Removal of Amaranth Dye from aqueous Solution using Pomegranate Peel

Hana'a Adii Ali, Hana'a Kadhem Egzar, Noor Mustafa Kamal, Naha abdulsaheb and Muthana Saleh Mashkour
Chemistry Department, College of Science, Kufa University, Najaf, Iraq

Abstract-- Pomegranate peel was tested for its ability to adsorb amaranth dye from solutions with alterations in the parameters such as pH, contact time, sorbent weight, and temperature. The adsorption process was analyzed on the basis of pseudo-first-order, pseudo-second-order kinetic models and also by Freundlich and Langmuir isotherm models. The maximum adsorption capacity for pomegranate peel as calculated by Langmuir model was found to be 3.448mg/g and 3.560 g L at 25°C. Thermodynamic parameters such as the changes of free energy, enthalpy, and entropy were also evaluated. The results indicated that the sorption amaranth dye onto the pomegranate peel was an endothermic process that could be well fitted with the Langmuir adsorption model and pseudo-second-order kinetic model.

Index Term-- Adsorption, amaranth dye removal, Pomegranate peel.

1. INTRODUCTION

In recent years, the search for low-cost adsorbents that have metal binding capacities has intensified. Agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, wool, orange peel, compost and leaves. Pomegranate peel, a by-product of the pomegranate juice industry is therefore an inexpensive, pomegranate, is one of the most popular fruits in the world due to its pleasant taste, high nutritional value, and many medical features. It consists of edible part, seeds, and peel. The pomegranate peel constitutes 5% to 15% of its total weight. Pomegranate peel is a material composed of several constituents, including polyphenols, ellagitannins and gallic and ellagic acids. The removal of dyes in the effluents is one of the major problems requiring solution by the textile industries. Some processes have been employed in order to solve this problem, such as adsorption, chemical flocculation, chemical oxidation, and biological techniques. Adsorption appears to be a good alternative for the treatment of effluents. Adsorption method may be one of environment friendly, economic and efficient techniques with considerable potential for the removal of dyes from contaminated water.

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewaters.

Amaranth is extensively used in textile industries, a dark red to purple azo dye once used as a food dye and to color cosmetics, but since 1976 it has been banned in the United States by the Food and Drug Administration as it is a suspected carcinogen. It usually comes as a trisodium salt. It has the appearance of reddish-brown, dark red to purple water-soluble powder that decomposes at 120 °C without melting. Its water soluble has absorption maximum at about 520 nm. Amaranth is an anionic dye. It can be applied to natural and synthetic fibers, leather, paper, and phenol-formaldehyde resins. Amaranth was, during the middle of the 20th century, made from coal tar modern synthetics are more likely to be made from petroleum byproducts. Its name was taken from Amaranth grain, a plant distinguished by its red color and edible protein-rich seeds.

Fig. 1. Structure of amaranth dye

The present work was undertaken to explore the feasibility of finding a low cost effective adsorbent, Pomegranate peel for the treatment of amaranth dye from aqueous solution as a function of temperature, dosage, contact time and pH by batch mode adsorption studies and to report the applicability of various kinetic models for the chosen dye by the adsorbent in a controlled system.

2. MATERIALS AND METHODS

2.1 Adsorbent

Pomegranate peel were first washed with double-distilled water and dried in an oven at 70°C for 24 hours. The dried pomegranate peels were crushing, and this material was then simmer with distilled water for two hour at polling point then filtered, this process was repeated to get rid of all colored or soluble materials then filtered and dried. The dried material was mixed with volume of concentrated H₂SO₄ (2N) at room temperature. After 2 hours then filtered, the excess of the acid was removed by washing the solid residue, repeatedly with distilled water till the residue was free from the acid and then dried the product at room temperature. The produce thus prepared was kept in hot air oven at 110°C for 8 hours. The activated carbon thus obtained was ground to yield a fine powder and fractionated into different mesh sizes.
2.2 Adsorbate
Amaranth dye (molecular formula: C\textsubscript{20}H\textsubscript{11}N\textsubscript{2}Na\textsubscript{3}O\textsubscript{10}S\textsubscript{3}; Molecular Weight 604.47 g/mol) is an anionic sulphonate azo dye derivative. Its water soluble dye has absorption maximum at about 520 nm.

