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Synthesis, characterization of hydroxyl-Fe-pillared-bentonite and its use in heterogeneous photo-fenton degradation of rose bengal

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Abstract

The degradation efficiency of rose bengal in aqueous medium using the heterogeneous photo-Fenton process has been assessed. It was found that, the heterogeneous photo-Fenton process was relatively more suitable as compared to its homogeneous counterpart. In heterogeneous system, the catalyst can be reused and the possible pollution caused by the ferrous ions in solution of homogeneous process can also be avoided. Through cation exchange reaction, Hydroxyl-iron-pillared-bentonite was prepared and used as a solid catalyst for photo-Fenton process. Effects of various parameters like pH, dye concentration, amount of hydrogen peroxide, light intensity and amount of catalyst on the rate of reaction was observed. A tentative mechanism has been proposed for photo-Fenton degradation of rose bengal.

Key words: Rose Bengal, Photo-Fenton, Photodegradation, Water pollution.

Introduction

Inspite of many uses, dyes, pesticides and other agrochemicals are toxic recalcitrant compounds which may accumulate in the environment. The waste characteristics vary according to the process employed. Discharge of waste water into water sources nearby industries causes water pollution and affects water quality adversely including temperature, turbidity, pH, alkalinity, acidity, BOD, COD, and color. Color in waste water is imparted by the dyes used in dyeing and printing industries. The inadequate management of these effluents can have harmful consequences to human health.

As the dyes present in waste water degrades very slow under normal conditions, some treatment methods have to be employed to either remove or degrade the dyes present in waste water. A number of homogeneous photo-Fenton reactions involving degradation of dyes and other pollutants have been reported [1-4]. However, the major drawbacks of the homogeneous photo-Fenton reagent are that the pH has to be adjusted to a limited range (2.0-4.0). Moreover, it is difficult to remove the sludge containing Fe ions after the treatment. It requires both; additional cost and labor. If these ions are not removed, then they add further to the pollution of water.

To overcome these drawbacks, an attention has been focused on development of some newer heterogeneous catalyst in photo-Fenton process. Chen and Zhu [5] catalytically degraded orange–II by UV-Fenton with hydroxyl-Fe-pillared-bentonite in water. Selective hydroxylation of cyclic ethers with tert-butylhydroperoxide and hydrogen peroxide catalyzed by iron (III) and manganese (II) bipyridine complexes included in zeolite and bentonite was reported by Niassary et al. [6]. Peyrovi et al. [7] investigated oxidation of alcohols with tert-butylhydroperoxide catalyzed by Co (II) complexes immobilized between silicate layers of bentonite. Pernyeszi and Dekany[8] photocatalytically degraded hydrocarbons by bentonite and TiO_2 in aqueous suspensions containing surfactants. Chirchi and Ghorbel [9] used various Fe-modified montomorillonite samples for 4- nitrophenol degradation by H_2O_2.

Discoloration and mineralization of orange-II by using a bentonite clay based Fe-nanocomposite film as a heterogeneous photo-Fenton catalyst has been reported by Feng et al. [10]. Daneshvar et al. [11] studied photocatalytic degradation of the insecticide diaginon in the presence of nanocrystalline ZnO powder under UV-C light irradiation; Miyoshi et al. [12] discovered acid-base buffering capacity of bentonite and strong acidic properties of H-Fe-P-B. Bottero et al. [13] and Charles and Flynn. [14] have found that added base was mainly consumed by Fe polycation in the bentonite interlayer, which decreases the pH of solution. Lin and Gurol [15] studied the effect of temperature on degradation of azo dye, Acid Light Yellow G by heterogeneous UV-Fenton process while Chen and Zhu [16] degraded dyestuffs in water by heterogeneous UV-Fenton catalyst i.e. hydroxyl-Fe-pillared-bentonite.

However, negligible attention has been paid to modify bentonite so that it can be successfully used under exposure to visible light. Therefore, in the present work, it has been proposed to use ferric ions for modifying bentonite and use it for bleaching of rose bengal under visible light irradiation.

Materials and Methods

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).

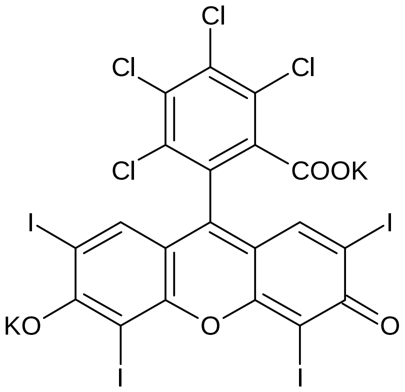

Fig. 1. Structure of rose bengal

Preparation of catalyst

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 1.25×10^{-1} 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 analyzed 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

