Bioadsorption of Eriochrome Black T (EBT) onto Iraqi Rice Husk as Adsorbent

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Abstract. The present study enclosed the employment of low cost industrial waste rice husk for the removal of Eriochrome Black T by adsorption technique. The impact of some parameters was studied like agitation time, biosorbent dose and temperature. The bioadsorption information were analyzed by Langmuir and Freundlich isotherm models at equilibrium. The adsorption capacities (Qm) obtained from the Langmuir isotherm plots were 40.00, 39.68, 38.91 and 38.00 mg/g respectively at pH adequate to of 7.0 at 30, 40, 50 and 60 C°. The study of the temperature diversity incontestible that the EBT adsorption is endothermic and spontaneous with distended irregularity at the solid-solution interface. thermodynamic quantities as change in (ΔH°), change in entropy (ΔS°) and change in free energy (ΔG°) were additionally investigated. Free energy change showed that bioadsorption of Eriochrome Black T was spontaneous in any respect studied temperatures (30–60 C°). It was implicit that rice husk could also be appropriate as an adsorbent for removal of Eriochrome Black T.

1-Introduction

Eriochrome Black T may be a complexometric indicator that's a part of the complexometric titrations, e.g. within the water hardness determination method. it's conjointly referred to as ET-00. In its protonated type, Eriochrome Black T is blue. It turns red once it forms a complex with calcium, magnesium, or different metal ions and it's an azo dye. (1) Dye pollutants created from the textile industries are a serious supply of environmental contaminations (2). regarding 15 August 1945 of the entire world production of dyes is lost throughout the coloring and finishing operations and is free within the textile effluents (3).

Azo dyes, that contain one or a lot of nitrogen to nitrogen double bonds (–N=N–) and represent a majorportion of dye colorants, are wide utilized in the coloring industry nowadays and are immune to aerobic degradation and below anaerobic conditions they will be reduced to probably carcinogenic aromatic amines (4-5). Color removal from textile effluents has been the topic of great attention not solely due to its toxicity however in the main as a result of its clarity (6).

Through many years, the size of production and therefore the nature of dyes have changed vastly, that the negative force of dyes on the environment has raised (7). adsorption process that produces
sensible quality effluents that are low in concentration of dissolved organic compounds, like dyes (8), are quickly gaining importance as treatment processes (9). Rice husks (or rice hulls)-RH-an extravagantly offered byproduct, the fibrous onerous outer covering the grain of rice, is generated at 120 million tonnes annually, accounting regarding simple fraction of the annual gross rice production throughout the world (10).

It's an agricultural waste that has been reported as a decent sorbent material of the many metals and basic dyes (11-13). Rice husk possesses a granular structure, is insoluble in water, has chemical stability, high mechanical strength and accounts for regarding 200th of the whole rice, tough, woody and characterised by its abrasive in Rice husk possesses a granular structure, is insoluble in water, has chemical stability, high mechanical strength and accounts for regarding two hundredth of the total rice, tough, woody and characterised by its abrasive inherent resistance behavior and silica-cellulose structural arrangement (14,15).

It consists of polysaccharide, hemicelluloses, lignin and oxides (10, 16-19) as shown in table 1 (20-22) and therefore the physicochemical characteristics of RH are shown in table 2 (23). It additionally contains plethoric floristic fiber, and a few functional groups like carboxyl, hydroxyl and amidogen, etc, representing a good characteristic of rice husk to be a potential sorbent (24). silica present on the outer surface of rice husks within the sort of silicon-cellulose membrane acts as a natural protecting layer against termites and different microbic attack on the paddy. This part is liable for low binding between accessible functional groups on rice husks surfaces and numerous adsorbate ions/molecules.

The inner surface of rice husk is swish and should contain wax and natural fats that offersensible shelter for the grain however the presence of those impurities on the inner surfaces of rice husks additionally affects the adsorption properties of rice husk chemically and physically (17). Rice husk is typically used as a low-value energy resource, burned within the field, or discarded, that is unfavorable to environment (25). it's conjointly utilized in power generation through combustion and its burning generates another residue, the rice husk ash (RHA) (26).

