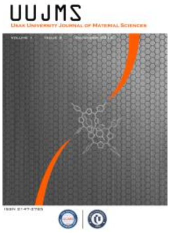
Usak University Journal of Material Sciences
journal homepage: http://uujms.usak.edu.tr



Research article

Optimization of the heterogeneous photo Fenton degradation of a model pollutant, benzyl alcohol using UV/ZnO process

Manohar Shanthi, Elias Ginish, Duraisamy Rajamanickam*

Department of Chemistry, Annamalai University, Annamalainagar, 608 002, Tamil Nadu, India

Received 19 August 2012 *Revised 06 December 2012* *Accepted 20 December 2012*

Abstract

Among advanced oxidation processes (AOPs), the photo chemically enhanced Fenton reaction (photo-Fenton) may be particularly effective for the treatment of industrial wastewater. In the present work, ferrous sulphate/ferrioxalate with H_2O_2 and ZnO particles was tested as a combined homogeneous and heterogeneous photo-Fenton process for the degradation of the model organic pollutant, benzyl alcohol. Enhancement in the photo-Fenton processes has been observed by the addition of ZnO. UV/ferrous/H_2O_2/ZnO and UV/ferrioxalate/H_2O_2/ZnO processes are found to be more efficient than the individual photo-Fenton and UV/ZnO processes. The use of ferrioxalate in the combined process is found to be more advantageous. The effect of various experimental parameters such as pH, initial H_2O_2, Fe^{2+}, Fe^{3+}, ZnO and pollutant concentrations on these combined photocatalytic process have been investigated. All these parameters strongly influenced the removal rate. The efficiency of chemical oxygen demand (COD) removal was tested. The optimum operating conditions of these combined processes are reported.

Keywords: Advanced oxidation processes, benzyl alcohol, photo-Fenton, ferrous ion, ferrioxalate, H_2O_2, ZnO, UV-light

1. Introduction

In recent years, advanced oxidation processes (AOPs) have been widely used for the destruction and mineralization of non-biodegradable organic pollutants in wastewater. The AOPs almost rely on the generation of very reactive free radicals such as hydroxyl radical ($^{\bullet}OH$). These radicals react rapidly and mineralize most of the organic compounds to CO_2 and H_2O.

Benzyl alcohol (BzOH) is used in a wide variety of cosmetic formulations as a fragrance component, pharmaceutical aid and viscosity-decreasing agent. Efficient treatment technologies are required to reduce the BzOH concentration in wastewater to acceptable levels because it is a membrane “fluidizer” that affects lipid bilayer structure and it also inhibits the activities of various glycosyl transferases of the liver Golgi membrane of some of the aquatic animals. Semiconductor photocatalysis was proved as a potential enhance technology for solar disinfection of water [1]. Photocatalytic degradation of

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*Corresponding author: Tel: +91 4144 237386, Fax: +91 4144 237386
E-mail: shanthimsm@gmail.com

pesticide in natural water using hydrogen peroxide was studied by [2]. Degradation of wastewater by using doped semiconductor photocatalysts were reported [3]. Sm_2FeTaO_7 act as an effective photocatalyst for the degradation of indigo carmine dye in aqueous solution [4]. The photocatalytic activity of the prepared zinc oxide hallow spheres was evaluated by photocatalytic decolorization of Rhodamine B aqueous solution at ambient temperature [5]. Hierarchical flower-like-C-doped ZnO superstructures (ZnO flowers) assembled from porous nanosheets are obtained by pyrolysis process and characterized by using various techniques, and its photocatalytic activity is evaluated [6]. Zhou et al reported [7] visible-light induced Rhodamine B degradation H_2O_2 at near neutral pH over hematite was strongly architecture-dependent, and the reactivity trend can be rationalized as exposed facets in the order {110} > {012} > {001}.

Recently, attention has been focused on the homogeneous photochemical advanced oxidation processes using Fenton reagent with UV light for the toxic chemical degradation. Photo-Fenton processes are found to be faster than heterogeneous photochemical process [8-10]. In the photo-Fenton process, the use of ferrioxalate process is found to be more advantageous than the ferrous and other ferric salts. The usefulness and applicability of UV-Vis/ferrioxalate/H_2O_2 process as compared to the UV/H_2O_2 and UV-vis/Fe (II)/ H_2O_2 processes had been well demonstrated [11]. The photo-Fenton processes are faster than ZnO mediated photocatalytic processes, but they are found to be less efficient in complete mineralization. Hence a combined homogeneous and heterogeneous process may be more efficient for degradation.

