Different Techniques for Enhancing the Removal of Methylene Blue (MB) dye From Aqueous Solution.

Hamdi M. H. Gad, Mahmoud M. S. Ali & Hisham S. Hassan
Hot Laboratories and Waste Management Center, Atomic Energy Authority, P. O. 13759, Inshas, Cairo, Egypt.
E-mail: drhamdigad@yahoo.com

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ABSTRACT
Different techniques were conducted for removal of MB dye from aqueous solution. These techniques which were used separately are: (i) adsorption using activated carbon (AC) prepared from composite of different ratios of Date Pits-Clay (DP-C); (ii) Chemical oxidation using \( \text{H}_2\text{O}_2 \); and (iii) photo degradation using UV irradiation. In the adsorption technique, a series of experiments were undertaken in an agitated batch to assess the effect of the system variables; types of activated carbon, pH, adsorbent and adsorbate concentration, temperature and interfering ions. From the isotherm studies, the Langmuir monolayer capacity was 416.67 mg/g. The kinetic parameters have shown that they could be fitted well to the pseudo-second-order kinetic and intra-particle diffusion models. The temperature study showed that the MB adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. The presence of interfering ions has an insignificant effect with the exception of \( \text{Cl}^- \) anion that slightly decreases the adsorption of MB. Finally, the addition of \( \text{H}_2\text{O}_2 \) and UV irradiation in the presence of AC enhances the removal of MB dye. The rates of the second order for the removal of MB dye take the following order: AC+\( \text{H}_2\text{O}_2 \)+UV > AC+UV > AC+\( \text{H}_2\text{O}_2 \) > AC.

Key words: MB/date pits-clay composite; \( \text{H}_2\text{O}_2 \) chemical oxidation; UV photodegradation.

INTRODUCTION
Two major sources of industrial dyes released into the environment are the effluents from synthesis plants and from dye-using industries, such as textile factories. For example, during textile processing, inefficiencies in the dyeing process results in 10–15% of all dyes being released directly into the wastewater. With a consumption of over 7×10^5 tons of dyes per year, a lot of pressure is imposed on the textile coloration industry, which is often considered as one of the major water polluters taking into account both volume discharged and effluent composition (1–3).

New ecolabels for textile products and tighter restrictions on wastewater discharges are forcing textile processors to reuse process water. Various traditional methods such as adsorption, coagulation, filtration, sedimentation and biological treatments have been used to treat textile dye wastewater, but none of these treatments is satisfactory because of the effluent’s high degree of polarity and complex molecular structure. Furthermore, they all end up in producing a secondary waste product which needs to be dealt with further. A variety of new technologies (e.g. fixed film bioreactors, anaerobic digestion, ozone/UV-oxidation, photocatalysis (UV/TiO\(_2\)), aerobic treatment with fungi) have been studied for textile wastewater treatments to meet this challenge. Though several of these new technologies are promising in terms of cost and performance, they still require further research and/or need broader validation (2, 4–6).

Promising results have been achieved using advanced oxidation processes (AOPs) which are based on in situ generation of strong oxygen-based oxidizers: hydroxyl radicals, ozone, atomic oxygen, hydrogen peroxide, perhydroxyl radicals, which promote destruction of the target pollutant...
until mineralization i.e., oxidation to CO$_2$ and H$_2$O. Especially, the formation of hydroxyl radicals and ozone is desired since they are among the strongest oxidizers, and their reactions with organic compounds are characterized by very high reaction rates. The remarkable advantage of AOPs over all chemical and biological processes is that they neither transfer pollutants from one phase to the other nor produce massive amounts of hazardous sludge. Advanced oxidation processes include ozonation, photocatalytic degradation, Fenton’s reagents (H$_2$O$_2$/Fe$^{2+}$), photo-Fenton, high energy radiation and wet air oxidation (WAO) $^{(4,5,7)}$. In the adsorption technique, a number of workers have used different waste materials. They have studied the feasibility of using low cost materials, such as waste orange peel, banana pith, cotton waste, rice husk, bentonite clay, neem leaf powder, perlite, sawdust carbon, bagasse pith, coal bottom ash, blast furnace slag $^{(8-13)}$ as adsorbents for removal of various dyes from wastewaters.

