

Removal of Dye from Textile Industry Dyeing Effluent using Adsorption and Coagulation Methods

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Abstract: This work deals with investigation of effectiveness of adsorption and coagulation on removal of color of simulated acid dye solutions. Dye stuff belonging to acid group is employed and batch tests were conducted with three coagulants (Calcium hydroxide, Ferric sulphate and Aluminium chloride) to access feasibility and also to study the optimum values for coagulant dosage, RPM, pH and time. The study clearly indicates that dye effluent responds effectively to Ferric sulphate. The removal is probably due to physicochemical mechanism of coagulation and flocculation and/or chelating complexation type reactions and color removal at lower pH ranges may be either due to physicochemical coagulation or chelating complex formation reactions. The study clearly indicates that there is significant reduction in the chemical dosage requirements and in some cases a further increase in color removal. From the above studies it may be concluded that some of the Acid dye stuffs are suitable for their color removal using various coagulants. In this study we have used commercial carbon as well as activated carbon prepared from sawdust (agriculture waste), and performed the same experiment by varying the variables (coagulant dosage, RPM, pH and time), the studies shows that in the process of coagulation the percentage color removal is more than when compared to that of adsorption.

Keywords: Adsorption, Coagulation, Dying effluent, Dosage, pH, Time, RPM

I. INTRODUCTION

More than 8000 chemically different typed of dyes are being manufactured and the major consumers are textile, tannery, paint, paper and pulp etc due to this type of dye effluent environment is getting polluted and is directly impacting on the receiving waters and soil. So we have to remove the color from dye effluent probably chemical and physical treatments. It is evident that this issues cannot be solved in a hit and miss fashion [1]. A systematic approach to investigate the response of acid dyes to various applications, classes and chemicals families though treatment with aluminium and probe into mechanistic aspect of color removal. Suspended and dissolved particles in water influence color. Color is essentially psychological sensation produced when the light of certain wavelengths reaches the eyes. This wavelength is in the range of 10^2 - 10^6 nm (ultraviolet rays, visible light, and infrared) [2].

Revised Manuscript Received on November 15, 2019

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Table- I: Main type of dyes, their main use and associated chemicals

| Dye | Use | Associated Process Chemicals |
|----------|-------------------|---|
| Acid | Wool, nylon | Sulphuric acid, acetic acid, sodium sulphate, surfactant |
| Azoic | Cotton | Metal salts, formaldehyde, sodium hydroxide, sodium nitrate |
| Basic | Acrylic | Acetic acid, softening agent |
| Direct | Cotton synthetics | Sodium salt, fixing agent metal salts |
| Disperse | Polyester | Carrier, sodium hydroxide sodium hydro sulphide |
| Mordant | Wool | Chromium and other metal salts |
| Reactive | Cotton, wool | Sodium chloride ethylene diamine |
| Sulphur | Cotton synthetics | Sodium sulphide and other salts, acetic acid |
| Vat | Cotton | Sodium hydroxide, sodium hydro sulphite and other salts |

Table- II: Dyes and their uses

| Type of dye | Used in |
|-------------|-------------------|
| Acid | Wood, nylon |
| Azoic | Cotton |
| Basic | Acrylic |
| Direct | Cotton synthetics |
| Disperse | Polyesters |
| Mordant | Wool |
| Reactive | Wool, cotton |
| Sulphur | Cotton synthesis |
| Vat | Cotton |

More than 8000 chemically different types of dyes being manufactured and biggest consumer are textile, tannery, paper, pulp, paint and electro plating industries [3].

As far as color pollution is concern the current annual world production of dyestuffs is about 800,000 tons of active substances. Some part of these dyes used is lost in residual liquors (spent dye bat) though incomplete exhaustion and washing process and may way into aquatic environment or may be disposed on land [4].

The gravity of the color pollution problems caused by dye colors can be well appreciated and realized from the fact that the whole of a small town engaged in traditional saree printing. Infect to quote the press reports, the Indian parliament (Loksabha) deputed a parliament

team to probe and suggest remedial measures [5]. Similarly at places like Jodhpur, Pali and Balotra in Rajasthan, Dharoji in Gujarat and North Arcot in Tamilnadu, public observed bandh and hartal to draw the attention of the government to the pollution problems caused by the indiscriminate and careless disposal of colored effluent [6].

