

Photodegradation of pentachlorophenol in room temperature ionic liquids

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Abstract

The photolytic degradation of chlorinated aromatics namely pentachlorophenol (PCP) in 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] room temperature ionic liquid (RTIL) has been investigated using UV radiation of 253.7 nm. At low concentrations (less than 1.57 mM), PCP could be degraded in this RTIL following pseudo-first-order kinetics. Addition of H₂O₂ at different concentrations in the presence of UV 253.7 nm radiation showed an inhibition effect on the PCP degradation rate. The degradation of PCP was also studied using a radical-enhanced degradation process using Fe(II)/UV activation of Oxone. Initial studies showed that the enhancement of reaction rate in this case was approximately 72% when compared to only UV at a high PCP concentration of 0.225 mM. However greater Oxone concentrations exhibited an inhibition effect similar to H₂O₂ addition. Quenching studies with tertiary butyl alcohol (TBA) suggested the generation of hydroxyl radicals in the ionic liquid. *In situ* degradation of PCP extracted from soils, namely, montmorillonite (MT) and glacial till (GT), using [BMIM][PF₆] showed enhanced reaction rates compared to those of the samples prepared by dissolving the compounds directly in the ionic liquid solvent. It is suggested that some species co-extracted with the target compound could facilitate the photodegradation reaction. This technique has shown potential for further development into a method for the removal of organic compounds from solid surfaces in the laboratory or in industry. This would involve the extraction of organic compounds using RTILs followed by *in situ* photodegradation of extracted compounds in the ionic liquid phases and recycling the extractants used.

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Keywords: Photodegradation; Ionic liquids; RTIL; [BMIM][PF₆]; Pentachlorophenol; PCP; UV; Iron; Fe(II); H₂O₂; Oxone; Hydroxyl radicals; *tert*-Butyl alcohol; TBA

1. Introduction

The scientific understanding of the nature of ionic liquids as a class of emerging solvents is still limited, and it is difficult to fully explain or precisely predict the physicochemical properties of these solvents. However, some connections between the properties and the chemical structure have been demonstrated. For example, increasing the size of the cation or anion decreases the melting point [1,2] and longer *N*-alkyl chain of the cation gives lower density [3]. Studies also revealed that ionic liquids are non-flammable, exhibit high thermal and chemical stability, and

have negligible vapor pressure as well as large electrochemical window [1]. The electrochemical window measures the stability of the cation against reduction and the anion against oxidation processes. This is an important property of the ionic liquids with respect to photodegradation process. Not much literature is available on the redox properties of [BMIM][PF₆] but formation of stable radiolysis intermediates indicated its resistance towards oxidation [1,2]. Values of the electrochemical window for some ionic liquids are given in Table 1.

Due to these unique properties, ionic liquids have been proposed as “green solvents” and potential substitutes for volatile organic compounds (VOCs). Since VOCs are usually flammable and toxic, their use can lead to severe environmental pollution problems. As a result, great efforts have been exerted for search of environmentally friendly replacements to VOCs. Although

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Table 1
Values of electrochemical window for some ionic liquids

Ionic liquid	Electrochemical window (V)	Reference
BuPyBF ₄ (<i>N</i> -butylpyridinium tetrafluoroborate)	−0.21 to 0.2	[2]
[EMIM][BF ₄] (1-ethyl-3-methylimidazolium tetrafluoroborate)	−2.45 to 2.10	[4]
[BMIM][BF ₄] (1-butyl-3-methylimidazolium tetrafluoroborate)	−2.55 to 2.13	[2,5]
1-Butyl-1-methyl pyrrolidinium trifluoromethylsulfonate	−3.1 to 3.4	[2,4]

many aspects of ionic liquids remain unknown and need further investigation, their non-volatility as well as some of their properties may render them as promising candidates for replacing VOCs. It has been reported that ionic liquids could be effective solvents in reactions in different fields including electrochemistry, chemical synthesis, catalysis, and photochemistry [1,3,6–10]. Recent studies also show that some organic compounds and several metals can be removed from the aqueous phase via liquid–liquid separations using ionic liquids as extractants [10].

Solvent extraction is also an effective technique for the removal of organic compounds from solids by transferring the target compounds from the solid matrices to the extracting solvent media. VOCs have traditionally been employed as extractants in this process and raised similar concerns to those of their application in other industrial processes. Ionic liquids can be considered as green alternative extractant solvents to VOCs in this process due to their negligible volatility, non-flammability and their affinity towards organic compounds. The solvent extraction of soils using the ionic liquid [BMIM][PF₆] has been described by Khodadoust et al. [11]. The application of ionic liquids as a substitute for VOCs in the extraction of environmental samples is only restricted to usage in the laboratory [11]. The extraction efficiencies are comparable to those of the conventional solvents. Since the disposal of the extracted compounds and the recovery of the used solvents are of environmental and economical importance, further treatment approach has to be considered for the destruction of the extracted compounds along with the recycling of the ionic liquids.

