Monitoring and control of environmental pollution due to dyeing effluents

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Abstract : All the water samples were found to contain higher levels of hardness and Total dissolved solids than their prescribed tolerance limits. The levels of Cl- ,Ca2+ were slightly higher than the tolerance levels. The pH levels of the water samples were found to be well within the tolerance limits.TCB/UV is an effective method for the photocatalytic degradation of RR2.The dye was completely degraded at 90 minutes in presence of TCB/UV. The degradation rate increase from neutral to alkaline pH and at pH 10 the dye is   completely degraded.The percentage of dye removal is inversely proportional to its concentration .i.e., the lower the dye concentration the higher the efficiency of dye removal. The kinetic model of Langmuir-Hinshelwood well describes the photodegradation results. The photocatalytic degradation of the Reactive Red 2 dye exhibited pseudo- first- order kinectics.
Key words : Hardness, Total dissolved solids, calcium, chloride, pH, Reactive Red 2 dye, TCB.

Introduction

Water

Water covers 70.9 % of the Earth's surface and is vital for all known forms of life. On Earth, 96.5 % of the planet's water is found in oceans, 1.7 % in groundwater, 1.7 % in glaciers and the ice caps of Antarctica and Greenland, a small fraction in other large water bodies, and 0.001 % in the air as vapor, clouds (formed of solid and liquid water particles suspended in air), and precipitation [1]. Only 2.5 % of the Earth's water is freshwater, and 98.8% of that water is in ice and groundwater. Less than 0.3 % of all freshwater is in rivers, lakes, and the atmosphere, and an even smaller amount of the Earth's freshwater (0.003 %) is contained within biological bodies and manufactured products [2]. Water on Earth moves continually through the hydrological cycle of evaporation and transpiration (evapotranspiration), condensation, precipitation, and runoff, usually reaching the sea. Evaporation and transpiration contribute to the precipitation over land. Safe drinking water is essential to humans and other lifeforms. Access to safe drinking water has improved over the last decades in almost every part of the world, but approximately one billion people still lack access to safe water and over 2.5 billion lack access to adequate sanitation. There is a clear correlation between access to safe water and GDP per capital. However, some observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability [3]. A recent report (November 2009) suggests that by 2030, in some developing regions of the world, water demand will exceed supply by 50 % [4]. Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Approximately 70 % of the fresh water used by humans goes to agriculture.

Pollution due to dyes

Over the last few decades, society has become increasingly sensitive towards the protection of the environment. Due to this problem, mankind now-a-days has concern about the potential adverse effects to the chemical industry on the environment, although the response in some parts of the world has been much faster and more intense than in others. The colour manufacturing industry represents a relatively small part of the overall chemical industry. Dyes and pigments are highly visible material. Thus even minor release into the environment may cause the appearance of colour, for example in open waters, which attracts the critical attention of public and local authorities. There is thus the requirement on industry to minimise environmental release of colour, even in cases where a small but visible release might be considered as toxicologically rather innocuous. A major source of release of colour into the environment is associated with the incomplete exhaustion of dyes onto textile fibre from an aqueous dyeing process and the need to reduce the amount of residual dye in textile effluent has thus become a major concern in recent years. An alternative approach to addressing the problem of colour in textile dyeing effluent has involved the development of effluent treatment methods to remove colour. These methods inevitably add to the cost of the overall process and some present the complication associated with the possible toxicity of degradation products.

Technologies for colour removal

There are more than 100,000 commercially available dye exist and more than 7x105 tonnes per year are produced annually [5]. Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light. A synthetic dye in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale in the textile and paper industries [6]. The technologies for colour removal can be divided into three categories: biological, chemical and physical [7-11]. All of them have advantages and drawbacks which is shown in Table 1.

