid phase was investigated. To the best of our knowledge, the preparation of HDTMA-modified montmorillonite and its application to the removal of these synthetic dyes have not been previously reported.

2 Material and methods

2.1 Materials

The dyes Alizarin Red S (CI 58005; CI name: Mordant Red 3) and Bromocresol Green (BCG) were purchased from Alvan Sabet Co, Iran. The former belongs to the anthraquinone class and the latter to the triarylmethane class. The clay, montmorillonite (Mt), and hexadecyl trimethyl ammonium bromide (HDTMA) were obtained from Laviosa Co, Italy and Aldrich Co, USA, respectively. H₂SO₄ and NaOH were purchased from Merck Co, Germany. The chemical structures and other properties of ARS and BCG are shown in Table 1. The pH was adjusted by a digital pH-meter (50-pp-Sartorious model) by adding 0.1 N H₂SO₄ or NaOH solution. Stock solutions (1000 mg/L) of each dye were made by dissolving 1 g of dye in one liter of deionized water. The stock solutions of the dyes were kept in the dark to avoid dye photodegradation.
Table 1: Properties of Alizarin Red S and Bromocresol Green.

<table>
<thead>
<tr>
<th>Scientific name</th>
<th>Chemical structure</th>
<th>Molecular Formula</th>
<th>Molecular weight</th>
<th>Maximum wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alizarin Red S</td>
<td><img src="image1.png" alt="Chemical structure" /></td>
<td>C_{14}H_{8}O_{7}S</td>
<td>320.271 g/mol</td>
<td>425</td>
</tr>
<tr>
<td>Bromocresol Green</td>
<td><img src="image2.png" alt="Chemical structure" /></td>
<td>C_{21}H_{14}Br_{4}O_{4}S</td>
<td>698.014 g/mol</td>
<td>455</td>
</tr>
</tbody>
</table>

2.2 Purification and modification of montmorillonite

To purify, 30 g of the raw montmorillonite (Mt) was placed in 1 L of deionized water. The solution was mechanically stirred at 250 rpm for 24 h at room temperature (25 °C ± 2 °C). Then the obtained suspension was centrifuged at 1790 × g for 20 min to eliminate impurities and the supernatant was collected, dried at 105 °C and sieved to a particle size less than 125 µm (Nourmoradi, Nikaeen, and Khiadani 2012).

In order to modify the clay by HDTMA in the amounts of 20–200% of the Mt cationic exchange capacity (CEC), 5 g of highly purified Mt was separately introduced in 100 mL of deionized water (1:20) and mixed with 0.393, 0.984, 1.37, 2.36, 2.95 and 3.93% g of the cationic surfactant to produce HDTMA-modified Mt at surfactant loadings of 20, 50, 70, 100, 150 and 200% of the Mt CEC, respectively. The suspensions were agitated on a stirrer at 250 rpm for 24 h at room temperature. The HDTMA-modified Mt was centrifuged at 1790 × g for 20 min, washed several times with deionized water, then dried at 60 °C and finally passed through an ASTM (American Standard Test Sieve Series) sieve of 125 µm (mesh No. 120).

2.3 Characterization and analysis

The specific surface area and the morphology of the raw-Mt and HDTMA-Mt were characterized by the Sears’s method and by SEM (Jeol Model Jsm-T330), respectively. FTIR spectral study of the raw and HDTMA-modified Mt was analyzed by Diffuse Reflectance FTIR spectroscopy (DRIFTS-FTIR) at a resolution of 1 cm⁻¹ in the region of 400–4000 cm⁻¹ (JASCO, FT/IR-6300, Japan). The characterization of the Mt was also determined by X-ray diffractometry (Bruker, D8 Advance, Germany) using Ni filtered Cu Kα radiation (1.5406 Å). The concentrations of ARS and BCG in the solution were measured by a UV-vis spectrophotometer (PG Instrument Limited Model) and associated with the maximum absorption peak in the visible wavelength spectrum (425 and 455 nm, respectively).

