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Synthesis and Characterization of Solid-state Fe-exchanged nano-Bentonite and Evaluation of Methyl orange Adsorption

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Abstract

A new adsorbent was synthesized using ion-exchange between iron salts and bentonite modified with acetyl trimethylammonium bromide (CTAB) in the solid phase. Ion exchange was performed in the solid-state at a temperature of 100 °C for 2 min. Various analyzes such as X-ray diffraction (XRD), scanning electron microscopy (SEM), porosity measurement (BET), infrared Fourier transform (FT-IR), transmission electron microscopy (TEM), X-ray energy diffraction (EDX), and thermal weighing (TGA) were used to characterize the synthesized nano-adsorbents. Under optimal conditions (pH = 7, time 60 min, concentration of dye solution 150 ppm, and amount of nano-adsorbent 0.75 g / l), the modified nano-adsorbent absorbed 73% of the methyl orange (MO) dye. Adsorption isotherm studies and kinetic model showed that the pseudo-second-order model and Langmuir equation agree with the obtained results. After three reductions of the modified nano-adsorbent in the photo-Fenton process, the dye absorption percentage was 69.50%.

Keywords: Solid-state ion exchange adsorption, Surfactant, Modified bentonite with iron, Photo-Fenton
1. Introduction

Environmental pollution is one of the global problems that affect biodiversity, ecosystems, and human health. One of the most challenging groundwater contamination problems is paint. Despite limited water resources, the treatment of industrial dye effluents is essential. Dye effluents reduce the penetration of sunlight into the water due to the formation of a visible layer above the water surface and affect photosynthesis, which is a threat to aquatic life (Chacko et al. 2011). Their contact with the skin irritates and causes shortness of breath when inhaled (Nguyen et al. 2013). Methyl orange (MO) is one of the most common water-soluble azo dyes widely used in various industries, including textile, cosmetics, paper, printing, and food industries (Zayed et al. 2018). Its effluents are mostly discharged in industrial wastewater. The acute toxicity of MO dyes is caused by oral ingestion and inhalation, and it is carcinogenic (Lellis et al. 2019). As MO dye is not easily decomposed and resistant to light and washing, it is essential to separate it from the effluent (Yu and Luo 2014; Ghaedi and Mosallanejad 2014).

Dye effluents can be treated by biological, chemical, and physical methods (Tang et al. 2018). Nanofiltration, ultrafiltration, membrane filtration, reverse osmosis, and adsorption are among the physical methods of dye effluents treatments. Among the mentioned techniques, adsorption has been widely considered by researchers due to its simplicity and availability (Gong et al. 2011; Agarwal and Singh 2017). Adsorption is a process for separation without the need for special equipment and high electrical energy. This mass transfer process from the effluents to the solid adsorbent is easy to design and does not produce hazardous by-products (Yagub et al. 2014; Rafatullah et al. 2010; Bouabidi et al. 2018). Another feature of the adsorption process is the possibility of regenerating the adsorbent. Today, by identifying low-cost adsorbents, this method is an economical way to remove dye effluents (Ahmad et al. 2015; Mojsov et al. 2016).

