Using Modified Montmorillonite by Methylene Blue for Removing Brilliant Red from Textile Wastewater

Abstract

Background: The presence of quantities of dye chemicals in the textile industry effluent is clearly visible and harmful environmental impacts caused by chemical compounds are also as a noticeable challenge. Regarding this issue, control of the pollution has been considered.

Methods: In this study, an absorbent of Sodium Montmorillonite modified by Methylene Blue dye was used to remove Brilliant Red dye from the textile effluent. All batch experiments were carried out in 250mL of solution of 640 mg/L Methylene Blue with 2g of adsorbent and performed on a shaker with a shaking of 120 rpm; the precipitate was placed in an oven at 60°C for 24 hours. The effective parameters on the adsorption including: pH, absorbance dose, dye concentration and contact time were optimized by using both one factor at a time technique and Central Composite Design method by designing 30 experiments with four variables (n=4) and two levels (low (-) and high (+)).

Results: The optimal values of the influencing parameters such as pH, absorbance dose, dye concentration and contact time were determined at 6, 0.3 g, 80 mg/L and 60 min with an approximate 92% removal percentage, respectively. The results illustrated that the process was more consistent with Langmuir adsorption isotherm and pseudo-second kinetics equation.

Conclusion: The adsorption behaviors of the modified absorbent showed that the adsorption kinetics and isotherms were in good agreement with pseudo-second-order equation and the Langmuir equation, respectively. The potential for regeneration and reuse of the modified absorbent was proved by the desorption studies.

Keywords: Adsorption, Montmorillonite, Wastewater

Introduction

The effluents produced from industrial activities are reported to afflict public health and biodiversity as they contain various hazardous materials. They reduce the transmitted sunlight into water streams and the presence of even minute amounts of coloring substance makes it undesirable due to its appearance. In addition, these dyes consume dissolved oxygen in aquatic system, interrupt processes such as photosynthesis, respiration, and finally cause eye burn and injury to human, and animals.

To remove dyes from textile effluent, various wastewater treatment methods, including adsorption, electro-coagulation and advanced oxidation, etc. are used. The natural adsorbents such as clay have been reported as effective materials of alternative adsorbent for the purpose.

Montmorillonite clay (MMT) has the largest surface area and the highest cation exchange capacity. In this respect, many studies have been carried out...
aiming to assess and improve the sorption capability of MMT in water for practical operation.\textsuperscript{19, 20}

Previously, adsorbent materials were optimized in the base of natural clay (MMT), and used to remove some pollutants such as BR from textile effluent.\textsuperscript{21-24} Recently, results have revealed that MMT clay is efficiently used as an effective adsorbent for the removal of the pollutant from aqueous solution.\textsuperscript{19}

Therefore, removal of Brilliant Red from textile effluent using the modified MMT\textsuperscript{25, 26} by Methylene Blue (MB), to develop more effective adsorbent, was studied in this paper. The uptake of BR on modified montmorillonite by methylene blue (MMT-MB) was examined as a function of contact time, adsorbent dose, pH and initial BR concentration. The optimization of the process was studied by employing both one factor at a time technique and response surface method (RSM).

Optimization of the process variables is needed to achieve the maximum adsorption capacity and removal efficiency. The conventional and classical method of optimization of process multivariable system involves “one factor at a time” techniques which requires performing a lot of experiments and also it could not reveal the effect of factor interaction in the system. RSM, a statistical experimental design, provides statistical models, helps to understand the interactions among the factors that have been optimized and also reduces the number of experiments. Central composite design (CCD) is a useful method to optimize the responses shaped under the influence of process variables.\textsuperscript{27} The RSM tool is employed in design optimization to minimize or reduce the cost of expensive analysis and the numerical noise associated with the analysis.\textsuperscript{28}

Isotherm, thermodynamic and kinetic studies for adsorption of Brilliant Red (BR) on MMT-MB have been reported. Finally, the possibility of the desorption studies was discussed. This paper reports on the ability of Modified montmorillonite clay (MMT) by methylene blue (MB) to remove Brilliant Red (BR) from aqueous solution. The uptake of BR on clay was examined as a function of temperature, absorbance dose, adsorbent concentration, and contact time.

