

Removal of Dyes from Aqueous Solution by Using Chitosan as an Adsorbent

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ABSTRACT

Due to colour emerging from unfixed dyes, textile industries faces the difficulty to treat the wastewater, chitosan are widely used for waste water treatments in many industries due to its availability, low cost, high biocompatibility, biodegradability and ease of chemical modification and eco-friendly adsorbent for removal of dyes from wastewater. In this thesis chitosan is utilised as adsorbent to remove Acid Scarlet dye and Skyblue FF dye. The sieved first chitin was deacetylated (deacetylation is the process of converting chitin to chitosan by the removal of acetyl group) to chitosan and then batch experiment were conducted to study the effect of pH, initial dye concentration, adsorbent dosage, temperature, contact time, the equilibrium adsorption data were analysed by using Langmuir isotherms model. In the laboratory test conducted chitosan was capable of adsorbing Sky blue FF dye, but it is not capable of absorbing acid scarlet dye n also for mix of both dyes. For adsorption of sky blue FF dye The optimum time was found 10 min, optimum catalyst dose was found to be 0.5g, optimum temperature was found to be 25°C, pH of solution was found to be 8.71. the initial dye concentration increases in solution the percentage removal of colour decreases. The adsorption capacity for skyblue FF is 80% by Langmuir isotherm model. The physical properties of adsorbent was characterised by BET surface analysis, FTIR-spectra.

Keywords - Adsorption, isotherm, chitosan, Skyblue FF, Acid Scarlet

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I. INTRODUCTION

Many industries are using dyes to colour their products, now the demand of synthetic dyes are increased. Dyes are harmful pollutants from industries like textile, leather, paper, food etc. and it causes water pollution and this is a common problem in worldwide but regarding dye ions water is getting polluted and is becoming a very serious problem. These cause adverse impact to the environment. Especially it is becoming threat to aquatic ecosystem and human beings.

1.1 Acid Scarlet

These dyes are mainly used as food colorants and effective on protein fibers and also used to colour basic tissue protein, in staining during microscopic examination for diagnosis are highly soluble in water, and as compared to basic dyes, they have better light fastness as it contain sulphonic acid groups, which are usually present as sodium sulphonate salts. These increase solubility in water, and give the dye molecules a negative charge. This experiment investigated the effect of such various factors as contact time, initial concentration,

catalyst dose, at different temperature, the initial pH value on the colour removal. The results of the experiment clearly indicated the rate of colour removal.

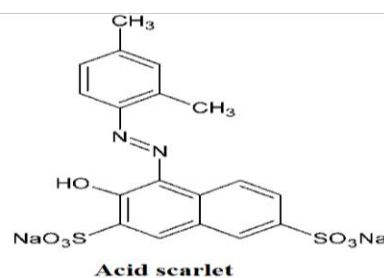
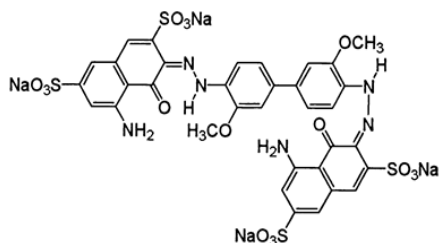


fig 1.1:- structure of acid scarlet [8]

1.2 Sky Blue FF

It reacts chemically with fiber polymer molecules and form covalent bond. Also has highly coloured organic substances, primarily used for tinting textiles, and then it gets attached themselves to their substrates through chemical reaction that forms a covalent bond between the molecule of and fiber, these are used mainly for coloration of cellulosic fibers, can also be applied on wool and nylon.



Sky blue FF

fig1.2:- structure of sky blue FF[8]

1.3 Chitosan

In these experiment chitosan is used as an adsorbent, Chitosan is a linear polysaccharide composed of randomly distributed β -(1 \rightarrow 4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is made by treating the chitin shells of shrimp and other crustaceans with an alkaline substance sodium hydroxide. Chitosan has a number of commercial and possible biomedical uses. Chitin and chitosan are widely used for waste water treatments in many industries that decrease the chemical oxygen demand and total nitrogen.