	O	**Si**	**Al**	**Fe**	**Mg**	**K**
Raw Bentonite (clay)	74.24	19.52	4.76	0.28	0.69	0.51
Pillared Bentonite (clay)	70.45	20.64	5.24	1.86	0.95	0.87

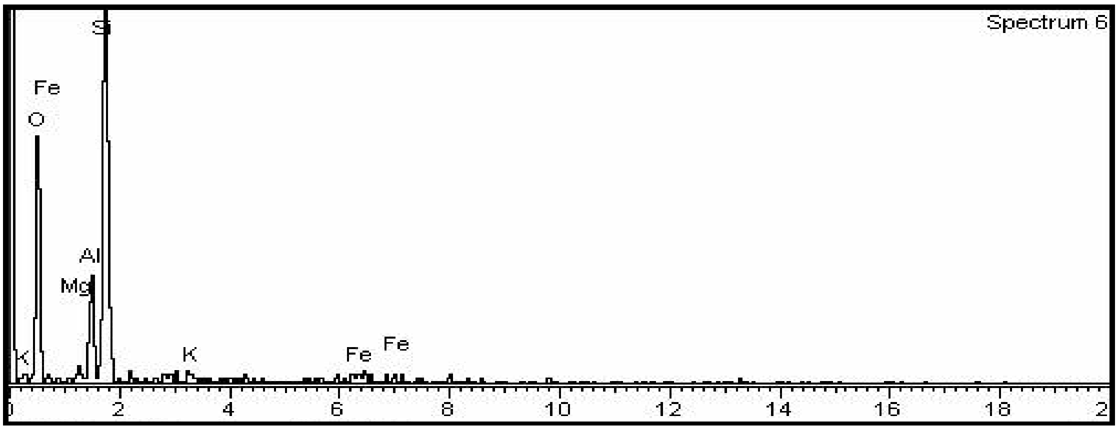

Fig. 2. EDX analysis of raw bentonite

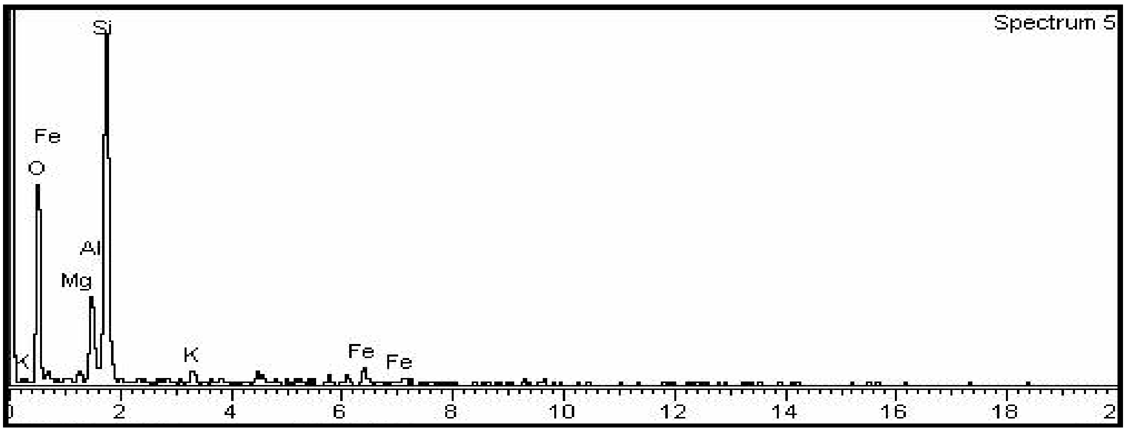

Fig. 3. EDX analysis of pillared bentonite

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 O.D. 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

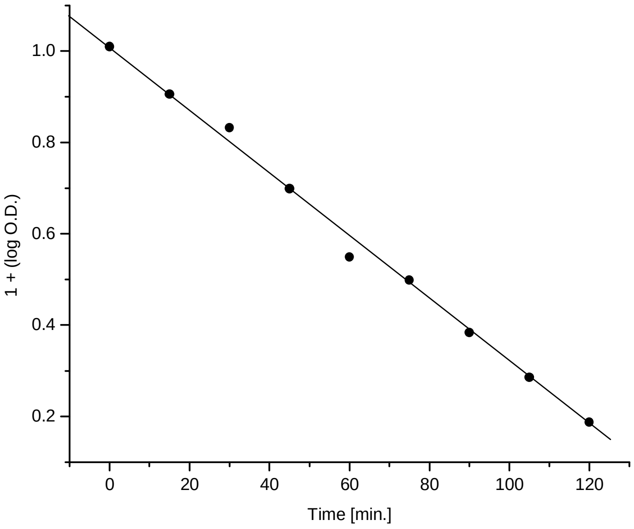

Fig. 4

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	1.27
6.5	1.55
7.0	1.90
7.5	**2.64**
8.0	1.79
8.5	1.17
9.0	0.75

[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 = 0.14 g

This effect may be explained on the basis of proposed mechanism; where the hydroxyl radicals are generated in eq. (3) and (5); both. The increase in the pH of the medium will favor the eq. (3) where H^+ ions are formed along with hydroxyl radicals, whereas hydroxyl ions are generated in eq. (5) and therefore, eq. (5) will not be favoured at higher pH values. The reverse trend is observed on decreasing the pH of the medium. Thus, it may be concluded that the eq. (5) dominates over eq. (3) in the pH range below optimum point. On the other hand, retardation of the reaction above optimum pH, suggests the dominance of eq. (3) over eq. (5).