This purpose can be achieved by a subsequent *in situ* degradation of extracted compounds in the ionic liquid phases using photolysis, which will simultaneously result in the regeneration of ionic solvents. Because VOCs are generally not inert when exposed to high energy UV radiation [12], the application of UV for the degradation of extracted compounds will result in the simultaneous degradation of the organic extractants, thus the recycling of the extractant phase is difficult. On the other hand, ionic liquids have been proved to be more stable than conventional organic solvents under harsh reaction conditions such as oxidation, photolysis and radiolysis [13,14]. Therefore, their recyclability under such condition is feasible. As a result, a two-step process that involves extraction of organic compounds from solid matrices using ionic liquids as solvents followed by *in situ* photodegradation of extracted compounds in the ionic liquid phases with simultaneous regeneration of the extractant phases can be explored as a new application of RTILs in chemical and industrial processes for the extraction of organic chemicals from solid surfaces.

Highly chlorinated compounds like PCP degrade relatively slowly under UV radiation and require longer exposure time [15,16]. In this study, we investigate the degradation of PCP with transition metal activated generation of radicals with some powerful oxidants to reduce treatment time and to increase the rate of the degradation reaction. The conventional Fenton systems have some pH limitations [15], require higher concentration of hydrogen peroxide and also do not achieve complete mineralization of the organic compounds. A similar system has been investigated previously in our laboratory by using the cobalt/peroxymonosulfate (Co/PMS) system for the removal of chlorophenols in aqueous media [17]. Here, we extend the process to ionic liquid medium using Fe(II) as the transition metal mediator instead of Co which may have some environmental concerns.

Halogenated aromatics such as 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP), are termed as priority pollutants by the USEPA [15,16]. Due to their toxicity to organisms, they are resistant to biodegradation and are persistent in the environment. Previously, UV-based photodegradation with or without addition of oxidants has been used to treat water contaminated by chlorophenols and some polycyclic aromatic hydrocarbons (PAHs) [15,16,18,19]. It is suggested that ionic liquids may be applied as a substitute for VOCs to extract chlorophenols from samples in the laboratory.

In this work, we report the photodegradation of PCP in 1-butyl-3-methylimidazolium hexafluorophosphate, known as [BMIM][PF₆], using UV radiation. The effects of addition of H₂O₂ on the degradation reaction are also discussed. UV/Fe(II)/Oxone-mediated photodegradation of PCP in [BMIM][PF₆] is also studied. In addition, an attempt was made to confirm the radical generation process using a quenching agent, tertiary butyl alcohol (TBA). *In situ* degradation rates of PCP extracted from real soils, montmorillonite (MT) and glacial till (GT), using [BMIM][PF₆] are compared with those of the samples prepared by directly dissolving the compounds into the ionic liquid. To the best of our knowledge, this is the first study that reports radical-enhanced degradation of organic compounds in the ionic liquid phase.

2. Experimental

2.1. Chemicals

PCP (98%) was purchased from Aldrich and used without further purification. [BMIM][PF₆] (97% purity, yellowish color) was obtained from Sachem, Inc. (Austin, TX) and either used as received or after saturation with water. H₂O₂ (30% in water)

was provided by Acros Organics (New Jersey). Oxone (KHSO_5 as active component) manufactured by DuPont was obtained from Aldrich. The water used in this study was double distilled deionized water (18 M Ω).

2.2. Methods

The ionic liquid was stored in the laboratory where the relative humidity of the air was approximately 54% [20]. This ionic liquid was assumed to be air equilibrated [20]. Photodegradation studies of PCP in [BMIM][PF₆] were conducted in air equilibrated ionic liquid by dissolving PCP directly into the ionic liquid. The ionic liquid containing PCP extracted from MT or GT was prepared following the procedure explained in Khodadoust et al. [11] in the Department of Civil and Materials Engineering of the University of Illinois at Chicago and used as received.

Different concentrations of PCP (0.06, 0.35, 0.68 and 1.57 mM) were obtained by directly dissolving PCP in the air equilibrated ionic liquid. Fe(II) in the form of FeSO_4 was used, directly dissolved in the ionic liquid. Experiments were conducted with a 1:1 molar ratio of PCP:Fe(II). Oxone was not found to be soluble in the ionic liquid. A concentrated solution of Oxone was prepared in water such that only a very small quantity (a few μL) was required in the reaction mixture. Oxone was used in molar ratios of 1:0.5, 1:1, 1:2, 1:5 and 1:10 with the Fe(II) for the higher concentrations of PCP. At 0.06 mM PCP, Fe(II)/Oxone tested was in the molar ratio of 1:1. H_2O_2 was also used in a similar way. Certain volumes of H_2O_2 or Oxone were added to the ionic liquid containing PCP to achieve different concentrations in the range of 0.382–6.12 mM. Two distinct phases were formed upon the addition of H_2O_2 . After the solution was mixed using a magnetic stirrer, the two phases could not be observed any more.