2.4 Adsorption experiments

All the experiments were performed in batch approach. The influence of surfactant loading rates (20–200 % CEC of the Mt), contact time (0–120 min), pH (3–11), adsorbent dosage (1–10 g/L) and adsorbate concentrations (20–100 mg/L for ARS and 50–500 mg/L for BCG) on the removal of ARS and BCG were examined. All the uptake experiments were conducted using 100 mL of dye solution at room temperature (25 °C ± 2 °C) in 250-mL conical flask containing 1 g/L of adsorbent on a mechanical stirrer (250 rpm). After attaining the equilibrium time, the suspensions were centrifuged at 1370 × g for 20 min, then the supernatant was determined through a UV-vis spectrophotometry. Batch experiments were conducted in duplicate and calculated averages were presented. The adsorption percentage (%) and adsorption capacity (mg/g) of the modified Mt for ARS and BCG removal were calculated by the following equations:

\[
\text{Adsorption (\%)} = \frac{(c_0 - c_e)}{c_0} \times 100
\]

\[
q_e = \frac{(c_0 - c_e)v}{m}
\]
where \( q_e \) (mg/g) is the uptake capacity of the dye, \( C_0 \) is the initial dye concentration and \( C_e \) (mg/L) is the equilibrium dye concentration. Also, \( V \) (L) is the solution volume and \( m \) (g) is the adsorbent mass (Elmoubarki et al. 2015).

### 3 Results and discussion

#### 3.1 Characterization

##### 3.1.1 Characterization of the adsorbent

The physico-chemical characteristics of the Mt are exhibited in Table 2. As can be seen, SiO\(_2\) and Al\(_2\)O\(_3\) were the major constituents of the adsorbent together with other oxides present in lower quantities (Omidi-Khaniabadi et al. 2016b). Therefore, it was expected the major oxides in the adsorbent was responsible for the dye uptake from the solutions. On the basis of the Sear’s method, the CEC of Mt was 108 meq/100 g (Nourmoradi, Nikaeen, and Khiadani 2012).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>60.00</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>20.03</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>2.31</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>3.02</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>4.02</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.13</td>
</tr>
<tr>
<td>CaO</td>
<td>1.46</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.24</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>8.71</td>
</tr>
<tr>
<td>Other</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>Limit of ignition (%)</td>
</tr>
</tbody>
</table>

##### 3.1.2 Surface area measurement

The results of surface area measurement showed that the adsorbent modification of the raw Mt by HDTMA led to a reduction of the Mt surface area from 32.6 m\(^2\)/g for the raw Mt to 27.8 m\(^2\)/g for HDTMA-modified Mt. This reduction in the surface area of the modified-Mt can be linked to the blocking of some of the internal layers of the HDTMA-modified Mt by the surfactant. The modification of Mt led to a smaller surface area, but its adsorption capacity increased due to the shift of the Mt surface from hydrophilic to hydrophobic.

##### 3.1.3 SEM images

The SEM images of the raw and modified-Mt are illustrated in Figure 1. As can be seen, the raw Mt (Figure 1(a)) has an irregular shape with an uneven surface structure. In contrast, the HDTMA-modified Mt (Figure 1(b)) has a homogenous and smooth surface and the surfactant particles are seen upon it.
Indeed, the organic surfactant-modified clay shows significant changes in the morphology. There are several small and aggregated particles and the sheets become relatively flat layers compared with the morphology of the Na–montmorillonite. In modified clay, the cationic surfactant easily intercalated into the clay interlayer space by cation exchange. In this case, intercalation of the cationic surfactants not only changes the surface properties of clays from hydrophilic to hydrophobic, but also increases the basal spacing of the clay interlayers (Tangaraj et al. 2017; Wang et al. 2004). There was found that modified montmorillonite by HDTMA expanded the average pore size and interlamellar space due to the insert of HDTMA cations into the aluminosilicate sheets of the clay. Zhang, Sparks, and Scrivner (1993) found that the adsorption of amines ions on montmorillonite surface involves three types of reactions including cation-exchange reaction, ion pair adsorption and interactions of tail–tail. So, the adsorption mechanisms are closely related to the size of quaternary amines. Wang et al. (2004) pointed out that the hydrophobic tails interaction between HDTMA surfactants can also bring out positive charge development on the surface of montmorillonite. Their results also showed that larger HDTMA cations may insert into the aluminosilicate sheets and then expand the interlamellar space.

