Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

J. Chem. Pharm. Res., 2010, 2(3):1-9

ISSN No: 0975-7384
CODEN(USA): JCPRC5

Heterogeneous photo-fenton discoloration of the dye rose bengal over pillared bentonite containing iron

Rajeshwari Arora, Indu Bhati, Pinki B. Punjabi and Vinod K. Sharma*

Photochemistry Laboratory, Department of Chemistry, Mohan Lal Sukhadia University, Udaipur(Raj.), India

ABSTRACT

Rose bengal degradation was investigated under a heterogeneous photo-Fenton system. This heterogeneous photo-Fenton process is very suitable than homogeneous because the catalyst can be reused and avoid the possible pollution caused by the metal ions in the solution. Hydroxyl-Iron-pillared-bentonite was developed as a noble catalyst through exchange reaction, by pillaring on the natural clay support. Effect of various parameters like solution pH, H_2O_2 amount, dye concentration, amount of pillared clay (catalyst) was observed on the efficiency of the reaction. A tentative mechanism has also been proposed for this photocatalytic degradation of rose bengal.

Key words: Hydroxyl-Iron-pillared-bentonite; Photo-Fenton; Photocatalytic; Water pollution.

INTRODUCTION

Dye pollutants from the textile industries are a principal source of environmental contamination. The extensive use of chemicals and water by the textile mills results in the generation of large quantities of highly polluted wastewater. In general, the current practice in textile mills is to discharge the wastewater into the local environment without any treatment. Environmental contamination by these toxic chemicals is emerging as a serious global problem. Colored solutions containing dyes from effluents of textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage.

On the other hand, bleached dye solutions are less toxic and almost harmless. Secondly, the dye containing colored water is almost of no use but if this colored solution is bleached to give colorless water, it may be used for washing, cooling, irrigation and cleaning purposes. Therefore, there is a need to search for water treatment processes which are economical, ecofriendly and less time taking.

Many homogeneous photo-Fenton or photo-Fenton likes processes, which could generate OH radicals and destroy organic pollutants significantly, have been reported for the treatment of dye effluents [1-4]. In these systems, the compounds of iron ions are dissolved in water so they are called homogeneous photo-Fenton systems [5].

However, Fenton and photo-Fenton processes in homogeneous media require the removal of the sludge containing Fe ions after wastewater treatment, which is expensive in labor, reagents and time [6, 7]. These drawbacks have been overcome by using supported Fenton catalysts. Various supports used in heterogeneous photo-Fenton reactions have been reported, such as zeolites [8, 9] Naflon film or Naflon pallet [10, 11] polythelene copolymers [12] and silica fabrics [13, 14].

Pillared clay (PILC) represents a new class of microporous materials that have potential for the use as catalysts due to their unique properties and structures as well as low cost [15, 16]. Waste water treatment by catalytic wet oxidation using H_2O_2 and pillared clays containing iron as heterogeneous catalysts has been widely investigated [17, 18].

In the present work Hydroxyl-iron-pillared bentonite using various molar ratios was prepared and tested as heterogeneous catalysts for the photo-Fenton discoloration of rose bengal. In addition, the structural characteristic of the catalysts were also examined by using EDX method.

EXPERIMENTAL

All the chemicals used were of analytical grade. Na_2CO_3, $Fe(NO_3)_3$ and Bentonite were supplied by Himedia. Distilled water was prepared in own laboratory. Rose bengal, was of industrial grade and used without further purification. The structure of rose bengal is shown as (Fig. 1).

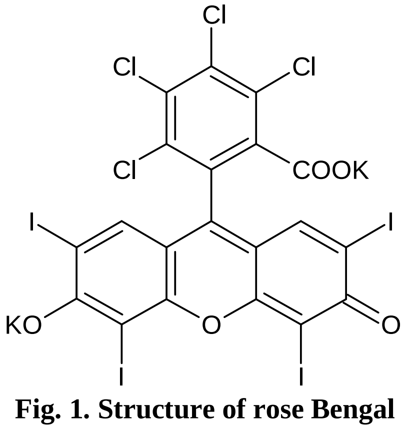

Fig. 1. Structure of rose Bengal

Preparation of catalysts

The hydroxyl-Fe-pillared-bentonite catalyst (H-Fe-P-B) was prepared by pillaring the bentonite (clay) through cation exchange process using the following procedure.