In present work, we have investigated the photodegradation of benzyl alcohol using the combined ZnO mediated photo-Fenton process with UV light. Benzyl alcohol has the absorption maximum at 207 nm. In our earlier studies, we have reported the degradation of some of the organic pollutants using the individual AOPs [12-16].

2. Experimental

2.1. Materials

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. The 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. Potassium ferrioxalate $K_3[Fe(C_2O_4)_3]$ was prepared and purified [17]. The experimental solutions were prepared using double distilled water. The pH of the solution was adjusted using H_2SO_4 and NaOH. The pH of the solution is measured by using HANNA Phep (model H 198107 digital pH meter).

2.2. Irradiation Experiments

For the photolysis experiment, a desired molar ratio of pollutant (benzyl alcohol)/ $Fe^{2+/3+}$/H_2O_2/ZnO solutions were freshly prepared from benzyl alcohol (BzOH) stock solution, $FeSO_4.7H_2O$, $K_3[Fe(C_2O_4)_3]$, H_2O_2 and ZnO. 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 using Heber photoreactor model HML-MP 88 (Fig.1). This model consists of eight medium pressure mercury vapour lamps (8 W) set in parallel and emitting 365 nm wavelength light. It has a reaction chamber with specially designed reactors made of highly polished aluminum and built in cooling fan at the bottom. It is provided with magnetic stirrer at the center. Open borosilicate glass tube of 50 mL of capacity, 40 cm height and 20 mm diameter was used as the reaction vessel with the total light exposure length of 330 mm. The irradiation was carried out using four parallel medium pressure mercury lamps (32 W) in open-air condition. The reaction mixture was continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. All the solutions prior to photolysis were kept in dark by covering with aluminum foil to prevent any photochemical reactions.

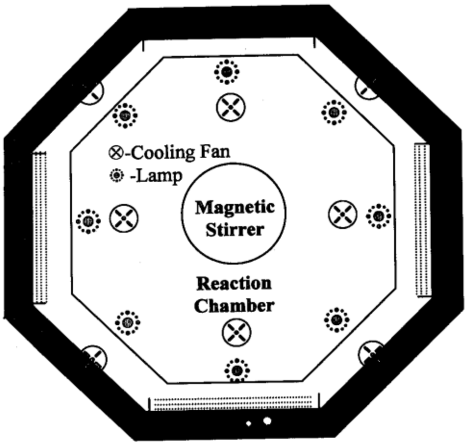


Fig. 1 Schematic diagram of photoreactor

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 was used to monitor the degradation of benzyl alcohol. UV spectral measurements were made using SHIMADZU UV 1650 PC UV-Visible spectrophotometer.

COD was determined using the following procedure [18]. Sample was refluxed with $HgSO_4$, known volume of standard $K_2Cr_2O_7$, Ag_2SO_4 and H_2SO_4 for two hours and titrated with standard ferrous ammonium sulphate (FAS) using ferrion indicator. A blank titration was carried out with distilled water instead of Pollutant (BzOH) sample. COD was determined using the following equation:

$$\text{COD} = \frac{(\text{Blank titre value} - \text{pollutant (BzOH) sample titre value}) \times \text{normality of FAS} \times 8 \times 1000}{\text{Volume of sample}}$$

where; COD: Chemical oxygen demand and FAS: Ferrous Ammonium Sulphate.

3. Results and Discussion

The controlled experiments have been carried and their efficiencies by various advanced oxidation processes are compared in Table 1.

Table 1
The degradation efficiencies of various processes

Process	**Condition***	**Reaction time (min.)**	**Degradation (%)**
BzOH/UV		120	0.0
BzOH/ferrous/UV	Fe^{2+} - 0.5 mmol	120	0.0
BzOH/ferrioxalate/UV	Fe^{3+} - 0.5 mmol	30	3.2
BzOH/ H_2O_2/UV	H_2O_2 – 10 mmol	30	5.7
BzOH/ZnO/UV	ZnO – 100 mg	30	7.9
BzOH/ferrous/ H_2O_2/dark	Fe^{2+} - 0.5 mmol H_2O_2 - 10 mmol	30	9.4
BzOH/ferrioxalate/ H_2O_2/dark	Fe^{3+} - 0.5 mmol H_2O_2 - 10 mmol	30	2.5
BzOH/ferrous/ H_2O_2/UV	Fe^{2+} - 0.5 mmol H_2O_2 - 10 mmol	30	16.9
BzOH/ferrioxalate/H_2O_2/UV	Fe^{3+} - 0.5 mmol H_2O_2 - 10 mmol	30	23.2
BzOH/ferrous/H_2O_2/ZnO/UV	Fe^{2+} - 0.5 mmol H_2O_2 - 10 mmol ZnO = 100 mg	30	29.0
BzOH/ferrioxalate/H_2O_2/ZnO/UV	Fe^{3+} - 0.5 mmol H_2O_2 - 10 mmol ZnO = 100 mg	30	46.6