MB is a thiazine cationic dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on. Although MB is not considered a very toxic dye, it can reveal very harmful effects on living things. After inhalation, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans $^{(14)}$. MB was selected in this study as a model compound for evaluating the potential use of three different techniques to enhance the removal of dye from wastewaters. Namely, adsorption technique using AC prepared from date pits-clay composite, chemical oxidation technique using H$_2$O$_2$ and photo degradation technique using UV irradiation. These techniques were used separately or in combination with each others.

**EXPERIMENTAL**

1. Preparation of activated carbon:

Date pits (DP) was supplied from El-Sharkeya Governorate in Egypt. It was washed with distilled water then, dried at 110 °C for 48 hr to facilitate subsequent crushing and grinding to the particle size in the range of 0.25 to 0.50 mm. The crushed DP was used in two forms; the first is the use of DP only, and the second is a mixture of DP and Clay composite (DP-C) in different weight ratios (clay was supplied from Ismailia canal at Inshas site near Egyptian Atomic Energy Authority). 40 grams of each type was transferred into a stainless steel tube; the tube was admitted into an electric tube furnace and heated at the rate of 50°C/10 min to attain 350 °C. This rate allows free evolution of volatiles, exhausts gases and liquid condensates to be drained. Pure steam was then introduced from the top of the tube using steam generator up to the hold temperatures at 800 °C and soaked at this temperature for 2 hr. The cooled mass was subjected to thorough washing with hot double distilled water until the washings was neutral in effect, then dried at 110 °C for 48 hr, and finally kept in tightly closed bottles.

1.1. Characterization of adsorbent:

The texture characteristics of prepared AC were determined by the standard N$_2$ adsorption isotherms using a NOVA 1000e instrument (Chromatic), USA, followed by their analysis to evaluate the porous parameters. Thermo Gravimetric Analysis (TGA) using Thermo Gravimetric Analyzer Shimadzu TGA-50 Japan evaluated the thermal stability of the adsorbent. The pH of the solution was measured using a 3151 MWT pH meter (MWTGmbH, Germany); the pH was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards.

2. Preparation of MB solutions:

MB is a monovalent cationic dye. It has a molecular formula C$_{16}$H$_{18}$N$_3$ClS and molecular weight of 319.85. Figure 1a illustrates the molecular structure of MB. A stock solution of 1000 mg L$^{-1}$ was prepared by dissolving an appropriate quantity of MB in a liter of double distilled water. The working solutions were prepared by diluting the stock solution to give the appropriate concentration. The concentration of the residual dye was measured using UV/visible spectrometer at a $\lambda_{max} = 664$ nm.
The amount of the dye adsorbed onto unit weight of the adsorbent, $q_e$ (mg/g), is calculated from the following mass balance equations:

$$q_e = \frac{(C_0 - C_e) V}{M} \text{ (mg/g)}$$

(1)

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

(2)

Where; $C_0$ is the initial dye concentration in liquid phase (mg/L), $C_e$ is the liquid phase dye concentration at equilibrium (mg/L), $V$ is the volume of dye solution used (L) and $M$ is the mass of adsorbent used (g).

![Molecular structure and UV Digester](image)

**Figure 1:** (a) Molecular structure of MB. (b) 705 UV Digester (220 V, 60 Hz).

3. Chemical oxidation and photodegradation techniques.

For chemical oxidation technique, hydrogen peroxide 30% (100 volumes) aqueous solution (SIGMA) was used. And for the photodegradation technique, the 705 UV Digester (220 V, 60 Hz) was used (figure 1b).

4. Isotherm models:

The most common sorption models used to fit the experimental data are Langmuir and Freundlich [15, 16] models. The linear form of Langmuir model is given by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

(3)

Where: $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $Q_e$ is the amount of adsorbate per unit mass of adsorbent (mg/g), $Q_0$ is the theoretical monolayer saturation capacity, $b$ (L/mg) is a constant related to the affinity between the adsorbent and adsorbate. The values of $Q_0$ and $b$ can be determined by plotting $C_e/Q_e$ versus $C_e$. The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless factor called separation factor ($R_L$, also called equilibrium parameter) which is defined by the following equation [17]:

$$R_L = \frac{1}{1+bC_0}$$

(4)

The value of $R_L$ indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The second model is the Freundlich model. The linear form of this model takes the form:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$

(5)

Where; $K_f$ (L/mg) and $n$ are Freundlich constants. $K_f$ is correlated to the maximum adsorption capacity, $n$ is an indication of how favorable is the adsorption process. The values of $K_f$ and $n$ can be obtained by plotting $\log Q_e$ versus $\log C_e$.

