Activated Red Mud as an Adsorbent in the Removal of Anionic Dye, Brilliant Yellow Dye, From Polluted Waters

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**Abstract:** The sorption nature of acid activated red mud towards anionic dye, Brilliant yellow dye, has been investigated with respect to various physicochemical parameters like pH, sorbent concentration, agitation time, temperature and initial concentration of the dye using simulated waters and the conditions have been optimized for the maximum removal of the dye. The interference of co-ions on the adsorption of the dye has been investigated. The adsorption data is analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. Correlation coefficient ($R^2$) and dimensionless separation factor ($R_L$) values have confirmed that adsorption obeys Langmuir adsorption ($R^2$: 0.9914; $R_L$: 0.0290) indicating monolayer formation while Temkin isotherm and Dubinin-Radushkevich isotherms indicate that the adsorption is ‘physisorption’ in nature. Pseudo-first-order, pseudo-second-order, Bangham’s pore diffusion and Elovich equations have been applied to identify the kinetics of adsorption process and found that adsorption follows pseudo-second-order kinetics. The thermodynamic study revealed that adsorption of the dye is an endothermic process and the adsorption increases with increase in temperature. The procedures developed in this investigation have been applied to the samples collected from the effluents of textile industries and found to be successful.

**Key Words:** Anionic Dye, Brilliant yellow dye, Pollution and Control, Activated Red mud, adsorption, applications.

1: Introduction

The removal of pollutants from waste waters using un-conventional methods based on adsorption is being widely investigated throughout the Globe to find simple, effective, economical and eco-friendly methodologies. Our research group has been probing these unconventional methods and developed producers for the removal of Chromium (VI)\(^1\)-\(^4\), Zinc\(^5\)-\(^6\), Aluminum (III)\(^7\)-\(^10\), Fluoride\(^11\)-\(^17\), Nitrite\(^18\),\(^19\), Nitrates\(^20\), Ammonia\(^21\)-\(^23\), Phosphate\(^24\),\(^25\) and some Dyes\(^26\)-\(^31\) and also bio-remediation methods for the removal of some heavy metal ions using oxidation ponds\(^32\).

In the recent past, red mud, a waste produced in Aluminum manufacturing industries, has attracted the attention of researchers. The adsorption nature of red mud either in its native or activated form, is being investigated in the removal of various pollutants such as As (III,V)\(^33\),\(^34\), Pb (II)\(^35\),\(^36\), Cr(VI)\(^37\), Co(II)\(^38\), Zn(II)\(^39\),\(^40\), Phosphate\(^41\)-\(^43\), Nitrate\(^44\), Dyes\(^45\)-\(^47\) from waste waters and thereby making a waste and potential pollutant material, red mud, for better use.

In the present work, acid activated red mud is investigated for its adsorption nature towards anionic dye, Brilliant Yellow. The presence of even traces of synthetic dyes in waste waters is a potential environmental
threat as the dyes or their degradation products are toxic owing to their complex aromatic nature to aquatic life and human beings. Further, the color of water in water bodies curtails the light and interferes with the photosynthesis and thereby affecting the biota and depending aquatic life. The contamination of water bodies with residues of synthetic dyes coming from the effluents of textile industries is endangering the biota and aquatic life prevailing in the water bodies due to the toxic nature of some of the dyes or their degradation products. Further, the color in water bodies due to the residues of dyes obstruct the sun-light to reach to the biota or aquatic life and thereby retarding or effecting the natural phenomenon such as photosynthesis, metabolisms etc.

It is reported that every year nearly 10% of dye used in Textile industry is lost through the sewage and if proper extraction and disposal methods are not envisaged by the industries, they enter into the water bodies causing grave threat to aquatic life.

Brilliant yellow dye is used in industries pertaining to textile, inks and tinting. It is widely used for dyeing the protein fibers like wool, angora, cashmere and silk. The effluents from these industries have to be treated for the complete removal of the dye. If the effluents contain even traces of dyes, they cause polluting the water bodies as it is not bio-degradable and it is hazardous. Hence, treating the wastewaters for the complete removal of this potential hazardous dye is essential.

