

## Photo-Fenton oxidation of dichlorophene in aqueous solution: kinetics investigation and effects of operational parameters

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### ABSTRACT

Dichlorophene (DCP), a widely detected contaminant in the aquatic environment, was removed under the UV-254 nm irradiations based on advanced oxidation processes. The removal efficiency of DCP from water was enhanced by coupling UV with oxidant (H<sub>2</sub>O<sub>2</sub>) and/or catalyst (Fe<sup>2+</sup>), that is, UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> owing to the <sup>•</sup>OH radical generation in the system, which is chiefly responsible for degradation of DCP. Removal of DCP was maximum, that is, 96% degradation after 50 min UV irradiation by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> at pH 3, with apparent rate constant ( $k_{app}$ ) of 0.058 min<sup>-1</sup>. The degradation rate of DCP increased with the increasing initial concentrations of DCP, represented by 0.011, 0.018 and 0.023 ppm min<sup>-1</sup> at using 3, 4 and 5 ppm initial concentrations of DCP, respectively. The presence of NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> deteriorated the degradation proficiency of DCP from 96% to 86% and 74%, respectively, attributed to scavenging of <sup>•</sup>OH radical.

**Keywords:** Dichlorophene; Advanced oxidation processes; Photo-Fenton process; Rate constant; Radical scavengers

### 1. Introduction

Water is not simply an economic commodity but also an imperative societal commodity. Though, due to cumulative human activities, aqueous environments have been exposed to thrilling microbial, chemical and biological toxins. Polluted water from anthropogenic sources is

discharged into fresh water bodies, and is destroying the aquatic system [1]. In most of the developing countries, one of the key environmental problem is water pollution [2]. Dichlorophene (DCP) is one of the harmful substances [3] used as an antihelmintic pesticide product, which enters into the aquatic environment and causes long-term chronic effects in the aquatic organisms, that is, fish, leading to

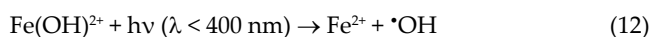
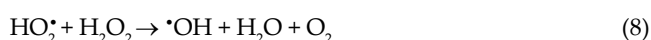
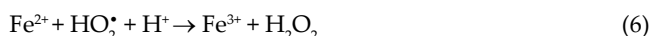
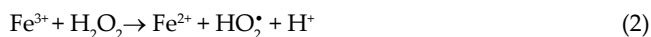
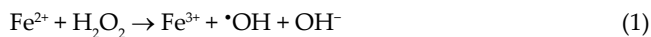
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disturbed aquatic life; it may also cause fatal diseases [4]. DCP is a non-biodegradable mutagen and has been reported to cause serious health issues directly or indirectly to human populations; it irritates the skin leading to serious skin diseases. It is also very harmful to the eyes and mucous membranes. It has the probability to develop cancer [5]. The removal of such hazardous substances from aquatic environment is necessary [6]. Previously many techniques such as filtration, froth filtration, adsorption, ultra filtration,  $\text{KMnO}_4$  oxidation, primary, secondary and tertiary treatment for the removal of such kinds of toxic material from water have thoroughly been conducted [7,8]. Most of the organic pesticides used in agriculture and other contaminants present on the surface of soil absorb ultraviolet (UV) radiation, which causes their degradation via molecular bond that in turn causes breaking [9,10]. The above mentioned techniques are more expensive and more complicated as well as the degradation efficiency of contaminant is not too much high [11]. Other drawbacks of these stated techniques are that non-biodegradable, mutagenic materials such as DCP may be converted into more toxic by-product; thus DCP is not completely mineralized in aquatic environment [12]. Therefore, new economically practicable and extra effective methods for pollution regulation and prevention are mandatory for environmental safety. Recently advanced oxidation process (AOP), a conventional technique, is utilized for the removal of harmful chemicals from wastewater [11]. AOPs have been found the most effective remediation technologies concerning the removal of non-biodegradable organic pollutants (NBOP) including pharmaceuticals into nontoxic and even complete mineralized constituents [13].