3.1.4 FTIR analysis

FTIR spectroscopy is a helpful tool for the determination of the functional groups of the adsorbent surface and to attain information regarding the interactions between the Mt and the surfactant. The FTIR spectra of the raw Mt and HDTMA-modified Mt are depicted in Figure 2(a). The raw Mt and the HDTMA-modified Mt showed similar peaks in the region of 400–2000 cm−1. FTIR spectra of the raw Mt and the HDTMA-modified Mt are different in the region of 2800–3000 cm−1 (Omidi-Khaniabadi et al. 2016b). As shown, the characteristic bands at 3627 cm−1 and the wide band at 3436 cm−1 are related to -OH and H2O stretching vibrations, respectively (Nourmoradi, Nikaeen, and Khiaadani 2012). The IR band at 1635 cm−1 is associated to water molecules bound to Al and Mg (Su et al. 2011). Also, the decrease in the IR band intensity of 1635 cm−1 in the HDTMA-modified Mt indicates a reduction of the water content due to the replacement of the hydrated cations with the surfactant.

These changes showed that the features of the adsorbent surface were altered from hydrophilic to hydrophobic by the modification with the HDTMA surfactant. The IR bands at 1036 cm−1, 525 cm−1 and 468 cm−1 were
attributed to the stretching vibration of Si-O, Al-O-Si and Si-O-Si groups, respectively (Omidi-Khaniabadi et al. 2016b; Silva et al. 2012). The new broad peak found in the region of 2800–3000 cm$^{-1}$ in the modified adsorbent can be assigned to the stretching vibration of the C-H groups. The appearance of this peak can be due to the intercalation of the surfactant into the Mt (Nourmoradi, Nikaeen, and Khiadani 2012). This renders Mt organophilic which plays an important role in the removal of the above-mentioned pollutants (i.e. anionic dyes).

### 3.1.5 XRD analysis

A powerful technique to prove the loading of the surfactants in the galleries of the resulting organoclays is XRD analysis (Chen et al. 2011a). The XRD patterns of the raw Mt and HDTMA-modified Mt are illustrated in Figure 2(b). As observed, the modification of the raw Mt by the HDTMA surfactant led to structural changes in the Mt (Omidi-Khaniabadi et al. 2016b). The XRD basal spacing in the raw Mt was 12.10 Å. The interlayer spacing of the HDTMA-modified Mt increased to 18.83 Å which showed that HDTMA molecules were inserted into the internal region of the Mt (Nourmoradi, Nikaeen, and Khiadani 2012).

### 3.2 Effects of the surfactant-loading rate on dye removal

The removal of ARS and BCG by HDTMA-modified Mt at different loading rates of the surfactant (20–200% of the CEC Mt) is displayed in Figure 3. As shown, the adsorption capacity ($q_e$) of the HDTMA-modified Mt increased up to 70 and 120% of the CEC Mt for ARS and BCG, respectively.

![Figure 3: Effect of the surfactant loading rate on the adsorption of Alizarin Red S (ARS) and Bromocresol Green (BCG) by HDTMA-modified Mt (ARS = 50 mg/L, BCG = 100 mg/L, contact time = 24 h, HDTMA-modified Mt dosage = 1 g/L and initial pH = 7).](image)

A high surfactant loading may occupy the whole internal layers spaces of the Mt and as a result, the diffusion of adsorbates into these layers was reduced. The adsorption capacities of ARS and BCG by the HDTMA-modified Mt for 70 and 120% of the CEC Mt were 40.5 mg/g and 88.02 mg/g, respectively. Therefore, the Mt with the surfactant-loading yields of 70 and 120% CEC of the adsorbent were considered for the subsequent experiments.

### 3.3 Effect of contact time on dye removal

The effect of different adsorption times on the removal efficiency of ARS and BCG by HDTMA-modified Mt is presented in Figure 4(a). As shown, at an initial amount of 50 mg/L for ARS and 500 mg/L for BCG, dye removal rapidly increased as contact time increased up to 40 min for the former and up to 20 min for the latter. After these times, dye removal slowed down up to 120 min. Because of the accessibility of high free active sites at the beginning uptake time, a rapid initial adsorption is observable. After a certain time, the gradual occupation...
of the active sites slowed down the adsorption process. Therefore, the contact times of 40 and 20 min were selected as the optimum contact times for ARS and BCG, respectively.