A. Impact on Soil

Safe disposal of effluent from communities and industries are practiced extensively in many countries throughout of the world. Effluents from industries contain significant quantities of waste and residual chemicals and their disposal lead to pollution of air, water and soil and hence required to be treated [7]. The drastic decrease in shear strength, plasticity and binding ability of the soils could be one of the consequences of contamination due to sedimentation of organic or inorganic and metallic compounds. Lukes et al., (1972) give a detailed account of the foundation failures of three industrial buildings as a result of chemical reactions between the subsoil and accidental chemical spillage, which were acidic into of the cases in the other. They attributed the large settlements recorded in each case to changes in soil properties as result of the dissolution of either the limestone in glacial till or the high silica sand subsoil's in the chemical contaminants [8].

B. Treatment of Dye Effluent

The composition of wastes varies widely even on the same site, as different process are usually conducted at the same works. Even a works that performs only dyeing produces wastes of differing strengths. Rinse- waters are relatively clean, whereas the effluent from scouring has high BOD and suspended solid concentrations. The BOD of wastes varies between 200 and 300 mg/l, with a COD between 500-5000mg/l suspended solids 50-500 mg/l and a pH of 4-12. Many of the chemicals listed in table I may be present at varying concentrations. Individually the dyes and the carries and other chemicals are usually measured in mg/l or g/l.

C. Types of Adsorption

Physical adsorption: The physical force of attraction or Vander wall forces of attraction exists between adsorb ate and adsorbent is called physical adsorption. It is a weak adsorption. It is reversible. Physical adsorption is multi –

layered adsorption .With increasing pressure physical adsorption increases. With increasing temperature physical adsorption decreases [9].

Chemical adsorption: Chemical forces of attraction exist between adsorbate and adsorbent is called chemical

adsorption. It is strong adsorption. It is a uni-layered. With increase in pressure, chemical adsorption decreases, with increase in temperature chemical adsorption increases.

Adsorbents: Depending on the requirements we have to select the appropriate adsorbent. For this let us see the various types of absorbent which are used industrially: Activated carbons, Bituminous coal, Fuller earth, Activated alumina, Activated clays, Bone char, Decolorizing carbons, Molecular sieves, Synthetic polymers, Silica gel, Saw dust, Fly ash [10].

Activated carbons are produced by two methods,

(a) Thermal decomposition of carbonaceous materials and subsequent controlled oxidation.

(b) Decomposition and activation by thermal treatment of cellulosic materials with H_3PO_4 or $ZnCl$.

By this activation, porosity is increased and the surface characteristics are altered which favor absorbability. Activated carbons are less polar than other adsorbents. So the absorbability of polar compounds like water on activated carbons is less. These are used from 4x6 mesh (coarse) to 12x20. Mesh for gas phase application the hardness of carbon is an important parameter particularly in case of regeneration, in which case thermal stresses in addition to the packing and fluid stresses [11].

D. Coagulation

In dye effluent treatment suspended particles to be removed is colloids and in suspended form. These colloids are destabilized by coagulation techniques [12].

Coagulation means agglomeration of suspended particles by adding a chemical substance. It involves the reduction of surface charges & formation of complex hydrous oxide. Colloids that don't agglomerate naturally are called stable. Surface phenomena predominate over mass phenomena. The most important surface phenomena are accumulation of electrically charged particle surface[13].

Coagulation involves the mechanisms of ionic layer compression, charge neutralization, sweep coagulation (or) entrapment and bridging [14].

E. Mechanisms of Coagulation

Ionic Layer Compression: Consider a negatively charge colloid, the opposite charges called counter ions will surround it [15]. The opposite charges will in turn be surrounded by charges opposite to them forming an electric double layer. When concentration of ions is small the thickness of double layer is larger. When concentration is increased colloid charge will be neutralized causing double layer shrink [16-20].

