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Photocatalytic Degradation Of An Organic Pollutant, Benzyl Alcohol Using An Enhanced Solar Photo-Fenton Process

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Abstract: A combined homogeneous and heterogeneous photocatalytic degradation of an organic pollutant, benzyl alcohol (BzOH) has been carried out using ferrous sulphate/ ferrioxalate with H_2O_2 and ZnO particles. Solar/ferrous/H_2O_2/ZnO and Solar/ferrioxalate/ ZnO processes are found to be more efficient than the individual photo-Fenton and Solar/ZnO processes. The experimental parameters such as pH, initial H_2O_2, Fe^{2+}, ferrioxalate and ZnO concentration strongly influenced the pollutant removal rate in Solar processes. The optimum operating conditions of these two combined processes are reported. The photodegradation kinetics is discussed in terms of Langmuir-Hinshelwood kinetic model.

Keywords: Benzyl alcohol, photo-Fenton, Ferrous ion, Ferrioxalate, H_2O_2, ZnO, Solar light.

1. Introduction

Hazard organic compounds released into the environment result in environmental damage as pollutants. The removal of toxic organic compounds from industrial wastewater effluents is of growing concern and there is an urgent need to develop strategies to deal with organic compound contaminated wastewater. Oxidation of Organic compounds in the presence of Fe^{2+} and hydrogen peroxide was first observed by Fenton in 1894[1], but its mechanism was not known till 1934. The oxidation power of this process was later attributed to the generation of hydroxyl radical formed during the catalytic decomposition of hydrogen peroxide in acid media[2] as shown in equ(1).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$

The efficiency of hydroxyl radical in Oxidation of organic compounds has been well established by various advanced Oxidation processes[3-6]. When Fenton's reagent combined with UV-Visible irradiation, the efficiency of organic compounds degradation has considerably improved due to the continuous regeneration of Fe^{2+} via photo reduction of Fe^{3+} [7]. The decomposition of hydrogen peroxide is also catalyzed by ferric ion[8] on irradiation. The utility of the Fe^{3+}/H_2O_2 reagent to destroy organic pollutants in water medium has been well demonstrated[9-13].

The ferric ion forms stable complexes. The photosensitivity of ferrioxalate is known for a long time and it has been widely used as chemical actinometer. Its photolysis has been reported as follows[14].

$$[Fe\,(C_2O_4)_3]^{3-} + h\nu \longrightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-\bullet} \qquad (2)$$

$$C_2O_4^{-\bullet} + [Fe\ (C_2O_4)_3]^{3-} \longrightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \qquad (3)$$

$$C_2O_4^{-\bullet} + O_2 \longrightarrow 2CO_2 + O_2^{-\bullet} \qquad (4)$$

The use of ferrioxalate in the photo-Fenton reaction for the degradation of organic pollutants was reported to be very effective by safarzadeh- Amri and cowokers[15]. They observed higher degradation efficiency of trichloroethylene and toluene with ferrioxalate than using either TiO_2 or Fe^{3+} in the presence of H_2O_2 under solar irradiation. Another interesting aspect of the use of ferrioxalate in photodegradation processes is that the higher portion of the solar spectrum can be utilized when compared to ZnO due to its high absorption upto 450 nm.

Photodegradation of pollutants using ZnO with solar light can make it economically viable process since solar energy is an abundant natural energy source nobody can claim for it, so we trap the solar energy and utilize it. This solar energy can be used instead of artificial light sources. The artificial light sources need high electrical power, which is costly and hazardous. When the process is carried out using solar radiation it becomes a green chemical process. This feature favours its application for wastewater treatment using solar energy as source of irradiation

The photodegradation of organic compounds using ZnO particles in the presence of UV/ Solar radiation has been known to have many advantages. (i).The large numbers of organic compounds dissolved (or) dispersed in water undergo complete mineralization. (2) ZnO is relatively inexpensive, so ZnO has been extensively used in the mineralization of toxic organic contaminants present in the wastewater[16-18]. Though solar light can been limited by low quantum yields due to its absorption up to 380 nm, which corresponds to about only 3% of total solar energy available. In the case of ferrioxalate, about 18% of solar irradiation can be absorbed by the complex[15]. Even though the homogeneous photo-Fenton processes are faster than semiconductor mediated photocatalytic processes, the semiconductor processes are found to be more efficient in complete mineralization. Hence, a combined homogeneous and heterogeneous process may be very efficient for degradation. In our earlier studies we have reported the degradation of some of the organic pollutants using the advanced oxidation processes[19-23].

In the present work, for we have investigated the solar photodegradation of an organic pollutant, benzyl alcohol (BzOH) with the combined ZnO-mediated photo-Fenton process using ferrous or ferrioxalate. The electronic spectrum of benzyl alcohol is given in Fig-1.