So, in the present study, we have applied AOP, which is cheap and easy to construct and also the removal/degradation efficiency of NBOPs from aquatic environment is high as compared with other techniques [4,5]. In AOPs, there are different methods such as homogenous catalysis, heterogeneous catalysis, electrochemical process, photo-oxidative process, etc. [5]. There are different systems present in AOPs such as UV/ $\text{O}_3$ , UV/ $\text{H}_2\text{O}_2$ , UV/peroxydisulfate, photo-Fenton, and Fenton such as AOPs, etc. In the present study, we used photo-Fenton process (PFP) for the degradation of DCP. In PFP, the  $\cdot\text{OH}$  radical is created from  $\text{Fe}^{2+}$  catalyzed activation of  $\text{H}_2\text{O}_2$ , following a chain reaction (i.e., reactions (1)–(13)) [14,15], and as a result,  $\cdot\text{OH}$  radical attacks on focused pollutant causing its debasement [16].  $\text{H}_2\text{O}_2$  may react with  $\text{Fe}^{3+}$  to regenerate  $\text{Fe}^{2+}$  as well. The  $\text{Fe}^{2+}$  may also be regenerated through UV light according to Eq. (12). Meanwhile, the less oxidant radical species, that is,  $\text{HO}_2\cdot$  may also react with  $\text{Fe}^{3+}$  to regenerate  $\text{Fe}^{2+}$  as well as forming additional  $\cdot\text{OH}$  radical. This Fenton process has the advantage over many other techniques as it causes complete mineralization of the target contaminant through safe and non-toxic route. Although the efficiency of a photocatalytic system was generally reduced by mass transfer from the solution to the photocatalyst surface in fixed film reactors, which may limit the degradation reaction rates. However, mass transfer effect was not significant in Fenton and PFPs using homogeneous photocatalyst. The Fenton's reagents are easily soluble in water, constituting a homogeneous solution in aqueous medium, thereby avoiding the mass transfer limitation effects. Thus, in PFP, the catalyst ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) may play

an essential role in the production of  $\cdot\text{OH}$  through electron exchange component by utilizing UV light radiation [17].



The  $\cdot\text{OH}$  radical basically assaults chlorinated carbon on benzene ring in DCP molecule. In PFP, the catalyst ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) decomposes  $\text{H}_2\text{O}_2$  to deliver  $\cdot\text{OH}$  through electron exchange component within the nearness of UV (ultra violet). The PFP is relatively cost effective and environmental friendly process, since no supplementary vitality is required when compared with many other AOPs. Similarly, both hydrogen peroxide and iron are moderately conservative and safe [18].

According to the above mentioned discussion, photo-Fenton oxidation (PFO) was adopted for the effective remediation of recalcitrant pollutant DCP. As to the best of our knowledge, no research study is available on the PF-based degradation of DCP. The nitrates and bicarbonates are two of the more commonly inorganic anions found in natural water systems, which might affect the degradation efficiency of the pollutants based on various AOPs [19]. Investigating the effect of those anions on pollutant degradation may be useful on laboratory scale, considering practical applications. The aim of the current study is to remove DCP from the water system through safe and economical route. The concentration of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  has been optimized for the effective degradation of DCP besides pH optimization, as pH of the aquatic system greatly affects the degradation. To boost WTPs (water treatment processes), pH is an important factor that significantly influences the efficiency of PFP. Due to the presence of various organic and inorganic ions, natural water impacts on the removal efficiency of DCP by UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  at predetermined ideal conditions. Therefore the influence of  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  on the

degradation of DCP by PFP has also been conducted in the current exertion.

## 2. Materials and methods

### 2.1. Materials

Dichlorophene ( $C_{15}H_{10}Cl_2O_2$ , Fig. 1),  $H_2O_2$  (hydrogen peroxide 30%),  $FeSO_4 \cdot 7H_2O$  (ferrous sulfate hepta hydrate), HCl (hydrochloric acid 37%),  $NaHCO_3$  (sodium nitrate),  $NaNO_3$  (sodium bicarbonate),  $CH_3OH$  (methanol),  $CH_3COOH$  (acetic acid), and  $CH_3CN$  (acetonitrile) were bought from Sigma-Aldrich (St. Louis MO, USA). All chemicals were used as received. All the solutions were prepared in Milli-Q water. The pH of the solution was adjusted by adding appropriate amount of 0.1 N HCl or NaOH.