5. Kinetic studies:

The decolorization of MB was investigated in a batch system. All experiments were conducted using 50 mL flasks. 10 mL of MB solution and a known weight of adsorbent added and the mixture were shaken in thermostated shaker (Kottermann D-1362 Germany) at the desired temperature for
different contact times at 250 rpm. The adsorbent separated from the solution by centrifugation at 4500 rpm for 10 min. A blank sample was performed under similar experimental conditions but in the absence of the adsorbent. Different kinetic models used to fit the experimental data; Pseudo-second order and half-adsorption time, \( t^{0.5} \) and intra-particle diffusion. The pseudo-second order model can be represented in the following form \(^{(18)}\):

\[
t/q_t = 1/k_2q_e^2 + t/q_e
\]

Where; \( k_2 \) is the rate constant of the pseudo-second-order model (g mol\(^{-1}\) min\(^{-1}\)). The equilibrium adsorption uptake \( (q_e) \) and rate constant \( (k_2) \) can be determined from the slope and intercept of the plot of \( t/q_t \) versus \( t \). Half-adsorption time, \( t^{0.5} \), is defined as the time required for the adsorption to take up half as much adsorbent as its equilibrium value. This time is often used as a measure of adsorption rate:

\[
t^{0.5} = 1/k_2q_e
\]

The nature of the rate-limiting step in a batch adsorption system can be also assessed from the properties of the solute and adsorbent. Weber and Morris \(^{(19)}\) stated that if intra-particle diffusion is the rate-controlling factor, the uptake of the adsorbate varies with the square root of time. The root time dependence may be expressed by the following equation:

\[
q_t = C + k_i t^{0.5}
\]

Where, \( k_i \) is an intra-particle diffusion rate parameter. According to Eqn.(8), a plot of \( q_t \) versus \( t^{0.5} \) should be a straight line with a slope \( k_i \) and intercept \( C \) when adsorption mechanism follows the intra-particle diffusion process. Values of intercept give an idea about the thickness of boundary layer, i.e., the larger the intercept the greater is the boundary layer effect \(^{(20)}\).

**RESULTS AND DISCUSSION**

The removal of MB dye from aqueous solution was determined in this study through three different techniques. These techniques are: adsorption, using AC prepared from composite of different ratios of date pits-clay (DP-C), chemical oxidation, using \( \text{H}_2\text{O}_2 \) and photo degradation using UV irradiation. The following will address these methods alone and then compared as grouped in one experiment to optimize the use of these methods.

![Scheme 1: Schematic diagram of the different techniques for enhancing the removal of MB dye from aqueous solutions](image-url)
1: Adsorption Technique:

In the adsorption technique, many factors affect the removal of MB dye from aqueous solution.

1.1: Effect of carbon type

As shown from table 1, preliminary tests indicated that the presence of clay with date pits during the carbonization and activation processes might lead to the creation of some new pores, leading to the increase of surface area or creation of new functional groups. This is reflected by the increase in the % removal of MB dye of sample DP-2%C (94.62%) than the DP only (88.95%). Increasing the clay over 2% decreases the % removal of MB. So, the DP activated carbon containing 2% clay (DP-2%C) was selected for further investigations.

Table 1: Effect of carbon type on the removal of MB from aqueous solution

<table>
<thead>
<tr>
<th>Carbon types prepared</th>
<th>Uptake $q_e$(mg/g)</th>
<th>% R</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP only</td>
<td>44.25</td>
<td>88.95</td>
</tr>
<tr>
<td>DP+ 2% clay (DP-2% C)</td>
<td>47.31</td>
<td>94.62</td>
</tr>
<tr>
<td>DP+ 5% clay</td>
<td>44.10</td>
<td>88.20</td>
</tr>
<tr>
<td>DP+ 10% clay</td>
<td>43.57</td>
<td>87.14</td>
</tr>
<tr>
<td>DP+ 20% clay</td>
<td>43.06</td>
<td>86.11</td>
</tr>
<tr>
<td>DP+ 30% clay</td>
<td>42.54</td>
<td>85.07</td>
</tr>
<tr>
<td>Clay only</td>
<td>41.51</td>
<td>83.03</td>
</tr>
</tbody>
</table>

1.2: Effect of pH

The influence of initial solution pH on the adsorption of MB was investigated in the pH range 2-10 at a constant temperature of 25°C. The maximum adsorption uptake ($q_e$) was obtained at pH range 9-10 is 199.1 mg/g at pH 9, as shown in Figure 2. Any adsorbent surface creates a charge positive or negative on it. This charge is proportional to the pH of the solution, which surrounds the adsorbent particles. A convenient index of the propensity of a surface to become either positive or negative charged, as a function of pH is the value required to give zero net surface charge $\Phi_c$.