2.3 Effect of Contact Time.

The adsorption of amaranth on pomegranate peel was studied as a function of shaking time at 25\textdegree C\textsuperscript{0}. A sample of 15 cm\textsuperscript{3} of dye (25 ppm) solution was taken in eight titration flasks, labeled them from 1–8, and shaken with 0.1g of carbon in each flask for different intervals of time ranging from 5min to 40 min in a shaker. After equilibration the suspension was centrifuged for 15minutes at 2000 rpm. The supernatant was carefully removed by a syringe with a long pliable needle and absorbance was determined photometrically at wavelength 520 nm. From it, calculate the equilibrium concentration (Ce) of dye, percentage removal, and equilibrium time was determined by plotting a graph between different time intervals and percentage removal.

Figure 2 shows the variation of percentage removal adsorption as a function of shaking time. The result shows that the adsorption of dye solution on pomegranate peel is symmetrically time dependant which increases with the shaking time rapidly and gets to an equilibrium stage after 25 minutes which dose not change latter on. So for all other experiments shaking time was kept 25 minutes.

At 25 minute, the maximum adsorption is observed due to the attractive forces developed between dye and surface. Initial adsorption of dye is on exterior surface of carbon. After complete adsorption on outer surface, the dye enters to the inner surface via pores\textsuperscript{(17)}. After 25 minutes desorption takes place.

![Fig. 2. Effect of contact time on adsorption of amaranth by pomegranate peel.](image)

2.4. Effect of pH.

The adsorption of amaranth dye on pomegranate peel was studied as a function of different pH. 3–11, that are, amaranth concentration (5-35 ppm), shaking time (25min). After equilibration, the suspension was centrifuged for 15minutes at 2000 rpm. The supernatant was carefully removed by a syringe with a long pliable needle and absorbance was determined photometrically at wavelength 520 nm.

From it, calculate the amount of equilibrium concentration (Ce) of amaranth, percentage removal, and determined the adsorption of amaranth on pomegranate peel at different pH by plotting a graph between different pH and percentage removal. Figure 3 shows the variation of equilibrium concentration (Ce) and percentage removal as a function of different pH. The result shows that the adsorption of amaranth on pomegranate peel increases in acid medium at pH 3. The similar trend of results was reported for colour removal \textsuperscript{(18,19)} The surface of the carbon become highly protonated under acidic conditions that favored the adsorption of dye in the anionic form. The increase in pH value caused a decrease in protonation of the surface, which led to a decrease in the net positive surface potential of sorbent. This decreased the electrostatic forces between sorbent and sorbate, leading to reduced sorption capacity\textsuperscript{(20,21)}. 

![Graph showing variation of percentage removal against time.](image)
2.5. Effect of Adsorbent amounts.

The adsorption of amaranth dye on pomegranate peel was studied as a function of different amount of adsorbent, that is, 0.1–1.0 g, while keeping all other parameters that is, dye concentration (25 ppm), shaking time (25 min), and pH (3.0), of the suspension constant. Calculate the equilibrium concentration \( (C_e) \) of dye and percentage removal adsorption and determine the adsorption of dye on pomegranate peel at different amount of adsorbent by plotting a graph between different amount of adsorbent and percentage removal adsorption. Figure 4 shows the variation of percentage removal adsorption as a function of different amount of adsorbent. The results show that the adsorption of dye on pomegranate peel increases spontaneously with increasing adsorbent concentration until 0.25 g then decrease. This may be due to the increase in the availability of surface active sites resulting from the increased dose\(^{(22)}\).