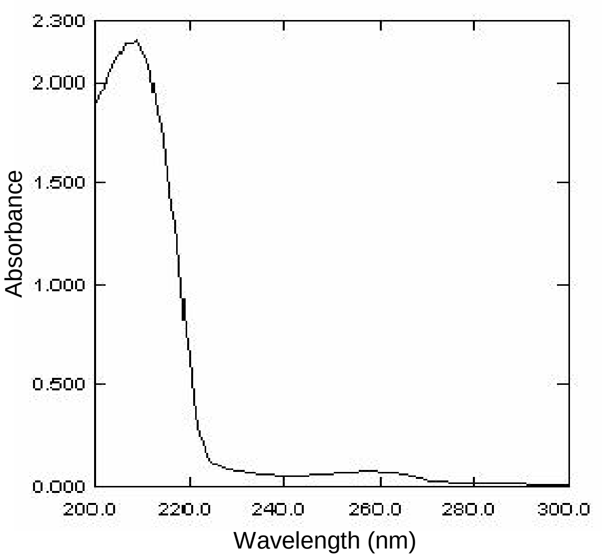

Fig. 1. Electronic spectrum of benzyl alcohol

2. Experimental

2.1. Materials

The photocatalyst Zinc oxide was purchased from E.Merck (99% purity). ZnO has a particle size 0.1-4 µm and surface area 10 m^2/g. The experiments were carried out in slurry form of the catalyst. Benzyl alcohol (E. Merck), AnalaR H_2O_2 (30% w/v), $FeSO_4.7H_2O$ (E.Merck) and all other reagents were used as received. Potassium-trioxalatoferrate(III)-$K_3[Fe(C_2O_4)_3]$-(ferrioxalate) was prepared and purified[24]. The experimental solutions were prepared using double distilled water.

2.2.1. Irradiation experiments

For the photolysis experiment, a desired molar ratio of benzyl alcohol/Fe^{2+}/$^{3+}$/H_2O_2/ZnO solutions were freshly prepared from benzyl alcohol stock solution, $FeSO_4.7H_2O$, $K_3[Fe(C_2O_4)_3]$, H_2O_2 and ZnO. Benzyl alcohol stock solution was used as a synthetic wastewater. Irradiated aqueous suspensions always contained 100 mg/50 mL of ZnO and 3×10^{-3} mol/L of initial benzyl alcohol concentration. All photochemical reactions were carried out under identical conditions. All photocatalytic degradations was carried out under similar conditions on sunny days between 11 A.M to 2 P.M. Open borosilicate glass tube of 50 mL of capacity, 40 cm height and 20 mm dia was used as the reaction vessel. The suspensions were magnetically stirred in dark for 30 min to attain adsorption-desorption equilibrium between BzOH and ZnO. Irradiation was done in the open-air condition. The reaction mixture continuously aerated by a pump to provide oxygen and for the complete mixing of the reaction solution.

2.3. Analysis

In all experiments 50 mL of reaction mixture was irradiated. At specific time intervals 1-2 mL of the sample was withdrawn and centrifuged to separate the ZnO. One mL of the sample was suitably diluted and its absorbance at 207 is used to monitor the degradation of benzyl alcohol. UV spectral measurements were made using SHIMADZU UV 1650 PC UV-Visible spectrophotometer. The pH of the solution is measured by using HANNA Phep (model H 198107 digital pH meter).

2.4 Solar light intensity measurement

Solar light intensity was measured for every 15 minutes and the average light intensity over the duration of each experiment was calculated. The sensor was always set at the position of maximum intensity. The intensity of Solar light was measured using LT Lutron LX-10/A digital Lux meter. The intensity was nearly constant during the experiments.

3. Results and discussion

3.1. Photodegradability of benzyl alcohol (BzOH) by Solar light

The photodegradation of BzOH using photo-Fenton process with ferrous (or) ferrioxalate in presence of ZnO using solar light was carried out. The results are given in Table 1. The controlled experiments have been carried out for the comparison of the efficiencies and the results are compiled in Table. 2 .

It is clear that the dye is resistant to direct photolysis by solar light and irradiation in the presence of ferrous ion alone. Irradiation with ferrioxalate causes 5.4% of degradation in 30 minutes. The photodegradation of pollutant is due to the formation of hydrogen peroxide and ferrous ion (Fenton reagent) during the photolysis of ferrioxalate eqs 2-7.

$$O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet} \qquad (5)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (6)$$

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (7)$$

Table 1: Photodegradability of BzOH by Solar light on combined processes

Time (min)	Percentage of BzOH remaining	
	Fe^{2+}/BzOH/H2O2/ZnO/Solar	Fe^{3+}/BzOH/H2O2/ZnO/Solar
0	**96.2**	**95.1**
15	**83.9**	**81.7**
30	**76.4**	**65.0**
60	**60.7**	**49.7**
90	**49.9**	**30.6**
120	**41.6**	**23.8**

[BzOH] = 3 ò 10^{-3} mol/L, pH = 3 ï 0.1, ZnO = 100 mg, H2O2 = 10 mmol,
Fe^{2+} = 0.6 mmol (Ferrous process), Fe^{3+} = 0.6 mmol (Ferric process).

Table 2: a The degradation efficiencies of various processes

Process	Condition*	Reaction time (minutes)	% of degradation
1. BzOH/Solar		**120**	**0**
2. BzOH/ferrous/Solar	Fe^{2+} - 0.6 mmol	**120**	**0**
3. BzOH/ferricoxalate/Solar	Fe^{3+} - 0.6 mmol	**30**	**5.4**
4. BzOH/H2O2/Solar	H_2O_2 - 10 mmol	**30**	**6.8**
5. BzOH/ZnO/Solar	ZnO - 100 mg	**30**	**7.5**
6. BzOH/ferrous/H2O2/dark	Fe^{2+} - 0.6 mmol H_2O_2 - 10 mmol	**30**	**10.1**
7. BzOH/ferricoxalate/H2O2/dark	Fe^{3+} - 0.6 mmol H_2O_2 – 10 mmol	**30**	**3.0**
8. BzOH/ferrous/H2O2/Solar	Fe^{2+} - 0.6 mmol H_2O_2 – 10 mmol	**30**	**15.6**
9. BzOH/ferricoxalate/H2O2/Solar	Fe^{3+} - 0.6 mmol H_2O_2 – 10 mmol	**30**	**21.3**
10. BzOH/ferrous/H2O2/ZnO/Solar	Fe^{2+} - 0.6 mmol H_2O_2 - 10 mmol ZnO = 100 mg	**30**	**23.6**
11. BzOH/ferricoxalate/H2O2/ZnO/Solar	Fe^{3+} - 0.6 mmol H_2O_2 - 10 mmol ZnO = 100 mg	**30**	**35.5**