First, Na_2CO_3 was added slowly as powder into the solution of $Fe(NO_3)_3$ under magnetic stirring, until the ratio of $[Na^+] / [Fe^{3+}]$ became 1:1. Then the solution was aged at 60˚C for 1 day.

Second, the pillared solution was added to the clay suspension under stirring. The final $[Fe^{+3}]$ / clay ratio was equal to 2.0×10^{-2} M / Kg. The product was then filtered, washed with distilled water several times. Finally, this hydroxyl-Fe-pillared-bentonite catalyst was dried at 105˚C overnight. After drying the catalyst, it was analysed and was used for the photocatalytic degradation of dyes.

Characterization of the catalyst

EDX Method

Elemental detection of raw bentonite and iron-pillared bentonite (clay) catalyst was carried out by EDX model-INCA oxford. It was observed that iron content increased in pillared clay. Results are tabulated in Table 1 and are represented in Fig. 2 and 3.

Table. 1. Elemental analysis of raw bentonite and pillared clay, as catalyst having different atomic percentage of elements

Raw Bentonite (clay)	**O**	**Si**	**Al**	**Fe**	**Mg**	**K**
	74.24	19.52	4.76	0.28	0.69	0.51
Pillared Bentonite (clay)	71.94	20.80	4.75	1.17	1.06	0.29

