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Removal of Acidic Dye from Aqueous Solution Using Surfactant Modified Bentonite (Organoclay): Batch and Kinetic Study

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ABSTRACT

Modified bentonite has been used as effective sorbent material for the removal of acidic dye (methyl orange) from aqueous solution in batch system. The natural bentonite has been modified using cationic surfactant (cetyltrimethyl ammonium bromide) in order to obtain an efficient sorbent through converting the properties of bentonite from hydrophilic to organophilic. The characteristics of the natural and modified bentonite were examined through several analyses such as Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Surface area. The batch study was provided the maximum dye removal efficiency of 88.75 % with a sorption capacity of 555.56 mg/g at specified conditions (150 min, pH= 2, 250 rpm, and 0.5 g/100 ml). The results showed that with the Freundlich isotherm model the sorption data was accurately described with (R²≥0.94) in comparison with the Langmuir model under the studied conditions. The kinetic studies were revealed that the sorption follows a pseudo-second-order kinetic model which indicates chemisorption between sorbent and sorbate molecules.

Keywords: methyl orange dye; modified-bentonite; sorption; isotherm; kinetic.

إزالة الصبغة الحامضية من المحلول المائي باستخدام البنتونيت المعدل: دراسة دفعية وحركية

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الخلاصة

تم في هذه الدراسة تم استخدام مادة البنتونيت المعدل كمواد مازة منخفضة التكلفة وفعالة لإزالة الصبغة الحامضية (الميثيل البرتقالي). تم تعديل البنتونيت الطبيعي باستخدام منشط السطح الموجب (cetyltrimethyl ammonium bromide CTAB) لتكوين مادة ممتزة فعالة من خلال تحليل طبيعتها من مادة محبة للماء إلى مادة محبة للمواد العضوية. تم فحص خصائص 

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64
البنتونايت الطبيعية والمعدلة من خلال العديد من التحليلات مثل المسح المجهرى الإلكتروني (SEM) وقياس الطيف بالأشعة تحت الحمراء (FTIR) والمساحة السطحية. تم الحصول على كفاءة لإزالة الصبغة تبلغ 88.75% مع قدرة امتصاص تبلغ 55.56 ملغم / غم في ظروف محددة (150 درجة، 200 دقيقة في الدقيقة، و 0.5 غم / 100 مل). ووضعت النتائج أن وتوضح تسمى سمود (R2≥0.94) بالمقارنة مع pseudo-second-order kinetic model في ظل الظروف المدروسة. وقد كشفت الدراسات الحركية أن الامتصاص يتبع Langmuir model يفسر الامتصاص الكيميائي بين جزيئات المادة المازه والممتزة بالكلمات الرئيسية: صبغة المثيل البرتقالي, البنتونايت المعدل. الأيسوثرم. الأيسوثرم. الأيسوثرم. الحركية.

1. INTRODUCTION

Water is one of the most important sources which man has availed for support of his life. Water can be regarded as polluted when its composition or quality changes or according to human activities(Alexander, et al., 2019). Due to the rapid increase in population and industrial activities, water demand doubles globally every 21 years. This is compounded by the decrease in the preceding decade (Concerns, 2013). In recent years, widespread water contamination by synthetic organic chemicals such as dyes has been recognized as a growing issue (Leodopoulos, et al., 2015). Methyl orange (MO) is one of the recognized acidic/anionic and non-biodegradable dye, it has a different structure depends on the acidity. It is an anionic dye belongs to the azo group of dyes. The presence of azo group (R-N=N-R) long chains of conjugation which allows them to be chromophores on MO and low biodegradability makes it an issue of concern for environmental science (Aziztyana, et al., 2019). In addition, the azo dyes that are very toxic can produce several environmental pollution problems by releasing toxic and carcinogenic compounds in the waters. It can cause cancer, contact dermatitis, skin irritation, tearing, exophthalmos, permanent blindness, acute tubular necrosis, gastritis, rhabdomyolysis, hypertension, toxic when swallowed and respiratory distress (Chung, 2016).