***BzOH = 3 ò 10^{-3} mol/L, pH = 3 ï 0.1 for all reactions.**

[25]reported the formation of H_2O_2 in ferrioxalate photolysis is related to pH, irradiation intensity and the concentration of ferrioxalate. The solar/H_2O_2 degradation process is less efficient 6.8% than solar/ZnO process 7.5%. For ferrous/H_2O_2 and ferrioxalate/H_2O_2, 10.1 and 3.0% of degradation were observed respectively in dark. BzOH removal was obtained in ferrous/H_2O_2 due to the production of hydroxyl, radical in the process. In the solar/H_2O_2 the removal efficiency is lower than that of ferrous/H_2O_2/dark process. Fe^{2+} catalyzed decomposition of H_2O_2 is more than the solar catalyzed decomposition of H_2O_2.

Though the ferric ion catalyzes the decomposition of H_2O_2 in dark (10) its efficiency is very low when compared to ferrous ion. Hence the degradation in ferrioxalate/H_2O_2/dark process is 3.0% whereas in ferrous/H_2O_2/dark process 10.1% in 30 minutes. This is because of the low reactivity of ferric ion towards hydrogen peroxide in dark. This iron oxalate complex generates Fe(II) only on irradiation and hence the removal efficiency is very much increased for ferrioxalate/H_2O_2 when irradiation for 30 min with ferrioxalate/H_2O_2 causes 21.3% degradation.

In ferrous/H_2O_2/solar process, the removal of BzOH (pollutant) is due to generation of hydroxyl radical by (i) Fenton reaction (equ. 7), (ii) direct photolysis of H_2O_2 (equ. 8) and (iii) photo reduction of Fe^{3+} formed during the irradiation (equ.9).

$$H_2O_2 \longrightarrow {}^{\bullet}OH + {}^{\bullet}OH \qquad (8)$$

$$Fe^{3+} + H_2O + h\nu \longrightarrow {}^{\bullet}OH + Fe^{2+} + H^+ \qquad (9)$$

In ferrioxalate/H_2O_2/solar process, the degradation of pollutant (BzOH) is due to the fast generation of Fe^{2+} ion by photolysis of ferrioxalate. Ferrioxalate absorbs strongly at longer wavelength generating Fe^{2+} ion and the reported quantum yield of Fe(II) generation is about 1.0-1.2 for the irradiation with the light in the range of 250-450 nm[26].

The degradation efficiencies of both photo-Fenton processes increases sharply in the presence of ZnO. For 30 min, ferrous/H_2O_2/ZnO/solar process causes 23.6% degradation, whereas in ferrioxalate/H_2O_2/ZnO/solar process 35.0% degradation are observed.

The relative efficiencies of the above processes are in the following order: BzOH/ferrioxalate/H_2O_2/dark<BzOH/ferrioxalate/Solar<BzOH/H_2O_2/Solar<BzOH/ZnO/Solar<BzOH/ferrous/H_2O_2/dark<BzOH/ferrous/H_2O_2/Solar<BzOH/ferrioxalate/H_2O_2/Solar <BzOH/ferrous/H_2O_2/ZnO/ Solar <BzOH/ferrioxalate/H_2O_2/ZnO/ Solar

Among all these processes, the combined ZnO (heterogeneous) and photo-Fenton (homogeneous) processes are found to be more efficient in the degradation. The higher efficiencies of these two processes are due to additional hydroxyl radicals produced by the ZnO on irradiation.

Among the two photo-Fenton processes, the ferrioxalate/H_2O_2/ZnO/solar process is found to be more efficient than ferrous/H_2O_2/ZnO/solar process. This is because of the high molar absorption coefficient of ferrioxalate in the wavelength region of 200-450 nm[15]. The effects of various parameters on these two combined (ferrous/H_2O_2/ZnO/solar and ferrioxalate/H_2O_2/ZnO/solar) Processes have been investigated.

3.2 Effect of pH

pH is an important parameter for photo-Fenton processes. The pH of the solution controls the production rate of hydroxyl radical concentration and the nature of iron species in solution. The effects of pH on degradation of BzOH are shown in Fig. 2. The results indicate that both processes are efficient at pH 3. Increase of pH from 1-3 increases the degradation from 1.2 to 23.6% and 10.6 to 35.0% at the time of 30 minutes for ferrous and ferrioxalate processes respectively.

Above pH 3 the degradation decreases in both processes. The optimum pH of 3 obtained for these two processes shows that the conditions of photo-Fenton processes are predominant over UV/ZnO process in these combined processes. In these process the decrease in degradation at pH above 3 is due to the coagulation of hydro complex of Fe^{3+} formed during the reaction[27] At low pH the removal rate is limited due to the hydroxyl radical scavenging effect of H^+ ion (equ. 10)[28]

$${}^{\bullet}OH + H^+ + e^- \longrightarrow H_2O \qquad (10)$$

3.3 Effect of initial ferrous and ferrioxalate dosage

The effects of addition of ferrous and ferrioxalate on the degradation of BzOH are shown in **Table 3.** Increase of ferrous dosage from 0.2 to 0.6 mmol increases the degradation from 7.0 to 23.6% in 30 minutes. Further increase from 0.6 to 2 mmol decreases the removal rate. The increase in the removal rate is due to increase in the hydroxyl radical production by ferrous ion.