Photodegradation experiments were carried out in a 5 mL cylindrical quartz photoreactor. The solution was continuously stirred throughout the photodegradation process with a magnetic stirrer. The initial volume of the solution used was 4 mL and 0.5 mL of sample was withdrawn at specified time intervals and quenched with 5 mL of acetonitrile. This dilution was carried out for HPLC analysis. Methanol was used to quench samples with Oxone. Photodegradation reactions were initiated by UV radiation provided by two UV radiation sources positioned opposite to the reactor cell. Each UV source comprised of two removable low pressure mercury tubes provided by Spectronics Corporation (Westbury, NY). The power for each tube is 15 W. The wavelength of the radiation is in the range of 250–258 nm, and the emission peak is at 253.7 nm (data from Spectronics Corporation). Atrazine was used as the target organic compound in the studies of determining the radical species. The experiments were conducted as previously with the addition of TBA being the only difference. The molar ratio of atrazine:Fe(II):Oxone:TBA was 1:1:1:50.

2.3. Analyses

Quantitative analysis of PCP and atrazine in ionic liquids was conducted using a Series 1100 HPLC (Agilent). A reverse

phase amide column (RP-16 Discovery Supelco) and a UV–vis Diode Array Detector were used for HPLC analysis. All ionic liquid samples were dissolved in HPLC grade acetonitrile due to the high viscosity of the solvent. A mixture of 0.01N sulfuric acid and acetonitrile (40:60 ratio) was used as the mobile phase for HPLC analysis, and the flow rate was 1.5 mL/min. The Fe content in [BMIM][PF₆] was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES)—Perkin Elmer. The samples were 2% acidic solutions for easy detection.

3. Results and discussion

3.1. Effect of concentration on the photodegradation of PCP

The concentration profile of PCP in [BMIM][PF₆] versus treatment time is shown in Fig. 1. The photodegradation of PCP followed a similar trend to that of 2-CP [15,16,21]. PCP possesses an absorbance peak at 254 nm, which is very close to wavelength of the UV source used (253.7 nm) [15,16]. Therefore, the degradation rate of PCP was not significantly slower than that of 2-CP [20]. Different initial concentrations of PCP were used in order to investigate the effect of PCP initial concentration on the degradation reaction. When the initial concentration of PCP was 1.57 mM, 90% reduction of the initial amount of the parent compound was achieved over 360 min under 253.7 nm UV radiation. PCP concentration detected at the end of the irradiation was 0.16 mM. The transformation rate of PCP in the first 60 min of the reaction was $8.8 \times 10^{-3} \text{ mM min}^{-1}$. This rate decreased to 5.6×10^{-3} and $3.2 \times 10^{-3} \text{ mM min}^{-1}$ at initial concentrations of PCP of 0.68 and 0.35 mM, respectively. The corresponding final PCP concentrations and removal efficiencies (i.e., % reduction of the initial amount) after 360 min of irradiation were 0.02 and 0.004 mM, 97.2 and 98.7%, respectively.

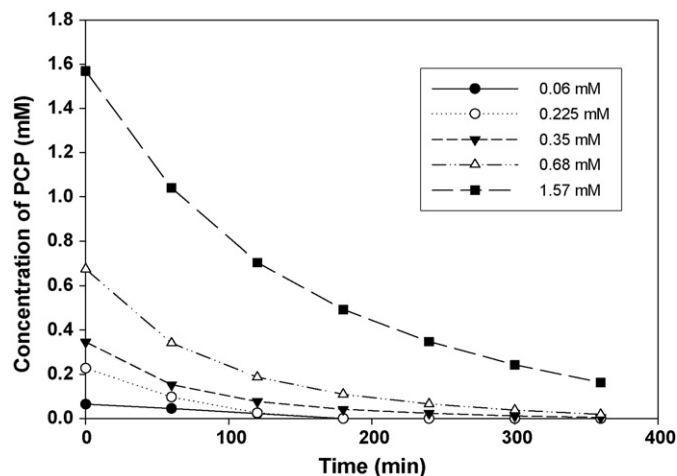


Fig. 1. Photodegradation of PCP with different initial concentrations in air equilibrated [BMIM][PF₆] under UV radiation.