*BzOH=3×10^{-3} mol/L, pH=3.0±0.1 for all reactions

From the results, it is clear that the pollutant (BzOH) is resistant to direct photolysis by UV light and irradiation in the presence of ferrous ion alone. The irradiation with ferrioxalate alone causes 3.2% of degradation of 30 min. The degradation of BzOH on irradiation in the presence of ferrioxalate is due to the formation of hydroxyl radical during its photolysis (Eqs. 1-6). The formation of hydroxyl radical ($^{\bullet}OH$) on the surface of photo-illuminated catalyst was reported by [6, 19, 20]. Zuo et al reported the formation of H_2O_2 in ferrioxalate photolysis and it is related to pH, irradiation intensity and the concentration of ferrioxalate [21].

After 30 minute of irradiation, 5.7% and 7.9% of degradation were observed in UV/H_2O_2 and UV/ZnO process respectively. The degradation of the BzOH in UV/H_2O_2 process is by the reaction of hydroxyl radicals generated upon photolysis of hydrogen peroxide (Eq. 7).

In UV/ZnO process, pollutant is oxidized by the reactive hydroxyl radical formed from the UV irradiated ZnO particles and by the holes formed on the UV irradiated ZnO surface.

$$[Fe^{III}(C_2O_4)_3]^{3-} + h\nu \longrightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-\bullet} \tag{1}$$

$$C_2O_4^{-\bullet} \longrightarrow CO_2^{-\bullet} + CO_2 \tag{2}$$

$$CO_2^{-\bullet} + O_2 \longrightarrow CO_2 + O_2^{-\bullet} \tag{3}$$

$$O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet} \tag{4}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \tag{5}$$

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{6}$$

$$H_2O_2 \xrightarrow{h\nu} {}^{\bullet}OH + {}^{\bullet}OH \qquad (7)$$

For ferrous/H_2O_2 and ferrioxalate/H_2O_2, 9.4 and 2.5% of degradation were observed respectively in dark. In UV/H_2O_2 process, the removal efficiency is lower than that of ferrous/H_2O_2 process. Fe^{2+} catalyzed decomposition of H_2O_2 is more than the UV catalyzed decomposition of H_2O_2. The quantum yield of formation of $OH^{\bullet}$ in UV/H_2O_2 is also dependent on the light intensity. The quantum yield of formation of hydroxyl radical is low; hence, low removal rate was observed [22].

The decomposition of hydrogen peroxide is also catalyzed by ferric ion [23]. However, the removal of BzOH by the ferrioxalate/H_2O_2 (dark) process has been found to be very less (2.5%) compared to ferrous/H_2O_2 process. This is because of the low reactivity of ferric ion towards hydrogen peroxide in dark. This iron complex generates Fe(II) only on irradiation. But on irradiation for 30 minutes the removal efficiency is improved for both ferrous and ferrioxalate reagent. Irradiation with ferrous/H_2O_2 and ferrioxalate/H_2O_2 causes 16.9 and 23.2% of degradation after 30 minutes.

In ferrous/H_2O_2/UV process, the removal of BzOH is due to generation of hydroxyl radical by (i) Fenton reaction (Eq. 6) and (ii) direct photolysis of H_2O_2 (Eq. 7). However, in ferrous/H_2O_2/UV process the reactions (Eq. 6 and 7) contribute only in a minor way to the degradation of BzOH. In ferrioxalate/H_2O_2/UV process, the degradation of BzOH is due to the fast generation of Fe^{2+} ion by photolysis of ferrioxalate (Eq. 1). A greater enhancement of removal rate was observed in ferrioxalate/H_2O_2/UV over ferrioxalate/H_2O_2/dark. This enhancement is due to light absorption of ferrioxalate strongly at longer wavelength generating Fe^{2+} ion with high quantum yield.

