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Adsorption of methylene blue onto natural Saudi Red Clay: isotherms, kinetics and thermodynamic studies

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Abstract

The current work investigates the adsorption behavior of methylene blue (MB) from aqueous solution using natural Saudi Red Clay (SRC) adsorbent. The surface characteristics of the adsorbent were investigated using surface area measurements (S_{BET}), Scanning Electron Microscopy (SEM), X-ray florescence (XRF) and Fourier-Transform Infrared Spectroscopy (FTIR) and x-ray diffraction (XRD). Various process parameters such as pH, adsorbent dosage, initial dye concentration, contact time and temperature were investigated. MB removal efficiency was noticed to increase with increasing adsorbent dosage while the effect of pH was noticed to be insignificant for the pH range studied. Applying the Langmuir isotherm fitting to the experimental data, a maximum adsorption capacity was found to be 50.25 mg g$^{-1}$ of clay at 298 K. Pseudo-first-order and pseudo-second-order models were applied to the experimental data to study the kinetics of the process. Pseudo-second-order model fitted well with the experimental as compared to the pseudo-first order model. The spontaneous and endothermic nature of the adsorption process was revealed by studying the thermodynamic parameters of the system. The positive $\Delta S^\circ$ value indicates the affinity of MB molecules to the adsorbent surface. Re-usability/recycling study showed that this material can be successfully reused at least four times in this study without significant loss in the adsorption capabilities.

1. Introduction

Rapid industrialization in recent past has led to the introduction of various stringent environmental and pollution control legislations. Organic dyes are a major source of wastewater effluents mainly from textile manufacturing facilities and various other industries such as paper and pulp, plastic and rubber, food, cosmetics and pharmaceutical [1, 2]. For example, on average, almost 1%–15% of the dye ends up in the effluent during a typical dying process depending on the class of dye. Organic dyes are color compounds and are classified into many different types mainly based on the functional groups present in their chemical structure [3]. Among the various cationic dyes, methylene blue is known to be used in cotton, wood and silk industries and may be linked to health issues such as severe headache, chest pain, breathing difficulty etc [4]. Presence of significant quantities of these dyes and colors not only endanger the aquatic systems by producing unpleasant colors and blocking the direct sunlight (photosynthesis process) but also presents indirect significant health risk due to the carcinogenic and toxic nature of these organic dyes [5]. The available techniques that can effectively remove these pollutants and decontaminate the concern effluents include adsorption, flocculation/coagulation, reverse osmosis and membrane technology, advanced oxidation processes, ozonation etc. However, they all come with their advantages and disadvantages.

Among the various available technologies, adsorption is known to have various advantages as compared to the other techniques. The adsorption technique is cost effective, simple and flexible, easy to operate and control etc [6, 7]. The choice and type of adsorbent may depend on parameters such as cost, availability, toxicity and regeneration and re-usability etc. The use of many different types of adsorbents for the removal of methylene blue (MB) is reported in literature. Granular activated carbon has been successfully used by many researchers,
but its high cost sometimes limits its use as an adsorbent for color removal [8, 9]. Other low-cost adsorbent materials that have been used for dye removal include fly ash [10, 11], agriculture wastes [12–16]. As for the clay minerals, usually clay minerals are used as natural without any chemical modification [17]. Natural clays as adsorbents for the removal of dyes from wastewater are; montmorillonite, [5, 18, 19], bentonite [20], zeolites [6, 21–24], perlite [25], sepiolite [26] kaolinite [1, 27, 28], fibrous clay minerals [29] and Algerian diatomite [30].

As a low-cost adsorbent material, clay minerals have been increasingly receiving attention and have been an important and challenging area of research in recent years. However, use of natural clay minerals as a low-cost adsorbent material from Kingdom of Saudi Arabia (KSA) especially from the southern region is scarce in literature. Hence, the objective of the current work is to explore and utilize the red clay mineral (abundantly available) for the adsorption of MB from artificial wastewater. One of the objectives of the current research is to gain an insight into the equilibrium kinetics, thermodynamic behavior of the adsorption processes, determine the maximum adsorption capacity and the possible mechanisms involved. Results from the current work will be compared with similar clay adsorbents from literature for MB removal to evaluate its suitability and efficiency.