A number of chemical, physical and biological technologies have been developed to reduce color in effluent streams such as, flocculation-coagulation, membrane separation, oxidation, ozonation, sedimentation, flotation, reverse osmosis, precipitation and aerobic or anaerobic treatment. Furthermore, these processes are found to be infeasible for an industrial application due to low performance, high operating costs and environmental impact (Leodopoulos, et al., 2015). Adsorption is one of the common methods used in the treatment of wastewater for color removal due to its high efficiency, simplicity in operation and availability of a wide range of adsorbents. (Salleh, et al., 2011; Kant, 2012). Many low-cost adsorbents such as natural and modified clays have been successfully implemented for dyes adsorption from wastewater (Sarma, et al., 2015). Natural clay has gained popularity as low-cost adsorbents in recent decades due to its local and plentiful availability and the ability to endure modifications to improve surface area, adsorption efficiency and range of practical application (monvisade and siriphannon, 2009). The modification of clay surfaces enhances their adsorptive properties through converting its nature from hydrophilic to organophilic, Therefore, the modified of bentonite has high potential for alternate adsorbents to the most commonly used (Jiuhui, 2008). The main objective of this study is to evaluate the possible application of modified bentonite as inexpensive and effective adsorbent material for the removal of methyl orange dye from aqueous solutions using batch experiments.
2. MATERIALS AND METHODS

2.1 Materials

*Natural bentonite* used in this study was local Iraqi bentonite in natural form (calcium type). It was supplied by the State Company of Geological Survey and Mining, (Baghdad) as rock bits. These rocks were washed with distilled water several times, dried at 90°C, crushed in granules of various sizes, then sieved using sieves (type: Restch, Germany) To produce size granules of bentonite (250-500) µm. The physical characteristics of natural bentonite were analyzed in the laboratories of the State Company of Geological Survey and Mining as presented in Table 1.

*Methyl orange dye (MO) [Acid Orange, C14H14N3NaO3S, M.W. = 327.33 g.mol⁻¹, and λmax: 484 nm] supplied by Sigma Aldrich Chemise (Germany) has been used in this study. The aqueous solution of dye was prepared by dissolving a fixed quantity of dye in distilled water to achieve a concentration of 100 mg/L.

*Surfactant cetyltrimethyl ammonium bromide (CTAB) [C19H42Br, M.W. = 364.45 g.mol⁻¹] supplied by Interchimiques SA company (France) used to modify bentonite through converting its nature from hydrophilic to organophilic. Deionized water was used in all experiment. 0.1 mol/L HCl and NaOH was used for adjusting different pH.

**Table 1.** Characteristics of Iraqi Bentonite. (State Company of Geological Survey and Mining, Baghdad).

| Characteristics       | Value         |
|-----------------------|---------------|
| **Physical**          |               |
| Particle size, mm     | Pass 0.35     |
| Moisture content, %   | 4.57          |
| Bulk density, kg/m³   | 845           |
| Specific surface area, m²/g | 63.5        |
| CEC, meq/100g         | 65            |
| **Composition (wt%)** |               |
| Silica(SiO₂)          | 57            |
| Aluminum(Al₂O₃)       | 13.5          |
| Ferric oxide(Fe₂O₃)   | 4.5           |
| Magnesium oxide (MgO) | 2.35          |
| Calcium oxide(CaO)    | 8             |
| Sodium oxide(Na₂O)    | 0.7           |
| Potassium oxide(K₂O)  | 0.4           |
| Titanium oxide(TiO₂)  | 0.75          |
| Loss on ignition (L.O.I)| 12.8         |

