

RESEARCH ARTICLE

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## Removal of Color from Different Dye Wastewater by Using Ferric Oxide as an Adsorbent

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### ABSTRACT

Dyes are colored organic compounds that are used to impart colour to various substrates including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. The discharges of industrial wastewater containing dyes cause serious environmental problems. There are many colour removal techniques amongst which adsorption process is popular. Many removal techniques have been applied. But, adsorption process is inexpensive and readily available to control the various pollutants from the water and wastewater. The practical performance evaluation in batch reactor is carried out because of its feasibility and simplicity in action and also involving less economic aspects.

Present work is carried out on colarane blue BGFS Anthraquinone dye. Powdered  $\text{Fe}_2\text{O}_3$  has been used for dye removal practical. It was observed that maximum dye removal efficiency at pH 2 with  $\text{Fe}_2\text{O}_3$  dosage of 0.3 gm and initial concentration is 125 ppm. Practicals were also carried out on actual wastewater. The work is right now done with the synthetic dye wastewater and will be focused with different parameters. The percentage removal efficiency by powdered  $\text{Fe}_2\text{O}_3$ , the dye waste water under experiment will be calculated. Kinetic study and adsorption study for dye wastewater under consideration.

### Keywords:

Dye, dye waste water, adsorption, Experimental work, kinetic study and adsorption study

### I. INTRODUCTION

Wastewater is liquid waste discharged by domestic residences, commercial properties, industry, agriculture, which often contains some contaminants that result from the mixing of wastewater from different sources [24, 35].

Based on its origin wastewater can be classed as sanitary, commercial, industrial, agricultural or surface runoff. Term wastewater need to be separated from the term sewage, sewage is subset of wastewater that is contaminated with feces or urine though many people use term sewage referring to any waste water [24, 35].

The sources of industrial wastewater are like cement industries, pharmaceutical industries, food industries, textile industries, pulp paper industries, rubber industries, color photography Leather industries, cosmetics industries, plastic industries, organic compost and other industries [9, 35].

The mentioned sources Industrialization of the textile industry and use of a large variety of chemical treatments and dyes has resulted in a public health threat created by pollution. 17 -20% of industrial freshwater pollution is caused by textile dyeing and treatment. Estimations state that 10-15% of total dyestuffs (equivalent to 280,000 tons of dyestuffs) used during the manufacturing of textile products is

released into the environment worldwide annually [10, 36].

The main release of pollution during manufacturing occurs during the dyeing and finishing processes and is released by the manufacturer into their local waterways. The wastewater produced is not always biodegradable and often poses severe environmental and health hazards to the community they operate within [18, 35, 36].

Among various industries, the textile industry ranks first in the usage of dyes for coloration of the fibers. The textile sector alone consumes about 60% of total dye production for coloration of various fabrics and out of it, it is estimated that around 10–15% of dyes are wasted into the environment upon completion of their use in the dyeing unit which generates a strongly coloured wastewater, typically with a concentration in the range of 10–200 ppm or mg/L [7,8].

Colour in the effluent is one of the most noticeable indicators of water pollution and the discharge of highly coloured synthetic dye effluents is aesthetically very displeasing and can damages the receiving water body by hindering the penetration of light. Moreover dyes are stable, recalcitrant, colorant, and even potentially carcinogenic and toxic [9,10], their release into the environment creates serious

environmental, aesthetical and health problems. Thus, industrial dye-laden effluents are an increasingly major concern and need to be effectively treated before being discharged into the environment in order to prevent these potential hazards [3, 4, 32, 33].

It has been noted Synthetic dyes are extensively as used it has many application in various branches of the textile industry, paper printing, and pharmaceutical. The discharges of industrial wastewater containing dyes cause serious environmental-problems because of its toxicity and possible accumulation in the environment. Synthetic dyes are a group of most dangerous pollutants in water. The presence of even very low concentrations of dyes in water reduces light penetration through the water surface, precluding photosynthesis of the aqueous flora. Many of these dyes are carcinogenic, mutagenic and teratogenic and also toxic to human beings, microorganisms, and fish species. Hence, their removal from aquatic wastewater becomes environmentally important [20, 35].