![Figure 4](image)

Rehman et al. (2011) reported an equilibrium time of 35 min for the removal of ARS (25 mg/L) from aqueous solutions by alumina as an adsorbent operating at optimal conditions (i.e., 30 °C, 300 rpm, pH 1.0) and a maximum removal about 92%. Ghaedi et al. (2012) found a maximum BCG (40 mg/L) removal of 93% by cadmium hydroxide loaded on activated carbon operating at an adsorbent dosage of 1 g/L, an initial pH of 1, room temperature and 10 min equilibrium time (Ghaedi et al. 2012).

### 3.3.1 Kinetics study

The establishment of adsorption kinetic models is valuable to assess the mechanism of the adsorption process (Moeinpour, Alimoradi, and Kazemi 2014). Three models, namely pseudo-first-order, pseudo-second-order and intra-particle diffusion were considered to evaluate the adsorption data of ARS and BCG by the HDTMA-modified Mt. The pseudo-first-order kinetic model can be depicted by eq. (3):

\[
\ln(q_e - q_t) = \ln q_e - K_1 t
\]

where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the quantities of dye adsorbed onto the HDTMA-modified Mt at the equilibrium time and at a given time \( t \) (min), respectively. \( K_1 \) (1/min) is the rate constant of the pseudo-first-order model (Cheng et al. 2015; Qiu et al. 2015). \( K_1 \) and \( q_e \) can be obtained from the slope and intercept of the lineal plotting of \( \ln(q_e - q_t) \) versus \( t \), respectively.

Experimental data were also explored using the pseudo-second-order kinetic model. This kinetic model is represented as follows:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

where \( K_2 \) (g/mg min) is the rate constant of the pseudo-second-order kinetic model. \( K_2 \) and \( q_e \) were acquired from the intercept and slope of plotting \( t/q_t \) against \( t \), respectively (Du et al. 2014).

The intra-particle diffusion model can be illustrated as follows:
\[ q_t = k_{id}t^{1/2} + c_i \]  

(5)

where \( k_{id} \) is the rate constant of the intra-particle diffusion model (mg/g min\(^{1/2}\)) and \( C_i \) (mg/g) is the thickness of the boundary layer. The values of \( k_{id} \) and \( C_i \) were estimated from the slope and intercept of the lineal regression of the plots of \( q \) versus \( t^{1/2} \).

The plots of the kinetic models and also the kinetic parameters of ARS and BCG are shown in Figure 4 and Table 3, respectively.

Table 3: Parameters of pseudo-first-order and pseudo-second-order kinetics models obtained from this study.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
<th>Intra-particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{e, \text{calculated}} ) (mg/g)</td>
<td>( q_{e, \text{calculated}} ) (mg/g)</td>
<td>( K_1 ) (1/min)</td>
</tr>
<tr>
<td>ARS</td>
<td>46.89</td>
<td>14.24</td>
<td>0.105</td>
</tr>
<tr>
<td>BCG</td>
<td>462.29</td>
<td>292.83</td>
<td>0.217</td>
</tr>
</tbody>
</table>

The lineal plotting of \( q \) versus \( t^{1/2} \) could present multi-linearity (Allen, Mckey, and Khadur 1989) and shows two or more steps occurring in the adsorption process. The external surface adsorption or rapid adsorption stage would correspond to the first sharp step. The second step would correspond to the gradual adsorption step, where the intra-particle diffusion controlled the rate and the last step would be the final equilibrium step, where the intra-particle diffusion slowed down due to the low adsorbate content in solution (Chiou and Chuang 2006). The slope of the plot in each step is written as the rate parameter \( k_{p,i} \) (\( i = 1 \rightarrow 3 \)) and their amounts are shown in Table 3. As can be seen, the amounts of \( C_i \) for the adsorption of ARS and BCG by the HDTMA-Mt were 39.6 mg/g and 399.9 mg/g, respectively. As observed, the regression lines of this model did not pass through the origin (Figure 4(d)), showing that the intra-particle diffusion is not the rate-limiting stage in the uptake of dyes.

As can be seen from Figure 4(b)–Figure 5(d) and Table 3, the pseudo-first-order and intra-particle diffusion model had correlation coefficient values much lower than that of the pseudo-second-order kinetic model, showing that the adsorption process of ARS and BCG dyes by HDTMA-Mt followed this latter model. Similar kinetic results were obtained for the removal of ARS onto some adsorbents including gold nanoparticles (Roosta, Ghaedi, and Mohammadi 2016), mint waste (Ahmad and Kumar 2008) and coconut shell (Wagh and Shrivastava 2014). Moreover, Ghaedi et al. (2012) and Shokrollahi et al. (2011) reported similar kinetic results for the adsorption of BCG onto cadmium hydroxide nanowire loaded on activated carbon and Ziziphus nummularia.

