Adsorption of Methylene Blue on Iraqibentonite, Narang Leaves and Corn Seeds Powder From Aqueous Solution

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Abstract
Background: use the bentonite, narang leaves and corn seeds as adsorbent surface for the removal of one of dyes from wastewater was studied.
Objective: The adsorption of methylene blue from aqueous solution are investigate on three adsorbents
Method: UV-Spectrophotometric technique to obtained the quantities of adsorption data at different of temperatures (37, 32, 30 °c) and at pH=1.2 in an attempt to simulate the acidity of gastric fluid.
Results: The quantities adsorbed of methylene blue on bentonite, narang leaves and corn seeds were increased at 37 °c Adsorption characteristics were described using frundlich isotherm.
Conclusion: The adsorption process has been found the value of ΔG showed the spontaneous nature of adsorption for three adsorbents and endothermic in nature and thermodynamic Parameters, Gibb’s free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) have been calculated.
Keyword: Adsorption, methylene blue, bentonite, narang leaves and corn seeds, thermodynamic parameters.

I. Introduction
There are more than 1,00,000 types of dyes commercially available of dyes produced annually, which can be classified according to their structure as cationic and anionic. Waste stream containing dyes is one of the major toxic industrial wastes. Various types of dyes are used in the process industries like textile, paints, pulp and paper, carpet and printing etc. The effluents containing dyes are highly colored and cause water pollution. Methylene Blue, is one of the dyes, it is a cationic dye. It is used in synthetic pigments sand is widely used in textile industry and in several processes such as acrylic, nylon, silk and wool dyeing. In addition it’s a hydrochloride salt are used in the coloring of paper and leather. Therefore the disposal of dye into receiving water causes pollution to the environment. In textile processing, a significant proportion of synthetic organic dyestuffs are released annually to wastestreams which eventually enter the environment. Elimination of dye in the textile dyeing process is very difficult by conventional wastewater treatment methods. These dyes are stable under the environmental effects, such as light, pH and microbial attack. The highest rates of toxicity were found amongst basic and diazo direct dyes. Therefore, it is highly necessary to lowering dye concentration in the wastewater. The elimination methods for treating dye containing wastewaters are electrochemical treatment, coagulation and flocculation, chemical oxidation, liquid–liquid extraction and adsorption. Among these methods, adsorption process is widely used for its simplicity. There are different types of adsorbents such as kaolin, activated charcoal, attapulgite, talc, magnesium triflicate and bentonite. Activated carbon is the most popular for the removal of pollutants from wastewater in the adsorption study the process effects by different parameters including pH, agitation rate and contact time on the adsorption efficiency. These adsorbents or clays have typical properties (large surface area, high cation exchange capacity, chemical and mechanical stability, and a layered structure) that improved them to be good adsorbents. Among these clays is bentonite. Therefore, the bentonite is considered as a good adsorbent material for heavy metal ions such as Pb in aqueous solution due to its typically elevated surface area, high availability and low cost. Bentonite surface consists of one octahedral alumina sheet lying between two tetrahedral layers of silica. Bentonite exhibit negative charge is attributed to the isomorphs replacement of Al for Si in the tetrahedral layer and Mg for Al in the octahedral layer. Langmuir isotherm: for simple solutes, the adsorption behavior is generally uncomplicated, and can be modeled accurately on the basis of the interactions between the adsorbing adsorbate and the surface of the adsorbent and describes the adsorption behavior to a monolayer level of coverage. The Langmuir equation could be expressed as:

$$C_e/Q_e = 1/K + a/k . C_e$$

Where $Q_e$ is the amount of adsorbate (mg/g), $C_e$ is the equilibrium concentration (mg/L), and $a, k$ are constants or sometimes called Langmuir constants. Related to adsorption capacity and energy of adsorption.
Freundlich Isotherm is one of the most important isotherms that found with the adsorption process at solid-liquid interface. Most of surfaces are heterogeneous, so the change in potential energy is regular, and the adsorption sites are not equivalent in energy hence the multilayer formation is highly expected. Freundlich equation could be written as follows:

\[ Q = k_F C_e^{1/n} \] ………(2)

\[ \log Q = \log k_F + \frac{1}{n} \log C_e \] ………(3)

Where \( Q \) is the adsorbate quantity (mg/g), \( C_e \) is the concentration of adsorbate at equilibrium (mg/L), \( k_F \), and \( n \) is the adsorption capacity and an empirical parameter, respectively and also called Freundlich constants (8).

