Photolytic degradation of chlorinated phenols in room temperature ionic liquids

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Abstract

The photolytic degradation of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP) and pentachlorophenol (PCP) in 1-butyl-3-methylimidazolium hexafluorophosphate $\{[bmim^+]PF_6{}^-\}$ and 1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide $\{[emim^+]beti\}$ room temperature ionic liquids (RTILs) has been investigated using UV radiation of 253.7 nm. Stability study revealed that these RTILs are relatively resistant to phototransformation when used as pure phases. At low concentrations (less than 1.57 mM), chlorinated phenols could be degraded in these RTILs following pseudo-first-order kinetics. Intermediate product identification using Electrospray TOF MS, GC–MS and HPLC revealed the formation of phenol among the stable phototransformation intermediates of 2-CP. It is proposed here that two possible pathways, via formation of phenoxyl radical or carbene, could lead to phenol generation. In these two mechanisms, $\{[bmim^+]PF_6{}^-\}$ may participate in the reaction as H-donor. The increase of the chlorine atoms in the phenolic ring generally resulted in a decrease in the phototransformation rates, with exception of 2,4,6-TCP. UV absorbing impurities present in the ionic liquids as received from the manufacturer had a significant negative effect on the phototransformation rate of chlorophenols. Purification of RTILs using activated carbon enhanced the photodegradation rates. On the other hand, these impurities could, at some extent, protect the ionic liquid from photolysis and enhance the stability of the solvent. Recyclability study indicated that the recycling of the solvents was hindered at some extend by the presence of organic impurities that were resistant to photolysis or by the generation of byproducts that were resistant to photolytic degradation and compete with the chlorophenols for photon absorption. While further research is necessary to examine all aspects of this system, including the use of non-toxic RTILs, it is feasible that this technology can be further developed into a two-step process for extraction of organic pollutants from solid matrices, such as contaminated soils or dredged sediments, using ionic liquid solvents followed by in situ photodegradation of the organic contaminants in the ionic liquid extractant phase while achieving simultaneously regeneration of the solvent.
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1. Introduction

During the last few years, room temperature ionic liquids (RTILs) have captured the interest of chemists and engineers as a new and novel generation of solvents and stimulated scientific curiosity, research and product and process development in a large number of innovative applications. Composed entirely of ions, RTILs are different than molecular solvents, water and organic solvents, and chemically analogous to molten salts. Conventional molten salts exhibit a high melting point (i.e., 801 °C for sodium chloride and 614 °C for lithium chloride), which greatly limits their use as solvents in most applications. RTILs, however, remain liquids at or below room temperature. These low melting points are a result of the chemical composition of RTILs, which contain larger asymmetric organic cations compared to their inorganic counterparts of molten salts. In some cases, even the anions are relatively large and play a role in lowering the melting point [1,2].

One of the most distinct advantages of RTILs that has been the rationale for their characterization as "Green Solvents" is their negligible volatility. This characteristic renters them promising replacements to volatile organic compounds (VOCs), which are used in large quantities in chemical and engineering industries and are a source of major environmental problems. In addition, RTILs possess a unique array of physicochemical properties that make them suitable in numerous task-specific applications in which conventional solvents are non-applicable or insufficiently

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effective [3–9]. Such properties include high thermal stability, high electrical conductivity, large electrochemical window, low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment. Moreover, by fine-tuning the structure, these properties can be tailor-designed to satisfy the specific application requirements [10,11]. It has also been found that RTILs are very good solvents for a wide variety of organic, inorganic and organometallic compounds [7,9]. In some cases, the solubility of certain solutes in RTILs can be several orders of magnitude higher than that in traditional solvents [12].

As a result, RTILs are currently considered as environmentally promising solvents and have been used for pollution prevention or minimization of waste production in a variety of chemical and engineering processes, especially in the fields of electrochemistry, catalysis, chemical synthesis, liquid–liquid separations, photochemistry and nuclear fuel cycle [1–20]. However, in most of these applications, the stability of ionic liquids, at least at a certain extent, is crucial for optimum process performance. Previous studies have indicated that, although not 100% inert, certain ionic liquids incorporating 1,3-dialkyl imidazolium cations are generally more resistant than traditional solvents under certain harsh process conditions, such as those occurring in oxidation, photolysis and radiation processes [3,16,17,20].

Chlorinated aromatics, such as chlorophenols, are environmental pollutants of great health concern [21,22]. Among the 19 different chlorophenols, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) have been listed by the US EPA as priority pollutants [23]. These compounds have widely been used in the production of pesticides, herbicides, and wood preservatives. They can also be generated as byproducts in industrial operations, such as the paper pulp bleaching process and water disinfection with chlorine. Being released into the environment, chlorophenols can enter water streams through various transport mechanisms and can also chemisorb onto soil surfaces and aquatic sediments. Due to their toxicity, these xenobiotics are consequently harmful to humans, animals, and fish that are exposed to such contaminated environments. Because of their toxic properties to microorganisms, these compounds are also recalcitrant to conventional biological treatment [24,25].

Such substances may, however, be treated using UV irradiation. Previous studies suggest that photolytic transformation is one of the major mechanisms contribute to the degradation of chlorophenols in aquatic environments [26–32]. Direct photolysis of chlorophenols involves both homolytic and heterolytic C–Cl bond cleavage followed by a series of subsequent reactions. Although photolytic degradation of chlorophenols in water has been proven to be feasible, this technique may not be cost effective when the contaminant concentration in water is low and the volume of polluted water is large. For those hydrophobic compounds [i.e., polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs)] that are tightly chemisorbed on the solid matrices such as soils and dredged sediments, VOCs are usually used to wash them off. This may cause other environmental problems.

RTILs can be used for the extraction of chlorophenols, PCBs or PAHs from contaminated solid matrices. The contaminants transferred to the ionic liquid phase can be subsequently degraded in situ using UV radiation. This two-step remediation technology avoids the use of VOCs and can also result in the regeneration of the ionic liquid solvent (step 2). Since ionic liquids are capable of solubilizing a wide variety of hydrophobic organic compounds to high concentrations [7,12], one batch of ionic liquid solvent can be repeatedly used for extraction in order to highly concentrate the organic compounds in the ionic liquid phase, while simultaneously achieving minimization is solvent use. For certain contaminants, such as PCP, PAHs, and PCBs, this approach is impractical when water is used as solvent due to their very low solubility in water. In addition, a higher contaminant concentration in the solvent during the photodegradation process will result in lowering process cost. This is because the photodegradation rates will be higher and the reactor volume will be smaller.