Table 1: Chemical composition of rice husk

| Compound | Percent (wt %) |
|----------|----------------|
| SiO₂     | 91.00          |
| LOI      | 5.00           |
| K₂O      | 3.00           |
| P₂O₅     | 0.70           |
| CaO      | 0.60           |
| MgO      | 0.30           |
| Al₂O₃    | 0.10           |
| Fe₂O₃    | 0.06           |
| TiO₂     | 0.02           |

Table 2: Physicochemical characteristics of rice husk

| Characteristics      | Value  |
|----------------------|--------|
| Solid density (g/ml) | 20.00  |
| Bulk density (g/mL)  | 0.70   |
| Ash content (%)      | 46.0   |
| Moisture content (%) | 7.00   |
| Surface acidity (meq/g) | 0.10 |
| Surface basicity (meq/g) | 0.50 |
The main objective of this work is to study the adsorption potential of low cost bioadsorbent, rice husk for the removal of hazardous azo dye Eriochrome Black T. Apart from this, another objective of this work is to evaluate the effect of dye concentration, adsorbent dose, contact time and temperature on the adsorption characteristic of rice husk. This paper also discusses the Langmuir and Freundlich adsorption isotherm model and various thermodynamic parameters such as Gibbs free energy change ($\Delta G^o$), heat of adsorption ($\Delta H^o$) and entropy change ($\Delta S^o$) as applied to the adsorption of Eriochrome Black T onto rice husk.

2. Experimental

2.1 Adsorption Studies

Equilibrium adsorption isotherms for the rice husk were determined at an agitation rate of 120-rpm at different temperatures and different concentrations of EBT and rice husk. 50 mg/50 mL of adsorbent was located in group 250-mL Erlenmeyer flasks and different initial EBT concentrations of (10-60 mg/L) were added to each flask. The contents were shaken for 60 min, a small amount was withdrawing and centrifuged at 3000 rpm for 5 min. The supernatant was analyzed for EBT contents. The adsorption performances of the samples were considered by assessing the percentage removal proficiency of EBT, from the relation:

$$\text{Removal efficiency} = \left[ \frac{(C_o - C)}{C_o} \right] \times 100$$  \hspace{1cm} (1)

Where $C_o$ is the original concentration of EBT, $C$ is the solution concentration after adsorption at any time. Impact of time on the EBT withdrawal at different fixed interims was observed by shaking the reaction mixture, centrifuged and examined for the EBT content toward the finish of each contact time. Every flask denotes to an interval, this mean one point on the plot. The time of experiments were contemplated for various adsorbent concentrations to think about the impact of adsorbent amounts on the adsorption of color. Analyses were performed utilizing adsorbent concentrations of (10-70) mg/50 mL, in a dye solution of 30 mg/L. The amount of EBT adsorbed onto the rice husk $Q_e$ (mg/g) was determined by the accompanying mass balance equation

$$Q_e = \frac{(C_o - C_e) V}{W}$$  \hspace{1cm} (2)

Where $C_o$ and $C_e$ are the initial and equilibrium concentrations (mg/L) of EBT respectively, $V$ represents the volume of solution in liter and $W$ refers to the weight of the rice husk in gram.

2.1.1. Preparation of adsorbent

Rice husk was obtained from local rice mills in Al-Diwaniya city and was washed several times with water followed by filtration. The cleaned rice husk was oven dried completely at 105°C, then cooled and sieved of 500 μm size used without additional handling.

2.1.2. Preparation of dye solution

EBT was obtained from Aldrich Company and was used without further purification. Its molecular formula is C20H12N3O7Sn. A stock solution of the EBT was prepared by dissolving 1 gram of EBT in 1 liter of distilled water to prepare a stock solution of 1000 mg/L. The experimental solution was prepared by diluting a definite volume of the stock solution to get the desired concentration. For absorbance measurements a UV-VIS spectrophotometer-1650 supplied from Shimadzu Company was employed using silica cells of path length 1 cm. The maximum wavelength $\lambda_{max}$ for the EBT was measured at 508 nm in the presence of 96 % ethanol (from Fluka) as a solvent. Concentrations during experimental work were determined from a standard calibration.
2.1.3. Effect of contact time

The experiments were carried out by taking 50 ml samples of EBT (concentration 30 mg/L) in separate flasks and treated with 50 mg of the adsorbent dose at room temperature, then shaking with different times (10,20,30,40,50,60,70 min) was done at pH=7.

2.1.4. Effect of adsorbent dose

The study was carried out with different doses of adsorbent (10,20,30,40,50,60,70 mg) then they were shaken with 50 mL of 30 mg/L concentration of EBT at 50 min agitation time and pH=7.