In this present work methodologies for the removal Brilliant Yellow Dye from waster waters using activated red mud as adsorbent have been investigated with respect to various physicochemical parameters and conditions for the maximum removal of the dyes have been optimized.

2: Materials and Methods

Table No:1 Chemical properties of red mud

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Result (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina as Al₂O₃</td>
<td>15.47</td>
</tr>
<tr>
<td>Iron as Fe₂O₃</td>
<td>58.78</td>
</tr>
<tr>
<td>Silica as SiO₂</td>
<td>6.58</td>
</tr>
<tr>
<td>Titanium as TiO₂</td>
<td>4.39</td>
</tr>
<tr>
<td>Soda as Na₂O</td>
<td>3.63</td>
</tr>
<tr>
<td>Calcium as CaO</td>
<td>1.49</td>
</tr>
<tr>
<td>Phosphorus as P₂O₅</td>
<td>0.159</td>
</tr>
<tr>
<td>Vanadium as V₂O₅</td>
<td>0.110</td>
</tr>
<tr>
<td>LOI (105-1000°C)</td>
<td>7.22</td>
</tr>
</tbody>
</table>

2.1. Adsorbent

The red mud was obtained from Utkal Alumina, Rayagada, Orissa. Red mud samples was washed with distilled water a number times until the pH of the filtrate is almost neutral. Then the red mud was dried at 105°C for two hours. Then the sample was grinded to a fine powder and then it was meshed to 150 µ. The meshed sample was stored. From it, a suitable amount of red mud was taken and to it, 1.0 N HCl was added in the ratio: 1:2 (by volume), stirred well and was digested for 12 hrs at 50°C temperature. Thus treated sample was filtered.
and the red mud was washed with distilled water repeatedly until, the pH of the filtrate was neutral. Then the sample was dried at 105°C for two hours. Thus obtained sample was used in this work. The composition of the active red mud is presented in Table 1.

2.2. Adsorbate:

An anionic dye, Brilliant Yellow (400 nm) purchased from S.D. fine chemical was used. Stock solution of 1000 ppm was prepared with distilled water and it was suitably diluted as per the need.

2.3 Reagents and Chemicals:

All the chemicals used were of Analytical Reagent Grade purchased from Merck. India Pvt. Ltd and Sd. Fine Chemicals and all the solutions were prepared using double distilled water throughout this study. Stock solution of 100 ppm of Brilliant yellow Dye was prepared and was suitably diluted as per need.

2.4: Method:

Batch modes of extraction were adopted. 100 ml of Brilliant Yellow Dye solution (100 ppm) was taken into 250ml conical flask and to it definite quantity the activated red was added. pH was adjusted to a desired value. Then the solution was shaken in horizontal shaker at 250rpm. After a definite contact time, the conical flask was removed from shaker and the solution was filtered through Whatman No.1 filter paper and the filtrate was analyzed for the residual dye concentration using Spectrophotometric method.

Estimation of the Dye:

The dye has λmax at 400 nm below pH: 6.5 and obeys Beers-Lamberts law even at low concentrations. The O.D. measurements were made at the said λmax using UV-Visible Spectrophotometer(Elico) against blank. The obtained O.D value for un-known solution was referred to standard graphs (drawn between O.D and concentration) prepared with known concentrations of the dye by adopting method of Least Squares to know the concentration of the dye.

The influence of pH, sorbent dosage, equilibration time, initial concentration of the dye and temperature on the % removal of the dye with the Activated red mud was studied and conditions were optimized.