There are many removal techniques such as chemical oxidation, precipitation, filtration, aerobic and anaerobic microbial degradation, coagulation, membrane separation, electrochemical treatment, flotation, hydrogen peroxide catalysis, and reverse osmosis, ozonation and biological techniques can be employed to remove various pollutant form the textile industry wastewater [6, 8, 9, 13,24,35].

Among the treatment methods, the adsorption process provides an attractive alternative to the above processes because of inexpensive and readily available to control the various pollutants from the water and wastewater. It is therefore necessary to treat textile effluents prior to their discharge into the receiving water. So, that the hazards to human health can be minimized [19, 35, 36].

There are so many techniques to remove colour from dye wastewater but these conventional treatment techniques are rather expensive. But adsorption process has been found to be more effective, efficient and economic process to remove dyes, pigments, and other colorants and also to control the bio-chemical oxygen demand [6, 8, 17, 27, 29].

## II. MATERIAL AND METHOD

### 2.1 Synthetic dye wastewater preparation

Anthraquinone blue dye was obtained from Colourtex, Surat (India) and was used as received without further purification. The available details of these dye is listed in Table 1. Double distilled water was used to prepare all the solutions. The stock solution was prepared by dissolving 1 g of the dye in 1 L of double distilled water to obtain working solutions of varying concentrations for further experiments.

TABLE 1

Dye detail	
Title	Dye 1
Commercial name of dye	Coralene blue BGFS
Chemical name of dye	Mix. Of 1,5-diamino-4,8-dihydroxy(p-hydroxy-phenyl)anthraquinone & 1,5-diamino-4,8-dihydroxy(p-methoxy-phenyl)anthraquinone
Chemical formula	$C_{20}H_{14}N_2O_5$ & $C_{21}H_{16}N_2O_5$
Class	Anthraquinone
C.I number	C.I disperse blue 73
Molecular weight	362 & 376

### 2.2 Adsorbent and Chemicals

Clays can be modified to improve their sorption ability. One of these modification methods is coated with magnetic particles. Use of the magnetic particle in the Nano scale have attracted by many authors. The extremely fine size of Nano-particles yields favorable characteristics. With a reduction in size, more atoms are located on the surface of a particle results to a remarkable increase in surface area of Nano powders. This imparts a considerable change in surface energies and surface morphologies. All these factors are altering the basic properties and the chemical reactivity of Nano-materials. Powdered  $Fe_2O_3$  (Ferric oxide), a brown powder, were recently used in several applications like adsorption, magnetic storage media, solar energy transformation, electronics, Ferro fluids and catalysis. It is used as an effective adsorbent in the wastewater treatment. The technique was found to be very useful and cost effective for better removal of dye. These particles showed the highest adsorption capacity of removal as compare to other adsorbents [3, 4, 7, 9, 12, 13, 15].

The pH was adjusted by using 0.1 N  $H_2SO_4$  and NaOH.

### 2.3 Batch Adsorption Experiments

The adsorption experiments were carried out as batch tests in magnetic stirrer. In a batch test, 100 mL dye solution of desired concentration was prepared in 250 mL glass flask by suitable dilution of the stock solution and its desired pH was adjusted. Then known amount of  $Fe_2O_3$  powder was added and the resulting suspension was kept under constant stirring for predefined time. After stirring, the suspension was centrifuged and the supernatant was analyzed for the dye removal capacity.

### 2.4 Analysis

Suspension was centrifuged at 3500 rpm in centrifuger (Centrifig, Model 228, Fisher Scientific). Samples of solutions before and after treatment were analyzed for the dyes using a UV 1100-Spectrophotometer (vortex) at their maximum

absorption wavelengths (Table 2). The dye concentrations were calculated from the standard calibration curve obtained from standard dye solutions. The pH of the liquid samples was measured using a pH meter (Sense Ion 378, Hack).