3.4 Effect of solution pH and adsorbent dosage

The solution pH affects the surface nature of the adsorbent and the ionization level of the adsorbate (Chaari et al. 2009; Chen et al. 2011a). The influence of solution pH on the removal efficiencies of ARS and BCG by HDTMA-modified Mt was examined in a range from 3 to 11. As observed, the removal rate of both dyes by HDTMA-modified Mt decreased with increasing pH owing to the competition between the OH\(^-\) and the anionic molecules of the dyes for the positive binding surface sites of the adsorbent (Figure 5(a)). The maximum removal
efficiencies of ARS and BCG dyes occurred at pH 3 and were equal to 94.3% and 95.8%, respectively. In view of the results obtained, pH 3 was chosen as the optimal pH for the removal of the ARS and BCG from the synthetic wastewater. Gautam, Mudhoo, and Ghattopadhyaya (2013) reported that with the increase of pH, the removal of ARS by mustard husk decreased due to the increasing of OH- ions in the solution. Ghaedi et al. (2012) also obtained similar results to that of the present study for the adsorption of BCG from solution onto cadmium hydroxide nanowire loaded on activated carbon.

The effect of the adsorbent dosage (1–12 g/L) on the adsorption capacities of dyes by HDTMA-modified Mt was investigated at initial amounts of 50 mg/L and 500 mg/L for ARS and BCG at pH 3, respectively (Figure 5(b)). As shown, dye removal diminished with the increase in the adsorbent dosage. The reason for this phenomenon can be attributed to the aggregation of the HDTMA-modified Mt particles at high dosages due to particle interaction resulting in the decrease of available active sites (Aksakal and Ucun 2010). Similar findings were reported by Kranşan et al. (2014) for the removal of Acid Orange 7 using a nanomaterial of cetyltrimethy- lammonium bromide-modified Mt. Thus, an adsorbent dosage of 1 g/L was preferred as the optimum to perform the next experiments.

### 3.5 Effect of dye concentration

The impact of dye concentration (20–100 mg/L for ARS and 50–500 mg/L for BCG) on the adsorption capacity of HDTMA-modified Mt with the adsorbent amount of 1 g/L at 25°C was investigated. The results are depicted in Figure 6. As observed, with the increasing dye concentration, the uptake capacities of the adsorbents increased. Thus, the adsorption capacity of HDTMA-modified Mt for ARS progressively increased from 18.18 mg/g for 20 mg/L to 81.89 mg/g for 100 mg/L, while for BCG it increased from 36.23 mg/g for 50 mg/L up to 468 mg/g for 500 mg/L. It has been previously reported that the increase of the driving force with increasing dye molecules overcomes the resistance to mass transfer between the liquid and solid phases (Banerjee and Chattopadhyaya 2013).

![Figure 6: The effect of initial dye concentration on the adsorption capacity of Alizarin Red S (ARS) and Bromocresol Green (BCG) by HDTMA-modified Mt (contact time = 40 min for ARS and 20 min for BCG, adsorbent dosage = 1 g/L and pH = 3).](https://example.com/figure6.png)

#### 3.5.1 Isotherm study

The adsorption isotherms are helpful to find out the adsorbate distribution onto the adsorbent at the equilibrium conditions (Dong et al. 2013; Silva et al. 2012). Therefore, the isotherms of Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich (D-R) models were considered to describe the ARS and BCG adsorption on the HDTMA-modified Mt. The Langmuir isotherm approximates the greatest monolayer adsorption on the uniform adsorbent surface (Elmoubarki et al. 2015; 2012; 2015).