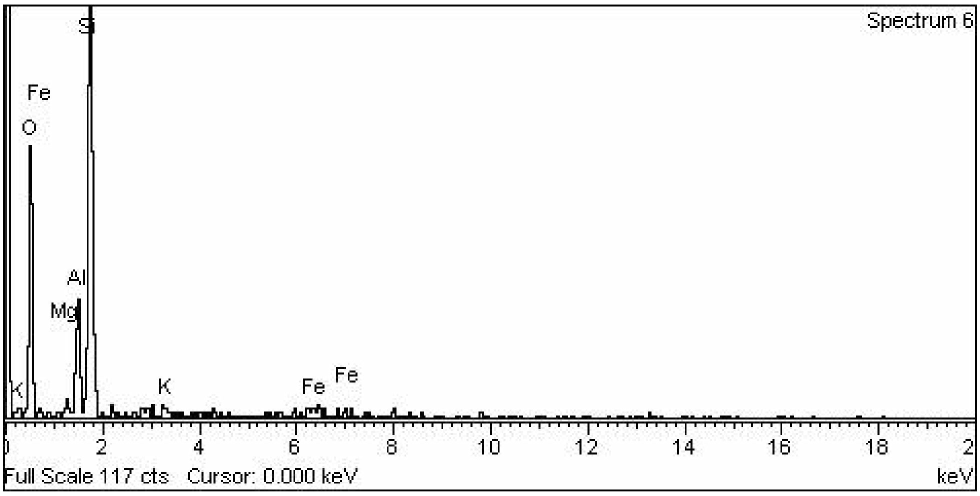

Fig. 2. EDX analysis of raw bentonite

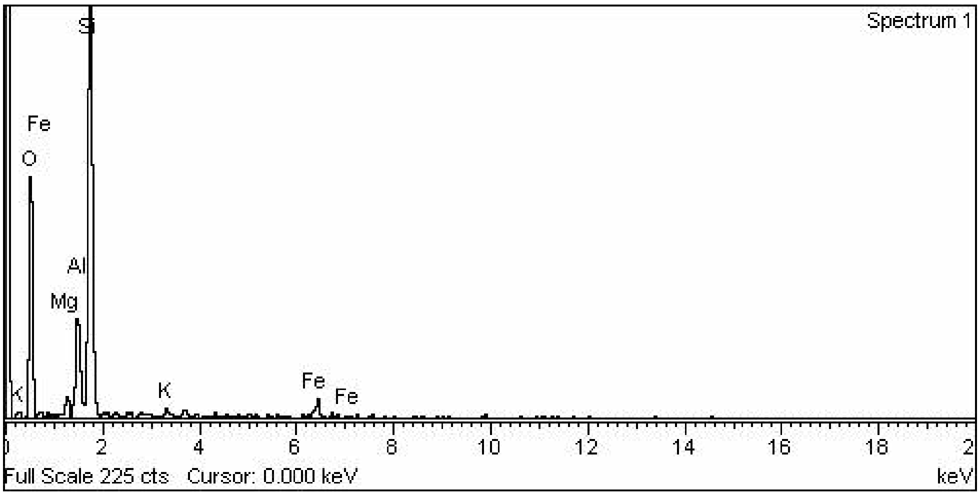

Fig. 3. EDX analysis of pillared bentonite

RESULTS AND DISCUSSION

An aliquot of 3.0 ml was taken out from the reaction mixture at regular time intervals and the absorbance was measured spectrophotometrically at λ max = 545 nm. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of rose bengal decreases with increasing time of exposure. A plot of 1 + log A versus time was linear and followed pseudo-first order kinetics. The rate constant was measured using following expression;

$$k = 2.303 \times \text{slope}$$

The typical run is graphically represented in Fig. 4

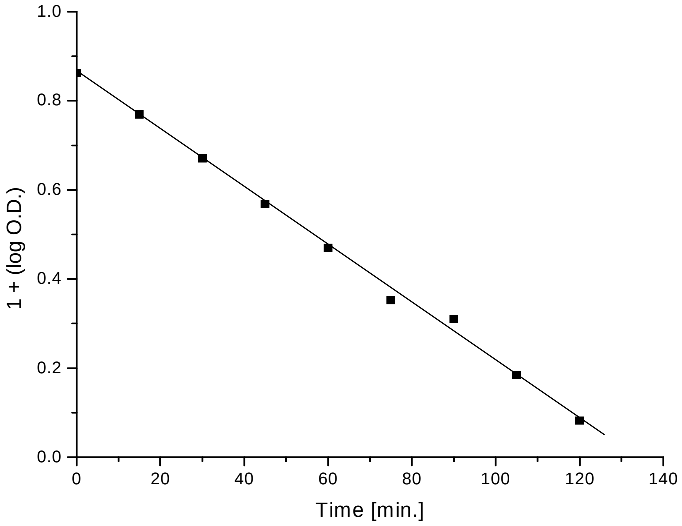

Fig. 4. A Typical run

Effect of pH

The effect of pH on the rate of degradation of rose bengal was investigated in the pH range of 6.0 to 9.0 using pillared clay as catalyst.

The photo-Fenton degradation depends strongly on the pH of the reaction medium as it is evident from Table 2. That the rate of photo-Fenton degradation of rose bengal increases with increase in pH up to 7.5 and then the rate of reaction decreases with increasing pH.

Table 2. Effect of pH

pH	**k x 10^4 (sec^{-1})**
6.0	1.37
6.5	1.43
7.0	1.80
7.5	**2.49**
8.0	1.68
8.5	1.08
9.0	0.64

[Rose Bengal] = 1.50 x 10^{-5} M, H_2O_2 = 1.0 mL, Light Intensity = 70.0 mW cm^{-2}, Amount of pillared clay = 0.12 g

The hydroxyl radicals are generated by two steps;

(i) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH$
(ii) $Fe^{3+} + H_2O \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+$

The increase in the pH of the medium will favour the step, (ii) where H^+ ions are formed along with hydroxyl radicals, whereas hydroxyl ions are generated in step (i). Thus, it may be concluded that the step (i) dominates over step (ii) in the pH range below 7.5. On the other hand, retardation of the reaction above pH 7.5 suggested, the dominance of step (ii) over step (i).

