REACTIVE DYE COLOUR REMOVAL BY USING PREFORMED FLOCS AS ADSORBENT

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ABSTRACT

Efficiency of preformed flocs of Ferric Sulphate, Aluminium Sulphate and Manganese Sulphate in decolourizing the C.I. Reactive green 19 dye was studied by conducting non-flow agitated batch sorption studies. Excellent colour removal at pH::4 with preformed flocs of Ferric sulphate and at pH:: 10 with preformed flocs of Manganese Sulphate was achieved. Equilibrium data was fitted well to Langmuir isotherm and kinetic data was fitted well to Pseudo-second –order stating chemisorption is the rate limiting step.

Keywords: Kinetic adsorption studies, equilibrium studies, aqueous solution, flocs, Ferric Sulphate, and Manganese Sulphate

I. INTRODUCTION

Dyes are an important class of pollutants which came in large amounts from textile, dyeing, paper and pulp, tannery and paint industries (Gupta, 2009). The dye effluents when discharged into watercourse without proper treatment leads to color which impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which produce micro-toxicity to fish and other organisms (Garg et al., 2004). Various treatment processes such as biological treatment, coagulation/flocculation, ozone treatment, chemical oxidation, membrane filtration, ion exchange, photocatalytic degradation and adsorption have been developed to remove these compounds from colored effluents (Shabnam Sheshmani et al., 2014). Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility (Aguayo Villarreal et al., 2013). Hence the present study were carried out by using flocs of Ferric Sulphate, Aluminium Sulphate and Manganese Sulphate as adsorbent to decolourize reactive dye.

2. Materials

2.1. Adsorbent
Ferric sulphate, Aluminium sulphate and Manganese sulphate flocs were used as adsorbents.

2.2. Adsorbate
C.I.Reactive green 19 was used as adsorbate solution with concentration of 50 mg/L.

2.3. Glass ware and chemicals
Coagulants of AR grade and good pyrex quality glass materials were used during the present study. Absorbance reading was made with systronics spectrophotometer.

2.4. Analyses
APPHA standard methods were used in the study.

3. Experimental Procedure
Dye colour solution having concentration of 50 mg/L was used in the study. Agitated non-flow batch sorption studies were conducted during the study. Adsorption studies were conducted using pre-formed flocs of coagulants which was made at its optimum pH and concentration. Equilibrium
studies with different doses of flocs varying from 100 to 1000 mg/L and kinetic studies with varying time intervals from 1 min to 60 min were used in the study. Absorbance readings were noted after 4 hours of sedimentation.

4. Results and Discussion

Optimum coagulant concentration at optimum pH of coagulant is given in Table 1.

**Table 1: Optimum dose of coagulant**

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Optimum pH</th>
<th>Acidic Medium</th>
<th>Basic Medium</th>
<th>Optimum dose, mg/100mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric Sulphate (Fe₂(SO₄)₃)</td>
<td>4</td>
<td>10</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Aluminium Sulphate (Al₂(SO₄)₃·18H₂O)</td>
<td>4</td>
<td>10</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Manganese Sulphate (MnSO₄·4H₂O)</td>
<td>4</td>
<td>10</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>

4.1. Kinetics of colour adsorption

4.1.1. Removal of colour at different contact time

The percentage of reactive green dye colour removal at different contact times at pH: 4 and pH: 10 are shown in Fig.1 and Fig.2.

From Fig.1, 96% of colour removal was observed with Ferric Sulphate flocs, 88% of colour removal with Aluminium sulphate flocs and 16% with Manganese sulphate flocs. The efficiency of Ferric sulphate is higher than Aluminium sulphate and Manganese Sulphate at pH: 4.
Fig. 2 Percentage of reactive green dye colour removal at pH:10 at different contact times
From Fig. 2, 69% of colour removal was observed with Manganese Sulphate flocs, a very low percentage of 8% of colour removal with Aluminium sulphate flocs and 5% with Ferric sulphate flocs. The efficiency of Manganese sulphate is higher than Aluminium sulphate flocs and Ferric Sulphate flocs at pH:10.

4.2. Equilibrium Isothermal studies by preformed flocs
The percentage of colour removal of reactive dye at different doses at pH:4 and PH:10 are given in Fig. 3 and Fig. 4

Fig. 3. Percentage colour removal of C.I. Reactive green 19 at different floc doses (pH:4)
Fig. 4. Percentage colour removal of C.I. Reactive green 19 at different floc doses (pH: 10)
From Fig. 3, 96% of C.I. Reactive green 19 colour removal was observed with Ferric Sulphate flocs, 88% with Aluminium sulphate and 15% with Manganese sulphate. The efficiency of Ferric sulphate is higher than Aluminium sulphate and Manganese sulphate at pH: 4.
From Fig. 4, 68% colour removal was observed with flocs of Manganese sulphate, 8% of colour removal was observed with Aluminium sulphate and 4% of colour removal was observed with Ferric sulphate. The efficiency of Manganese sulphate is higher than Aluminium sulphate and Ferric sulphate at pH: 10.