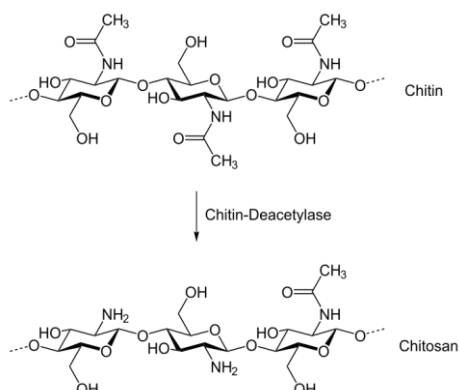


Fig 1.3 Structures of Chitin And Chitosan [9]

1.4 Research objective

The specific objectives are as follows-

1. To investigate the feasibility of chitosan for the removal of Acid scarlet and Sky blue FF dyes from aqueous solution.

1. Preparation of adsorbent from chitin powder to chitosan

2. To study the physical and chemical properties of chitosan

3. To study the effectiveness of chitosan for the adsorption of Acid scarlet and Sky-blue FF

4. To study the adsorption isotherm model

1. Langmuir isotherm model

2. Freundlich isotherm

5. To examine effect of the following factors on the removal of Acid scarlet dye and Sky blue FF dye by adsorption on chitosan

- Effect of Initial concentration.
 - Effect of catalyst doses.
 - Effect of contact time.
 - Effect of temperature.
 - Effect of mixed dye.
6. To characterize the adsorbent by particle size, FTIR values and BET surface areas

II. METHEDOLOGY

Table 2.1 List of all materials used

Material	Manufacturer/Type
HCl (1 M)	Merck, India
NaOH (1 N)	Merck, India
Sky Blue Ff (Dye)	Commercial Grade (616 Nm)
Acid Scarlet (Dye)	Commercial Grade (506 Nm)
Chitin	Tokyo Chemical Industry Co., Ltd.
Mixed Dye (Dye) : Mixture Of Sky Blue Ff + Acid Scarlet (506 Nm), Distilled water.	

Table 2.2 List of all instruments used

INSTRUMENTS	MANUFACTURER/TYPE
Electronic weight balance	Sartorius
Hot Plate Magnetic stirrer	Make: REMI, Model: 4R
Digital pH meter	Make: EI, Model: 111
UV-Vis spectrophotometer	Make: Shimadzu, Model: UV-1800
Brunauer-Emmet-Teller (BET)	Smart Sorb-93
Fourier-transform infrared spectroscopy (FTIR) spectrometer	Bruker, the Alpha model

2.1 Preparation of Adsorbent "Chitosan"

The sieved chitin was deacetylated (deacetylation is the process of converting chitin to chitosan by the removal of acetyl group) to chitosan by using 48% sodium hydroxide solution (w/w) at 100 °C. Then, the product was washed with deionized water completely, dried at 70 °C in an oven overnight, and sieved according to desired particle size range 355-500 μ m. The fractions were further dried in a vacuum oven for 1 day and stored in desiccators.

2.2 Dye Solution Preparation

Precisely weighed amount (1gm) of dye dissolved in distilled water (1000 ml) to prepare a stock solution (1000 ppm). Solution used in the testing for the desired concentration obtained by consecutive dilution (10 ppm to 50 ppm). Dye concentration was measured by absorbance values measured before (C_i) and after (C_f) the treatment at 616nm and 506nm and linear equation (obtained from calibration curve) using UV-visible spectrophotometer.

2.3 Calibration of Sky Blue FF (Dye)

The dye sample calibrated in order to find out various optical densities at various concentration. The calibrated results are very effective to identify colour removal capacities of various adsorbents

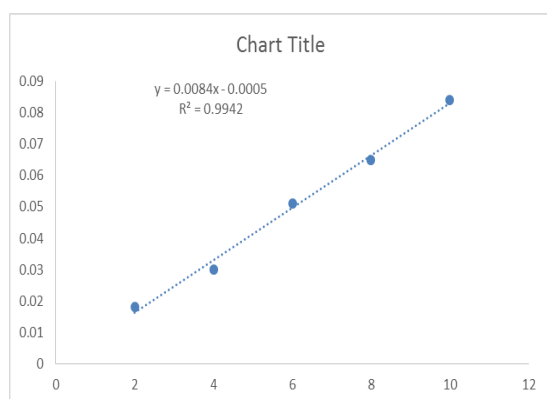


Fig 2.1 showing a graphical representation of sky blue FF

III. EXPERIMENTAL METHOD

3.1 Analysis

The adsorption process was started adding the certain amount of Chitosan in to prepared dye solution. At specific time intervals, the solution was extracted (2×5 min) from the beaker stirring with at 400 rpm. The following equation was applied to calculate the dye removal efficiency:

$$\% \text{ Colour removal (\% CR)} = \frac{C_i - C_f}{C_i} \times 100$$

Where, C_i and C_f are initial and final concentration of solution.

