Equilibrium and Thermodynamic studies of Adsorption of Remazol Brilliant Blue dye on snail shell powder

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Abstract

Remazol Brilliant Blue dye is a noxious dyes, so the snail shell powder was used as an adsorbent surface because of its high efficiency to remove the remazol brilliant blue dye from aqueous solutions where the removal percent was (99.09%). Also, the factors affect the efficiency of adsorption (equilibrium time, adsorbent weight, PH, ionic strength, temperature and using "Langmuir, Freundlich and Temkin" models were studied. The experimental data of isotherm showed that it is in good agreement with the freundlich and temkin equation it to take the form (S-curve) according to the Giles classification, and it does not agree with the Langmuir equation. The thermodynamic functions (ΔS, ΔH, ΔG) were calculated and explained in the mean of the chemical structure of the adsorbant.

Keywords:- Remazol Brilliant Blue, Adsorption, Isotherms, Snail shell, Langmuir, Freundlich and Temkin.

1. Introduction

RBB is considered a harmful dyes where it is used in textile industriis and because the residues factories will run by rivers and lakes so it will pose great problems for aquatic life and organisms in general. It is an anthraquinone dye and is an acidic dyes. Dyestuffs are one of the most important pollutants in water systems. The amount of dyes produced in 1996 reached 4.5 million tons. Due to the increase in population expansion and technological advancement, this has led to the emergence of a phenomenon which is the problem of pollution. Where pollution seemed to pose a great danger to the environment and life and this prompted many researchers and those interested in this area to think in order to access ways to treat or remove this pollution from water. There are many methods used to treat pollution are filtration, chemical oxidation, adsorption, ion exchange, etc. One of the most important methods used to remove water pollution is adsorption because of its high efficiency and also low cost and simple compared to other methods. The adsorption method uses simple materials such as adsorbent surfaces to remove contaminants from aqueous solutions including Bentonite clay, sugar beet pulp, rice husk, banana peels, orange waste. The purpose of adsorption is to dispose of water pollutants from industrial waste and make them usable and this is done by using adsorbent surfaces that are capable of adsorption of pollutants from their aqueous solution. Snail shell powder has been used as an alternative to Pumice in cleaning and removal of dental dyes and polishing because they are available in nature and cheap price. And also which is used for removal some dyes like AzureB and Coomassie brilliant blue G-250 dye. In this study snail shell powder was used to remove the dye remazol brilliant blue from its aqueous solutions.

2. Experiments

2.1. Materials

All the chemicals were of high purity, commercially available.
Organic Remazol Brilliant Blue dye was used.
The adsorbent (snail shell powder).

2.2. Preparation the adsorbent (snail shell powder)
The Snail shell was obtained after it was collected and washed with distilled water in order to remove impurities and particulate material from their surface. And leave it to dry at 100°C, and then grind in order to get the snail shell powder.

2.3. Preparation of the dye
Prepare Remazol Brilliant Blue dye solution with concentration 100.000 mg/L by dissolving 0.0200 g from dye in 200 ml of distilled water. The properties of the selected dye are given in Table (1) and their structures are shown in Fig. (1).

| Table 1. Specifications of Remazol Brilliant Blue |
|-----------------------------------------------|
| Empirical Formula | C_{22}H_{16}N_{2}Na_{2}O_{11}S_{3} |
| Class | Thiazine |
| Source | Aldrich |
| Solubility in water | Soluble |
| Molecular Weight | 626.54 g/mol |
| λ max | 608 nm |
| C. I. No | 61200 |

![Fig. 1: Structural formula of Remazol Brilliant Blue dye](image)

2.4. Batch Adsorption Experiments
By using 0.0200 g adsorbent with 25 ml of dye solutions 30.000 mg/L at 150 rpm on a thermo stated shaker water bath. The unabsorbed supernatant liquid of the residual dye in each treatment solution was analyzed by Shimadzu UV-Vis 1800 digital double beam instrument at a wavelength corresponding to the λ max. The contact time, PH, effect of ionic strength and temperature effects were studied. The amount of adsorption is expressed by the ratio x/m which is defined as the quantity of adsorbate in mg held by weight of adsorbent (g).

Removal %=[(C_0-C_e)/C_0]×100 \hspace{1cm} \ldots \ldots \hspace{1cm} (1)

Where : C_0 and C_e (mg/L) are the concentration of dye at initial and equilibrium respectively.