2.2 Preparation of modified bentonite (organobentonite)

The organobentonite was prepared by adding 10 g of natural bentonite to 100mL of distilled water, then the mixture was stirring for 2 hr in order to swell and become homogeneous (Jeeva and Wan Yaacob, 2018). After that, the different amount of modified surfactant (0.05, 0.1, 0.2, 0.25, 0.3,
0.35, 0.4, 0.45 and 0.5g CTAB/1g natural bentonite) added to determine the best ratio of “CTAB/bentonite” that gives the highest MO removal efficiency. The mixture was stirred for 2 hr, the resulting organobentonite was filtered with (Whatman No. 40) and washed with distilled water several times to remove excess salts and afterward dried at 105 °C (Kıranşan, et al., 2014). The produced samples of the modified bentonite were ground and sieved with a size range from 250 to 500 µm. The sample with a specified amount of CTAB which achieves the highest MO removal percent will be adopted in subsequent experiments.

2.3 Characterization of organobentonite
The characteristics of the natural and modified bentonite were examined through several analyses as follows:

- **Fourier transform infrared spectroscopy (FTIR):** The study of FTIR enables spectrophotometric observation and provides means to identify functional groups on the sorbent surface. The spectrum analysis was carried out within the range 400–4000 cm⁻¹ using Bruker Tenso 27 spectrophotometer with the KBr pellet technique. It is achieved at the University of Baghdad, College of Science.
- **Scanning electron microscopy (SEM):** The bentonite surface morphology was tested by SEM (NOVASEM, FEL450L) analysis under 10 KV voltage and a 6-mA flux. This taste clarifies the changes in bentonite structural properties before and after CTAB modification.
- **Surface area:** Surface area is an important factor in determining the active sites that will be occupied with the contaminants. The specific surface area was determined by surface area analyzer the BET method from the nitrogen adsorption at 77 K, using an automatic Micrometrics ASTM D 3663, USA. It performed at the Ministry of Oil (Institute of Oil Training and Development).

2.4 Adsorption experiments
The adsorption of MO dye by modified bentonite was studied using batch experiments under different conditions, the removal experiments were carried out by adding the modified bentonite to 100 mL of the synthetic solution of MO with initial concentration of 100 mg/L, then the mixture was shaken using thermostatic shaker (Type LSI-3016A, Korea). Batch tests were implemented with different initial pH of the solution (2 - 12), contact time (10 - 240 min), agitation speed (50 - 300 rpm), sorbent dosage (0.05 - 0.7 g/ 100 mL). A fixed amount (25 mL) of the solution was taken from each flask, and filtered to separate the adsorbent from the aqueous solution using filter paper type (Whatman No. 40), then the filtered solution was analyses using double beam UV-visible spectrophotometer (PG Instruments, Model UV T80, Japan) at λmax = 484 nm to determine the remain MO concentration. The amount of pollutant (MO) adsorbed on modified bentonite, qe (mg/g), was calculated from the mass balance Eq. (1):

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

(1)

Where qe is the amount of MO adsorbed per unit adsorbent mass (mg/g), C₀ and Cₑ (mg/L) is the initial and equilibrium concentration of dye, m (g) is the adsorbent mass and, V (L)
is the volume of dye solution. The removal efficiency ($R\%$) of MO onto modified bentonite at time was calculated by:

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100$$  \hspace{1cm} (2)

### 3. Description of sorption data

Sorption isotherms are mathematical models that demonstrate the propagation of sorbate species between sorbent and liquid based on a set of presumptions linked primarily to the heterogeneity / homogeneity of sorbents (degree of coverage and potential interaction between the sorbate species). These isotherms related to the adsorption of pollutants per unit mass of sorbent, $q_e$, to the equilibrium concentration of sorbate in the bulk solution phase, $C_e$ (Hamdaoui and Naffrechoux, 2007; Abd, et al., 2019). The sorption data for MO is fitted with a linearized form of Langmuir and Freundlich isotherm models as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_e$$ \hspace{1cm} (Langmuir model) \hspace{1cm} (3)

$$lnq_e = lnK_F + \frac{1}{n}lnC_e$$ \hspace{1cm} (Freundlich models) \hspace{1cm} (4)

where $q_{max}$ is the maximum adsorption amount for the adsorbent (mg/g), $q_e$ is the amount of MO adsorbed on the adsorbent (mg/g) at equilibrium, $C_e$ the equilibrium MO concentration in solution (mg/L). $K_F$ (L/g) is the Freundlich sorption coefficient, $K_L$ is the Langmuir adsorption constant (L/mg) and $n$ is an empirical coefficient related to the intensity of the sorption. (Naji et al., 2019)