II. Methods

The instruments used were UV - VIS Spectrophotometer (UV-1800) Shimadzu, thermostatic Shaker bath/GFL (D-3006), Germany, pH Meter/HM -73, TDA Electronics Ltd., Centrifuge /eppendorf 5804 R, electronic Balance/Sartorius Lab. BP 3015. The material used is NaOH (Emscope laboratories Ltd). The dye used in this study methylene blue that is obtained from chemical and biochemical department. The chemical formula and molecular weight for methylene blue are \( \text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl} \cdot 4\text{H}_2\text{O} \) and 320 g mol\(^{-1}\).(14) Acid, basic, reactive and direct and soluble dyes, while dispersed pigments and oxidized dyes are insoluble in water. (5)

![Fig (1): structure of methylene blue.](image)

A stock of (500ml) aqueous solution of methylene blue(0.003 mg L\(^{-1}\)) was prepared and its (\( \lambda_{\text{max}} \)) was determined. The maximum absorbance (\( \lambda_{\text{max}} \)) was (495) nm. As shown at figure (2).

![Fig (2):Spectra of aqueous solution of methylene blue at temperature 37\(^{\circ}\)c.](image)

Various drug solutions with different concentrations were prepared by diluting the stock solution with distilled water (0.001, 0.0008, 0.0006, 0.0004, 0.0002  mgL\(^{-1}\)). In order to obtain the calibration curve for aqueous solutions of methylene blue at pH =1.2 the absorbance values of these drug solutions were measured at the specific (\( \lambda_{\text{max}} \)) using UV-Vis double beam Spectrophotometer and plotted versus the concentrations of these drug solutions (in figure 3).
Bentonite: The bentonite clay size 75 µm used in this study was supplied by Geological scanning company and has the following composition (by percentage weight): SiO$_2$ (56.77%), Al$_2$O$_3$ (15.67%), Fe$_2$O$_3$ (5%), CaO (4.48%), MgO (3.42%), K$_2$O (0.60%), Na$_2$O (1.11%), L.O.I (12.49%).

Narang leaves, corn seeds and bentonite adsorbents were in powder form. Also for narang leaves powder and corn seeds powder size 75 µm used in this study, the function groups were supplied by Nano center in university of technology. As shown in figure (5) and (6).
Each of them was washed several times with excessive amounts of distilled water then dried at (150 °C) in the oven for three hours and kept in airtight containers. Each adsorbent was ground and sieved using Retch test sieve 150μm. The time to reach equilibrium state, that is required for full saturation of adsorbent surface at 37 °C by the adsorbate has been determined by the following procedure: 500 ml initial concentration (0.003 mg/L) of adsorbate solution was shaken with (0.5 g) of each adsorbent. The absorbance of adsorbate solutions were measured by UV/Visible spectrophotometer at different intervals 10, 20, 30, 60 …minutes until reaching equilibrium (no further uptake of adsorbate by adsorbent as the time proceeds). A systematic procedure
was followed to determine the adsorption isotherms for each pair of adsorbent-adsorbate systems. A volume of (50ml) of five different concentrations of drug solution (0.001, 0.0008, 0.0006, 0.0004, 0.0002 mg/L) was shaken with (0.5 g) of adsorbent at a certain temperature in a thermostatic shaker. The speed of shaking was 60 cycles per minute. After the equilibrium time (15 min) elapsed, the mixtures were allowed to settle and the clear liquids were either centrifuged at 3500 round per minute (rpm) for 10 minutes. The absorbencies of the filtrate solutions were measured at (λmax). The equilibrium concentrations of the prepared solutions can be determined from the calibration curve using their absorbencies. Adsorbed amount of the drug was calculated at certain conditions from the concentration of solution before and after adsorption according to equation (1):

