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Photocatalytic degradation of basic Fuchsin over quaternary oxide iron zinc cuprate ($FeZn_2cu_3O_{6.5}$)

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ABSTRACT

The photocatalytic activity of iron zinc cuprate was investigated taking photodegradation of Basic fuchsin dye as a model system under visible light. The photocatalyst $FeZn_2Cu_3O_{6.5}$ was synthesized by the ceramic technique. Photocatalytic degradation of Basic fuchsin dye was observed spectrophotometrically and progress of the reaction was monitored at 544 nm. The optimum rate was observed as pH = 6.0, concentration of Basic fuchsin = 1.2×10^{-5} M, amount of $FeZn_2Cu_3O_{6.5}$ = 0.10 g and light intensity = 50.0 $mWcm^{-2}$. Quality parameters of water were also determined before and after treatment. Products received after degradation of dyes were also analyzed. A tentative has been mechanism proposed.

Keywords: Quaternary oxide, Photocatalyst, Basic fuchsin, Iron zinc cuprate.

INTRODUCTION

Effective removal of organic dyes has attracted increasing interest because of the long term environmental toxicity and short term hazards of organic dyes to public health. Solar energy, an abundant natural energy source has been successfully used for photocatalytic degradation of pollutants. Photocatalytic water splitting technology for hydrogen production has great potential as it is low cost and environmentally friendly to support the future hydrogen economy [1]. Many of the binary and ternary oxides like TiO_2, ZnO, $SrCrO_4$, $ZnAl_2O_4$, etc. have been used as photocatalyst in waste water treatment. Smith et al. [2] and Lazar et al. [3] have described recent developments in the field of photocatalytic water treatment using nanocrystalline titanium dioxide.

Mobtaker et al. [4] synthesized TiO_2/magnetite and TiO_2/Nd/magnetite using sol-gel method for decomposition of the Methyl orange as a pollutant. whereas photodegradation and mineralization of two azo dyes, Acid orange 7 (AO7) and Reactive red 2 (RR2) in aqueous TiO_2 suspension under UV irradiation was examined by Juang et al. [5] Photocatalytic degradation of Methyl orange was also observed by Chen et al. [6] using Ag/ZnO catalyst under UV irradiation. Ebrahimi et al. [7] have carried out photocatalytic decolourization of aqueous solution of Red-81 (5-Solamine) in presence of UV light irradiation and zinc oxide nanoparticle catalysts on granule glass at acidic pH.

Xu et al. [8] have reviewed the applications of iron oxide nanomaterials in waste water treatment. A range of environmental clean-up technologies has been proposed in waste water treatment with iron oxide nanomaterials as photocatalyst. Zhang et al. [9] synthesized $SnO_2/\alpha\text{-}Fe_2O_3$ semiconductor hierarchical nanoheterostrutures for photocatalytic degradation of Methylene blue under visible light irradiation. The photocatalytic degradation of Crystal violet in aqueous solution on suspended copper oxide semiconductor has been carried out by Shah et al [10].

Photocatalytic degradation of Malachite green and Crystal violet in aqueous suspension has been reported using $BaO_3TiO.SrO_3TiO$.[11] Vijay et al. [12] have carried out the photocatalytic degradation of Azure B in aqueous solution using barium tungsten oxide as semiconductor under UV irradiation. Ghorai and Biswas [13] synthesized $SrCrO_4$ and TiO_2 nano-sphere mixed oxides and used as catalyst for photodegradation of Rhodamine 6G in aqueous solutions. Zinc aluminate ($ZnAl_2O_4$) spinal was synthesized and used in degradation of organic pollutant in aqueous solution under sunlight [14]. Sadiq and Nesaraj [15] have investigated the use of NiO-Co_3O_4 nano-ceramic composites materials in photocatalytic degradation of Rhodamine B and Methyl orange under UV light irradiation. Huang et al. [16] synthesized $CdIn_2S_4$ and evaluated its photocatalytic activity by the decomposition of azo dye, Methyl orange under visible light irradiation.

Very little work has been carried out on the use of quaternary oxides and sulphides as photocatalyst as compared to binary and ternary oxides. Sharma et al. [17] studied the photocatalytic degradation of Celestine blue B in the presence of ammonium phosphomolybdate semiconductor under UV irradiation. The photocatalytic degradation of Methylene blue dye was also investigated with Bi_2AlVO_7 or Bi_2InTaO_7 as catalyst under visible light irradiation [18].

