Adsorption of Malachite Green Dye by Bio- micro-adsorbent from Aqueous Solution at Different Temperatures

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Abstract. The objective of this study is to test the ability of algae bio adsorbent to absorb green malachite (MG) from aqueous solutions. The properties of the bioadsorbent surface have been diagnosed through several spectral techniques such as FTIR and SEM / EDX. The batch adsorption system was used to study the effect of both temperature and equilibrium time parameters on the adsorption capacity of the algal biomass. The percentage of adsorption of dye was obtained at a concentration of 80 mg L\textsuperscript{-1}, biosorbent size 150 μm, 0.02 g dose, and 60 min of equilibrium time by Biomass reached to (100%). The adsorption kinetics were tested using several kinetics models. The results showed that malachite green adsorption by algae biomass follows pseudo-second order model with a high coefficient (R\textsuperscript{2} = 0.99). We conclude from this study that algal biomass is highly efficient in cationic dyes adsorption from aqueous solutions.

Keyword: Adsorption, Malachite Green, Bioadsorbent, Algae , Adsorption kinetics, Activation Energy.

1. INTRODUCTION

Textile industries include the process of tissue dyeing. As a result of this process, large amounts of liquid waste are produced into the water, causing widespread environmental problems. There are more than 10000 of the commercially known dyes which are produced in large quantities of about 700,000 tons per year and are widely used in industry such as paper, plastics, cosmetics and rubber on a large scale, [1].

Waste water Dyeing textile industries cause growing environmental concern because the dyes are non-biodegradable materials in nature, leading to their accumulation in the environment. Several methods have been used to try to solve this problem by relying on the reduction of biological oxygen but found it ineffective to remove these pigments. But the combination of some techniques such as adsorption and degradation contribute to solving this problem. [2]

Absorption processes have proven to be an useful method of treating sewage dye [3]. Tracking the adsorption kinetics of batching is important for the format of the industrial adsorption column [4]. Chemical Kinetics show how quickly the rate of chemical reaction occurs and also the parameters affecting the reaction rate. The adsorption process affected by the physiochemical properties of the
adsorption systems In addition to system conditions. In order to study the kinetic behavior of a solid-liquid adsorption process, several kinetic expressions were used as are the pseudo first order kinetic, pseudo second-order kinetic and Second order model (Elovich) [5].

A specific study examined a test to determine the optimal conditions for the process of Methyl violet adsorption (100 mg / L concentration) from aqueous solutions using response surface methodology (RSM). As a result of this test, optimum conditions were found to be temperature 33 ° C, contact time 180 min, adsorbent size 250 meshes, adsorbent dose 500 mg and agitation speed 200 rpm. The results of these conditions examined the kinetic adsorption of the Methyl violet by compensating the practical results in several kinetic models (Elovich’s, intraparticle diffusion equations). The results elucidated that they applied to the intraparticle diffusion model which indicate importance of intraparticale diffusion in the adsorption mechanism of dye.[6]

The bioadsorption of nickel ions from aqueous solutions was studied on a bioadsorbent surface (Sargassum swartzii), the diagnosis of the active groups of the bioadsorbent surface using FT-IR spectroscopy. The morphophilic surface was observed through the scanning electron microscopy (SEM), EDX technique ability to analyze the elementsand their contribution for the biosorption of Ni (II) ions, from adsorption data which obtained from the continuous process was found to be the highest adsorption at pH 4. This indicates that the Sargassum swartzii can be used as an effective bioadsorbent surface for adsorption of nickel ions from wastewater.[7]

Several types of biomass, such as algae, fungi, yeast cells and bacteria, are used to remove contaminants from water bodies through the association of contaminants with the active groups of these biomass. In this study, algae (algae ponds) are used to adsorb malachite green from their aqueous solutions.[8]

Thus, the objective of this study is the possibility of using these algae to adsorption MG of aqueous solution at several adsorption conditions adsorbent dose, temperature, contact time on adsorption in a batch system and achieve kinetic models of adsorption,

2. MATERIALS AND METHODS

2.1 Biosorbent preparation: For this study algae biomass was used as a low-cost bioadsorbent. The amounts of algal biomass were collected from ponds in the al-Griatt area farms / Baghdad city. The biomass collected with distilled water was then washed several times to dispose all undesirable materials such as plant residues and soil. And then subjected to sunlight for 15 days for the purpose of drying while kept in a desiccator and then drying in the oven (Labtech Oven LDO-60e, South Korea) at 80 ° C for 24 hours. The dried biomass is then grated by a mortar and agate stone mortar, using a sieve, to determine the particle size of a 150 μm sieve. This algal biomass is symbolized by G.

2.2 Adsorbate: The basic dye, Malachite green (chemical formula C_{23}H_{25}ClN_{2}, nature basic blue, molar mass 364.91g/mole and the maximum absorption wave length (λ_{max}) for MG dye has been used in this study is 616nm. The chemical structure of MG dye is shown in figure 1.

