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The influence of inorganic oxidants and metal ions on semiconductor sensitized photodegradation of 4-fluorophenol

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Abstract

This paper mainly focuses on the influence of inorganic oxidants and metal ions on the TiO_2, ZnO sensitized photodegradation of 4-fluorophenol (4-FP) by UV-A light. TiO_2-P25 is more efficient than ZnO. Among the oxidants periodate ion was found to be more efficient than others in improving the degradation of 4-FP via formation of reactive radicals. The effect of oxidants on the degradation of 4-FP was found to be in the order of $IO_4^- > BrO_3^- > S_2O_8^{2-}$ $H_2O_2 > ClO_3^-$. The effect of metal ions on degradation of 4-FP was found to be in the order of $Mg^{2+} > Fe^{3+} > Fe^{2+} > Cu^{2+}$. The degradation of 4-FP follows *pseudo*-first order kinetics according to the Langmuir–Hinshelwood model. The photomineralisation has also been confirmed by COD, gas chromatography and fluoride ion measurements.

Keywords: 4-Fluorophenol; TiO_2-P25; ZnO; UV-A light; Photocatalysis

1. Introduction

The major organic contaminants in industrial wastewater are phenols and phenolic compounds. They are released to the environment from effluents discharged by industries such as petroleum refining, coal tar, steel, dye stuff paper and pulp mills, tanning, fibre wood, pharmaceuticals, preservatives of food stuffs and high quality polymer. Fluorophenols represent a group of organics found in some of industrial effluents and reported in hazardous wastes [1]. In recent years advanced oxidation processes (AOPs) have been reported to be very useful for the photodegradation of organic pollutants in wastewater [2–4]. Among the various AOPs, semiconductor mediated photocatalysis has been accorded greater importance over the last few years due to its potential to degrade a wide range of organic and inorganic pollutants [5–7]. The major mechanism in the degradation is due to oxidation by hydroxyl radical produced in this process by the following reactions:

$$\text{Semiconductor} + h\nu \rightarrow e_{VB}^- + h_{VB}^+ \tag{1}$$

$$h_{VB}^- + OH_{(ads)}^- \rightarrow {}^{\bullet}OH \tag{2}$$

$$h_{VB}^+ + H_2O_{(ads)} \rightarrow {}^{\bullet}OH + H^+ \tag{3}$$

$$e_{CB}^- + O_2 \rightarrow O_2^{\bullet -} \tag{4}$$

$$2O_2^{\bullet -} + 2H_2O \rightarrow 2{}^{\bullet}OH + 2OH^- + O_2 \tag{5}$$

The resulting hydroxyl radicals, being very strong oxidising agent can oxidise most of organic and inorganic pollutants. It is well known that O_2 is essential for the photocatalytic oxidation of organic compounds. Its presence in the liquid phase inhibits the recombination of electron/hole pairs and increases hydroxyl radical concentration [8]. Oxygen over the TiO_2 surface acts as electron acceptor to form superoxide radical ion ($O_2^{\bullet -}$). This superoxide anion radical then forms more hydroxyl radicals (Eq. (5)).

The inorganic oxidants such as IO_4^-, $S_2O_8^{2-}$, BrO_3^-, ClO_3^-, H_2O_2 can also be used as additives instead of oxygen to enhance the photodegradation rates of organic substrates by quenching the conduction band electrons and by the formation of reactive radical intermediates [9–11]. The influence of inorganic additives must be accurately checked before their application since they may exhibit negative effect depending on experimental parameters.

It has been observed that addition of some transition metal ions to aqueous TiO_2 dispersions improves UV/TiO_2 system's power in degrading organic substrates [12,13]. The enhancement

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effect due to the presence of metal ion arises mainly from two different effects. The first reason is the quenching of the ejected electrons from TiO_2 surface by the metal ions according to the following equation:

$$M^{n+} + e_{CB}^{-} \rightarrow M^{(n-1)+} \quad (6)$$

Where M^{n+} represents Cu^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+} metal ions.

The second reason is by inducing Fenton and photo-Fenton type reactions to produce more hydroxyl radicals

$$M^{n-1} + H_2O_2 + H^{+} \rightarrow M^{n+} + {}^{\bullet}OH + H_2O \quad (7)$$

In the present study we examined the effect of additives such as inorganic oxidants, anions and metal ions on the photocatalytic degradation of 4-FP with TiO_2-P25 or ZnO using UV-A light. In 1990, first work on fluorophenols was reported by Minero and Aliberti [1]. They have studied the kinetics of photocatalysis of fluorophenol with AM1 simulated sunlight over titania. Later not much work had been carried out on 4-fluorophenol. The present work is a continuation of our on going work on photocatalytic/photochemical degradation of dyes [14–17].

