EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDY OF ADSORPTION OF ERYTHROSINE-B FROM AQUEOUS SOLUTION BY ACTIVATED CARBON FROM BLACK GRAM HUSK (Vigna mungo L.)

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ABSTRACT

Erythrosine–B dye, which causes carcinogenicity and neurotoxicity, is removed by adsorption technique using low cost Activated Carbon prepared from Black Gram Husk (ACBGH). ACBGH was characterized by SEM, FTIR, XRD and Raman Spectroscopy. SEM image of ACBGH showed porous and irregular external surface. It is clear that there is a good possibility for the dye molecules to be adsorbed on the surface of ACBGH. The surface area (480.10 m²/g) was determined by BET method. Batch experiments were performed to study the effects of contact time, adsorbent dose, temperature and pH on the percentage removal of Erythrosine-B dye. The data best fitted with the Langmuir model. The adsorption capacity of ACBGH for Erythrosine-B was 882.68 mg g⁻¹. The adsorption process followed the pseudo second order equation kinetics. Thermodynamic studies showed that the adsorption was spontaneous, endothermic and entropy controlled. Desorption studies were done.

Key Words: Activated carbon, Adsorption, Isotherms, Kinetics, Thermodynamics

INTRODUCTION

Dyes are synthetic organic aromatic compounds that are molecularly dispersed and bound to the substrates by intermolecular forces and have high application potential in the industrial sectors as colouring materials¹. These dyes can cause allergic dermatitis, skin irritation, cancer and mutation in living organisms. Erythrosine - B (EB) is a water-soluble xanthenes class of dye. It is widely used as colourant in food, textile, drug and cosmetics. In large doses it causes various types of allergies, thyroid activities, carcinogenicity, DNA damage behaviour, neurotoxicity and xenoestrogen nature in the humans and animals. The photochemical and biochemical degradation of the erythrosine is not recommended due to formation of toxic by-products². Photo degradation, electrochemical oxidation³ and adsorption are effective for removing reactive dyes without producing unwanted by-products. Adsorption is considered to be superior to other techniques because of its low cost, easy availability, simplicity of design, high efficiency and ease of operation, biodegradability and ability to treat dyes in more concentrated forms.

Black Gram belongs to the family Leguminoseae bearing the botanical name as Vigna mungo L. It is one of the important pulse crops in India. It is reported that Black gram is originated in India and is the largest producer and consumer in the world. It is a rich protein food which contains about 26 percent protein, almost three times that of cereals. The coastal Andhra region in Andhra Pradesh is famous for black gram after paddy.

AIMS AND OBJECTIVES

To develop a low cost and efficient adsorbent by chemical activation of Black Gram husk by using orthophosphoric acid and to evaluate the equilibrium isotherms, kinetics and thermodynamics of EB dye adsorption by the Activated Black Gram Husk (ACBGH).

MATERIAL AND METHODS

Method of preparation of the adsorbent (ACBGH)

Raw Black gram husk was collected, washed with water and dried at room temperature. It was

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subjected to grinding and drying at 110°C. The dried mass was impregnated with Orthophosphoric acid in the ratio of 5:1 (g H₃PO₄/g Black gram husk powder) and allowed to carbonize at 450°C in a muffle furnace for 1h. The carbon was washed to remove all the free acid and then dried at 110°C overnight (ACBGH).

**Batch and kinetic studies**

In order to evaluate the feasibility of adsorption, batch studies were carried out using 100ml conical flasks each containing 50ml of the dye solution and a known amount of ACGGH adsorbent and then mechanically agitated in a water bath shaker (Remi) to elucidate the values of the test parameters including solution pH, dose, temperature and contact time. The supernatant solution after centrifuge the remaining EB was determined at 526 nm by using a UV Visible spectrophotometer. The kinetic and thermodynamic studies were performed by determining removal conditions. The amount of adsorbed q (mg/g) capacity was calculated using the following equation.

\[
\text{Amount Adsorbed (q) = } (C_0 - C_t) \times \frac{V}{m} \]

where \(C_0\) and \(C_t\) (mol/L) are the concentrations of the dye solution initially and at time \(t\) respectively. \(V\) (L) is the volume of dye solution and \(m\) (g) is the mass of the adsorbent used.