However, the adsorption capacity showed a decreasing trend with increasing adsorbent dosage. If the adsorbent amount is increased by keeping the dye concentration constant, the amount of adsorbed per unit mass showed a decrease due to availability of less number of dye ions per unit mass of the adsorbent. The drop in adsorption capacity is basically due to the site remaining unsaturated during the adsorption process. The same trend was also reported by other researchers\(^{(23)}\).

On the basis of these results, 0.25 g of pomegranate peel was selected for further studies.

2.5 Effect of Temperature.

The adsorption of dye on pomegranate peel was studied as a function of different temperature, that are, (20, 30\(^{\circ}\)C, 40\(^{\circ}\)C and 50\(^{\circ}\)C), dye concentration(5-35 ppm), shaking time (25 min), sorbent concentration (0.25 g), and at natural pH. From it calculate the equilibrium concentration \( (C_e) \) of dye and percentage removal and determined the effect of temperature on adsorption of dye on pomegranate peel by plotting a graph between different temperature and % age adsorption. Figure 5 shows the variation of percentage removal adsorption as a function of different temperature. The results show that the adsorption of dye on pomegranate peel was increased with increasing temperature which indicates that adsorption of dyes in this system was an endothermic process\(^{(24)}\). The result same to also reported by other researcher\(^{(24)}\).

Increase in adsorption at elevated temperature is due to the enlargement of pore size from where dye adsorbed\(^{(17)}\), and may be attributed to increased penetration of reactive dyes inside adsorbent at higher temperatures or the creation of new active sites\(^{(25)}\).
2.6 Adsorption Isotherm.

The adsorption of amaranth dye on pomegranate peel was studied as a function of different dye concentration that is, 5–35 ppm, while keeping all other parameters that are, shaking time (25 min), pH (3), and sorbent concentration (0.25 g) constant. 15 cm$^3$ of dye (5 ppm to 35 ppm) solution was shaken with 0.25 g of pomegranate peel for 25 min in a shaker. After 15 minutes, the absorbance was determined photometrically at wavelength 520 nm. Then calculated the adsorbed amount of dye and equilibrium concentration ($C_e$) and determine the adsorption isotherms dye on pomegranate peel carbon by plotting a graph between extent of adsorption ($\log q$) and equilibrium concentration $\log C_e$.

There are two types of adsorption isotherm: Langmuir Adsorption Isotherm, and Freundlich Adsorption Isotherm. The adsorption isotherms were used to investigate the relationship between the concentration of sorbed species and sorption capacity of sorbing species.

**A-Langmuir Adsorption Isotherm.** Linear form of Langmuir adsorption isotherms is shown as follows:\(^{27}\):

$$\frac{1}{q_e} = \frac{1}{Q_{\text{max}}} + \frac{1}{bQ_{\text{max}}} \cdot \frac{1}{C_e}$$  \hspace{1cm} (1)

$q_e$: sorption capacity, $C_e$: equilibrium concentration, $Q_{\text{max}}$: maximum possible amount of dye that can be adsorbed per unit dry weight of sorbent, $b$: Empirical constant, indicating the affinity of sorbent towards the sorbate\(^{28}\).

A curve $1/q_e$ versus $1/C_e$ has been plotted to investigate the fitting of Langmuir model for the equilibrium data of carbon-dye sorption a straight line was obtained. The correlation coefficient $R^2$ was found to be 0.9436 indicating that the data was fitted well the Langmuir model (Figure 6). From the Langmuir plot, $Q_{\text{max}} = 3.448$ mg/g and $b = 3.560$ L/mg. The characteristics of the Langmuir isotherm can be expressed as another constant separation factor or equilibrium parameter given by $R_L$:\(^{29}\).

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} (2)

where $K_L$ is Langmuir’s Equilibrium Constant which is related to the affinity of binding sites and ($K_L = Q_{\text{max}} \cdot b$), $C_0$ is the initial dye concentration. $R_L$ between 0 and 1 indicates favorable adsorption. In the current experiment $R_L$ is found to be 0.007961 and again the adsorption is found to be favorable\(^{30}\). The results of present investigation were compared with the earlier reports\(^{31,32}\); which were carried out as adsorption studies by using different types of dyes and on low cost adsorbent.
B-Freundlich Absorption Isotherm. Linear form of Freundlich adsorption isotherms is shown as (33).