The dye uptake capacity was calculated using formula:

\[ q_e = \frac{(C_0 - C_e) \times V}{m} \]

where:
- \( q_e \) is the amount of dye quantity adsorbed (mg/g).
- \( C_0 \) is the initialConcentration of dye (mg/L), \( C_e \) is the equilibrium dye concentration (mg/L).
- \( m \) is the mass of adsorbent (g).
- \( V \) is the volume of the solution (L).

The percent removal of dye from the solution was calculated by the following equation:

\[ \% \text{ removal} = \left( \frac{C_0 - C_i}{C_0} \right) \times 100 \]

where \( C_0 \) (mg/L) and \( C_i \) (mg/L) are the initial and final dye concentrations.

The obtained results were presented in the Graph No. 1-9Table No.2 and 3.

3: Results and Discussions

The sorption of characteristics of the activated Red mud towards the Brilliant yellow dye by varying pH, adsorbent dosage, temperature, initial concentration of dye and interfering ions has been investigated and the finding are presented comprehensively hereunder:
3.1: Effect of pH:

The pH of the dye solution plays an important role in the whole adsorption process. The effect of pH has been studied by varying the pH from 2 to 10 under other optimum parameters: initial conc. of dye: 100ppm; adsorbent dosage: 0.6gm/100ml, contact time:25 minutes; rpm:250; temperatures: 30⁰ C. The results are presented in Graph No.1. It is observed from the Graph that 100% removal is possible at pH 2; and% of extraction is progressively decreased as Ph is increased from 2 to 10. So it is inferred that acidic conditions favour the adsorption of dye.

This can be attributed to the function groups present on the surface of the adsorbent and anionic nature of the dye. The pHzpc is found to be 6.5 (vide Graph No. 2) and below this pH, the surface acquires+ positive charge and a thrust for anions. This is reflected in the adsorption nature of the dye. As the dye is anionic in nature, the % removal is progressively increased with the decrease in the pH because, the surface acquires +ve charge at low pH values and the dye being anion is held to the surface due to electrostatic interactions. If the pH is more than 7, adsorption of the dye is marginal because, above pH: 6.5, the surface acquires negative charge and thus causes repulsion of the negatively charged anion

3.2: Effect of adsorbent dosage:

The effect of adsorbent dosage was studied by varying the sorbent dosage from 100mg to 1000mg/ 100ml at other optimum extraction conditions namely: pH: 2, time of equilibration: 25 min, rpm: 250; initial conc. of dye: 100 ppm; temp.:30⁰C. The results are depicted in the Graph No. 3.
From the graph it is inferred that with increasing the sorbent dosage, the % removal of the dye also increased but after certain dosage, it remains constant. It is observed from the Graph that the % removal of the dye is increased from 92.0% to 100% as the sorbent dosage is increased from 100 mg to 600mg/100 ml. As the concentration of the sorbent is increased, the availability of active sites increases and hence, the increase in the % removal of the dye. But at high concentrations of the adsorbent, some of the active sites may be blocked resulting a study state at optimum dosages of the adsorbent concentrations.

3.3: Effect of Contact time:

To determine the optimum equilibrium time, the time is varied from 0 to 30 minutes at optimum conditions of pH: 2, dosage: 600 mg/100ml, rpm: 250 and temp. 30°C. It is observed from the Graph No: 4, that the % removal of the dye is 87.0% within 5 minutes of equilibration and the adsorption process is slowed down and 100% removal is observed only after 25 minutes of agitation. The rapid adsorption at the initial contact time can be attributed to the large number of vacant adsorbent sites and the high gradient of solute concentration, whereas the slower rate with the increasing time may be ascribed to the saturation of the available adsorbing sites.
3.4: Effect of initial concentration:

In the Graph No. 5, the effect of initial concentration of the dye on the % of extraction when all the other conditions are constant is depicted. % of extraction of the dye decreases from 100 to 64% with the increase in the initial concentration from 25 to 250 mg/L for a fixed concentration of the adsorbent, 600 mg/100ml. This is expected because at low concentrations of the dye, many active sites are available on the adsorbent. At high concentrations of the dye, the demand of active sites is more but the available active sites are limited as the concentration of the adsorbent is constant and hence, % removal is less.