Table.1. Advantages and disadvantages of physical and chemical methods of dye removal from industrial effluent

	Technology	Advantages	Disadvantages
Conventional treatment process	Coagulation Flocculation	Simple, economicall feasible.	High sludge production, handling and disposal problems.
	Biodegradation	Economically attractive, publicly accepted treatment.	Optimal favourable environment, maintenance and nutrition requirements.
	Adsorption of activated carbon	The most effective adsorbent, produce a high quality treated effluent.	Ineffective against disperse and vat dyes. The regeneration is expensive.
Established recovery process	Membrane separations	Removes all dye types, produce a high quality treated effluent.	Expensive, incapable of treating large volumes.
	Ion exchange	No loss of sorbent on regeneration.	High cost and not effective for disperse dye
	Oxidation	Rapid and efficient process.	Needs high energy and costly chemicals.
Emerging removal process	Advanced oxidation process	No sludge production, little or no consumption of chemicals.	Economically unfeasible due to formation of by-products which leads to technical constraints.

Reactive Red 2

Reactive Red dye (RR2) is widely used for dyeing cellulosic fibers .Only 60-70% of the reactive dyes reacts with the fiber during the dyeing process,the remaining is hydrolysed and is released into the environment. Reactive red dye are mainly used for dyeing of silk,wool,leather etc.,.In reactive red 2,N=N (Azo) group is attached.

Molecular structure
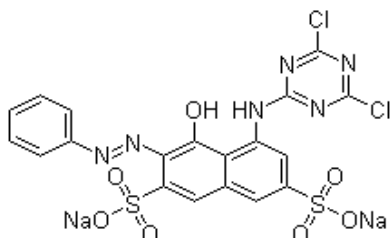
Name	: Reactive Red 2
Molecular formula	: $C_{19}H_{10}Cl_2N_6O_7S_{22}Na$
Molecular weight	: 615.33
Synonyms	: Disodium5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino] -4-hydroxy-3-(phenylazo) naphthalene-2,7-disulphonate

Aim and scope of the present work

Chinnalapatty is one of the famous textile center of Tamil Nadu.There are about 22 domestic dyeing units present in and around Chinnalapatty village. The effluents from these units were let out without any treatment. Hence, it is proposed to analyse the water quality of the textile effluent polluted area and to find out the remedial measures for the reversal of textile effluents.

The main objectives are,

1. To assess the water quality of the drinking water collected near by dye polluted area.
2. To study the effect of various experimental parameters like contact time, dose of catalyst, pH, initial concentration and on the extent of removal of dye by the sorbent TCB.

The results of the present study will be highly useful in designing the cost effective and efficient treatment plant for the economical removal of dye (RR2) from water and industrial wastewater / textile effluents.

Materials And Methods

Analysis of ground water samples [19]

    I.   Determination of hardness

Hardness of the H_2O samples were determined by complexometric titration method.

Reagents used

1.Disodium salt of EDTA solution(0.01M)

3.723 g of AR disodium salt of EDTA is dissolved in water and made upto 1litre.

2. Buffer solution

1. 16.9 g AR NH_4Cl dissolved in 143 ml of concentrated NH_4OH.
2. 1.179 g of disodium salt of EDTA and 0.780g AR $MgSO_4$ were dissolved in 50ml of distilled water.

3.   Solution first and second are mixed with each other and diluted to 250ml.

3. Eriochrome Black-T

0.40 g of EBT was mixed with 100 g of NaCl and ground to fine powder.

Procedure

1.   10 ml of water sample was taken in a conical flask.
2.   2-3 drops of buffer solution added to this sample.
3.   25 mg of EBT was added to the above.
4.   The contents in conical flask were titrated against disodium salt of EDTA solution taken in burette.
5.   End point is sharp colour change from wine red to blue.

Calculation

Hardness as $CaCO_3$ mg/l   = $\dfrac{\text{ml of EDTA} \times 1000}{\text{ml of sample}}$

II. Total dissolved solids

1.   10 ml of water evaporated to dryness in a previously weighed beaker at110 ºC for half an hour in oven.
2.   The beaker was cooled in a desiccators and weighed.
3.   The heating, cooling and weighing were repeated till the beaker gave constant weight.

The TDS present in all the samples were calculated using the formula

TDS mg/l   = $\dfrac{(A-B) \times 1000 \times 1000}{\text{ml of the sample}}$

A= Final weight of the beaker in g

B= initial weight of the beaker in g

III. Determination of calcium – Ca^{2+}

Principle

        Many indicators such as ammonium pupurlate, calcon, etc. form a complex with only calcium but not with magnesium at higher pH. As EDTA is having a higher affinity towards calcium the former complex is broken down and a new complex is formed.

