Development of photocatalytic degradation and kinetic study for imidazolium based ionic liquids in Fe-Cu/TiO_2-AC system

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Abstract. Ionic Liquids (ILs) are already recognized by the chemical industry as they possess a wide spectrum of physical and chemical properties (solubility, polarity, viscosity or solvent miscibility). However, a release of ILs from industrial processes into aquatic environments may lead to water pollution, because of their high solubilities in water. Due to these reasons, this work is conducted to investigate the photodegradation on ILs structure varies in alkyl chain length and anion group. The photocatalytic degradation was conducted based on fixed parameter optimized which includes pH = 6, [photocatalyst] = 1g/L, [IL_o] = 0.11 mM and [H_2O_2] = 0.75 ml/L. The reaction for emimCl follows zero order whereas both bmimCl and bmimBF_4 follow the first order reaction.

1. Introduction

Ionic liquids (ILs) are characterized by properties such as negligible vapour pressure and non-flammable under ambient conditions, high thermal conductivity, a wide electrochemical window and high polarity [1]. They also have the ability to dissolve a wide diversity of materials, including salts, fats, proteins, amino acids, surfactants, sugars, polysaccharides and organic solvents. However, the most important attribute of ILs is the possibility of designing their properties to order. The enormous number of cation and anion combinations causes ILs to possess a wide spectrum of physical and chemical properties (solubility, polarity, viscosity or solvent miscibility), and they are already recognized by the chemical industry as new, target-oriented reaction media [1].

Although the low vapor pressure of ILs may reduce air pollution with respect to the typical volatile organic solvents, it is not insufficient to justify calling them as “green” solvent. It must be considered that a release of ILs from industrial processes into aquatic environments may lead to water pollution, because of their high solubilities in water [1].

Most ILs are not readily biodegradable, so advanced oxidation processes (AOPs) are frequently suggested as an alternative disposal strategy to handle this character of ILs [2,3]. AOPs are characterized by a common chemical feature: the capability of exploiting the high reactivity of hydroxyl radicals (*OH) in driving oxidation processes that are suitable for achieving the complete abatement and mineralization of even less reactive pollutants [4].

The low biodegradability and considerable ecotoxicity of some ILs are the reasons why we should prevent their leakage into the environment, choosing effective means of removal and recovery from...
wastewater as well as minimizing their presence in such a matrix. The identification of transformation products (TPs) is a crucial aspect to provide important information on the degradation system, the formed transformation TPs may have a very different impact on the environment compared to the parent molecules. Most of the methods suggested for ILs treatment have the possibilities for the intermediate products to become more toxic than their former species. Since photodegradation is a heterogenous techniques and the pH of the solution do not need to be adjusted, this method already get rid of a few possibilities for the intermediates to turn harmful due to less compound reacted in the solution [5].

This study is to investigate the influence of visible light radiation on the stability of imidazolium ILs conducted primarily to determine the role of radiation itself with the presence of other optimum variables set within the system which includes the combination of H2O2 and photocatalyst. This information can be quite helpful especially in the water treatment industry to predict the consequences and prevention in order to preserve the environmental fate by estimation of the long-term degradation of the analyzed compounds. Thus, this work aims to analyze the capability of photocatalytic degradation process employing Fe-Cu/TiO2-AC for degrading different type of ILs. In this study, we are investigating the effect of varying alkyl chain length and anion group.

2. Materials and Methods

2.1. Chemicals
All of the chemicals were purchased and used without further purification. The ILs used in this work were the following: 1-butyl-3-methylimidazolium chloride (bmimCl), 1-ethyl-methylimidazolium chloride (emimCl), 1-butyl-methylimidazolium tetrafluoroborate (bmim(BF4)), methanol (CH3OH, 99.8%), potassium dihydrogen phosphate (KH2PO4), phosphoric acid (H3PO4, 85%) and triethylamine (C6H15N, AR) were purchased from Merck (Darmstadt, Germany).

2.2. Synthesis of photocatalyst
Nano-TiO2 was synthesized using the water-in-oil microemulsion method, followed by modification with the desired Fe and Cu via the wetness impregnation method. The resultant powder from the impregnation method was calcined at 400 ºC for 1.5 h. In a different set-up, the pre-carbonized AC was oxidized using 1 M of nitric acid in a boiling condition for 20 min. The oxidized AC was washed repeatedly with distilled water until the filtrate became neutral. The oxidized AC was then dried overnight in an oven at 80 ºC. Finally, the developed Cu-Fe-TiO2 and AC were mixed (10 wt % AC) using the impregnation method. The final photocatalyst was denoted as 0.2 Cu:Fe-TiO2/10AC [7].

2.3. Photodegradation Study
Photocatalytic degradation process was carried out in an open glass reactor using a fixed parameter optimized which includes pH = 6, [photocatalyst] = 1g/L, concentration of initial ILs [ILo] = 0.11 mM and hydrogen peroxide [H2O2] = 0.75 ml/L. A pre-determined amount of photocatalyst and H2O2 was added into the reactor containing the desired concentration of ILs solution. The system was stirred in dark for 30 mins to allow for equilibrium adsorption–desorption process, followed by 4 h irradiation under a 500-W halogen lamp.