Adsorption capacity and surface area are the most critical characteristics of adsorbents. Bentonite is an aluminum phyllosilicate clay consisting of montmorillonite (and a small
amount of beidellite depending on the sources). Bentonite structure consists octagonal
aluminum layer sandwiched between two quadrilateral silica layers, which give a high aspect
ratio to it (Alexandre et al. 2009; Ballav et al. 2018). Bentonite can be used in a wide range of
applications due to its high porosity, high viscosity, high ion exchange capacity
(Ahmaruzzaman 2008; Doulia et al. 2009). One of the advances in nanomaterials is the use of
nano-adsorbents to remove industrial effluents. They are more efficient than traditional
adsorbents (Liu et al. 2008; Singh et al. 2011; Simelane et al. 2016; Fosso-Kankeu et al. 2016).
To increase the adsorption capacity of bentonite; can be used thermal activation (Al-Asheh et
al. 2003), acid activation (Hussin et al. 2011), ion exchange (Hadjltaief et al. 2014), Simultaneous modification with surfactant (Huang et al. 2017) and pillaring (Ma et al. 2005).
The presence of iron oxide nanoparticles on nanolayers makes it possible to regenerate the
prepared adsorbent in the photo-Fenton process (Khelifi and Ayari, 2019). In the process of
photo-Fenton reduction, organic dyes adsorbed on the adsorbent, in the presence of hydrogen
peroxide and ultraviolet light, bind to produced hydroxyl radicals, which leads to the
degradation of organic dyes and the production of water, carbon dioxide, and other chemical
compounds (Babuponnusami and K. Muthukumar 2014). In this study, bentonite nanolayers
were selected as the adsorbent, and CTAB was used to increase the d-spacing between its
layers. The photo-Fenton process was used to regenerate the adsorbent, and acceptable results
were obtained. At each stage of surface modification, X-ray diffraction (XRD), Energy
Dispersive X-ray (EDX), Brunauer-Emmett-Teller (BET) surface area, thermal gravimetric
analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) analyzes were used to
prove the successful process and the effect of MO and initial MO concentration, contact time
and adsorbent amount on adsorption performance was investigated. Also, isotherms and
adsorption kinetics were studied, and thermodynamic studies were used to investigate the
adsorption process.
2. Experimental

Bentonite (B, the surface area of 85.03 m$^2$/g, basal spacing of 1.40 nm, and moisture content of $\leq$ 10.00 wt.%) kindly provided by Kanysazejam Co. Cetyltrimethylammonium bromide (CTAB, $\geq$98 %), Iron(II) chloride tetrahydrate (FeCl$_2$.4H$_2$O, $\geq$99%), Hydrogen peroxide (H$_2$O$_2$, 30% w/v), Chloridric acid (HCL, 37%), Sodium hydroxide (NaOH, $\geq$99%), Methyl orange (MO) were purchased from Merck.

According to procure (Huang et al. 2017; Darvishi and Morsali 2011), the 4 g of bentonite; was dispersed in 200 ml deionized water (20 g/L) under vigorous stirring for 72 hr. In the next step, 100% cation exchange capacity of the bentonite; CTAB was added to the mixture. After ultrasonication with acoustic intensity of 400 W for 30 minutes at 50 °C, the resulting slurry was washed and centrifuged (at 6000 rpm) three times to remove bromide ion. Then it was dried at 50 °C for 24 hr, and the obtained pretreated Bentonite; was named B-CTAB. For pillaring, 0.5 g of B-CTAB was sonicated with 1 g of FeCl$_2$.4H$_2$O in the aqueous phase, then the mixture was centrifuged three times with distilled water to ensure the removal of residual ions, and finally dried at 50 °C overnight. The dried powder was collected and named B-CTAB-Fe. The color of B-CTAB changed from white to cream during the pillaring process.

Transmission electron microscopy was performed by a Phillips EM 208 S 100 kV. The bentonite samples were embedded and then cut with an ultramicrotome into layers with 60–100 nm thickness, which were cryo-ultramicrotome at $-145$ °C with a diamond knife cooled at $-60$ °C. Morphology of samples was analyzed by a scanning electron microscope (SEM) (LEO model 1430 VP, England) equipped with a backscattered electrons detector. Before analysis, all samples were coated with a thin layer of gold-palladium using an Edwards S-150 sputter coater (Wilmington, Massachusetts, USA). The elements in the samples were observed using energy dispersive spectroscopy (EDS) (Mira 3-XMU, Berno, Czech Republic). Samples X-ray
Diffraction (XRD) patterns were collected on an Intel, France, EQUINOX 3000 X-ray diffraction with Cu K-α radiation while the accelerating voltage and applied currents were 40 kV and 30 mA, respectively. Thermal gravimetric analyses (TGA) of the prepared polymers and composites were performed on a LENSES STAPT-1000 instruments (Linseis STA PT1000, Selb, Germany) using about 4 mg of material as a probe. The samples were heated up to 700 °C with a heating rate of 10 °C·min⁻¹. The residue in the N₂ atmosphere at 700 °C consider as the inorganic content of samples. The FT-IR spectrum of the samples was recorded in the region 4000–400 cm⁻¹ using a spectrum 400 instrument (PerkinElmer Inc., USA). The Brunauer-Emmett-Teller (BET) surface area measurements of bentonite samples were performed on BELSORP-mini, Bell Japan, Inc. To compare the percentage of methyl orange dye removal and the adsorption capacity of the samples, different amounts of adsorbents (B, B-CTAB, or B-CTAB-Fe) were added to 40 ml of seven different MO concentrations (20, 75, 100, 125, 150, 175 and 200 ppm) and then placed on a shaker for 2 hours. Absorbent concentration in MO water solution was varied from 0.25 to 4.5 g·L⁻¹. To evaluate the effects of the pH, temperature, and time on the absorption process, different pH (ranging from 2 to 9), temperature (303, 313, and 323), and absorption time (from 5 to 120 min) values were used in experiments. After 60 minutes, the mixture was centrifuged at 60,000 rpm. Dye removal percentage was calculated using Eq. 1.