Motivated by the potential of RTILs as a new generation of solvents and aiming at exploring some of their properties as alternative solvents to replace VOCs, this study deals with a new application of RTILs as solvent media for the photodegradation of organic compounds of environmental concern. Here, we report the photolytic degradation of certain chlorinated phenols from one to five chlorine atoms in two RTILs, namely, 1-butyl-3-methylimidazolium hexafluorophosphate $\{[\text{bmim}^+]\text{PF}_6{}^-\}$ and 1-ethyl-3-methylimidazolium bis-(perfluoroethylsulfonyl)imide $\{[\text{emim}^+]\text{beti}\}$. The stability of the ionic liquids, the influence of impurities present in these ionic liquids, the role of oxygen on the photodegradation reaction, and the recyclability of the solvents are also discussed in this work. It should be noted that in this study, relatively water immiscible ionic liquids have been used. The selection of $\{[\text{bmim}^+]\text{PF}_6{}^-\}$ was mainly based on the fact that it is the most common RTIL used in most recent studies and it can be obtained at a relatively low price. $\{[\text{emim}^+]\text{beti}\}$ was selected because of its lower water solubility and its high electrochemical window. It should be emphasized that the purpose of the study was mainly to explore the potential of this approach. Further development of the process will require water immiscible RTILs that are less expensive, non-toxic (or at least significantly less toxic than relevant VOCs), and recyclable.

2. Experimental

2.1. Chemicals

The following chlorophenols with purity ranging from 97 to 99% were used in this study: 2-CP, 4-chlorophenol

(4-CP), 2,4-DCP, 2,4,6-TCP, 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP), and PCP. These compounds were obtained from Aldrich and used as received. Two different ionic liquids, $\{[bmim^+]PF_6^-\}$ and $\{[emim^+]beti\}$ were used in this study. $\{[bmim^+]PF_6^-\}$ has been involved in a number of studies concerning ionic liquids. These two ionic liquids are commercially available and are used as probes to investigate applicability of ionic liquids in this process. $\{[bmim^+]PF_6^-\}$ with 97% purity (yellowish color) was provided by Sachem, Inc. (Austin, TX). $\{[bmim^+]PF_6^-\}$ and $\{[emim^+]beti\}$ of 98% purity (both are colorless) were provided by Covalent Associates, Inc. (Woburn, MA). The ionic liquids with 98% purity were used without further purification. The less pure ionic liquid was used either as received or after purification using activated carbon. Whenever used, aqueous solutions of chlorophenols were prepared using double deionized water (18 MΩ).

2.2. Methods

UV-C photodegradation experiments were performed in an approximately 20 mL cylindrical quartz photoreactor with reaction space of 5 mL. The initial solution used was 4 mL. Samples were taken every 60 min. UV radiation (predominantly of 253.7 nm) was generated by two UV-C radiation sources positioned opposite to the reactor cell. Each UV source contains two 15 W UV tubes provided by Spectronics Corporation (Westbury, NY). A magnetic stirrer was used for continuous mixing of the solutions during the photodegradation process.

The photodegradation experiments of 2-CP in $\{[bmim^+]PF_6^-\}$ were conducted using air or water-equilibrated ionic liquid. It has been reported that ionic liquids are able to absorb moisture from air and that equilibrium can be reached provided the contact time is long enough [2,33,34]. The ionic liquids used in this study were kept in the containers shipped by the manufacturers. The air in the laboratory had approximately 54% relative humidity. When not specified, the glass reactor headspace (approximately 15 mL at the beginning of the experiment) was air with 54% relative humidity. As explained later, pure oxygen (dry; water content 1 ppmv) or nitrogen (dry; water content 3 ppmv) was also used in certain experiments. Air equilibrated ionic liquids containing 2-CP were obtained by directly dissolving the compound in the solvent. Water saturated ionic liquids containing 2-CP were prepared by vigorously mixing the ionic liquid with 2-CP aqueous solutions at the ratio of 1:5 (v/v) for 15 min. Afterwards, the aqueous and ionic liquid phases were separated by gravity. Two distinct phases, both of which contained small droplets, were obtained. The ionic liquid phase was at the bottom because of its higher density (i.e., 1.32 g/cm^3 for 97% $[bmim^+]PF_6^-$) while the aqueous phase was on the top. Further separation was achieved using centrifugation at 5000 rpm (3578 g) for 30 min. Afterwards no visible droplet of one phase could be seen in the other phase. The aqueous phase (upper phase)

was then removed by decanting. This process also resulted in achieving equilibrium of 2-CP between the two phases [12]. By carefully adjusting the concentration of 2-CP in the aqueous phase, it was feasible to obtain ionic liquid phases containing the desired initial concentration of 2-CP after achieving equilibrium between the two phases. Some loss of $\{[bmim^+]PF_6^-\}$ due to its solubilization in water was observed. The solubilities of $\{[bmim^+]PF_6^-\}$ and $\{[emim^+]beti\}$ in water and those of water in these two ionic liquids were reported in one of our previous studies [12]. Photodegradation studies of the other chlorophenols in $\{[bmim^+]PF_6^-\}$ were conducted by using air-equilibrated ionic liquid after dissolving the chlorophenols directly in this RTIL.

FILTRASORB 400 activated carbon produced by Calgon Carbon Corp. (Pittsburgh, PA) was used for the removal of impurities from the less pure ionic liquid. The activated carbon was pretreated with double deionized water washing and then dried at 105 °C overnight. The residual acids present in the ionic liquid were reduced with water washing for several times until the pH of washing water remained constant. Afterwards, one more water washing was followed and the separation of water and ionic liquid phases was accomplished as described above. Afterwards, 2-CP was dissolved in the resulting water-equilibrated ionic liquid phase and the photodegradation experiments were conducted. To investigate the effect of oxygen (presence or absence) on the photodegradation reactions, the ionic liquid containing 2-CP was purged in the dark with pure oxygen or nitrogen for 1 h followed by oxygen or nitrogen purging during the UV photodegradation process. The prolonged nitrogen purging was assumed to provide an anoxic or almost anoxic condition since dissolved oxygen measurements were not performed. It should be noted that no detectable reduction in the concentration of 2-CP over 2 h of purging was observed.

The initial degradation rates (averaged in the first 60 min) of 2-CP in $\{[bmim^+]PF_6^-\}$ not recycled, recycled once and recycled twice were compared to evaluate the recyclability of the solvent in this process. UV treatment time of 6 h for one cycle and 2-CP initial concentration of 0.4 mM were selected for this series of experiments. Previous experimental data have demonstrated that under this initial 2-CP concentration and radiation time, the final 2-CP concentration was 0.003 mM. To obtain this rate in $\{[bmim^+]PF_6^-\}$ recycled once, 2-CP was added into the ionic liquid to achieve a concentration of 0.40 mM. Then 5 mL solution was transferred to the photoreactor. The solution was irradiated for 6 h without taking any sample. Afterwards, a second dose of 2-CP was added into the 5 mL ionic liquid in the reactor to reach 0.40 mM. After taking 0.5 mL sample, another 0.5 mL solution was removed to achieve 4 mL solution, the same volume as that used to obtain the initial degradation rate of 2-CP in the ionic liquid not recycled. Then, the photodegradation process was continued for one more hour. At the end of the reaction, 0.5 mL sample was taken for analysis. To determine the rate in the ionic liquid recycled twice, 5 mL of 0.40 mM