2. Experimental

2.1. Material

4-Fluorophenol was purchased from Aldrich. A gift sample of TiO_2-P25 was obtained from Degussa (Germany). It has particle size of 30 nm and BET specific area 56 m^2/g. ZnO had a particle size of 0.1–4 μm and surface area 10 m^2/g. AnalaR grade reagents H_2O_2 (30 w/w%), $(NH_4)_2S_2O_8$, $KBrO_3$, $KClO_3$, KIO_4, Na_2CO_3, Na_2SO_4, $NaHCO_3$, $NaNO_3$ and NaCl were used as received. The double distilled water was used to prepare experimental solutions. The pH of the solutions was adjusted using H_2SO_4 or NaOH.

2.2. Photoreactor

Heber multilamp photoreactor model HML-MP 88 was used for photoreaction (Fig. 1). This model consists of eight medium pressure mercury lamps (8 W) set in parallel and emitting 365 nm wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminium and built in cooling fans at the bottom. It is provided with a magnetic stirrer at the centre. Open borosilicate glass of 50 ml capacity, 40 cm height and 20 mm diameter was used as a reaction vessel with the total light exposure of 330 nm. The irradiation was carried out at using four parallel medium pressure mercury lamps in open air condition. The UV power of the four lamps is 32 W. The reaction mixture was continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. The airflow rate was maintained at 8.1 ml s^{-1}. All solutions prior to photolysis were kept in dark by covering with aluminium foil to prevent any photochemical reactions.

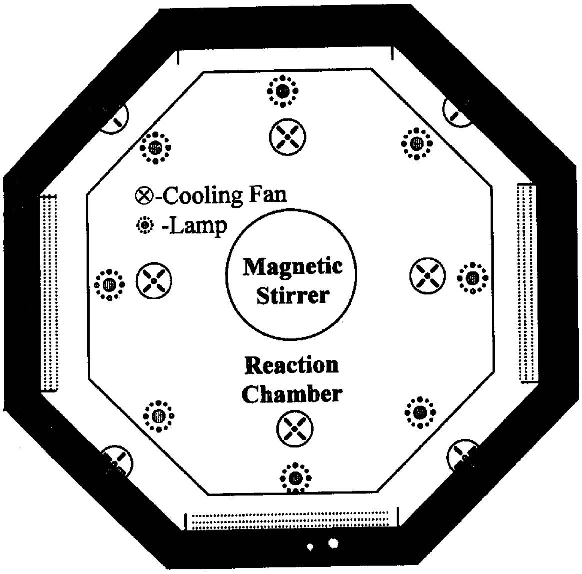

Fig. 1. Photoreactor.

2.3. Analysis

In all experiments 50 ml reaction mixture was irradiated. At specific time intervals 1–2 ml of the sample was withdrawn and centrifuged to separate the TiO_2 or ZnO. About 1 ml of sample suitably diluted and its absorbance was measured. UV spectral measurements were made using Hitachi U-2001 spectrophotometer. Gas chromatography (GC-9000, Perkin-Elmer) using a capillary column (VF-5) and flame ionization detector (FID) was used to quantify the 4-fluorophenol. The pH of the solution was measured using HANNA Phep (model 4 198107) digital pH meter. The fluoride ion concentration was measured using Orian ionometer.

3. Results and discussion

3.1. Primary degradation

Initially the experiments were carried out under the following conditions to test the photodegradability by TiO_2 and ZnO catalysts (i) 4-FP + UV, (ii) 4-FP + TiO_2 + UV and (iii) 4-FP + ZnO + UV. The results are presented in Fig. 2. Addition of TiO_2 and ZnO without irradiation had a negligible effect on the degradation rate. After 90 min of irradiation only 9% decomposition was observed. However, a rapid degradation of 4-FP occurred by irradiation in the presence of TiO_2 or ZnO. In the presence of TiO_2-P25 complete degradation of 4-FP was achieved in 60 min while with ZnO the complete degradation occurred in 90 min. ZnO is reported to be a suitable alternative to TiO_2-P25 since its photodegradation mechanism has been proven to be similar that of TiO_2 [18]. ZnO is found to be more efficient than TiO_2 in phenol degradation under certain conditions [19–21]. Hence 4-FP degradation have been studied using both photocatalysts. The high efficiency of TiO_2-P25 is due to larger surface of TiO_2-P25 than ZnO. The photocatalytic degradation occurs mainly on the catalyst surface by hydroxyl