\[ X_m = \frac{(C_o - C_e) V}{m} \quad \text{(1)} \]

where \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of drug solution (mg/L) respectively, \( V \) is the volume of solution in liter, \( X_m \) is the maximum quantity of adsorbate (in mg) that is adsorbed on the adsorbent at certain value of \( C_e \) that was fixed for all temperatures used in the study, \( m \) is the weight of adsorbent in grams.

\[ Q_e = \frac{X_m}{m} \quad \text{(2)} \]

where \( Q_e \) is the quantity of adsorbate (in mg) held by (0.5 g) of adsorbent. The equilibrium constant (k) for the adsorption process at each temperature is calculated from equation (3):

\[ K = \frac{(Q_e)(0.5 \text{ g})}{(C_e)(0.05 \text{ L})} \quad \text{(4)} \]

where (0.5 g) represents the weight of the clay that has been used, (0.05 liter) represents the volume of the drug solution used in the adsorption process.

The change in free energy (ΔG) could be determined from equation (4):

\[ \Delta G = -RT \ln k \quad \text{(4)} \]

where \( R \) is the gas constant (8.314 J/mol. deg) and \( T \) is the absolute temperature.

The heat of adsorption (ΔH) may be obtained from equation (5):

\[ \ln X_m = \frac{-\Delta H}{RT} + \text{constant} \quad \text{(5)} \]

The change in entropy (ΔS) can be determined from equation (6):

\[ \Delta G = \Delta H - T\Delta S \quad \text{(6)} \]

III. Results

Temperature effects and thermodynamic parameters:

The general shapes of the adsorption of methylene blue on bentonite, narang leaves and corn seeds at different temperatures (37 and 32°C) are given in figures (7, 8 and 9). Figures show that the adsorption of methylene blue increases at 37°C temperature.

![Fig (7): adsorption isotherm of methylene blue on bentonite at different temperatures (37 and 32°C) and at pH=1.2.](image-url)

Fig (8): adsorption isotherm of methylene blue on narang leaves at different temperatures (37 and 32°C) and at pH=1.2.

Fig (9): adsorption isotherm of methylene blue on corn seeds at different temperatures (37 and 32°C) and at pH=1.2.

The study of the temperature effects on adsorption helps in finding the basic thermodynamic functions (ΔH, ΔG, ΔS) of the adsorption processes. Show as that in table (1) gives $X_m$ values at different temperatures and at pH=1.2. Table (1): effect of temperature on the maximum adsorbed quantities of methylene blue on bentonite, narang leaves and corn seeds.

Where $X_m$ is the maximum uptake of adsorbate at certain value of ($C_e$) for all temperatures.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$T_c$</th>
<th>$T_k$</th>
<th>$\frac{1000}{T}$</th>
<th>$X_m$ (mg)</th>
<th>In $X_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>37</td>
<td>310</td>
<td>3.22</td>
<td>0.009</td>
<td>-4.71</td>
</tr>
<tr>
<td>Narang leaves</td>
<td>37</td>
<td>310</td>
<td>3.22</td>
<td>0.007</td>
<td>-4.96</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>305</td>
<td>3.27</td>
<td>0.005</td>
<td>-5.29</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>310</td>
<td>3.22</td>
<td>0.0025</td>
<td>-5.99</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>305</td>
<td>3.27</td>
<td>0.0015</td>
<td>-6.5</td>
</tr>
<tr>
<td>Corn seeds</td>
<td>37</td>
<td>310</td>
<td>3.22</td>
<td>0.009</td>
<td>-4.82</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>305</td>
<td>3.27</td>
<td>0.005</td>
<td>-5.29</td>
</tr>
</tbody>
</table>

Plotting (In $X_m$) versus 1000/T produced a straight line with a slope = - ΔH/R as shown in figures (10,11 and 12).
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Fig 10. In Xm plotted against reciprocal absolute temperature for the adsorption of methylene blue on bentonite at pH=1.2.