**Material and Methods**

**Materials and Instruments**

All the chemicals used were of analytical grade and were used without purification. Na\textsuperscript+-Montmorillonite (Southern Clay Products), Methylene Blue (Figure 1) (chemical formula=C\textsubscript{16}H\textsubscript{18}N\textsubscript{3}SCl, MW=319.85 g/mol), Brilliant Red (Figure 2) were purchased from Merck Co, Germany.

Also, the pH adjustments were carried out using diluted NaOH and HCl solutions. Adsorption measurement was performed on a UV-visible spectrophotometer (UV- 20D, USA). Surface morphology was studied by scanning electron microscope (LEO-SEM, 1420, Germany). All experiments were studied at room temperature.

**Preparation of Adsorbent**

The MMT sample was used as the adsorbent (Figure 3). To optimize it, 2 g of Montmorillonite was added to 250 ml of solution of 640 mg/ml Methylene Blue (MB). After performing on a shaker (Grant operation, UK), the precipitate was placed in an oven at 60 ° C for 24 hours.

**Adsorption Study**

Batch adsorption experiments were carried out using a shaker at a constant speed of 140 rpm. The four effective parameters consisting of pH, adsorbent concentration, initial BR concentration and contact time were studied. In this respect, chemical analysis of adsorption was first performed by adjusting different amounts of adsorbent (0.05-0.3 g) for various concentrations of BR (60-250 mg/l) for different times (10- 100 minutes) and at pH values (2 to 10). The pH of the solution was adjusted by adding a small amount of the NaOH and HCl. The kinetics, isotherms and thermodynamic parameters adsorption were investigated till the equilibrium was achieved. The absorbencies of the samples were measured using a UV-visible spectrophotometer (UV- 20D, USA) at 530 nm (λ\textsubscript{max}) corresponding to a maximum absorbency of BR. The adsorbed amounts (q) of BR were calculated by Eq. 1:

$$q = \frac{(C_0-C_e)v}{m}$$  \hspace{1cm} (1)
Removing textile dyes with modified montmorillonite

Where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of dye (mg/L), \( m \) is the mass of sorbent (g), and \( V \) is the volume of solution (L).

Experiments and Statistical Analysis

The effect of the four parameters on the adsorption process (contact time, adsorbent concentration, pH and initial BR concentration) was investigated using a factor at a time technique; also, to find the optimum conditions the experimental plan was carried out by using a Response Surface Methodology (RSM), Central Composite Design (CCD) method. There are three major steps involved in the process optimization by RSM technique including: statistically experimental design, estimation of coefficients in the mathematical model and prediction of the response and checking the accuracy within the range of experimental variables. In the current research, four independent operating parameters were selected for the statistical analysis. The parameters are pH, absorbance dose, dye concentration and contact time. All the independent parameters at their specific ranges were observed as significant parameters for efficient BR removal from solution on the modified adsorbent (MMT-MB). Therefore, the response is represented as a function of all independent variables. An empirical model equation has been developed which correlate the response, removal efficiency with process variables by a second-degree polynomial equation and reproduced below in Equation (5). A number of tests (N) can be performed by considering the typical \( 2^n \) factorial design consisting of the distance from the center (-1.0,+1), as mentioned earlier. A quadratic term was generated by the axial fixing of the \( 2^n \) points at the distance \( \alpha \) from the center. Independent variable was defined as \( (n) \).\(^{30-32} \) To design the experiment, we determined four variables \( (n=4) \) and two levels (low (-) and high (+)), based on which the total number of experiments was determined 30 times. The parameters were pH, adsorbent concentration, initial BR concentration and contact time identified as A, B, and C and D, respectively. The percentage of removal amount was considered as a target function (response).