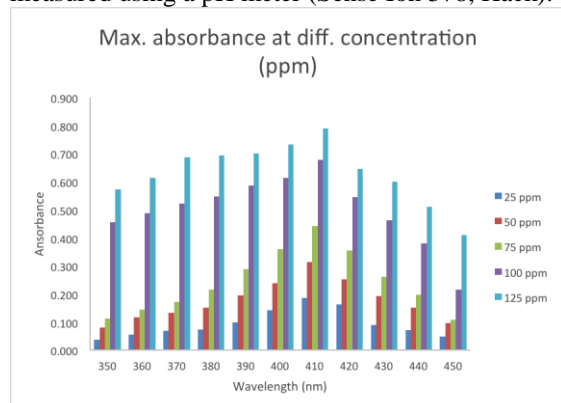


Fig 1: Peak wavelength

### III. RESULTS AND DISCUSSION

#### 3.1 Effect of pH

pH is an important parameter that affects adsorption of dye molecules. The effect of the initial pH of the solution on the anthraquinone blue adsorption onto adsorbents was assessed at different values, ranging from 2 to 12, with a stirring time of 65 min. The initial dye concentrations and dosage of each adsorbent were kept constant at 125 mg/L and 0.3 g per 100 mL dye solution, respectively, for all batch tests in this experiment. Fig. 2 presents the results of the effect of the solution pH on the anthraquinone blue dye removal efficiencies for  $\text{Fe}_2\text{O}_3$  powder. As shown in Fig. 2, removal of dye decreased from 88 to 37% when the pH was increased from 2 to 9. Since the maximum removal of anthraquinone blue dye is achieved at a pH of 2, acidic condition is favorable for  $\text{Fe}_2\text{O}_3$  powder.

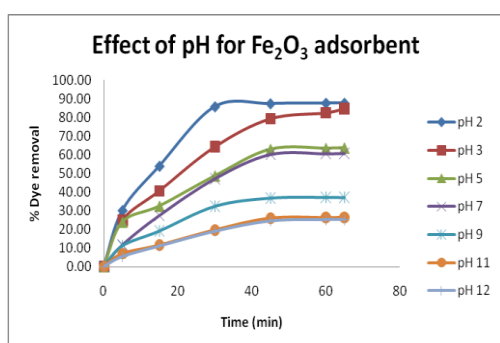


Fig 2: Effect of Different pH

#### 3.2 Effect of Adsorbent Dosage

The effect of adsorbent quantity on removal of anthraquinone blue was investigated in batch experiments by adding various amount of adsorbent in the range of 0.2–0.35 g powder into the flask containing 100 mL of dye solution. The initial dye

concentrations and the pH of the solutions were fixed at 125 mg/L and 2, respectively, for all batch experiments. The suspension was then stirred for 65 min, after which time the solution was coagulated and settled and the supernatant was analyzed for the remaining dye. Results are shown in Fig. 3. As earlier indicated, 94% of anthraquinone blue was removed at the initial dosage of 0.3 g, respectively. After that there is no significance change in % dye removal by increasing in  $\text{Fe}_2\text{O}_3$  dosage to 0.35 g. This observation can be explained by that further increasing the adsorbent dose did not affect the removal of dye. Hence, the optimum dosage of  $\text{Fe}_2\text{O}_3$  powder for removing anthraquinone blue dye was found to be 0.3 g.