3.5: Effect of temperature:

The effect of temperature on the extraction of the dye of concentration 200 ppm has been studied in the temperature range: 303 to 333 K at optimum extraction conditions: pH: 2, agitation time: 25 minutes, rpm: 250 and dosage: 600mg/100 ml and the results have been depicted in the Graph No. 6a & 6b.

Free energy change \((\Delta G)\) (KJ/mole), enthalpy change \((\Delta H)\) (KJ/mole) and entropy change \((\Delta S)\) (KJ/mole) were determined using the equations:

\[
\Delta G = -RT \ln K_d; \ln K_d = \Delta S / R - \Delta H / RT; K_d = q_e / C_e; \Delta G = \Delta H - T\Delta S,
\]

where \(K_d\): distribution co-efficient of the adsorption, \(q_e\): the amount of dye adsorbed, \(C_e\): equilibrium conc. of dye, \(T\): the absolute temperature in Kelvin, \(R\): the gas constant. The values of \(\Delta H\) and \(\Delta S\) were obtained from the slope and intercept of the plot between \(\ln K_d\) and \(1/T\). The values are presented in the Table No: 2. % of extraction increases from 75% to 88% with the increase in temperature from 303 to 333 K for dye solution of 200 ppm concentration.
Table No: 2 Thermodynamic Parameters of Adsorption of dye on acid activated red mud

<table>
<thead>
<tr>
<th>ΔH (KJ/mole)</th>
<th>ΔS (KJ/mole)</th>
<th>ΔG (KJ/mole)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.94</td>
<td>81.27</td>
<td>-4.677 (303k)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-5.490 (313k)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-6.303 (323k)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-7.115 (333k)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.993</td>
<td></td>
</tr>
</tbody>
</table>

The negative values of ΔG indicate that the adsorption of the dye is feasible and spontaneous in nature. The positive value of ΔH (19.94 kJ/mol) reflect the endothermic nature of the adsorption process. The positive ΔS value reflects an increase in randomness at the solid/solution interface with the increasing of temperature, which implies the more possible arrangement during the adsorption of the dye.

3.6: Effect of Co-ions:

The interference of co-ions (fivefold excess) on the % of extraction of the dye has been
Presented in Graph No. 7a & b. It can be inferred from the data that the studied co-ions have either not interfered or marginally affected the % of extraction and at any condition, the % of extraction has not come down below 98.0%.

3.7: Adsorption Isothems:

Four well known adsorption isotherm models, Freundlich\\textsuperscript{59}, Langmuir\\textsuperscript{60}, Temkin\\textsuperscript{61} and Dubinin-Radushkevich\\textsuperscript{62} isotherms have been selected to evaluate nature of adsorption. Linear form of Freundlich equation is 
\[
\log (q_e) = \log k_f + \frac{1}{n} \log C_e
\]

According to Hall et al\\textsuperscript{63}, the nature of the adsorption process is unfavorable (R\textsubscript{L} > 1), linear (R\textsubscript{L} = 1), favorable (0 < R\textsubscript{L} < 1) and irreversible (R\textsubscript{L} = 0) and the significant feature of the Langmuir isotherm model can be defined by the dimensionless separation factor, R\textsubscript{L} = 1 / (1 + a\textsubscript{L}C\textsubscript{i}) . The linear plots of these two adsorption isotherms were as shown in Graph Nos :8a &b and isothermal constants along with the correlation coefficient values were presented in Table 3.
Freundlich isotherm \{log (q_e) vs log (c_e)\} and Langmuir isotherm \(\left(\frac{C_f}{q_e}vS\frac{1}{C_e}\right)\) have been presented in the Graph No. 8a and 8b respectively. The slope \(a_t/k_l\), intercept \(1/k_L\), and \(R^2 \) and \(R_L\) values have been calculated and presented in the Table No. 3.