### 2.2. Degradation experiments

The photo-Fenton experiments were carried out in a bench-scale photochemical reactor comprising of a Pyrex Petri dish covered with a quartz plate. The solution was irradiated by a 15 W low pressure mercury UV lamp, which emitted UV light primarily at 254 nm. The intensity of the UV light was measured as 0.1 mW/cm<sup>2</sup> by using a calibrated radiometer. The reacting solution was constantly stirred using a magnetic bar to thoroughly mix the solution. The experiments were performed in triplicate. The error bars in the figures denote the standard error of the mean. A schematic diagram of PFP is depicted in Fig. 2.

### 2.3. Chemical analysis

The concentration of DCP was determined by using high performance liquid chromatograph (HPLC, Agilent 1200) with UV detector. An Eclipse (XDB-C18) column (150 × 4.6 mm, 5 micrometer particle size) was employed for the separation of the analyte. The UV detection was performed at 280 nm, and the column temperature was maintained at 25°C. The mobile phase comprised of acetonitrile, methanol and acetic acid (50:30:20% v/v) at a flow rate of 1 mL/min.

## 3. Results and discussion

### 3.1. Direct UV photolysis of DCP

Fig. 3 depicts the result of direct UV photolysis of DCP in aqueous solution. The results showed that DCP was significantly degraded by direct UV photolysis, represented

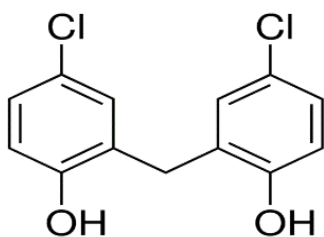


Fig. 1. Chemical structure of dichlorophene.

by 40% DCP removal in 50 min. Furthermore, the results revealed that the degradation efficiency of DCP increased with increasing UV radiation time, represented by 9%, 15%, 27%, 35% and 40% degradation, after 10, 20, 30, 40 and 50 min UV irradiation, respectively. The result was consistent with the studies of Dantas et al. [20] showing 50% and 30% removal of metronidazole and propranolol, respectively, in an 8-h UV-C irradiation. Mondal et al. [21] showed 60% degradation of ciprofloxacin in 120 min, using UV-C light irradiation. Similarly, Xie et al. [22] showed 83% degradation of 4-bromophenol in 20 min, by using direct UV photolysis. A plausible reason was the presence of a chromophore structure, such as unsaturated bond or aromatic ring, which have the capacity of UV light absorption [20].

### 3.2. Degradation of DCP by UV/ $H_2O_2$

The degradation of DCP by UV/ $H_2O_2$  is shown in Fig. 3, indicating 60% degradation of 5 ppm in 50 min. The results revealed that the UV photolytic degradation of DCP was significantly enhanced by adding  $H_2O_2$ , attributed to  $\cdot OH$

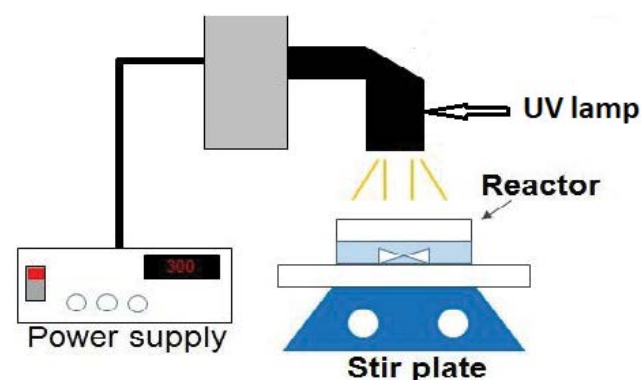


Fig. 2. A schematic diagram of photo-Fenton experimentation.