Reagents used

1. 0.01M EDTA solution

   0.01 M EDTA solution was prepared as in total hardness estimation

2.1N Sodium Hydroxide

   4g of NaOH is dissolved in distilled water ane made up to 100 ml in smf.

3. Murexide indicator

   Mixed 0.2g of ammonium purpurate with 100 g of AR NaCl and grinded

Procedure

        10 ml of water sample was taken in a conical flask 2 ml NaOH solution was added followed by 100 to 200 mg of Murexide indicator , titrated against EDTA solution.The end point of the titration was shown by a sharp colour change from pink to purple. The amount of the calcium present was determined using the formula.

Calculation

$$\text{Calcium as } CaCO_3 \text{ mg / l} = \frac{\text{ml of EDTA} \times 400.8}{\text{ml of sample}}$$

IV. Determination of Chloride

Principle

Silver nitrate reacts with chloride to from very slightly soluble white precipitate of AgCl. At the end point when all the chlorides get precipitated, free silver ions react with chromate to from silver chromate of reddish brown colour.

Reagents Required

1.Sodium chloride solution 0.05N

0.2923 g of AR NaCl was dissolved in distilled water and made up to 100 ml

2.Silver Nitrate 0.02N

3.4 g of dried AR $AgNO_3$ was dissolved in distilled water and made upto 1 liter and kept in a dark coloured bottle.

3. Potassium chromate indicator 5%

5 g of AR potassium chromate was dissolved in distilled water and made upto 100 ml.

Procedure

Standardisation of $AgNO_3$ solution

10 ml of standard NaCl solution was taken in a conical flask, 3 drops of potassium chromate was added as indicator and the content were titrated against $AgNO_3$ solution. The end point was the appearance of permanent reddish brown precipitate.

Estimation of chloride

100 ml of water sample was taken in a conical flask. 3 drops of potassium chromate was added to it and then the solution was titrated against standardized $AgNO_3$ solution. The end point was the appearance of permanent reddish brown precipitate.

Calculation

The amount of chloride present in the water samples were determined the using the formula

$$\text{Chloride as mg / l} = \frac{\text{Volume of } AgNO_3 \times \text{Normality of } AgNO_3 \times 1000 \times 35.5}{\text{ml of sample}}$$

V.Determination of pH

Principle

pH is the negative $\log_{10}$ of the hydrogen ion concentration

Procedure

The pH measurements of the water samples were carried out using digital pH meter. The pH meter calibrated was first checked with the buffer solution of pH 4 and again cross-checked with another solution of pH 9.Then pH values of different water samples were measured.

Analysis of the sample

The expandable ion analyzer was calibrated using two solutions of known concentrations. The difference in concentration of the two standards should be at least ten times and furthermore, the concentration of the unknown sample to be measured should fall between the two standards. Concentration of fluoride ion in the water samples was measured directly from the calibrated ion analyzer by mixing with equal volume of the TISAB II buffer.

Photodegradation of RR2 dye using Titanium dioxide impregnated chitosan beads TCB)

Materials

All the chemicals used were of analytical reagent grade.Reactive Red 2 dye is taken for photo degradation studies. TiO_2 was used as photocatalyst. Double distilled water was used throughout the study.

Equipment

The photodegradation studies were carried out using "HEBER" multilamp photoreactor of 8W mercury lamps(4 Nos.) at the wave length of 254 nm. The concentration was measured using spectroquant pharo 300, MERCK and pH studies were done using Expandable Ion Analyser EA 940 ion selective meter with pH electrode (ORION,USA).

Instrumental studies

FTIR spectra of the samples as solid by diluting in KBr pellets were recorded with JASCO – 460 PLUS model. The result of FTIR spectra was used to confirm the functional group present in sorbent before and after sorption of dyes.