![Figure 2: Effect of pH on the adsorption of MB onto DP-2% C activated carbon. ($C_0$=100 mg/L, $W$ = 10 mg, $V$ = 20 ml, time = 5hr and Temp.=25°C).](image-url)
MB is a cationic basic dye as denoted by the presence of the positive charge in its structure. At low pH values, the low adsorption observation is expected due to the increase in positive charge (protons) density on the surface sites and thus, electrostatic repulsion occurred between the MB+ cations and the edge groups with positive charge on the surface as follows:

\[-\text{OH} + \text{H}^+ \leftrightarrow -\text{OH}_2^+\]  \hspace{1cm} (9)

At higher pH, the surface of DP-2%C becomes negatively charged and electrostatic repulsion decreases with raising pH resulting in an increase in the adsorption process. This mechanism can be shown as follows:

\[-\text{OH} + \text{OH}^- \leftrightarrow -\text{O}^- + \text{H}_2\text{O}\]  \hspace{1cm} (10)

\[-\text{O}^- + \text{MB}^+ \leftrightarrow -\text{O}-\text{MB}\]  \hspace{1cm} (11)

A similar theory proposed by several earlier workers for metal adsorption on different adsorbents \((22, 23)\). Therefore, a pH value = 9 was selected as optimum pH for further studies.

### 1.3. Effect of adsorbent dose

Figure 3 illustrates the effect of varying adsorbent doses on the uptake of MB. The uptake of MB will not indicate the optimum amount of adsorbent used because both the % removal and the amount of MB adsorbed show an increasing trend. With the increase in adsorbent concentration from 0.01 to 0.20 mg, the amount of adsorbed MB increases from 20 to 99 %. However, the adsorption uptake decreases from 400 to 99.2 mg/g. In order to determine the optimum amount of adsorbent, the trade-off between the adsorption uptake and the % removal has to be studied. The increase in % removal of MB with an increase in the DP-2%C amount is due to the increase in surface area and active sites available for adsorption. The drop in adsorption uptake is due to the sites remaining unsaturated during the adsorption process \((24)\). For the determination of optimum adsorbent dosage, the optimum value of MB % removal and the adsorption uptake were taken at 86.5 % and 345.8 mg/g, respectively which is equal to 0.1 mg. The amount of adsorbed dye was observed to vary exponentially in accordance with the fractional power term of the adsorbent dose i.e. \((\text{dose})^n\), where \(n=\text{fraction}\). The plots of \(\log q_e\) vs. \(\log (\text{dose})\) are found to be linear \((r=0.997 \approx 1.0)\). This suggests that the adsorbed species/solute may either block the access to the internal pores or cause particles to aggregate and thereby resulting in the unavailability of active sites for adsorption \((24)\).

![Graph 1](image1.png)

**Figure 3**: Effect of adsorbent dose on the % removal of MB by DP-2%C carbon. 
\([C_0= 100 \text{ mg/L}, V = 20 \text{ ml}, \text{ temp.}=25^\circ\text{C and Time = 5 hr.}]\)

### 1.4. Adsorption kinetics

Figure 4 shows the influence of contact time on MB adsorption using DP-2% C. It can be seen that sorption efficiency, in terms of \(q_e\), of MB increases with the increase of shaking time up to 240
min. Maximum sorption efficiency was attained as 92.05% at 25°C. In order to investigate the mechanism of adsorption, various kinetic models were suggested in this study.

Figure 4: Equilibrium uptake of MB by DP-2%C modified carbon composite.

Figure 5 (A) shows the curve-fitting plot of the pseudo second-order equation and the parameters obtained for this model are shown in Table 2. The curve-fitting plot of t/q versus t gives a straight line, and the correlation coefficient was observed to be close to 1.0 for the contact time of 300 min. Also, the theoretical q<sub>e</sub> values for the MB-DP-2%C system are very close to the experimental q<sub>e</sub> values confirming the applicability of the pseudo second-order equation. It is clear from the accuracy of the model that the adsorption kinetic of the MB can be described by a pseudo second-order chemical reaction and that this reaction is significant in the rate-controlling step.

