Photodegradation of 1-butyl-3-methylimidazolium chloride [bmim]Cl via synergistic effect of adsorption-photodegradation of Fe-TiO$_2$/AC

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Abstract: Ionic liquids (ILs) have gained interest among researchers due to its tunable properties that can be used in wide applications. However, toxicity and bio-degradation studies of ILs proved that most of the aromatic ILs, such as imidazolium is highly toxic and non-biodegradable. Several advance oxidation processes (AOPs) have been investigated by researchers to evaluate the efficiency of the systems for the removal of ILs from wastewater. However, the issue on relative high cost and environmental concern has limited the application of these AOPs in industry. In this research, photocatalytic study using hybrid nano-materials was conducted to evaluate the efficiency of this system as an alternative AOP system for removal of ILs from wastewater. The synergistic effect of adsorption-photodegradation was introduced by depositing Fe-TiO$_2$ onto the functionalized activated carbon (AC). Nano-TiO$_2$ was synthesized using micromulsion method before modification with transition metal and deposited onto the oxidized AC. Photodegradation reaction of 1-butyl-3-methylimidazolium chloride [bmim]Cl was investigated under simulated visible light irradiation. It was observed that the overall efficiency of the system was increased with the increasing amount of Fe dopant. Investigation on the extrinsic factors such as solution pH, initial concentration of ILs and photocatalyst dosage showed to significantly affect the overall efficiency of the systems where the optimum condition for the system was observed at pH 10, with initial ILs at 1mM at 1 g/L of photocatalyst. The best performance photocatalyst was 0.2Fe-TiO$_2$/AC.

Keywords: photodegradation; TiO$_2$; ionic liquids; activated carbon; synergistic effect

1. Introduction

Ionic liquids (ILs) is a chemicals that can be synthesized either via metathetic exchange of anion, neutralization with Bronsted acid, direct alkylation and alkylimidazole or carbonate route [1]. Depending on its specific applications, the physical and chemical properties of ILs are tunable by varying its cation and anion. ILs is currently being used in industry for both large scale production and pilot plant study. For instance, PETRONAS has applied ILs for mercury removal process while BASF and Institutes Francis de Petrole Axens (IFP) have employed ILs in biphasic acid scavenging liquid processes (BASIL) PROCESS and dimersol process, respectively [2].

The increasing number of ILs applications has raised the concern towards the impact of ILs to the environmental due to its high solubility and persistence in water. Biodegradation studies on ILs which was conducted by a few researchers have concluded that ILs with aromatic ring cation such as imidazolium is non-biodegradable [3-5]. On the other hand, this type of IL has been widely used in bio industry [1]. Hence, efficient treatment system that is able to overcome the high solubility properties of ILs in water is urgently required. Advance oxidation process (AOP) is widely known for its efficient for degradation of wide range of organic pollutants [6]. Photocatalytic degradation employing semiconductor as the photocatalyst is one of the AOP that is efficient to treat ILs in wastewater [7]. This process can be considered as relatively low cost and sustainable since it is able to harvest solar energy into chemical reaction [8].
Among the semiconductor available for the application, titania (TiO\textsubscript{2}) is the most researched semiconductor used as photocatalyst [9]. The major drawback of TiO\textsubscript{2} that hinders its application in industry as photocatalyst, however, is the limited range of light absorption in UV region only. In addition, TiO\textsubscript{2} has a comparatively slow diffusion rate between the target pollutant and its surface [10, 11]. These limitations could be overcome through modification of the TiO\textsubscript{2} via several methods such as doping with metals, depositing TiO\textsubscript{2} onto AC as support and doping another semiconductor onto TiO\textsubscript{2} as co-catalyst. The introduction of metal dopants onto TiO\textsubscript{2} has significant enhanced its activity under visible light, thus improving its overall performance of the system [9]. The modification process causes defect to the TiO\textsubscript{2} structure such as oxygen vacancy (Vo) and Ti\textsuperscript{3+} leading to the reduction of band gap energy. Hence, absorbance of TiO\textsubscript{2} is shifted towards the visible light region [12].

Furthermore, addition of activated carbon to TiO\textsubscript{2} has a dual function; as a support and at the same time as the center of accumulation for the pollutant. The presences of hydroxyl groups (OH) on AC surface are able to attract [bmim]Cl towards the surface of the photocatalyst thus enhance the diffusion rate of [bmim]Cl into TiO\textsubscript{2}. The synergistic effect of adsorption-photodegradation of composite photocatalyst has consequently increased the overall efficiency of the system [13]. Apart from intrinsic factors, the extrinsic factors such as initial ILs concentration, initial pH of ILs solution and photocatalyst dosage has been reported to have significant effect to the overall efficiency of the systems [14].

In this paper, the work is focused on the development of hybrid nano-photocatalyst consisting of nano-TiO\textsubscript{2} synthesized via microemulsion method followed by modification with Fe and deposited on AC surface. The efficiency of the developed photocatalyst was evaluated in a photocatalytic degradation system containing [bmim]Cl solution at the desired concentration under 500W visible light energy source. Several parameters that were reported to be highly significant to the photodegradation process will be investigated.