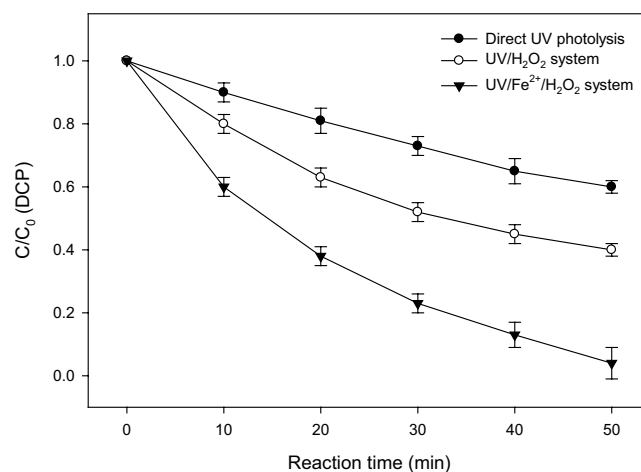


Fig. 3. Degradation of DCP with (i) direct UV photolysis, (ii) UV/ $H_2O_2$  and (iii) UV/ $Fe^{2+}$ / $H_2O_2$  processes.  $[H_2O_2]_0 = 3$  mM;  $[Fe^{2+}]_0 = 7$   $\mu$ M;  $[DCP]_0 = 5$  ppm; pH = 3.0.

radical generated in Eq. (13). Furthermore, the results showed that the degradation efficiency of DCP by UV/ $H_2O_2$  increased with the increasing concentration of  $H_2O_2$ , indicated by 47%, 55% and 60% degradation of DCP in 50 min at using 1, 2 or 3 mM  $H_2O_2$ , respectively (Fig. 4). The result was attributed to the elevated concentration of  $\cdot OH$  at using high concentration of  $H_2O_2$ . This result was consistent with the literature studies regarding the degradation of organic pollutants by UV/ $H_2O_2$  system. Mondal et al. [21] showed the degradation of ciprofloxacin by UV-C light irradiation increased from 60% in 120 min to 100% in 40 min, by adding 100 mM  $H_2O_2$  to the system, attributed to the generation of  $\cdot OH$  radicals. Khan et al. [23] found the degradation efficiency of lindane by UV/oxidant system increased from 58% to 92%, 98% and 100% after 180 min UV irradiation, by increasing the oxidant concentration from 125 to 250; 500 and 1,000  $\mu M$ , respectively. Gu et al. [24] reported the apparent rate constants ( $k_{obs}$ ) of ketamine and methamphetamine increased radically from  $0.001 \text{ min}^{-1}$  to  $0.027$  and  $0.049 \text{ min}^{-1}$  by increasing the  $H_2O_2$  concentration from 0 to 1,000  $\mu M$ , respectively.

### 3.3. Degradation of DCP by PFP (i.e., UV/ $Fe^{2+}/H_2O_2$ )

The degradation of DCP by PFP (i.e., UV/ $Fe^{2+}/H_2O_2$ ) is shown in Fig. 3, indicating 96% removal of DCP ( $C_0 = 5 \text{ ppm}$ ) in 50 min, at using  $[Fe^{2+}]_0 = 7 \mu M$  and  $[H_2O_2]_0 = 3 \text{ mM}$ . The enlarged degradation of DCP was attributed to enhanced  $\cdot OH$  radical generation owing to the involvement of  $Fe^{2+}$  according to reactions (1)–(13). Furthermore, the results showed that the degradation efficiency of DCP by UV/ $Fe^{2+}/H_2O_2$  increased with the increasing concentration of  $H_2O_2$ , indicated by 80%, 90%, 93% and 96% degradation of DCP at using 0.5, 1, 2 or 3 mM  $H_2O_2$ , respectively, in 50 min (Fig. 4). The results also showed that the degradation efficiency of DCP by UV/ $Fe^{2+}/H_2O_2$  increased with the increasing concentration of  $Fe^{2+}$ , indicated by 45%, 58% and 96% DCP removal in 50 min at using 2, 5 and 7  $\mu M$   $Fe^{2+}$ , respectively (Fig. 5). This was