2-CP solution was irradiated by UV-C radiation for 6 h without taking any sample. Afterwards, a second dose of 2-CP was added following the procedure described above but without taking any samples. After another 6 h of irradiation, a third dose of 2-CP was added to achieve the concentration of 0.4 mM. By taking 0.5 mL sample and removing another 0.5 mL solution, 4 mL of the solution was obtained and the photodegradation process was continued for one more hour at the end of which 0.5 mL sample was taken for analysis. Since UV radiation of the solvent itself (ionic liquid) may also affect the initial degradation rate of the solute (2-CP), control experiments were conducted to evaluate this effect and the rate was also used as an indicator. In the control experiments, 5 mL sample of ionic liquid containing no 2-CP was irradiated for 6 or 12 h for one-time and two-time recycling, respectively. 2-CP was added afterwards to reach an initial concentration of 0.40 mM. After taking 0.5 mL sample and removing 0.5 mL solution, the photodegradation process was continued as in the previous approach for one more hour followed by taking 0.5 mL sample for analysis. The initial reaction rates for 2-CP photodegradation were then compared under these conditions (control, 1 cycle, 2 cycles). All the experiments on recyclability were performed in triplicate. These experiments were repeated with the duration of photodegradation cycle at 12 h (or 24 h) instead of 6 h as described above. In addition, for comparison, recyclability of the photodegradation process was also tested for water as the solvent.

2.3. Analysis

^{1}H, ^{13}C NMR (Bruker AC-250) and UV-Vis spectrometer (Hewlett-Packard 8452A) were employed for examining the stability of the ionic liquids. For ^{1}H NMR analysis, the samples were dissolved in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Neat ionic liquid samples and the internal standard, tetramethylenesulfoxide (TMSO), were used for ^{13}C NMR analysis. Neat samples were used for UV-Vis analysis and the path length of the cuvette in which the sample was contained was 1 cm. Quantification of chlorophenols in ionic liquids was carried out using a Series 1100 HPLC (Agilent) equipped with a reverse phase amide column (RP-16 Discovery Supelco) and a UV-Vis Diode Array Detector. Due to the high viscosity of the ionic liquids, the samples were dissolved in HPLC grade acetonitrile prior to injection into the column. The mobile phase used for HPLC analysis was a mixture of acidic water (0.01 N sulfuric acid) and acetonitrile. The flow rate of the mobile phase was in the range of 1.0–1.5 mL/min. Depending on the characteristics of chlorophenols and ionic liquids to be analyzed, the composition and flow rate of the mobile phase were optimized for better peak separation. Details of the analytical procedures for the quantification of chlorophenols in $\{[bmim^+]PF_6^-\}$ and $\{[emim^+]beti\}$ are described elsewhere [35]. Both Electrospray Q-TOF II MS (Waters) and HP 6890 series GC–MS (Hewlett-Packard) equipped

with a Zebron ZB-5 column (15 m × 0.25 mm, 0.25 μm film thickness) and a single quadruple mass analyzer were utilized for identification of photogenerated intermediate compounds. Since detection of non-polar compounds is difficult with Electrospray Q-TOF II MS, coupling of this instrument with GC–MS was employed to avoid overlooking possible reaction intermediates. The samples were prepared following the same procedures applied in HPLC analysis.

3. Results and discussion

3.1. Stability of ionic liquids

If this application involving the use of ionic liquids as both extractants and photodegradation reaction media is to be feasible, the reaction media must exhibit certain stability upon exposure to UV radiation. ^{1}H NMR, ^{13}C NMR and UV-Vis spectrometer were utilized to examine the stability of the ionic liquids under UV-C radiation. Comparison of ^{1}H NMR spectra of $\{[bmim^+]PF_6^-\}$ before and after UV-C radiation for 6 h indicated no detectable destruction or any other alteration of the molecular structure and bonding. When the treatment time was extended to 96 h, some small extraneous peaks emerged in ^{1}H NMR spectroscopy. The chemical shifts of these peaks appear at 2.10, 2.85, 3.49, and 8.01 ppm. The intensity of these peaks was enhanced with increasing treatment time up to 148 h, which indicated the accumulation of these compounds. However, ^{13}C NMR spectroscopy did not record any change of the ionic liquid over 148 h of irradiation. This may be due to the presence of such photogenerated species at concentrations that were too low to be detected by the instrument. It has previously been reported that less than 1% conversion of 1,3-dialkylimidazolium-based ionic liquids containing nitrate and chloride anions under gamma irradiation could not be observed using NMR [20]. We then utilized UV-Vis spectrometer to examine the structure of the ionic liquids. Figs. 1–3 show the absorbance of ionic liquids after UV radiation. The results indicate that 1 h of UV-C irradiation was sufficient enough to cause some changes to the ionic liquid solvents. For $\{[bmim^+]PF_6^-\}$ with purity of 97%, the absorbance in the region between 250 and 300 nm decreased after 1 h of UV radiation, but in the region between 300 and 400 nm, a new absorbance peak emerged, as shown in Fig. 1. This new peak decreased with further radiation. Compared to the absorbance of 98% $\{[bmim^+]PF_6^-\}$ not irradiated with UV shown in Fig. 2, it seems in this case that UV radiation plays a role to purify the ionic liquids with respect to UV absorbance in the region between 250 and 300 nm. Although UV radiation eliminated some UV absorbing species, newly formed compounds could absorb in a higher wavelength and could be more persistent in the reaction solution. The interaction between these compounds and 2-CP or other reaction intermediates may shift the reaction pathway or inhibit the reaction.
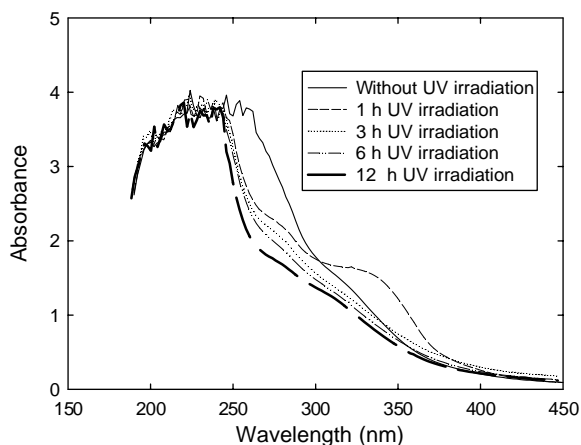
Fig. 1. Absorbance of $\{[bmim^+]PF_6^-\}$ (97% purity) before and after 253.7 nm UV irradiation.
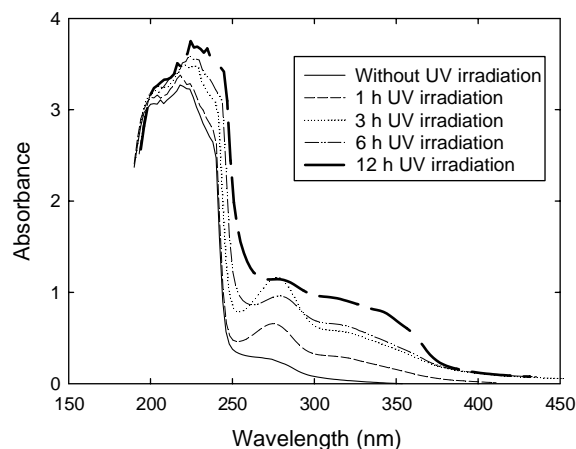