2.1.5. Effect of temperature

The effect of temperature was investigated with 0.05 mg dose of adsorbent mixing in 50 ml aqueous solutions of EBT (concentration 30,40,50,60 mg/L) and the samples were shaken at 50 min agitation time and pH=7.

2.2. Determination of the calibration curve

Various solutions (concentrations: 5,10,20,30,40,50,60,70 mg/L) were prepared from the stock solution of EBT (concentration 1000 mg/L) by diluting, then the absorbance of each concentration was measured at $\lambda_{\text{max}}=508$ nm. Plot the value of concentration against the value of absorbance showed straight line.

3-Discussion

3.1. Determination the calibration curve of Eriochrome Black T

EBT has structural formula demonstrated by fig.1. From the structure it is clear that EBT is an azo compound due to presence of $\text{–N=N–}$ group.

![Structural formula of eriochrome black T](image-url)

Fig.1: Structural formula of eriochrome black T
The UV-Visible spectrum was taken to identify the maximum wave length which was 567 nm in aqueous solution of ethanol (fig.2). A set of solutions of EBT with different concentrations (5-70 mg/L) were prepared from the stock solution (1000 mg/L) by dilution using 96% ethanol as a solvent. Then the absorbance at 508 nm was determined for each solution to represent the calibration curve which was done by plot the values of absorbance against the values of concentration which showed an straight line that obeyed the law of Lambert-Beer \( ^{(27)} \).

Fig.2: Electronic spectrum of eriochrome black T

A positive deviation from Lambert-Beer law above 5 mg/L was appeared, thus the optimum concentration range was (5-50 mg/L) as illustrated in fig.3.

Fig.3: Calibration curve of Eriochrome Black T at 508 nm
3.2. Effect of initial dye concentration and contact time

The experimental results of adsorption at various concentrations (10, 20, 30, 40, 50 and 60 mg/L) were collected in table 1.

Table 3: Equilibrium parameters for the adsorption of EBT onto rice husk

|          | C_e |          | C_e |          |
|----------|-----|----------|-----|----------|
|          | 30  | 40       | 50  | 60       |
| 10       | 83.50| 83.50    | 83.50| 83.50    |
| 20       | 84.10| 84.10    | 84.10| 84.10    |
| 30       | 85.40| 85.40    | 85.40| 85.40    |
| 40       | 87.50| 87.50    | 87.50| 87.50    |
| 50       | 88.80| 88.80    | 88.80| 88.80    |

The effect of contact time on adsorption of EBT was investigated. Fig. 4 shows the adsorption of EBT by rice husk as a function of contact time at different initial concentrations.

Fig.4: Effect of contact time on the removal of EBT at different concentrations.

pH=7, adsorbent dose = 50 mg/ 50mL, temperature = 25 C°

It is seen that the adsorption of EBT expanded with the ascent in contact time up to 50 min. Further increment in contact time did not upgrade the adsorption. At first, the rate of adsorption was quick because of the adsorption of dye particles onto the outside surface. From that point onward, the particles go into pores (inside surface), a moderately sensible way. The underlying quicker rates of adsorption may likewise be credited to the existence of a large number of binding positions for adsorption and the slower adsorption rates toward the end is because of the capacity of the coupling places and accomplishment of equilibrium (28). The adsorption achieved equilibrium about 60 min. It was found from the outcomes represented in fig.5 that the percent of adsorption reduced with increment in initial dye concentration, however, the genuine quantity of adsorbed dye per unit mass of carbon expanded with increment in dye concentration. It implies that the adsorption is deeply dependent on the initial concentration of dye. It is a direct result of that at a lower concentration, the
proportion of the primary number of dye particles to the accessible surface area is low successively the fractional adsorption becomes independent of initial concentration. At high concentration, the reachable sites of adsorption end up less and thus the rate removal of dye is needy upon starting concentration (29,30).

3.3. Effect the adsorbent dose

The adsorption of EBT onto rice husk was studied with varying the dose of adsorbent (10-70 mg/50 mL) for dye concentration of 30 mg/L. It was found that the increasing in the adsorbent dose raise the percentage of adsorption (fig.5). This was due to increase in the surface area and availability of more adsorption sites (28,29).