Preparation of sorbent TCB

Chitosan (10g) was dissolved in 2 % glacial acetic acid solution. To this solution 5g of titanium dioxide was added and stirred until a homogeneous solution was achieved .Beads were formulated by dispensing the solution into 0.5M NaOH solution .Beads sat in 0.5 M NaOH over night and were washed with distilled water to a neutral pH. The wet beads were cross- linked with 2.5 wt. % glutaraldehyde solution. Cross- linking reaction occurred for 48 h and then cross– linked beads were washed with distilled water to remove any free glutaraldehyde and dried at room temperature.

Characterization of sorbent Material

(a) pH Zero Point Charge (pHzpc)Measurement

The pH at the potential of zero charge of was measured using the pH drift method.The pH of solution of 0.01M NaCl was adjusted between 2 and 12 by adding either HCl or NaOH. TCB (0.15mg) was added to 50ml of the solution. After the pH had stabilized, the final pH was recorded. The graph of final Vs initial pH were used to determine the point at whichn initial pH and final pH values were equal. This was taken as pHzpc of the TCB.

(b) pH of aqueous solution

The adsorbent (50mg) was mixed with 50 ml of distilled water and equilibrated for 1 hr agitating in the thermostated shaker at 120 rpm. The pH of supernatant wasmeasured using 2 pH meter . The pH meter was calibrated with 4.0 and 9.2 buffers.

Preparation of dye solution

About 1g of reactive red 2 dye was accurately weighed and dissolved in distilled water and made up to1 liter in standard measuring flask to prepare 1000 mg/L of dye solution .This solution was used as stock solution . Known concentration solutions for the experiments were prepared from this stock solution.

Removal of Reactive Red 2 using UV/TCB by Photocatalytic degradation studies

In the present work the photodegradation experiments were carried out by employing the TCB under different experimental conditions. In the photodegradation experiments, the extents of removal of dye in terms of the value of percentage removal of dye have been calculated using the following relationship.

Percentage removal = $100(C_i - C_f)/C_i$ ----------(1)

C_i Initial concentration of dye (mg/l)

C_f ⟶ Final concentration of dye (mg/l)

(a) Effect of Contact Time

In order to study the effect of contact time on the removal of Reactive Red 2 dye by photodegradation on TCB, the degradation experiments were carried out at the constant dose (0.1 g) and optimum initial concentration at room temperature by varying the contact time such as 15, 30, 45, 60, 75 and 90 minutes and then the solution was centrifuged several times. The final concentration of the dye solution was determined spectrophotometrically

(b) Effect of dose of sorbent

To study the effect of dose of sorbent, the initial concentration of the dye solution (10 mg /L) and the contact time (75 min) was kept constant and the dose of the sorbent was varied such as 0.05, 0.075, 0.1, 0.125, 0.15 g. The final concentration of the dye solution was determined and the amount of sorbent required for maximum removal of dye was determined.

(c) Effect of pH

The photodegradation experiment was carried out at different initial pH (2 to10), at constant initial concentration of the dye solution (10mg/l), the dose of the sorbent (0.1g), and contact time (75 min) in order to study the effect of initial pH on the extent of removal of dye by photodegradation.The initial pH of the dye solution was varied (2 to 10) by adding the required volume of HCl and NaOH .After photodegradation of the dye solution, the final concentration was determined spectrophotometrically as usual. The percentage removal of the dye was calculated.

(d) Effect of concentration of dye

 The photodegradation experiments were carried out at concentrations varied from 10 mg/L to 50 mg/L, keeping the contact time (75 min) and dose of the catalyst (0.1 g) as constant. The final concentration of the dye solution was determined.

Kinetics of photodegradation

A Langmuir-Hinshelwood type of relationship was used to describe the effect of dye concentration on its degradation. The limitation of surface sites for the reaction may control the dye decomposition.

The degradation experiments by UV irradiation of Reactive Red 2 dye containing sorbent TCB follow pseudo first order kinetics with respect to the contact time(t).

The following first order kinetics equation was used to study the kinetics of photodegradation of RR2 dye.

$\ln (C_o / C_t) = kt$

where, C_o = initial concentration of dye solution (in mg/L)

C_t = concentration of dye solution at various time (in min)

k = first order rate constant for degradation of dye (in min^{-1})

The values of $\ln (C_o / C_t)$ are plotted against time (in min) and the plots were found to be linear. From the slope , the rate constants were calculated .