Results

The Surface Morphology

For morphological analysis, the samples were investigated by scanning electron microscopy SEM. Morphology of the absorbent level of unmodified MMT (Figure 4-a) and modified MMT-MB (Figure 4-b) with MB was studied. The changes on the edges are common in layered silicates, which leads to the formation of hydroxyl groups. Hence, the images indicate that the sharp edges of MMT clay have been changed due to the potential stabilization of the modifying agent (MB).

The Parameters Affecting Adsorption of BR

Effect of pH

Many studies have been carried out to investigate the effect of pH as one of the important factors affecting the capacity of adsorbent since variation in pH leads to the variation in adsorption process.\(^{31, 32} \) Based on Table 1, pH=6 of BR is appropriate.
Effect of Adsorbent Concentration

The effect of MMT-MB concentration on BR adsorption at contact time of 60 min was studied at room temperature by varying the sorbent amounts from 0.05 to 0.3 g in 50 mg/L BR solution. Table 1. indicates that the percentage of BR removal after the 0.3 g absorbent remains almost unchanged and the adsorption process has attained equilibrium.

Effect of Initial BR Concentration

The effect of initial dye concentration in the range of 60 to 250 mg/L on adsorption is shown in Table 1. Considering the relationship between the acceptability of pollutant removal rate and its maximum removal potential, it can be seen that at a concentration of 80 mg/L, the percentage of removal is about 90% and then the removal percentage is reduced. Therefore, this concentration was determined as an appropriate amount of the dye concentration.

Effect of Contact Time

According to Table 1, it is clear that the adsorption capacity increased promptly in the first time slot (0-45 min), but after the contact time reached approximately 60 min, the adsorption capacity remained almost unchanged. Therefore, this time was chosen as the equilibrium and optimal time for the adsorbent.

Optimization of the Removal Percentage

The effects of the four operative conditions, A, B, C and D on adsorption process were investigated using CCD method in terms of the removal content (%). A total of 30 experiments were necessary to estimate the coefficients of each model using linear regression analysis. The one dependent output responses, percentage removal and quadratic model, was obtained from the independent input variables for CCD and are presented in Table 2 and Eq. 2:

(Eq 2)

The statistical significance of the full quadratic models was verified by the analysis of variance (ANOVA) technique. The ANOVA results of the models are shown in Table 3. The significance of the model can be evaluated by considering either the F-values or the p-values of the model.

The model F value of 63/53 indicates the model is significant for percentage removal. For percentage removal A, B, C, D, BC, BD, \( A^2 \) and \( B^2 \) are significant model terms. However, if any one of these conditions is not fulfilled, the model will be only accepted when the correlation coefficient (\( R^2 \)) is higher than 0.95, which means that 95% of the data is explained by the model.

**Comparison of the Optimized Process Variables Value for Adsorption of BR by a Factor at a Time Technique and CCD Method**

The predicted and the experimental optimum values of the effective variables for the maximum percentage removal are shown in Table 4.

According to Table 3, the optimum values of independent variables were determined: pH 6.28, adsorbent dosage 0.16 (g), Contact time 59.47 (min) and initial dye concentration 88 mg/L. To confirm the result, we carried out an extra experiment according to the model prediction. The interaction effect of analyzed parameters by CCD for percentage removal of BR using MMT-MB was visualized through three dimensional views of response surface plot, as shown in Figure 5. Accordingly, the combination effect of...