In ferrioxalate process, increase of initial ferrioxalate concentration from 0.2 to 0.6 mmol increases the degradation from 23.5 to 35.0% in 30 minutes. Further increase from 0.6 to 2 mmol decreases the removal rate. The generation of Fe^{2+} is likely to be the main step of photodegradation in ferrioxalate system. Since the light absorption fraction particularly at longer wavelength region is greater than Fe^{2+} ion the increase of ferrioxalate concentration increases photon absorption producing more Fe^{2+} ion. The reported quantum yield of formation of Fe^{2+} from ferrioxalate above one in the wavelength region 250-400 nm also confirms this. This results in the increase of removal rate. But when the ferrioxalate concentration is above 0.6 mmol, the light penetration through the irradiated solution decreases and the ferrioxalate at higher concentration produces less reactive hydroperoxy radicals[29].

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (11)$$

The optimum amount of ferrous and ferrioxalate is found to be 0.6 mmol for both the processes.

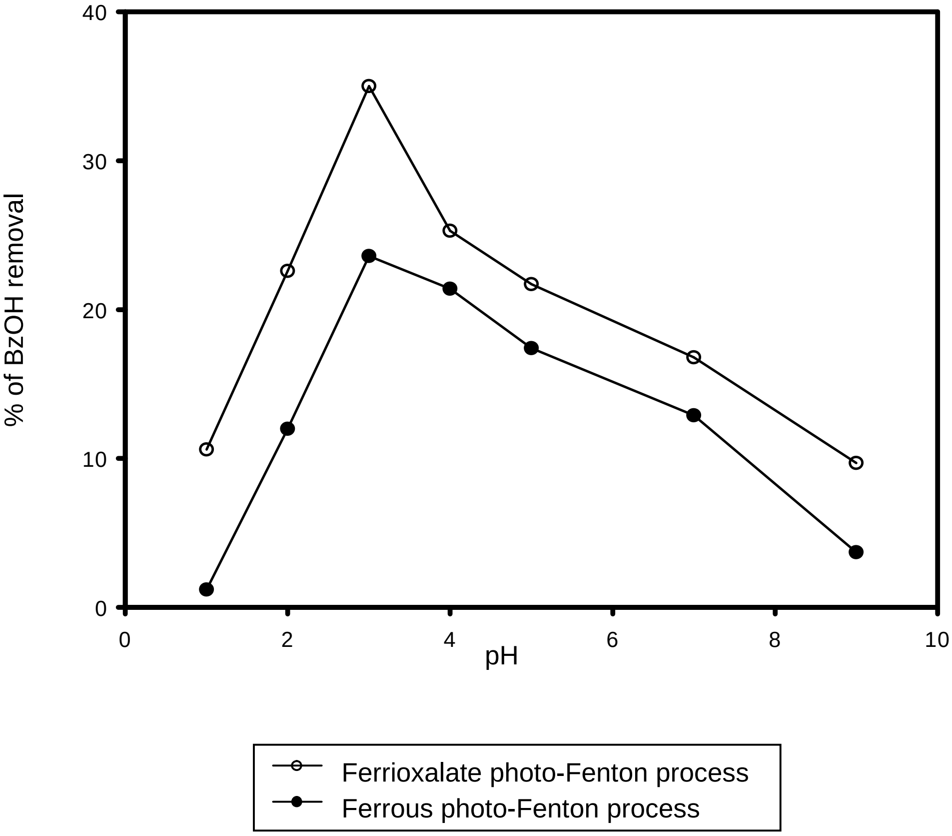

Fig. 2. The effect of pH on combined processes (Solar)
$[BzOH] = 3 \times 10^{-3}$ mol/L, H_2O_2 = 10 mmol, ZnO = 100 mg,
Fe^{2+} = 0.6 mmol (Ferrous process), Fe^{3+} = 0.6 mmol (Ferric process),
Irradiation time = 30 minutes.

Table 3: Effect of initial ferrous and ferricoxalate dosage on combined processes

Amount of ferrous/ferric added in mmol	Percentage of degradation	
	Fe^{2+}/BzOH/H2O2/ZnO/Solar	Fe^{3+}/BzOH/H2O2/ZnO/Solar
0.2	**7.0**	**23.5**
0.4	**14.7**	**28.8**
0.6	**23.6**	**35.0**
0.8	**22.2**	**30.3**
1.0	**20.0**	**28.5**
1.5	**10.6**	**19.5**
2.0	**4.4**	**7.9**

[BzOH] = 3 ò 10^{-3} mol/L, pH = 3 ï 0.1, ZnO = 100 mg, H2O2 = 10 mmol,
Irradiation time = 30 minutes.

3.4 Effect of added hydrogen peroxide

The initial concentration of H_2O_2 plays a very important role in the oxidation of organic compounds in photo-Fenton processes. The effects of addition of H_2O_2 on the ferrous and ferrioxalate photo-Fenton process are shown in Fig.3.