Results And Discussion

In this chapter, the impacts of dyeing effluents on the quality of nearby drinking water samples have been assessed. Also, various sorption conditions for the maximum sorption of Reactive Red2 (RR2) by photodegradation method using TCB as a sorbent have beenoptimized.

Table.2. Tolerance limit for various quality parameter

S.No.	Parameters	Minimum	Maximum
1	pH	6.5	8.5
2	Hardness	300	500
3	Calcium	60	75
4	Chloride	250	600
5	TDS	500	1000

Assessment of quality of water samples collected

Fifteen (15) representative ground water samples from the chinnalapatty of dindigul district were collected and analyzed for various water quality parameters like pH, alkalinity, hardness, fluoride, calcium, magnesium, chloride, sodium and potassium and are shown in Table 3.

Table 2 The results analysis of various water quality parameter

Sample nos.	Cl⁻ mg/L	Ca²⁺ mg/L	pH	TDS mg/L
1	482.8	272.5	7.31	1600
2	298.2	96.19	8.29	700
3	298.2	200.4	8.10	2200
4	284	176.3	7.82	1200
5	255.6	144.2	8.06	1600
6	355	80.16	8.25	1900
7	298.2	128.2	8.10	1900
8	326.6	120.2	8.14	2500
9	397.6	224.4	7.98	2000
10	323.6	136.2	7.70	2200
11	369.2	160.3	8.17	1500
12	497	200.4	8.20	2400
13	284	240.4	8.20	700
14	255.6	144.2	8.12	800
15	426	200.4	7.94	3000

The levels of pH of all drinking water samples ranged between 6.81 and 8.65 .The pH of all these water samples were within the tolerance limit of 7.31 to 8.29 which is given in Table 3. Almost all the samples the concentration of Cl⁻ ions was found well within the tolerance limit of 250 mg/L to 600 mg/L. The amount of

hardness for all samples are higher than the prescribed levels of 300 mg/L .A maximum of 1500 mg/L was observed for the sample 6. The range is between 720 -2200 mg/L. Hardness would results in scaling of the utensils thus leading in high fuel wastage. Further,it does not quench thirst and pulses cannot be cooked. The levels of calcium in almost all the samples were found to be very high. The concentration of calcium varies from 80.160 to 272.544 mg/L where as its tolerance level is 60 mg/L. The higher concentration of calcium makes the water hard and render unsuitable for drinking and cooking. The level of the TDS of all drinking water samples ranged between 700 to 3000 mg/L. The TDS of all these water samples were higher than the tolerance limit of 1000 mg/L except samples 2, 13 and 14. A maximum of 3000 mg/L was observed for the sample 15. From the above discussion, it has been concluded that, the water quality parameters viz., pH level is well within the tolerance limits where as calcium, chloride, levels are slightly higher than the prescribed limits. The value of Total hardness and Total dissolved solids are extremely higher than the tolerance limits indicating that the water is unfit for drinking and irrigation purposes.

 Photocatalytic degradation of Reactive Red 2 using UV / TCB

**Properties of TiO_2 – impregnated chitosan beads (TCB)**

The TCB was characterized by calculating the factors such as pH_{ZPC} and pH and the results are shown in the Table 4.