In the combined ZnO mediated photo-Fenton process, 29.0% and 46.6% of degradation was observed in the ferrous/H_2O_2/ZnO/UV and the ferrioxalate/H_2O_2/ZnO/UV processes respectively after 30 minutes irradiation. The degradation efficiencies of photo-Fenton processes are enhanced sharply in the presence of ZnO.

The comparison of degradation efficiencies of all the processes for the treatment time of 30 min. reveals the following order BzOH/ferrioxalate/H_2O_2/dark < BzOH/ferrioxalate/UV < BzOH/H_2O_2/UV < BzOH/ZnO/UV < BzOH/ferrous/H_2O_2/dark < BzOH/ferrous/H_2O_2/UV < BzOH/ferrioxalate/H_2O_2/UV < BzOH/ferrous/H_2O_2/ZnO/UV < BzOH/ferrioxalate/H_2O_2/ZnO/UV.

Among all these processes, the combined heterogeneous and homogeneous processes are found to be more efficient in the degradation. The efficiencies of photo-Fenton processes are enhanced by the addition of ZnO particles. The efficiency of this combined process is due to additional hydroxyl radical produced by the ZnO on irradiations.

Fig. 2 shows the changes in the UV-visible spectrum of BzOH on UV irradiation with ZnO in the presence of ferrous photo-Fenton process.

The ferrioxalate/H_2O_2/ZnO/UV process was found to be more efficient than the ferrous/H_2O_2/ZnO/UV process. This is because of the high molar absorption coefficient of ferrioxalate for the wavelength above 200 nm [11]. The effect of various parameters on these two (ferrous/H_2O_2/ZnO/UV and ferrioxalate/H_2O_2/ZnO/UV) combined processes have been investigated.

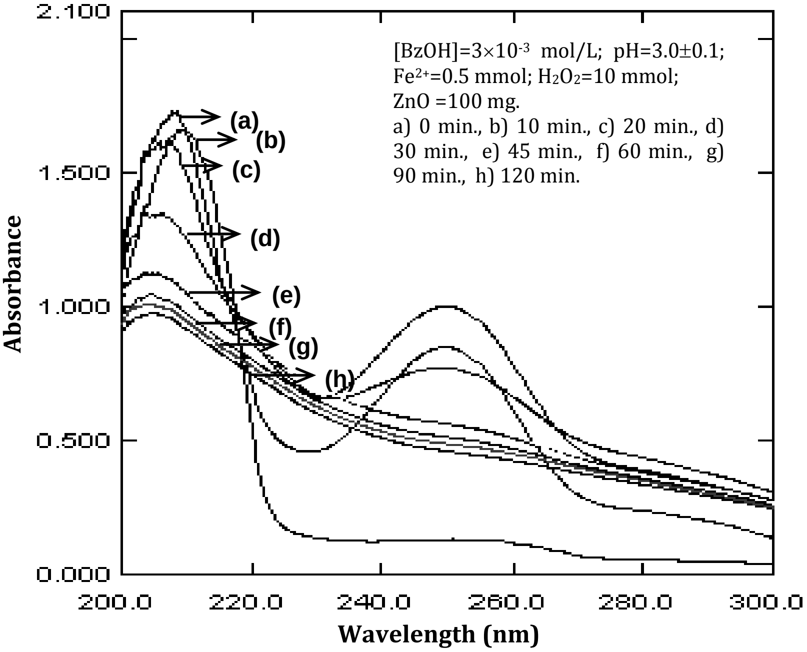


Fig. 2 The changes in UV-visible spectrum of BzOH on irradiation with UV-light in the presence of ferrous photo-Fenton process

3.1. Effect of pH on Combined Processes

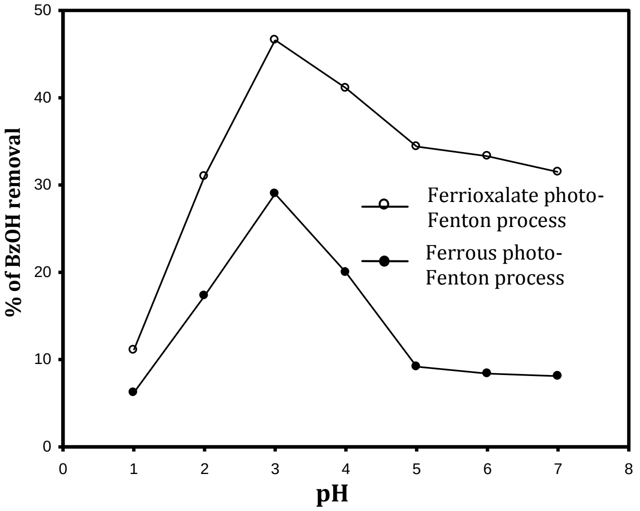
pH is an important parameter for photo-Fenton processes. The pH of the solution controls the production rate of hydroxyl radical concentration and the nature of iron species in solution. The effects of pH on degradation of BzOH are shown in (Fig.3).