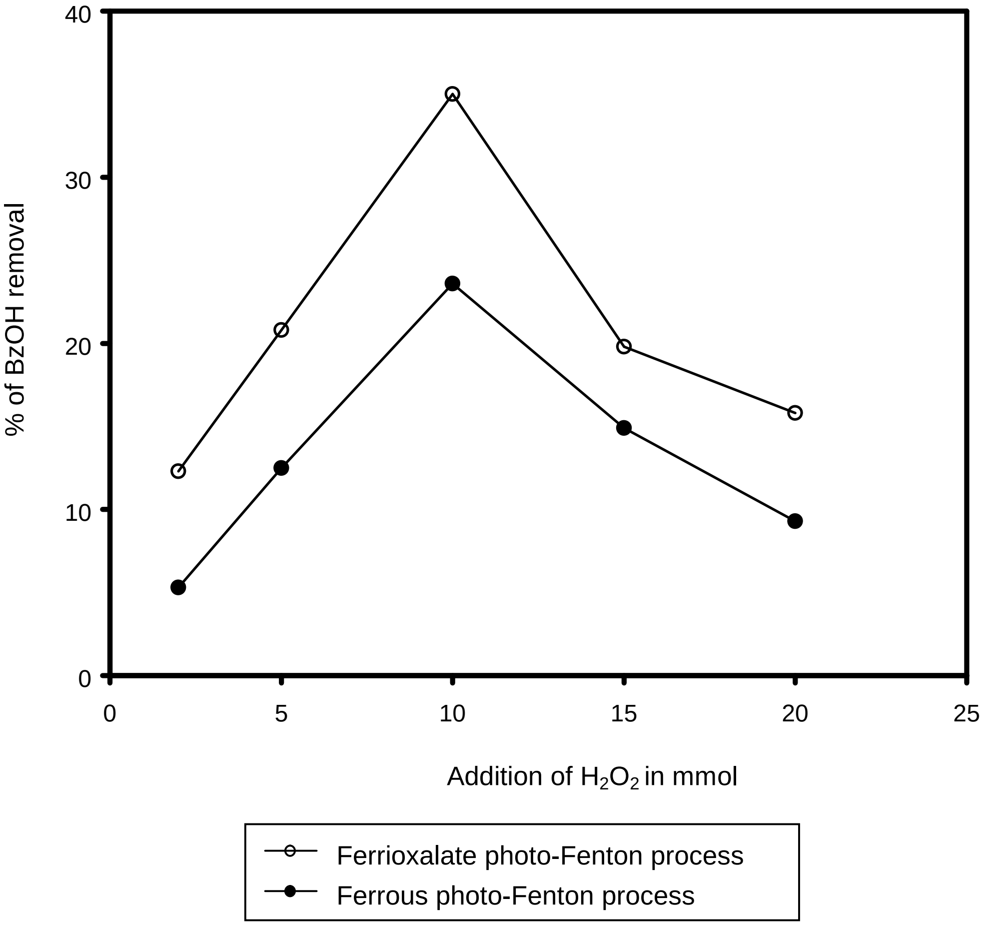

Fig. 3. The effect of addition of H_2O_2 on combined processes (Solar)
BzOH] = 3×10^{-3} mol/L, pH = 3 ± 0.1, ZnO = 100 mg,
Fe^{2+} = 0.6 mmol (Ferrous process), Fe^{3+} = 0.6 mmol (Ferric process),
Irradiation time = 30 minutes.

Addition of H_2O_2 increases the removal rate in both processes upto a certain concentration and then the removal rate decreases In ferrous photo-Fenton process addition of 2 to 10 mmol of H_2O_2 increases the degradation from 5.3 to 23.6% in 30 minutes. Further addition of H_2O_2 above 10 mmol decreases the removal rate. For ferrioxalate process addition of H_2O_2 upto 10 mmol increases the degradation from 12.3 to 35.0% in 30 minutes. Further increase of H_2O_2 dosage decreases the removal rate. The optimum concentration of H_2O_2 for both processes is 10 mmol. The enhancement of degradation by the addition of H_2O_2 is due to the higher production of hydroxyl radicals by these processes. (eqns 12, 13)

$$H_2O_2 + e^{-}{}_{CB} \longrightarrow {}^{\bullet}OH + OH^{-} \qquad (12)$$

$$H_2O_2 + O_2\ {}^{\bullet} \longrightarrow {}^{\bullet}OH + H\ \ + O_2 \qquad (13)$$

At excess dosage (above 10 mmol) the removal rate decreases due to its hydroxyl radical and hole scavenging effects (eqns. 12-14).

$$H_2O_2 + {}^{\bullet}OH \longrightarrow HO_2{}^{\bullet} + H_2O \qquad (14)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad (15)$$

$$H_2O_2 + h^{+}_{VB} \longrightarrow HO_2^{\bullet} + H^{+} \quad (16)$$

3.5 Effect of addition of ZnO

The optimum amount of ZnO has to be added in order to avoid excess catalyst and to ensure total absorption of light for efficient removal. The effect of ZnO loading on the photodegradation of BzOH has been investigated in ferrous and ferrioxalate photo-Fenton processes and the results are given in Table 4. In ferrous photo-Fenton process increase in ZnO loading from 50 to 100 mg, the degradation increases from 10.3 to 23.6% in 30 minutes. In ferrioxalate process the degradation increases from 15.0 to 35.0%. Further increase of ZnO loading in both processes decreases the removal rate. In both the processes the enhancement of removal rate is due to (i) increase of hydroxyl radical concentration, (ii) increase of active sites in ZnO and (iii) the absorption of more light 100 mg of ZnO for the degradation of 3×10^{-3} mol/L BzOH solution is found to be the optimum dosage for both ferrous and ferrioxalate photo-Fenton processes.

Table 4: Effect of addition of ZnO on combined processes

Amount of catalyst ZnO added in mg	Percentage of degradation	
	Fe^{2+}/BzOH/H2O2/ZnO/Solar	Fe^{3+}/BzOH/H2O2/ZnO/Solar
50	**10.3**	**15.0**
75	**18.3**	**24.8**
100	**23.6**	**35.0**
125	**22.8**	**30.0**
150	**21.0**	**25.4**
175	**18.8**	**23.5**

[BzOH] = 3 ò 10^{-3} mol/L, pH = 3 ï 0.1, H2O2 = 10 mmol, Fe^{2+} = 0.6 mmol (Ferrous process), Fe^{3+} = 0.6 mmol (Ferric process), Irradiation time = 30 minutes.