2. Materials and methods

Saudi Red Clay minerals (SRC) were collected from the Southern region of KSA. The clay minerals were crushed by hand using a mortar and pestle and sieved through a sieve size less than 100 μm. The collected clay powder was used in the adsorption experiments without any further treatment/modification. Methylene blue was purchased from Sigma Aldrich.

2.1. Characterization

X-ray florescence (XRF) analysis were performed on the ZSX Primus II (Rigaku, USA) to determine the metal oxide contents of the clay sample as presented in table 1. The samples for XRF analysis were prepared according to the procedure mentioned in [31] and finally analyzed using XRF spectrometer. Surface area measurements (SBET) together with other relevant data were carried out from the nitrogen adsorption-desorption plots using Brunauer–Emmett–Teller (BET) method. Morphological characteristics of the clay sample were obtained using Scanning Electron Microscope (SEM, TM3030Plus, Hitachi). Fourier Transform Infrared Spectroscopy (FT-IR) measurements were carried out on the samples before and after adsorption using Cary 630 FTIR (Agilent Technologies). The range of spectrogram was from 4000–400 cm$^{-1}$. X-ray diffraction (XRD) pattern of the SRC was obtained in the 2θ range of 5° to 50° in a Shimadzu X-600 powder diffractometer with CuKα1 radiation operated at 40 kV.

2.2. Adsorption experiments

Adsorption experiments were carried out in batch operations using 50 ml conical flasks. Stock solutions of MB dye were prepared by dissolving 0.3 g of solid MB in one litre distilled water. This was followed by subsequent dilutions to prepare the appropriate concentrations as required. In order to study the effect of initial solution pH, a series of MB dye solutions (50 ml volume, 100 mg l$^{-1}$ MB concentration) were prepared with different pH ranging from 1.46–11.25. The pH of these solutions was adjusted using 1M HCl and 1 M NaOH solutions. The optimum pH was selected (neutral solution, pH = 6.42) and was used for all subsequent experiments. To investigate the effect of other parameters, MB concentration of 100 mg l$^{-1}$ was chosen. As for the effect of adsorbent dosage, different amount of adsorbent ranging between 0.05 to 0.6 g was used from which 0.3 g of adsorbent was chosen to be the optimum dose for 50 ml sample of 100 mg l$^{-1}$ MB concentration. Mixing speed of the temperature-controlled shaker was chosen to be 150 rpm. MB solutions of different initial concentrations were also prepared and investigated. The contents after mixing were filtered, and the filtrate was collected and

| Chemical compound | Weight % |
|-------------------|----------|
| SiO$_2$           | 51.77    |
| Al$_2$O$_3$       | 29.17    |
| Fe$_2$O$_3$       | 13.22    |
| TiO$_2$           | 1.80     |
| CaO               | 1.53     |
| MgO               | 1.14     |
| Others            | 1.37     |

Table 1. Chemical composition (wt%) of the SRC adsorbent obtained by XRF analysis.

The samples for XRF analysis were prepared according to the procedure mentioned in [31] and finally analyzed using XRF spectrometer. Surface area measurements (SBET) together with other relevant data were carried out from the nitrogen adsorption-desorption plots using Brunauer–Emmett–Teller (BET) method. Morphological characteristics of the clay sample were obtained using Scanning Electron Microscope (SEM, TM3030Plus, Hitachi). Fourier Transform Infrared Spectroscopy (FT-IR) measurements were carried out on the samples before and after adsorption using Cary 630 FTIR (Agilent Technologies). The range of spectrogram was from 4000–400 cm$^{-1}$. X-ray diffraction (XRD) pattern of the SRC was obtained in the 2θ range of 5° to 50° in a Shimadzu X-600 powder diffractometer with CuKα1 radiation operated at 40 kV.
analyzed using UV spectrophotometer Shimadzu 1600 with wavelength of 665 nm. The effect of contact time was also studied with contact time ranging from 5 min up to 1 h. In order to study the batch kinetics of the adsorption process, the remaining concentration of MB in the solution was studied at pre-determined intervals of time. According to [31] the percentage dye removal can be calculated as follows:

\[
\text{% dye removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

where \(C_0\) is the initial dye concentration (mg l\(^{-1}\)), \(C_e\) is the equilibrium concentration. The amount of dye adsorbed per unit weight of the adsorbent; \(q_e\) (mg g\(^{-1}\)) was calculated using equation (2) [31]:

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

where \(V\) is the volume of dye solution (L) and \(m\) is the adsorbent mass (g). All experiments were carried out in duplicate and the average values were used in further calculations.

3. Results and discussions

The nitrogen adsorption/desorption isotherms of the SRC is shown in figure 1. BET surface area of the SRC adsorbent was found to be 63.15 m\(^2\) g\(^{-1}\), while the average pore diameter was around 6.288 nm and the total pore volume was 0.0993 cm\(^3\) g\(^{-1}\). Figure 2 presents SEM image of the SRC adsorbent that shows almost regular shapes and fine sizes.

In order to evaluate the roles of the functional groups on the clay surface in the adsorption process, FT-IR analysis were carried before and after MB adsorption and the results are shown in figure 3. As can be seen from figure 3, beside the classical and well-known bands of Si–O stretching vibrations and OH stretching of the hydroxide groups, some new bands appeared at 1336, 1394 and 1600 cm\(^{-1}\) which are very close to the observations reported by [32, 33]. These bands are most likely to be associated with the stretching of –C–N–, –C=N–, and –C=C– in polyheterocycles that may be used as evidence for the adsorption of the MB dye on clay. The SRC sample was also characterized by XRD in order to identify the phase compositions present in the mineral clay. The clay mainly composed of kaolinite (K), montmorillonite (MMT), quartz (Q), calcite (Ca), hematite (H) and edinite (E) as shown in figure 4.

3.1. Adsorption kinetics

Adsorption kinetics were explored by studying the effect of contact time, initial dye concentration, adsorbent dosage and pH of the dye solution.

3.1.1. Effect of SRC dosage

The effect of adsorbent dosage was investigated in order to identify the optimum dosage with respect to the amount of dye concentration. Generally, as the adsorbent dosage increases, so the removal efficiency also increases. This is expected because there are more adsorption sites available at the adsorbent surface. As shown in figure 5, there is a very sharp increase in the adsorption efficiency below 0.2 g but reaches almost a plateau.
from 0.2 g onwards and the increase in removal efficiency is very small. These results are in good agreement with the observation reported by [34] for kaolin, [35] for red mud, [22] for zeolite and [36] for natural clay.

3.1.2. Effect of pH

Initial pH of the dye solution is known to affect the adsorption process of dye removal. The initial pH is known to be affected by various factors such as surface charge of the adsorbent, degree of ionization of the adsorbate molecule, and the extent of dissociation of functional groups on the active sites of the adsorbent. Generally, the percentage of dye removal is low at low pH range but is known to increase at high pH range for cationic dyes. The minimum % removal of MB was observed between pH 1.5 and pH 3. However, no significant change in % removal was observed at higher pH values as shown in figure 6. Lower % MB removal at the low pH may be due to the availability of excessive H\(^+\) ions that may compete with the cationic dye for adsorption sites as reported by [37] for Moroccan clay.

3.1.3. Effect of contact time

Changes observed in the adsorption of MB as a function of contact time are presented in figure 7. As can be seen, the removal efficiency increases with increasing and the maximum adsorption of dye takes place in the first five minutes, indicating spontaneous adsorption. After the initial first five minutes, there is a very gradual increase in dye adsorption and almost reached equilibrium within 40 min of the initial contact. During the first five minutes
Figure 4. XRD pattern of the SRC adsorbent.

Figure 5. Effect of adsorbent dosage on MB removal efficiency. (pH = neutral, initial dye concentration = 100 mg l\(^{-1}\), contact time = 60 min, mixing speed = 150 rpm and volume = 50 ml).