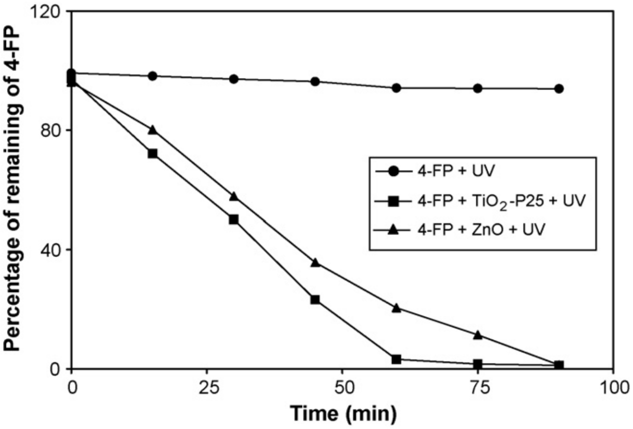

Fig. 2. Photodegradability of 4-FP: [4-FP] = 100 ppm; catalyst suspended = 100 mg; $I = 1.381 \times 10^{-3}$ einstein l^{-1} s^{-1}; airflow rate = 8.1 ml s^{-1}.

radicals. The oxidizing power of hydroxyl radicals produced by these catalysts is strong enough to break C–C, C–F, C=C bond of 4-FP adsorbed on their surfaces leading to the formation of CO_2 and mineral acids.

3.2. *Effect of photocatalyst dosage*

The influence of the photocatalyst dosage on the degradation of 4-FP has been investigated employing different concentrations of TiO_2 and ZnO. The results are presented in Fig. 3. The *pseudo*-first order rate constants, determined using Eq. (8) increase from 0.0152 to 0.0358 min^{-1} with the increase of TiO_2-P25 from 50 to 150 mg

$$\ln\left[\frac{C_0}{C}\right] = k't \qquad (8)$$

where k' is the *pseudo*-first order rate constant, C_0 the initial concentration of 4-FP and C is the concentration at time 't'. Further increase from 150 to 250 mg decreases rate constant from 0.0358 to 0.0296 min^{-1}. In the case of ZnO increase of catalyst loading from 50 to 200 mg increase the rate constant from 0.0147 to 0.0291 min^{-1}. Further increase of catalyst concentration decreases the removal rate. Hence under experimental conditions 150 mg of TiO_2 and 200 mg of ZnO were found to be optimum for efficient removal of 4-FP. The deviation from linearity at higher concentrations is probably due to aggregation of free catalyst particle and screening effect resulting from the excessive opacity of the solution [22,23].

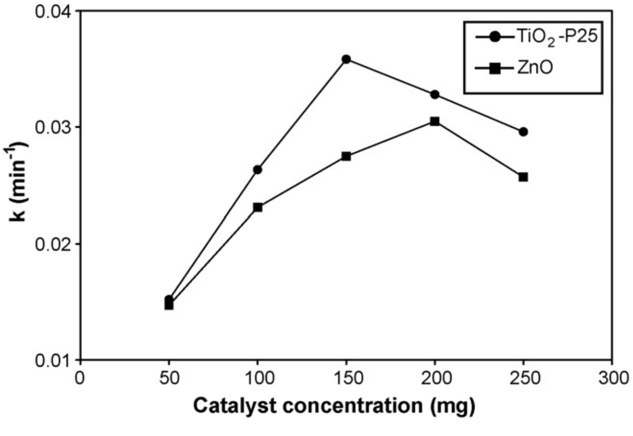

Fig. 3. Effect of pH on photodegradation of 4-FP: [4-FP] = 100 ppm; catalyst suspended = 100 mg; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}; airflow rate = 8.1 mL s^{-1}.

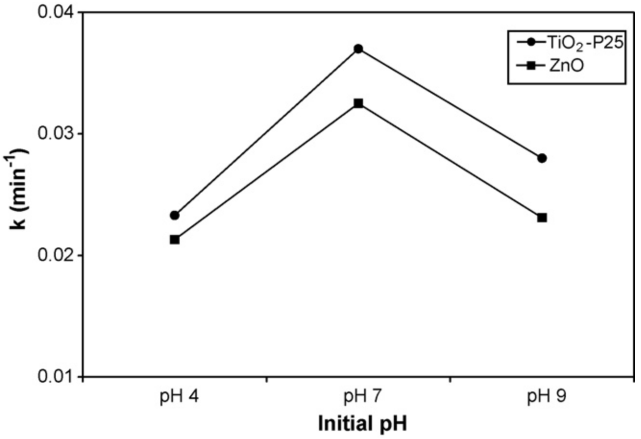

Fig. 4. Effect of photocatalyst dosage of 4-FP: [4-FP] = 100 ppm; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}; airflow rate = 8.1 mL s^{-1}.