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e 
\]

where \( q_e \) is the equilibrium dye concentration sorbed in sorbent (mg g\(^{-1}\)), “\( C_e \)” is the dye equilibrium concentration in solution (mg L\(^{-1}\)). \( K_f \) is Freundlich constant related to the sorption capacity, and \( \frac{1}{n} \) is an empirical parameter related to sorption intensity, which varies with heterogeneity of the material\(^{34,35}\). The equilibrium data was also used to investigate Freundlich model. A plot of \( \log q_e \) versus \( \log C_e \) was obtained to study the model. The correlation factor \( R^2 \) was 0.8982 that data also fit the Freundlich model. The values of \( K_f \) and \( n \) were 1.3 and 2.4. The values of \( n \) were greater than one indicating that the adsorption onto pomegranate peel is favorable physical process except at 50 C\(^0\) , where its value is less than one indicating the adsorption may be chemical\(^{36}\).

![Graph between logCe and log qe for Freundlich absorption isotherm.](image)

D- Dubnin-R Equation.

This equation is used to determine sorption mean energy which enabled us to estimate whether adsorption is carried out by ion exchange mechanism, physisorption or, chemisorptions\(^{37}\).

\[
\ln q_e = \ln q_m - \beta \varepsilon^2 
\]

\[
\varepsilon = R T \ln (1 + \frac{1}{C_e}) 
\]

where \( q_m \) is a theoretical saturation capacity, \( \beta \) is a constant related with sorption energy, mol\(^2\).J\(^{-2}\). \( \varepsilon \) is a polonyi potential. Mean sorption energy \( E \) is determined by (38)

\[
E_s = \frac{1}{\sqrt{2\beta}} 
\]

\( \beta \) is calculated from slope of a linear graph \( \ln q_e \) versus \( \varepsilon^2 \) shown in Figure 8.

The value of sorption mean energy is 0.519 KJmol\(^{-1}\). It is positive and less than 8 KJmol\(^{-1}\). This shows that there is a physisorption and ion exchange\(^{39}\).

![Graph between polonyi potential \( \varepsilon \) and \( \ln q_e \) for activation energy.](image)

\[
y = -0.0179x + 0.4475 \\
R^2 = 0.925
\]
2.10. Thermodynamic Parameters.

The effect of a change in temperature on the sorption system was studied to determine the thermodynamic parameter and to investigate the nature of the process. The sorption capacity increases with the temperature. Thermodynamic parameters for adsorption of amaranth on pomegranate peel such as ΔH, ΔS, and ΔG were calculated from the equilibrium constant Ke. The equilibrium constant (Ke) of the adsorption process at each temperature, is calculated from the equation:

\[ Ke = \frac{Q_e}{C_e} \times \frac{0.252 \text{ gm}}{0.015 \text{ L}} \]  \hspace{1cm} (7)

Where \( Q_e \) is the amount adsorbate (mg/gm), \( C_e \) is the equilibrium concentration of the adsorbate expressed in mg/L. The change in the Gibbs energy could be determined from the equation:

\[ \Delta G^\circ = -RT \ln Ke \]  \hspace{1cm} (8)

The enthalpy of adsorption may be obtained from the Clausis-Clapeyron equation:

\[ \ln X_m = \frac{\Delta H}{RT} + \text{Constant} \]  \hspace{1cm} (9)

When \( X_m \) (mg/gm) is the maximum value of adsorption at a certain value of equilibrium concentration \( (C_e) \). Table I gives \( X_m\) values at different temperatures for amaranth dye.

Plotting \( \ln X_m \) versus \( 1/T \) should produce a straight line with a slope \(-\Delta H/R\) as shown in Figures (8).