**Table 3:** ANOVA for the quadratic models predicted for response variable

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F value</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>10</td>
<td>87/2196</td>
<td>84/217</td>
<td>63/53</td>
<td>0001/0&lt;</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>47/301</td>
<td>47/301</td>
<td>21/74</td>
<td>0001/0&lt;</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>33/458</td>
<td>33/458</td>
<td>83/112</td>
<td>0001/0&lt;</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>42/104</td>
<td>42/104</td>
<td>90/38</td>
<td>0001/0&lt;</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>00/158</td>
<td>00/158</td>
<td>03/6</td>
<td>0001/0&lt;</td>
</tr>
<tr>
<td>AD</td>
<td>1</td>
<td>50/24</td>
<td>50/24</td>
<td>90/38</td>
<td>0325/0</td>
</tr>
<tr>
<td>BC</td>
<td>1</td>
<td>46/34</td>
<td>46/34</td>
<td>48/8</td>
<td>0816/0</td>
</tr>
<tr>
<td>BD</td>
<td>1</td>
<td>56/17</td>
<td>56/17</td>
<td>32/4</td>
<td>0039/0</td>
</tr>
<tr>
<td>A^2</td>
<td>1</td>
<td>31/860</td>
<td>31/860</td>
<td>79/211</td>
<td>0001/0&lt;</td>
</tr>
<tr>
<td>B^2</td>
<td>1</td>
<td>69/320</td>
<td>69/320</td>
<td>95/78</td>
<td>0009/0</td>
</tr>
</tbody>
</table>

SS, sum of squares; DF, degree of freedom; MS, mean square. *p value less than 0.05 indicates model terms are significant.

**Table 4:** Optimized process variables value for adsorption of BR by a factor at a time technique and CCD method

<table>
<thead>
<tr>
<th>Optimal values</th>
<th>Initial BR concentration (mg/L)</th>
<th>Contact time (min)</th>
<th>Adsorbent dosage (g)</th>
<th>pH</th>
<th>Removal%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predicted values by CCD method</td>
<td>88</td>
<td>47/59</td>
<td>16/0</td>
<td>28/6</td>
<td>90/251</td>
</tr>
<tr>
<td>Experimental results based on CCD predicted values</td>
<td>90</td>
<td>60</td>
<td>2/0</td>
<td>6</td>
<td>91/36</td>
</tr>
<tr>
<td>Predicted values by a factor at a time technique</td>
<td>80</td>
<td>00/60</td>
<td>2/0</td>
<td>00/6</td>
<td>92</td>
</tr>
</tbody>
</table>

Figure 5: Effect of pH on the removal due to adsorption of BR on to MMT-MB
initial dye concentration and adsorbent concentration on percentage removal indicates that the percentage removal of BR was increased with increased adsorbent dosage and their combination showed a strong significant effect on the response value (%).

Adsorption Isotherms

The adsorption equilibrium data was analyzed by Langmuir\textsuperscript{33} and Freundlich\textsuperscript{34} models as commonly used to describe the adsorption isotherms and adsorption capacities of the adsorbent. In spite of the increasing number of recent developments for modeling equilibrium adsorption phenomena, the Langmuir isotherm remains popular. Correlation coefficients ($R^2$) and other parameters computed by fitting the experimental equilibrium data to Langmuir isotherm equation were tabulated in Table 5. Accordingly, the adsorption capacities of MMT-MB for BR is 27/39 mg/g.

Thermodynamic Studies

According to Figure 6, the thermodynamic parameters $ΔH_{ads}$, $ΔS_{ads}$, and $ΔG_{ads}$ associated with the adsorption process can be determined using the following Eq. 7.

$$ΔG^0 = -RT\ln K_c$$

where $R$ is the gas constant ($R = 8.314$ Jmol$^{-1}$K$^{-1}$). A convenient form of the van’t Hoff equation then relates $K_L$ to the standard enthalpy and entropy changes of adsorption, $ΔH_{ads}$ and $ΔS_{ads}$, respectively. Figure 6 and the Table indicate just a plot with a correlation coefficient of 0.967. The $ΔH_{ads}$ and $ΔS_{ads}$ values are thus found to be +15617 (J/mol) and +63.24 J/K, respectively, while the $ΔG_{ads}$ value is -4756.91 J/mol in 298 K. The positive value of $ΔH_{ads}$ confirms the endothermic nature of the adsorption process, as has been found in most cases.\textsuperscript{35, 36}

Adsorption Kinetics

The adsorption kinetics of BR on MMT-MB was evaluated by using the first and second-order pseudo-kinetic models at a time interval of 10 to 60 min and already apparent in Table 6.