3.3. *Effect of pH*

The effect of pH is an important parameter in photocatalytic degradation. It is related to the ionization state of the surface of the photocatalyst as well as pollutants. pH changes can influence the adsorption of pollutants on the photocatalyst surface, an important step for the photocatalytic oxidation to take place. The effect of initial pH of 4-FP on degradation is shown (Fig. 4). After 30 min of irradiation the *pseudo*-first order rate constants were 0.0233, 0.0370 and 0.0280 min^{-1} for TiO_2-P25 and 0.0213, 0.0325 and 0.0231 min^{-1} for ZnO at pH 4, 7 and 9, respectively. In both catalysts higher efficiency was observed at neutral pH of 7. The order of efficiency was found to be pH 7 > pH 9 > pH 4. The photocatalytic efficiency of the catalysts is also influenced by acid–base properties of the catalyst. The zero point charge PZC of TiO_2-P25 is 6.8 [24]. The TiO_2-P25 surface is positively charged in acidic medium (pH < 6.8) whereas it is negatively charged in alkaline medium. In case of ZnO the PZC is 8 and its surface is also positively charged at pH 4 and negatively charged at pH 9. Since the pK_a value of 4-FP is 9.89, it exists in molecular form at all these pH. Hence in both catalysts the maximum adsorption and consequently maximum efficiency in degradation were observed at neutral pH. As 4-FP exists in molecular form, both acidic and basic media are not favorable for 4-FP adsorption on catalyst surface.

3.4. *Effect of substrate concentration*

The effect of various substrate concentrations on the degradation of 4-FP in TiO_2-P25 and ZnO surface have been investigated. Fig. 5 shows that the increase of substrate concentration from 50 to 200 mg/l decreases the rate constant from 0.034 to 0.009 for TiO_2 and 0.037 to 0.011 for ZnO in 30 min.

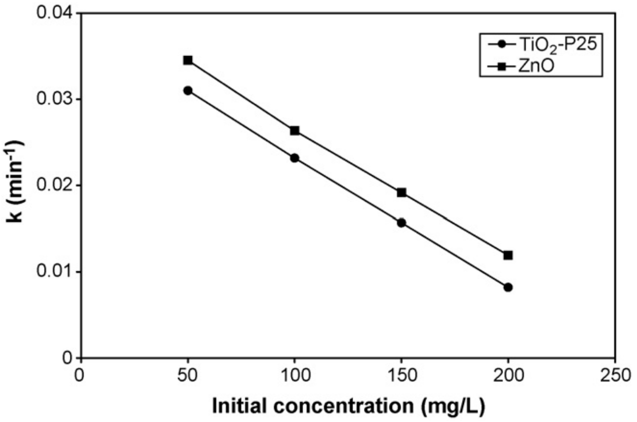

Fig. 5. Effect of various initial substrate concentration of 4-FP: catalyst suspended = 100 mg; $I = 1.381 \times 10^{-3}$ einstein L^{-1} s^{-1}; airflow rate = 8.1 mL s^{-1}.

The results reveal that the degradation is less in solution of higher initial 4-FP concentration when compared to the degradation at lower concentration. The rate of degradation relates to the probability of $^{\bullet}$OH radical formation on catalyst surface and probability of $^{\bullet}$OH radical reacting with 4-FP molecule. For all initial phenol concentration, the catalyst, oxidant and UV power are same. Since the generation of hydroxyl radical remains constant the probability of phenol molecule to react with hydroxyl radical decreases. At high initial phenol concentrations the path length of photon entering into the solution decreases, and also the amount of phenol adsorbed on catalyst surface increases. These processes also affect catalytic activity.