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

(1)

where \(c_0\) and \(c_e\) denote the MO concentration (mg·L⁻¹) at initial and equilibrium time, respectively. Also, the equilibrium capacity (\(q_e\)) was calculated using Eq. 2.

\[
q_e = \frac{c_0 - c_e}{M} \times V \quad \text{(mg/ g)}
\]  

(2)

where \(M\) is the weight of absorbent (g), and \(V\) is the volume of the solution (L).
After adsorption under optimal conditions (0.75 g L$^{-1}$ of B-CTAB-Fe was mixed with 150 ppm of MO at pH=7 for 60 min), the photo-Fenton process was used to reduce B-CTAB-Fe nano-adsorbent. The B-CTAB-Fe separating by centrifugation at 6000 rpm, then dispersed in 40 ml of distilled water, and the pH of the mixture was reached 4. The mixture was introduced into a photoreactor and placed on a magnetic stirrer. The reduction process was performed by adding H$_2$O$_2$ (22.5 mM) and turning on the UVC lamp (4 W, Philips) for 90 min. The reduced B-CTAB-Fe was separated by centrifugation and dried at 50 °C in an oven for 24 hours for reuse.

3. Results and Discussion

The XRD pattern of B, B-CTAB, and B-CTAB-Fe is shown in Fig. 1. The main peak in the XRD pattern of bentonite; appeared at 36.82° and the peak at 20.08°, corresponding to the structural feature of smectites (De-León et al. 2017). Also, the peaks at 2θ=21.01°, 26.80°, and 42.73° are related to the quartz mineral in bentonite (Khatamian et al. 2019). In this pattern, the peak d$_{001}$ has changed from 2θ=6.28° for B to 2θ=5.30° for B-CTAB. The d-space between the bentonite layers (d$_{001}$) increased from 1.40 nm to 1.66 nm for the surface-modified modified sample (B-CTAB). Ion exchange between the surfactant and bentonite; has increased the distance between the layers (Dos-Santos et al. 2018). The reason for such an increase is the replacement of the long CTAB alkyl chain with cations located between the bentonite layers (Huang et al. 2017). In the B-CTAB-Fe XRD pattern, no characteristic peak related to d-space is observed. The absence of a peak in d001 indicates a very irregularly formed structure called clay exfoliation. So, the layers are delaminated by the polarization, and it seems to be no aggregated layers in its structures (Chen et al. 2017; Chen et al.1995; Yuan et al. 2006).

SEM images of B, B-CTAB, and B-CTAB-Fe are shown in Figure 2. Bentonite aggregates have a smooth, irregular surface (2a). Bentonite sample after CTAB treatment and sonication forms collapsed structure with more irregularity. Also, in Figure 2b, bentonite nanosheets are
primarily broken. Figure (2c) shows the morphology of nanosheets after the iron nanoparticle’s entrance. As shown in figure (2d) TEM image of sample B-CTAB-Fe confirms the entry of iron nanoparticle’s into the gallery of clay nanosheets. The TEM image next to the X-ray patterns shows the exfoliation of the clay. Also, the TEM image proves that the synthesis method of B-CTAB-Fe has been successful, and the iron salt has been able to enter the nanometer distance between the clay plates in two minutes at temperature, close to its melting temperature, and the pillaring process has been performed successfully. The darker parts of the images show iron oxide nanoparticles, which are denser and restrict the passage of electrons.