Figure 6. Effect of solution pH on MB removal efficiency. (adsorbent dosage = 0.3 g, initial dye concentration = 100 mg l\(^{-1}\), contact time = 60 min, mixing speed = 150 rpm, temperature = 25 °C and volume = 50 ml).
of the initial contact time, very rapid adsorption was observed. This may be attributed to the availability of the negatively charged surface of adsorbent which caused rapid electrostatic adsorption of cationic dye methylene blue from the solution at neutral pH similar to the results reported by [38] for kaolin.

3.1.4. Effect of initial concentration
Keeping all other parameters such as pH, adsorbent dosage, temperature, contact time, mixing speed and volume constant but increasing the initial concentration, the removal efficiency decreases as shown in figure 8, implying that the % removal efficiency inversely proportional to surface loading. This is most likely due to the lack of availability of active sites for the adsorbate to interact with i.e. more and more active sites are occupied and the adsorbent is saturated. Higher loading (more adsorbent) leads to greater competition among the MB ions with fixed surface adsorbing sites. Thus, the % MB removal decreases. Similar observations were reported by [39] for spend activated clay.

3.1.5. Effect of temperature
The effect of temperature on adsorption uptake of MB was studied in the temperature range of 25 °C–55 °C. The removal of MB by the clay adsorbent was observed to increase with increasing temperature as shown in figure 9. This is most likely due to the increase in the entropy of the system resulting in more collisions and activities at the interface between the adsorbent and adsorbate.
3.2. Adsorption equilibrium

Adsorption isotherms are frequently used to study the equilibrium parameters and the adsorption properties and to gain an insight into the nature of interactions taking place between the adsorbent and the adsorbate. They provide information about the optimum use of adsorbents. Three well known adsorption isotherms: the Langmuir, Freundlich and Temkin are utilized in the current investigation. The Langmuir isotherm provides information regarding the availability of active sites on the adsorbent surface and the saturation of these sites once all the available sites are occupied and maximum adsorption is attained. The linear equation of the Langmuir model is represented by the following equation according to [2, 40]:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

where \(C_e\) is the equilibrium concentration of MB dye, \(q_e\) is the dye uptake capacity of the adsorbent, \(K_L\) is the Langmuir constant related to the adsorption energy and \(q_{\text{max}}\) is the maximum adsorption capacity (mg g\(^{-1}\)) of adsorbent. The maximum adsorption capacity \(q_{\text{max}}\) and \(K_L\) values are usually obtained from the slope and intercept of the graph shown in figure 10(a). Other important information that can be obtained from the Langmuir isotherm is about the separation factor, \(R_L\). This factor gives an insight into the characteristics of adsorption. \(R_L\) values may be calculated from the following equation:

\[
R_L = 1 + K_L C_o
\]

where \(C_o\) is the maximum preliminary concentration of the dye solution. \(R_L\) values indicate the type of adsorption such as unfavorable adsorption when \(R_L\) values are greater than 1, favorable when the values are between 0 and 1 and irreversible if the \(R_L\) values are equal to 0. Thus, the adsorption process in the current investigation is favorable since the \(R_L\) values are in the range of 0 and 1 as listed in table 2.

The Freundlich isotherm model proposes an exponential decrease in the adsorption energy upon completion of the sorption centers of the sorbent. The linear form for the Freundlich model can be expressed by the following equation [2, 40]:

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

where \(K_F\) and \(n\) are Freundlich constants and may provide information regarding the adsorption capacity of the sorbent that is associated with the bonding energy and adsorption strength (intensity). A linear plot of this model is presented in figure 10(b) from which values of \(K_F\) and \(n\) were determined from slope and intercept respectively. Since the 1/n value is greater than 1 as shown in table 2, thus it is consistent with cooperative adsorption [41].