3.2 Experiment

Batch adsorption experiments were carried out to examine effects of adsorbent dosage, initial dye concentration, solution pH, and time on the adsorption of color on chitosan. For each adsorption experiment, 100 ml of the dye solution with a specified concentration was stirred at 400 rpm in a beaker. The pH of solutions was adjusted to a desired value by adding 1 N NaOH or 1 M HCl solution. Batch adsorption experiments were carried out using

hot plate magnetic stirrer for a certain contact time. At predetermined time intervals, samples were withdrawn by a pipette. Then, the residual concentration was determined from a constructed calibration curve by measuring the absorbance at $\lambda_{\text{max}} = 616 \text{ nm}$ and 506 nm using UV-V is spectrophotometer.

3.3 Optimization Parameters for Adsorption:

3.3.1 Effect of Adsorbent Dose

The adsorbent effect chitosan dose on the Sky blue FF and Acid scarlet (dyes) adsorption is determined by the varying the amount of dose of 0.1g, 0.2g, 0.3g, 0.4g, 0.5g in 100 ml dye solution. Concentration of dye solution used was 50ppm and take initial pH 8.71. Kept for agitation at 400 rpm using an hot plate magnetic stirrer for the regular interval of 10min. At the end the agitated sample taken from the shaker and filtered using Whatman filter paper and tested by using UV spectrophotometer. From the results it is clearly understood that the effect of adsorbent dosage is also plays a very vital role in adsorption process for colour removal. The maximum colour removal was found at dosage of 0.5g for time duration of 30 min.

3.3.2 Effect of Initial Concentration

The initial adsorbate concentration of Sky blue FF and Acid scarlet on the adsorption by chitosan has studied by ranging the initial concentration from 10, 20, 30, 40, 50ppm. This study conducted with adsorbate dose 0.5g.

3.3.3 Effect Of pH

The sample containing concentration of Sky blue FF and Acid scarlet of 50 ppm in five beaker sample volume 100ml/2 was taken and the pH 3, 4, 5, 6, 8 was established. A chitosan of 0.5 g was added to all the samples and shaken at 400rpm.

3.3.4 Effect of Time

The chitosan of 0.5g added and sample containing concentration of Sky blue FF and Acid scarlet of 50 ppm 1/4 sample volume 100ml/2 were taken in five different flasks at different retention time of 2, 4, 6, 8, 10 min.

3.3.5 Effect of Temperature

The effect of temperature for the adsorption of Sky blue FF and Acid scarlet has studied at pH 8.71 with adsorbent dose 0.5g with sample volume 100ml, pollutant concentration 50ppm of Sky-blue FF, Acid scarlet solution and solution having different temperature of 25°C, 35°C, 55°C.

3.3.6 Effect of Mixed Dye

The both dyes Sky blue FF and Acid scarlet was mixed and prepare sample volume 100ml 50ppm both dyes concentration at pH 8.71 with adsorbent dose 0.5g.

3.4 Isotherm Studies

Adsorption equilibrium is established when amount of solute being adsorbed on to the adsorbent is equal to the amount being desorbed. By plotting solid phase concentration q_e against liquid phase concentration C_e of solute adsorption isotherm explains interaction between adsorbate and adsorbent and is critical for design of adsorption process. The Langmuir isotherm models are most frequent model to describe the experimental data of adsorption. At present these isotherm were applied to investigate the adsorption process of Sky blue FF and Acid scarlet on chitosan at different conditions of process parameters.

3.4.1 Langmuir Isotherm Model

Langmuir adsorption isotherm model is usually adopted for homogenous adsorption and it is used successfully in monomolecular adsorption processes.

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

The linearized form of Langmuir isotherm is:

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

Where C_e equilibrium pollutant dyes concentration, q_m and K_L are the Langmuir constant related to maximum adsorption capacity in mg/g and the relative energy of adsorption respectively.

3.4.2 Freundlich Isotherm

The Freundlich isotherm is also used for isothermal adsorption for heterogeneous surface energy because of the variation of the sorption in the Langmuir equation the energy term varies as a function of surface coverage.