3.6. Effect of various initial dye concentrations

Pollutant concentrations become important in wastewater treatment. The effects of various initial pollutant (BzOH) concentrations on the degradation of BzOH by ferrous and ferrioxalate photo-Fenton processes with ZnO are shown in Fig. 4. Increase of the initial BzOH concentration from 1 to 7 × 10-3 mol/L decreases the degradation from 31.4 to 12.5% and 38.7 to 16.6% in 30 minutes for ferrous and ferrioxalate processes respectively. Since, the concentration of catalyst, oxidant and the solar power are same for all dye concentration, the generation of hydroxyl radical remains constant. So with the increase of dye concentration, the probability of dye molecules to react with hydroxyl radical decreases. At high initial dye concentrations the path length of photon entering into the solution decreases and the amount of dye adsorbed on catalyst surface increases. This also affects the photocatalytic activity of ZnO.

3.7. Kinetics of photocatalytic degradation of BzOH

In the combined ZnO mediated photo-Fenton process photocatalytic degradation of BzOH containing ZnO obey apparently pseudo-first order kinetics at low initial substrate (BzOH) concentration and the rate expression is given by eqn. 17.

$$\frac{-\,d[C]}{dt} = k'\,[C] \quad (17)$$

Where k' is the pseudo-first order rate constant. The rate constants of degradation of BzOH by ferrous and ferrioxalate combined processes using Solar light are given in Table 5.

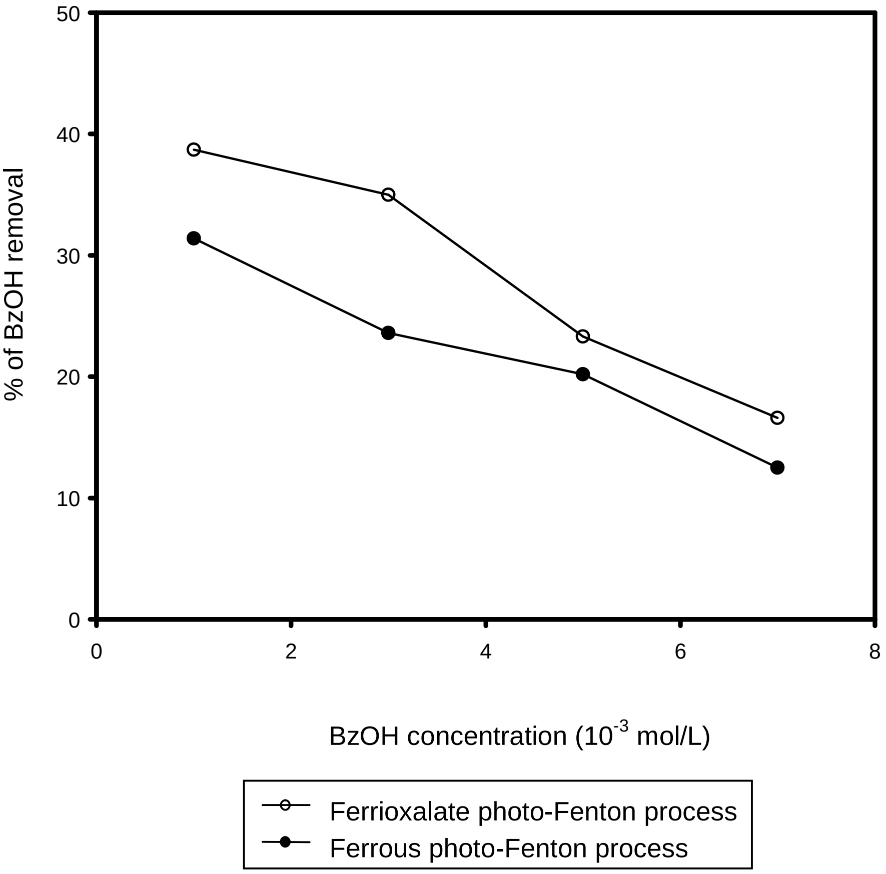

Fig. 4. The effect of various BzOH concentrations on combined processes (Solar)
pH = 3 ± 0.1, H_2O_2 = 10 mmol, ZnO = 100 mg, Fe^{2+} = 0.6 mmol (Ferrous process), Fe^{3+} = 0.6 mmol (Ferric process), Irradiation time = 30 minutes.

Table 5: Rate constants of degradation of BzOH by ferrous and ferricoxalate process using Solar light

Initial concentration of BzOH × 10^{-3} mol/L	Degradation k' (min^{-1})	
	Fe^{2+}/BzOH/H2O2/ZnO/Solar	Fe^{3+}/BzOH/H2O2/ZnO/Solar
1	**0.0100**	**0.0132**
3	**0.0070**	**0.0118**
5	**0.0049**	**0.0055**
7	**0.0027**	**0.0031**

pH = 3 ï 0.1, ZnO = 100 mg, H2O2 = 10 mmol, Fe^{2+} = 0.6 mmol (Ferrous process), Fe^{3+} = 0.6 mmol (Ferricoxalate process).

BzOH is adsorbed onto ZnO surface and the adsorption-desorption equilibrium is reached. After adsorption, the equilibrium concentration of BzOH solution is determined and it is taken as the initial BzOH concentration for kinetic analysis. Integration of the above equ. 17 with the limit of C = C_0 at t = 0 with C_0 being the equilibrium concentration of the bulk solution gives equ. 18.

$$\ln\left[\frac{C_0}{C}\right] = k' \, t \qquad (18)$$

C_0 = Equilibrium concentration of BzOH
C = Concentration of BzOH at a given time

A linear relation between BzOH concentration and irradiation time has been observed for Solar light degradation of BzOH by ferrous and ferrioxalate combined processes as shown in plots of ln C_0/C versus time (Figs. 5& 6). Many authors[30,31] have used the Langmuir-Hinshelwood (L-H) kinetic expression to analyse the photocatalytic reaction successfully. The experimental data has been rationalized in terms of the modified form of L-H kinetic model to describe the solid-liquid reaction[32].