Fig 11. In Xm plotted against reciprocal absolute temperature for the adsorption of methylene blue on narang leaves at pH=1.2.

Fig 12. In Xm plotted against reciprocal absolute temperature for the adsorption of methylene blue on corn seeds at pH=1.2.
Table (2) shows the basic thermodynamically values of adsorption of methylene blue on bentonite, narang leaves and corn seeds.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>ΔH</th>
<th>ΔG</th>
<th>ΔS</th>
<th>pH</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>bentonite</td>
<td>+12.14</td>
<td>-5.9</td>
<td>+0.05</td>
<td>1.2</td>
<td>37</td>
</tr>
<tr>
<td>Narang leaves</td>
<td>+12.78</td>
<td>-2</td>
<td>+0.04</td>
<td>1.2</td>
<td>37</td>
</tr>
<tr>
<td>Corn seeds</td>
<td>+15.91</td>
<td>-15.7</td>
<td>+0.1</td>
<td>1.2</td>
<td>37</td>
</tr>
</tbody>
</table>

The negative values of ΔG for the adsorption of methylene blue on bentonite, narang leaves and corn seeds indicated that the adsorption process of folic acid is spontaneous. The positive values of ΔH at different temperatures indicated an endothermic reaction. The positive values of ΔS indicated the increase in the degree of freedom of the adsorbed species (methylene blue). Adsorption isotherms of methylene blue on bentonite, narang leaves and corn seeds at pH=1.2 and different temperatures are shown in figures (7,8 and 9), as indicate offrundlich isotherm depend on Giles classification. Figures (13,14 and 15) show a linear relationship between (log Qe) and (log Ce).

Figure 13. Linear form of freundlich isotherm of methylene blue adsorbed on bentonite at 37 °C and pH=1.2.

Figure 14. Linear form of freundlich isotherm of methylene blue adsorbed on narang leaves at 37 °C and pH=1.2.
IV. Discussion