Table .4. Properties of TCB

Parameters	Results
pH_{ZPC}	6.6
pH	7.0

Effect of contact time

         In order to study the contact time (range 15 to 90 min for RR2 dye by using TCB)   on the extent of removal of dye by photodegradation, the photodegradation experiment was carried out at constant dose of the catalyst (0.1 g) and optimum initial concentration of dye (10 mg/L) at room temperature. The dye solutions were analyzed for the final concentration and the percentage removal of dye was found to increase by increasing the contact time. After 75 min, the percentage removal of dye has a tendency for saturation and the dye was completely degraded at 90 min. Hence, 75 min was fixed as contact time for further studies.
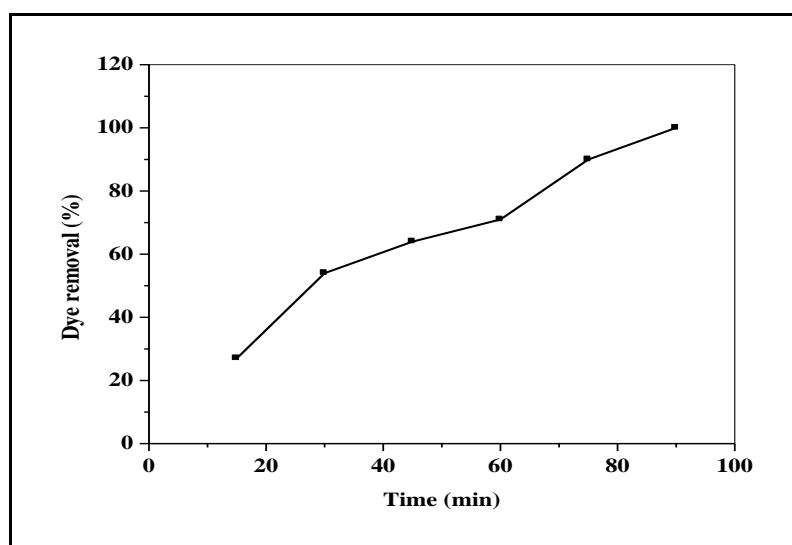
Fig.1.Effect of contact time

Effect of dose of TCB

The effect of dosage of TCB on the extent of removal of dye was studied. For the degradation studies, the amount of TCB varied from 0.05 g to 0.15 g. The initial concentration was maintained as 10 mg/L and the irradiation time was 75 min. As the dosage increases, obviously the percentage removal of dye also increases. This is due to the increase in the availability of surface active sites. The results are shown in Fig.2.
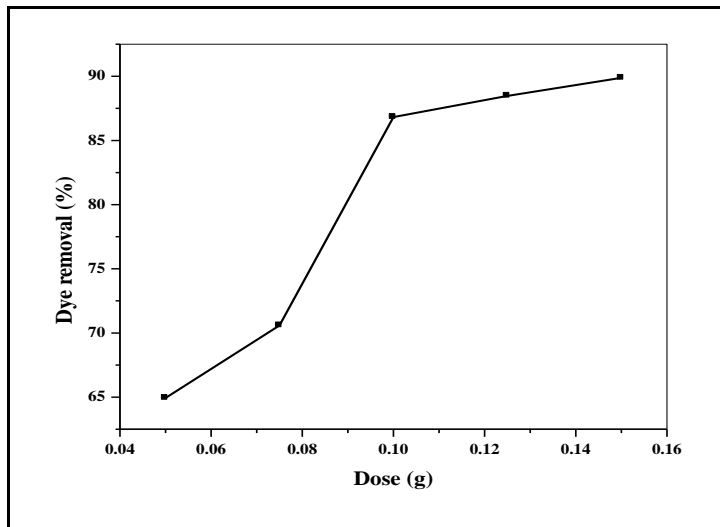

Fig .2. Effect of dose of sorbent

Effect of pH

To study the influence of solution pH on the removal of dye molecules, test mixtures containing 10 mg/L of dye solution and 0.1 g of TCB was adjusted to various pH values (2 to 10). The irradiation time was fixed as 75 min. The effect of pH on the removal of dye is depicted in Fig .3. It was observed that the degradation rate increases in the neutral to alkaline pH as compared to the acidic pH conditions.Enforcement of the reaction rate under alkaline conditions could be attributed to the increase of hydroxyl ions, which in turn induces the formation of more hydroxyl radical formation. This formed hydroxyl radical initiates the degradation process by ion-exchange mechanism.
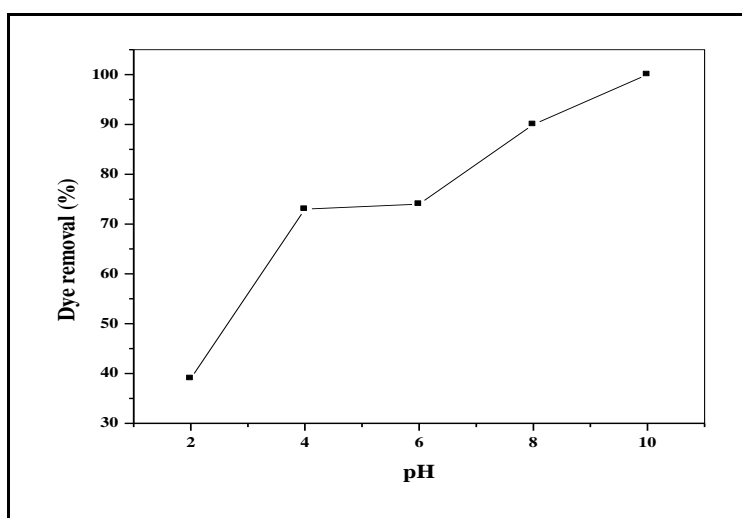