Fig. 2. Absorbance of $\{[bmim^+]PF_6^-\}$ (98% purity) before and after 253.7 nm UV irradiation.
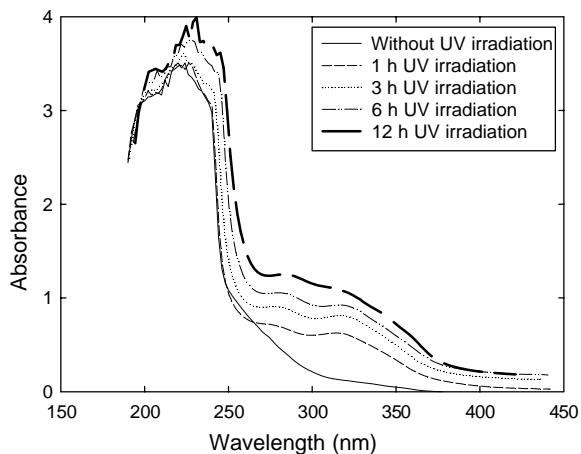

Fig. 3. Absorbance of $\{[emim^+]beti\}$ (98% purity) before and after 253.7 nm UV irradiation.

For $\{[bmim^+]PF_6^-\}$ and $\{[emim^+]beti\}$ ionic liquids with 98% purity, the purification effect of UV-C radiation was not observed. The absorbance in the region between 200 and 400 nm of both ionic liquids increased significantly after UV-C radiation, as shown in Figs. 2 and 3. These results suggest that 2% of impurities present in these ionic liquids or even the ionic liquids themselves might undergo degradation to some extent. This resulted in the formation of UV-absorbing intermediates. Predictably, the degradation rate of the probe compounds in these ionic liquids could be reduced due to the competition of the intermediates with the compounds on photon absorbance when using the UV-C irradiation source. Combined with the results shown in Fig. 1, these data also indicate that the UV-absorbing impurities present in the less pure ionic liquid could compete not only with the probe compounds but also with the ionic liquid for photon absorption. This competition could result in the reduction of degradation rate of the probe compounds as well as the reduction of possible degradation of the ionic liquid.

3.2. Photodegradation of 2-CP

The HPLC chromatograms in Fig. 4 show the decrease in the height of 2-CP peak with extending irradiation time. The concentration of remaining 2-CP in $\{[bmim^+]PF_6^-\}$ versus treatment time is shown in Fig. 5. Different initial concentrations of 2-CP were used. In the presence of UV-C radiation, 2-CP was degraded, while no reaction had taken place in the absence of UV-C radiation. Reduction in 2-CP concentration from 1.57 to 0.06 mM was accomplished in 6 h of irradiation. The transformation rate of 2-CP in the
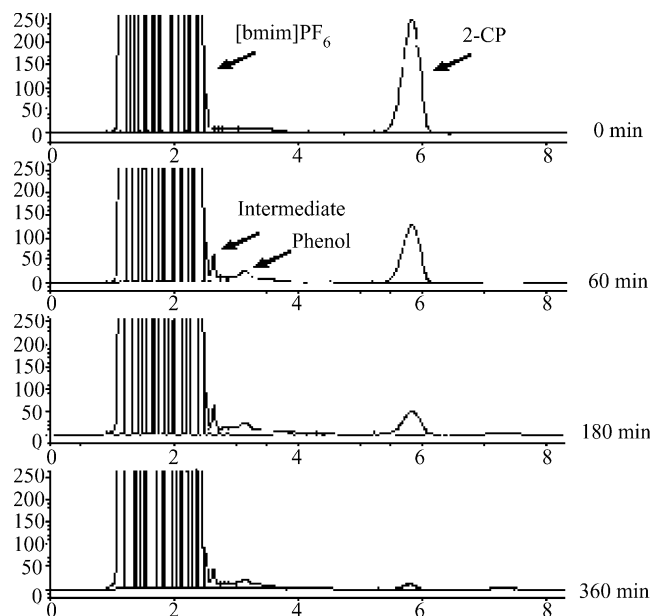

Fig. 4. HPLC chromatograms showing the photodegradation of 2-CP ($C_0 = 1.57$ mM, $\lambda_{UV} = 253.7$ nm) in $\{[bmim^+]PF_6^-\}$ during a 6-h treatment process.
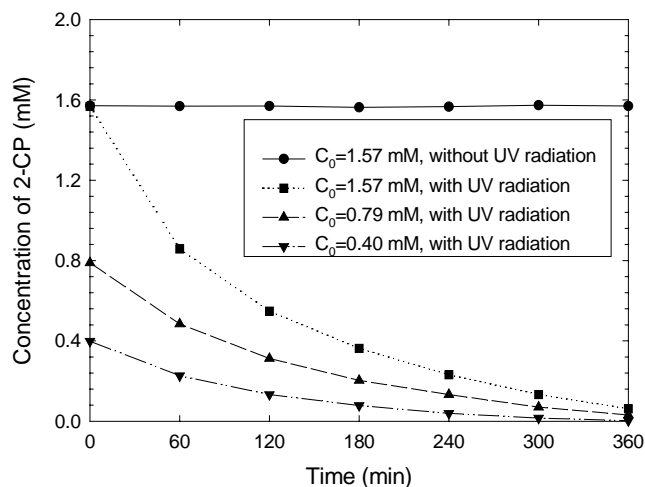
Fig. 5. Concentration profiles of 2-CP in water-saturated $\{[bmim^+]PF_6^-\}$ in the absence and presence of 253.7 nm radiation during the photolytic degradation of 2-CP.
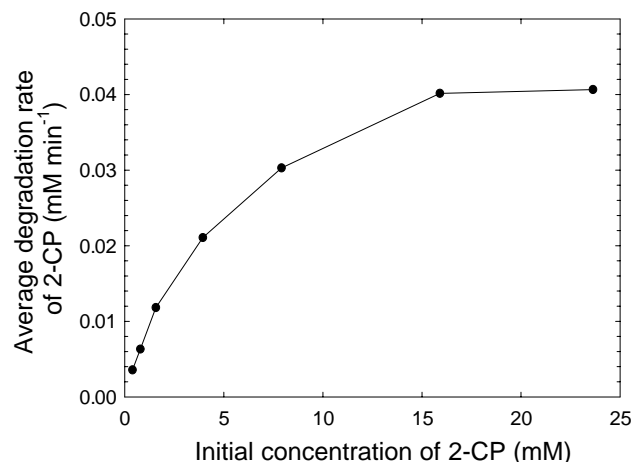