![Chemical structure of Malachite green dye (MG)]
2.3 Batch adsorption studies: Biosorption tests were achieved in batch system to find the effect of contact time and temperature parameters. The stock solution of MG dye was prepared in distilled water is (80 mg L\(^{-1}\)) and PH = 2.9 (pH meter BP3001, Singapore). To investigate the effect of contact time and temperatures on dye adsorption, different times and temperatures were used. The many of tests were conducted by putting 15 ml of dye solution in an Erlenmeyer flask and adding (0.02g) of bioadsorbent to that in a shaker water bath (Labtech, South Korea). After attainment of equilibrium The adsorbent in the sample (MG dye solution + adsorbent) were separated by centrifugation (Centrifuge.6000rpm.Hittelch(EBA-20),Germany) and the concentration of MG dye at any time was determined in the supernatant solutions. the aqueous phase was analyzed for remaining dye concentration using UV-visible spectrophotometer (Double beam shimadzu.1800, Jaban). All the tests were carried in twice and the result expressed as the mean values. The percent of dye adsorbed (A%) on adsorbent was calculated by equation:

\[
A\% = \left(\frac{C_o - C_t}{C_o}\right) \times 100
\]

Where \(C_o\) is the initial concentration of dye (mg L\(^{-1}\)), \(C_t\) are the remaining concentration of dye (mg L\(^{-1}\)) at time.

3. RESULTS AND DISCUSSION
3.1 Characterization of the Adsorbent

Infrared spectra were recorded using FTIR Spectrophotometer (Shemadzu IRAffinity-1S FTIR, Jaban) within 400-4000 cm\(^{-1}\). From the figure (2), there are several distinct peaks of the functional groups of the surface of the biomass (G), reflecting the complex nature of the surface, which includes a wide peak of 3100-3700 cm\(^{-1}\) that may be due to the O-H stretching vibrations for the glucose molecule. Within the structure of the cell walls and NH\(_3\) (amine group) stretching vibrations of the proteins. The reason for the broad band is due to the intra or inter-bonded of hydrogen bonding between functional groups and the presence of a weak peak at 3080 cm\(^{-1}\) site belonging to the symmetry CH chiral group. In 1627 cm\(^{-1}\) site, which are due to vibration of the carbonyl, aldehyde, ketone or carboxylic acid groups and a weak peak at 1257 cm\(^{-1}\) site belonging to the (SO\(_3\)) stretching vibrations, and the presence of a medium peak at 1001 cm\(^{-1}\), which is return to the vibration of the group of (C-O), which is due to alcohols or carboxylic acids.[9-11]

![Figure 2. FTIR spectrum of the Biomass (G)](image)
Scanning Electron Microscopy technique SEM Inspect S 50 (FEI, NETHERLAND) was used for analysis of biomass surface structure characteristics. The photomicrographs were recorded at 2000x magnification with accelerating voltage of 15 kv. The SEM image clearly showed the surface texture and morphology of the bioadsorbent G (Figure 3). Which include cylindrical structure (diatoms) which are a type of bacillary algae that have different diameters and lengths. Also, biomass include the microstructure bodies with different porous and irregular diameters, reflecting the heterogeneous nature of the surface, more porosity and therefore high specific surface area. This surface characteristic would result in the higher ability for adsorption [12,13]

![Figure 3. SEM images of biomass (G)](image1)

the elements were detected in the bioadsorbent by using EDX X Flash6110 (Bruker, German). In the present study various elements were identified from biomass. The peaks of carbon, silicon and aluminum were analyzed in EDX spectrum (Figure 4).

The presence of carbon indicates the presence of organic compounds, while the presence of both the silicon and aluminum to the mineral oxides, on the other hand, the high weight ratios of carbon, aluminum and silicon relative to other elements in the biomass work to give it the capacity of adsorption and ion exchange. [14]

![Figure 4. EDX spectrum of the Biomass (G)](image2)
3.2 Effect of Contact Time

The time of contact was an influence on the dye adsorption balance (MG), which was studied in the batch system at a constant concentration of dye (MG) 80 mg L⁻¹. The results were represented on the graph between qt versus contact time (t). Figure 6 shows that the adsorption ability of dye increases with rising contact time. The dye adsorption rate is high initially due to the availability of adsorption sites. Rapid transfer of dye molecules from aqueous solution to the bulk makes adsorption fast. Then the speed begins to gradually decrease to a specific value representing the state of saturation or depletion of all the dye in the solution to the surface. In this study, the maximum adsorption occurred within the first 60 minutes as shown in the figure below [15]. On the other hand, we observed the adsorption percent increase with increasing temperatures so the adsorption percent reached to ratio 100% at time 60 min and temperature 308K these lead to indicate the nature of (MG) adsorption processes on biomass (G) are endothermic. [16]

![Figure 5. Effect of contact time on the biosorption of malachite green dye at constant concentration 80mg L⁻¹ at different temperatures.](image)

3.3 Kinetic Studies

Adsorption kinetics depend on adsorbent-sorbate interactions and Operating conditions such as temperature, contact time. Several kinetic models are used to explain the nature of adsorbents and also to check the control mechanism. The practical data was examined using many kinetic models: pseudo-first order, pseudo-second order and elecovich equation models.