![Graph](image)

Fig. 5: Effect of adsorbent dose on the removal of EBT, [EBT] = 30 mg/L, contact time = 50 min, pH 7

3.4. Adsorption isotherm

The direct types of the Langmuir and Freundlich isotherms were utilized to examine the exploratory information (31). The Langmuir isotherm was described by the accompanying equation:

\[ \frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \]  

Where \( C_e \) is the concentration on equilibrium (mg/L), \( Q_e \) is the quantity adsorbed at equilibrium (mg/g) and \( Q_m \) and \( b \) are Langmuir constants identified with adsorption productivity and energy of adsorption, respectively. The linear plots of \( C_e/Q_e \) versus \( C_e \) propose the relevance of the Langmuir isotherms (Fig.6).
Fig.6: The linearized Langmuir adsorption isotherms for EBT adsorption by rice husk at different temperatures. [EBT] = 30 mg/L, contact time = 50 min, adsorbent dose = 50 mg/50 mL, pH 7

The values of $Q_m$ and $b$ were determined from slope and intercepts of the plots and are presented in Table 4.

**Table 4: Langmuir isotherm results**

| Temp. (°C) | $R^2$ | $Q_m$  | $b$  |
|-----------|-------|--------|------|
| 30        | 0.9874| 40.00  | 0.17 |
| 40        | 0.9849| 39.68  | 0.18 |
| 50        | 0.9843| 38.91  | 0.21 |
| 60        | 0.9838| 38.00  | 0.24 |

The results of adsorption energy $b$ of the adsorbent and adsorption efficiency $Q_m$ conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The observed $b$ values show the endothermic nature of the process involved in the system $^{(32,33)}$.

The Freundlich equation was used for the adsorption of EBT dye onto the adsorbent. The Freundlich isotherm was illustrated by:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (4)

Where $Q_e$ is the adsorbed amount of Eriochrome Black T (mg/g), $C_e$ is the concentration of dye in solution (mg/L) at equilibrium and $K_f$ and $n$ are constants refer to the adsorption capacity and intensity of adsorption, respectively. Linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of Eriochrome Black T obeys the Freundlich adsorption isotherm (Fig.7).
The values of n and Kf gave in Table 5 demonstrate that the rise in negative charges on the adsorbent surface makes electrostatic forces, for example, van der Waals between the dye particle and adsorbent surface. The molecular weight, size, and radii either breaking point or increment the likelihood of the adsorption of the dye onto the adsorbent. The qualities demonstrate the strength in adsorption limit. The intensity of adsorption is characteristic of the bond energies among dye and adsorbent and the likelihood of slight chemisorptions as opposed to physisorption (33, 34). The multilayer adsorption of EBT through the permeation procedure might be conceivable. The values of n are more noteworthy than one showing the adsorption is substantially more good (34-36).

Table 5: Freundlich isotherm results

| Temp. (°C) | Statistical parameters/ constants |
|------------|-----------------------------------|
|            | R²      | k_f | n   |
| 30         | 0.938   | 7.89 | 2.18 |
| 40         | 0.945   | 8.45 | 2.27 |
| 50         | 0.955   | 9.14 | 2.40 |
| 60         | 0.951   | 9.77 | 2.51 |

3.5. Effect of temperature

The adsorption capacity of the adsorbent expanded with increment in the temperature of the framework from 30°-60°C. Thermodynamic parameters, as Gibbs free energy $\Delta G^o$ (kJ/mol), enthalpy $\Delta H^o$ (kJ/mol) and entropy $\Delta S^o$ (J/K/mol) were resolved utilizing the accompanying equations:

$$ K_o = \frac{C_{\text{solid}}}{C_{\text{liquid}}} $$  \hspace{1cm} (5)

$$ \Delta G^o = -RT \ln K_o $$  \hspace{1cm} (6)

$$ \Delta G^o = \Delta H^o - T \Delta S^o $$  \hspace{1cm} (7)

$$ \ln K_o = \frac{\Delta G^o}{RT} = \frac{\Delta S^o}{(R)} - \frac{\Delta H^o}{(RT)} $$  \hspace{1cm} (8)

$$ \log K_o = \frac{\Delta S^o}{(2.303R)} - \frac{\Delta H^o}{(2.303RT)} $$  \hspace{1cm} (9)

Where $K_o$ is the equilibrium constant, $C_{\text{solid}}$ is the concentration of solid phase at equilibrium (mg/L), $C_{\text{liquid}}$ is the concentration of liquid phase at equilibrium (mg/L), T is the temperature in Kelvin and R
is the gas constant. The \( \Delta H^o \) and \( \Delta S^o \) values obtained from the slope and intercept of Van’t Hoff plots have presented in Table 6.