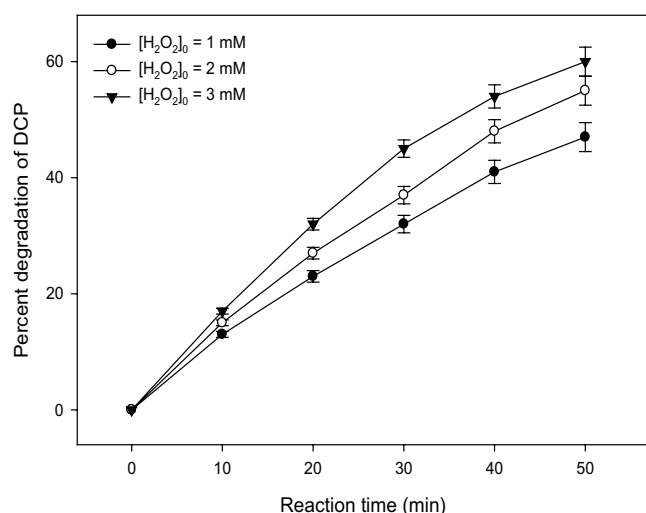


Fig. 4. Effect of initial concentration of  $H_2O_2$  on DCP degradation by UV/ $H_2O_2$  process.  $[Fe^{2+}]_0 = 7 \mu M$ ;  $[DCP]_0 = 5 \text{ ppm}$ ;  $pH = 3.0$ .

attributed to the elevated concentration of  $\cdot OH$  at high concentration of  $Fe^{2+}$ . This result was consistent with the literature about the degradation of organic pollutants by using UV/ $Fe^{2+}/H_2O_2$  systems. Lucas and Peres [25] reported that the decolorization of the azo dye Reactive Black 5 by Fenton and PFO increased with the increasing concentration of  $Fe^{2+}$ . In case of Fenton process, by increasing the  $[Fe^{2+}]_0$  from  $5.0 \times 10^{-5}$  to  $2.0 \times 10^{-4} \text{ M}$ , the discoloration of Reactive Black 5 was enhanced from 72% to 95% after 7.5 min UV irradiation, while PFP enhanced the discoloration efficiency from 75% to 96% within the same reaction time. Khan et al. [26] also found the degradation of atrazine by UV/ $H_2O_2/Fe^{2+}$  dramatically increased by increasing the concentration of  $Fe^{2+}$  from 1.79 to 35.81  $\mu M$ .

### 3.4. Factors affecting the degradation efficiency of DCP

#### 3.4.1. Effect of solution pH

The pH of the solution is an important factor affecting the efficiency of Fenton and PFPs. The pH effects on Fenton and PFPs could be related to several reasons, for example, varying the solution pH may change the oxidation state of  $Fe^{2+}$ , etc. [27]. pH is also marked as an effective parameter in the optimization of WTPs, as it considerably affects the efficiency of many AOPs as well [28]. At both very low and high pH, iron is not soluble rather precipitates as manifested by Eq. (9); thereby hindering the degradation efficiency of the pollutants. In the current study, optimization of pH was done by studying DCP degradation at various pH, that is, ranging from acidic to basic conditions, including neutral pH, that is, investigating pH 2, 3, 6 and 9, while keeping other parameters constant, such as concentration of DCP,  $H_2O_2$  and  $Fe^{2+}$ .

Table 1 shows the effect of pH on degradation efficiency of DCP by UV/ $Fe^{2+}/H_2O_2$ , represented by 65%, 96%, 91% and 59% DCP removal in 50 min, at pH 2, 3, 6 and 9, respectively. Based on experimental findings, pH 3 was selected as ideal pH for the degradation of DCP by photo-Fenton

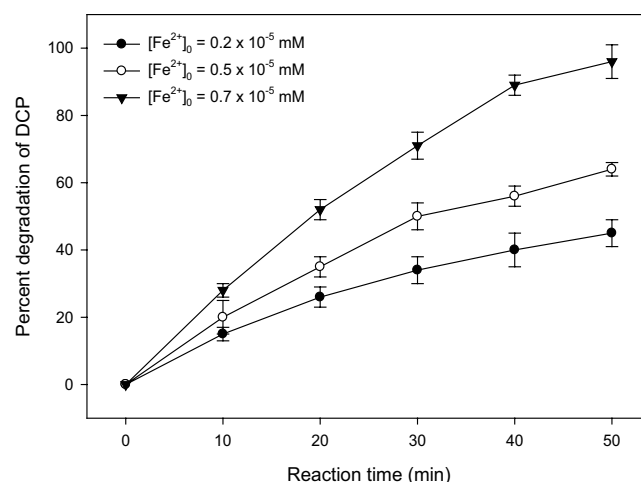


Fig. 5. Effect of initial concentration of  $Fe^{2+}$  on DCP degradation by UV/ $H_2O_2$  process.  $[H_2O_2]_0 = 3 \text{ mM}$ ;  $[DCP]_0 = 5 \text{ ppm}$ ;  $pH = 3.0$ .