The rate of oxidation of BzOH at surface reaction is proportional to the surface coverage of BzOH on the ZnO, assuming that BzOH is strongly adsorbed on the catalytic surface than the intermediate products[33]. The effect of BzOH concentration on the rate of degradation is given in the form of eqns.19&20[34].

$$r = \frac{K_1 K_2 C}{1 + K_1 C} \tag{19}$$

$$\frac{1}{r} = \frac{1}{K_2 K_1 C} + \frac{1}{K_2} \tag{20}$$

Where ‘C’ is the concentration of the BzOH at time‘t’, K_1 is the constant related to adsorption and K_2 is to the reaction properties of the substrate (BzOH)

The applicability of L-H equation for the degradation has been confirmed by the linear plot (Fig. 7) obtained by plotting the reciprocal of initial rate $\left(\frac{1}{r}\right)$ against reciprocal of initial concentration of the BzOH$\left(\frac{1}{C}\right)$. The values of K_1 and K_2 have been determined from the slope and intercept of these plots. The values of K_1 and K_2 obtained for the degradation of BzOH by ferrous and ferrioxalate combined processes using Solar light are found to be $2.02 \times 10^2\ M^{-1}$, $8.25 \times 10\text{-}5\ Mm^{-1}$ and $2.63 \times 10^2\ M^{-1}$ and $8.55 \times 10\text{-}5\ Mm^{-1}$.

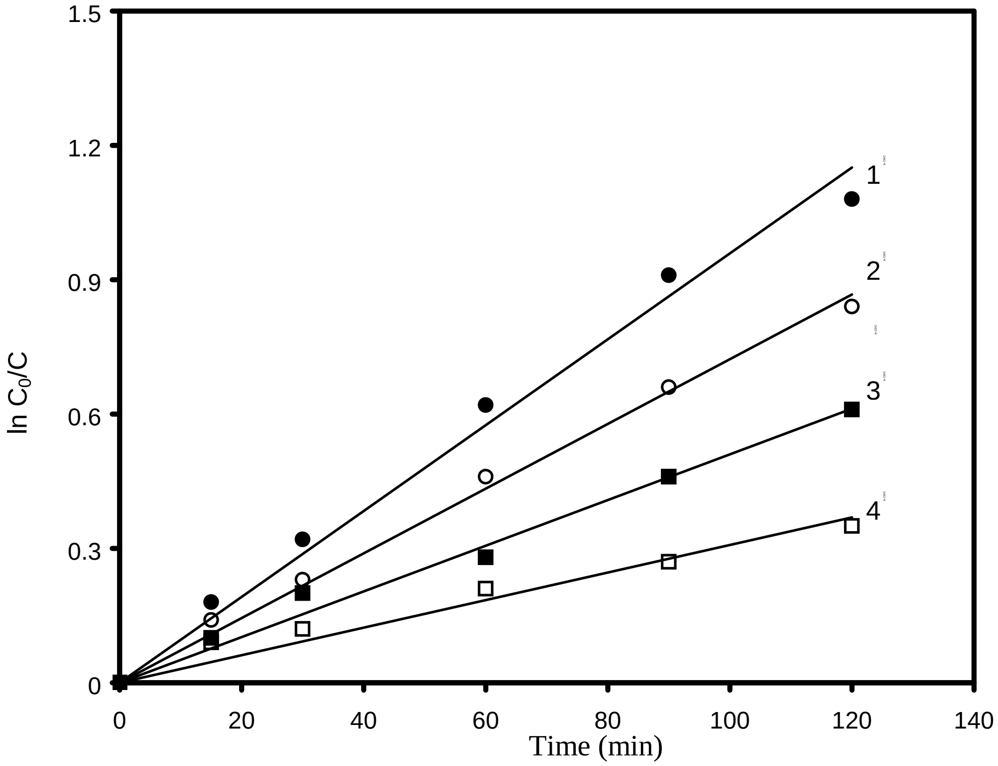

Fig. 5. Kinetics of BzOH degradation for different initial concentration by $Fe^{2+}/H_2O_2/ZnO$/Solar process
1 – 1×10^{-3} mol/L; **2** – 3×10^{-3} mol/L, **3** – 5×10^{-3} mol/L; **4** – 7×10^{-3} mol/L
H_2O_2 = 10 mmol, pH = 3 ± 0.1, ZnO = 100 mg, Fe^{2+} = 0.6 mmol.