\(R^2\) values are: 0.9914 for Langmuir isotherm model and 0.9549 for Freundlich model indicating that the Langmuir isotherms are more suitable for describing the adsorption proves. Further, \(R_L=0.0290\) indicates that the adsorption of the dye is onto the surface of the adsorbent. Thus, the adsorption of the dye on the surface of the adsorbent is monolayer and homogeneous.

Further, the adsorption process is modeled with Linear form of Temkin equation: 
\[q_e = B\ln C_e + BlnA\]

where \(RT/b = B\) and Linear form of Dubinin-Radushkevich equation: 
\[lnq_e = -\beta \varepsilon^2 + lnq_m\]

where \(\varepsilon = RT \ln(1+1/C_e)\). The linear plots of these two adsorption isotherms are depicted in Graph No: 8c & d and isothermal constants along with the correlation coefficient values are presented in Table 2. The mean free energy (E) and heat of sorption (B) are characteristics of adsorption and as E value is less than 8 kJ/mol and B is less than 20kJ/mol, the adsorption is “physisorption” in nature i.e. non-specific adsorption due long range weak Vander Waals forces.

### 3.8: Adsorption kinetics:

#### Table 3: Adsorption and Kinetic parameters

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Adsorption and Kinetic parameters</th>
<th>Slope</th>
<th>Intercept</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Freundlich Isotherm</td>
<td>0.1891</td>
<td>1.2418</td>
<td>0.9549</td>
</tr>
<tr>
<td>2.</td>
<td>Langmuir Isotherm (R_L=0.0290)</td>
<td>0.0267</td>
<td>0.0799</td>
<td>0.9914</td>
</tr>
<tr>
<td>3.</td>
<td>Temkin Isotherm (B=5.1873)</td>
<td>5.1873</td>
<td>15.785</td>
<td>0.9492</td>
</tr>
<tr>
<td>4.</td>
<td>Dubinin-Radushkevich Isotherm (E=1.118)</td>
<td>-4E-07</td>
<td>3.4072</td>
<td>0.6173</td>
</tr>
<tr>
<td>5.</td>
<td>Pseudo-first-order model</td>
<td>-0.0903</td>
<td>0.8755</td>
<td>0.9752</td>
</tr>
<tr>
<td>6.</td>
<td>Pseudo-Second-order model</td>
<td>0.0578</td>
<td>0.055</td>
<td>0.9999</td>
</tr>
<tr>
<td>7.</td>
<td>Elovich Model</td>
<td>-7.4449</td>
<td>23.768</td>
<td>0.9446</td>
</tr>
<tr>
<td>8.</td>
<td>Bangham’s pore diffusion model</td>
<td>0.6539</td>
<td>0.5359</td>
<td>0.9543</td>
</tr>
</tbody>
</table>

Kinetics of adsorption is studied using pseudo first-order model\(^{54,65}\), pseudo second-order model\(^{66,67}\), Bangham’s pore diffusion model\(^{68,69}\) and Elovich equations\(^{70,71}\). The pseudo first-order equation is \(\log (q_t - q_e) = \log q_e - k_1t/2.303\); the pseudo second-order equation is \(t/q_t = 1/k_2 q_e^2 - (1/q_e) t\); Bangham’s pore diffusion equation is \(\log \left[\log \left(C_f/C_t - q_m\right)\right] = \log \left(k_o/2.303V\right) + a \log(t)\); Elovich equation is \(q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t)\).

The data of these four kinetic models are presented in Graph Nos: 9-a to d, and rate constants along with the correlation coefficient values are presented in Table 3.
On perusal of the correlation coefficient ($R^2$) values, it may be inferred that the kinetics of adsorption follows the order: pseudo second-order $>$ pseudo first-order $>$ Bangham’s pore diffusion $>>$ Elovich model. Hence, the adsorption kinetics can be well defined by pseudo second-order and least by Elovich model.