**RESULTS AND DISCUSSION**

**Boehm titration**

The Boehm titration was used to calculate the amount of surface acidic and basic functional groups. The surface chemistry was determined with the use of four independent solutions of NaHCO₃ (0.05N), Na₂CO₃ (0.05N), NaOH (0.05N) and (0.05N) HCl with 0.5g of ACGGH with 24 hrs shaking. Subsequently the aqueous solutions were titrated against HCl (0.05N) for basic and (0.05N) NaOH for acidic sites. The amount of HCl was used to calculate the number of surface basic sites while the amount of NaOH, Na₂CO₃ and NaHCO₃ were used to calculate the number of surface acidic sites. The most common oxygen groups on the surface are carboxylic (0.52 meq/g), phenolic (0.3 meq/g), lactonic (0.12 meq/g) and basic sites (0.818 meq/g).

**FT-IR spectroscopic studies**

In raw black gram husk the broad band around 3374 cm⁻¹ is observed (Fig.1) which is attributed to the O-H stretching vibration of hydrogen bonded hydroxyl groups in carboxylic, phenolic or alcoholic functional groups. The peaks at 2925.77 cm⁻¹, 1635.26 cm⁻¹ and 1429.88 cm⁻¹ are due to –CH₃, C-C and C-O stretching respectively. The bands around 1000-1300 cm⁻¹ are usually found in oxidized carbons and are assigned to C - O stretching in acids, alcohols, phenols, ethers and/or ester groups. The band at 1024.14 cm⁻¹ is associated with the stretching vibration and may indicate the presence of phenols, epoxide structures, aromatic ethers and lactone groups. The sharp intense band at 3696.83 cm⁻¹ is due to the O-H stretching in alcohols. The spectra obtained at 2921.54 cm⁻¹ may be due to the C-H stretching in alkanes. The spectra of the ACGGH showed a strong band at 1590.92 cm⁻¹ which could be attributed to the carbonyl (C=O) stretching vibration of carboxylic acids and lactones.

**XRD Spectrum of ACGGH**

The phase composition details of ACGGH were determined from the XRD pattern studies. The crystallite size along the directions (Lc or La) was determined using Scherer equations.

\[
L_\text{c} = \frac{K_c \lambda}{\beta_c \cos \theta_c} \quad \text{(2)}
\]

\[
L_\text{a} = \frac{K_a \lambda}{\beta_a \cos \theta_a} \quad \text{(3)}
\]

The X-ray diffraction results shown in Fig. 2 had a sharp peak at 2θ of 25.58° which confirmed the formation of graphitic structure corresponding to [002] plane of graphite. A broad peak around 20 of 43.18° indicated the formation of [101] plane of the graphitic structure (Fig. 2). The two peaks at 20 of 25.58° and 43.18° were used to calculate \(L_c\) and \(L_a\) respectively which are attributed to the reflections from the [002] and [101] planes of the ACGGH. The value of interlayer distance between two planes was found to be 0.347nm. Typically in crystalline carbonaceous structures such as graphite, the interlayer distance between two adjacent carbon sheets is 0.335 nm. The calculated interlayer spacing of ACGGH was approximately equal to the standard interlayer spacing of pure graphitic carbon. This indicates that ACGGH was graphitic and crystalline in nature.

**Raman spectrum of ACGGH**

The crystallographic parameter for the ACGGH was got from Raman Spectral studies (Fig. 3). The D-band (1340 cm⁻¹) is often referred to the disorder band which results from the
imperfection or loss of hexagonal symmetry of
the graphite structure.\textsuperscript{a} The second order Raman
lines show that the bands at the positions around
2577 cm\(^{-1}\) - 2960 cm\(^{-1}\) are very much similar to
that of graphite. This confirms the presence of
graphite in ACBGH.