Fig.3.Effect of pH

Effect of Initial concentration

To study the effect of initial concentration on the removal of dye, the concentrations are varied from 10 mg/L to 50 mg/L and the dosage of sorbent 0.1 g at equilibrium time 75 min was maintained. The effect of

initial concentration on the removal of dye is illustrated in fig.4. As the initial concentration increases, the dye removal capacity found to decrease. This may be attributed that as the concentration increases, the available surface area may not be sufficient to accommodate all the dye molecules at that fixed dosage of sorbent.
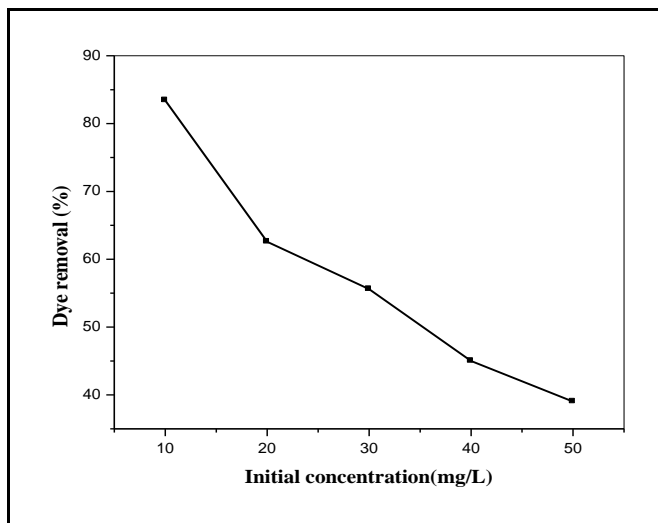
Fig.4.Effect of initial concentration

Characterisation of the sorbent

FTIR spectra of (a) TCB and (b) RR2 sorbed TCB are shown in Fig.5. Although there is a possibility of overlapping between –NH$_2$ and –OH stretching vibrations, the strong broad band at the wave number region of 3300-3500cm^{-1} is the characteristic of –NH$_2$ stritching vibration. The major bands for TCB can be assigned as follows: 3400cm^{-1} (-OH and –NH$_2$ stretching vibrations), 1660 cm^{-1} (N-H for primary amine band especially for chitosan), 1070 cm^{-1} (-CO stretching vibration in –COH), 530 cm^{-1}(band corresponds to TiO$_2$). The sorbent TCB have not shown any significant change in adsorption intensity after dye sorption [22]. This implies that for TCB, the sorption process is by physical means and not by chemical interaction.
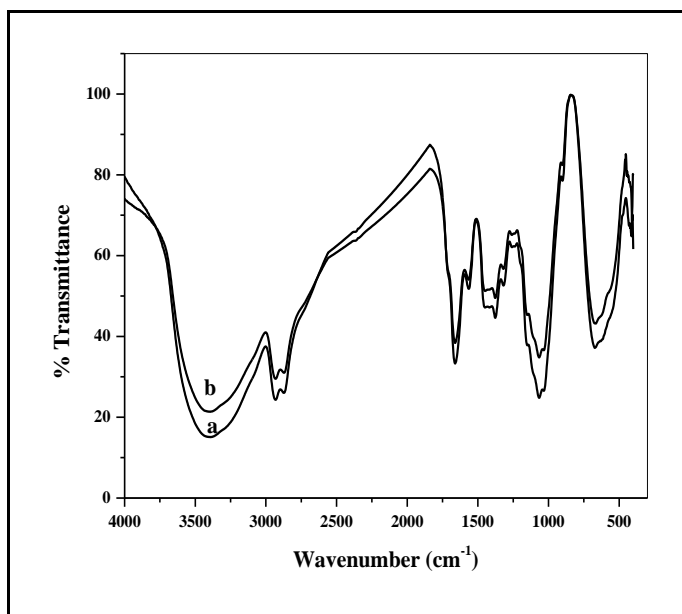
Fig.5. FTIR spectra of a) TCBb) RR2 sorbed TCB