**Table 5:** Isotherm constants for MB on adsorbents

<table>
<thead>
<tr>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$ (mg/g)</td>
<td>$K$ (L/mg)</td>
</tr>
<tr>
<td>39/27</td>
<td>261/0</td>
</tr>
</tbody>
</table>

**Table 6:** Kinetic parameters for the removal of BR onto MMT-MB

<table>
<thead>
<tr>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{eq}$ (mg g$^{-1}$)</td>
<td>$q_{eq}$ (mg g$^{-1}$)</td>
</tr>
<tr>
<td>1/19</td>
<td>58/4</td>
</tr>
</tbody>
</table>

Discussion

Results obtained from this study showed that the adsorption capacity of the modified adsorbent for the removal of Brilliant Red dye (BR) increased by pH = 6. Accordingly, at pH values below 6, BR is converted to its cationic form; hence, its tendency to absorb decreases. Similar results have been reported for the effect of the
electrostatic interactions in the study of the removal of Brilliant Red dye (BR) by using tannin adsorbent.\textsuperscript{23} The study of the effect of initial dye concentration indicated that more BR was retained by the MMT-MB, and the adsorption mechanism also became more efficient, as the initial dye concentration increased to 80 mg/L. Since the removal percentage for 0.2 g of adsorbent is approximately the same as 0.3 g of MMT-MB, the use of less absorbent is more cost effective; 0.2g of adsorbent in the experiments has been used as an appropriate amount. According to the study by Royer et al., the increase in the adsorbent mass at a fixed dye concentration and volume could lead to unsaturation of adsorption sites through the adsorption process.\textsuperscript{37} The amount of adsorption should be proportional to a period of contact time.\textsuperscript{38, 39} According to the results, the maximum removal of the BR occurs when contact time increases from initial contact time to 60 min.

Up to now, many publications ($>10^4$) have been reported for the study of equilibrium adsorption using this model, especially for liquid phase systems.\textsuperscript{40} Based on the study, the best-fit adsorption equilibrium isotherm was achieved with the Langmuir model, illustrating that homogeneous adsorption occurs. The thermodynamic parameters are considered as a better way of the effect of temperature on adsorption.\textsuperscript{32} The enthalpy changes for the adsorption process (+15617 J/mol) confirms the endothermic nature of adsorption. Adsorption kinetic studies are important in the treatment of aqueous effluents because they provide valuable information on the mechanism of the adsorption process.\textsuperscript{41, 42}

**Conclusion**

In summary, modified Montmorillonite by Methylene Blue was efficiently used as an adsorbent for the removal of Brilliant Red dye (BR) from the textile effluent. The optimal values of the effective parameters on the adsorption process including: pH, adsorbent dosage, initial dye concentration and contact time with one factor at a time technique and Central Composite Design method were investigated. The results indicated acceptable fitting of the used methods with 6, 0.3 g, 80 mg/L and 60 min determination of the analyzed parameters, respectively. The best-fit adsorption equilibrium isotherm was achieved with the Langmuir model, illustrating that homogeneous adsorption occurs. The enthalpy changes for the adsorption process (+15617 J/mol) confirmed the endothermic nature of adsorption. The kinetic data of adsorption using modified adsorbent followed pseudo-second-order kinetics model, consistent with the description of the chemical sorption, indicating that it is the rate-limiting step for the sorption process. In desorption studies, a comparatively high desorption of dye was obtained using Methanol which indicates the modified adsorbent provides the potential for reuse after dye adsorption. As a result, it can be concluded that modified Montmorillonite by Methylene Blue is an effective adsorbent for the removal of BR from textile effluent.

**Conflict of Interest:** None declared.

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