3. Results and discussion
3.1. Effect of Contact Time
The relation between contact time(Tmin) and Removal percentage of Remazol Brilliant Blue dye(Re%) is done through batch experiments to achieve the balance as shown in Fig.2. Results showed that equilibrium time was reached within 10 minutes.
Fig. 2: Effect of contact time on adsorption of Remazol Brilliant Blue by snail shell powder at temperature 298 K, Conc. of dye 30 mg/L and weight of adsorbent 0.0200 g

3.2. Effect of adsorbent weight

The effect of weight on the adsorption process was studied using different weights of adsorbate (0.0050-0.0800 g) at 30 mg/L of dye, 298 K, and 10 min equilibrium time, where we note when increasing the weight of the surface adsorbent (snail shell powder) will increase the rate of removal and the reason is due to the provision of a large surface area and also increase in the effective sites adapted for adsorption, as show the Fig. 3.

Fig. 3: Effect of adsorbent weight on adsorption of Remazol Brilliant Blue by Snail shell powder at 298 K.

3.3. Effect of pH

The effect of pH on the adsorption process was studied at the concentration of 30 mg/L of the dye, 298 K, equilibrium time 10 min, the weight of adsorbate is 0.0200 g, and the range of the function is (2-12) using 0.1 N of HCl and 0.1 N of NaOH. Fig. 4 shows that the best removal percent at the PH = 6.

Fig. 4: Effect of pH on adsorption of Remazol Brilliant Blue by snail shell powder at 298 K.
3.4. Effect of ionic strength

The effect of ionic strength on removal of Remazol Brilliant Blue dye on the surface of snail shell powder was studied using different concentrations ranging from (0.0700-0.0200) M of salts (NaCl, KCl, MgCl$_2$ and CaCl$_2$). Fig.5 show the result obtained in the effect of the ionic strength on dye removal.

![Fig.5: Effect of ionic strength on the adsorption of Remazol Brilliant Blue by snail shell powder at 298 K.](image)

3.5. Effect of Temperature

Remazol Brilliant Blue was studied using Snail Shell at a range from 298 to 338 K. Determination of thermodynamic parameters such as Gibbs energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) find them using equations (2 - 5), which are given in table 2, Fig.6. An effect appears effect the temperature.

$$Keq = \frac{(Qe_m)}{Ce V} \quad \ldots \ldots \ (2)$$
$$\Delta G = -RT \ln Keq \quad \ldots \ldots \ (3)$$
$$\ln Keq = \frac{-\Delta H}{RT} + \text{con.} \quad \ldots \ldots \ (4)$$
$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad \ldots \ldots \ (5)$$

![Fig.6: Effect the temperature of the adsorption Remazol Brilliant Blue dye on the snail shell powder.](image)
Table 2. Thermodynamic parameters \( \Delta G, \Delta H \) and \( \Delta S \) of Remazol Brilliant Blue dye on the adsorbent surface Snail shell powder at (298-338) K.

| Adsorbate | Temp. K | \( \Delta G \) (KJ/mol) | \( \Delta H \) (KJ/mol) | \( \Delta S \) (KJ/mol) |
|-----------|---------|------------------------|------------------------|------------------------|
| RBB       | 298     | -12.3477               | -45.8018               | -0.1122                |
|           | 308     | -11.0213               | -45.3418               | -0.1128                |
|           | 318     | -9.7960                | -45.3418               | -0.1132                |
|           | 328     | -8.7329                | -45.3418               | -0.1130                |
|           | 338     | -7.8124                | -45.3418               | -0.1123                |

Negative value of \( \Delta G \) indicate the spontaneous nature of adsorption, the process is exothermic due to the negative value of \( \Delta H \), and negative value of \( \Delta S \) indicate decrease in randomization in the solid interface / solution during the adsorption process.\(^{24,25}\)

### Adsorption Isotherm

The adsorption isotherms of Remazol Brilliant Blue dye onto Snail shell powder show at Fig.7 pH =6.0, temperature from 298 to 338 K, 0.0200 g of the adsorbent, 30 mg/L of dye concentration, and the time of 10 min, where we note that the adsorption capacity for Remazol Brilliant Blue dye increases with the increasing equilibrium Remazol Brilliant Blue concentration. The amount of the adsorbed can be calculated by the equation\(^{26}\):

\[
Q_e = \frac{V(C_o - C_e)}{m} = \frac{x}{m} \quad \ldots \ldots \ldots \ldots (6)
\]

![Fig.7: Adsorption Isotherm of Remazol Brilliant Blue adsorption from aqueous solution on the surface of the snail shell powder at different temperatures.](image)

### Langmuir Isotherm

The Langmuir adsorption isotherm model suppose that adsorption occur at specific homogeneous sites within the adsorbent, the Langmuir equation is expressed by the following relation:

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

Where:
- \( Q_e \) is the amount of Remazol Brilliant Blue dye adsorbed at equilibrium time (mg/g).
- \( C_e \) is equilibrium concentration of Remazol Brilliant Blue dye in solution (mg/L).
- \( a \) and \( b \) are the Langmuir constants.\(^{27}\)

\[
R_L = \frac{1}{1 + b C_0} \quad \ldots \ldots (8)
\]

Where:
- \( C_0 \) is the initial dye concentration in solution mg/L.
b is the Langmuir constant L/mg  
$R_L$ is the Separation Factor  
Where $R_L$ values indicate the type of adsorption to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), liner ($R_L = 1$) or unfavourable ($R_L > 1$), $R_L$.