### 4. Sorption Kinetic Study

Kinetic sorption models are helpful to understand the mechanism of the sorption process of MO onto modified bentonite. These models include pseudo-first-order, pseudo-second-order as follows:

- **Pseudo-first-order rate equation:** is quantified by (Abd Ali, 2016):

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$ \hspace{1cm} (5)

Where $q_e$ is the amount of contaminant sorbed at equilibrium (mg/g), $K_1$ is the rate constant of pseudo first order adsorption (min$^{-1}$), and $q_t$ is the quantity of contaminant sorbed at time $= t$ (mg/g). Eq. (5) is integrated for the boundary conditions $q=0$ to $q=q_e$ and $t = 0$ to $t=t$.

- **Pseudo-second-order rate equation:** is based on adsorption equilibrium capacity can be expressed as (Saad et al., 2019)

$$\frac{dq_t}{dt} = K_2(q_e - q_t)(q_e - q_t)^2$$ \hspace{1cm} (6)
Where \( K_2 \) is the rate constant of pseudo second order adsorption \((g/mg.min)\). Taking into account, the boundary conditions \( q_t=0 \) to \( q_t=q_e \) and \( t=0 \) to \( t=t \). The integrated form of Eq. (6).

5. Result and discussion

5.1 Modification of bentonite

Modified bentonite was prepared by adding different ratios of surfactant \((g\, CTAB / 1g \, of \, natural \, bentonite)\). Figure showed the removal percent of MO from aqueous solutions as a function of adsorbent at different ratios of surfactant \((CTAB)\) for specific conditions \((Co=100 \, mg/L, \, time=180\, min, \, pH=7, \, agitation \, speed=200\, rpm, \, dosage=0.2g)\) at 25 °C. The results showed that the removal efficiency was increased with increasing the amount of CTAB because the positive charges of surfactant covered the surface of natural bentonite which lead to increase electrochemical interactions between the surface of modified clay and anionic dye molecules (Huang, et al., 2017; Jeeva and Wan Yaacob, 2018). Moreover, the natural bentonite was tested for the removal of MO from aqueous solution; it found that the modified bentonite was 4.9 times adsorption capacity than natural bentonite. This was due to the fact that the spacing of the bentonite layer increased after modification and the bentonite hydrophilic surface converted to hydrophobic to increase adsorptive properties (Mierczynska-Vasilev and Smith, 2016). The samples of modified bentonite that achieve the higher removal percent \((0.5 \, g \, CTAB/1g \, NB)\) will be adopted for removal of dye from contaminated water in all subsequent experiments.

![Figure 1. Effect of the ratio of CTAB/bentonite for the adsorption of MO.](image-url)
5.2 Characterization of bentonite