Fig. 1: FTIR spectra of raw Black gram husk and ACBGH

Fig. 2: XRD pattern of ACBGH

Fig. 3: Raman spectrum of ACBGH
BET analysis of ACBGH

Surface area and pore size distribution were obtained by BET studies. The N$_2$ adsorption - desorption isotherm of ACBGH sample is shown in Fig. 4. It is found that the isotherm is type IV character as defined by IUPAC classification with H1 hysteresis. The presence of hysteresis confirms that the surface of ACBGH is of mesoporous in nature. The BET surface area of the ACBGH is found to be 480.10 m$^2$/g. The average pore diameter is obtained by $D_{av} = 4V_{tot}/S_{BET}$, where $V_{tot}$ is total pore volume and $S_{BET}$ is the surface area from BET method. The average pore diameter of ACBGH is found to be 4.1 nm which further confirms the presence of mesopores. From Table 1, the mesopore volume and micropore volume are found to be 96.4% and 3.6% respectively indicating that the ACBGH was mesoporous in nature.

![Nitrogen adsorption – desorption isotherm of ACBGH obtained at 77K](image)

**Fig. 4**: Nitrogen adsorption – desorption isotherms of ACBGH obtained at 77K

Scanning Electron Microscopy images of ACBGH

The surface morphology of ACBGH adsorbent was obtained using Scanning Electron Microscopy. Fig. 5 shows the SEM image of the activated carbon before subjecting to the adsorption. The surface morphology of the observed ACBGH indicated the presence of various sizes of pores on its surface. The surface seems to be rough and hence suitable for the adsorption of dyes from aqueous solution.

Zero point charge of ACBGH

The point of charge pH$_{zpc}$ is defined as the pH of the aqueous solution in which the solid presents a neutral electrical potential. The pH$_{zpc}$ of ACBGH was determined by salt addition method which is also called as drift method. It is accounted that if the pH < pH$_{zpc}$, the surface has a net positive charge and that if pH > pH$_{zpc}$ it is negative. The pH$_{zpc}$ of ACBGH is found to be 2.0 (Fig. 6). This low pH$_{zpc}$ value was consistent with Boehm titration result, which showed dominance of acidic group at the surface of the ACBGH.

Effect of contact time

The effect of contact time on the adsorption of EB was studied for different concentrations like $1.2 \times 10^{-3}$M, $1.4 \times 10^{-3}$ M and $1.8 \times 10^{-3}$M with a time range from 5 to 120 min and a fixed dose of 0.1g ACBGH. The contact time needed for the
dye solution to reach equilibrium was 120 min (Fig. 7). The percentage removal increased with increase in contact time. The extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation. It is because initially the number of vacant surface site may be available for adsorption and after some time, the remaining vacant surface site may be exhausted.$^{10}$

Fig. 5: SEM image of ACBGH

![SEM image of ACBGH](image)

Fig. 6: Zero point charge of ACBGH

![Zero point charge graph](image)
Effect of adsorbent dose
Effect of the amount of adsorbent was carried out in the range of 0.04–0.32 g of ACBGH with a dye concentration of $1.8 \times 10^{-3}$ M. Fig. 8 represents that an increase in the amount of the adsorbent leads to an increase in the removal of the dye onto ACBGH. Such a trend is mainly attributed to the fact that with increase in the amount of the adsorbent the adsorptive surface area increases which provides a greater number of active sites for adsorption. An amount of 0.1 g was chosen as optimum amount for dye adsorption onto ACBGH.

Effect of concentration at different temperatures
Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process\textsuperscript{11}. Fig. 9 shows that adsorption of dyes increases with increase in temperature. Increase in the adsorption capacity with temperature suggests that active centers on the surface available for adsorption increase with temperature. This could also be attributed to the change in pore size. Chemisorption occurs when the extent of adsorption is enhanced at elevated temperature.\textsuperscript{12}
Adsorption isotherms

Langmuir isotherm
The Langmuir sorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with a finite number of identical sites\textsuperscript{13}. The Langmuir equation is written as:

\[
\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e
\]  \hspace{1cm} (4)

Where \(q_e\) (mol/g) and \(C_e\) (mol/l) are the amounts of dye adsorbed per unit weight of adsorbent and the concentration of the dye solution at equilibrium (Fig. 10). The \(Q_m\) (mol/g) is the adsorption capacity and \(K_L\) (L/mol) is the Langmuir equilibrium constant. The adsorption capacity for EB is 882.68mg/g. The feasibility of Langmuir adsorption isotherms was tested by using dimensionless constant called separation factor or equilibrium parameter (\(R_L\)).

\[
R_L = \frac{1}{1 + K_L C_0}
\]  \hspace{1cm} (5)

Freundlich isotherm
The Freundlich equation explains surface heterogeneity. The Freundlich adsorption isotherm equation can be expressed as:

\[
\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e)
\]  \hspace{1cm} (6)

where \(q_e\) (mol/g) is the amount of dye adsorbed at equilibrium, \(C_e\) (mol/L) is the equilibrium dye concentration in solution, \(K_f\) (mol/g) and \(n\) (dimensionless) (Fig. 11).