Kinetics of photodegradation of RR2 using TCB

The kinetics of disappearance of RR2 at different concentrations is illustrated in fig.6. The results show that the photocatalytic decolorization of RR2 dye can be described by the first order kinetic model,

$\ln (C_0 / C_t) = kt$

The plots of the concentration data gave a straight line .The correlation constant for the fitted line was calculated for RR2 concentrations 10, 20, 30, 40, 50 mg/L respectively. The rate of the reaction was calculated by plotting $\ln (C_0/C_t)$ as a function of time. The rate constants were calculated and given in Table.5.
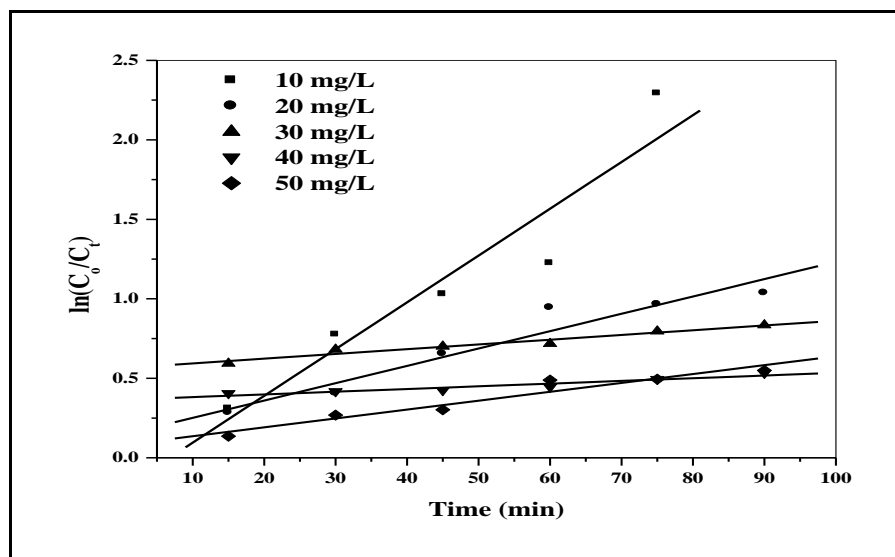

Fig.6. Kinetics of photodegradation of RR2 using TCB

Table.5. Rate constants for photodegradation of RR2 dye using TCB

Concentration of RR2 (mg/l)	R	k (min^{-1})
10	0.948	0.029
20	0.965	0.011
30	0.976	0.003
40	0.953	0.0012
50	0.967	0.006

where k = rate constant (min^{-1})

The plots gave different straight lines which confirmed the degradation process follows a pseudo-first-order reaction

Conclusions

The following conclusions could be made from the results of this work.

1. All the water samples were found to contain higher levels of hardness and Total dissolved solids than their prescribed tolerance limits.
2. The levels of Cl$^-$,Ca^{2+} were slightly higher than the tolerance levels.
3. The pH levels of the water samples were found to be well within the tolerance limits.
4. TCB/UV is an effective method for the photocatalytic degradation of RR2.
5. The dye was completely degraded at 90 minutes in presence of TCB/UV.
6. The degradation rate increase from neutral to alkaline pH and at pH 10 the dye is   completely degraded.
7. The percentage of dye removal is inversely proportional to its concentration .i.e., the lower the dye concentration the higher the efficiency of dye removal.

8. The kinetic model of Langmuir-Hinshelwood well describes the photodegradation results. The photocatalytic degradation of the Reactive Red 2 dye exhibited pseudo- first- order kinectics.

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