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Research Article

# STUDIES ON PHOTODEGRADATION OF BISMARCK BROWN AND RHODAMINE B DYE FROM AQUEOUS SOLUTIONS OF THEIR BINARY MIXTURE BY THE SYNTHESIZED IRON OXIDE NANO PARTICLES USING SUNLIGHT AND PHOTOREACTOR

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## ABSTRACT

Photo degradation study has been most widely used in waste water treatments and it appears to be thebestmethod for theoverall treatment of dyestuff effluent. Photodegradation of Bismarck Brown and Rhodamine B dyes from aqueous solutions of their binary mixture was carried out usingsynthesized iron oxide nanoparticleas photocatalyst. The nano particles are produced by using the co-precipitation method. The optimum condition for degradation is obtained by varying the experimental parameters like concentration, dose, pH and contact time.The photodegradation was done by using different source of energy like solar radiation and ultra violet radiation.Solar degradation was carried out in direct sunlight and UV degradation was carried out using photo reactor. Thedegradation was carried out at differenttemperaturesso as to calculate the rate constant.The degradation ofboth dyes followspseudo first order reaction. These resultswill be helpful in designing effluent treatment plants in industries.

**Keywords**: Photodegradation, Rhodamine B, Bismarck Brown,iron oxide, Photo Reactor.

## INTRODUCTION

Textile industry causes considerable higher impacts to water pollution by discharging their effluents into various water bodies like rivers, ponds etc. Azodyes represent the largest class of textile dyes in industrial use. These reactive azodyes cannot be easily removed by conventional treatment methods due to their stability and non biodegradable nature. Some azodyes are assumed to be carcinogenic due to the formation of aromatic amines[1,2]. Advanced oxidation process seems to be one of the best suitable method for the removal ofazo dyes[3].Among the various advanced oxidation process (AOPs) heterogeneous photo catalysis on metal oxide semiconductor particles has been found to be very effective for removing the organic pollutants from wastewater [4-6].

## EXPERIMENTAL

The Bismarck brown and the Rhodamine B dyes were obtained froms.d.fine chemicals, Mumbai. In the current work the iron oxidenanoparticles are prepared by the co-precipitation technique. Photocatalyst iron oxide was prepared by addition of 0.6M of ammonium hydroxide(purchased from E. Merck chemicals Ltd, Mumbai.) on 0.2 Msolution of ferric chloride (obtained from E.Merck chemicals Ltd, Mumbai.) with constant stirring,the mixture was kept at roomtemperature under constant stirring usingmagnetic stirrer for a period of 2 – 3 hours. Allthe reagents and solutions were prepared byusing this DD water. The resultantprecipitateobtained wasirradiated with microwave in a microwave oven.The sample was irradiated at 100W for 1hour.The co-precipitation reaction can be represented as follow.

$$FeCl_3 + 3NH_4OH \quad Fe(OH)_3 + 3NH_4Cl \longrightarrow \quad (1)$$

$$2\,Fe(OH)_3\,Fe_2O_3 + 3\,H_2O \longrightarrow \quad (2)$$

## 2) PHOTO CATALYTIC DEGRADATION STUDIES

### 2.1 Preparation of dye solution

The stock solution of dyes (Rhodamine B & Bismarck brown) with known concentration (2000 ppm) was prepared and stored in brown bottles. It was diluted to get different required initial concentration of the dye and used in the photo degradation of dye experiment.

### 2.2 Measurement of concentration of dye solution

The stock solution is diluted to different initial concentration 10, 20,30….ppm for Rhodamine B and 10, 20 ,30……ppm for Bismarck brown in standard measuring flask by making necessary dilution with required volume of DD water.

The optical density (OD) of each dye solution was measured by visible spectrometer at $\lambda_{max}$ 493 and 532 for Bismarck brown and Rhodamine B respectively.

Plot of optical density versus initial concentration were drawn for both dyes. These arestandard graphs for estimation of dyes by interpolation technique. The values of optical density for dye solution before and after the degradation of dye were also obtained by using spectrophotometer. Using these optical densities the corresponding dye concentration were obtained from standard graphs by the interpolation technique.

### 2.3) BATCH KINETIC EXPERIMENT

Stock solution of dyes (2000ppm of Bismarck brown and 2000ppm of Rhodamine B ) were suitably diluted to the required initialconcentration of dye with DD water. Fifty ml of the dye solutions of known initial concentration ($C_i$) was taken in 100ml beaker.