The results indicate that both processes are efficient at pH 3. The increase of pH from 1 to 3 increases the degradation. Above pH 3 the degradation decreases in both processes. Hence, pH 3 is found to be the optimum pH for the combined ZnO mediated photo-Fenton processes. In these processes, the decrease in degradation at pH above 3 is due to the coagulation of hydroxo complex of Fe^{3+} formed during the reaction [24]. At low pH the removal rate is limited due to the hydroxyl radical scavenging effect of H ion (Eq. 8) [15,25,26].

$$^{\bullet}OH + H^{+} + e^{-} \longrightarrow H_2O \qquad (8)$$

3.2. Effect of Initial Ferrous and Ferrioxalate Dosage on Combined Process

The effects of addition of ferrous and ferrioxalate on the degradation of BzOH are shown in Table 2. The increase of ferrous dosage from 0.1 to 0.5 mmol increases the degradation from 13.3% to 39.6% in 45 minutes. Further increase from 0.5 to 1.5 mmol decreases the degradation rate. The increase in the removal rate is due to the increase in the hydroxyl radical production by ferrous ion.



[BzOH] = 3 × 10^{-3} mol/L, H_2O_2 = 10 mmol, ZnO = 100 mg, Irradiation time = 30 min
Fe^{2+} = 0.5 mmol (Ferrous process), Fe^{3+} = 0.5 mmol (Ferrioxalate process).

Fig. 3 The effect of pH on combined processes (UV)

Table 2
Effect of initial ferrous and ferrioxalate dosage on combined processes

Amount of ferrous/ferric added in mmol	Percentage of degradation	
	Fe^{2+}/BzOH/H_2O_2/ZnO/UV	**Fe^{3+}/BzOH/H_2O_2/ZnO/UV**
0.1	13.3	42.5
0.3	31.4	48.4
0.5	39.6	55.5
0.7	35.5	45.6
1.0	28.3	41.6
1.5	19.0	31.0

[BzOH]=3×10^{-3} mol/L, pH=3.0±0.1, ZnO=100 mg, H_2O_2=10 mmol, Irradiation time=45 min.

In the ferrioxalate process, the increase of initial ferrioxalate concentration from 0.1 to 0.5 mmol increases the degradation from 42.5% to 55.5% in 45 minutes. Further increase from 0.5 to 1.5 mmol decreases the removal rate. The generation of Fe^{2+} is likely to be the main step of photodegradation in ferrioxalate system. Ferrioxalate concentration determines the light absorption fraction and so the increase of ferrioxalate concentration increases the photon absorption, producing more Fe^{2+} ion. This results in the increase of removal rate. But when the ferrioxalate concentration is above 0.5 mmol the light penetration through the irradiated solution decreases, and the ferrioxalate at higher concentration produces less reactive hydroperoxy radicals (Eq. 9) [27].

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (9)$$

0.5 mmol of ferrous and 0.5 mmol of ferrioxalate are optimum dosages of both the ferrous/H_2O_2/ZnO/UV and ferrioxalate/H_2O_2/ZnO/UV processes respectively.

3.3. Effect of Added H_2O_2 on Combined Processes

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. 4.

The addition of H_2O_2 increases the removal rate in both processes up to a certain concentration. In the ferrous photo-Fenton process, the addition of 2 to 10 mmol of H_2O_2 increases the degradation from 11.3% to 29.0% in 30 minutes. Further addition of H_2O_2 above 10 mmol decreases the removal rate.

For the ferrioxalate process addition of H_2O_2 up to 10 mmol increases the degradation from 14.4% to 46.6% in 30 minutes. Further increase of H_2O_2 dosage decreases the removal rate. Hence, 10 mmol of H_2O_2 is found to be optimum concentration for the ferrous and ferrioxalate processes. The increase in the degradation is due to the increase in hydroxyl radical concentration by the addition of H_2O_2 (Eqs. 10,11).