Effect of Dye 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	0.52
0.50	0.80
0.75	0.95
1.00	1.03
1.25	1.55
1.50	**2.64**
1.75	1.66

pH = 7.5, H_2O_2 = 1.0 mL, Light Intensity = 70.0 mW cm^{-2}, Amount of pillared clay = 0.14 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	1.28
1.0	**2.64**
1.5	1.55
2.0	1.19
2.5	1.17

[Rose Bengal] = 1.50 x 10^{-5} M, pH = 7.5, Light Intensity = 70.0 mW cm^{-2}, Amount of pillared clay = 0.14 g

The rate of photocatalytic degradation of dyes increases with an increase in the amount of H_2O_2 up to a certain value i.e. 1.0 mL and starts decreasing beyond this limit. This can be explained on the basis that more H_2O_2 molecules are available, on increasing the amount of H_2O_2 for Fe^{2+} ions to react. It increases the number of $^{\bullet}OH$ radicals, which are responsible for oxidative degradation of dye. But after a fixed amount of H_2O_2, any further increment in the amount of H_2O_2 results into increase in the rate of eq. (5). $^{\bullet}OH$ radicals are consumed rapidly in eq. (6) due to availability of more H_2O_2 molecules. From eq. (4) and (6), $^{\bullet}OOH$ radicals are generated in large amounts. This $^{\bullet}OOH$ radical is utilized in eq. (8) and H^+ ions are produced. The production of H^+

ions was confirmed by a slight decrease in pH of the reaction mixture at the end of reaction. As a consequence, the rate of photodegradation decreases.

Effect of amount of pillared clay catalyst

The effect of variation in the amount of catalyst on photodegradation of rose bengal was investigated in the range of 0.04 to 0.16 g. and results are summarized in Table 5.

Table 5. Effect of amount of catalyst

Amount of catalyst (g)	**k x 10^4 (sec^{-1})**
0.04	0.78
0.06	0.95
0.08	1.03
0.10	1.74
0.12	2.34
0.14	**2.64**
0.16	2.12

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

It has been observed that initially, the rate of degradation of dye increases with an increase in the amount of catalyst but rate of dye degradation decreases after 0.14 g. This may be attributed due to the fact that an increase in the amount of pillared clay sample results into increase in rate of eq. (3). But after a certain limit, a reverse trend was observed. This may be explained on the basis that an increase in the amount of clay sample results into a corresponding increase in concentration of Fe^{3+} ions. This results into an increase in the rates of eq. (4) generating $^{\bullet}$OOH radical, which consumed more amount of Fe^{3+} ions in eq. (8) 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	0.40
30	0.75
40	1.18
50	1.98
60	2.40
70	**2.64**

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

The rate of degradation of dyes was accelerated as the intensity of light was increased because an increase in the intensity of light will increase the number of photons striking the catalyst particles per unit time per square cm. As a result, more photons will be responsible for an increase in the number of active species i.e. the hydroxyl radicals. This will result in corresponding increase in the rate of reaction. However; at higher light intensities, some thermal side reactions may also start, and hence, higher intensities of light were avoided.

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).

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

$$\text{Bentonite-OH}_2^+ \underset{+H^+}{\overset{+OH^-}{\rightleftharpoons}} \text{Bentonite-OH} \underset{+H^+}{\overset{+OH^-}{\rightleftharpoons}} \text{Bentonite-O}^- \tag{2}$$

$$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \tag{3}$$

$$Fe^{3+} + H_2O_2 + h\nu \longrightarrow Fe^{2+} + HOO^{\bullet} + H^+ \tag{4}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH \tag{5}$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow HOO^{\bullet} + H_2O \tag{6}$$

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + {}^{-}OH \tag{7}$$

$$Fe^{3+} + HOO^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^+ \tag{8}$$

$${}^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \tag{9}$$

$$\text{Dye} + {}^{\bullet}OH \longrightarrow \text{Products} \tag{10}$$

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. The rate of photodegradation was drastically reduced in presence of isopropanol.

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 reveals that, the iron content, of H-Fe-P-B increased remarkably. Secondly, it is also interesting to know that pillared clays (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 drawbacks 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.

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