As MB is a basic dye it ionizes in solution to form a positive ion. The structure of DP-2%C composite is a carbon and metal oxides-based and the surface of metal oxides in contact with water is negatively charged at studied pH range, so it is likely that a chemical reaction may take place, which appears to be the main rate determining factor in the adsorption process. The mechanism of adsorption can also be described as chemisorptions, involving valence forces through sharing or the exchange of electrons between adsorbent and adsorbate as covalent forces. If the intra-particle diffusion is involved in the adsorption processes, then the plot of the square root of time versus the uptake (q<sub>t</sub>) would result in a linear relationship and the intra-particle diffusion would be the controlling step if this line passes through the origin. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control. The plots have intercept of 176.6 mg/g as shown in figure 5(B) and table 2.

Figure 5: (A) Pseudo-second-order kinetic plot and (B) Intra-particle diffusion for the adsorption of MB onto DP-2%C.
This further shows that the intra-particle diffusion is not the only rate controlling step, but also some other mechanisms play an important role and control the rate of adsorption process. The results show that the plots presented a Multi linearity, which indicates that two or more steps occur in the process. As shown in Figure 5(B), the external surface adsorption, stage 1: sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. Stage 1 is the fast and completed before 30 min and then the stage of intra-particle diffusion control starts. Stage 2 describes the gradual adsorption stage, where intra-particle diffusion is rate limiting, is attained and continues from 30-60 min. Finally, stage 3 starts after 60 min. The third stage is attributed to the final equilibrium stage where intra-particle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. Surface adsorption and intra-particle diffusion were likely to take place simultaneously and control the kinetics of dye-adsorbent interaction.

### Table 2: Kinetic parameters for the adsorption of MB on DP-2%C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Q&lt;sub&gt;exp&lt;/sub&gt; (mg/g)</th>
<th>Q&lt;sub&gt;cal&lt;/sub&gt; (mg/g)</th>
<th>K&lt;sub&gt;2&lt;/sub&gt; g.mg&lt;sup&gt;-1&lt;/sup&gt;.min&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>r</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-Second order</td>
<td>199.2</td>
<td>208.3</td>
<td>0.002</td>
<td>0.999</td>
<td>0.003</td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td>199.2</td>
<td>C=176</td>
<td>K&lt;sub&gt;i&lt;/sub&gt;=1.59</td>
<td>0.944</td>
<td>2.849</td>
</tr>
</tbody>
</table>

(PH= 9.0, temp.=25°C, C<sub>0</sub>=100 mg/L, V=20 ml and W=0.01 gm.)

### 1.5. Adsorption isotherm

The experimental data are analyzed according to the linear form of the Langmuir and Freundlich isotherms. The linear plots of C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> suggest the applicability of the Langmuir isotherms, Figure 6. From the slope and intercept of the plot the values of Q<sub>m</sub>, b and R<sub>L</sub> are calculated and represented in Table 3. The values of q<sub>m</sub>= 416.67 mg/g, b = 0.545 (mg/l)<sup>-1</sup> and R<sub>L</sub>= 0.018 confirming the favorability of the adsorption process. The Freundlich equation is also employed, K<sub>f</sub> and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively.

![Figure 6: Linear form of Langmuir and Freundlich models for adsorption of MB using DP-2%C AC.](image)

The value of K<sub>f</sub> and n shows the increase of negative charge on the surface which enhances the electrostatic force between the carbon surface and the dye ion, and increases in turn the adsorption of the dye. The values clearly show the dominance of adsorption capacity. The intensity of adsorption is an indication for the bond energies between the adsorbate and the adsorbent and the possibility of a slight chemisorption rather than physisorption. The possibility of multilayer adsorption of dyes
through the percolation process cannot be ruled out. However, the value of n is greater than one indicating that the adsorption is favorable (17, 28, 29).