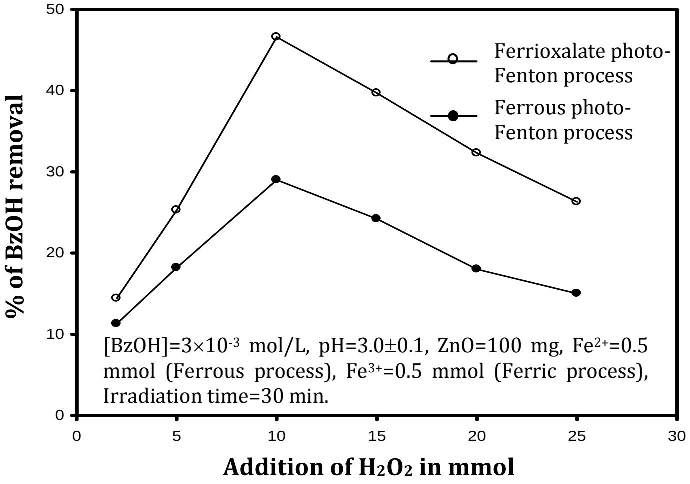


Fig. 4 the effect of addition of H_2O_2 on combined processes (UV)

$$H_2O_2 + e^-_{CB} \longrightarrow {}^\bullet OH + OH^- \qquad (10)$$

$$H_2O_2 + O_2^{-\bullet} \longrightarrow {}^\bullet OH + H^+ + O_2 \qquad (11)$$

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

$$H_2O_2 + {}^\bullet OH \longrightarrow HO_2^\bullet + H_2O \qquad (12)$$

$$HO_2^\bullet + {}^\bullet OH \longrightarrow H_2O + O_2 \qquad (13)$$

$$H_2O_2 + h^+_{VB} \longrightarrow HO_2^\bullet + H^+ \qquad (14)$$

3.4. Effect of Addition of ZnO on Combined Processes

For economic removal of pollutant from wastewater, it is necessary to find the optimum amount of catalyst for efficient degradation. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process [28-30].

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 3. In the ferrous photo-Fenton process increase in ZnO loading from 50 mg to 100 mg/50 mL, the degradation increases from 7.2% to 29.0% in 30 minutes. In the ferrioxalate process, the degradation increases from 14.1% to 46.6%. Further increase of ZnO loading in both processes decreases the removal rate. The increase of the catalyst loading beyond 100 mg/50 mL, and an increase in turbidity of the solution reduced the light penetration through the solution. While below this level, it is assumed that the catalyst surface and absorption of light by the catalyst are the limiting factors [31]. With regard to the photoreactor used in this study, 100 mg/50 mL was selected as the optimal ZnO load.

Table 3
Effect of addition of ZnO on combined processes

Amount of catalyst ZnO added in mg	**Percentage of degradation**	
	Fe^{2+}/BzOH/ H_2O_2/ZnO/UV	**Fe^{3+}/BzOH/ H_2O_2/ZnO/UV**
50	7.2	14.1
75	21.1	33.3
100	29.0	46.6
125	27.9	37.9
150	24.0	32.2
175	20.4	27.1

[BzOH]=3×10^{-3} mol/L, pH= 3.0±0.1, H_2O_2=10 mmol, Fe^{2+}=0.5 mmol (Ferrous process), Fe^{3+}=0.5 mmol (Ferric process), Irradiation time=30 min.

3.5. Effect of UV Light on Combined Processes

The UV power is mainly used for (i) photolysis of H_2O_2 (Eq. 7), (ii) photolysis of ferrioxalate, (iii) production of e^- and hole in ZnO. All these processes are strongly dependent on wavelength and light intensity. The effects of UV light powers on the combined processes are shown in Fig. 5. The figure clearly shows that increase of UV power from 16 to 64 W increases the degradation in the ferrous and the ferrioxalate processes. The increase of light intensity from 16 to 64 W increases the degradation from 28.7% to 57.8% and 40.8% to 71.6% at the time of 45 minutes for the ferrous and the ferrioxalate processes respectively.

The enhancement of removal rate is due to the increase in hydroxyl radical concentration. The rate of photolysis of H_2O_2 depends directly on the incident power. At the low UV power the photolysis of H_2O_2 is limited. At high UV power more hydroxyl radicals are produced upon the photo dissociation of H_2O_2; hence, removal rate increases. It appears that the UV power tested in our steady lies within the linear range and hence all the photons provided were effectively used.