According to the results of Table 1, calcium is present in the interlayer structure of primary bentonite. In the B-CTAB sample, there is 5.41% carbon and no calcium, which indicates that the cation exchange in the B-CTAB sample is complete, and calcium has been removed from the bentonite layers (Dos-Santos et al. 2018). Also, the removal of negative bromide ions indicates proper and sufficient washing and centrifugation. In the B-CTAB-Fe sample, iron ions and the absence of chloride ions indicate the success of iron entry into the bentonite structure and proper washing after the modification process. In the bentonite modification process, iron oxide nanoparticles were exposed to the B-CTAB sample for two minutes. This time is shorter than other studies in the liquid phase (Chen et al. 2017; Hadjltaief et al. 2014). The low time required in this method for complete removal of calcium and the entry of the surfactant CTAB and the entry of iron oxide nanoparticles into the interlayer space of bentonite; indicates the efficiency of this method.

According to BET results (Table 2), the surface area of bentonite; decreased by 49.15 m$^2$/g after modification with CTAB. The reduction in pore size and volume in the B-CTAB sample is due to the entry of CTAB organic molecules, which leads to the overlap of the nanolayers surface and blocked interlayer channels (Huang et al. 2017). Such a decrease can be attributed to the reduced access of nitrogen molecules to the inner surfaces of nanosheets during the
adsorption process (Dos-Santos et al. 2018; Deniz and Karaman, 2011). In the pillaring process, the specific surface area is reduced by placing oxidized iron nanoparticles in the bentonite structure and closing more cavities. According to FTIR spectra (Fig. 3), in all samples, the absorption band occurring at 3,624 cm\(^{-1}\) was due to the stretching vibration of the hydroxyl groups of water adsorbed in the bentonite structure (Tyagi et al. 2006). The absorption band at 1,640 cm\(^{-1}\) was the characteristic of bending vibration of the OH group of water molecules between the bentonite layers (Zhang et al. 2010). The strong absorption band at 1,037 cm\(^{-1}\) in the bentonite sample is related to the Si-O stretching vibration. The absorption band at 797 cm\(^{-1}\) is also related to the stretching vibration of Al-O (Li et al. 2016). The absorption peak at 522 cm\(^{-1}\) is related to the layer vibration of the Al-O-Si network (Yan et al. 2016). The absorption peak at 466 cm\(^{-1}\) is attributed to the layer vibration of the Si-O-Si network (Moslemizadeh et al. 2016). Figure 3b shows the FT-IR spectrum of the B-CTAB sample. Absorption occurs at 2,928 cm\(^{-1}\) and 2,928 cm\(^{-1}\), subject to symmetric and asymmetric stretching vibrations -CH\(_2\) and -CH\(_3\) in the CTAB aliphatic chain (Huang et al. 2017). The presence of a new peak at 1,481 cm\(^{-1}\) is related to the flexural vibration of the methyl group (Schampera et al. 2016). FT-IR spectrum of B-CTAB-Fe shows that the heat of the pillaring process did not cause the CTAB degradation. The vibrational absorption peak of the Fe-O band, which should be observed at 1,020 cm\(^{-1}\), is covered by a strong montmorillonite peak (Ma et al. 2005).

The thermal stability of the samples was studied by TGA. Figure 4 shows TGA thermograms for B, B-CTAB, and B-CTAB-Fe samples. The weight loss of bentonite; (5.28%) in the temperature range of 40 to 150 °C is due to water evaporation absorbed between the bentonite layers (Ma et al. 2005; Gourouza et al. 2011). Mass reduction of bentonite in the temperature range of 550 to 700 °C (0.92%) mass is related to bentonite dehydroxylation (Bounab et al. 2017). This high-temperature range causes the crystalline structure of bentonite; to fail. The
weight reduction of the B-CTAB sample (33%) from ambient temperature to 150 °C is due to the loss of absorbed water on the surface and between the layers (Dos-Santos et al. 2018). This amount is lower than unmodified bentonite; because some of the absorbed water in the sample was removed by the CTAB modification process. In the TGA graph, from 100 to 500 °C, both B-CTAB and B-CTAB-Fe samples have a mass reduction of about 10.16 % is due to the entry of the surfactant into the bentonite structure. The organic structure of CTAB decomposes in this temperature range (Ma et al. 2005). The presence of a peak in this temperature range is also a confirmation of the success of bentonite treatment with CTAB. In the temperature range of 500 to 700 °C, a mass reduction of 3.52 can be observed, caused by the loss of OH groups in the silicate layers (Ma et al. 2005).