The equation is given as:

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

In the above equation it can be linearized by taking logarithms to determine the parameters K_F and $1/n$.

$$\ln(q_e) = (1/n) \ln C_e + \ln K_F$$

Where K_F is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity. K_F and $1/n$ can be determined from the linear plot of $\ln(q_e)$ versus $\ln(C_e)$.

IV. RESULT AND DISCUSSION

4.1 Characterization of Chitosan

4.1.1 FT-IR Analysis of Chitosan

Fourier-transform infrared spectroscopy (FTIR) spectra of prepared catalyst were recorded using a Bruker, the Alpha model in the range of 500 cm^{-1} to 3500 cm^{-1} .

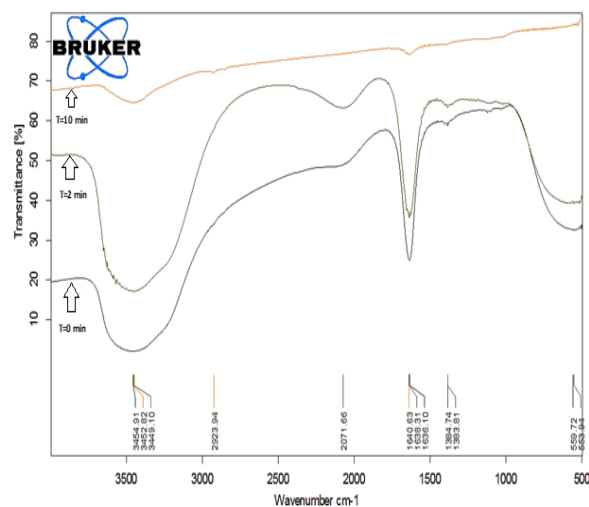


Fig 4.1 FT-IR analysis of chitosan

4.1.2 Bet Surface Analysis Of Chitosan

Bet Surface Area

The specific surface area and pore volume of synthesized catalyst was measured by Brunauer-Emmet-Teller (BET) method in a surface area analyzer Smart Sorb-93 apparatus.

Table 4.1 BET surface analysis of chitosan

S.No.	BET surface area (m ² /g)	Total pore volume (m ³ /g)
1.	16.75	0.0071

4.2 Sky Blue FF Dye

4.2.1 Effect of Catalyst Dose

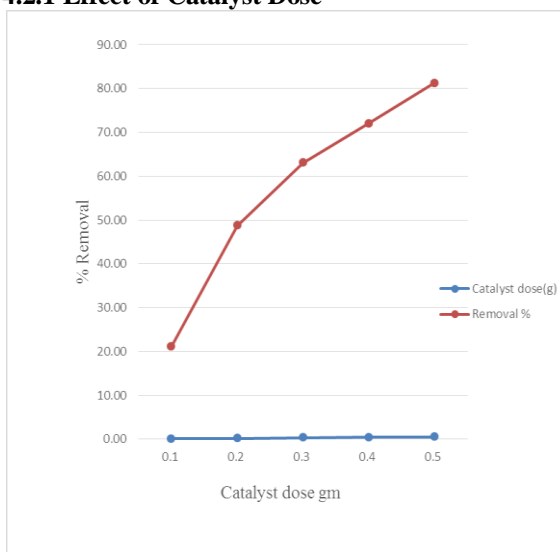


fig 4.2 effect of catalyst dose on adsorption of sky blueFF

4.2.2 Effect of Initial Dye Concentration

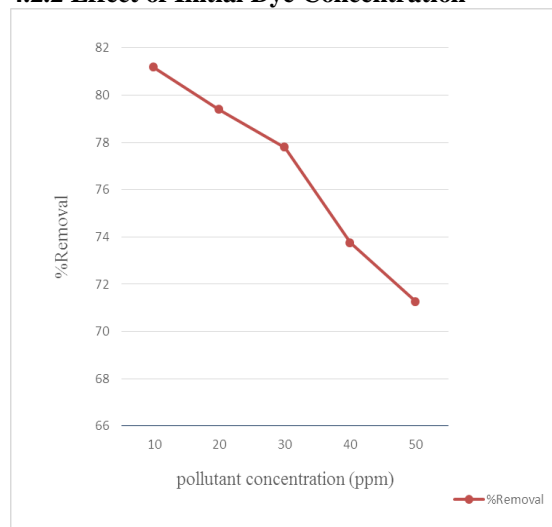


fig 4.3 effect of initial dye concentration on adsorption of sky blue FF dye.