Effect of Rose bengal concentration

Effect of variation of dye rose bengal concentration on rate of reaction was also studied by taking different concentration of dye solution. The results were given in Table 3.

Table 3. Effect of dye concentration

[Rose bengal] x 10^5 M]	**k x 10^4 (sec^{-1})**
0.25	0.34
0.50	0.55
0.75	0.69
1.00	0.95
1.25	1.45
1.50	**2.49**
1.75	1.59
2.00	1.11

pH = 7.5, H_2O_2 = 1.0 mL, Light Intensity = 70.0 mW cm^{-2}, Amount of pillared clay = 0.12 g

The rate of photo-Fenton degradation was found to increase with increase concentration of dye rose bengal up to 1.50 × 10^{-5} M. On further increase of its concentration, a sudden decrease in the rate of degradation was observed. This may be explained on the basis that on increase the concentration of dye, more molecules of dye are available for degradation. However, on increase the concentration above 1.50×10^{-5} M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of dye was increased, it started acting like a filter for the incident light, where its larger concentration will not permit the desired light intensity to reach the dye molecule in the bulk of the solution and thus, a decrease in the rate of photo-Fenton bleaching of dye was observed.

Effect of hydrogen peroxide

The effect of amount of hydrogen peroxide on photodegradation of rose bengal was also investigated. The results are reported in Table 4.

Table 4. Effect of Hydrogen peroxide

H_2O_2 (mL)	k x 10^4 (sec^{-1})
0.5	1.20
1.0	**2.49**
1.5	1.46
2.0	1.12
2.5	1.09

[Rose Bengal] = 1.50×10^{-5} M, pH = 7.5, Light Intensity = 70.0 mW cm^{-2}, Amount of pillared clay = 0.12 g

It was observed that the rate of reaction increases on increase the amount of H_2O_2 and it attained an optimum value at H_2O_2 = 1.0 mL. Thereafter, the rate of degradation decreases on increase the amount of the hydrogen peroxide above 1.0 mL. This can be explained on the basis that more H_2O_2 molecules are available, on increase the amount of H_2O_2, for Fe^{2+} ions to react, which increases the number of $^{\bullet}OH$ radicals responsible for oxidative degradation of rose bengal. But after a fixed amount of H_2O_2 (1.0 mL), further increment in amount of H_2O_2 results into increase in the rates of eq. (5). $^{\bullet}OH$ radicals are consumed rapidly in eq. (5) due to availability of more H_2O_2 molecules. From eq. (3) and (5), $^{\bullet}OOH$ radicals are generated in large amounts. This $^{\bullet}OOH$ radical is utilized in eq. (7) and H^+ ions are produced. The production of H^+ ions is confirmed by a slight decrease in pH of the reaction mixture at the end of reaction. As a consequence, the rate of photodegradation decreases.

Table 5. Effect of amount of catalyst

Amount of catalyst (g)	k x 10^4 (sec^{-1})
0.04	1.33
0.06	1.92
0.08	2.01
0.10	2.13
0.12	**2.49**
0.14	2.30
0.16	1.40
0.18	0.84

[Rose Bengal] = 1.50×10^{-5} M, pH = 7.5, Light Intensity = 70.0 mW cm^{-2}, H_2O_2 = 1.0 mL

Effect of amount of pillared clay sample (catalyst)

The effect of variation in the amount of catalyst on photodegradation of rose bengal was investigated in the range of 0.04 to 0.18 g. and results are summarized in Table 5.

The rate of photo-Fenton degradation was found to increase with increase concentration of catalyst. Optimum value for the amount of different pillared clay samples was found to be 0.12 g. This can be explained on the basis that on increase amount of pillared clay sample results into increase in rate of eq. (ii). But after a certain limit, a reverse trend was observed. This may be explained on the basis that on increasing amount of clay sample results into increase in concentration of Fe^{3+} ions, this results into increase in the rates of eq. (3) generating $^{\bullet}OOH$ radical, which consumed more amount of Fe^{3+} ions and hence, Fe^{3+} ions are now less available for generation of $^{\bullet}OH$ radicals and the rate of photodegradation also decreases.