The change in entropy (\( \Delta S \)) was calculated from Gibbs-Helmholtz equation (41):

\[ \Delta G = \Delta H - T \Delta S \]  \hspace{1cm} (10)

Table II gives the quantitative thermodynamic data of dye on the adsorbent surface. The value \( \Delta H \) of amaranth dye is positive indicating that the adsorption process is endothermic reaction (42,43). All process of adsorption consider no spontaneous (44) from the positive value of \( \Delta G \). While, \( \Delta S \) have positive value for dye that refer the interaction of molecules caused random of the total system.

![Graph](image-url)

Fig. 9. Plot of \( \ln X_m \) versus \( 1/T \) of adsorption on the pomegranate peel surface.

<table>
<thead>
<tr>
<th>T/K</th>
<th>1/T*10^-3</th>
<th>C_e=1.548mg/L</th>
<th>X_m(mg/gm)</th>
<th>\ln X_m</th>
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<td>293</td>
<td>3.4</td>
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<td>0.001</td>
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<tr>
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<td>0.14</td>
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<td>323</td>
<td>3.09</td>
<td>1.987</td>
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<table>
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<tr>
<th>Adsorbate</th>
<th>( \Delta G ) / (kJ mole(^{-1}))</th>
<th>( \Delta S ) / (J mole(^{-1})K(^{-1}))</th>
<th>( \Delta H ) / (kJ mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amaranth dye</td>
<td>15.18</td>
<td>29.25</td>
<td>23.75</td>
</tr>
</tbody>
</table>
2.1 Kinetic modeling

One of the most important characteristics in evaluating adsorption efficiency is kinetics. In order to clarify the adsorption kinetics of amaranth dye onto pomegranate peel, the kinetic models, Lagergren's pseudo-first-order (45) and pseudo-second-order models (46), were used. The Lagergren model as a pseudo-first-order rate equation is obtained under the ideal assumption of a totally homogenous adsorption surface and is given as follows:

\[
\log q_e - q_t = \log q_e - \frac{K_1 t}{2.303}
\]

where \( q_e \) and \( q_t \) are the amounts of adsorbed dye (mg g\(^{-1}\)) at equilibrium and at time \( t \), respectively. \( K_1 \) is the Lagergren rate constant relating to adsorption energy (L min\(^{-1}\)). Linear plot of \( \log (q_e - q_t) \) versus \( t \) was plotted to evaluate this kinetic model and to determine rate constant \( K_1 \). The values of \( R^2 \) is 0.6371 and \( K_1 \) is 0.10501. Similar results were reported for metal ion adsorption onto activated carbon cloths (47, 48) shown in Figure 10. It depicts that Lagergren model is not fitted in sorption of amaranth on pomegranate peel.

The pseudo-second-order kinetic model of McKay and Ho can be expressed as follows:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

(12)

The parameters \( q_e \) and \( K_2 \) are calculated from slope and intercept of a plot \( t/q_e \) versus time shown in Figure 11. The value of \( R^2 \) is 0.9811 that shows pseudo-second-order model is best fitted. The best fit of the second-order expression suggests that the chemisorptions mechanisms involved in the adsorption. Similar phenomenon was observed for the adsorption of malachite green onto bentonite (49).

![Fig. 10. First-order adsorption kinetics of amaranth on pomegranate peel.](image)

![Fig. 11. second-order adsorption kinetics of amaranth on pomegranate peel.](image)

3. CONCLUSION

In this study, pomegranate peel carbon was applied successfully for the removal of amaranth dye from aqueous solution. The optimum parameters for equilibrium study are time of contact 25 min, pH 3, and dose of adsorbent 0.25 g L\(^{-1}\) under optimum conditions. The kinetic studies proved that the second-order kinetic was the best applicable model. The isotherm equilibrium studies confirmed that the Langmuir form and generalized models were the highest fitted models for the adsorption process. The maximum adsorption potential of pomegranate peel adsorbent for dye removal was 3.448 mg g\(^{-1}\). Thermodynamic parameters showed that the adsorption process was endothermic. The comparison of this study with the previous studies shows that the new biosorbent has more ability than the other waste biomasses for removing dye.

REFERENCE