The linearized form of the Langmuir isotherm is presented by eq. (6):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \tag{6}$$

where $C_e$ (mg/L) is the initial adsorbate concentration, $q_e$ (mg/g) is the adsorbate adsorption capacity at the adsorption equilibrium time, $Q_m$ and $b$ are the maximum adsorption capacity (mg/g) and the rate constant of Langmuir (l/mg), respectively. $Q_m$ and $b$ are acquired from the slope and intercept of the linear plotting of $C_e/q_e$ versus $C_e$, respectively. The Langmuir isotherm can be shown via a dimensionless constant separation factor ($R_L$). This factor, also called the equilibrium parameter, is obtained from the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{7}$$
where \( C_0 \) is the maximum initial concentration of adsorbate in mg/L. The value of separation factor \( (R_L) \) indicates the adsorption conditions as unfavorable \( (R_L > 1) \), linear \( (R_L = 1) \), irreversible \( (R_L = 0) \) and favorable \( (0 < R_L < 1) \). Based on the obtained values of \( R_L \) (Table 4), the adsorption process of ARS and BCG by HDTMA-modified Mt is favorable.

### Table 4: Parameters of Langmuir and Tempkin isotherm models for the adsorption of ARS and BCG by HDTMA-modified Mt.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Langmuir isotherm</th>
<th>Tempkin isotherm</th>
<th>D-R isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_m ) (mg/g)</td>
<td>( b ) (L/g)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>ARS</td>
<td>666.6</td>
<td>0.001</td>
<td>0.991</td>
</tr>
<tr>
<td>BCG</td>
<td>1250</td>
<td>0.0005</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The Freundlich isotherm is often expressed for multilayer adsorption onto a heterogeneous surface of adsorbent (Elmoubarki et al. 2015; 2011) as illustrated by eq. (8):

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

where \( K_f \) (L/g) is the Freundlich constant and \( n \) indicates the intensity level of the adsorption (Xiao et al. 2013). The plot of \( \ln q_e \) versus \( \ln C_e \) is used to generate the intercept \( K_f \) and the slope \( 1/n \). A value of \( 1/n \) higher than 1 indicates that saturation is not achieved.

The isotherm of Tempkin shows the effect of some indirect adsorbent/adsorbate interactions on the adsorption and can be illustrated by eq. (9):

\[
q_e = B_1 \ln K_t + B_1 \ln C_e
\]

where \( K_t \) is the Tempkin isotherm constant (L/g) and \( B_1 = RT/b \). Also, \( b \) is the Tempkin constant associated with the heat of adsorption (J/mol), \( R \) is the gas constant (8.314 J/mol K), and \( T \) is the absolute temperature (K). The constants \( B_1 \) and \( K_t \) are acquired from the plot of \( q_e \) versus \( \ln C_e \).

To determine the adsorption condition as physical or chemical, the isotherm of Dubinin–Radushkevich (D–R) is commonly used. The D-R isotherm is given by eq. (10):

\[
\ln q_e = \ln q_m - \beta \epsilon^2
\]

where \( q_m \) (mg/g) and \( \beta \) (kJ/mol) are the theoretical sorption capability at saturation form and a constant associated with the adsorption energy, respectively (Nourmoradi, Nikaeen, and Khiadani 2012). The \( \epsilon \) parameter, namely Polanyi Potential, is achieved by the eq. (11):

\[
\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]

where \( R \) (kJ/mol) and \( T \) (K) are the universal gas constant and the media temperature, respectively.

The parameters of \( q_m \) and \( \beta \) are obtained from the intercept and the gradient of plot of \( \ln q_e \) versus \( \epsilon^2 \), respectively. \( E \) (kJ/mol), the average adsorption energy, is calculated via eq. (12).

\[
E = \frac{1}{\sqrt{2\beta}}
\]

The calculated values of the isotherms parameters for ARS and BCG adsorption by HDTMA-modified Mt are shown in Table 4 and Table 5. As seen, the values of \( n \) obtained from the Freundlich model were 1.06 and 1.126 for the adsorption of ARS and BCG, respectively. Therefore, 1/n values were lower than 1 indicating that saturation occurred (Davila-Jimenez, Elizalde-Gonzalez, and Pelaez-Cid 2005).

### Table 5: Freundlich constants and calculated and experimental \( q_e \) values for different initial ARS and BCG concentrations at pH 3.
Rendering to the results given in Figure 7 and Table 4 and Table 5, the Freundlich isotherm led to higher \( R^2 \) values than the Langmuir, Tempkin and D-R isotherms, showing the heterogeneity of the adsorbent surface and a multilayer adsorption. The physical and chemical adsorptions occur for \( E < 8 \text{ kJ/mol} \) and \( E > 16 \text{ kJ/mol} \), respectively. As listed in Table 4, the \( E \) values of 0.36 and 0.102 \text{ kJ/mol} were obtained for the adsorption of ARS and BCG from aqueous media, respectively. Thus, it can be concluded that the adsorption of the pollutants by the HDTMA-Mt was of physical nature.