2.4. Analytical Method
Liquid samples were collected at regular time intervals and analyzed using high performance liquid chromatography (Agilent 1100 HPLC, Santa Clara, CA, USA). For better separation and sharp analysis, column symmetry C-18 (250 × 4.6 mm, 5 µm) and a mobile phase mixture of methanol (35 vol %) and 25 mM of phosphate buffer (KH2PO4/H3PO4) containing 0.5% of triethylamine were used. The analysis was performed at a column temperature of 30 ºC, a 5-µL sample injection, and an 0.8 mL/min flow rate. The separated ILs was detected at a 212-nm wavelength using a UV detector (Agilent, Santa Clara, CA, USA).
3. Results and Discussion

BmimCl and emimCl are compared in terms of alkyl chain length effect as their structure varies in the number of methyl chain (–CH$_3$–) presence whereas bmimCl and bmimBF$_4$ are compared in terms of anion group. Table 1. shows the structure and the comparison between the ILs tested. BmimCl is used as reference.

| Type of ILs  | Chemical formula | Structure | Cation       | Anion   |
|-------------|------------------|-----------|--------------|---------|
| EmimCl      | $\text{N} N+\text{C}_3\text{H}_3\text{C}_3\text{H}_3\text{Cl}^{-}$ | –CH$_2$CH$_3$ | Cl$^-$       |
| BmimCl      | $\text{N} N+\text{C}_3\text{H}_3\text{C}_3\text{H}_3\text{Cl}^{-}$ | –CH$_2$CH$_2$CH$_3$ | Cl$^-$       |
| BmimBF$_4$  | $\text{N} N+\text{C}_3\text{H}_3\text{C}_3\text{H}_3\text{BF}_4^{-}$ | –CH$_2$CH$_2$CH$_3$ | BF$_4^{-}$|

3.1. Effect of alkyl chain length of ILs

The results for degraded ILs based on alkyl chain length are presented in Figure 1. From the photocatalytic degradation of both ILs tested, it can be observed that both bmimCl and emimCl were removed almost at the same rate since the ILs show a total of 76 ± 2% removal after 240 mins of irradiation.

![Figure 1. Degradation of imidazolium-based IL with different alkyl chain length (bmimCl,emimCl)](image)

Although they degrade within the same rate, the best fit curve for emimCl prove that the degradability of bmimCl is slightly higher in comparison. This may be due to the presence of free radical cation which believed to play a major role in its ability to degrade [8]. The n-alkyl chain also seems to be responsible for the stability of imidazolium ionic liquids. These fragments can undergo various
geometric intramolecular interactions in aqueous solutions such as flexing or strengthening as a result of solvation forces around positively charged nitrogen atoms. This can additionally improve resistance to photodegradation. In addition, Stepnowski and Zaleska [8] work also found 1-ethyl-3-ethylimidazolium to be the most stable entity among the compounds studied in enhanced photodegradation systems. The degradability in the system tested decreases in the order bmim < emim and depends on the length of the alkyl chain substituted at position 1 of the 1-alkyl-3-methylimidazolium ring.

3.2. Different anion
Within the system studied here, bmimBF$_4$ displays the highest degradability since it achieved a total removal after 180 mins of irradiation whereas only 63% of bmimCl is degraded over this period of time.

![Figure 2. Degradation of imidazolium-based IL with different anion group (bmimCl,bmimBF$_4$)](image)

The best fit curve in Figure 2. shows a huge different between this two ILs in terms of degradation rate which can be associated with their stability. The stability of the ILs with respect to the degradation reaction of the active species appeared to be structure-related [9]. The removal efficiency of the ILs decreased in the order of [BF$_4$]$^{-}$ > [Cl]$^{-}$. Halogen containing anions such as [BF$_4$]$^{-}$ are unstable and tend to decompose to hydrogen fluoride (HF) in the presence of water and disrupts the purity of ILs. Another relaying factor affecting the thermal stability of ILs is the nucleophilicity and the hydrophobicity of the corresponding anions [6]. In addition, BF$_4$$^{-}$ was typically a weak coordinating fluorocations. This fact is probably related to H–F interactions present [11].
3.3. Kinetic Study

The degradation kinetics of the degradation processes of bmimCl, emimCl and bmimBF₄ in photocatalytic systems was analysed as in Figure 3.

![Figure 3. Reaction order of degraded ILs](image)

A good linear relationship was found for emimCl that follows the zero-order reaction with \(R^2 = 0.9732\). The linear equation describes as follows:

\[
[A]_t = -kt + [A]_0
\]  

Meanwhile, the disappearance of bmimCl and bmimBF₄ can be illustrated by first-order kinetics describes as follows:

\[
\ln[A]_t = -kt + \ln[A]_0
\]

The \(k\) value or the rate constant for bmimBF₄ was the highest with \(2.65 \times 10^{-2}\) M⁻¹s⁻¹, whereas emimCl was the lowest with \(k\) value equals to \(3 \times 10^{-4}\) M⁻¹s⁻¹ as the initial concentration of these ILs was the same. The high value of \(k\) indicates a faster reaction. Therefore, the degradation of bmimBF₄ followed the fastest kinetics, and the lowest was that of emimCl. Thus the degradability of this system decreases in the following order: \([\text{bmimBF}_4] > [\text{bmimCl}] > [\text{emimCl}]\).

Conclusion

This study showed that imidazolium-based ILs can be readily and rapidly degraded with visible light in Fe-Cu/TiO₂-AC system. The stability of the ILs with respect to the degradation reaction of the active species appeared to be structure-related. The removal efficiency of the ILs decreased in the order of \([\text{bmimBF}_4] > [\text{bmimCl}] > [\text{emimCl}]\) and emimCl was found to be more stable than bmimCl and bmimBF₄. Both bmimBF₄ and bmimCl follow the first-order reaction with \(R^2\) value of 0.982 and 0.9863 respectively while emimCl fits zero-order the best with \(R^2\) value of 0.9732.

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