MATERIALS AND METHODS

2.1 Chemicals and Measurement

In the present study Basic fuchsin 4-[(4-aminophenyl)-(4-imino-1-cyclohexa-2,5- dienylidene)methyl]aniline hydrochloride, copper oxide, zinc oxide, Fe_2O_3, acetone, $HgSO_4$, Ag_2SO_4 and other chemicals were produced from Hi-Media chemicals (Figure 1) Basic fuchsin was used as a model system. The structure of Basic fuchsin is given in Figure 1.

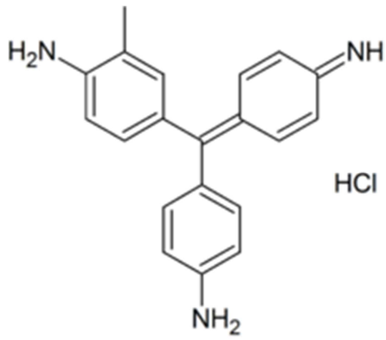

Figure 1: Structure of Basic fuchsin

Its molecular formula is $C_{20}H_{20}N_3.HCl$ and molar mass 337.86 g mol^{-1}. 1.0 × 10^{-3} M solution of Basic fuchsin (0.0364 g in 100 mL water) was prepared in doubly distilled water, which is used as stock solution. A solution of 1.2 × 10^{-5} M Basic fuchsin was prepared in doubly distilled water and 0.10 g of semiconductor was added to it. The pH of the reaction mixture was adjusted to 6.0 and this solution was exposed to a 200 W tungsten lamp (50.0 mW cm^{-2}). The pH of the solution was measured by digital pH meter (Systronic model 335) and the intensity of light was measured with the help of a solarimeter Surya Mapi (Model CEL 201). Visible spectrophotometer (Systronic Model 166) was used for measuring absorbance for Basic fuchsin different at time intervals. Some water parameters like pH, conductivity, salinity, TDS (Total dissolved solids) and DO (Dissolved oxygen) were determined with the help of water analyzer (Systronic water analyzer Model 371).

2.2 Synthesis of the Semiconductor

Iron zinc cuprate ($FeZn_2Cu_3O_{6.5}$), a quaternary oxide was prepared by ceramic technique. Mixture of fine powders of Fe_2O_3, CuO and ZnO were mixed and ground in mortar using 50 mL of acetone for maintaining homogeneity.

2.3 Calcination of Semiconductor

Mixture of quaternary oxide were fired at 800°C for 20 hr for calcination and then at 950°C for 25 hr. Electric Muffle furnace (Shivaki T-701) was used for calcination. After the firing was over, the mixture was cooled slowly to room temperature and ground to fine particles.

2.4 Photocatalytic Degradation

The photocatalytic degradation of Basic fuchsin dye by iron zinc cuprate as photocatalyst under visible light irradiation has been studied. The absorbance of Basic Fuchsin solution was determined with the help of spectrophotometer at λ_{max} = 544 nm. The progress of reaction was observed by measuring absorbance of the reaction mixture containing dye and semiconductor a regular time intervals during exposure. Decreasing trend of absorbance showed that dye was degraded during this process. A typical run is presented in Figure 2. It was observed that the absorbance of Basic fuchsin solution decreased with increasing time of exposure. A plot of 1 + log A against time was found to be linear, which indicates that the catalytic degradation of Basic fuchsin follows pseudo-first order kinetics. The rate constant for this reaction was determined with the help of equation k = 2.303 × slope. Rate constant (k) for a typical run was observed as 7.19×10^{-5} s^{-1}. It was observed that the color of Basic fuchsin regenerate after sometime, which means that this dye does not degrade completely, but only part of it was bleached.