Fig. 6. Average photodegradation rate of 2-CP in $\{[bmim^+]PF_6^-\}$ during the first 60 min of reaction at different initial concentrations of 2-CP.

first hour of the reaction was 1.2×10^{-2} mM min^{-1}. This initial reaction rate decreased to 5.2×10^{-3} and 2.8×10^{-3} mM min^{-1} at initial concentrations of 2-CP of 0.79 and 0.40 mM, respectively. The corresponding final 2-CP concentrations after 6 h of irradiation were 0.02 and 0.003 mM, respectively. Since the incident photon flux was the same in all three cases, the removal efficiency (i.e., % reduction of the initial amount) of 2-CP over 6 h of irradiation was expected to decrease with an increase in the initial concentration. The calculated values at three different initial concentrations (0.40, 0.79 and 1.57 mM) were 99, 97 and 96%, respectively.

Under the same experimental conditions, the degradation of 2-CP in water-saturated $\{[bmim^+]PF_6^-\}$ followed the same trend as that observed when the contaminant was dissolved directly in the ionic liquid equilibrated with air. The calculation of both initial degradation rate ($t = 1$ h) and overall removal ($t = 6$ h) of parent compound in water saturated ionic liquid gave the values of 1.2×10^{-2} mM min^{-1} and 96%, respectively. These results were approximately the same as those (1.2×10^{-2} mM min^{-1} and 97%, respectively) obtained in air equilibrated ionic liquid, when starting with the same initial concentration (1.57 mM). It has been reported that the water content in $\{[bmim^+]PF_6^-\}$ exposed to air at a relative humidity of 59% for 24 h was 2640 ppm [36], and the water saturated $\{[bmim^+]PF_6^-\}$ contained 2.3 ± 0.2 wt.% water at 25 °C [34]. Water has been reported to participate in the photodegradation of 2-CP in aqueous phase [27–30]. In this study, the increase of water content in the ionic liquid phase did not show significant effect on the initial reaction rates. However, the water content has an influence on the viscosity of the ionic liquids. Viscosity measurement indicated that ionic liquids became less viscous with increasing water content [2,33]. For example, the viscosity of $\{[bmim^+]PF_6^-\}$ is 397 cP, at 25 °C for water-saturated sample and 450 cP, at 25 °C for a dried

sample [2]. In previous pulse radiolysis studies dealing with second-order reactions between $CCl_3O_2^{\bullet}$ radicals and chlorpromazine or between $CCl_3O_2^{\bullet}$ radicals and Trolox, the lower reaction rate constants in ionic liquids compared to those in water were attributed to the higher viscosity of ionic liquids [37,38]. Similar effects were also reported in other bimolecular photochemical reactions carried out in ionic liquids [15,18,19]. However, in our study, it seems that the viscosity of $\{[bmim^+]PF_6^-\}$ has little effect, if at all, on the early stage of the phototransformation reaction of 2-CP.

Fig. 6 shows the effect of initial concentration of 2-CP on the initial reaction rate in water-saturated $\{[bmim^+]PF_6^-\}$. In the lower concentration region (less than 1.57 mM), the reaction followed a pseudo-first-order degradation process with respect to concentration. When the experiments were performed at initial contaminant concentration above 15.89 mM, the reaction kinetics shifted from the pseudo-first-order to zero-order, and a transition zone existed between the low and high concentration regions. In the low concentration region, the amount of photons incident in the photochemical reactor is adequate for the number of 2-CP molecules available to absorb photon energy. The degradation rate is limited by the amount of contaminant molecules available, and increasing the concentration of 2-CP molecules enhances the initial degradation rate. When the initial contaminant concentration is high enough, the degradation rate is limited by the amount of photons incident in the reaction solution. In this region, increasing the contaminant concentration has little effect on the degradation rate. It should also be emphasized that the use of high initial contaminant concentration may not only change the kinetics of the reaction but may also affect the reaction mechanism. Previous studies on photochemistry in aqueous solutions have reported that bimolecular and polymolecular reactions are favored in concentrated solutions, while in dilute solutions, photochemical reactions follow a monomolecular process [28,39].

During the preparation of water-saturated $\{[bmim^+]PF_6^-\}$, the pH of the aqueous phase decreased significantly from the initial value of 5.8 to 3.0, which suggests the presence of acids as impurities in the ionic liquid. Since acids have been employed as catalysts in certain chemical reactions such as nitration of benzene and hydrolysis of ester, we suspected that such acidic impurities might affect the photodegradation of 2-CP. To elucidate this, comparison of the degradation rate of 2-CP in $\{[bmim^+]PF_6^-\}$ in the presence and in the absence of acids was carried out. Then, 2-CP was added directly into the ionic liquid after washing and the photodegradation of 2-CP was performed following the same procedure. The experiments revealed that the degradation rate of 2-CP was the same as that in the ionic liquid without treatment. In addition, UV-Vis spectroscopy showed that the absorbance of the ionic liquid before and after water washing was identical. Therefore, acid impurities seem not to affect the initial reaction rates.

To investigate the effect of other impurities on the degradation reaction, 2-CP was dissolved directly in $\{[bmim^+]PF_6^-\}$ of 98% purity and the degradation experiment was performed following the same procedure. Although the purity of this ionic liquid is enhanced only by 1% (i.e., compared to the yellowish one of 97% purity), the degradation rate of 2-CP was increased considerably, as illustrated in Fig. 7. Although the absorbance of the ionic liquids with higher purity increased after UV-C irradiation as shown in Figs. 2 and 3, their absorbance at 253.7 nm was still less than that of the less pure ionic liquid even after 12 h of UV-C irradiation. As a result, the competition of reaction intermediates generated from both the impurities and the ionic liquids themselves with 2-CP on photon absorption was relatively weaker and the degradation rate was higher. The degradation rate of 2-CP in $\{[emim^+]beti\}$ with the same purity of 98% was slightly slower than that in $\{[bmim^+]PF_6^-\}$. Considering that the viscosity of $\{[bmim^+]PF_6^-\}$ is 450 cP (25 °C, dried) [2] which is much higher than that of $\{[emim^+]beti\}$ (61 cP at 26 °C),

the results suggest that the viscosity may not be a critical parameter in this photodegradation reaction. It should be noted that the density of $\{[emim^+]beti\}$ (98%, $1.57 \, g \, cm^{-3}$) is higher than that of $\{[bmim^+]PF_6^-\}$ (98%, $1.38 \, g \, cm^{-3}$). It is obvious that the chemical composition and physical properties of ionic liquids are significant in investigating the reaction and further studies are necessary. As a comparison to the reaction in the ionic liquids, the degradation of 2-CP in aqueous solution was also investigated under the same experimental conditions ($C_0 = 1.57$ mM; $\lambda_{UV} = 253.7$ nm, $V_0 = 4$ mL). It was found that the degradation rate of 2-CP in water was similar to those in the transparent $\{[bmim^+]PF_6^-\}$ and $\{[emim^+]beti\}$ (98% purity) samples obtained from Covalent Associates. Considering the large difference in viscosity between water (0.8904 cP at 25 °C) and $\{[bmim^+]PF_6^-\}$ (450 cP at 25 °C, dried) [2] and based on the comparable results obtained on the photodegradation rates of 2-CP in these two different solvents, it is suggested that solvent viscosity is not a critical parameter in this process and that 2-CP phototransformation may proceed following a monomolecular photochemical pathway, at least in the early stage of 2-CP transformation. This will be further discussed in the proposed reaction mechanism.