- **FTIR analysis:** The FTIR spectra of natural and modified bentonite before and after sorption of MO were shown in Fig. 2. The FTIR spectrum of natural bentonite (NB) showed that the characteristic smectitic bentonite mineral peaks at 462, 532, 792, 1633, 2328, 2926, 3400, 3632, 3681, 3699 and 3905 cm\(^{-1}\) (Zhang, et al., 2019). While the organic matter in modified bentonite showed peaks at 2848 and 2933 cm\(^{-1}\) that are sharper than those of the natural bentonite, were assigned to the CH\(_2\) scissor vibration band and the symmetrical CH\(_3\) stretching absorption band respectively. The groups CH\(_3\) and CH\(_2\) indicating that the CTAB molecules were intercalated between the bentonite mineral layers (Wang et al., 2014), and the higher intensity of the characteristic of modified bentonite peaks compared with that in natural bentonite, indicate the organophilic nature of the modified bentonite. Also, after modification with CTAB, the deformation and bending mode of Si-O-Si band at 792 and 806 cm\(^{-1}\) have also shifted to 754 and 827 cm\(^{-1}\). The supplemental peaks at 2933 cm\(^{-1}\) in modified bentonite, which are truant in natural bentonite indicate the presence of CH oscillation in modified bentonite (Dhodapkar et al., 2006). Through comparing the FTIR spectra of modified bentonite before and after sorption of MO. The peak at 1633 cm\(^{-1}\) is caused by vibrations of the C–N bond while the comparing the FTIR analysis of modified bentonite before and after sorption of MO, the additional peaks at 3379.28 cm\(^{-1}\) shows NH group aliphatic and group of MO. The shift in peaks 3630 cm\(^{-1}\) indicates the dye adsorption on the silanol group (Pavia, 2010). The peak at 1641 cm\(^{-1}\) is caused by vibrations of the C–N bond (Jing-yil, et al., 2007).

![FTIR analysis of natural and modified bentonite before and after sorption of dye.](image-url)
• **SEM analysis:** The microstructure and surface morphology of natural bentonite before and after modification by CTAB were displayed using SEM analysis as shown in Error! Reference source not found.. This Fig detected considerable changes in the surface morphology of the natural bentonite after modifying with CTAB (Zha et al., 2013). (Error! Reference source not found.) shows that the Natural bentonite has a porous structure, an infrequent and rough appearance with a dispersed block structure and different sizes. On other hand, the modified bentonite surface morphology has been converted into an ultra-fine thin 'cornflake' like a fluffy-crystal appearance (Error! Reference source not found.). This fluffy appearance is obviously occurring due to the reduction in certain amorphous phases that were typically associated with bentonite because the surfactant has generally covered the surface of the bentonite (Huang, et al., 2017).

![Figure 3. SEM images of (a) Natural bentonite (b) Modified bentonite.](image)

• **Surface area** The results of this test showed that the surface area of the modified bentonite was lower than the natural bentonite. The surface area of natural bentonite is found to be 63.32 m²/g. This value was decreased to 27.51 for modification bentonite. This can be attributed to the agglomeration property of bentonite after modification by CTAB. In addition, the organic molecules entered the surface of the bentonite interlayers and blocked the channel between these layers that reducing the surface area and the volume of the pore. (Jeeva and Zuhairi 2018; Huang et al., 2017; Siregar et al. 2018).

### 5.3 Batch Experiments

Batch experiments were conducted to investigate the impact of surface modification of bentonite on the MO removal percent as follows:

#### 5.3.1 Equilibrium Time

The equilibrium time should be determined to ensure achieving equilibrium concentrations. shows The impact of 0.1 g of CTAB-bentonite on MO removal added to 100 mL of contaminated batch tests solutions at 25 °C. This Fig shows that with an increase in contact time, the percentage
of removal of these contaminants increased significantly. At the initial stage, the sorption rate was rapid and slowly slowed down. The slower sorption was probably due to a reduction in sorption sites on the modified bentonite surface (Khatib, et al., 2012). The sorption data show that 33.7% of MO it was mostly removed at 150 min. After these equilibrium times up to 180 min, there was no significant change in residual concentration.