Table 3: Langmuir and Freundlich adsorption parameters of MB dye by selected carbon obtained from modified carbon composite.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b(mg/l)</td>
<td>Q_m(mg/g)</td>
</tr>
<tr>
<td>MB</td>
<td>0.545</td>
<td>416.67</td>
</tr>
</tbody>
</table>

1.6: Effect of temperature

Temperature has a direct influence on the amount of the adsorbed MB, Figure 7. The uptake of the DP-2% C increased with the increase in the temperature of the system from 25° to 50°C. The thermodynamic parameters were determined using the following equations (30):

\[
K_c = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \quad (12)
\]

\[
\Delta G^\circ = -RT \ln K_c \quad (13)
\]

\[
\log K_c = \frac{\Delta S^\circ}{2.303RT} - \frac{\Delta H^\circ}{2.303RT} \quad (14)
\]

Where, \(\Delta G^\circ\) (KJ/mol) is a change in free energy, \(\Delta H^\circ\) (KJ/mol) is the enthalpy change and \(\Delta S^\circ\) (KJ/mol) entropy change. \(K_c\) is the equilibrium constant, \(C_{\text{solid}}\) is the solid phase concentration (mg/g), \(C_{\text{liquid}}\) is the liquid phase concentration at equilibrium (mg/L), \(T\) is the temperature in Kelvin degree and \(R\) is the universal gas constant.

![Figure 7 (A): Effect of temperature on the removal of MB from aqueous medium by DP-2% C composite, (B) Plot of ln Kc vs. 1/T for estimation of thermodynamic parameters.](image)

The value of \(\Delta H^\circ\) and \(\Delta S^\circ\) obtained from the slope, and intercept of Van’t Hoff plots are represented in Table 4. The value of \(\Delta H^\circ\) is in the range of 1.0 - 93.0 KJ/mol. The positive value of \(\Delta H^\circ\) confirms the endothermic nature of adsorption and the very low \(\Delta H^\circ\) value shows that the dye is physisorbed onto the adsorbent (31, 32).

Table 4: The thermodynamic parameters of the adsorption of MB onto DP-2% C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(\Delta G^\circ)</th>
<th>(\Delta S^\circ)</th>
<th>(\Delta H^\circ)</th>
<th>r</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>-3.98</td>
<td>12.35</td>
<td>8.69</td>
<td>0.989</td>
<td>0.012</td>
</tr>
<tr>
<td>35 °C</td>
<td>-4.50</td>
<td>13.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>-5.05</td>
<td>13.68</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The negative values of \(\Delta G^\circ\) show that the adsorption is highly favorable and indicates that the dye adsorption is spontaneous. The positive value of \(\Delta S^\circ\) refer to increasing disorder and randomness.
at the solid solution interface of the adsorbent. The enhancement of adsorption uptake at higher temperatures may be attributed to the increase of the mobility of MB molecules, enlargement of pore size and activation of the adsorbent active sites surface (33).

1.7. Effect of the presence of cations or anions

The presence of cations: Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\) or anions: Cl\(^{-}\), NO\(_3\)\(^{-}\), SO\(_4^{2-}\) was studied to investigate the effect of interfering ions on the uptake of MB by DP-2\%C. The obtained results represented in table 5 show that Cl\(^{-}\) anions slightly decreases the adsorption of MB, whereas most of the other investigated ions have an insignificant effect on the removal process.

### Table 5: Effect of interfering ions on the MB removal using DP-2\%C composite.

<table>
<thead>
<tr>
<th>Type of cations (50 mg/L)</th>
<th>Type of anions (50 mg/L)</th>
<th>Uptake q(_e) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB only</td>
<td>MB only</td>
<td>198.36</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>Cl(^{-})</td>
<td>198.40</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>NO(_3)(^{-})</td>
<td>198.54</td>
</tr>
<tr>
<td>K(^{+})</td>
<td>SO(_4^{2-})</td>
<td>198.00</td>
</tr>
</tbody>
</table>

1.8: Physico-chemical Characterization of DP-2\%C.

The above results show that the prepared activated carbon with a carbon yield of 16.33% has a promising capacity for removal of MB from aqueous solutions. Therefore, some of its physico-chemical characterization have been discussed and summarized in table 6.

### Table 6: Chemical composition of (D P) and Clay used in preparation of (DP-C) composite

<table>
<thead>
<tr>
<th>Chem. comp. of DP (wt %)</th>
<th>Chemical composition of clay (estimated by XRF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>Moisture</td>
<td>8.0</td>
</tr>
<tr>
<td>Oil</td>
<td>8.8</td>
</tr>
<tr>
<td>Protein</td>
<td>5.0</td>
</tr>
<tr>
<td>Carbohydrates (cellul., hemicellu &amp; lignin.)</td>
<td>61</td>
</tr>
<tr>
<td>Fibre</td>
<td>16</td>
</tr>
<tr>
<td>Inorganic percent</td>
<td>1.4</td>
</tr>
<tr>
<td>Ca %</td>
<td>2.803</td>
</tr>
</tbody>
</table>

1.8.1: Thermo Gravimetric Analysis (TGA)

The TGA of DP-2\%C was studied to investigate its thermal stability at high temperature operating condition and thermal regeneration processes of loaded activated carbon. Figure 8 shows the TGA of DP-2\%C which contains three main steps.