Many treatment methods have been used to remove dyes from wastewater, which can be divided into chemical, biological and physical methods. Physical methods which include adsorption. The Adsorption is one of the methods commonly used to remove any substance from various aqueous solutions with relatively low concentrations. The efficiency of adsorption relies on the capability of the adsorbent to absorb molecules from the solutions onto its surfaces in addition, a number of intermolecular forces have been suggested to explain this aggregation, these forces include van der Waals forces, ion dipole forces and dipole–dipole forces. The most important in the investigation of adsorption mechanism is the equilibrium adsorption isotherm. These properties such as surface property and the maximum adsorption capacity can be determined from the adsorption isotherm and correlative constants. The process of dye removal by adsorption is being from of use the lower cost adsorbents so that the process becomes economically feasible. Therefore, the researchers are focused on the use of low-cost, reusable, locally available, biodegradable adsorbents made from natural sources like wheat bran, rice husk, waste apricot, bagasse fly ash, powdered peanut hull etc. Natural and modified clays like zeolite, perlite and bentonite are being considered as low-cost adsorbents. Three adsorbents used in this work for adsorption methylene blue dye Bentonite, narang leaves and corn seeds powder were chose. From this work the adsorption isotherms is Freundlich Isotherm S type depend on Giles classification it used to describe the adsorption characteristics for the heterogeneous surface and formation multilayers. This is indicate for bentonite, narang leaves and corn seeds surfaces is heterogeneous. From structure of methylene blue ionic in nature as shows in figure (1) it is carry a net positive charge in the presence of protonated amine or sulfur containing groups. It can be adsorbed on different site of each adsorbent due to the polar ends of the dye molecule have a tendency to adhere to the heterogeneous surfaces of adsorbent and can separates out from aqueous solution. Therefore, in this work the adsorption processes between the methylene blue and negative site of hydroxyl group in the bentonite site surface is attributed to the isomorphous replacement of Al\(^{3+}\) for Si\(^{4+}\) in the tetrahedral layer and Mg\(^{2+}\) for Al\(^{3+}\) in the octahedral layer. This negative charge is balanced by the presence of replaceable cations (Ca\(^{2+}\), Na\(^{+}\), etc.) in the structure. In addition the functional groups of heterogeneous surfaces analysis for narang leaves surface and corn seeds surface were detected by used the FT-IR spectrum it found at 3400 cm\(^{-1}\) is O-H bond of these surface compounds, a 2922 cm\(^{-1}\) vibration of CH\(_2\), 2852 cm\(^{-1}\) vibration of CH\(_3\), 1797 cm\(^{-1}\) C=O of carboxylic acids band ,1637 cm\(^{-1}\) vibration of COO, C=O and C-N bands, peptide bond of proteins, a 1426 cm\(^{-1}\) was of phenolic O-H and C-O stretching bond,a 1033 cm\(^{-1}\) band was vibration of aliphatic C=O bands. The <1000 cm\(^{-1}\) indicated finger print zone which were phosphate and sulphuregroups. And there are two bands at 1022 cm\(^{-1}\) and 465 cm\(^{-1}\) could be attributed to the stretching and bending vibrations of the SiO\(_2\) in the structure of narang leaves surface the functional groups of corn seeds surface are two bands at 1022cm\(^{-1}\) and 465 cm\(^{-1}\) could be attributed to the stretching and bending vibrations of the SiO\(_2\) in the structure. Also there is at 2900 cm\(^{-1}\) could be attributed to C-H band stretching for aliphatic chain and at 1720 cm\(^{-1}\) there is a band related to the C=O of the carboxylic group.

![Figure 15](image-url)
In this studied used pH (1.2) at low pH showing that adsorbents have positively charged surface. Which enhance adsorbing basic dyes, e. the adsorbent have a zero point charge at pH lower, the surface of the adsorbent becomes positive charged which enhances the adsorption of negatively charged from functional groups of the adsorbate as shown in figure (1)through the electrostatic forces of attraction on the surface of adsorbent. In this study found the temperature effect on the adsorption process increasing with increasing temperature. It might be that stronger bonds are formed at higher temperatures and in this fact that the adsorption is endothermic. Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) used to know the nature of adsorption process. In this work the negative values of ΔG° for all temperatures indicate the spontaneous nature of adsorption with a higher preference of Methylene Blue onto (bentonite, narang leaves and corn seeds). The value of ΔH° was positive, indicated that the adsorption reaction was endothermic. The positive value of ΔS° shows that increasing randomness at the solid/liquid interface during the adsorption of Methylene Blue on adsorbents.

V. Concluded

It conclude the bentonite surfaces showed ability to adsorb the methylene blue dye from its aqueous solution it higher than narang leaves surface and its higher than the corn seeds surface at pH=1.2 and different temperatures, therefore, these adsorbents can be used as antides to decreasing of methylene blue dye concentration. The adsorption isotherms of methylene blue on bentonite, narang leaves and corn seeds project a Freundlich isotherm model. These results indicated the surface heterogeneity of the adsorbents leading to different adsorption affinities towards dye molecules and adsorption strengths from site to site. The FT-IR spectrum results showed the adsorbents have characteristic bands of proteins, lipids and carboxylic acid groups which are able to react or adsorbed with functional groups of dye molecules from aqueous solutions. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) showed that the adsorption process of methylene blue dye on each adsorbents was spontaneous and endothermic.

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