3.2. Effect of H_2O_2 on the degradation of PCP

In order to investigate the effect of H_2O_2 on the photodegradation reaction of PCP, different amounts of H_2O_2 were added to the ionic liquid phase containing PCP directly dissolved in the ionic liquid to achieve various concentrations ranging from 0.382 to 6.12 mM. As illustrated in Fig. 2, the degradation rate of PCP in [BMIM][PF₆] was inhibited by H_2O_2 . Compared to the initial degradation rate of PCP ($0.009 \text{ mM min}^{-1}$) under UV radiation in the absence of H_2O_2 , addition of 0.382 mM (1:0.5 molar ratio) H_2O_2 yielded a rate of $0.006 \text{ mM min}^{-1}$, which indicates approximately 34% reduction. Increase of H_2O_2 loading resulted in further reduction of the degradation rates. When H_2O_2 concentration was increased to 6.12 mM (1:8 molar ratio), the degradation rate was reduced by approximately 57% ($0.004 \text{ mM min}^{-1}$).

In the aqueous phase, the conjunction of H_2O_2 and UV radiation is proven to enhance degradation rates when compared to only UV. Decomposition of H_2O_2 results in formation of $\bullet OH$ which are very reactive radical species and attack the organic compounds. Increase in H_2O_2 concentration has been observed to further enhance the reaction rate [14,17]. However, when the reaction rate reached a maximum, addition of more H_2O_2 led to inhibition of the reaction, suggesting the existence of an optimum H_2O_2 concentration. This has also been observed in several other studies including the photochemical oxidation of 4-chlorophenol [22], photodegradation of 4-nitrophenol and nitrobenzene [23] and degradation of acetone [24,25] in aqueous phases by UV/ H_2O_2 processes. Such a case has also been observed in the photodegradation of 2-CP in [BMIM][PF₆] [20,26]. It was suggested that, when the concentration exceeded the optimum, H_2O_2 behaved as a strong $\bullet OH$ scavenger that competed with the target compounds, and consequently reduced the reaction rates.

The $\bullet OH$ could also attack the ionic liquid which was the predominant compound (solvent) in the system to form OH-adducts. The reaction between $\bullet OH$ and [BMIM]⁺ has been observed in pulse radiolysis of 2 mM 1-butyl-3-

methylimidazolium chloride aqueous solutions saturated with N_2O and adjusted to pH 7.0 [3]. There is also evidence of reaction occurring between [BMIM]⁺ and $\bullet OH$ [24]. However, this reaction was not observed in pure ionic liquid. The hydroxyl radicals in our case can also attack the impurities which constitute 3% of our ionic liquid sample [23,25]. In the ionic liquid, the reactions may be different from those in the aqueous system. Reactions between $\bullet OH$ and chlorophenols have been suggested to be diffusion controlled and might be hindered due to the high viscosity of [BMIM][PF₆] and thus mixing effect in such a system could also affect the observed reaction rates [12,27].

3.3. Effect of iron and Oxone

PCP with the low concentration (0.06 mM) was also degraded with Oxone activated by the conjunction of Fe(II) (Fe(II):Oxone = 1:1) and UV irradiation. Fig. 3 depicts the degradation of PCP with the Oxone activation reagents. From Fig. 3, it can be seen that the combined UV/Fe(II)/Oxone as well as the UV/Fe(II) led to complete transformation of the chlorophenol in 1 h of reaction. When UV alone was used, complete transformation of the chlorophenol was achieved only after 3 h of radiation time. The average degradation rate at 30 min was 0.0014 mM/min with UV/Fe(II)/Oxone compared to 0.0006 mM/min when UV/Oxone were used. The UV/Fe(II)/Oxone demonstrated a slightly faster rate of degradation than UV/Oxone between the 30th and 120th min, most probably due to the additional presence of iron. Complete degradation of PCP was observed in less than 10 min when the Fe(II):Oxone ratio was increased to 1:2 (Oxone 0.12 mM). The control experiment with Fe(II) in the absence of UV proves that there is no significant absorption of the PCP by iron.

In the case of the higher PCP concentration of 0.225 mM, the degradation of PCP with different molar ratios of PCP:Oxone were tested, namely, 1:0.5, 1:1, 1:2, 1:5 and 1:10. The comparison of the initial degradation rates at 30 min with Oxone ratios is shown in Fig. 4. Compared to UV alone, the enhancement in the reaction rate was 72% when a 1:1:1 ratio of PCP:Fe(II):Oxone