In the Temkin adsorption model, the sorption heat of all molecules in the layer is assumed to decrease linearly with coverage of the adsorbent surface due to a decrease in the interactions between the adsorbent and adsorbate. A linear model of Temkin isotherm can be described by the following equation [40]:

\[
q_e = B \ln K_T + B \ln C_e
\]

where \(B = (R_T/b_t)\), \(T\) is the absolute temperature and \(R\) is the universal gas constant and \(K_T\) is equilibrium binding constant corresponding to the maximum binding energy. The constant \(b_t\) is related to the heat of
adsorption ($J \text{ mol}^{-1}$) that was found to be 383.75 $J \text{ mol}^{-1}$. The model fitted relatively good with the experimental data as shown in figure 10(c). Overall, comparing the correlation coefficient $R^2$ values of the three models, the Langmuir model best fits the experimental data suggesting a monolayer adsorption on the homogeneous surfaces of the adsorbent.
3.3. Kinetic studies
In order to investigate the adsorption kinetics of MB dye on the SRC surface, pseudo-first-order and pseudo-second-order kinetic models were applied to study the controlling mechanism of adsorption process. The pseudo-first-order can be expressed as follow:

\[ \ln (q_e - q_t) = \ln q_e - k_1 t \]  

where and are the concentration of MB dye adsorbed at the equilibrium and at time (t) respectively, and is the rate constant of adsorption. As for the pseudo-second-order model, the following equation was fitted to the experimental data:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

Pseudo-first-order model did not fit well with the experimental data (figure 11(a)) while pseudo-second-order kinetic model fitted very well with R^2 values very close to unity (R^2 > 0.999) as shown in figure 11(b). Kinetic model results reveal that the adsorption of MB dye onto SRC could be better explained by pseudo-second-order kinetic model which is in good agreement with the work of [27] for kaolin, [34] for Algerian kaolin and [35] for activated red mud. The results are summarized in table 3. Since it is well known that the pseudo-second-order model assumes that the rate limiting step is chemisorption, it may be concluded that the interaction between the dye ions and the adsorbent are either by charge neutralization or electrostatic attraction.

3.4. Thermodynamic parameters
Adsorption processes are frequently influenced by temperature; thus, the effect of temperature was investigated in the temperature range of 298 to 328 K. Using the following equation, the thermodynamic parameters for the adsorption of MB were calculated:
where $K_d$ is the distribution coefficient of adsorption and equal to $q_e/C_e$, $D_H^0$ (kJ mol$^{-1}$) and $D_S^0$ (J mol$^{-1}$ K$^{-1}$) are respectively, the standard enthalpy and the standard entropy; $T$ is the absolute temperature; and $R$ is the gas constant.

The Gibbs free energy change $D_G^0$, indicating the spontaneity of the adsorption process, is calculated as:

$$
\ln(K_d) = -\frac{D_H^0}{RT} + \frac{D_S^0}{R} \tag{9}
$$

A linear plot of $\ln(K_d)$ versus $1/T$ was obtained as shown in figure 12 with a slope and intercept giving values of $D_H^0$ and $D_S^0$. The obtained thermodynamic parameters are tabulated in table 4. The negative values of $D_G^0$ indicates that the adsorption process on the SRC is spontaneous and the increase in negative value with increasing temperature shows that the adsorption process on SRC becomes more favorable at higher temperatures. Also, since the $D_G^0$ values are in the range between $-20$ and $0$ kJ mol$^{-1}$, indicating that the physisorption was likely the mechanism as reported [42].

The standard enthalpy of adsorption $D_H^0 = 11.79$ kJ mol$^{-1}$ indicates an endothermic process and the positive value of $D_S^0$ reflects the affinity of SRC for MB and suggests an increase in disorder/randomness at the adsorbate-adsorbent interface i.e. some structural changes in dye and SRC which agrees with the observations.