Required amount of photo catalysts wasexactly weighed and then transferred into the dye solution with different $C_i$. The solutions were then exposed to any one of the energy source, namely direct sunlight, UV irradiation for a fixed period of contact time.After bleaching, the OD of these solutions were measured using spectrophotometer at 493nm and 532nm. Then the final or equilibrium concentrations ($C_e$) were obtained from the standard graph by interpolation technique. In all the batch degradation of dye experiments, the extent of removal of the dye in terms of the value of percentage removal of dye has been calculated using the following relationships.

$$\text{Percentage removed} = 100(C_i - C_e)/C_i \text{ -----------1}$$

Where

$C_i$= initial concentration of dye (ppm)

$C_e$=equilibration concentration of dye (ppm)

In the batch dye degradation technique, the effect of several factors governs the degradation process. The effect of various experimental parameters on degradation of Rhodamine B and Bismarck brown dyes in the aqueous suspension by iron oxide was studied.

## RESULT AND DISCUSSION

### 3.1) XRD pattern

The average particle size of the iron oxide particle was determined using theDebye – Scherrer's equation applied to major,peaks corresponding to intensity and is found tobe around 10 nm.The size of the synthesized iron oxide nanoparticleswas calculated from powder XRD pattern using Scherrer's formula.

$$t = 0.9\lambda/\beta\cos o$$

Where

$\lambda$ is the wavelength of incident X-Ray (1.5406Å)

$\beta$ isthe full width for half maximum and

$\theta$ is the Bragg's angle for the peak.

$\beta$ can be calculated using the equation

$\beta = (2\theta 2 - 2\theta 1)$

### 3.2) Effect of variation of initial concentration of Dyes from Aqueous solution of Their Binary Mixture

Keeping all other experimental parameters constant, the concentration of dye was changed from 100 to 800 ppm for photo degradation using iron oxide nano particles . It was exposed to sunlightand its effect on rate of bleaching was studied.The variation can be graphically represented asin Figure (3).

The photo catalytic bleaching was found to decrease with increase in concentration of dye. This may be due to the excess of dye molecule to be degraded by a small amount of catalyst and it will be up to optimum concentration of dye.

From this we can find the optimum concentration as 600 ppm each for Rhodamine B and Bismarck brown dyes for degradation by solar radiationand UV radiation for both the catalyst.

### 3.3) Effect of variation of Dose of Photo catalyst on the Photo degradation of dye

To study the effect of variation of dose of photo catalyst on the photo degradation,the kinetic experiment was carried out keeping the intial concentration (as600 ppm for both the dyes in all beakers) and pH (4.4) as constant and varying the dose of photo catalyst from 100 to 1300 mg .The photo catalytic removal of dye at optimum initial concentration and pH were carried out following the general procedure. From the spectrophotometric analysis the equilibrium concentration ($C_e$) can be determined. The variation can be represented graphically as in Figure (4).

Minimum amount of photo catalyst required for themaximum removal of dye was determined and fixed as optimum dose of photo catalyst.From this we can fix the optimum dose of photocatalyst as 600 mgfor degradation of mixture of dyes.

### 3.4) Effect of variation of pH on photo degradation of dyes

The effect of variation of pH of dye solution on photo degradation was determined by keeping the initial concentration and dose at optimum values in all experimentand varying thepH.The initial pH of dye solution was varied (1 to 8) by adding the required volume of 1N solution of HClorNaOH. Then pH was measured using digital pen pH meter ( Henna Instrument ).The degradationstudies were carried out following the general procedure.The variation can be graphically represented as in Figure (5).

It is established that surface properties of semiconductor are responsible for photo catalytic process. The hole generated by semiconductor creates $H^+$ ions in the solution from $H_2O$ .These protons are utilized by dissolved oxygen in solution.

$$2H^+ + H_2O \longrightarrow \frac{1}{2} O_2 + 2H^+ \quad (1)$$

$$2H^+ + O_2 + 2e^- \longrightarrow H_2O_2 \quad (2)$$

These two reaction counter balance each other to a particular extent.The surface charge on semiconductor favors the reaction when it is positive. This surface charge depends on the pH of the solution being positive in acidic and negative in alkali media .After a particular pH net charge on semiconductor surface become zero and is called point of zero discharge. Therefore with increasing pH surface concentration of dye molecules and $OH^-$radicals increases. All these factors are responsible for optimal value of pH in the decolourisation rate of dyes.

From this we can fix the optimum pH value for degradation studies. The optimum value was found out as 8 for degradation usingiron oxide ascatalyst.

### 3.5) Effect of Variation of Contact Time on the photo degradation of dye

In order to study theeffect of variation of contact time on the degradation ofRhodamine B and Bismarck brown dyes by exposure to sunlight and UV light experiments were carried out with optimum initial concentration of dye solution, optimum pH and optimum dose of photo catalyst at different values of contact time at $28^0$C.