Table- III: Properties of coagulants

| Name | Formulae | M.Wt | Sp. gravity | Melting point | Boiling point | Solubility in 100 parts | |
|--------------------|-----------------------------|--------|-------------|---------------|---------------|-------------------------|----------------------|
| | | | | | | Cold H ₂ O | Hot H ₂ O |
| Alum | $Al_2(SO_4)_3 \cdot 16H_2O$ | 916.5 | 1.675 | 61 | --- | 106.4 | 121.7 |
| Iron Sulphate | $FeSO_4 \cdot 7H_2O$ | 278.02 | 1.899 | 64 | 300 | 32.8 | 149 |
| Ferric Chloride | $FeCl_3$ | 162.22 | 2.804 | 282 | 315 | 74.4 | 535.8 |
| Barium Chloride | $BaCl_2 \cdot 2H_2O$ | 244.31 | 3.907 | 100 | ---- | 39.3 | 76.8 |
| Aluminium Chloride | $AlCl_3$ | 133.34 | 2.44 | 194 | 182.7 | 68.87 | s.d |
| Aluminium Oxide | Al_2O_3 | 101.94 | 3.99 | 1999 to 2032 | ---- | ---- | ---- |

II. MATERIALS AND METHODS

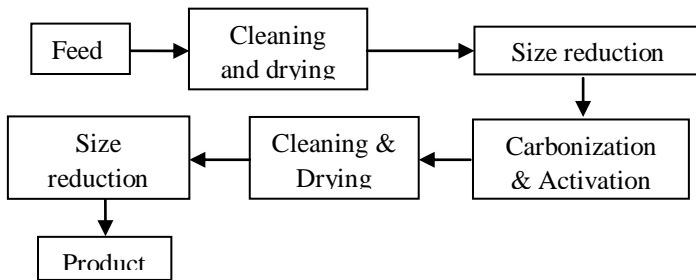
Instruments used for present work were Colorimeter and pH system, horizontal shaker (100 rpm). List of dyes along with some of their characteristic and chemical properties chosen for the present study are given previously. All the chemicals used for chemical treatment are of analytical grade and their characteristics as presented previously. Acetic acid and Sodium Hydroxide were used for adjusting the pH values of dye test solution to assess the effect of color removal.

A. Experimental Procedure

Dye effluent treatment by coagulation; To determine the optimal concentrations of dye and coagulant, optimum pH, optimum speed and optimum time for maximum removal of dye.

Apparatus: Photo electric colorimeter, Reagent bottles, Horizontal shaker, pH meter, Conical flasks, Measuring jar
Coagulants: Alum, Ferrous sulphate, Barium chloride, Calcium hydroxide, Aluminium hydroxide, Aluminium chloride.

Preparation of activated carbon from agricultural waste:



III. RESULTS AND DISCUSSION

A. Choice of Coagulant

1. Response of selected effluents to chemical treatment with Calcium hydroxide, $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, Al_2Cl_3 were assessed using batch test procedure. The color removal with different coagulants is tabulated.
2. It may be observed that effluent is amenable to chemical treatment with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. These variations in color removal made generalization in terms of chemical class difficult. And the results are tabulated below.

Table- IV: Selection of coagulant

| Coagulant | % Transmissivity | | |
|--------------------|------------------|------------|------------|
| | Effluent-1 | Effluent-2 | Effluent-3 |
| Alum | 24 | 77 | 16 |
| Ferrous sulphate | 25 | 88 | 72 |
| Aluminium oxide | 10 | 66 | 10 |
| Barium Chloride | 19 | 67 | 78 |
| Aluminium Chloride | 14 | 91 | 40 |
| Calcium hydroxide | 15 | 56 | 80 |