Dubinin-Radushkevich adsorption isotherm
Dubinin-Radushkevich adsorption isotherm is used to describe the adsorption on both homogeneous and heterogeneous surfaces. The linear form of the isotherm can be expressed as follows.

\[
\ln(q_e) = \ln(Q_m) - K \varepsilon^2
\]  \hspace{1cm} (7)

The plots of \(\ln(q_e)\) versus \(\varepsilon^2\) give straight line (Fig. 12) and \(\varepsilon\) is the Polanyi potential that can be calculated from the equation.

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]  \hspace{1cm} (8)

where \(R\) is the universal gas constant (8.314 J/mol/K), \(T\) is the temperature (K) and \(C_e\) is the concentration at equilibrium. The mean energy of sorption, \(E\) (kJ/mol), is calculated by the following equation.

\[
E = \frac{1}{\sqrt{2 K}}
\]  \hspace{1cm} (9)

From the experimental study the values of \(E\) were found to be in the range of 16 kJ/mol to 18 kJ/mol for EB. Comparing the \(R^2\) values from the Table 2 for the three adsorption isotherm models, the Langmuir model gives the highest \(R^2\) values for all the dyes which imply that it is the best fit model for the adsorption of dyes onto ACBGH.

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**Fig. 9**: Effect of concentration on the uptake of EB on ACBGH at different temperatures
Fig. 10: Langmuir adsorption plots

Fig. 11: Freundlich adsorption plots

Fig. 12: D-R adsorption plots
Table 2: Adsorption isotherm parameters for adsorption of EB onto ACBGH

<table>
<thead>
<tr>
<th>Adsorption Isotherm</th>
<th>Temperature (K)</th>
<th>305</th>
<th>315</th>
<th>325</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir adsorption isotherm</td>
<td>Qm (mol/g)</td>
<td>10.032 x 10^{-4}</td>
<td>10.520 x 10^{-4}</td>
<td>13.724 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>K_L (1/mol)</td>
<td>5.528 x 10^{4}</td>
<td>6.989 x 10^{4}</td>
<td>9.389 x 10^{4}</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.985</td>
<td>0.987</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>R_L</td>
<td>0.043</td>
<td>0.034</td>
<td>0.025</td>
</tr>
<tr>
<td>Freundlich adsorption isotherm</td>
<td>K_f (mol/g)</td>
<td>0.011 x 10^{-3}</td>
<td>0.210 x 10^{-3}</td>
<td>0.292 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>0.287</td>
<td>0.272</td>
<td>0.213</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.943</td>
<td>0.949</td>
<td>0.718</td>
</tr>
<tr>
<td>D-R adsorption isotherm</td>
<td>Qm (mol/g)</td>
<td>1.922 x 10^{-3}</td>
<td>3.579 x 10^{-3}</td>
<td>5.892 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>1.184 x 10^{-9}</td>
<td>1.465 x 10^{-9}</td>
<td>1.435 x 10^{-9}</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.865</td>
<td>0.918</td>
<td>0.786</td>
</tr>
</tbody>
</table>

Adsorption kinetics

In order to explore the kinetics involved in dye adsorption, the results obtained were fitted into the following equations (Fig. 13 and Fig. 14).

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{10}
\]

Pseudo first order

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{11}
\]

Pseudo second order

From the Table 3, it is clear that the correlation coefficients are closer to unity for pseudo second order kinetics than for the pseudo first order kinetics. This suggests that the adsorption system follows pseudo second order kinetic model for the adsorption of EB onto ACBGH.\textsuperscript{16,17} The \( q_e \) (calc) values are in good agreement with the \( q_e \) (exp) data, which further confirms that the adsorption of EB dye onto ACBGH follows pseudo second order reaction.