![Graph showing removal percent of dyes on modified bentonite as a function of contact time.](image)

**Figure 1.** Removal percent of dyes on modified bentonite as a function of contact time.

5.3.2 Initial pH of the Solution

The most important single parameter influencing the sorption capacity is the initial pH of the solution. Therefore, the sorption of MO on the modified bentonite was investigated at different pH ranges from 2 to 12 with an initial concentration of 100 mg/L and 0.1 g of modified bentonite. Figure 2. The solution pH was adjusted with 0.1 M HCL and NaOH solutions to the desired value. It was observed that the increase in the pH value of the solution leads to decreases in the sorption capacity of MO. This behavior can be attributed, as the pH increases, the positive charge on the surface of modified bentonite decreases while the number of negatively charged increases (Chaari et al., 2015). A negatively charged surface reduces the sorption of anionic dyes such as MO dye due to electrostatic repulsion force (Laysandra, et al., 2019). The maximum removal percent of MO was 51% at a pH = 2.
5.3.3 Agitation Speed

The effect of agitation speed on the removal percent of MO was studied by varying the shaking speed from (0 to 250) rpm and maintaining other parameters identical to the best obtained in the previous steps.

**Figure 3** shows that approximately 27.59% of the MO was removed before shaking and the uptake increases as the shaking rate increases. However, the uptake of contaminant increased when the agitation rate increased from zero to 250 rpm, at which approximately 53.14% of MO was removed. These results can be affiliated with the fact that the diffusion of dye towards the surface of the adsorbent improves with increase the agitation speed. Thus, contact between sorbate in solution and binding sites is created to promote the effective transfer of sorbate to the sorbent sites (Khattri and Singh, 2009).
5.3.4 **CTAB-bentonite dose**

The dependence of MO sorption on sorbent dosage was studied by using various amounts of CTAB-bentonite from (0.05 to 0.7 g) added to 100mL of contaminated solution for batch experiments at 25 C°, while reserving other parameters as follows (Co=100 mg/L, pH=2, agitation speed=250 rpm and contact time specified previously).

**Figure 4** shows the percentage of MO removal as a function of various CTAB-bentonite amounts. It is clear that the of removal efficiency has been increased with an increasing sorbent dose up to (0.5g/100mL), then they remain almost constant. This behavior was expected because of the greater availability of sorption sites when increase the dose of sorbent in the solution, the. Also, it indicated that, after certain dose of sorbent, the total sorption sets the quantity of MO bound to the sorbent and that the quantity of this dye in the solution remains constant even with the addition of the sorbent dose (Kiranşan et al., 2014; Kankeu et al., 2016).
5.4 Sorption Isotherms
The experimental data were fitted with the Langmuir and the Freundlich models. Accordingly, the empirical coefficients for each model were determined from the slope and intercept of the linear plot using Microsoft Excel 2016 software as shown in Fig. 8 and Table 2. The Freundlich model obviously provided the best determination coefficient (R²) compared to the Langmuir model. Therefore, the Freundlich model was more appropriate for the representation of sorption data of MO onto CTAB-bentonite.

Figure 5: Linear form of isotherm models for sorption of MO onto CTAB-bentonite. (C₀=100 mg/l, dose=0.5 g/100 ml, pH=2, agitation speed=250 rpm, contact time=150 min).
Table 2. Sorption isotherm constants with coefficients of determination for sorption of MO onto CTAB-bentonite.

| Model        | Parameters           | Values     |
|--------------|----------------------|------------|
| **Langmuir** | $q_{\text{max}}$ (mg/g) | 555.56     |
|              | $b$ (l/mg)           | 0.0206     |
|              | $R^2$                | 0.4998     |
| **Freundlich** | $K_F$ (mg/g)(l/mg)^{1/n} | 1.4803     |
|              | $N$                  | 1.116      |
|              | $R^2$                | 0.9433     |

In order to determine the accuracy of the Freundlich model, recalculating the sorbed amounts using the concentration equilibrium values and Freundlich parameters is important and essential. Figure 6. However, generally good fitness between the experimental and predicted values (Freundlich model).

![Figure 6](image.png)

Figure 6. Comparison of the experimental results with the $q_e$ values obtained by Freundlich model for MO sorbed by CTAB-bentonite.