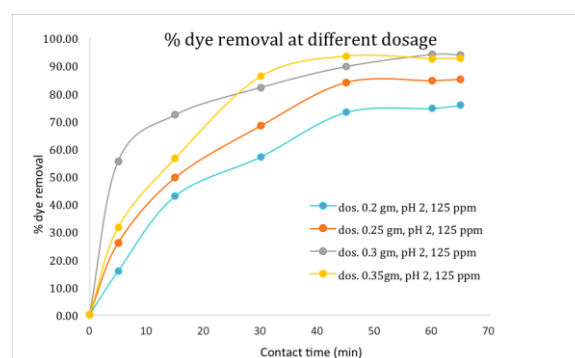


Fig 3: Effect of Different Adsorbent dosage

#### 3.3 Effect of Dye concentration

The initial dye concentration is another important variable that can affect the adsorption process. The effect of initial concentration of anthraquinone blue dye between 25 and 125 mg/L was studied on their adsorption onto  $\text{Fe}_2\text{O}_3$  powder under previously determined optimum conditions. The results, in terms of removal efficiency versus initial concentration of dye, are indicated in Fig. 7. According to Fig. 4, dye removal slightly decreased from around 96% at a concentration of 25 mg/L to 94% when the concentration was increased to 125 mg/L. Overall, we found that the prepared  $\text{Fe}_2\text{O}_3$  powder had high adsorption affinities for anthraquinone blue, which are models of anthraquinone class dyes.

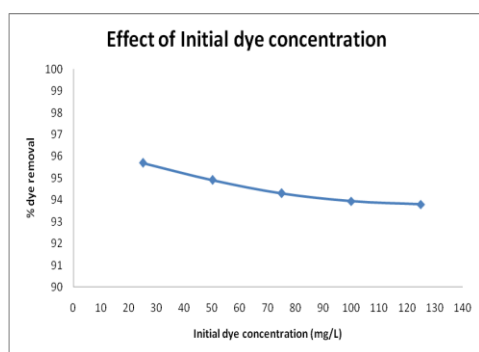


Fig 4: Effect of Initial dye concentration

### 3.4 Isotherm modeling

Equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. Langmuir and Freundlich isotherms were used to describe the equilibrium characteristics of adsorption. An accurate isotherm is important for design purposes. Linear regression is commonly used to determine the best fit model, and the method of least squares has been widely used for obtaining the isotherm constants [19, 25, 35, 36].

One of the most popular adsorption isotherms used for liquids to describe adsorption on a surface having heterogeneous energy distribution is Freundlich isotherm. It is given as:

$$q_e = K_F C_e^{1/n}$$

**Freundlich isotherm** is derived assuming heterogeneity surface.  $K_F$  and  $n$  are indicators of adsorption capacity and adsorption intensity, respectively. Rearranging Equation we get,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

A plot of  $\log q_e$  versus  $\log C_e$  yields a straight line, with a slope of  $1/n$  and intercept of  $\ln K_F$ . The value of Freundlich constant ( $n$ ) should lie in the range of 1–10 for favorable adsorption [19, 25, 35, 36].

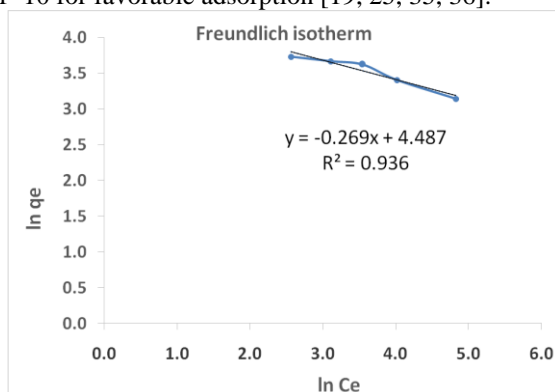


Fig 5: Freundlich isotherm

**Langmuir isotherm**, applicable for homogenous surface adsorption, is given as:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$$

Above equation can be rearranged into linear form:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$$

By plotting  $1/q_e$  versus  $1/C_e$ , the Langmuir constants can be obtained. The essential characteristics of Langmuir isotherm can be expressed by a separation or equilibrium parameter, which is a dimensionless constant defined as:

$$R_L = \frac{1}{1 + K_L C_0}$$

$R_L$  indicates the nature of adsorption as indicated below:

- Unfavorable  $R_L > 1$ ;
- Linear  $R_L = 1$ ;
- Favorable  $0 < R_L < 1$ ;
- Irreversible  $R_L = 0$ .