Effect of light Intensity

The effect of light intensity on the photocatalytic degradation of rose bengal was studied in the range 20.0 – 70.0 mW cm^{-2} and results are summarized in Table 6.

Table 6. Effect of light intensity

Light intensity(mW sec^{-2})	k x 10^4 (sec^{-1})
20	0.36
30	0.66
40	1.03
50	1.80
60	2.30
70	**2.49**

[Rose Bengal] = 1.50 x 10^{-5} M, pH = 7.5, H_2O_2 = 1.0 mL

The rate of photocatalytic bleaching of dye was found to increase on increasing light intensity because an increase in the intensity of light will increase the number of photons striking catalyst particles per unit time per square cm. As a result, more photons reacts with Fe^{+3} ions and there is an increase in the number of active species, the hydroxyl radicals and corresponding increases in the rate of reaction.

Mechanism

On the basis of experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for heterogeneous photo-Fenton degradation of rose bengal using H-Fe-P-B.

In the acidic solution, the exchange between the cations (Ca^{2+}, K^+, Na^+) in the bentonite interlayer and the H^+ in the solution resulted in increase of pH eq. (1). While in the alkaline solution, part of base will be consumed by surface hydroxyls of bentonite, which decreases the pH of solution eq. (2).

$$\text{Bentonite-}M^{n+} \qquad +H^+ \qquad \text{Bentonite–}H^+ + M^{n+} \tag{1}$$

$$\text{Bentonite-}OH_2^+ \xrightleftharpoons[+H^+]{+OH^-} \text{Bentonite–}OH \xrightleftharpoons[+H^+]{+OH^-} \text{Bentonite-}O^- \tag{2}$$

It is believed that the added base was mainly consumed by Fe polycation in the bentonite interlayer considering of hydrolysis process of Fe (III) salts [19-21]. As a result, the degradation of dye could proceed effectively by heterogeneous photo-Fenton process. The formation of hydroxyl radical is due to Fe^{2+} catalyzed decomposition of H_2O_2 eqs. (3 and 4).

$$Fe^{3+} + H_2O_2 + h\nu \longrightarrow Fe^{2+} + HOO^{\bullet} + H^+ \quad (3)$$
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH \quad (4)$$
$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + {}^{-}OH \quad (5)$$
$$Fe^{3+} + {}^{\bullet}O_2H \longrightarrow Fe^{2+} + O_2 + H^+ \quad (6)$$
$${}^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \quad (7)$$
$$\text{Rose Bengal} + {}^{\bullet}OH \longrightarrow \text{Products} \quad (8)$$

The ferric ions generates ${}^{\bullet}OOH$ radicals due to dissociation of H_2O_2 in presence of light. The incorporation of ${}^{\bullet}OH$ with H_2O_2 also produces ${}^{\bullet}OOH$ radical. Ferrous ions will undergo oxidation to ferric ions by addition of ${}^{\bullet}OH$ radicals while ferric ions get reduced to ferrous ions by incorporation of ${}^{\bullet}OOH$ radical, producing H^+ ion.

${}^{\bullet}OOH$ radicals are highly unstable in water and they undergo facile disproportionation rather than reacting slow with dye molecules. The participation of hydroxyl radical as an active oxidizing species was confirmed by using hydroxyl radical scavenger like isopropanol, where the rate of photodegradation was drastically reduced.

Further, this method has more advantages over other methods. It does not add to pollution any further. The active oxidizing species i.e. the hydroxyl radicals will dimerize to give hydrogen peroxide, which may degrade ultimately to water and oxygen. As in this reaction, very low concentration of chemicals is used and the process is cyclic in nature also, it may be concluded an ecofriendly method for the treatment of waste water.