The beakers containing required optimum initial concentration and pH were taken. Then the optimum dose of catalyst was added and immediately they were subjected to radiation. The beakers were removed at different intervals viz, 0.30, 1, 1.30, 2……..hours for sunlight and 0.30, 1, 1.30…… hours for UV light respectively. The solutionwereanalysed by the UV-Spectrophotometer. The equilibrium concentration of dye solution was obtained by measuring its Optical Density(OD).The variations are represented graphically in Figures (6&7).

The optimum contact time required for the maximum removal was found to be 2.30 hours for solar radiation and UV radiation.

### 3.6) Kinetic Studies

The photo catalytic degradation experiments were carried at various temperatures namely $28^0$ C, $38^0$C, $48^0$C foriron oxide as catalyst using solar radiation. The rate constant k , was determined from the first order plots of 2 + log ODvs Time . An increase in temperature helps the reaction to complete more efficiently with $e^-/H^+$ recombination.

The plots are represented in Figures (8&9).The calculated values of rateconstants are given in Table (1). With increase in temperature the rate constant values increases.The optimum condition required for maximum degradation is given in the Tables 2 &3.

## CONCLUSION

The co-precipitation technique has been used for the synthesis of iron oxide.The photo catalytic degradation of Bismarck brown and Rhodamine B dye from binary mixture of their aqueous solution can be carried out using$Fe_2O_3$.

Photo catalytic degradation of dyes can be carried out with two sources of radiation namely solar radiation and UV radiation and the reaction can process to almost degradation.Using this study the optimum conditions required for maximum degradation were determined

Solar radiation bring out 95 % degradation while UV, degrade up to 96%.The photo catalytic degradation of mixture of dye obeyed pseudo-first order kinetics. We are using minimum quantity of salts and there will be no harm in mixing small quantity of these salt in water stream.So we can use iron oxide for the degradation process. These resultswill be helpful in designing treatment plant in industries.