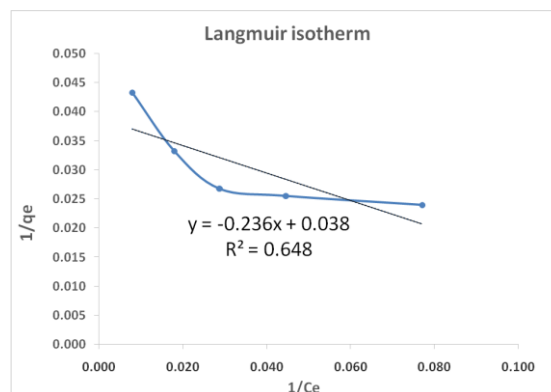


Fig 6: Langmuir isotherm

**Temkin Adsorption isotherm** model is given by,

$$q_e = \left( \frac{RT}{b} \right) \ln AC_e$$

It's linear expression,

$$q_e = \left( \frac{RT}{b} \right) \ln A + \left( \frac{RT}{b} \right) \ln C_e$$

Where  $A$  is the equilibrium binding constant related to the heat of adsorption. The plot of  $q_e$  Vs  $\ln C_e$  is used to determine the isotherm constant  $A$  and  $b$ . The basic assumptions of this model are that the heat of adsorption of the ions in a layer decreases linearly

due to the adsorbent – adsorbate interaction and that the binding energies are uniformly distributed.

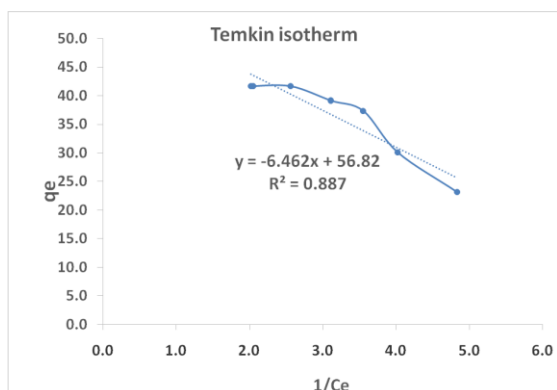


Fig 7: Temkin isotherm

TABLE 2

The value of parameters and correction coefficient of Langmuir, Freundlich and Temkin equations.

Langmuir			Freundlich			Temkin		
Qm	K <sub>L</sub>	R <sup>2</sup>	N	K <sub>F</sub>	R <sup>2</sup>	A	b	R <sup>2</sup>
25.707	0.165	0.643	3.706	88.872	0.936	6592.2	387.26	0.887

### 3.5 Adsorption Kinetics

The transient behavior of the dye sorption process was analyzed by using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Application of a single kinetic model to sorption on solid adsorbents may be questionable because of the heterogeneity of adsorbent surfaces and diversity of adsorption phenomena [19, 25, 35, 36].

The pseudo-first-order kinetic model has been widely used to predict dye adsorption kinetics. Lagergren based on solid capacity originally expresses the pseudo-first-order rate expression suggested as follows.

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

Integrating and applying boundary conditions  $q_t|_{t=0} = 0$  and  $q_t|_{t=t} = q_t$  we get,

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

Values of  $q_e$  and  $K_1$  can be obtained from the slope and intercept of the plot  $\ln(q_e - q_t)$  versus  $t$ .