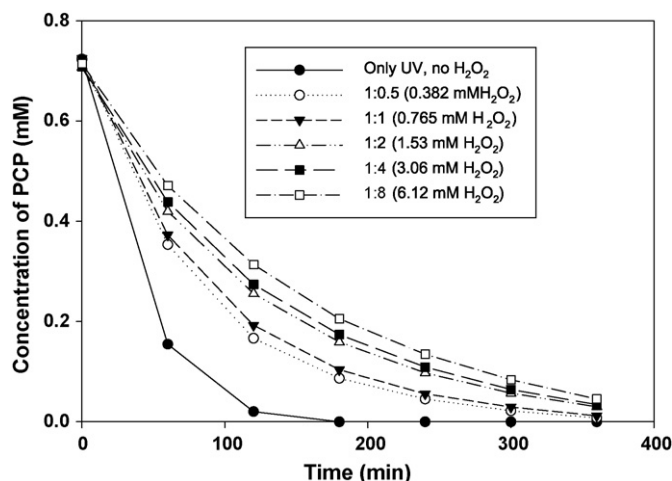


Fig. 2. Degradation of PCP in the presence H_2O_2 with different PCP: H_2O_2 molar ratios under UV.

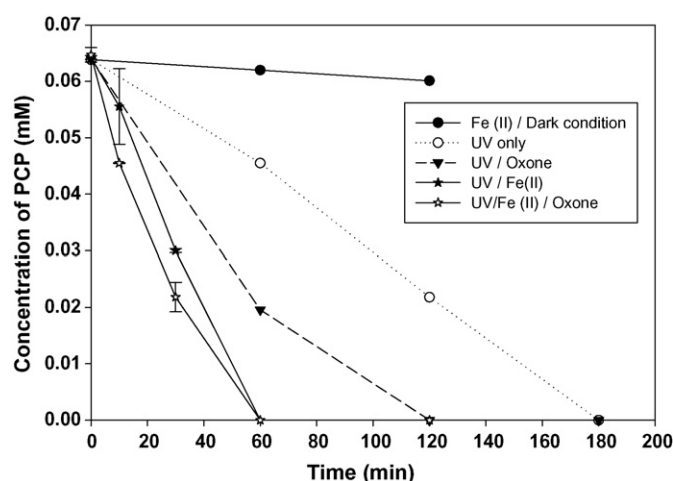


Fig. 3. Degradation of PCP (0.06 mM) with the conjunction of Fe(II) and Oxone under UV irradiation.

was used, and complete degradation was observed in less than 30 min whereas 60 min with UV alone. However, retardation of the rates was observed with increasing concentration of Oxone as in the case of hydrogen peroxide. When UV alone was used, the initial degradation rate at 30 min was 0.002 mM/min and it increased to 0.004 and 0.005 mM/min at 1:1:0.5 and 1:1:1 ratio of PCP:Fe(II):Oxone, respectively. Then, it decreased to 0.003 mM/min at a high ratio of 1:1:10. This trend is similar to inhibition by H_2O_2 and suggests the presence of an optimum dose of oxidant.

The degradation of organic contaminants by Oxone in conjunction with transition metals, such as Fe(II), Fe(III), Co(II) and Ag(I), in the aqueous media has been studied recently [15,28]. In many cases, Fe(II) has been found not just to catalyze the reaction but to also participate directly in reaction by undergoing redox or electrochemical transformations. In a study of the chemical oxidation of 2-CP and 2,4-DCP in aqueous solutions, it was found that the degradation rate with Fe(II)/UV without the addition of Oxone or H_2O_2 was still significant [17]. Fernandez et al. studied the Co activated Oxone treatment of dye Orange II and reported that there was no dye mineralization or photobleaching when Co(II) and Oxone were added separately, showing that Co(II) only acts as an activator and does not take part in the reactions [29,30]. In this study, there was significant degradation when Oxone or iron was present with UV, indicating that a possible branched radical chain reaction can occur even when the Oxone decomposition was not activated by the Fe(II) ions. In the solutions of organic compounds, peroxides are formed due to the branched radical chain mechanisms [29]. Anipsitakis and Dionysiou [17] and Yamazaki and Piette [31] have reported reactions of Fe ion due to the formation of the ferryl ion and other such oxidizing species. Compared to aqueous medium, ionic liquids are believed to be a microenvironment that can retain the reactants for longer periods [32]. This could be an additional reason for enhanced degradation by UV/Fe(II), since contact time is an important parameter in radical processes.