process, which led to 96% DCP removal in 50 min. The results obtained were supported by the literature studies [29,30]. Ghaly et al. [31] reported the degradation of p-chlorophenol by photo-Fenton process varied from 83% to 96%, 82% and 72% by increasing the pH from 2 to 3, 4 and 5, respectively. In our previous study, it was shown that the removal efficiency of lindane by photo-Fenton-like process was 98.2%, 42.5% and 36.4% after 40 min UV irradiation, when the initial pH was 3.0, 6.0 and 9.0, respectively [14], indicating pH 3 as the best pH condition. The maximum efficiency of DCP at pH 3 was attributed to the solubility of  $\text{Fe}^{2+}$  catalyst in the aqueous medium. Furthermore, Table 1 also depicts that the degradation efficiency of DCP at natural pH (i.e., pH 6) was also comparatively high, suggesting that the current process was an efficient approach for treating natural water and wastewater systems.

#### 3.4.2. Effect of initial concentration of DCP

For conducting the kinetic studies, the photo-Fenton degradation of DCP was investigated at using different initial concentrations of DCP (i.e., 3, 4 and 5 ppm) at using constant concentrations of  $\text{Fe}^{2+}$  (7  $\mu\text{M}$ ) and  $\text{H}_2\text{O}_2$  (3 mM) at pH 3. The results showed that degradation rate of DCP (calculated by the concentration change in the first 20 min) by photo-Fenton process under the optimized situation increased with the increasing initial concentrations of DCP, represented by 0.011, 0.018 and 0.023 ppm  $\text{min}^{-1}$  at using initial DCP concentrations of 3, 4 and 5 ppm, respectively (Fig. 6). Fig. 6 suggests that the degradation rate of DCP enhanced with increasing DCP concentration, imitating direct relationship of degradation rate with DCP concentration [29]. Meanwhile, it was shown that the apparent rate constant ( $k_{\text{obs}}$ ) of degradation of DCP decreased with increasing concentration of DCP (Fig. 6). The observed

rate constant ( $k_{\text{obs}}$ ) of DCP was found to be 0.058, 0.043 and 0.034  $\text{min}^{-1}$ , respectively, at initial DCP concentrations of 3, 4 and 5 ppm, respectively (Fig. 6). Khan et al. [14] found that the degradation rate of lindane by photo-Fenton-like process increased from 0.023 to 0.175  $\mu\text{M min}^{-1}$  by varying initial lindane concentrations of lindane from 0.5 to 5.0 mM, respectively. A probable reason was the greater number of DCP molecules being exposed to the  $\cdot\text{OH}$  radicals, which might led to an enhanced degradation rate of DCP [14]. Degradation of pollutants by Fenton and photo-Fenton based advanced oxidation processes generally followed first order kinetics [13]. In this study, the degradation of DCP was carried out at using three different concentrations of DCP, that is, 3, 4 and 5 ppm, and the graphs of  $-\ln C/C_0$  vs.  $k$  were plotted at different time intervals ( $t$ ) that gave straight lines with  $R^2$  values greater than 0.95 in each case (Fig. 7). These graphs were successfully explained by first order kinetics equation, as shown by reaction (14) [14]. Table 2 presents a comparative degradation analysis of various contaminant by conventional methods with our established system, which clearly signifies the superiority of our approach.

