Adsorption of Basic Dye Using Environmental friendly adsorbent

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Abstract. This study was included using the walnut husks powder as efficient adsorbent material to remove the Azure C dye from its aqueous solution, the effects of (pH), contact time, temperature and the adsorbent quantity were evaluated, the highest adsorption efficiency 98.17% was recorded with 5 ppm of dye according to the law of Beer Lambert (calibration curve for dye), 0.02g of adsorbent material 10 min as contact time and 328 K. The removal data using Freundlich , Langmuir and Temkin models were analyzed at various temperature varying from 298 to 328 K, and the adsorption thermodynamic parameters were studied. In which ΔG values indicates spontaneous process, ΔH refers to endothermic property of the adsorption process and ΔS prove increase in randomness at the solid/solution interface.
1. Introduction

Many industries such as pulp and paper, leather treatment, manufacturing, dyeing of cloth, textiles, printing, paper and food products etc. are uses the synthetic chemical dyes\[1]. Indeed, the pollution because of textile industry considers the main problem that Infects the environment due to the effluents lost by this industry bearing high levels of dyes and floating solid materials\[2]. These dyes are toxic and threatens the environment and human life. In which many previous studies reported that the direct contact with dye leads to health problems such as mutagenic and carcinogenic effects, allergy and asthma, hypersensitivity, skin eczema and immunosuppressive effects. The wastewaters of textile industry which discharged into rivers and lakes contains many kinds of toxic materials for instance alkaline cleaning agents, cyanides degreasing solvents, heavy metals (in case of inorganic dyes)\[3,4]. These substances work to absorb the water’s oxygen as well as prevents the sunlight and oxygen exchange with the air\[5]. Usually this kind of pollution is treats with the chemical(chemical analysis, chemicoagulation), physical and advanced oxidation methods because the classical biological treatment process is not very effective, take much time, some synthetic dyes murderous to microorganisms, cannot degrade the complex dyes and costly, because the used dyes are low biodegradability. chemicoagulation leads to formation an colloids in the water which also considers as pollutions. Common chemical oxidation process for instance using chlorine needs to long time and additional reactive materials that are dangerous to store and transport. The advanced oxidation method like ozonation and photocatalyst are uneconomical and costly\[6,7]. Therefore, the adsorption process has been reported to be used as effective method to gives promising results, utilizes smallest amounts of chemicals and consumes low energy\[8]. Amongst the adsorbent materials is the activated carbon which is widely explored as the most efficient adsorbsents.. So in the nowadays researchers looking for low cost adsorbent as alternates to activated carbon . Many authors have investigated the ability for using the cheaper materials like wheat peel\[9] Sunflower Seed\[10] pomegranate peel\[11] Coconut (Cocos nucifera)\[12] avocado, hamimelon and dragon fruit peels\[13] etc for removing the contaminations from the wastewater that discharged into rivers and lake. So in the present study walnut husks was used to study the removal Azure C dye from its aqueous solution. The results showed that the process spontaneous, endothermic and increase in randomness at the solid/solution interface. Temkin isotherm is more applicable from Langmuir and Freundlich isotherm.

2. Methods and materials

2.1. Specifications of the dye

All the chemical that used during experiments were commercially available with high purity. The solution of Azure C dye (Aldrich) {N-(7-aminopheno thiazine-3-ylidene) Methanaminiumchloride} was set up with concentration of (100 ppm) as a stock solution, in which (0.0200 g) of the used dye was dissolved in (200 ml) distilled water. Chemical formula of the dye C\textsubscript{13}H\textsubscript{12}ClN\textsubscript{3}S , water Soluble, Molecular Weight 277.77 g/mol, \(\lambda\) sub 616 nm\[14]

![Figure 1: Structural formula of Azure C dye\[15]](image-url)
2.2. Specifications of the adsorbent (Walnut husks powder)

Walnut husks firstly were gathered, then washed precisely with the tap water and deionized water respectively. Thereafter Walnut husks was dried then ground and sieved with the aid of a mechanical sieve to get adsorbent particles with the With a diameter of (0.2) mm approximately.