The results obtained in UV/Fe(II)/Oxone system shown in Fig. 4 illustrate the presence of an optimum oxidant dosage. In the degradation of the dye Orange(II), it was found that variation of Oxone concentration up to an Oxone concentration of 40 mM did not influence the degradation rate and the TOC (total organic

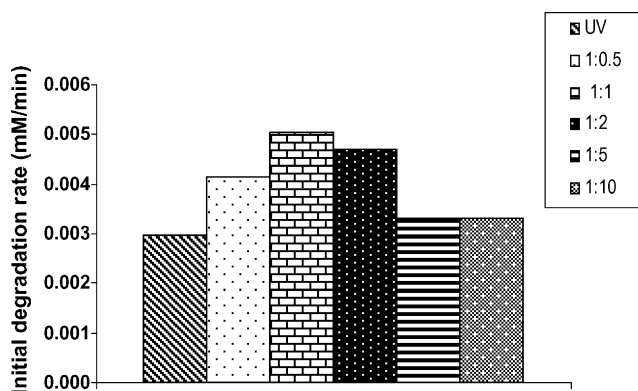


Fig. 4. Comparison of initial degradation rates of PCP (0.225 mM, PCP:Fe(II) = 1:1) at 30 min using different molar ratios of PCP:Oxone.

carbon) removal rate was constant over 5.5 mM Oxone [29,30]. These trends are similar to the pattern observed in our study. The reason could be the radical scavenging effect which competes with PCP and reduce the reaction rates. In a previous study on the degradation of 2,4,6-trichlorophenol by H_2O_2 and Oxone using complex iron activators based on ligands of nitrogen. Lente et al. [33] reported the formation of Cl^- in the primary reaction and Oxone oxidizing it to chlorine gas under catalytic conditions. This reaction is not desirable as it consumes oxidizing agent and generates a toxic gas. The consumption of oxidant could be the possible reason for the reduced rates with Oxone and UV in our study.

3.4. In situ degradation of PCP extracted from soils

The photodegradation of PCP extracted from MT or GT in the presence of UV 253.7 nm radiation was also investigated. PCP was extracted either from MT or GT and different concentrations in the ionic liquid were obtained depending on its availability in the soils used. When starting with an initial concentration of 0.076 mM of the MT extract, all PCP could be transformed after 120 min of UV 253.7 nm radiation, as shown in Fig. 5. This transformation could be achieved over 100 min when the initial concentration was 0.023 mM for GT, as shown in Fig. 6. Since the soils have other components which may transfer into the ionic liquid along with PCP and such species may affect the degradation reaction, we conducted control experiments by dissolving PCP directly in the ionic liquid to achieve the same concentrations as those obtained by extraction. For both initial concentrations used (0.076 and 0.023 mM), the control experiments gave a relatively slower degradation rate. The calculated average degradation rates in the first 60 min were 1.1×10^{-3} and 9.3×10^{-4} mM min $^{-1}$ for the extraction and control sample, respectively, with initial PCP concentration of 0.076 mM. When the initial PCP concentration was 0.023 mM, the average degradation rates in the first 20 min were 1.9×10^{-4} and 1.6×10^{-4} mM min $^{-1}$ for PCP extracted and dissolved directly, respectively.

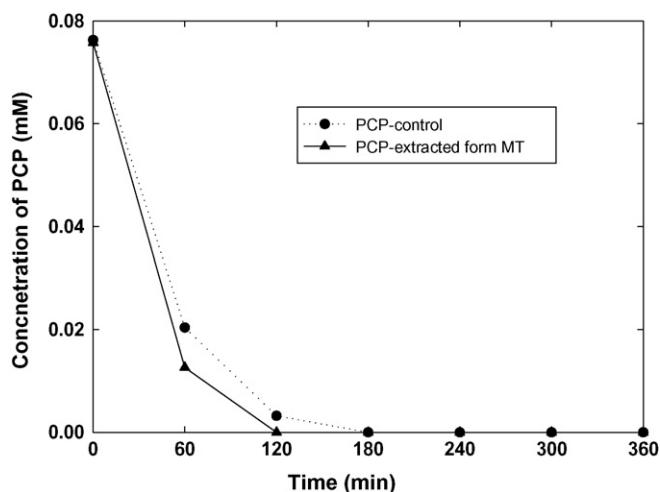


Fig. 5. Degradation of PCP extracted from MT and dissolved directly in air equilibrated [BMIM][PF $_6$] (control) under UV radiation.

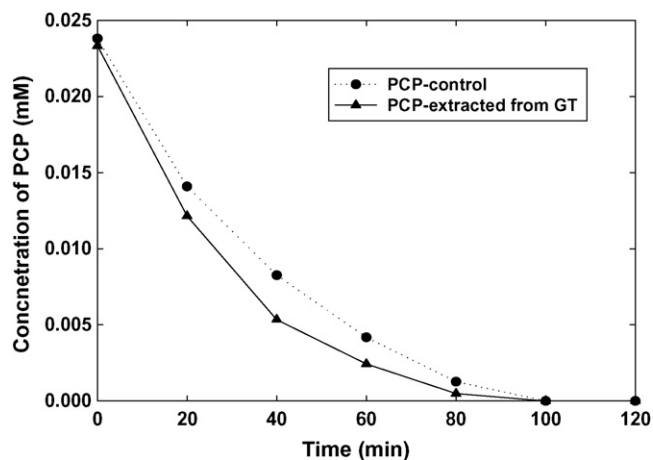


Fig. 6. Degradation of PCP extracted from GT and dissolved directly in air equilibrated [BMIM][PF₆] (control) under UV radiation.