The effect of pH on the adsorption of MO onto B-CTAB-Fe was shown in Fig. 5. The lowest and highest percentages of dye removal were obtained at pH 2 and 7, respectively. At acidic pH, due to the positive surface of the nano-adsorbent and the presence of H⁺ ions, the electrostatic repulsion force between them does not allow dye removal to the nano-adsorbent surface. Because in the competition between H⁺ ions and the positive surface of the nano-adsorbent, the MO (anion dye) is absorbed by H⁺ acid ions. Therefore, with increasing pH and decreasing acidity, dye removal by nano-adsorbent increases. At pH above 7, due to OH⁻ positive ions, the nano-adsorbent surface is covered by these small ions. As a result, the electrostatic repulsion force between the negative MO ions and the negatively absorbed surface charge decreases the dye removal percentage.

The optimum pH value was considered 7 for adsorption experiments. The results showed that with increasing MO concentration, the equilibrium adsorption capacity has an upward trend (Figure 6). Above 150 ppm, due to the saturation of adsorption sites on nanosheets, adsorption efficiency decreases.
The effect of contact time on the amount of MO adsorption with a concentration of 150 ppm and a pH of 7 is shown in Figure 7. The presence of empty adsorption sites on the nano-adsorbent surface in the early times increases the adsorption rate. The time of 60 minutes can be seen as the equilibrium time of absorption. The percentage of MO removal by bentonite, B-CTAB and B-CTAB-Fe is 46.8%, 76.88%, and 73.18%, respectively. The B-CTAB-Fe sample is less adsorbed than the B-CTAB sample (approximately 3%) due to the presence of oxidized iron nanoparticles in its structure.

Figure 8 shows the effect of changing the amount of B-CTAB-Fe from 0.25 - 4.5 g/lit at pH = 7, time 60 minutes, and concentration of 150 ppm. With increasing the amount of nano-adsorbent and increasing the number of active sites, the effluent deposition on the nano-adsorbent surface has increased. The slope of the changes varies from 0.75 g/l onwards. A concentration of 0.75 g/lit is likely to be optimal for the availability of active adsorbent sites. Absorption isotherms such as Langmuir and Freundlich were used to describe the relationship between the initial concentration of colored effluent and the amount of adsorbed effluent. The linear form of the Langmuir equation (Eq. 3) and Freundlich equation (Eq. 4) is as follows:

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{Q_m k_L} \cdot \frac{1}{c_e}$$

$$\log q_e = \log k_f + (1/n) \log c_e$$

$q_e$ (mg/g) is the amount of dye adsorbed for a given amount of adsorbent at equilibrium. $k_L$(mg/L) is Langmuir adsorption equilibrium constant. $Q_m$ (mg/g) is the maximum amount of adsorption in the monolayer formation state, and $c_e$ (mg/L) is the equilibrium concentration of the dye. $k_f$ and $n$ are Freundlich absorption constants. The other parameters of Eq. 4 are the same as Eq. 3. The Freundlich equation is used for heterogeneous systems, irreversible adsorption, and non-monolayer adsorption. In comparison, the Langmuir adsorption isotherm is suitable for homogeneous surface and monolayer adsorption (Nataša et al. 2008). The basic
properties of the Langmuir equation can be expressed by a dimensionless constant called the Langmuir $R_L$ equilibrium parameter (Eq. 5).

$$R_L = \frac{1}{1+K_L C_0}$$  \hspace{1cm} (5)

Where $C_0$ (mg/L) is the initial concentration of the adsorbent and $K_L$ (L/mg) is the Langmuir constant. The results of the sample absorption model are shown in Table 3. According to the data, the Langmuir isotherm diagram has a better regression coefficient than the Freundlich isotherm. Therefore, the Langmuir adsorption model is better suited to describe the adsorption of MO on the adsorbent. The results show that the surface of the synthesized adsorbents is homogeneous, and the available sites are uniformly present on the adsorbent surface. Given the value of $R_L$ between zero and one, it can be concluded that the adsorption process is optimal for all three adsorbents. According to the results, the addition of CTAB has improved $q_{\text{max}}$ and $k_l$. Although the addition of iron slightly reduces $q_{\text{max}}$ and $k_l$, it adds regenerative properties to the adsorbent.