Experimental results for each dye are presented in the following tables and a discussion of results is included along with the presentation. However, before presentation of results and discussion, it is appropriate to be acquainted with behavioural, aspects or organic direct dyes and metallic salts in the aqueous phase to serve as background for

understanding the response of textile direct dyes to chemical treatment and associated metal-dye interaction. Most of the organic direct dyes in aqueous phase exhibit a tendency to associate and form dimmers (double molecules) or polymers (higher molecular aggregates). This self-aggregation of direct dyes in aqueous solution is universal reversible process being promoted by an increase dye concentration, electrolyte concentration, higher pH and a decrease in temperature. Such aggregate are micelles may be ionize and forms the positive and negative charges. The negative charge is localized most often on an ionized sulfonate group or oxide group. The colloidal property of direct dyes in aqueous solution and their role has been recognized. The organic direct dyes in aqueous phase exhibit marked concentration effects and this has been related to deviation from the Beer's law at higher concentration range and correlated to the formation of dimer and polymer colloidal aggregates in water. It is also established that the dye anion aggregate usually contain absorbed gentians or undissociated grouping. Various mechanisms have been put forward to explain aggregation of in aqueous phase and the nature of forces that overcome the mutual coulombic repulsion forces of similar ions to favor aggregation is not clear. It is very likely that Van der waal forces, hydrogen bonding, and interaction of π -electrons or coupling of electronic oscillators and hydrophobic interactions may be responsible. In present study, deviation from the Beer's Law was observed for all the dyes. Several factors such as dye concentration or dissociation and at high temperatures, the effects of dye concentration are reversible. Effect of various parameters on % Color Removal: Coagulant: FeSO_4

Table- V: Effect of RPM on % CR

| RPM | % T | % CR |
|------------|-----------|--------------|
| 30 | 52 | 91.05 |
| 60 | 64 | 95.52 |
| 90 | 74 | 97.15 |
| 120 | 83 | 98.37 |
| 150 | 91 | 99.18 |
| 180 | 87 | 98.67 |

It is observed that maximum color removal, 99.18 % occurs at optimum RPM of 150.

Table- VI: Effect of time on % CR

| Time, min | % T | % CR |
|-----------|-----------|--------------|
| 30 | 91 | 99.18 |
| 60 | 93 | 99.38 |
| 90 | 94 | 99.59 |
| 120 | 91 | 99.18 |
| 150 | 91 | 99.18 |
| 180 | 93 | 99.38 |

It is observed that maximum color removal, 99.59 % occurs at an optimum time of 90 min.

Table- VII: Effect of dosage on % CR

| Dosage, gm | % T | % CR |
|------------|-----------|--------------|
| 0.5 | 94 | 99.59 |
| 1.0 | 89 | 99.18 |
| 1.5 | 95 | 99.62 |
| 2.0 | 89 | 99.18 |
| 2.5 | 92 | 99.28 |
| 3.0 | 90 | 99.08 |

It is observed that maximum color removal, 99.62 % occurs at an optimum dosage of 1.5 gm.

Table- VIII: Effect of pH on % CR

| pH | % T | % CR |
|------------|-----------|--------------|
| 2.2 | 95 | 99.62 |
| 4.13 | 95 | 99.62 |
| 6.4 | 84 | 98.67 |
| 8.9 | 96 | 99.72 |
| 10.01 | 89 | 98.88 |
| 11.89 | 78 | 97.85 |

It is observed that maximum color removal, 99.72 % occurs at an optimum pH of 8.9.

Table- IX: Effect of RPM on % CR with activated carbon

| RPM | % T | % CR |
|-----------|-----------|--------------|
| 30 | 12 | 28.86 |
| 60 | 10 | 18.69 |
| 90 | 13 | 30.89 |
| 120 | 12 | 28.86 |
| 150 | 10 | 18.69 |
| 180 | 10 | 16.69 |

It is observed that maximum color removal, 30.89 % occurs at an optimum RPM of 90.

Table- X: Effect of time on % CR using activated carbon

| Time | % T | % CR |
|------------|-----------|--------------|
| 30 | 10 | 18.69 |
| 60 | 20 | 51.22 |
| 90 | 20 | 51.22 |
| 120 | 22 | 59.34 |
| 150 | 18 | 47.15 |
| 180 | 20 | 51.22 |

It is observed that maximum color removal, 59.34 % occurs at an optimum time of 120 min.