The decrease of the reaction rate in the less pure $\{[bmim^+]PF_6^-\}$ (yellowish color) may be due to the presence of impurities that could also absorb incident photons, competing thus with 2-CP for photon absorption. The immediate impact of these impurities on this photochemical process lies has two effects. First, the color is associated with substances that absorb in the visible range but nevertheless can interfere in the various photochemical reactions taking place. In addition, impurities present in such solvents may alter the reaction mechanism and give unpredictable results [14]. Second, other impurities that absorb in the UV-C range (i.e., 250–260 nm) will absorb portion of the incident photon energy and will attenuate the effective photon flux used by 2-CP and its phototransformation intermediates. Therefore, the availability of spectroscopic grade ionic liquids for studying photochemical reactions in ionic liquids is of great importance. Moreover, impurities can considerably affect the physical properties of ionic liquids. As mentioned before, water can lower the viscosity of the ionic liquids. On the other hand, the presence of chloride impurity makes the solvents more viscous [2,33].

High quality ionic liquids incorporating $[bmim]^+$ cation and a variety of anions, such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[CF_3CO_2]^-$ and $[(CF_3SO_2)_2N]^-$ have been reported to be colorless, even though they are not 100% pure [40]. The color of less pure ionic liquids generally ranges from yellowish to orange. The formation of the color has been attributed to the use of raw materials with color or excessive heating during the synthesis of imidazolium salt [40,41]. A number of precautions for synthesis of colorless ionic liquids have been described [41], and a procedure for removal of color from impure ionic liquids using acidic alumina and activated charcoal has also been proposed [40]. Activated
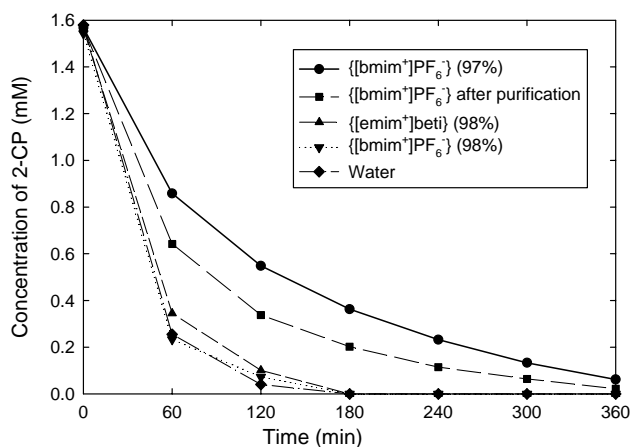

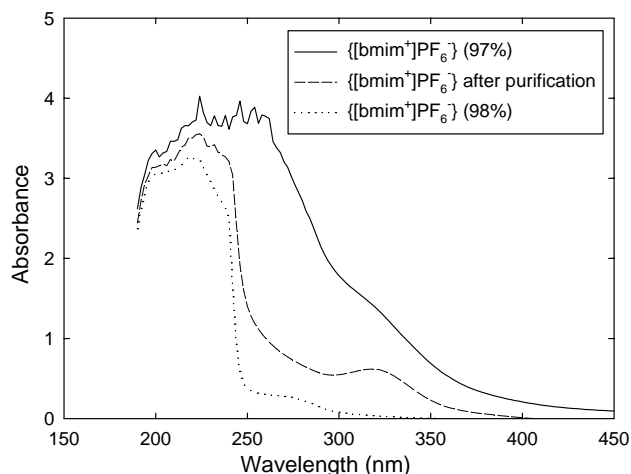Fig. 7. Degradation of 2-CP (dissolved directly) in different solvents under 253.7 nm UV radiation.

Fig. 8. UV-Vis absorption spectra of $\{[bmim^+]PF_6^-\}$ samples obtained under different conditions.

Fig. 9. Concentration profile of phenol during the photodegradation of 2-CP in $\{[bmim^+]PF_6^-\}$ under 253.7 nm UV radiation.

carbon was also used in our work for the purification of $\{[bmim^+]PF_6^-\}$ with yellowish color (97% purity) obtained from Sachem. After prolonged treatment using activated carbon, the yellowish color of the ionic liquid faded. The extent of purification achieved using activated carbon treatment was examined by comparing the UV-Vis spectra of the ionic liquid prior to and after purification. As presented in Fig. 8, significant reduction in the region between 245 and 300 nm was achieved after treatment. In addition, removal of most impurities that absorb in the visible light was also achieved. This is consistent with the significant fading of the yellowish color after treatment. Considering that the UV radiation used in this study has a wavelength mainly at 253.7 nm and based on the results of Fig. 8, it was hypothesized that higher reaction rates could be achieved after purification of this ionic liquid using activated carbon. The degradation of 2-CP in the purified ionic liquid is also shown in Fig. 7. The results showed that the degradation rate in the purified $\{[bmim^+]PF_6^-\}$ is higher than that prior to purification but still is lower than those in the electrochemical grade ionic liquids (98% purity, colorless) and water. These results along with those of Fig. 8 suggest that certain impurities could not be removed with the activated carbon purification step and that these impurities inhibited the photodegradation of 2-CP.