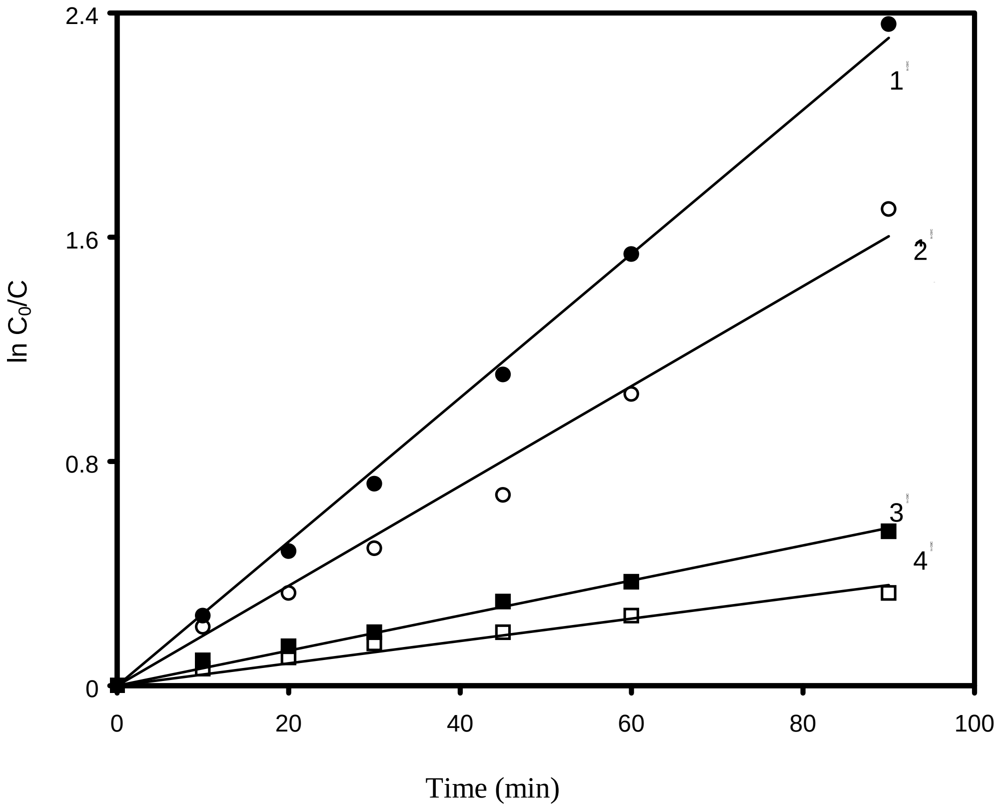

Fig.6. Kinetics of BzOH degradation for different initial concentration by $Fe^{3+}/H_2O_2/ZnO$/Solar
1 – 1 × 10^{-3} mol/L; **2** – 3 × 10^{-3} mol/L, **3** – 5 × 10^{-3} mol/L; **4** – 7 × 10^{-3} mol/L
H_2O_2 = 10 mmol, pH = 3 ± 0.1, ZnO = 100 mg, Fe^{3+} = 0.6 mmol.

4. Conclusion

BzOH (organic pollutant) is effectively degraded by the combined solar photo-Fenton processes using either ferrous ion (or) ferrioxalate. Among these two combined processes, the ferrioxalate process is most efficient than ferrous process in solar light. The degradation efficiency is maximum at 0.6 mmol of Fe^{2+}/Fe^{3+}, 10mmol of H_2O_2 and 100 mg of ZnO for both ferrous and ferrioxalate processes. Both processes are efficient at pH 3 and decrease at both sides. Though both processes are viable, ferrioxalate process is more efficient in solar light than ferrous process for the wastewater treatment.

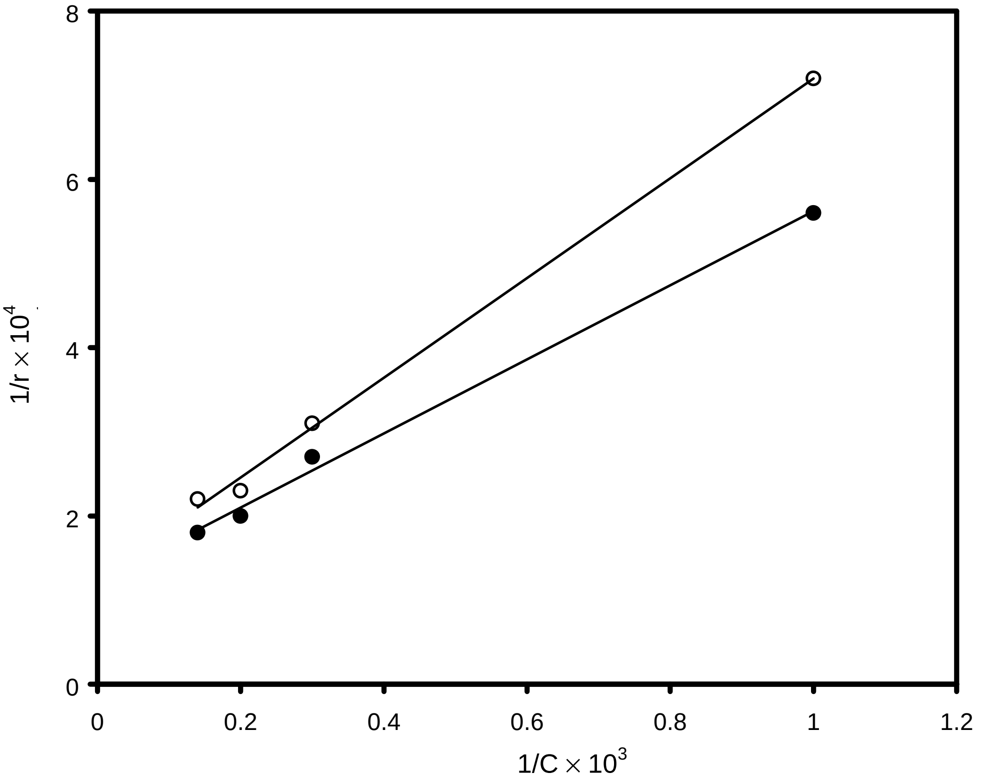

Fig.7. Linearised reciprocal kinetic plot of the degradation of BzOH by $Fe^{2+}/ZnO/H_2O_2$/Solar and $Fe^{3+}/ZnO/H_2O_2$/Solar

[BzOH] = 3×10^{-3} mol/L, pH = 3 ± 0.1, ZnO = 100 mg, Fe^{2+} = 0.6 mmol, Fe^{3+} = 0.6 mmol, H_2O_2 = 10 mmol.

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