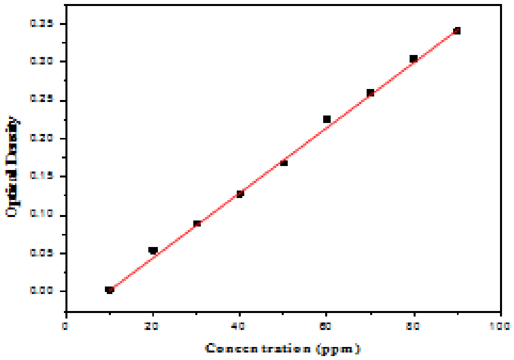

Fig. 1: Standard curve for Bismarck brown

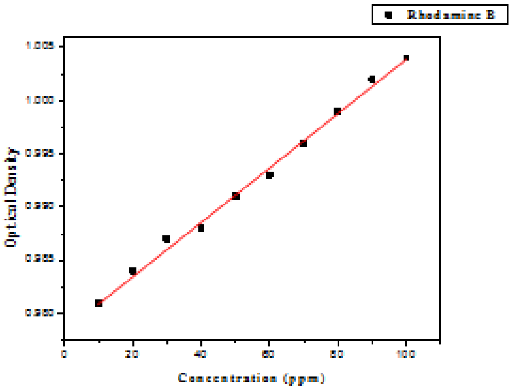

Fig. 2: Standard curve for Rhodamine B

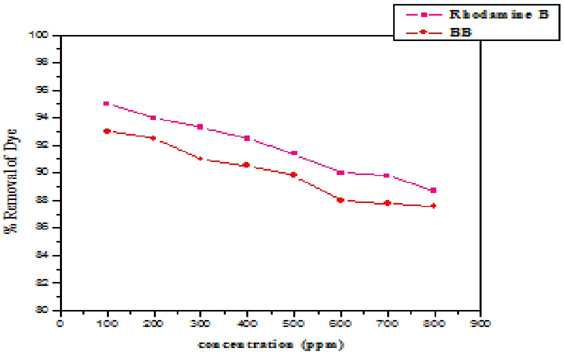

Fig. 3: Effect of variation of initial

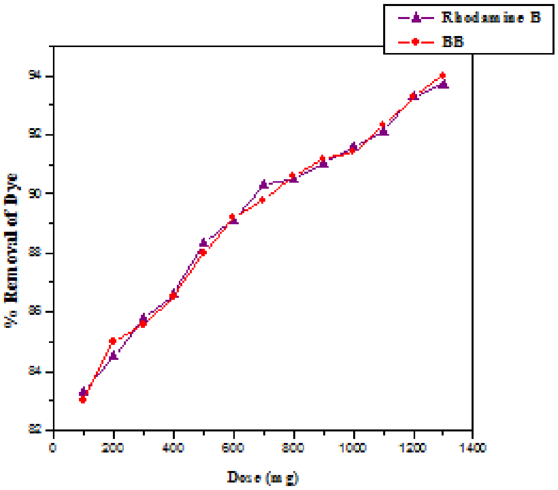

Fig. 4: Effect of variation of dose of photo catalyst concentration of dyes

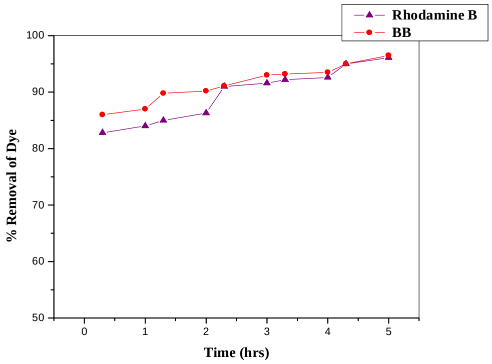

Fig. 5: Effect of variation of pH on the photo degradation

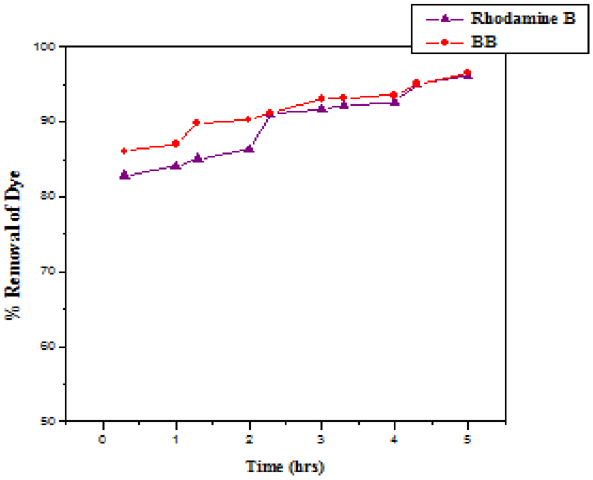

Fig. 6: Effect of variation of contact time on the photo degradation of dyesat 28$^0$C using sunlight

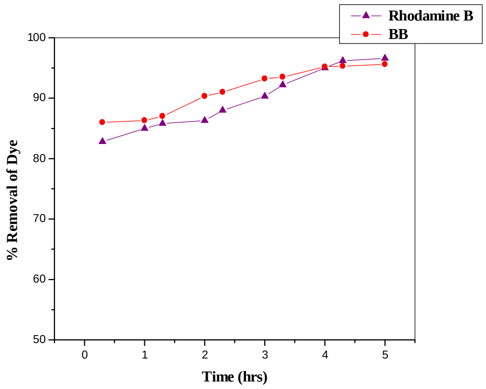

**Fig. 7: Effect of variation of contact time on the photo degradation of dyes at $28^0$C using photo reactor**

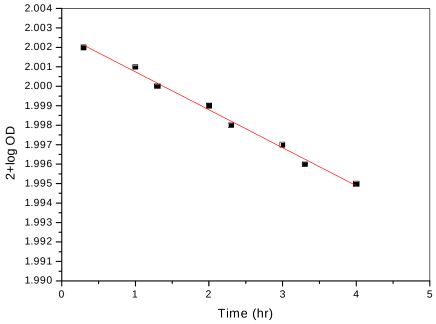

**Fig. 8: Kinetic plot for the degradation of Rhodamine B using solar radiation at $28^0$C.**

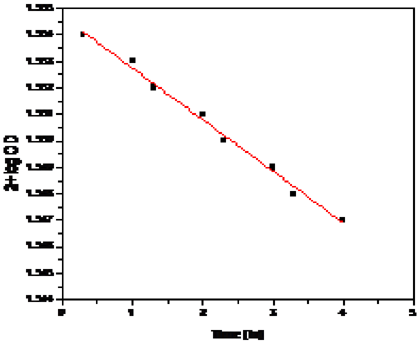

**Fig. 9: Kinetic plot for the degradation of Bismarck brown using solar radiation at $28^0$C.**

**Table 1: The rate constant values for degradation of dyes using iron oxide photo catalyst**

| Catalyst | Temperature | Rate constant (k) | |
|---|---|---|---|
| | | Rhodamine B | Bismarck brown |
| Iron oxide | $28^0$C | $0.45\times10^{-2}$ | $0.43\times10^{-2}$ |
| | $38^0$C | $0.61\times10^{-2}$ | $0.67\times10^{-2}$ |
| | $48^0$C | $1.2\times10^{-2}$ | $0.95\times10^{-2}$ |

**Table 2: Optimum condition required for degradation using synthesized iron oxide as catalyst**

| Radiation | Initial concentration (ppm) | pH | Dose (mg) | Contact Time (hrs) | % Removal of Dye | |
|---|---|---|---|---|---|---|
| | | | | | RhodamineB | Bismarck brown |
| Solar | 600 | 8 | 600 | 5 | 96.1 | 95.5 |
| UV | 600 | 8 | 600 | 5 | 96.5 | 95.6 |

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