3.6. Effect of Various Initial Pollutant (BzOH) Concentrations on Combined Processes

Pollutant concentration becomes important in wastewater treatment. The effect of various initial BzOH (pollutant) concentrations on the degradation of benzyl alcohol by the ferrous and the ferrioxalate photo-Fenton processes with ZnO is shown in (Fig.6) The increase of the initial pollutant concentration from 1 to 7 × 10^{-3} mol/L decreases the degradation from 63.0 to 19.8% and 71.4 to 25.0% in 45 minutes for the ferrous and the ferrioxalate processes respectively. For all, pollutant (BzOH) concentrations, the concentration of catalyst, oxidant and UV power are the same. Hence, the generation of hydroxyl radical remains constant. So the probability of pollutant molecule to react with hydroxyl radical decreases. At high initial pollutant concentrations the path length photon entering into the solution decreases, and the amount of BzOH adsorbed on catalyst surface increases. This also affects the photocatalytic activity of ZnO [32].

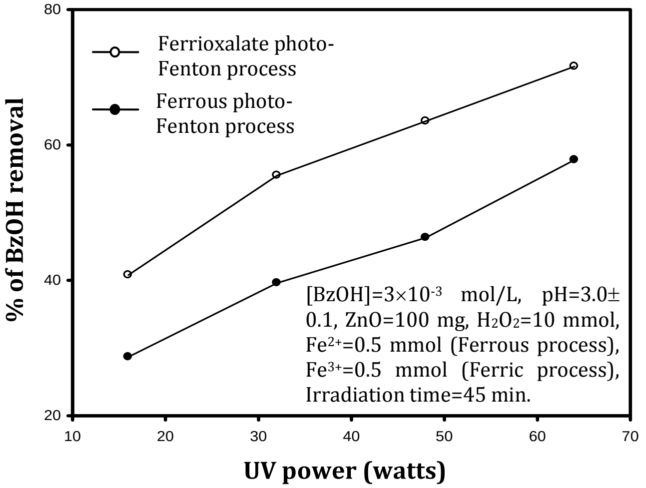


Fig. 5 The effect of UV power on combined processes

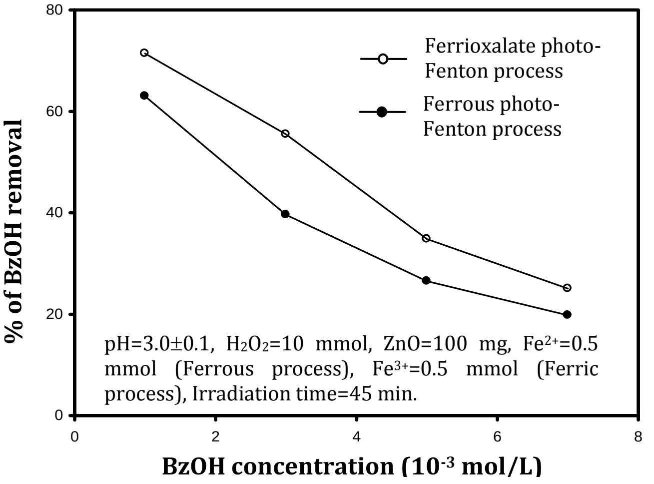


Fig. 6 The effect of various BzOH (pollutant) concentrations on combined processes

3.7. Chemical Oxygen Demand (COD)

To confirm the mineralization of the pollutant (BzOH) the degradation was also analyzed by COD values. The percentage of COD reductions is given in Table 4. From the Table 4, it is evident that the solutions obtained after photodegradation show a significant increase in COD removal efficiencies for both processes. In the ferrous photo-Fenton process 63.6% of COD removal was observed after 90 minutes of irradiation. In the ferrioxalate process 75.0% was observed. The substantially lower toxicity of the photodegraded products clearly indicates the high potential of the ZnO-catalysed photodegradation process for the removal of pollutant (BzOH) from wastewater. This indicates that the mineralization of pollutant is carried out. The degradation of the sample can also be accounted by analyzing the concentration by photometric measurements of the sample before and after irradiation. The degradation efficiency increases from 2.2 to 60.9% for the ferrous process and 5.4 to 71.4 for the ferrioxalate process in 90 minutes. This indicates that the combined heterogeneous and homogeneous process is found to be more efficient in the degradation of organic pollutant (BzOH).