$$\ln \frac{C}{C_0} = kt \quad (14)$$

#### 3.4.3. Effect of inorganic anions, that is, $\text{NO}_3^-$ and $\text{HCO}_3^-$

Depending upon the anthropogenic and ecological conditions, natural water bodies are abundant in a variety of inorganic anionic species, especially nitrates and bicarbonates, in unpredictable levels ranging from 0.00005 to 0.003 [34]. These inorganic anionic species are reported to have elevated rate constants with  $\cdot\text{OH}$  radical and hence can act as scavengers of  $\cdot\text{OH}$  radical, which may affect the degradation kinetics of the pollutants [35,36]. Fig. 8 shows the effect of  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  on the degradation efficiency of DCP by PFF, while keeping all other parameters constant, that is,  $[\text{DCP}]_0 = 5$  ppm,  $[\text{H}_2\text{O}_2]_0 = 3$  mM and  $[\text{Fe}^{2+}]_0 = 7$   $\mu\text{M}$ , at pH 3. The results showed that in the presence of 1 ppm  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  ions, the degradation efficiency of DCP decreased from 96% to 86% and 74%, respectively. The corresponding apparent rate constant ( $k_{\text{app}}$ ) also decreased from 0.058  $\text{min}^{-1}$  to 0.035 and 0.033  $\text{min}^{-1}$ , in the presence of 1 ppm  $\text{NO}_3^-$  and  $\text{HCO}_3^-$ , respectively. The retarding effect due to the presence of  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  was attributed to the scavenging of  $\cdot\text{OH}$  radical by these anions according

Table 1  
Parameters for degradation of DCP (5 ppm)/ $\text{H}_2\text{O}_2$  (3 mM)/ $\text{Fe}^{2+}$  (7  $\mu\text{M}$ ) at various pH

pH	% Degradation at reaction time of 50 min	$k_{\text{app}}$ ( $\text{min}^{-1}$ )	$R^2$
2	65	0.054	0.985
3	96	0.057	0.982
6	91	0.047	0.987
9	59	0.053	0.917

Table 2  
Comparative degradation analysis of various contaminants by conventional methods

Compound	Methods/material	% Degradation	Reference
Methylene blue	ZnO reduced grapheme, oxide-carbon composites	96%	[32]
DCP	Photoelectrocatalytic mechanism by using $\text{TiO}_2$ and active polytetrafluoroethylene	91.1%	[33]
Phenol	In the presence of hydrogen peroxide	48%	[8]
Carbamazepine	Photo-Fenton process	90.6%	[11]
DCP	UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}^{2+}$	95.5%	Present study

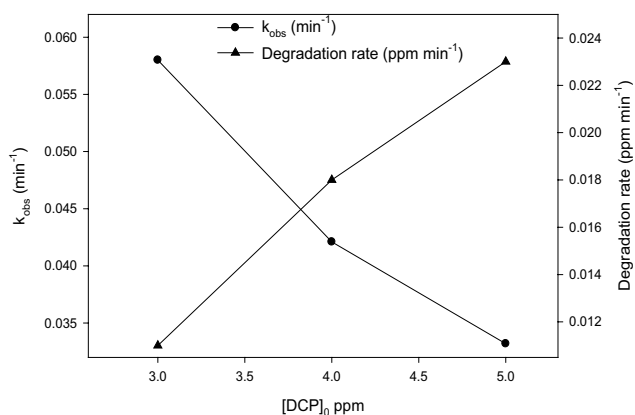


Fig. 6. Variation of  $k_{obs}$  and degradation rate with different initial concentration of DCP by UV/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> process. [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 3 mM; [Fe<sup>2+</sup>]<sub>0</sub> = 7 μM; pH = 3.0.

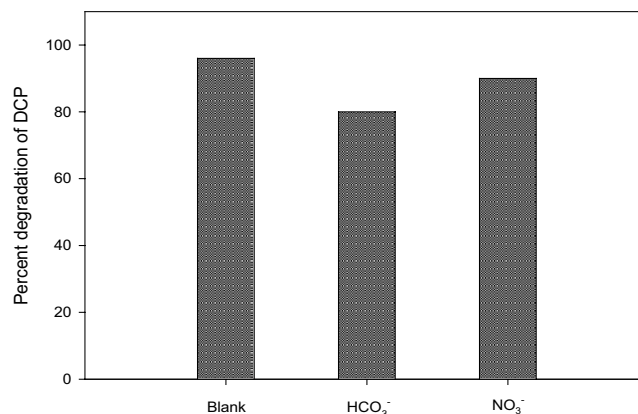


Fig. 8. Effect of NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> on percentage removal of DCP in 30 min. [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 3 mM; [Fe<sup>2+</sup>]<sub>0</sub> = 7 μM; [DCP]<sub>0</sub> = 3 ppm; [NO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 1 ppm; [HCO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 1 ppm; pH = 3.0.