![Fig. 13: Pseudo first order plots of EB](image-url)
Thermodynamic parameters such as Gibbs free energy change ($\Delta G^\circ$), enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) were determined to evaluate the spontaneity and the nature of the adsorption process. The value of $\Delta G^\circ$ ranges from $-27.69$kJ/mol to $-30.93$kJ/mol, $\Delta H^\circ$ value is $25.12$kJ/mol and $\Delta S^\circ$ value is $173.17$J/mol/K and this reflects the affinity of the adsorbent materials towards ACBGH and the adsorption mechanism is an entropy controlled process.

### Treatment of real effluent

Real effluent collected from a textile industry in Thirupur was subjected to experiments for the removal of dyes from the industrial waste water. The effluent before and after treatment was subjected to physical and chemical examination and the results are given in Table 4. The results obtained on examination showed that the COD value was reduced from $6060$ mg/L to $281$ mg/L and BOD value was reduced from $1800$ to $100$ mg/L. The turbidity level decreased from $36$NTU to $16.9$. The total dissolved solids also decreased from $7170$ to $5299$. The chemical examination studies showed a decrease in all the parameters calculated.
Table 4: Physical and chemical examination of ACBGH with real effluent

<table>
<thead>
<tr>
<th>Physical examination Parameters</th>
<th>Real effluent before treatment with ACBGH</th>
<th>Real effluent after treatment with ACBGH</th>
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</thead>
<tbody>
<tr>
<td>Odour</td>
<td>Offensive</td>
<td>None</td>
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<tr>
<td>Turbidity NTU</td>
<td>36</td>
<td>16.9</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>7170</td>
<td>5299</td>
</tr>
<tr>
<td>Electrical conductivity Micro mho/cm</td>
<td>10243</td>
<td>7570</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical examination Parameters</th>
<th>Real effluent before treatment with ACBGH</th>
<th>Real effluent after treatment with ACBGH</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.22</td>
<td>6.966</td>
</tr>
<tr>
<td>Alkalinity total</td>
<td>1840</td>
<td>456</td>
</tr>
<tr>
<td>Total hardness</td>
<td>3200</td>
<td>476</td>
</tr>
<tr>
<td>Calcium as Ca mg/L</td>
<td>760</td>
<td>133</td>
</tr>
<tr>
<td>Magnesium as Mg mg/L</td>
<td>312</td>
<td>30</td>
</tr>
<tr>
<td>Potassium as K mg/L</td>
<td>160</td>
<td>45</td>
</tr>
<tr>
<td>COD(mg/L)</td>
<td>6060</td>
<td>281</td>
</tr>
<tr>
<td>BOD(mg/L)</td>
<td>1800</td>
<td>100</td>
</tr>
</tbody>
</table>

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling the spent adsorbent and the dye. If alkaline water is needed, then the adsorption is by ion exchange. If organic solvents (CH₃COOH, C₂H₅OH) can desorb the dye then adsorption is chemisorption. Attempts were made to regenerate the adsorbed dyes and adsorbent with Ethanol, acetone, 0.1N acetic acid, 0.1 hydrochloric acid, 0.1N sodium hydroxide and water as desorbing agents. Maximum desorption was obtained by using ethanol as the solvent.

CONCLUSION

It is concluded that ACBGH has good capability to remove EB dye from aqueous solution. ACBGH has got a surface area of 480.10m²/g and has high percentage of mesopores (96.4%) as proved by BET studies and SEM. The rates of adsorption for EB dye at various initial concentrations were rapid at the beginning, followed by a more gradual process and equilibrium was attained within 2 hours. The adsorption process of EB onto ACBGH was better explained by Langmuir Adsorption Isotherm and pseudo-second order kinetic model. The maximum adsorption capacity of ACBGH was 882.68mg /g and hence ACBGH can serve as a good and low cost adsorbent to replace costly adsorbents in dye removal. Desorption studies show that ethanol is the best suitable solvent for desorption. The effectiveness of ACBGH is also proved with the treatment of real effluent.

REFERENCES