Since the adsorption kinetics of industrial effluent is an essential parameter in evaluating the effect of adsorbent, two kinetic models, pseudo-first-order and pseudo-second-order, were used to examine the data. The pseudo-first-order adsorption kinetics model has already been used for the adsorption of solid/liquid systems (Zaghouane-Boudiaf 2014). These models are Eq. 6 and 7.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$$  \hspace{1cm} (6)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (7)

Where $k_1$ (min$^{-1}$) is the adsorption rate constant, $q_e$, and $q_t$ (mg/g) are the adsorbent adsorption capacity at equilibrium time, $t$ (s) time, and $k_2$ (g.mg$^{-1}$ min$^{-1}$) are the adsorption rate constant. Figure 9 shows the agreement of the experimental data with the kinetic models. These results are summarized in Table 4. The correlation coefficient for all three adsorbents is higher in the
pseudo-second-order equation. Also, the values of $q$ obtained from the pseudo-second-order
equation for all three types of adsorbents are more consistent with the values obtained with
$q_{\text{exp}}$.

The thermodynamics of the adsorption process were studied using Equations 8 to 11.

$$G^\circ = -RT \ln K_C$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$K_C = \frac{c_{Ae}}{c_e}$$

$$\ln K_C = + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$K_C$ is the ratio of the equilibrium concentration of the adsorbent surface $c_{Ae}$ (mg/g) to the
equilibrium concentration of the effluent in the solution $c_e$ (mg/g). $T$ (K) is the absolute
temperature, and $R$ (J/mol.K) is the gas constant. The data in Table 5 are obtained by
considering $pH = 7$, time 60 min, the concentration of dye solution 150 ppm, and amount of
nano-adsorbent 0.75 g/l at three different temperatures. According to the results, enthalpy and
entropy are positive, so the adsorption of methyl orange by the modified nano-adsorbent is an
endothermic process, and with increasing temperature, the amount of colored effluent
adsorption on the nano-adsorbent surface increases. A positive entropy value indicates that the
randomness of the interface between the nano-adsorbent and the methyl orange dye solution
increased during the adsorption process, indicating that structural changes occurred between
the active nano-adsorbent sites the methyl orange dye solution (Uslu and Tanyol 2006; Abbasa
and Trari 2015). According to Table 5, the negative amount of Gibbs free energy shows the
spontaneity of the adsorption process for the synthesized nano-adsorbent (Eser et al.2012).

Re-recycling of B-CTAB-Fe nano-adsorbent was performed by photo-Fenton. The adsorbed
organic compounds on the adsorbent were bonded to the produced hydroxyl radicals and
converted to $CO_2$, $H_2O$, $SO_4^{2-}$ and $NO_3^-$ then separated from the adsorbent surface, resulting in
a white nano-adsorbent free of organic compounds. The percentage of dye removal efficiency
by B-CTAB-Fe nano-adsorbent was 72.61% in the first recycling, 71.48% in the second time, and 69.50% in the third time. Yield percentages after three times recycling indicate that the nano-adsorbent is well recycled in the photo-Fenton process.

4. Conclusion

Under optimal conditions (pH = 7, time 60 min, concentration of dye solution 150 ppm and amount of nano-adsorbent 0.75 g / l), maximum adsorption capacity and removal percentage were obtained. Data from the photo-Fenton method for regenerating synthesized B-CTAB-Fe nano-adsorbent showed that solid-state ion exchange bentonite with iron could be used as an effective nano-adsorbent.