CONCLUSION

Through the cation exchange process, hydroxyl-Fe pillared bentonite was developed as heterogeneous catalyst for photo-Fenton system.The elemental analysis as compared to the data of raw bentonite reveal that, the iron content, of H-Fe-P-B increased remarkably. Secondly, it is also interesting to know that PILCs could extend the range of pH values for Fenton-type oxidation. This observation seems to be important, since it is known that one of the major drawback of homogeneous photo-Fenton system is the limited range of pH (2.0-4.0). The acidification process to convert basic effluents to get acidic medium is more costly than the energy and oxidant used in Fenton degradation, which can be avoided by using H-Fe-P-B as a catalyst for degradation of rose bengal.

Acknowledgement

Authors are thankful to Dr. D. M. Phase, UGC-DAE-CSR, Indore for recording EDX.

REFERENCES

[1] K Wu; Y Xie; J Zhao; H Hidaka. *J. Mol. Catal. A*:, **1999**, 144, 77-84.
[2] EG Solozhenko; NM Soboleva; VV Goncharak. *Water Res.*, **1995**, 29, 2206-2210.

[3] F Herrara; J Kiwi; A Lopez; V Nadtochenko. *Environ. Sci. Technol*., **1999**, 33, 3145-3151.
[4] M Neamtu; A yediler; I Siminiceanu; A Kettrup. *J. Photochem. Photobiol. A*:, **2003**, 161, 87-93.
[5] J Feng; X Hu; PL Yue; HY Zhu. *Water Res*., **2003**, 37, 3776-3784.
[6] S Chou; C Huang. *Chemoshere*, **1999**, 38, 2719-2731
[7] DA Saltmiras; AT Lemley. *J. Agric. Food chem*., **2000,** 48, 6149-6157.
[8] M Rios-Enriquez; N Shahin; C Duran-de Bazua; J Lang; E Oliveros; SH Bassmann; AM Braun. *Solar Energy*, **2004**, 77, 491-501.
[9] SH Bossmann; E Oliveros; S Gob; M Kantor; A Goppert; L lei; PL Yue; AM Braun. *Water Sci. Technol*., **2001**, 44, 257-262.
[10] J Fernandez; J Bandara; A lopez; P Buffat; J Kiwi. *Langmuir*, **1999**, 15, 185-192.
[11] J Fernandez; J Bandara; A lopez; P Alberz; J Kiwi. *Chem. Commun*., **1998**, 1493-1494.
[12] MR Dhananjeyan; E Mielzcarski; KR Thampi; P Buffat; M Bensimon; A Kulik; J Mielcarski; J Kiwi. *J. Phys. Chem. B*:, **2001**, 105, 12046-12055.
[13] D Li; T Yuranova; P Albers; J Kiwi. *Water Res*., **2004**, 38, 3541-3550.
[14] A Bozz; T Yuranova; E Mielzcarski; J Mielzcarski; J Mielzcarsi; PA Buffat; P Latis; J Kiwi. *Appl. Catal. B: Environ*., **2003**, 42, 289-303.
[15] C Oaka; H Yoshida; M Horio; K Suzuki; T Hattori. *Appl. Catal. B: Environ*., **2003**, 41, 313-321.
[16] K-I. Shimizu; T Kaneko; T Fujishima; T Kodama; H Yoshida; Y Kitayama. *App. Catal. A Gen*., **2002**, 225, 185-191.
[17] E Guelou; J Barrault; J Fournier; J-M Tatibouet. *Appl. Catal. B: Environ*., **2003**, 44, 1-8.
[18] J Guo; M Al-Dahhan. *Ind. Eng. Chem. Res*., **2003**, 42, 2450–2460.
[19] JT Kloprogge. *J. Porous Mater*., **1998**, 5, 5-41.
[20] JY Bottero; A Manceau; F Villieras; D Tcoubar. *Langmuir*, **1994**, 10, 316-319.
[21] M. Charles; J.R. Flynn. *Chem. Rev*. **1984**, 84, 31-41.