![Figure 8: TGA and DTA analysis of DP-2\%C prepared AC.](image-url)
The first step, which began at 25°C and ended at 65°C, is attributed to the loss of external water molecules. The second main step began at 70°C and ended at 225°C, which is explained by the removal of surface adsorbed water in structure together with degradation of alginate chain in the DP. The third step is obviously due to the complete loss of the organic components and it started at 455°C and ended at 620°C, with the final weight loss of 71.6%.

From the DTA curve, the first endothermic peak appears in the temperature range of 65 to 225°C. Such endothermic effect corresponds to water release and light volatile organic compounds and the size of its area speaks about the amount of water and organic loss and temperature limits in which the release takes place. It is well known that the endothermic effect in the heating process of composite in the temperature range 455 to 620°C is in a consequence of the consumption of the heat or energy for dehydration of the hydrated cations positioned in the framework of composite and the release of water molecules from the nano-channels of the composite structure. According to literature data, the heat needed to remove water molecules from materials channels decreases with the increase in the effective diameter of these channels.

1.8.2: surface area

The surface area of DP-2%C was achieved by the adsorption of N₂ at 77k, Figure 9. The adsorption isotherm was analyzed to get various porous parameters. The BET-surface area was found to be: \( S_{\text{BET}} = 671.27 \text{ m}^2/\text{g} \), total pore volume at \( P/P_0 = 0.95 \) is \( V_P = 0.38 \text{ cc/g} \) and average pore radius from equation: \( r = 2V_P/S_{\text{BET}} \), was evaluated =11.34 Å.

![Figure 9: adsorption and desorption isotherm of N₂ by DP-2% C activated carbon.](image-url)

2. Chemical oxidation and Photodegradation investigations

In these techniques, hydrogen peroxide decomposition and photo-degradation of MB were studied in the presence of AC. As shown from figure10, at the same experimental conditions, the % removal of AC is 92.05 % and increases to 95.3 % by the addition of \( \text{H}_2\text{O}_2 \). If the \( \text{H}_2\text{O}_2 \) was replaced by UV irradiation, the % removal increased to 97.2 %. In the presence of the AC, \( \text{H}_2\text{O}_2 \) and UV irradiation, a significant % removal, 99.8 %, was obtained. It is proposed that the AC can activate \( \text{H}_2\text{O}_2 \) to generate \( \text{HO}^- \) radicals, which can lead to two competitive reactions, i.e. the hydrogen peroxide decomposition or the oxidation of organics in water. In fact, in this work we observed that AC...
presented high removal of MB dye combining the adsorption, oxidation and photo degradation processes.

2.1. Kinetics of MB removal in the combined system

The kinetics of MB removal was studied at different times as shown in figure 11 as it provides information about the mechanism of MB removal from aqueous solutions. The applicability of the pseudo-first order, pseudo-second-order and half removal time were tested for separate and combined systems. The best-fit model selected is based on the linear regression correlation coefficient (r) values.

2.1.1. According to the first order reaction:

The values of the Lagergren first-order rate constant (k₁) determined from the model are presented in table 7 along with the corresponding correlation coefficients (r) and standard deviation (SD). In spite of correlation coefficients r > 0.99 for all used techniques, the first order rate constant
takes the following order: AC+$H_2O_2$+UV $>$ AC+$H_2O_2$ $>$ AC+UV $>$ AC. This means that combination of all techniques is preferred for enhancing the treatment of MB.