The influence of the initial concentration of 4-FP on the photocatalytic degradation rate of most organic compounds is described by *pseudo*-first order kinetics (Eq. (8)), which is rationalised in terms of modified Langmuir–Hinshelwood model to accommodate reaction occurring at solid–liquid interface

$$r = \frac{K_1 K_2 [\text{4-FP}]_0}{1 + K_1 [\text{4-FP}]_0} \tag{9}$$

$$\frac{1}{r} = \frac{1}{K_1 K_2 [\text{4-FP}]_0} + \frac{1}{K_2} \tag{10}$$

where $[\text{4-FP}]_0$ is the initial concentration in mg/l, K_1 the reaction rate constant and K_2 is taken to be the langmuir adsorption constant. This Langmuir–Hinshelwood (L–H) kinetic equation has been used by several authors to analyze the heterogeneous photocatalytic reaction [25–27]. The rate of degradation of 4-FP at the surface is proportional to the surface coverage of 4-FP on the photocatalyst assuming that 4-FP is strongly adsorbed on the catalyst surface than the intermediate products [28]. In the L–H equation K_1 reflects the limiting rate of the reaction at maximum coverage under the given experimental conditions and K_2 represents the equilibrium constant for adsorption of 4-FP on the illuminated photocatalysts. The applicability of L–H equation for degradation has been confirmed by the linearity of the plot (Fig. 5) obtained by plotting the reciprocal of initial rate ($1/r$) against reciprocal of initial concentration ($1/C$). This indicates that the degradation of 4-FP occurred mainly on the surface of photocatalysts. The values K_1 and K_2 are found to be 0.0165 $(\text{mg/l})^{-1}$ and 3.168 (mg/l) m^{-1} for TiO_2 and 0.0116 $(\text{mg/l})^{-1}$ and 2.4331 (mg/l) m^{-1} for ZnO processes, respectively.

Table 1
Effect of oxidants on photodegradation of 4-FP (%)

Oxidants	TiO_2-P25		ZnO	
	pH 4	pH 9	pH 4	pH 9
KIO_4	79.86	76.71	76.33	73.86
$KBrO_3$	66.89	62.85	60.33	57.85
H_2O_2	60.88	28.81	40.85	13.90
$(NH_4)_2S_2O_8$	53.85	40.85	49.82	39.29
$KClO_3$	46.35	41.89	42.85	37.88

[4-FP] = 100 ppm; catalyst suspended = 100 mg; oxidants = 0.01 M; irradiation time = 15 min; airflow rate = 8.1 ml s^{-1}; $I = 1.381 \times 10^{-3}$ einstein l^{-1} s^{-1}.

3.5. *Effect of inorganic oxidants*

In heterogeneous photocatalytic reaction molecular oxygen is used as an electron acceptor for the prevention of electron-hole recombination. Inorganic oxidants H_2O_2, $S_2O_8^{2-}$, BrO_3^{-}, IO_4^{-} and ClO_3^{-}, can compensate for the O_2 lack of either because of oxygen consumption (or) slow oxygen mass transfer. They also play a dual function as strong oxidant themselves and as electron scavengers. The effect of addition of these oxidants on photocatalytic degradation of 4-fluorophenol was investigated. Irradiation of UV light with the oxidants enhances the 4-FP degradation rate in both TiO_2 and ZnO systems (Table 1). After 15 min irradiation at pH 4 79.86%, 66.89%, 60.88%, 53.85%, 46.35% of degradations were observed in UV/TiO_2/IO_4^{-}, UV/TiO_2/BrO_3^{-}, UV/TiO_2/H_2O_2, UV/TiO_2/$S_2O_8^{2-}$, UV/TiO_2/ClO_3^{-} processes, respectively.

From the results the most effective oxidant for the degradation of 4-FP is found to be IO_4^{-}. The higher reactivity of UV/TiO_2/IO_4^{-} is due to the production of a number of highly reactive intermediate radicals such as $IO_3^{\bullet}$, $OH^{\bullet}$ and $IO_4^{\bullet}$. These radicals and radical anion also assisted the degradation by free radical pathways

$$IO_4^{-} + h\nu \rightarrow IO_3^{\bullet} + O^{\bullet -} \tag{11}$$

$$O^{\bullet -} + H^{+} \rightarrow {}^{\bullet}OH \tag{12}$$

$${}^{\bullet}OH + IO_4^{-} \rightarrow {}^{-}OH + IO_4^{\bullet} \tag{13}$$

In the second effective oxidant BrO_3^{-} the enhancement of removal rate is due to reaction between BrO_3^{-} and conduction bond electron [29]. This reaction reduces the recombination of electron hole pair.

$$BrO_3^{-} + 6e_{CB}^{-} + 6H^{+} \rightarrow Br^{-} + 3H_2O \tag{14}$$

$S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet -}$) both thermally and photolytically in aqueous solution. $SO_4^{\bullet -}$ then reacts with H_2O to produce $^{\bullet}$OH radicals

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} \tag{15}$$

$$SO_4^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^{+} \tag{16}$$

In the addition of H_2O_2 the enhancement of degradation is due to the increase in the hydroxyl radical concentration as shown by Eqs. (17) and (18):

$$H_2O_2 + e_{CB}^- \rightarrow {}^{\bullet}OH + OH^- \tag{17}$$

$$H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \tag{18}$$

The order of enhancement is $UV/TiO_2/IO_4^- > UV/TiO_2/BrO_3^- > UV/TiO_2/S_2O_8^{2-} > UV/TiO_2/H_2O_2 > UV/TiO_2/ClO_3^-$.