5.5 Sorption kinetic study

Adsorption kinetic study is very important in the development and analysis of adsorbents to remove the adsorbents from the solution. The kinetic data were correlated with the pseudo-first and pseudo-second-order models. The parameters for each model were obtained by fitting the linearized form of these models to the experimental data as shown in Figure 7. Table (3) represent...
all parameters with the empirical coefficients that were determined from the slope and intercept of the linear plot using Microsoft Excel 2016 software. It is clear that the sorption of MO is likely to be second-order because the values of $q_e$ (experimental) and $q_e$ (calculated) are close, irrespective of the magnitude of the correlation coefficient. These results show that the chemo sorption or ion exchange mechanisms have been dominant in MO sorption on modified bentonite, these results are consistent with the results of other researchers such as (Juang et al., 2007; Anirudhan and Ramachandran, 2015; Zhang et al., 2016; Makkiya and Al-baldawi, 2019; Salem and Majeed, 2019).

Figure 7. The pseudo-first-order kinetic for the sorption of dyes onto CTAB-bentonite

Table 3. Pseudo-first-order and Pseudo-second-order kinetic model.

| Model                | Parameter                          | M.O |
|----------------------|------------------------------------|-----|
| **Pseudo-first-order** | $k_1$(min$^{-1}$)                  | 0.581 |
|                      | $q_e$ (experimental ,mg/g)         | 18.067 |
|                      | $q_e$ (calculated ,mg/g)          | 23.855 |
|                      | $R^2$                              | 0.658 |
| **Pseudo-second-order** | $k_2$(mg/g min)                   | 0.0079 |
|                      | $q_e$ (experimental ,mg/g)         | 18.067 |
|                      | $q_e$ (calculated ,mg/g)          | 18.587 |
|                      | $R^2$                              | 0.998 |
6. CONCLUSIONS
The CTAB-bentonite has been synthesized by replacing exchangeable calcium cations in natural-bentonite with cationic surfactant (CTAB). The characterization analysis of bentonite before and after modification proved that the CTAB created some improvements to the bentonite surface properties and structure, and convert it from hydrophilic to hydrophobic nature. The experiments have shown that:

1. The CTAB-bentonite was found to be effective for removing MO from aqueous solution with maximum sorption capacity of 555.56 mg/g.
2. The removal percent of MO was dependent on specific conditions such as contact time, initial pH of the solution, agitation Speed, and CTAB-bentonite dose. The values of these conditions which provide the highest removal percent (88 %) were 150 min, pH 2, 250 rpm, and 0.5 g/100 mL.
3. The isotherm study refers that the sorption data correlated well with Freundlich in comparison with the Langmuir isotherm model with \( R^2 \geq 0.94 \).
4. The kinetic study showed that experimental data obeyed to the pseudo-second-order rather than pseudo-first-order confirming that chemisorption has been predominant with \( R^2 \geq 0.99 \).

7. NOMENCLATURE
MO = methyl orange
CTAB = cetyltrimethyl ammonium bromide.
SEM = Scanning electron microscopy.
FTIR = Fourier transform infrared spectroscopy.
\( C_0 \) = the initial concentration of dye, (mg/L).
\( C_e \) = the equilibrium concentration of dye, (mg/L).
\( m \) = the adsorbent mass, (g).
\( V \) = the volume of dye solution, (L).
\( q_{max} \) = the maximum adsorption amount for the adsorbent, (mg/g).
\( q_e \) = the amount of dye adsorbed on the adsorbent (mg/g) at equilibrium.
\( q_t \) = the quantity of contaminant sorbed at time = t (mg/g).
\( K_F \) = the Freundlich sorption coefficient, (L/g).
\( KL \) = the Langmuir adsorption constant, (L/mg).
\( K_1 \) = the rate constant of pseudo first order adsorption (min\(^{-1}\))
\( K_2 \) = the rate constant of pseudo second order adsorption, (g/mg.min)
\( n \) = an empirical coefficient related to the intensity of the sorption.
\( R^2 \) = determination coefficient

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