Decolourization of Reactive Dye by using Novel Adsorbent

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Abstract: The color of dye aqueous solution which cannot be removed by coagulation was selected to decolourize it through adsorption process by using novel adsorbents namely Flocs of Ferric Sulphate, Aluminium Sulphate and Manganese Sulphate. In order to know efficacy of adsorbents, batch sorption studies and equilibrium studies were conducted. Good color removal was achieved with Ferric sulphate at pH: 4 and Manganese Sulphate at pH: 10, which will be applicable to reduce the industrial dye effluent pollution. Equilibrium data applied to Langmuir Isotherm, was best fitted, stating monolayer formation and kinetic data applied to pseudo second order equation, was well fitted, stating that chemisorption is the rate limiting step.

Keywords: Adsorption, Kinetic Data, Equilibrium Data, Preformed Flocs, Isotherms and Chemisorption.

I. INTRODUCTION

Dyes containing azo-aromatic groups are highly dispersible pollutants. The effluents from various textile, paper industries contributes water toxicity representing an increasing danger for the environment and human beings [7]. Some of the organic dyes have mutagenic or carcinogenic effect on human beings [2]. 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 [6]. Adsorption is an excellent process in removing dye colour from textile dye effluent [5]. Hence experiments was done using preformed flocs of Ferric sulphate, Aluminium sulphate & Manganese sulphate as adsorbents to decolourize reactive dye.

II. MATERIALS

2.1. Adsorbent
Pre-prepared Ferric sulphate, Aluminium sulphate and Manganese sulphate flocs.

2.2. Adsorbate
5mg/L concentration stock solution of C. I. Reactive Blue 5.

2.3. Materials
Chemicals of grade AR and Borosil glassware, /pH meter and Spectrophotometer of Systronics.

III. METHODOLOGY

Reactive dye solution having concentration of 50 mg/L was subjected to batch sorption studies with preformed flocs of coagulant which is prepared at its optimum dose and optimum pH. Equilibrium studies were conducted with different doses of flocs. Kinetic studies were conducted at varying intervals of 1 min, 3 min, 5 min, 7 min, 9 min, 12 min, 15 min, 30 min, 45 min and 60 min. Absorbance readings were taken after 4 hours of sedimentation.

4. Results followed by Discussion
Optimum dose concentration of coagulant is mentioned in the Table 1.

Table 1 Coagulants optimum dose

| Name of coagulant          | Optimum pH | Optimum dose, mg/100mL |
|----------------------------|------------|------------------------|
| Ferric Sulphate (Fe₂S₃O₈₃) | 4          | 1000                   |
| Aluminium Sulphate (Al₂(SO₄)₃.18H₂O) | 4          | 1000                   |
| Manganese Sulphate (MnSO₄.4H₂O) | 4          | 1000                   |

4.1. Adsorption Kinetics

4.1.1. Removal of colour at different contact time
The percentage of colour removal of reactive dye at different contact times at pH :: 4 and pH :: 10 are given in Figure 1 and Figure 2.

From Fig.1, it was observed that colour removal of 89% was observed with an adsorbent of Ferric Sulphate, 80% of colour removal was obtained with Aluminium sulphate and 15% colour removal was obtained with Manganese sulphate. The efficiency of Ferric Sulphate is higher than Aluminium Sulphate and Manganese Sulphate at pH :: 4.

Fig.1 Percentage of colour removal at pH: 4 at different contact times

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Fig. 2 Percentage of colour removal at pH:10 at different intervals of contact time

From Fig.2, 73% of colour removal was obtained with an adsorbent dose of Manganese Sulphate flocs, 10% colour removal was obtained with flocs of Aluminium sulphate and 7% colour removal was obtained with Ferric sulphate. The efficiency of Manganese Sulphate is higher than Aluminium Sulphate and Manganese Sulphate at pH :: 10.

4.2. Equilibrium studies

The colour removal percentage of reactive dye at various floc doses at pH :: 4 and pH :: 10 are given in Figure 3 and Figure 4.

Fig.3. Percentage colour removal of C.I. Reactive Blue 5 at different adsorbent doses at pH:4

Fig. 4 C.I. Reactive Blue 5 dye color removal at various floc doses at pH: 10

Figure 3 indicates that 88% color removal was obtained with an adsorbent of Ferric Sulphate, 80% of colour removal was obtained with Aluminium sulphate and 14% colour removal was obtained with Manganese sulphate. The efficiency of Ferric Sulphate is higher than Aluminium Sulphate and Manganese Sulphate at pH :: 4.

From Figure 4, 73% colour removal was obtained with an adsorbent of Manganese Sulphate, 9% colour removal was obtained with Aluminium sulphate flocs and 7% color removal was obtained with Ferric sulphate. The efficiency of Manganese Sulphate is higher than Aluminium Sulphate and Manganese Sulphate at pH :: 10.