4.3. Equilibrium study
In order to know the quantity of dye adsorbed per unit mass of adsorbent isotherms namely Langmuir, Freundlich and Temkin are used generally.

3.1. Langmuir Isotherm
The Langmuir is other m (Langmuir, 1916) is represents as:
\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e}
\]
Where \(q_m\) and \(K_L\) represents Langmuir Constants.
Langmuir Isotherm graph for the equilibrium adsorption data of C.I. Reactive green 19 is as given in the Fig. 5.
From Figure 5, it was observed that the data follows the Langmuir isotherm, as the graph is of straight line.

### 4.3.2. The Freundlich isotherm

The Freundlich equation in the form of log is given by

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Where \( K_F \) and \( n \) are Freundlich constants. The Plot between \( \log C_e \) and \( \log q_e \) for C. I. Reactive green 19 is as given in Fig. 6.

![Fig.6 Freundlich Isotherm](image)

The value of correlation coefficient (\( R^2 \)) and maximum sorption concentration of different sorbents are presented in Table 2.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_m ) (mg/g)</td>
<td>( K_L ) (L/mg)</td>
</tr>
<tr>
<td>Ferric Sulphate flocs</td>
<td>166.67</td>
<td>0.4615</td>
</tr>
<tr>
<td>Aluminium Sulphate flocs</td>
<td>125</td>
<td>0.421</td>
</tr>
<tr>
<td>Manganese Sulphate flocs</td>
<td>2.096</td>
<td>0.021</td>
</tr>
</tbody>
</table>

From Table 2, it states that Langmuir isotherm is the best fit as its \( R^2 \) value is nearer to 1.0 than Freundlich isotherm.

### 4.4. Kinetic Study

Lagergren Pseudo-First-Order equation (Lagergren, 1898) was used to find the nature of sorption reaction involved which is given by,

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

Where \( q_e \) is the quantity of color adsorbed (mg/g) at time \( t \), and \( q_t \) is the amount of color sorbed at equilibrium time \( t \) and \( k_1 \) is the rate constant of the pseudo-first-order adsorption process (min\(^{-1}\)).

In order to achieve correlation coefficients, graph between \( \log (q_e - q_t) \) and time was drawn which was presented in the Fig.7.
The equation of pseudo-second-order Kinetics is expressed as:

\[ \frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \]

Where \( h = k_2 q_e^2 \) (mg g\(^{-1}\) min\(^{-1}\)) and \( k_2 \) is reaction constant (g mg\(^{-1}\) min\(^{-1}\)).

The graph of pseudo-second-order kinetics was as shown in Fig.8. The value of correlation coefficient of pseudo-first-order and pseudo-second-order plots are presented in Table 3.
Table 3
The values of correlation co-efficient from Pseudo-first-order and Pseudo – second-order kinetic reactions

<table>
<thead>
<tr>
<th>floc</th>
<th>Pseudo First Order</th>
<th></th>
<th>Pseudo Second order</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K₁(min⁻¹)</td>
<td>qₑ(mg/g)</td>
<td>R²</td>
<td>K₂(gmg⁻¹min⁻¹)</td>
</tr>
<tr>
<td>Ferric Sulphate</td>
<td>0.027</td>
<td>1.3868</td>
<td>0.415</td>
<td>5.8026x10⁻³</td>
</tr>
<tr>
<td>Aluminium Sulphate</td>
<td>0.032</td>
<td>1.3333</td>
<td>0.472</td>
<td>5.902x10⁻³</td>
</tr>
<tr>
<td>Manganese Sulphate</td>
<td>0.064</td>
<td>1.4962</td>
<td>0.674</td>
<td>0.0359</td>
</tr>
</tbody>
</table>

From the Table 3, as R² value of Pseudo-second-order is nearer to 1.0 than Pseudo-first-order which implies that chemisorption is the rate limiting step.

5. CONCLUSIONS
Ferric sulphate, Aluminium sulphate and Manganese sulphate flocs was used as adsorbents in the colour removal of C.I Reactive green 19 dye and adsorption studies were conducted at both pH:4 and pH:10. From the results, it can be concluded that efficiency of ferric sulphate is more at pH:4 and efficiency of Manganese sulphate is more at pH:10. Langmuir isotherm was fitted well to equilibrium data and kinetic data was fitted well to Pseudo-second-order stating formation of monolayer in the sorption process and chemisorption is the rate limiting step.

REFERENCES