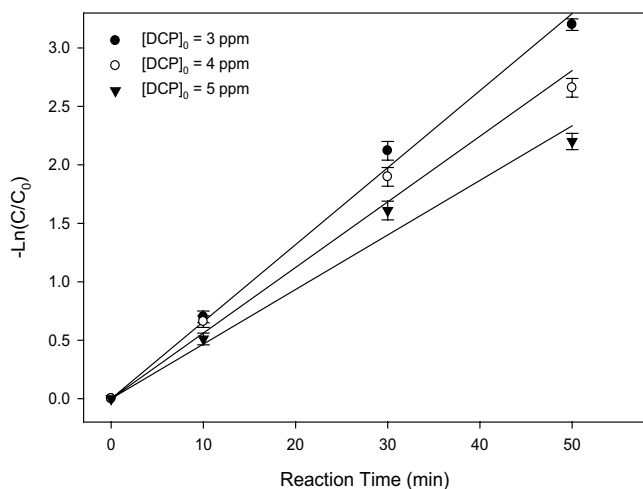


Fig. 7. Plot of  $-\ln(C/C_0)$  vs. time for degradation of DCP with UV/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> processes. [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 3 mM; [Fe<sup>2+</sup>]<sub>0</sub> = 7 μM; [DCP]<sub>0</sub> = 3, 4 and 5 ppm; pH = 3.0.

to reactions (15) and (16), respectively. Khan et al. [37] found that the apparent rate constants ( $k_{obs}$ ) of degradation of antipyrine by UV/H<sub>2</sub>O<sub>2</sub> decreased from 1.99 to 1.96 h<sup>-1</sup> and 1.34 h<sup>-1</sup>, in the presence of 100 mM of NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>, respectively. Keen et al. [15] reported that UV ( $\lambda < 200$  nm) photolysis may generate additional •OH radical from NO<sub>3</sub><sup>-</sup>; however, in the current study, the reaction is not likely to be efficient owing to the low quantum yield of •OH from NO<sub>3</sub><sup>-</sup> under the UV-C ( $\lambda = 254$  nm) light. Tan et al. [38] found the degradation of the pharmaceutical compounds, such as ibuprofen, diphenhydramine and phenytoin was reduced in the presence of NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>, attributed to the scavenging of •OH radicals by these anions.

#### 4. Conclusions

Dichlorophene (DCP), a widely detected contaminant in the aquatic environment was removed under the

UV-254 nm irradiations based on AOPs. The removal efficiency of DCP from water is enhanced by coupling UV with oxidant (H<sub>2</sub>O<sub>2</sub>) and/or catalyst (Fe<sup>2+</sup>), that is, UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> process. The •OH radical generated under UV/H<sub>2</sub>O<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> or UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> systems was mainly responsible for the substantial removal proficiency of DCP. The degradation of DCP was high in indirect photolysis due to the ample production of •OH radicals, which could attack DCP molecules. The degradation rate of DCP increased with the increasing concentration of DCP from 3 to 5 ppm, since large number of DCP molecules get exposed to •OH radicals resulting in enhanced degradation rate of DCP. Optimization studies by fixing other parameters constant ratified that degradation of DCP increased with increasing concentration of H<sub>2</sub>O<sub>2</sub> till 3 mM H<sub>2</sub>O<sub>2</sub> and then suffers decline with further increase in H<sub>2</sub>O<sub>2</sub> till 5 mM suggesting its role as •OH radicals scavenger. Optimization of Fe<sup>2+</sup> catalyst at DCP (5 ppm)/H<sub>2</sub>O<sub>2</sub> (3 mM) suggested 7 μM concentration as a best dose resulting in 96% degradation in 50 min, with 0.051 min<sup>-1</sup> apparent rate constant. The most competent degradation of DCP after 50 min of irradiation time under ideal PF environment, that is, DCP (5 ppm)/H<sub>2</sub>O<sub>2</sub> (3 mM)/Fe<sup>2+</sup> (7 μM) was achieved in acidic media at pH 3 with 96% degradation efficacy and 0.058 min<sup>-1</sup> suggesting our present system an economic, rapid and effective tool for environmental reclamation. Studies of scavenger effect elucidated that the presence of NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> ions decreased the degradation efficiency of DCP from 96% to 86% and 74%, respectively.

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