4.3. Equilibrium study

4.3.1. Langmuir Isotherm

The Langmuir isotherm [4], was given by

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e}
\]

Where, \(q_e\), \(q_m\) are Langmuir Constants. Langmuir Isotherm graph for the adsorption data of C.I. Reactive Blue5 is given in the Figure 5.

Fig. 5 Langmuir Isotherm

Figure 5 states that data of the isotherm follows the Isotherm of Langmuir, as graph obtained is straight line.

4.3.2. The Freundlich isotherm

The Freundlich isotherm is given by

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

Where, \(n\), \(K_F\) are Freundlich constants. The graph of \(\log C_e\) Vs \(\log q_e\) for C.I. Reactive Blue 5 is as given in Fig. 6.

Fig.6 Freundlich Isotherm

The maximum adsorption concentration along with \(R^2\) of different flocs are given in Table 2.
From Table 2, The value of Langmuir correlation coefficient is equal to 1.0 when compared to Freundlich isotherm, which states that data was fitted well to Langmuir isotherm.

**4.4. Kinetic Study**

Adsorption data was applied to Lagergren Pseudo first order equation

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

Where \( q_t \) is the amount of color adsorbed (mg/g) on sorbent at time \( t \) and \( q_e \) is the amount of color adsorbed on sorbent at an equilibrium time \( t \) and \( k_1 \) is pseudo first order rate constant adsorption process (min\(^{-1}\)). The plot between \( \log(q_e - q_t) \) and time was presented in the Fig.7.

![Fig. 7 Pseudo first order kinetics of dye sorbent interaction](image)

**Table 2. Langmuir and Freundlich Isotherm Constants**

| Adsorbent                | Langmuir isotherm | Freundlich isotherm |
|--------------------------|-------------------|---------------------|
|                          | \( q_m \) (mg/g)  | \( K_L \) (L/mg)    | \( R^2 \) | \( K_F \) (mg of color/g of flocs) | \( n \) | \( R^2 \) |
| Ferric Sulphate flocs    | 500               | 0.01234             | 0.951    | 25.9786                      | 1.497   | 0.918   |
| Aluminium Sulphate flocs | 250               | 0.0417              | 0.968    | 21.2930                      | 2.155   | 0.932   |
| Manganese Sulphate flocs | 1.3004            | 0.0213              | 0.943    | 1.122018x10\(^{-3}\)        | 0.0524  | 0.905   |

The equation of pseudo-second - order Kinetics is expressed as:

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

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 between \( t/q_t \) and \( t \) was given in Figure 8.

The value of correlation co-efficient of pseudo first order and pseudo second order plots are presented in Table 3.

![Fig. 8 Pseudo second order kinetics of dye adsorbent interaction](image)

**Table 3 The correlation co-efficient values of Pseudo first order and Pseudo second order kinetic reactions**

| floc                | Pseudo first order | Pseudo second order |
|---------------------|--------------------|---------------------|
|                     | \( K_1 \) | \( q_e \) | \( R^2 \) | \( K_2 \) | \( q_e \) | \( R^2 \) | \( h \) |
| Ferric Sulphate     | 0.0276  | 1.2589  | 0.570     | 5.831x10\(^{-3}\) | 45.4545 | 0.991    | 12.0482 |
| Aluminium Sulphate  | 0.0299  | 1.0046  | 0.822     | 6.686x10\(^{-3}\) | 40      | 0.991    | 10.989  |
| Manganese Sulphate  | 0.0645  | 1.652   | 0.658     | 0.0375           | 7.192   | 0.992    | 1.9417  |

From Table 3, the correlation coefficient value of Pseudo second order is nearer to 1.0 when compared to Pseudo first order indicating that chemisorption is the rate-limiting step.

**IV. CONCLUSIONS**

Aqueous dye solution of C.I. Reactive Blue 5 which was not able to decolourize using coagulation was subjected to adsorption process using novel adsorbents of pre-formed flocs of Aluminium sulphate, Ferric sulphate and Manganese sulphate at pH :: 4 and pH :: 10. From the experimental results, It can be concluded that excellent colour removal was achieved with pre-formed flocs. The efficiency in colour removal by Ferric sulphate flocs is greater than Aluminium Sulphate and Manganese Sulphate at pH :: 4 and the efficiency of colour removal by pre-formed flocs of
Manganese Sulphate is greater than Aluminium Sulphate and Ferric Sulphate at pH: 10. Sorption equilibrium data of the experiments conducted was suited well to Langmuir Isotherm stating that monolayer formation is involved in the adsorption process. Experiment results of Adsorption kinetic values are suited well to Pseudo second order equation stating that Chemisorption was the rate limiting step involved in the adsorption process.

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