![Figure 7: Freundlich isotherm model for the adsorption of ARS and BCG by HDTMA-modified Mt.](image)

These data are similar to others reported for the adsorption of ARS on various adsorbents including nanocrystalline \( \text{Cu}_{0.5}\text{Zn}_{0.5}\text{Ce}_3\text{O}_5 \) (Jadhava, Khetre, and Bamane 2011), coconut shell (Wagh and Shrivastava 2014), mint waste (Ahmad and Kumar 2008) and cynodon dactylon (Samusolomon and Martin Devaprasath 2011) and for BCG adsorption onto cadmium hydroxide loaded on activated carbon (Ghaedi et al. 2012), granite (Kadhim 2012) and \( \text{Ziziphus nummularia} \) (Shokrollahi et al. 2011).

In the present study, the maximum adsorption capacities of HDTMA-modified Mt for ARS and BCG dyes were 666.6 and 1250 \text{ mg/g}, respectively. The comparison of these values to those reported for other adsorbents show that HDTMA-Mt can be considered as a very effective adsorbent for the removal of ARS and BCG dyes from liquid phases (Table 6).

### Table 6: Comparison of the maximum monolayer adsorption capacities of various adsorbents from literature with the present study.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Ads-</th>
<th>Equi-</th>
<th>( Q_m )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive stone</td>
<td>ARS 72 h</td>
<td>16.01</td>
<td>Albadarin and Mangwandi (2015)</td>
<td></td>
</tr>
<tr>
<td>Coconut shell</td>
<td>ARS 120 min</td>
<td>19.6</td>
<td>Wagh and Shrivastava (2014)</td>
<td></td>
</tr>
<tr>
<td>Cynodon dactylon</td>
<td>ARS 60 min</td>
<td>23.80</td>
<td>Samusolomon and Martin Devaprasath (2011)</td>
<td></td>
</tr>
<tr>
<td>AC-modified by iron oxide</td>
<td>ARS 90 min</td>
<td>32.7</td>
<td>Feng et al. (2011)</td>
<td></td>
</tr>
<tr>
<td>Mint waste</td>
<td>ARS 180 min</td>
<td>94.59</td>
<td>Ahmad and Kumar (2008)</td>
<td></td>
</tr>
<tr>
<td>AMNS</td>
<td>ARS 50 min</td>
<td>200.0</td>
<td>Li et al. (2011)</td>
<td></td>
</tr>
<tr>
<td>HDTMA-Mt</td>
<td>ARS 40 min</td>
<td>666.6</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Granite</td>
<td>BCG60 min</td>
<td>2.11</td>
<td>Kadhim (2012)</td>
<td></td>
</tr>
<tr>
<td>( \text{Ziziphus nummularia} )</td>
<td>BCG8 min</td>
<td>6.21</td>
<td>Shokrollahi et al. (2011)</td>
<td></td>
</tr>
<tr>
<td>( \text{Cd(OH)}_2\text{-NW-AC} )</td>
<td>BCG10 min</td>
<td>108.7</td>
<td>Ghaedi et al. (2012)</td>
<td></td>
</tr>
<tr>
<td>HDTMA-Mt</td>
<td>BCG20 min</td>
<td>1250</td>
<td>This study</td>
<td></td>
</tr>
</tbody>
</table>
ARS = Alizarin Red S.
BCG = Bromocresol Green.

4 Conclusion

In this work, hexadecyl trimethyl ammonium bromide-modified montmorillonite (HDTMA-modified Mt) was applied as an appropriate adsorbent for the removal of two anionic dyes, Alizarin Red S (ARS) and Bromocresol Green (BCG), from aqueous solutions. The influences of some parameters, such as surfactant-loading rate, contact time, pH, adsorbent dosage and initial dye concentration on dye adsorption were investigated. Experimental data appeared to be accurately described by the pseudo-second-order kinetic and the Freundlich isotherm models. The results illustrated that HDTMA-modified Mt can be used as an effective, low cost, eco-friendly and non-toxic adsorbent for the removal of ARS and BCG from aqueous solutions.

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References