These results suggest that some species were mobilized from the soils and transferred along with the target compounds into the ionic liquid phase. Since MT has no organic matter, these co-extracted species are believed to be mostly inorganic species or metals. The metal content of both MT and GT is given in Table 2. From Table 2 it is seen that GT has higher level of Fe, Mn, Zn, Cu, S but lower level of Al. This could explain the difference between MT and GT at PCP concentration of 0.20 mM. Ionic liquids are known to extract metal ions. Visser et al. explored the properties of ionic liquids to extract metal ions from aqueous solutions. Fe³⁺, Cd²⁺, Co²⁺ and Ni²⁺ were easily extracted by [BMIM][PF₆] because of its exceptional partitioning properties [10]. Natural iron minerals are known to be UV activating agents. In the studies involving the remediation of PCP contaminated soil, naturally occurring iron minerals in soil namely hematite and magnetite were found to effectively catalyze the Fenton-like reactions [34]. There is also evidence of formation of ferrihydrite which can degrade the PCP by itself without oxidants by the formation of species other than hydroxyl radicals [34], thus concluding that the increase in the degradation rates is most probably due to the direct participation of natural iron in the photodegradation reactions. Natural iron minerals present in soil have been utilized for Fenton-like reactions to degrade PCP [34], diesel compounds in contaminated soil [35] and hexachlorobenzene [36]. In our study, there is definitely a high concentration of Fe in both soils to facilitate degradation of PCP in the photocatalytic reactions. The increase in the reaction rates is not proportionally as high as the Fe concentration in soil. A probable reason is attributed to lesser Fe concentra-

Table 2

Concentration of metal in montmorillonite and glacial till

Soil	Montmorillonite (MT)	Glacial till (GT)
Total iron (ppm)	10,580	22,400
Total manganese (ppm)	30	388
Total zinc (ppm)	16	450
Total copper (ppm)	<1	26
Total aluminum (ppm)	21,000	11,540
Total sulfur (ppm)	400	4,600

tions extracted into the ionic liquid. The Fe analysis of our ionic liquid soil extracts exhibited extraction efficiencies of less than 2%. The concentrations of Fe in [BMIM][PF₆] extracted from MT and GT was 107.5 and 310.5 mg/L, respectively.

Although natural soils contain various mineral and mineral oxides, iron minerals are dominant (0.5–5 wt%) [36]. The above mentioned studies have also suggested that for these treatments, it is more efficient to utilize natural iron minerals than addition of soluble iron [37]. It has been reported that because such contaminants are strongly sorbed into the soil, increased degradation occurs because the degradation takes place at the surface of the iron minerals through electron transfer [38].

3.5. Quenching studies for radical investigation

tert-Butyl alcohol (TBA) is an effective quenching agent for hydroxyl radicals and has been used to determine radicals in several systems [15,21,24,39,40]. In the degradation of ozone in an aqueous system where TBA has been investigated as a quenching agent for hydroxyl radicals, it was reported that TBA did not react with the oxidant and did not undergo significant degradation under UV 253.7 nm alone [27,41]. In the present study, the degradation of atrazine in the ionic liquid system with or without TBA in the dark was investigated (not shown here). No degradation of atrazine was found in the presence of TBA and Fe(II)/Oxone, without UV. After 2 h of reaction, only 9.1% atrazine was degraded with Fe(II)/Oxone without TBA. It is demonstrated here that Oxone cannot be effectively activated by Fe(II) in the dark. The reason could be associated with the viscous properties of the ionic liquid [2]. Moreover, the photolytic degradation of atrazine in the presence and absence of TBA was also studied as shown in Fig. 7. In the control study, no degradation of TBA was observed after 2 h with UV 253.7 nm radiation. In Fig. 7, no degradation of atrazine is observed in the presence of TBA under UV radiation, similar to the process in the dark. In addition, the removal efficiency of PCP in