The pseudo-first order rate equation used for the adsorption of solute from a liquid solution using the following expression [17]:

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

Where \( q_e \) is the quantity of (MG) dye adsorbed at equilibrium [mg/g], \( q_t \) is the quantity of (MG) dye adsorbed at any time [mg/g] and \( K_1[\text{min}^{-1}] \) is rate constant of the pseudo first order adsorption these can be calculated from the linear plot (figure 6) of ln (\( q_e - q_t \)) Vs t [slope = \( K_1 \), \( q_e \) = intercept]. The adsorption of pseudo first order rate constant and correlation coefficient \( R^2 \) values are summarized in Table [3].
The second order equation was examined on the same range of time. The pseudo second order equation [18]:

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (3)

Where $K_2 \text{[g mg}^{-1}\text{min}^{-1}]$ is the rate constant of the pseudo second order adsorption. $q_e$ and $K_2$ can be determined from the slope and intercept a linear relationship from of the plot of $t/q_t$ Vs $t$ respectively (figure 7). $q_e$, $K_2$ and the correlation coefficient $[R^2]$ values are recorded in Table [3].

The elovich model equation is generally expressed as [19]

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$  \hspace{1cm} (4)

Where $\alpha$ is the initial adsorption rate [mg g$^{-1}$ min$^{-1}$], $\beta$ is the desorption constant [g.mg$^{-1}$] during any one tests. A plot (figure 8) of $q_t$ Vs $\ln t$ should yield a linear relationship with a slope and an intercept were equal to $[1/\beta]$ and $1/\beta \ln(\alpha\beta)$ respectively. The elovich model parameters $\alpha$, $\beta$ and $[R^2]$ are recorded in Table [3].

**Figure 6.** First-order kinetic modeling of MG dye adsorption

**Figure 7.** Second-order kinetic modeling of MG dye adsorption
Table 1: The kinetic parameters for the adsorption of malachite green dye on the biomass (G)

| Model            | Temperature /K | R²    | Pseudo first-order | Pseudo second-order |
|------------------|----------------|-------|--------------------|---------------------|
|                  |                |       | qₑ,cal (mg/g)      | k₁ (min⁻¹)         |
|                  |                |       |                    |                     |
| Pseudo first-order | 293            | 0.979 | 1.086              | 0.025               |
|                  | 298            | 0.966 | 1.039              | 0.031               |
|                  | 303            | 0.808 | 1.647              | 0.062               |
|                  | 308            | 0.939 | 0.686              | 0.056               |
| Pseudo second-order | 293            | 0.999 | 60.096             | 0.0032              |
|                  | 298            | 0.999 | 61.012             | 0.0047              |
|                  | 303            | 0.999 | 60.864             | 0.0080              |
|                  | 308            | 0.999 | 60.313             | 0.0227              |
| Elovich equation |                |       |                    |                     |
|                  |                |       | β (g.mg⁻¹)         | α (mg.g⁻¹.min⁻¹)    |
|                  |                |       |                    |                     |
|                  | 293            | 0.970 | 0.194              | 2863                |
|                  | 298            | 0.990 | 0.246              | 72727               |
|                  | 303            | 0.926 | 0.290              | 1119589             |
|                  | 308            | 0.866 | 0.630              | 4.06×10⁻¹⁴          |

From table (1) we observed the value of R² for pseudo second order higher than pseudo first order and elovich models and the quantity of dye adsorbed (qₑ,cal) for pseudo second order more than pseudo first order and elovich models, these indicate The pseudo second order kinetic model fitted better than pseudo first order and elovich models [20]. This means that the adsorption of MG dye on bioadsorbent is by chemisorptions [21].

Based on the above we use the rate constant (k₂) of the pseudo-second-order model to determination the activation energy of the methyl green adsorption process using the Arrhenius equation (22):

\[ \ln k₂ = \ln A - \left( \frac{E_a}{RT} \right) \]
where \( k_2 \) = the rate constant of the second-order model (g/mg min), \( A \) = the frequency factor, \( E_a \) = activation energy of adsorption process (KJ/mol), \( R \) = the universal gas constant (8.314 J/mol K) and \( T \) = the temperature (K), respectively. From the slope of the plot of \( \ln (k_2) \) versus \( 1/T \) as fig. 6 the activation energy could be calculated which equal to 94.6 kJ/mol this value refer to type adsorption process is chemical adsorption.[23]

![Figure 9. A plot \( \ln k_2 \) versus \( 1/T \)](image)

4. CONCLUSIONS
This study shows that algal biomass has high efficiency in adsorption of green malachite (MG) aqueous solution and can be an effective and valuable means of controlling water pollution due to cationic dyes. The batch absorption tests showed that the absorption percent of MG dye by bioadsorbent (G) reached 100%. The results of kinetic experiments show that adsorption continues through the pseudo-second order kinetics. This study showed that the algae bioadsorbent (G) has the potential of total adsorption of MG dye from aqueous solutions.

Knowledge
The authors is thankful to the collage of Education for pure sciences (Ibn Al-Haitham) providing the requirements research and their nice services during the study period.

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