In basic medium at pH 9 a similar trend of degradation was observed. The degradation efficiency of UV/TiO_2/oxidant process is slightly more in acidic medium than in basic medium.

In the case of H_2O_2 a drastic decreases in the removal rate in basic medium occurs when compared to acidic medium. In basic medium H_2O_2 undergoes photodegradation to water and oxygen rather than hydroxyl radical [30]

$$2H_2O_2 \xrightarrow{h\nu} 2H_2O + O_2 \tag{19}$$

Irradiation of 4-FP with ClO_3^-, IO_4^-, H_2O_2, $S_2O_8^{2-}$ and BrO_3^- in the absence of photocatalyst results in 2.25%, 25.87%, 12.49%, 20.47% and 4.42% degradations, respectively. The degradation is negligible in UV/ClO_3^-, UV/BrO_3^- processes.

The order of photodegradation without photocatalyst is $UV/IO_4^- > UV/S_2O_8^{2-} > UV/H_2O_2 > UV/BrO_3^- > UV/ClO_3^-$. The higher efficiency of UV/IO_4^- is due to the formation of reactive free radicals upon irradiation (Eqs. (11)–(13)) and that of $UV/S_2O_8^{2-}$ is due to generation of $SO_4^{\bullet-}$ ($E^\circ = 2.6$ eV) by thermally and photolytically. The same trend is observed in both acidic and basic medium for UV/ZnO/oxidant processes (Table 1). But UV/TiO_2/oxidant process is slightly more efficient than UV/ZnO/oxidant process (Fig. 6).

In order to clarify the efficiency of UV/oxidant system UV absorption spectra of each oxidant at the same concentration were examined. The UV spectrum of these oxidants is shown in Fig. 7. As seen in figure, IO_4^- has very high UV absorption. But ClO_3^- has no UV absorption. The oxidant IO_4^- is more effective on degradation due to high absorption of UV light and ClO_3^- is least efficient. In addition to light absorption electron-scavenging effect of these oxidants also play a significant role. The higher efficiency of BrO_3^- than $S_2O_8^{2-}$ is due to the electron scavenging effect of BrO_3^-.

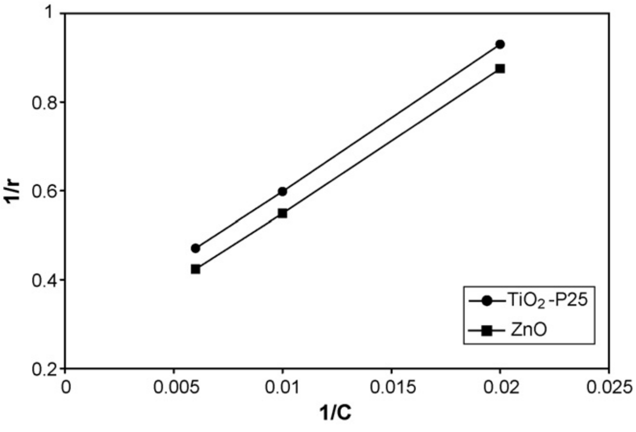

Fig. 6. Linearised reciprocal kinetic plot of the photodegradation of 4-FP: [4-FP] = 100 ppm; catalyst suspended = 100 mg; $I = 1.381 \times 10^{-3}$ einstein l^{-1} s^{-1}; airflow rate = 8.1 ml s^{-1}.

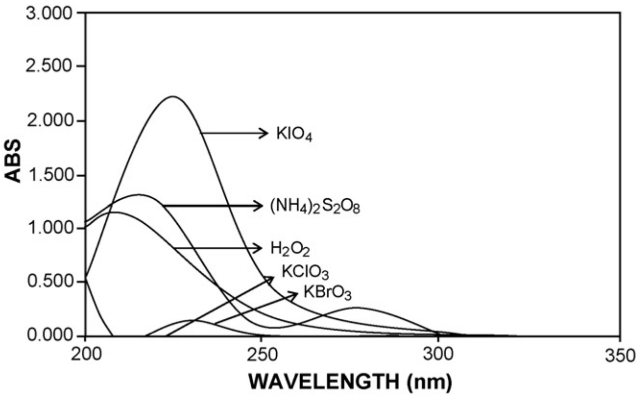

Fig. 7. UV absorption spectra of KIO_4, H_2O_2, $(NH_4)_2S_2O_8$, $KBrO_3$ and $KClO_3$ (0.01 M).