Oxygen was found to have no significant influence on the photo-transformation of 2-CP. The degradation rates of 2-CP under aerobic and anoxic conditions were approximately the same. This is in agreement with results reported in a previous study where neither the quantum yields nor product distribution was affected by the presence of oxygen [26]. As depicted in Fig. 4, HPLC chromatographs revealed the formation of new peaks after 60 min of UV irradiation. These peaks were not observed when irradiating neat ionic liquids suggesting that they are associated with intermediates originated from the parent contaminant (2-CP). As treatment time
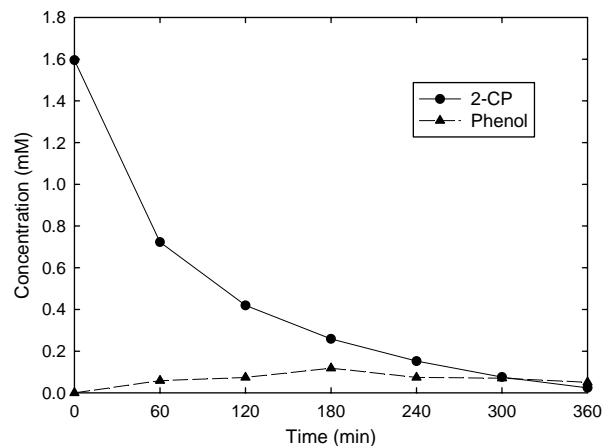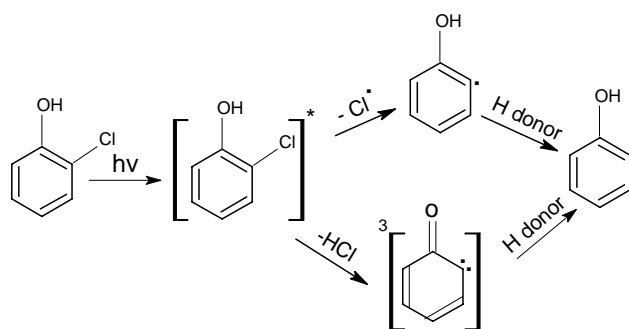
increased, the height of the peaks enhanced and then diminished. The retention time and UV-Vis absorption spectrum of one major intermediate corresponded to those of phenol. Electrospray TOF MS analysis revealed that a compound with mass to charge value (*m/z*) of 95 was generated after UV radiation. GC–MS analysis also indicated the formation of a compound with *m/z* value of 94. The retention time of this intermediate in the GC–MS column was also the same as that of phenol standard. Fig. 9 shows the increase and decrease of phenol concentration during the photodegradation of 2-CP. The concentration increased from 0 to 0.12 mM after 180 min reaction. Afterwards, the quantity of phenol decreased, and at the end of the reaction, the concentration was 0.05 mM. This result suggests that the photo-formation rate of phenol was faster than its photo-degradation rate when the parent compound was in abundance. As the reaction continued, 2-CP was consumed, and the formation rate of phenol decreased and became less than its degradation rate. Consequently, phenol concentration profile in Fig. 9 goes downward after 180 min of reaction. Due to the simultaneous degradation of phenol, it is difficult to calculate the amount of 2-CP transformed to this compound. Some low molecular weight compounds could not be identified. High molecular weight compounds other than $\{[bmim^+]PF_6^-\}$ were also observed, but could not be identified. It is also possible that some of these compounds may result from impurities originally present in the ionic liquid.

Phenol has been previously identified as minor product in the photolysis of 2-CP in dilute aqueous solutions of the surfactants polyoxyethylene lauryl ether and sodium dodecyl sulfate alkaline where the surfactants behaved as H-donors for the transformation of 2-CP to phenol [42]. The major products identified were cyclopentadiene carboxylic acid and catechol. However, when concentrated surfactant solutions (above their critical micellar concentration) were used, phenol was the only product. Both C–Cl homolysis and triplet carbene mechanism were proposed

Scheme 1.

Fig. 10. Comparison of the photo-degradation rates under 253.7 nm radiation of different chlorophenols in {[bmim$^+$]PF$_6$$^-$} equilibrated with air.

for the product formation. In the same study, photolysis of 2-CP in dimethoxyethane, cyclohexane, hexane and methanol also generated phenol [42]. The formation of carbene 2-oxocyclohexa-3,5-dienylidene has been observed in laser flash photolysis of 2-bromophenol [43]. The involvement of carbene 4-oxocyclohexa-2,5-dienylidene has also been proven in the photolysis of 4-CP in aqueous phase [44–46]. In water, in the absence of H source, phenol was not observed, and the major photolysis products of 2-CP were cyclopentadiene carboxylic acid and catechol [26–30]. In our system, these two products were not observed. Two possible pathways may result in the formation of phenol in the ionic liquids. One pathway involves homolytic dissociation of chlorine from 2-CP excited state, which resulted in the formation of phenoxyl radical. This radical could abstract a hydrogen atom from an H donor and form phenol as shown in Scheme 1. C–Cl bond may also undergo heterolytic dissociation to form triplet carbene that reacts with the H donor to give phenol. Singlet carbene has also been reported to be involved in the photodegradation of *ortho*-substituted halophenols [42,43]. This carbene can produce ketene via a Wolff rearrangement to form triplet carbene via intersystem cross. Ketene can undergo further photolysis to yield cyclopentadienyl carbene in the absence of a good nucelophile. Subsequent reaction of this carbene can result in the formation of other products [42]. In our system, the evidence of ketene formation has not been observed. However, this possibility can not be excluded. As can be seen, the formation of both phenolic radical and carbene involves only the excitation of 2-CP, which is not limited by the viscosity of the environment. In the final step to form phenol, the interaction between the active species and the H-donor can be diffusion controlled and affected by the solvent properties as well as the concentration of the reactants. In a previous photochemical study, it was found that an alkyl chain H atom of imidazolium-based ionic liquid cations could be abstracted by the triplet excited state of benzophenone [16]. In our study, [bmim$^+$] may have the same behavior in phenol formation during the photo-transformation of 2-CP. However, this step may be diffusion controlled and will be influenced by solvent viscosity.
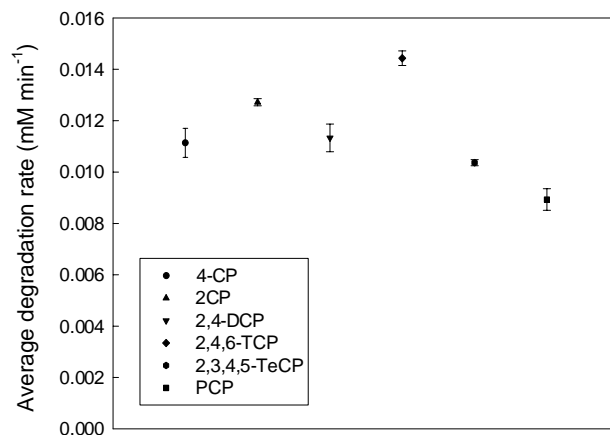
3.3. Photodegradation of other chlorophenols

Using the same protocol, photodegradation of 2,4-DCP, 2,4,6-TCP, 2,3,4,5-TeCP and PCP in {[bmim$^+$]PF$_6$$^-$} was performed. Similar degradation trends to that of 2-CP were observed. As depicted in Fig. 10, starting with the same initial concentration (1.57 mM), the transformation rate of chlorophenols decreases as the number of chlorines on the phenolic ring increases; with exception for 2,4,6-TCP. The addition of chlorine atom has previously been found to reduce the degradation rate of chlorophenols, but, in some cases, the position of chlorine substituent exhibited dominant effect and a reverse order could be obtained [47]. In this study, it seems that *ortho*-substituent on the phenolic ring enhanced the activity of chlorophenols toward UV radiation. Consequently, for 2,4,6-TCP, which has two *ortho* positions substituted with chlorine atoms, the photo-transformation rate was higher. A capillary electrophoretic study of the interactions between halophenols and ionic liquids suggests that, for the halophenol isomers, the *ortho*-substituted isomer is more affinitive to the dialkylimidazolium cation of the ionic liquid than the *para* one [48]. The stronger interaction may be associated to the activation effect on chlorophenols with respect to photo-transformation. If this is possible, the degradation rate of 4-CP in the ionic liquid should be lower than that of 2-CP. We thus conducted experiments to study the photodegradation of 4-CP. It was found that the degradation rate of 4-CP was lower than that of 2-CP. Although this result supports our hypothesis, more studies are required to further elucidate the details of such interaction and how this interaction activates the chlorophenols.