Table 7: Kinetic parameters of the removal of MB in the different techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>%R exp.</th>
<th>$k_1$ $\times 10^{-3}$</th>
<th>r</th>
<th>SD</th>
<th>$k_2$ $\times 10^{-4}$</th>
<th>r</th>
<th>SD</th>
<th>$k_{1/2}$ $\times 10^{-4}$</th>
<th>r</th>
<th>SD</th>
<th>$T^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>92.1</td>
<td>7.876</td>
<td>0.9968</td>
<td>0.01762</td>
<td>5.02</td>
<td>0.9959</td>
<td>0.2398</td>
<td>24.8</td>
<td>0.9963</td>
<td>9.0917</td>
<td>22.92</td>
</tr>
<tr>
<td>AC+$H_2O_2$</td>
<td>95.3</td>
<td>29.06</td>
<td>0.9999</td>
<td>0.01164</td>
<td>42.1</td>
<td>0.9994</td>
<td>0.0241</td>
<td>7.387</td>
<td>0.9073</td>
<td>14.700</td>
<td>51.12</td>
</tr>
<tr>
<td>AC+UV</td>
<td>97.2</td>
<td>26.34</td>
<td>0.9996</td>
<td>0.01899</td>
<td>52.4</td>
<td>0.9998</td>
<td>0.0140</td>
<td>5.862</td>
<td>0.9127</td>
<td>11.200</td>
<td>57.07</td>
</tr>
<tr>
<td>AC+$H_2O_2$+UV</td>
<td>99.8</td>
<td>29.82</td>
<td>0.9995</td>
<td>0.02606</td>
<td>58.6</td>
<td>0.9998</td>
<td>0.0144</td>
<td>5.046</td>
<td>0.9196</td>
<td>9.2265</td>
<td>61.65</td>
</tr>
</tbody>
</table>

2.1.2. According to the second order reaction:

The experimental kinetic data were further analyzed using the pseudo-second-order model. A straight line was obtained in all cases and the second order rate constant ($k_2$) and correlation coefficient (r) determined from the plots are summarized in Table 7. It can be noticed that $k_2$ takes the same order as first order reaction which is the following: AC+$H_2O_2$+UV $>$ AC+$H_2O_2$ $>$ AC+UV $>$ AC confirming the preference of the combination of all techniques in the treatment of MB dye form aqueous solution. From Table 7 it is clear that the highest values of (r) and lowest values of SD are obtained in the case of AC+$H_2O_2$+UV and AC+UV. This indicates that, according to the second order, the AC+$H_2O_2$+UV is the best one for treatment of MB. A number of authors have reported pseudo-second-order kinetics for adsorption of MB on wheat shells (34, 35), polygorskite (36) and dehydrated wheat bran carbon (37).

2.1.3. According to half removal time:

The half-removal time, $t^{0.5}$, is defined as the time required for removal to take up half as much removal as its equilibrium value. The half removal time is often used as a measure of the removal rate. Table 7 shows the corresponding parameters which indicates that the half removal time rate takes the following order: AC $>$ AC+$H_2O_2$ $>$ AC+UV $>$ AC+$H_2O_2$+UV. This means that the adsorption with DP-2%C is faster than any other technique. The adsorption technique has the highest value of correlation coefficient (r) and lowest value of SD confirming that it is the fastest technique in the removal of MB dye in our study.

CONCLUSION

The present study shows that the prepared DP-2%C composite is an effective adsorbent for removal of MB dye from aqueous solution whether it is used separately in adsorption technique or in combination with other techniques such as chemical oxidation by $H_2O_2$ or photo degradation by UV irradiation. In adsorption technique, the composite which consists of DP and 2% of clay (DP-2%C) was found to have the highest adsorption value therefore it was used in all further investigations in this work. The removal of MB dye is pH dependent and the maximum removal is attained at pH 9. The equilibrium adsorption was practically achieved through a time of 300 min. It is also a function of initial adsorbent dose, dye concentration, type of interfering anions or cations and temperature of the solution. In addition, adsorption equilibrium data follow Langmuir isotherm model with the monolayer capacity of 416.67 mg/g. The kinetic study indicates that the adsorption follows the pseudo-second-order model with intra-particle diffusion as one of the rate determining steps. The thermodynamic parameters; $\Delta G^\circ$, $\Delta H^\circ$ indicate the spontaneous and endothermic nature of the adsorption process. The positive value of $\Delta S^\circ$ indicates the increasing randomness at the solid/liquid interface. In the combination of adsorption technique with $H_2O_2$ chemical oxidation and/or UV photo-degradation techniques, it was found that according to the first and the second order, the rate constant takes the
following order: AC+H₂O₂+UV > AC+H₂O₂ > AC+UV > AC. Consequently, these techniques in presence of each other lead to enhancement of the removal of MB from aqueous solution.

REFERENCES