2.3. Batch Adsorption Experiments

The diluted dye solution 5 ppm contains 0.02 g of adsorbent material (Walnut Husks Powder) was putted in a thermostat water bath shaker, 105 rpm. The filtered solution which contains the unadsorbed (the residual) dye was analysed by UV – Visible Spectrophotometer Double Beam -1800 at a wavelength equal to \( \lambda \) sub. Also the effects of temperature and acidity were examined. The expression of \( \frac{x}{m} \) refers to the amount of adsorption which defined as a quantity of the adsorbate in (mg) that held by a specific weight of adsorbent in (g).

\[
\text{Removal} \% = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{…………….. (1)}
\]

\[
Q_e = \frac{V(C_0 - C_e)}{m} \quad \text{……….(2)}
\]

Where :
- \( Q_e = \frac{x}{m} \): is the amount of adsorbed substance in (mg/g) adsorbent
- \( V \): is the volume of pesticide solution L that was used
- \( C_0 \): Is the concentration at the initial (mg/L)
- \( C_e \): Is the concentration of the equilibrium state (mg/L)
- \( m \): is the weight of adsorbent substance in(g)

3. Results and Discussion

3.1. Effect of Contact Time

The adsorption of Azure C on the Walnut husks powder was investigated as a function of shaking time at 298K. In which the experiments were done in the range of time (5-120) min., 5 ppm of the studied dye and 0.0200 g of walnut husks powder. The obtained results were refers that the adsorption process depend on the time. So the time used for all other experiments was 10 min. because the change in adsorption ratio was unnoticeable after 10 min. Figure 2 illustrate the removal percent with time effect.

![Figure 2](image_url)

Figure 2. Illustrate the contact time effect on adsorption of the examined dye by Walnut husks at Temperature 298K.

3.2. Effect of adsorbent weight:

The adsorbent weight was tested in range of (0.005-0.08) g. Figure 3. gives a clear vision, that the ratio of dye removal from its solution was increase with increasing the weight of the adsorbent. And that attributed to increasing the surface area of the adsorbent and consequently increasing the active
sites of adsorption, then the weight of adsorbent was fixed at 0.02g due to, above this weight the adsorption was unnoticeable. 

Figure 3: Show the Walnut husks weight effects on the ratio of adsorption of Azure C at 298 K.

3.3. Acidity(pH) effects:
The pH value effects on the adsorption process consider one of an important factor. So to understanding this effect, we prepared the Azure C solutions at constant concentration and various pH (2, 4, 6, 8, 10 and 11.2) by using 0.1 N of HCl and 0.1 N of NaOH. Figure 4 indicates that the minimum dye removal was at (pH 2), and the amount of adsorbed dye was increases as the pH increase in the pH range (2-8). But above pH 8 the change in adsorption ratio was unnoticeable, thus the pH value was fixed at 8 for all other experiments.

Figure 4. Acidity value effects on the adsorption ratio of Azure C by the studied adsorbent at 298 K.
3.4. Effect of Temperature:
The thermodynamic parameters $\Delta G$, $\Delta H$ and $\Delta S$ for the Azure C adsorption on the walnut husks powder in the range of temperature (298-328)K were calculated by using equations 3 and 6. and their values are shown in the table. Figure 5 shows the effect of temperature.\(^{[20]}\)

\[
K_{eq} = \frac{Q_E \times m}{c_e \times V} \quad \text{.................. (3)}
\]

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

\[
\ln K_{eq} = \frac{-\Delta H}{RT} + \text{con.} \quad \text{.................. (5)}
\]

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

![Figure 5](image_url)

Figure 5. Temperature effect on the adsorption ratio of Azure C dye over the walnut husks surface.

Table 1:- Thermodynamic functions $\Delta G$, $\Delta H$ and $\Delta S$ of the adsorption process over temperature range (298-328)K.

| Adsorbate | Temp. K | $\Delta G$ (kJ/mol) | $\Delta H$ (kJ/mol) | $\Delta S$ (J/mol.K) |
|-----------|---------|---------------------|---------------------|----------------------|
| Azure C   | 298     | 9.3756              |                     | 0.05001              |
|           | 308     | 9.8505              |                     | 0.04993              |
|           | 318     | 10.3464             | 5.5296              | 0.04992              |
|           | 328     | 10.8635             |                     | 0.04997              |

the negative values of the free energy $\Delta G$ gives an indication on the spontaneity of the adsorption process.\(^{[21]}\), the positive sign of the $\Delta H$ refers to endothermic property of the adsorption reaction of Azure C.\(^{[22]}\), finally, the positive signs of the $\Delta S$ values revels the increasing the degree of freedom at the interface of solid-liquid during the adsorption of Azure C.\(^{[23]}\).

3.5. Adsorption Isotherm:
The filtered aqueous solution of the studied Azure-C was analyzed then the amount of adsorbed dye (adsorption ratio) measured through using equation (2). Figure 6. displays the adsorption isotherms...
Figure 6. Adsorption isotherm of Azure-C by Walnut husks over a range of temperature.