Fig.8: The Langmuir isotherms for Adsorption Remazol Brilliant Blue dye at different temperatures

**Freundlich isotherm**

The Freundlich isotherm model considers a multilayer adsorption (heterogeneous surface). Where the form of Freundlich isotherm is given by the following equation:

$$\log Q_e = \ln K_f + 1/n \log C_e \quad \ldots \ldots \ (9)$$

Where:

- $K_f$ is Approx indication of adsorption capacity
- $n$ is Adsorption strength.

Fig.9: The Freundlich isotherms for Adsorption Remazol Brilliant Blue dye at different temperatures.

**Temkin Isotherm**

The Temkin isotherm model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, has been generally applied in the following form:
\[ Q_e = B \ln AT + B \ln Ce \] 

\[ \ldots (10) \]

Where:

- \( AT \) is the adsorption equilibrium constant,
- \( B \) is the maximum adsorption energy,

Fig.10 shows the Temkin curves for Remazol Brilliant Blue dye adsorption.

Table 3. Langmuir, Freundlich and Temkin parameters of adsorption isotherms of RBB at (298 – 338) K.

| T(K) | Langmuir isotherm | Freundlich isotherm | Temkin isotherm |
|------|-------------------|---------------------|-----------------|
|      | \( a \) (mg/g)  | \( b \) (mg/L)  | \( R^2 \) | \( K_f \) | \( n \) | \( r^2 \) | \( B \) | \( A_T \) | \( r^2 \) |
| 298  | 178.5714         | 0.5091              | 0.2868          | 0.0614 | 55.3604 | 1.3042 | 0.9675 | 12.871 | 32.0757 | 0.7501 |
| 308  | 45.4545          | 0.3893              | 0.0788          | 0.0788 | 30.7114 | 0.7461 | 0.9924 | 21.931 | 4.7312  | 0.8206 |
| 318  | 163.9344         | 0.0816              | 0.2900          | 0.2900 | 6.3299  | 0.6275 | 0.8505 | 14.006 | 3.5672  | 0.8672 |
| 328  | 416.6666         | 0.0217              | 0.6056          | 0.6056 | 9.2789  | 0.9388 | 0.9927 | 16.652 | 2.3464  | 0.8895 |
| 338  | 90.9090          | 0.0802              | 0.2935          | 0.2935 | 8.0315  | 0.8083 | 0.9824 | 21.392 | 1.7422  | 0.9142 |

The isothermatic constants \((a,b,R_L)\) were calculated for Langmuir hypothesis \((K_f, n)\) for Freundlich hypothesis and \((A_T, B)\) for Temkine hypothesis with linear correlation coefficients \(R^2\) as shown in the table (3). The value of \(a\) (mg/g) of the Langmuir equation is a constant that is related to the capacity of the adsorption, so when you increase the value of \(a\) (mg/g) we will get the best adsorption capacity and \(b\) (mg/L) is related to the adsorption energy. The value of \(K_f\) in the Freundlich equation indicates and \((1/n)\) in the Freundlich equation indicates the intensity of the adsorption. The value of the constant \(A_T\) in the Temkine equation would represent the adsorption equilibrium constant and
(B) represents the maximum adsorption energy\(^{[32]}\). Note that the result of the slope and correlation coefficient in the table (3) that the result of the Freundlich equation is more applicable than the Langmuir and Temkine equation in the process of adsorption of the RBB dye.

**Conclusion:-**
The snail shell powder is highly efficient as a adsorbent surface to remove the RBB dye from aqueous solutions, the removal percent was 99.09% at 298K, 10min, 30mg/L of dye concentration and 0.0200g of the adsorbate weight, it was noted that the adsorption process is exothermic because the enthalpy is negative, also decreases random due to negative entropy, and also the process is spontaneous because the Gibbes energy is negative. The results of the experimental data of isotherm showed that it does not agree with the Langmuir isotherm but agreement with Freundlich and Temkine isotherms where takes the shape (S-curve) of according to Giles classification.

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