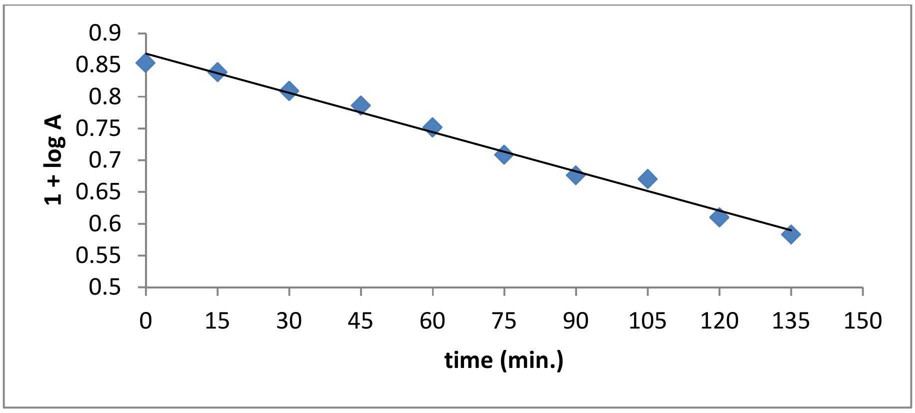

Figure 2: A typical run

RESULTS AND DISCUSSION

3.1 Effect of pH

The effect of pH on the rate of degradation of Basic fuchsin was investigated in the pH range 5.0-7.0. The results are reported in Table 1.

Table 1: Effect of pH

[Basic fuchsin] = 1.2×10^{-5} M

Light intensity = 50.0 mW cm^{-2}

Iron zinc cuprate = 0.10 g

pH	Rate Constant (k) × 10^5 (s^{-1})
5	2.81
5.5	4.87
6	**7.19**
6.5	5.76
7	4.65

It has been observed that the rate of photocatalyic degradation of Basic fuchsin increases as pH was increased and it attained optimum value at pH 6.0. Oxygen anion radicals are produced from the reaction between O_2 molecule and electron (e^-) in conduction band of the semiconductor. As the optimum pH is in acidic range, this super oxide anion radical will combine with proton forming $HO_2^{\bullet}$ radical. With the formation of more $HO_2^{\bullet}$ radicals, the rate of photocatalytic degradation of the dye increases. Above 6.0, a decrease in the rate of photocatalytic degradation of Basic fuchsin was observed, which may be due to the fact that cationic form of Basic fuchsin is converted to its neutral form, which does not face any attraction towards almost neutral or slightly positively charged surface of the semiconductor.

3.2 Effect of Basic fuchsin concentration
The effect of dye concentration was observed by taking different concentrations of Basic fuchsin. The results are summarized in Table 2.

Table 2: Effect of basic fuchsin concentration
pH = 6.0
Light intensity = 50.0 mW cm^{-2}
Iron zinc cuprate = 0.10 g

[Basic fuchsin] × 10^5 M	Rate Constant (k) × 10^5 (s^{-1})
0.7	1.86
0.8	3.36
0.9	4.22
1	5.18
1.1	5.84
1.2	**7.19**
1.3	5.7
1.4	4.54
1.5	3.71
1.6	3.07

It was observed that the rate of photocatalytic degradation of dye increases on increasing the concentration of Basic fuchsin up to 1.2×10^{-5} M. It may be attributed to the fact that as the concentration of the Basic fuchsin was increased, more dye molecules were available for excitation and consecutive energy/electron transfer and hence, an increase in the rate of degradation of the dye was observed. There was a decrease in degradation rate on increasing the concentration of dye above 1.2×10^{-5} M. This may be due to the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the sufficient light intensity to reach the surface of the photocatalyst at the bottom of reaction vessel.

3.3 Effect of amount of iron zinc cuprate
The amount of semiconductor may also affect the degradation of dye and hence, different amounts of iron zinc cuprate were used. The results are reported in Table 3.

Table 3: Effect of iron zinc cuprate
pH = 6.0
Light intensity = 50.0 mW cm^{-2}
[Basic fuchsin] = 1.2×10^{-5} M

Iron zinc cuprate (g)	Rate Constant (k) × 10^5 (s^{-1})
0.02	2.27
0.04	3.36
0.06	5.25
0.08	6.5
0.1	**7.19**
0.12	7.15
0.14	7.1
0.16	7.13

The rate of reaction was found to increase on increasing the amount of semiconductor, iron zinc cuprate. The rate of degradation reached to its optimum value at 0.10 g of the photocatalyst. Beyond 0.10 g, the rate of reaction becomes almost constant. After a particular value (0.10 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

3.4 Effect of light intensity
The effect of light intensity on the photocatalytic degradation of Basic fuchsin was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor. The results are given in Table 4.