4.2.3 Effect Of PH

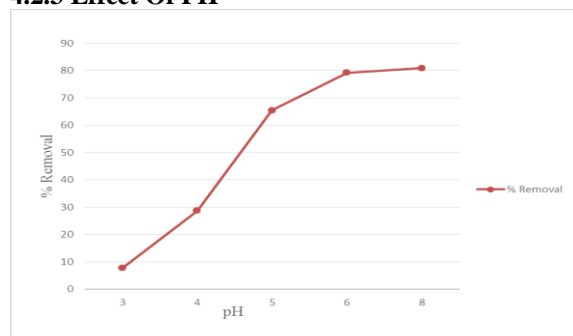


fig 4.4 effect of pH on adsorption of sky blue FF dye.

4.2.4 Effect of Contact Time

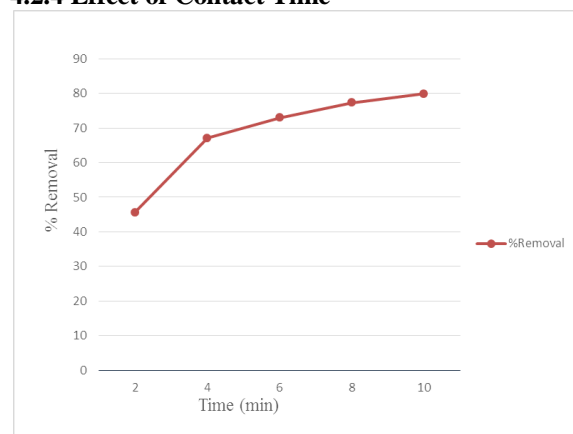


fig 4.5 effect of contact time on adsorption of sky blue FF dye

4.2.5 Effect of Temperature

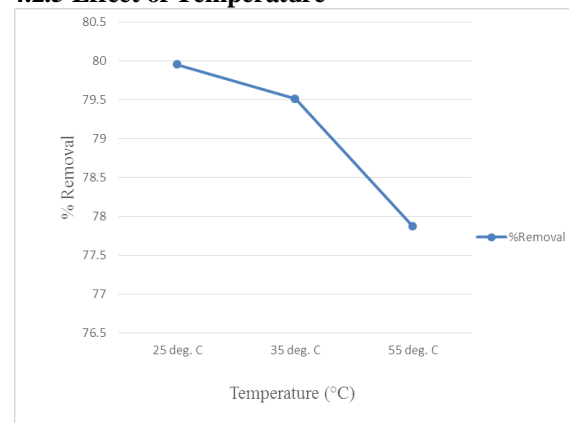


fig 4.6 effect of temperature on adsorption of sky blue FF dye.

4.3 Acid Scarlet Dye

Table 4.2 effect of time on adsorption of acid scarlet dye

Time	Ci	Cf	%Removal
10 min	1.113	0.942	15.36

4.4 Effect Of Mixed Dye

Table 4.3 Effect of Time On Adsorption of Mixed

Time	Ci	Cf	%Removal
10min	0.391	0.338	13.55

V. CONCLUSION

5.1 Based on the results of this study following conclusions could be drawn:

- In the laboratory test conducted chitosan was capable of adsorbing Sky blue FF dye,
- The Effect of all the parameters such as catalyst dose, contact time, initial dye concentration, temperature, pH, mixed dyes of solution were at temperate levels such as they can affect the removal effectiveness of the dyes were concerned.
- The percentage of removal of sky blue FF dye increases as the adsorption dose increases in solution. The optimum catalyst dose was found to be 0.5g.
- The optimum time for adsorption of sky blue FF dye was found to be 10 min.
- The optimum temperature of solution for sky blue FF dye was found to be 25°C.
- As the initial dye concentration increases in solution the percentage removal of colour decreases. i.e. at lower levels the adsorption was higher.
- The optimum pH of solution for sky blue FF was found to be 8.71.

5.2 Scope for Future Work

- Present studies were focused on the removal of Sky blue FF dye at various contact time, initial dye concentration, adsorbent dose, temperature, pH some other parameters like mixed dye are also recommended for studies.
- Present study shows that the chitosan is cheaper and easily available but it was not compared with any other adsorbents which are found suitable by other researchers.

This study was performing using prepare a dye solution laboratory conditions. The result may vary applied to real sample, the real sample are complicated because industries use various types of dyes for different applications. Thus a real waste water from industries which contain dyes effluent, separate study on this type effluent is needed

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- [9] Research gate, Structure-of-chitin-and-chitosan, figure.



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