3.6. *Effect of inorganic anions*

Wastewater contains not only organic contaminants but also considerable amount of inorganic anions such as nitrate, sulphate, carbonate, etc. These ions change the ionic strength of medium and thus affect of catalytic activity of the photocatalyst. Table 2 gives the results on the effect of added inorganic anions like chloride, carbonate, bicarbonate, sulphate and nitrate of sodium salts at two different pH. In the illuminated TiO_2 system at pH 4, 37.55%, 40.12%, 48.22%, 64.80% and 72.17% of degradations were observed with Na_2CO_3, $NaHCO_3$, NaCl, $NaNO_3$, Na_2SO_4, respectively, after 30 min irradiation. The order of inhibition of these anions are $CO_3^{2-} > HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$. The main inhibition effect is due to adsorption on TiO_2 surface [31]. As can be seen from the values (Table 2) the degradation efficiency of TiO_2/UV was significantly decreased in the presence of CO_3^{2-}, HCO_3^-, Cl^- whereas the efficiency increased in the presence of SO_4^{2-} and NO_3^-. The SO_4^{2-} ion reacts with hydroxyl radical to form $SO_4^{\bullet-}$ ions. The sulphate radical anion can accelerate the reaction (Eqs. (15) and (16)) and no quenching was reported for NO_3^- ion. Addition of CO_3^{2-}, HCO_3^-, Cl^- ions decreases degradation of 4-FP due to the hydroxyl radical quenching by

Table 2
Effect of anions on photodegradation of 4-FP (%)

Anions	TiO_2-P25		ZnO	
	pH 4	pH 9	pH 4	pH 9
Na_2CO_3	37.55	35.87	34.89	30.81
$NaHCO_3$	40.12	38.57	39.63	37.11
NaCl	48.22	46.22	46.82	43.66
Na_2NO_3	64.80	62.87	59.71	56.82
Na_2SO_4	72.17	70.17	62.17	60.39

[4-FP] = 100 ppm; catalyst suspended = 100 mg; anions = 0.1 M; irradiation time = 30 min; airflow rate = 8.1 ml s^{-1}; $I = 1.381 \times 10^{-3}$ einstein l^{-1} s^{-1}.

these ions. The effect is similar in basic medium also

$$CO_3{}^{2-} + OH^{\bullet} \rightarrow OH^- + CO_3{}^{\bullet -} \quad (20)$$

$$HCO_3{}^- + OH^{\bullet} \rightarrow H_2O + CO_3{}^{\bullet -} \quad (21)$$

$$OH^{\bullet} + Cl^- \rightarrow Cl^{\bullet} + OH^- \quad (22)$$

A similar trend was observed for ZnO system both in acidic and basic medium by the addition of these anions.

3.7. *Effect of transition metal ions*

The results on effect of addition of metal ions on photocatalytic degradation of 4-FP in UV/TiO_2 and UV/ZnO system are given in Table 3. At time of 30 min of irradiation 57.58%, 62.56%, 76.63% and 35.46% of degradations with TiO_2-P25 were observed for Fe^{3+}, Fe^{2+}, Mg^{2+} and Cu^{2+} in acidic medium whereas in basic medium 38.13%, 30.43%, 73.37% and 31.83% degradations occurred. The negative effect of Fe^{3+} and Fe^{2+} in basic medium is due to coagulation of hydroxo complex of Fe^{3+} formed during the reaction [32]. Addition of Mg^{2+} is most effective and 76.63% of degradation was achieved in 30 min. The enhancement of degradation by addition of these ions except Cu^{2+} is due to increase of charge separation by accepting the conduction band electron

$$M^{n+} + e_{CB}{}^- \rightarrow M^{(n-1)+}$$

where M^{n+} represents Cu^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+} metal ions.

The same order of reactivity was observed for ZnO/UV by the addition of transition metal ions. Except Cu^{2+} the addition of transition metal ions causes enhancement of reaction rate in both TiO_2 and ZnO systems. The reason for the negative effect of Cu^{2+} ions on the photocatalytic degradation of 4-FP in both TiO_2 and ZnO system may be attributed to the low reduction potential Cu^{2+}/Cu^{1+} couple. This value is 0.1 eV with respect to NHE. The reduction of Cu^{2+} by photogenerated electrons may compete with the formation of superoxide anion radicals and consequently may reduce the formation of hydroxyl radical [33]. In the literature there are reports of formation of surface complexes of Cu^{2+} with organic compounds present in the suspensions, which can also act as surface poison [34].