### Table 3. Constants and correlation coefficients of the two kinetic models for MB adsorption onto clay.

| Pseudo-first-order rate constants | $k_1$ (1 min$^{-1}$) | $q_e$, cal (mg g$^{-1}$) | $R^2$ |
|----------------------------------|----------------------|------------------------|-------|
|                                  | 0.1237               | 0.4255                 | 0.8052 |

| Pseudo-second-order rate constants | $k_2$ (g mg$^{-1}$ . min$^{-1}$) | $q_e$, cal (mg g$^{-1}$) | $R^2$ |
|------------------------------------|-------------------------------|------------------------|-------|
|                                    | 0.552                         | 16.611                 | 1.000 |

### Table 4. Thermodynamic parameters of adsorption of MB onto SRC.

| Thermodynamic parameters | $\Delta H^0$ (kJ mol$^{-1}$) | $\Delta S^0$ (J mol$^{-1}$ K$^{-1}$) | $\Delta G^0$ (kJ mol$^{-1}$) |
|--------------------------|-------------------------------|--------------------------------------|-------------------------------|
|                          | 11.791                        | 82.489                               | 298.15 308.15 318.15 328.15 |
|                          | −9.931                        | −13.60                               | −14.48 −15.25                |
of [19] for surfactant modified MMT and [20] for bentonite clay. These structural changes may be reflected by FT-IR analysis of the SRC before and after MB adsorption as shown in figure 3.

3.5. Reusability of the SRC adsorbent
Results from the reusability analysis are presented in figure 13. As shown, the removal efficiency gradually decreases but still maintaining relatively high removal efficiency (more than 95%) after 4 cycles suggesting that SRC adsorbent can be efficiently used even after 4 cycles of recycling and reusing.

3.6. Evaluation of SRC as an adsorbent for MB removal
In order to evaluate the adsorption performance of adsorbents, the maximum adsorption capacity, $q_{\text{max}}$ parameter from Langmuir isotherm is commonly used. For comparison, the $q_{\text{max}}$ values from literature for clay adsorbent materials for MB removal are presented in table 5. The reported SRC adsorbent used in the current investigation shows reasonably good adsorption capacity for MB dye removal. The abundant availability and low cost together with good adsorption capacity justify utilization of SRC for MB dye removal from wastewater.

![Figure 13. MB removal efficiency versus number of cycles and reusability of SRC adsorbent.](image-url)

### Table 5. Comparative assessment of MB adsorption capacity of some clay adsorbent materials.

| Adsorbent                        | $q_{\text{max}}$ (mg g$^{-1}$) | References |
|----------------------------------|---------------------------------|------------|
| Zeolite (raw clay)               | 8.67                            | [22]       |
| Moroccan illitic clay           | 13.69                           | [43]       |
| Kaolin (Raw clay)               | 13.99                           | [4]        |
| Zeolite (Egyptian)              | 21.41                           | [24]       |
| Natural zeolite                 | 21.78                           | [21]       |
| Natural clay Portugal           | 22.2                            | [1]        |
| Natural illitic clay mineral    | 24.87                           | [44]       |
| Natural zeolite                 | 25                              | [6]        |
| Ball clay (Malaysia)            | 25.01                           | [45]       |
| Kaolin (Persia)                 | 28.95                           | [8]        |
| Plasma treated bentonite        | 30.2                            | [2]        |
| Kaolinite                       | 45.45                           | [7]        |
| Natural clay                    | 50.25                           | Current study |
| Kaolin                           | 52.76                           | [28]       |
| Zeolite-reduced graphene oxide  | 53.3                            | [23]       |
| Natural clay (Turkey)           | 58.2                            | [46]       |
| Natural clay                    | 100                             | [29]       |
| Green clay minerals             | 241.9                           | [47]       |
| Montmorillonite                 | 289.1                           | [9]        |
4. Conclusion

Results from the current investigation show that the SRC adsorbent can be effectively used for the removal of MB from waste water. The adsorption efficiency was observed to be highly dependent on process parameters such as adsorbent dosage, initial concentration and temperature. The experimental data fits well with Langmuir model. Correlation coefficient higher than 0.999 was obtained for the pseudo-second-order kinetic model. Thermodynamic parameters suggest that the adsorption process is spontaneous, endothermic and physical in nature. The positive entropy value indicates that there is an increase in the randomness at the adsorbent/adsorbate interface. The overall conclusion is that the investigated adsorbent is a natural (environmentally friendly), effective, economical and efficient for the removal of MB from wastewater. SRC adsorbent can be used without any surface modification/treatment and without any pH adjustment of the adsorbate solution.

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