Table 4: Effect of light intenstiy
pH = 6.0
[Basic fuchsin] = 1.2×10^{-5} M
Iron zinc cuprate = 0.10 g

Light intensity (mW cm^{-2})	Rate Constant (k) × 10^5 (s^{-1})
20	3.7
30	5.11
40	6.58
50	**7.19**
60	3.58
70	2.79

These data indicate that photocatalytic degradation of Basic fuchsin was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond 50.0 mW cm^{--2}. This may be due to some side reaction, and therefore, light intensity of medium order was used throughout the experiments.

3.5 Determination of quality parameters of water
Quality of water before and after photocatalytic degradation has been tested by measuring some parameters and results are summarized in Table 5.

Table 5: Water quality parameters

Parameter	Before photocatalytic degradation	After photocatalytic degradation
pH	6	7
Conductivity (µS)	151	180
TDS (ppm)	71.2	98.6
Salinity (ppt)	0.15	0.15
DO (ppm)	14.2	17.2
COD (mg/L)	40	20

3.5.1 pH – pH of reaction mixture was in acidic range before the degradation but after the photocatalytic degradation of the dye, pH reaches to almost neutral range, because dye particles are mineralized to a significant extent.
3.5.2 Conductivity – Conductance is the measurement of the level of concentration of ions in solution. After photocatalytic degradation, the conductivity of treated water was increased as the dye has mineralized into ions. Slight decrease in pH and increase in conductivity also confirms the minerlization of dye into CO_2 and inorganic ions such as CO_3^{2-}, NO_3^-, etc.

3.5.3 Total dissolved solids (TDS) and salinity – Dissolved solids refer to any minerals, salts, metal, cations, or anions dissolved in water. In general, the TDS results in an undesirable taste, which could be salty, bitter or metallic. It could also lead to gastrointestinal irritation .The dye has been mineralized into ions and as a result, the TDS and salinity of the dye solution was found to increase after degradation.

3.5.4 Dissolved oxygen (DO) – Dissolved oxygen gives an idea about physical and biological activity in water. The minimum standard limit is 5 ppm. Dissolved oxygen has been observed to increase in treated water, which also indicates mineralization of dye to a significant extant.

3.5.5 Chemical oxygen demand (COD) – COD of the dye solution before and after illumination has been determined by redox method. COD is measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO_2 and water. The photodegradation efficiency after 2 hrs of illumination has been found to be 50% for Basic fuchsin. As clear from data, COD of dye solution decreases after exposure indicating that dye undergoes photocatalytic degradation.

3.6 Mechanism
On the basis of these observations a tentative mechanism for photocatalytic degradation of Basic fuchsin dye has been proposed as follows:

$$^{1}BF_0 \xrightarrow{h\nu} {}^{1}BF_1$$

$$^{1}BF_1 \xrightarrow{ISC} {}^{3}BF_1$$

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB)$$

$$e^- + O_2 \longrightarrow O_2^{\cdot -}$$

$$O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet}$$

$$HO_2^{\bullet} + {}^{3}BF_1 \longrightarrow \text{Leuco BF}$$

$$\text{Leuco BF} \longrightarrow \text{Products}$$

Basic fuchsin absorbs radiations of desired wavelength and it is excited giving its first excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting iron zinc cuprate (SC) also utilizes this energy to excite its e^- to conduction band of the semiconductor. This electron can be abstracted by oxygen molecule (present in the form of dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will react with aproton to form $HO_2^{\cdot}$ radicals as the medium is acidic $HO_2^{\bullet}$ radicals will oxidize Basic fuchsin to its leuco form, which may be ultimately degrade to products. $^{\bullet}$OH radical does not participate as an active oxidizing species in the degradation as it was not affected reasonably in presence of hydroxyl radical scavenger (2-propanol). The presence NH_4^+ and Cl^- ions were confirmed by their usual chemical test. Carbon dioxide and water were the major products of degradation.

CONCLUSION

Iron zinc cuprate ($FeZn_2Cu_3O_6$; quaternary oxide) was synthesized by ceramic technique. The photocatalytic activity of iron zinc cuprate was observed. Result showed that the dye degradation was affected by pH, dye concentrations, catalyst amount and light intensity. The optimum rate of photocatalytic degradation was $k = 7.19 \times 10^{-5}\ s^{-1}$ was obtained. The results indicated that this quaternary oxide can be used as an effective catalyst for the photodegradation of Basic fuchsin. Quality of water before and after photocatalytic degradation has been determined by water parameters, after degradation the treated water can be reused in daily activity like cleaning, washing, etc.

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