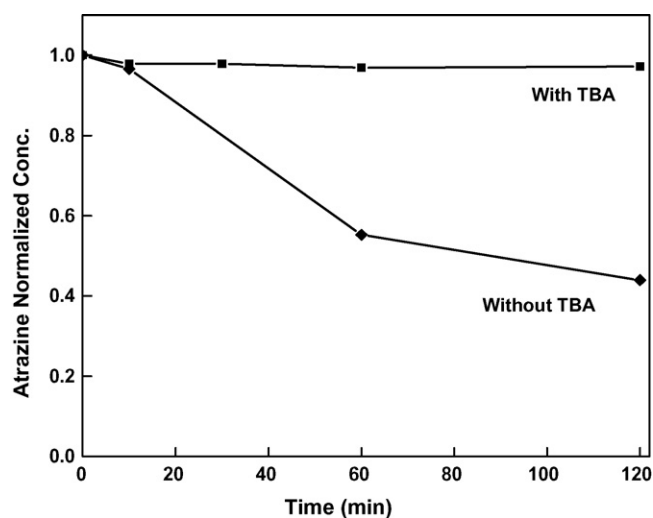


Fig. 7. Degradation of atrazine in the presence and absence of TBA under UV irradiation. Conditions: atrazine:Fe(II):Oxone = 1:1:1 (mol) and Oxone:TBA = 1:50 (mol).

2 h of reaction increased dramatically to 56% in the absence of TBA.

It has been published previously that the pulse radiolysis of several ionic liquids including [BMIM][PF₆] could generate organic radicals [2]. In the radiolysis of [BMIM][BF₄], TBA was found to scavenge hydroxyl radicals effectively in the ionic liquid system [40]. Combined with the present quenching studies, it is suggested that hydroxyl radicals could be generated in the UV/Fe(II)/Oxone system in the ionic liquid and attack the target compounds. In our previous studies, sulfate radicals were found to be the dominant species in aqueous systems with Fe(II)/Oxone [15]. In this current study, however, the presence of sulfate radicals was not identified. This suggests that the mechanism may be different in the ionic liquid medium in comparison to aqueous media. Earlier published works have shown differences in reaction mechanisms in ionic liquid and aqueous media due to properties such as viscosity and polarity [1,8]. Further research is required to confirm the type of the active species. There is also evidence that the viscosity of these ionic liquids retarded the recombination processes of the radicals [2]. For these reasons, ionic liquids have been suggested to be effective media for radical generation and investigation [40].

The recycling of the ionic liquid medium after such treatment has also been investigated [20]. It was reported that the reduction in the rates was not significant when ionic liquid was recycled after photodegradation of 2-CP. Such a process has both environmental and economic advantages when recycling of the ionic liquid medium is possible. Disposal and treatment costs are reduced. In the course of this study, we also became aware of various concerns regarding the stability of the ionic liquids. The degradation of [BMIM][PF₆] has been reported to produce toxic products such as HF [42,43]. Issues of persistence of ionic liquids in the environment particularly in soils and sediments are also being considered [44]. There are published reports on the stability of ionic liquids in the presence of UV, UV/H₂O₂ and UV/TiO₂ used at small concentrations of 100 mM [45]. Studies on the stability of ionic liquids in the presence of Fe(II)/Oxone/UV are lacking. Such investigations on ionic liquids as both pure phases and in aqueous media are necessary. This process can also be further extended to new environmentally friendly ionic liquids which do not have issues of toxic product release.

4. Conclusions

PCP could be degraded in room temperature ionic liquids under UV 253.7 nm radiation. UV radiation is very efficient due to the characteristic absorbance of the compound. Addition of H₂O₂ at any concentrations in the presence of UV radiation resulted in small inhibition of the degradation rate of PCP in the ionic liquid. At small contaminant concentrations (less than 1.57 mM), the photodegradation reactions of PCP follow pseudo-first-order kinetics. In the presence of Fe(II)/Oxone/UV systems, the results of our quenching studies suggest that the active species for atrazine degradation are probably hydroxyl radicals. The degradation rates of PCP extracted from soils, MT and GT, using the ionic liquid were enhanced compared to those

of the samples prepared by dissolving the compounds in the ionic liquid. Some mineral species transferred to the ionic liquid phases together with the target compounds may facilitate the degradation reaction. This technique is promising for the extraction of organic compounds from solid matrices such as soil or sediments. RTILs can replace VOCs for the extraction of organic compounds followed by the subsequent *in situ* photodegradation of extracted compounds in the ionic liquid phases with simultaneous regeneration of the ionic liquids. In this case, there is also no need for the addition of transition metal activators as there is potential of extracting and using the natural soil iron as an efficient activator as well as its direct participation in the degradation reaction.

Overall this extraction and subsequent photodegradation of organic compounds in the ionic liquid phase are effective procedures for reduction of volume of solvents and hence easier disposal. This study assessed the effectiveness of ionic liquid in a laboratory scale solvent extraction of soils and subsequent photodegradation process. Further economic and feasibility studies are required before application can be carried out on a larger scale. However, this work can be thought of as the first step towards the development of a process for removal and subsequent destruction of organic compounds in industrial processes.

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