3.4. Recycling of {[bmim$^+$]PF$_6$$^-$} (Sachem)

Compared to the ionic liquid sample used as obtained from the manufacturer, the degradation rate of 2-CP was slower in recycle samples. Moreover, the degradation rate
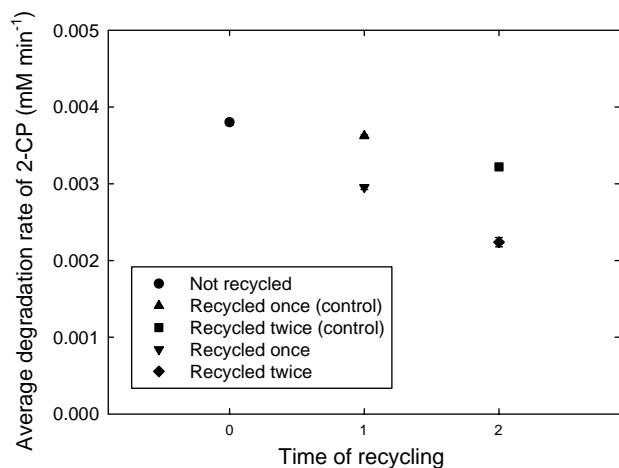
Fig. 11. Effect of recycling of $\{[bmim^+]PF_6^-\}$ on the average photodegradation rate of 2-CP during the first 60 min.

decreased as the number of recycles increased, as illustrated in Fig. 11. This could be attributed to the formation of degradation intermediates of 2-CP that are resistant to UV-C radiation. Although 99% of 2-CP was transformed over 360 min, reaction intermediates were still persistent in the ionic liquid and competed with 2-CP for photon adsorption. The results obtained from the control experiments supported this hypothesis. The degradation rate of 2-CP decreased also in the control experiments, but the decrease was less than that obtained in the recycling experiments. In the case of the control experiments, the decrease in the degradation rate of 2-CP could be attributed to the formation of intermediate compounds from the impurities originally present in the ionic liquid or even from the ionic liquid. Such intermediate compounds could absorb more in the UV region or they could interact with 2-CP or other reaction intermediates and shift the reaction pathway or inhibit the degradation rate of 2-CP. Further experimental results presented later in this work suggest the latter effect may more likely contribute to the reduction of the reaction rate. Therefore, the combined effects of intermediates originated from different sources contributed to lowering the degradation rate of 2-CP with time. As a comparison, recycling experiments using water as the solvent were also conducted following the same protocol. The degradation rates of 2-CP for the control experiments were the same as expected since pure water is transparent to UV. Similar trend of decreasing rates was observed during the recycling experiments, although this decrease was less than that in the ionic liquid due to the higher degradation rate in water as mentioned before. To test the hypothesis if prolong treatment time could reduce the concentration of photogenerated intermediate products and thus enhance the recyclability of ionic liquids, a following recycling experiment was performed in which the treatment time increased from 6 to 12 or 24 h during each cycle. The results indicated that, instead of increasing, the degradation rate slightly decreased. This suggests that extended treatment could generate higher concentrations of intermediates that can inhibit 2-CP photodegradation.

4. Conclusions

Chlorophenols are degradable in room temperature ionic liquids under 253.7 nm UV radiation. At small contaminant concentrations (less than 1.57 mM), the photo-degradation reactions follow pseudo-first-order kinetics. Phenol was found to be among the stable photo-transformation products of 2-CP in $\{[bmim^+]PF_6^-\}$. Both the formation of phenoxyl radical and carbene may lead to phenol, while the ionic liquid may act as H-donor. Increasing the number of chlorines on the aromatic ring generally resulted in a decrease in the photo-transformation rates, with exception of 2,4,6-TCP. UV absorbing impurities present in less pure ionic liquid samples significantly lower the photo-degradation rate of chlorophenols. On the other hand, the competition between these impurities and the ionic liquid for photon adsorption to some extent protect the ionic liquid from photolysis and enhanced the stability of the solvent. Although the ionic liquids tested in this study may also be affected by UV-C radiation, their stability is expected to be larger than that of volatile organic compounds. Use of longer wavelength radiation (i.e., UV-B or UV-A) may help to destroy some organic impurities or reaction byproducts that absorb in this range and could minimize photochemical degradation of the ionic liquid solvents. While we were preparing this manuscript, a published study demonstrates that the toxic aspect of $\{[bmim^+]PF_6^-\}$ needs to be carefully investigated due to the formation of its decomposition product, 1-butyl-3-methylimidazolium fluoride hydrate, during the purification of the ionic liquid and possible formation of toxic product HF [49]. In our study, although the photodegradation of chlorophenols in the ionic liquids is feasible, the application of this process for environmental remediation purpose certainly requires the use of ionic liquids that will give no harmful or acceptable impact on the environment. In any case, synthesis of environmentally friendly task-specific ionic liquids that are resistant to UV photolysis or harsh oxidation conditions could improve the applicability for such solvents in this process.

After further study, improvement, and optimization, the approach presented in this study could be further developed into a two-step process for the remediation of solid matrices, such as soils and dredged sediments, contaminated with recalcitrant hydrophobic organic impurities. AlNashef et al. [50] reported that stable superoxide ion could be generated electrochemically in ionic liquids in the absence of impurities and water, and suggested that the superoxide ion could be used to degrade halogen–carbon compounds. In a similar approach, UV-based photolysis may provide another technology to degrade these compounds. Conventional liquid–liquid or liquid–solid extraction technologies

currently used to remove the pollutants from water or sediments involve the use of toxic and flammable VOCs, which are the source of major environmental problems and contamination of water, soil and air. The use of ionic liquids may be a promising alternative to VOCs assuming that the cost of ionic liquids will be reduced in the future when larger quantities are produced and such compounds proved to have no or minimal toxicity. In addition and after proper selection of the UV wavelength, this technology can be used to eliminate a variety of organic impurities and byproducts from contaminated ionic liquids during several chemical and engineering processes dealing with chemical synthesis, catalysis, and electrochemistry. This study is the first demonstration that the destruction of chlorinated aromatics is feasible in room temperature ionic liquids using photolysis. Several fundamental experiments are currently underway in our laboratories for elucidating the interactions between ionic liquids and chlorophenols and other organic contaminants or compounds.

Acknowledgements

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