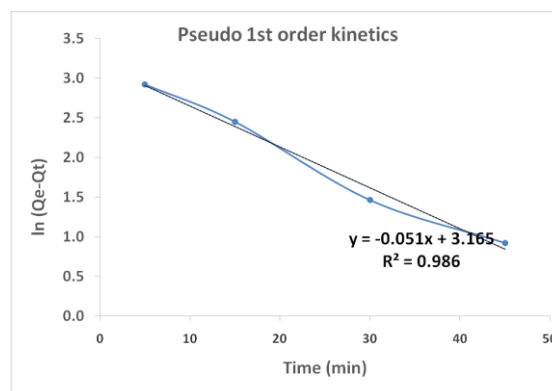


Fig 8: Pseudo first order

Pseudo-second order model is expressed by the equation.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

Integrating and applying boundary conditions  $q_t|_{t=0} = 0$  and  $q_t|_{t=t} = q_t$  we get,

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t$$

We can rearrange above equation as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Values of  $q_e$  and  $K_2$  can be obtained from the slope and intercept of the plot  $t/q_t$  Vs  $t$ .

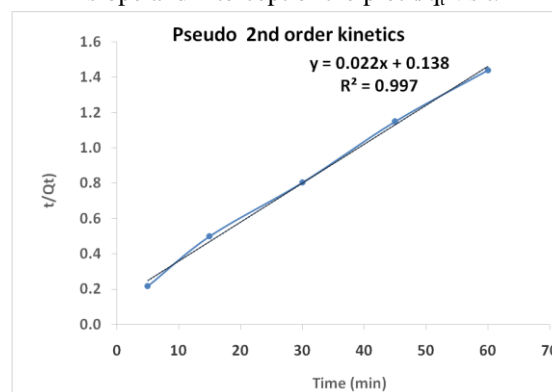


Fig 9: Pseudo second order

**Intraparticle diffusion studies,** It is necessary to identify the steps involved during adsorption in order to interpret the mechanism of adsorption. It is assumed that the adsorption process consists of several steps. Migration of the dye from the bulk of the solution to the sorbent surface, diffusion of the dye through the boundary layer, Intraparticle diffusion, and adsorption of the dye on the internal sorbent surface [19, 25, 35, 36].

The intraparticle diffusion rate can be expressed in terms of the square root time. The mathematical dependence of  $q_t$  versus  $t^{0.5}$  is obtained if the sorption process is considered to be influenced by diffusion in the spherical particles and convective diffusion in the solution. The root time dependence, the intraparticle diffusion model is defined as follows:

Multiple linear regions representing the external mass transfer followed by intraparticle or pore diffusion give the plot  $q_t$  versus  $t^{0.5}$  [19, 25, 35, 36].

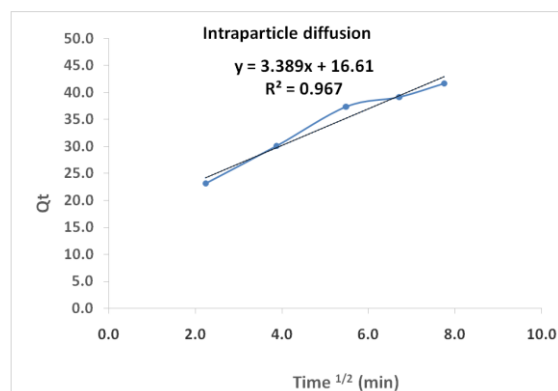


Fig 9: Intraparticle diffusion

TABLE 3  
Adsorption rate constant and coefficient of  
Pseudo first order, Pseudo second order  
and Intraparticle diffusion

Pseudo first Order Kinetics			Pseudo second Order kinetics			Intraparticle Diffusion	
$K_1$	$Q_e$	$R^2$	$K_2$	$Q_e$	$R^2$	$K_i$	$R^2$
0.0516	23.71	0.986	0.004	45.249	0.997	3.3897	0.967

#### IV. CONCLUSION

- $Fe_2O_3$  powder is used for removal of Color from textile dye wastewater by batch experiments.
- Adsorption Equilibrium is attained within 45 min.
- It obeyed Freundlich isotherm model as compared to Langmuir isotherm and Temkin isotherm.
- The order of disperse blue 73 (Anthraquinone dye) adsorption was governed by pseudo-second-order kinetics.

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