The shapes of the isotherms were received from the experimental data were found to be similar in all cases to the (S- curve) type according to Giles rating. The results was received on the adsorption of Azure C were analyzed by the well-known models given by Langmuir, Freundlich and Temkin.

3.6. Langmuir isotherm:

The Langmuir model isotherms mathematical were determined as follow equations \[24\].

\[
\frac{C_e}{Q_e} = \frac{1}{a b} + \frac{C_e}{a} \quad \text{...............(7)}
\]

Where :-

- \(a\) (mg/g) the maximum adsorption capacity according to Langmuir monolayer adsorption.
- \(b\) (mg/L) is the Langmuir constant relates to affinity and free energy of adsorption \[25\].

A linear plot was obtained when \(C_e/Q_e\) was plotted vis \(C_e\) \[26\] as shown in Figure 7.

Figure 7. Langmuir isotherms for Azure-C over the studied temperatures.

The ability of occurring and the feasibility of adsorption reaction was measured by applying the factor \(R_L\), that defined by equation (8).
The value of $R_L$ refers to the category of the isotherm to be either unfavourable ($R_L > 1$), linear $R_L = 1$, irreversible $R_L = 0$ or favourable $0 < R_L < 1^{[27]}$.

### 3.7. Freundlich Isotherm:

The second model is Freundlich model is given by:

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

(9)

where : $Q_e$ and $C_e$ are similarly to its defined above. $K_f$ (L/mg) and (n) are constants of Freundlich equation which its depends on the capacity of adsorption and the intensity of adsorption respectively$^{[28]}$.

![Figure 8. Freundlich isotherm model for the adsorption of Azure-C dye at different temperatures](image)

### 3.8. Temkin Isotherm model:

Temkin isotherm have a factor that give illustration about the adsorbent interactions and adsorbing species. In which Temkin isotherm assumes that the heat of adsorption for all molecules in the adsorption layer decreases linearly with increase the surface coverage due to the nature of the adsorbent–adsorbate interactions.

The Temkin isotherm is given as

$$Q_e = Bln A_t + B \ln C_e$$  

(10)

where :

$A_t$ is the binding constant at equilibrium that corresponds the maximum binding energy

$B$ is constant which related with heat of adsorption. A linear plot was obtained when $Q_e$ was plotted vst ln $C_e$ $^{[29]}$.

![Figure 9. Temkin isotherm model](image)
Figure 9. Temkin isotherm model for the adsorption Azure-C dye at different temperatures.

Table 2. Langmuir, Freundlich and Temkin functions of adsorption reaction at the studied range of temperature (298 – 328) K.

| Temp. K  | Langmuir isotherm | Freundlich isotherm | Isotherm Temkin |
|----------|-------------------|---------------------|-----------------|
|          | -a (mg/g)        | -b (mg/L)           | (r²) -R_L        | (K_L) | (n)  | (r²) | B    | A_T  | (r²) |
| 298      | 27.1739          | 0.6433              | 0.0628          | 0.4511 | 33.6046 | 0.8895 | 0.7182 | 7.3432 | 16.8778 | 0.9561 |
| 308      | 29.9401          | 0.6485              | 0.0569          | 0.4459 | 36.5594 | 0.8962 | 0.7200 | 7.3318 | 18.3439 | 0.9595 |
| 318      | 36.6300          | 0.6066              | 0.0427          | 0.4918 | 39.7557 | 0.9075 | 0.7126 | 7.3273 | 20.3239 | 0.9625 |
| 328      | 33.5570          | 0.7358              | 0.0490          | 0.3732 | 47.1085 | 0.8899 | 0.7165 | 7.5046 | 22.1935 | 0.9616 |

We notice from the correlation coefficient (r²) shown in the table 3 that Temkin isotherm is more applicable from Langmuir and Freundlich isotherm [38]. This indicating that the adsorption of Azure-C on the walnut husks surface, that the enthalpy of adsorption for all molecules in the adsorption layer was decrement linearly raises the surface coverage of husks surface.

4. Conclusions
1- This investigation proved the possibility of using walnut husks as efficient adsorbent material for remove Azure-C dye from its aqueous solutions.
2- The removal ratio was 98.17 % at optimal conditions 5 ppm dye concentration, the absorbent material weight 0.02 g and the contact time 10 min) at 328 K.
3- It was found that the equilibrium data fitted very well with Temkin isotherm model, this indicating that the adsorption of Azure-C on the walnut husks surface, that the enthalpy of adsorption for all molecules in the adsorption layer was decrement linearly raises the surface coverage of husks surface.
4- Thermodynamic studies mention that the adsorption process was endothermal, spontaneous, and increase in randomness at the solid/solution interface.
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