Table 3
Effect of transition metal ions on photodegradation of 4-FP (%)

Transition metal ions	TiO_2-P25		ZnO	
	pH 4	pH 9	pH 4	pH 9
Fe^{3+}	57.58	38.13	52.35	31.23
Fe^{2+}	62.56	30.43	57.83	26.73
Mg^{2+}	76.63	73.37	69.82	63.87
Cu^{2+}	35.46	31.83	36.82	32.85

[4-FP] = 100 ppm; catalyst suspended = 100 mg; transition metal ions = 10 mg; irradiation time = 30 min; airflow rate = 8.1 ml s^{-1}; $I = 1.381 \times 10^{-3}$ einstein l^{-1} s^{-1}.

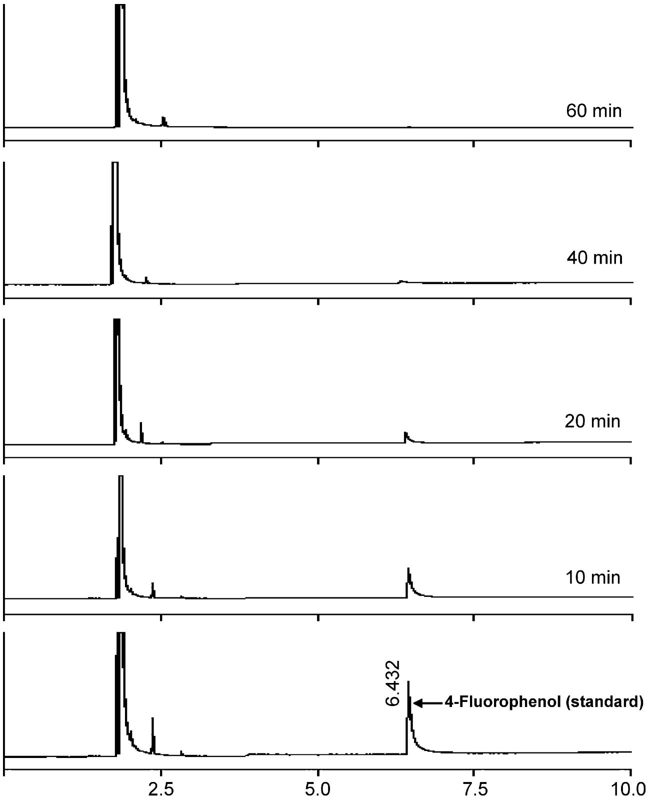

Fig. 8. Gas chromatograms of 4-FP (100 ppm) during the UV irradiation in presence of TiO_2.

3.8. *Mineralization*

The mineralization of 4-FP was also studied by COD measurements, gas chromatography and fluoride ion releasing in UV/TiO_2 system. The COD measurements revealed that the COD of 248 mg/l of the initial concentration of 100 ppm gradually decreased with increasing irradiation period under optimum conditions with TiO_2 system and after 1 1/2 h irradiation, the COD value becomes zero indicating the complete degradation of 4-FP. The gas chromatograms of 4-FP taken at different irradiation times are shown in Fig. 8. The signal of 4-FP at 6.432 decreases gradually and disappears completely at 60 min irradiation. The fluoride ion measurements also revealed that the compound released 18 mg/l fluoride ion after 1 1/2 h. The amount of fluoride ion released is equivalent to the theoretical value. The results confirm the mineralization of 4-FP by heterogeneous photocatalysis using UV light.

3.9. *Conclusions*

4-Fluorophenol is effectively degraded by both TiO_2-P25 and ZnO under irradiation with UV-A light. TiO_2-P25 is more efficient than ZnO. Addition of oxidants such as KIO_4, $KBrO_3$, $(NH_4)_2S_2O_8$, H_2O_2, $KClO_3$ increase the photocatalytic degradation significantly. Among the oxidants periodate ion is found to be more efficient than others. The effect of metal ions on degradation of 4-FP was found to be in the order of $Mg^{2+} > Fe^{3+} > Fe^{2+} > Cu^{2+}$. The degradation of

4-FP follows *pseudo*-first order kinetics. The applicability of Langmuir–Hinshelwood kinetic equation reveals that the degradation of 4-FP occurs mainly on the surface of the photocatalysts.

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