Table 4
COD and BzOH removal by UV light on combined processes

Type of process	COD removal rate (%)	BzOH removal rate (%)
Fe^{2+}/BzOH/ H_2O_2/ZnO/UV	63.6	60.9
Fe^{3+}/BzOH/ H_2O_2/ZnO/UV	75.0	71.4

[BzOH]=3×10^{-3} mol/L, pH=3.0±0.1, H_2O_2=10 mmol, Fe^{2+}=2 mmol, Fe^{3+}=2 mmol, irradiation time=90 min.

3.8. Comparison of UV and Solar Light on Combined Processes

The percentage of degradation of BzOH by ferrous and ferrioxalate combined processes using UV and Solar light under the same conditions are given in Table 5.

Table 5
Comparison of efficiencies in UV and Solar light

Process	Degradation (%)
Fe2+/ H2O2/ZnO/UV	40.4
Fe3+/ H2O2/ZnO/UV	69.0
Fe2+/ H2O2/ZnO/Solar	39.3
Fe^{3+}/ H_2O_2/ZnO/Solar	50.3

[BzOH]=3×10^{-3} mol/L, pH=3.0±0.1, H_2O_2=10 mmol, Ferrous=0.5 mmol, Ferrioxalate=0.5 mmol, ZnO=100 mg, Irradiation time=60 min.

Among all these processes, the Fe^{3+}/H_2O_2/ZnO/UV process is found to be more efficient. The percentage of degradation of Fe^{2+}/H_2O_2/ZnO/UV is almost same for Fe^{2+}/H_2O_2/ZnO/Solar. In the case of Fe^{3+}/H_2O_2/ZnO process, the degradation efficiency is more in UV than in Solar light. The results reveal that the ferrioxalate process is more suitable in UV light.

3.9. Reusability

Stability of the catalysts was tested for the degradation of benzyl alcohol in UV light and is given in Table 6. It shows the degradation of benzyl alcohol using the catalysts after recovery for 3 consecutive runs. In the ferrous photo-Fenton process 60.9% and in the ferrioxalate process 71.4% of degradation was occurred at 90 minutes in the first run. The percentages of degradation in the second and the third runs are 59.7% and 58.3% in the ferrous process, 70.6% and 68.7% in ferric process. Even in the third run the catalysts show significant efficiency. This shows that the catalysts are remained effective and reusable under UV light.

Table 6
Effect of reusability

Type of process	1st run	2nd run	3rd run
Fe^{2+}/BzOH/ H_2O_2/ZnO/UV	60.9	59.7	58.3
Fe^{3+}/BzOH /H_2O_2/ZnO/UV	71.4	70.6	68.7

[BzOH]=3×10^{-3} mol/L, pH=3.0±0.1, H_2O_2=10 mmol, Ferrous=2 mmol, Ferrioxalate=2 mmol, ZnO=100 mg, Irradiation time=90 min.

4. Conclusion

The degradation efficiencies of the photo–Fenton process are enhanced by the use of the ZnO particles. Benzyl alcohol (a pollutant) is effectively degraded by the combined ferrous and ferrioxalate photo–Fenton processes with ZnO. The higher efficiency of the combined processes relative to individual processes is due to the degradation taking place both in solution and in surface of ZnO. The ferrioxalate process is most efficient among all the processes. The optimum physico-chemical conditions for the efficient photodegradation of 3×10^{-3} mol/L Benzyl alcohol (pollutant) solution at room temperature was found to be: ZnO concentration 100 mg/50 mL, radiation intensity 32W; Fe^{2+} concentration 0.5 mmol, ferrioxalate concentration 0.5 mmol, H_2O_2 concentration 10 mmol for both processes .Both processes are efficient at pH 3 and decrease at both sides. The removal rate decreases with the increase in initial pollutant concentration. Increased COD removal efficiency confirms the photodegradation process. It is found that both the combined ferrous and ferrioxalate processes are viable and efficient methods for organic pollutant (benzyl alcohol) wastewater treatment within a short time.

Acknowledgement

One of the author Dr. M. Shanthi thanks to UGC, New Delhi, India for financial assistance (Project number F.No.41-288/2012 (SR)). Authors are thankful to Dr. M. Swaminathan, Professor and Emeritus Scientist (CSIR), Annamalai University for his valuable suggestions and encouragement.

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