Ethical Approval: Not applicable

Consent to Participate: Not applicable

Consent to Publish: Not applicable

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Table 1. Chemical composition of the Bentonite, B-CTAB, and B-CTAB-Fe.

| Element | Bentonite | B-CTAB | B-CTAB-Fe |
|---------|-----------|--------|-----------|
| O       | 55.19     | 57.15  | 55.04     |
| Mg      | 1.58      | 1.29   | 1.20      |
| Al      | 8.10      | 6.34   | 6.39      |
| Si      | 32.80     | 28.17  | 29.33     |
| K       | 0.79      | 0.97   | 0.63      |
| Ca      | 0.61      | 0      | 0         |
| Fe      | 0.92      | 0.67   | 2.58      |
| C       | 0         | 5.41   | 4.83      |
Table 2. Chemical composition of the Bentonite, B-CTAB, and B-CTAB-Fe.

| Sample       | Surface area (m²/g) | Pore size (nm) | Pore volume (cm³/g) |
|--------------|---------------------|---------------|---------------------|
| Bentonite    | 85.03               | 1.66          | 0.11                |
| B-CTAB       | 35.88               | 1.66          | 0.05                |
| B-CTAB-Fe    | 25.26               | 1.88          | 0.04                |
Table 3. Isotherm parameters analysis coefficient for the adsorption of MO onto B, B-CTAB, and B-CTAB-Fe

| Isotherm constants | B      | B-CTAB | B-CTAB-Fe |
|--------------------|--------|--------|-----------|
|                    | Langmuir |        |           |
| $q_m$(mg/g)        | 181.8181| 212.7659| 208.3333  |
| $K_L$(L/mg)        | 0.0114  | 0.0570  | 0.0402    |
| $R^2$              | 0.9895  | 0.9906  | 0.9744    |
| $R_L$              | 0.3048  | 0.0806  | 0.1106    |
|                    | Freundlich |        |           |
| $K_f$(mg^{-1}(L/n)g^{-1}L^{1/n}) | 6.4387 | 31.4195 | 21.8172   |
| $n$                | 1.7056  | 2.4943  | 2.1431    |
| $R^2$              | 0.9443  | 0.8885  | 0.9044    |
Table 4. Kinetic models parameters obtained in adsorption of MO onto B, B-CTAB, and B-CTAB-Fe

| Dynamics constants | B         | B-CTAB    | B-CTAB-Fe |
|--------------------|-----------|-----------|-----------|
|                    | Pseudo-first-order |          |           |
| $q_e$ (mg/g)       | 38.1416   | 82.3948   | 79.2318   |
| $k_1$ (min$^{-1}$) | 0.0430    | 0.0506    | 0.0449    |
| $R^2$              | 0.8965    | 0.9581    | 0.9309    |
|                    | Pseudo-second-order |        |           |
| $q_e$ (mg/g)       | 98.0392   | 161.2903  | 153.8461  |
| $k_2$ (g.mg$^{-1}$.min$^{-1}$) | 0.0052    | 0.0021    | 0.0019    |
| $R^2$              | 0.9995    | 0.9991    | 0.9988    |
| T(K) | Kc  | ΔG°(KJ/mol) | ΔH°(KJ/mol) | ΔS°(J/mol.K) |
|------|-----|-------------|-------------|--------------|
| 303  | 6.94| -4.78       |             |              |
| 313  | 8.28| -5.48       | 13.37       | 60.23        |
| 323  | 11.12| -6.08       |             |              |
Figure 1

The XRD pattern of B, B-CTAB, and B-CTAB-Fe
Figure 2

SEM images of B, B-CTAB, and B-CTAB-Fe
The absorption peak at 466 cm$^{-1}$ is attributed to the layer vibration of the Si-O-Si network (Moslemizadeh et al. 2016).
Figure 4

The thermal stability of the samples was studied by TGA.
Figure 5

The effect of pH on the adsorption of MO onto B-CTAB-Fe
The optimum pH value was considered 7 for adsorption experiments. The results showed that with increasing MO concentration, the equilibrium adsorption capacity has an upward trend.
Figure 7

The effect of contact time on the amount of MO adsorption with a concentration of 150 ppm and a pH of 7
The B-CTAB-Fe sample is less adsorbed than the B-CTAB sample (approximately 3%) due to the presence of oxidized iron nanoparticles in its structure.
Figure 9

Where $k_1$ (min$^{-1}$) is the adsorption rate constant, $q_e$ and $q_t$ (mg/g) are the adsorbent adsorption capacity at equilibrium time, $t$ (s) time, and $k_2$ (g.mg$^{-1}$ min$^{-1}$) are the adsorption rate constant.