Table- XI: Effect of dosage on % CR using activated carbon

| Dosage, gm | % T | % CR |
|------------|-----------|--------------|
| 0.5 | 22 | 59.34 |
| 1.0 | 11 | 22.76 |
| 1.5 | 13 | 30.89 |
| 2.0 | 25 | 69.51 |
| 2.5 | 24 | 67.47 |

| | | |
|-----|----|-------|
| 3.0 | 23 | 63.41 |
|-----|----|-------|

It is observed that maximum color removal, 69.51 % occurs at a dosage of 2.0 gm.

Table- XII: Effect of pH on % CR using activated carbon

| pH | % T | % CR |
|-------------|-----------|--------------|
| 2.55 | 35 | 87.47 |
| 5.57 | 40 | 83.73 |
| 7.46 | 25 | 69.51 |
| 10.83 | 36 | 81.70 |
| 12.04 | 38 | 82.92 |
| 13.89 | 24 | 67.47 |

It is observed that maximum color removal, 87.47 % occurs at a pH of 2.55.

Table- XIII: Effect of RPM on % CR using activated carbon prepared from saw dust

| RPM | % T | % CR |
|-----------|-----------|--------------|
| 30 | 10 | 18.69 |
| 60 | 15 | 39.02 |
| 90 | 16 | 45.12 |
| 120 | 15 | 39.02 |
| 150 | 12 | 26.82 |
| 180 | 13 | 30.89 |

It is observed that maximum color removal, 45.92 % occurs at an optimum RPM of 90.

Table- XIV: Effect of time on % CR using activated carbon prepared from saw dust

| Time | % T | % CR |
|------------|-----------|--------------|
| 30 | 16 | 45.12 |
| 60 | 13 | 30.89 |
| 90 | 15 | 39.02 |
| 120 | 18 | 49.59 |
| 150 | 15 | 39.02 |
| 180 | 16 | 45.12 |

It is observed that maximum color removal, 49.59 % occurs at an optimum time of 120 min.

Table- XV: Effect of dosage on % CR using activated carbon prepared from saw dust

| Dosage, gm | % T | % CR |
|------------|-----------|--------------|
| 0.5 | 18 | 49.59 |
| 1.0 | 19 | 51.21 |
| 1.5 | 17 | 45.36 |
| 2.0 | 19 | 51.21 |
| 2.5 | 22 | 59.34 |
| 3.0 | 21 | 58.28 |

It is observed that maximum color removal, 59.34 % occurs at an optimum dosage of 2.5 gm.

Table- XVI: Effect of pH on % CR using activated carbon prepared from saw dust

| pH | % T | % CR |
|--------------|-----------|--------------|
| 2.56 | 15 | 39.02 |
| 4.17 | 19 | 51.21 |
| 6.32 | 17 | 45.12 |
| 8.23 | 18 | 47.15 |
| 10.45 | 32 | 78.04 |
| 11.99 | 24 | 69.56 |

It is observed that maximum color removal, 78.04 % occurs at an optimum pH of 10.45.

IV. CONCLUSION

It is observed that maximum color removal, 99.72 % is obtained for green color dye effluent at optimum RPM of 150, time of 90 minutes, dosage of 1.5 gm and pH of 8.9 using coagulation technique.

It is observed that maximum color removal, 87.47 % is obtained for green color dye effluent at optimum RPM of 90, time of 120 minutes, dosage of 2 gm and pH of 2.55 using adsorption technique.

It is observed that maximum color removal, 787.04 % is obtained for green color dye effluent at optimum RPM of 90, time of 120 minutes, dosage of 2.5 gm and pH of 10.45 using adsorption technique with activated carbon prepared from agricultural waste (saw dust).

Some textile dyes belonging to various application classes and chemical family responded favorable in terms of color removal by chemical treatment with chemical coagulants like alum, ferrous sulphate, calcium hydroxide and aluminum chloride. Removal of color was interpreted to be due to specific chemical interactions between dye ligands and aqua metallic ions resulting information of insoluble metal-dye complexes like adsorption and interaction between metal hydroxide species leading to aggregation. The color removal probably is due to physiochemical mechanism of coagulation and flocculation.

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