| Co (mg/L) | \( K_a \) | \( \Delta G \) (J.mol\(^{-1}\)) | Temperature (C\(_o\)) | \( \Delta H \) (J.mol\(^{-1}\)) | \( \Delta S \) (J.mol\(^{-1}\).k\(^{-1}\)) |
|----------|--------|-----------------|-----------------|-----------------|-----------------|
|          |        | \( \gamma^c \) | \( \gamma^v \) | \( \gamma^t \) | \( \gamma^s \) | \( \gamma^o \) |
| 1\(^o\)  | 7.93   | 7.00            | 5.85            | 5.06            | -5732.73        | -5225.59         | -4596.78         | -4084.45         | 12827.67         | 55.78             |
| \( \gamma^v \) | 6.35   | 5.67            | 5.29            | 4.88            | -5117.56        | -4659.72         | -4334.93         | -3993.21         | 7194.52          | 36.86             |
| \( \gamma^t \) | 3.27   | 3.15            | 3.05            | 2.92            | -3280.16        | -3081.26         | -2901.91         | -2699.47         | 3123.90          | 19.23             |
| \( \gamma^s \) | 1.98   | 1.93            | 1.90            | 1.82            | -1891.20        | -1765.72         | -1670.28         | -1508.55         | 2261.66          | 12.49             |
| \( \gamma^o \) | 1.56   | 1.53            | 1.51            | 1.50            | -1231.14        | -1142.02         | -1072.43         | -1021.42         | 1091.30          | 6.94              |
| 60\(^o\)  | 1.38   | 1.36            | 1.34            | 1.27            | -891.71         | -825.73          | -761.61          | -602.12          | 2235.39          | 9.45              |

**Table 6**: Equilibrium constants and thermodynamics parameters for the adsorption of EBT onto rice husk

The qualities of \( \Delta H^o \) are inside the scope of 1 to 93 KJ/mol demonstrates the physisorption.

The outcome calls attention to physisorption is considerably more ideal for the adsorption of EBT and the endothermic idea of adsorption (34-36). Since on account of physisorption, while rising the temperature of the framework, the degree of dye adsorption increase, these standards out the likelihood of chemisorption (34, 35, 37, and 38). The low \( \Delta H^o \) value portrays dye is physisorbed onto the adsorbent. The negative values of \( \Delta G^o \) (Table 6) exhibit the adsorption is very great and unconstrained. The positive values of \( \Delta S^o \) (Table 6) demonstrate the raised disorder and arbitrariness at the solid solution interface of EBT with the adsorbent, while the adsorption there are some basic changes in the dye and the adsorbent happen. The adsorbed water molecules, which were uprooted by the adsorbate species, acquire translational entropy than is lost by the adsorbate particles, consequently allowing the prevalence of randomness in the system. The promotion of adsorption capacity of the adsorbent at higher temperatures was credited to the amplification of pore size and activation of the adsorbent surface (35-38).

**Conclusion**

The present investigation contracts with the expulsion of EBT by rice husk. The accompanying ends, proposals, and essentialness were drawn: The report anticipated from the present work obviously recommends that utilization of rice husk as the adsorbent is much prudent, successful and feasible. It very well may be proficiently used to expel EBT without representing any mischief to the nature of water. The various operational parameters detected through the procedure of examinations uncover that the concentration of adsorbate, adsorbent dose, contact time and temperature oversee the total procedure of adsorption. The batch studies visibly recommend that rice husk shows nearly at lower concentration adsorbates than at higher concentration.

Adsorption of EBT dye occurred and the equilibrium time has gotten in 60 min. at optimal dose 50 mg/50mL of the adsorbent. The outcomes acquired are all around fitted with straight type of both Freundlich and the Langmuir isotherms. But, Langmuir demonstrate is progressively proper for depicting the adsorption equilibrium information than the Freundlich model. Maximal sorption capacities determined from the Langmuir model were 40mg/g in EBT solution on rice husk at 298K. The determined values of thermodynamic parameters clearly demonstrate that the adsorption of EBT onto rice husk is possible, spontaneous and endothermic in nature. The \( \Delta H \) for EBT was in the scope of 12827.67 - 1091.30 kJ/mol. Experimental results of the present investigation uncover that rice husk is an operative low-cost adsorbent for the removal of dyes from water.

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