3.9: I R Spectral Data:

FTIR data before and after adsorption of the dye are presented in the Fig No. 2a&b. It is revealed from the data that the broad band around 3418 cm$^{-1}$ and the narrow band around 1638 cm$^{-1}$ assigned to the $\text{OH}$ stretching vibration and bending vibrations of adsorbed water are shifted to 3099.30 and 1625.33 cm$^{-1}$ respectively with decrease of intensity. This indicates the involvements of the $-\text{OH}$ functional groups in the adsorption process. Further, the appearance of new bands in the range 1380 to 1510 cm$^{-1}$ (characteristics of aromatic nature) in the spectrum of dye adsorbed red mud indicate the presence of dye on the red mud. The shifting of band at 1016.61 cm$^{-1}$ pertaining to $\text{Si-O-Si}$, to 1025.72 and appearance of bands at 960.46 and 800 cm$^{-1}$ also indicated the sorption of the dye on the surface of the red mud.
4: Applications

The procedures developed in this investigation were applied to the samples collected from effluents of textile industries at Mangalagiri and Machilipatnam of Andhra Pradesh. The samples were analyzed for the actual amounts of the said dye and then the samples were fed with known amounts of the dye.

Table No:4 Removal of color in swages of dying industries

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Water samples</th>
<th>C_i (mg/lit) (initial concentration of dye)</th>
<th>C_f (mg/lit) (concentration of dye after removal)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sample 1</td>
<td>50</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Sample 2</td>
<td>62</td>
<td>5</td>
<td>91.9</td>
</tr>
<tr>
<td>3</td>
<td>Sample 3</td>
<td>75</td>
<td>9</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>Sample 4</td>
<td>100</td>
<td>21</td>
<td>79</td>
</tr>
</tbody>
</table>
Then these samples were subjected to extraction adopting the methodologies developed in this work. The obtained results were presented in the Table No. 4. It can be seen from the table that the procedure developed in this work successfully remove the said anionic dye.

5: Conclusions

- The adsorption nature of Activated red mud towards anionic dye, Brilliant Yellow Dye, has been investigated by varying various physicochemical parameters such as pH, sorbent concentration, agitation time, temperature and initial concentration of the dye. Batch methods of extractions have been adopted using simulated water. The extraction conditions are optimized for the maximum removal of the dye.
- Complete removal of the dye is observed pH: 2; extraction time: 25 minutes; 250 rpm, temp: 30°C, initial conc. of the dye: 100 ppm and sorbent dosage: 0.6 g/100ml.
- Fivefold excess of co-ions normally exists in sewages viz., Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^2-\), PO\(_4\)\(^3-\), CO\(_3\)\(^2-\), Ca\(^2+\), Zn\(^2+\), Fe\(^2+\), Mg\(^{2+}\) and Cu\(^{2+}\) have shown marginal interference.
- The adsorption data is analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. Correlation coefficient (R\(^2\)) and dimensionless separation factor (R\(_L\)) values have confirmed that adsorption obeys Langmuir adsorption (R\(^2\): 0.9914; R\(_L\): 0.0290) indicating monolayer formation while Temkin isotherm and Dubinin-Radushkevich isotherms indicate that the adsorption is ‘physisorption’ in nature.
- Pseudo-first-order, pseudo-second-order, Bangham’s pore diffusion and Elovich equations have been applied to identify the kinetics of adsorption process and found that adsorption follows pseudo-second-order kinetics.
- The thermodynamic study revealed that adsorption of the dye is an endothermic process and the adsorption increases with increase in temperature.
- The procedures developed in this investigation have been applied to the samples collected from the effluents of textile industries and found to be successful.

Acknowledgement:

The authors thank the Ministry of Environment & Forests (MOEF), New Delhi, for granting the project entitled “Red mud as an adsorbent for the removal of pollutants” (File No: 19/16/2014-RE) and under whose financial aid, this work has been carried out.

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