2. Materials and Methods

2.1. Materials

All chemicals were purchased and used without further purification. Hexanol (C\textsubscript{6}H\textsubscript{14}O, 98%), ferum nitrate nonahydrate (Fe.(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O), 1-butyl-3-methylimidazolium chloride, [bmim]Cl (C\textsubscript{8}H\textsubscript{15}ClN\textsubscript{2}), heptane (C\textsubscript{7}H\textsubscript{16}, 99%), Ethanol (C\textsubscript{2}H\textsubscript{3}OH, 95%) and titanium tetraisopropoxide, TTIP (C\textsubscript{12}H\textsubscript{28}O\textsubscript{4}T, 97%) were purchased from Merck (Germany). Meanwhile other chemicals such as nitric acid (HNO\textsubscript{3}, 65%), triton X-100 (C\textsubscript{34}H\textsubscript{62}O\textsubscript{11}, AR), potassium dihydrogen phosphate (KH\textsubscript{2}PO\textsubscript{4}) and triethylamine (C\textsubscript{6}H\textsubscript{15}N, AR) were supplied by R&M Chemicals (Malaysia) and phosphoric acid (H\textsubscript{3}PO\textsubscript{4}, 85%) was purchased from QreC (New Zealand).

2.2. Methods

Nano-TiO\textsubscript{2} was synthesized using water-in-oil microemulsion method as reported from previous study [7] followed by modification with the desired Fe via wetness impregnation method. The resultant powder from the impregnation method was calcined at 400 °C for 1.5 h. In a different set up, the pre-carbonized AC was oxidized using 1M of nitric acid in a boiling condition for 20 minutes. 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 °C. Finally, the developed, Fe-TiO\textsubscript{2} and AC were mixed (10 wt% AC) using impregnation method as reported in our previous study [15]. The final photocatalyst was denoted as aFe where a refer to amount of Fe dopant ie; 0.2Fe refer to 0.2 wt% Fe deposited onto TiO\textsubscript{2}/AC.

2.3. Characterization Photocatalyst

Characterization of the photocatalyst was conducted to analyze its physical and chemical properties. The effect of adding AC to the photocatalyst surface was evaluated by analyzing the
existing functional group using Fourier Transform Infrared (FTIR). The analysis was conducted using Shimadzu FTIR-8400S Spectrophotometer. Absorbance and band gap of the photocatalyst was conducted using UV-Visible Spectroscopy. An optical property of the photocatalyst was conducted using Agilent Technologies Cary 100 UV-Vis Spectrophotometer Model G9821A. The pHZC of the photocatalyst was employed using mass titration method as reported from previous study [16].

2.3. Photodegradation Study

The performance of the developed photocatalyst was evaluated in the photocatalytic degradation of [bmim]Cl using open glass reactor in ambient conditions. In a typical experiment work, a pre-determined amount of photocatalyst was added into the reactor containing desired concentration of [bmim]Cl solution. The system was stirred in dark for 30 mins to allow for equilibrium adsorption-desorption process, followed by 2 h irradiation under 500 W halogen lamp. Liquid samples were collected at regular time intervals and analyzed using high performance liquid chromatography (Agilent 1100 HPLC). For better separation and sharp analysis, column symmetry C-18 (250 x 4.6 mm, 5 µm) and 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 30 °C column temperature, 5 µL sample injection and 0.8ml/min flow rate. The separated [bmim]Cl was detected at 212 nm wavelength using UV detector.

3. Results

3.1. Characterization of the photocatalyst

3.1.1. Fourier Transform Infrared (FTIR)

Figure 1 shows the vibration peak of different photocatalysts with respect to Fe content.

![Figure 1. FTIR spectra of photocatalyst at different amount of Fe](image)

3.1.2. Optical Property (UV-Vis)

The absorption spectra of the photocatalyst at different amount of Fe are presented in Figure 2.
The TiO$_2$ band gap energy was estimated from the extrapolation of Tauc plot and tabulated in Table 1. As a control, the synthesized TiO$_2$ has been treated in similar procedure as for the preparation of TiO$_2$/AC and Fe-TiO$_2$/AC. Similar procedure steps were also taken to P25 to ensure comparable data analysis.

### Table 1. Band gap energy of photocatalyst

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 25</td>
<td>2.80</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>2.77</td>
</tr>
<tr>
<td>0.0 Fe</td>
<td>2.57</td>
</tr>
<tr>
<td>0.1 Fe</td>
<td>2.58</td>
</tr>
<tr>
<td>0.2 Fe</td>
<td>2.35</td>
</tr>
<tr>
<td>0.3 Fe</td>
<td>2.17</td>
</tr>
<tr>
<td>0.4 Fe</td>
<td>2.06</td>
</tr>
<tr>
<td>0.5 Fe</td>
<td>2.03</td>
</tr>
</tbody>
</table>

#### 3.1.3. Surface Charge (pH$_{PZC}$)

Point zero charge (pH$_{PZC}$) of photocatalyst can be defined as the limiting pH when the net surface charge of photocatalyst is zero. The pH$_{PZC}$ study of photocatalyst was determined using titration method as reported from previous study [16].

![Figure 2. Absorption spectra of the photocatalyst](image-url)

![Figure 3. Surface charge of photocatalyst for 0.2Fe-TiO$_2$/AC](image-url)
3.2. Photodegradation Study of [bmim]Cl

The photodegradation analysis of [bmim]Cl was optimized by using one factor at a time experiment (OFAT) analysis. Factors such as composition of dopants, initial concentration of [bmim]Cl \([\text{IL}_0]\), initial pH of solution and photocatalyst dosage were investigated to study the effect of the parameters in degradation of [bmim]Cl.

3.2.1. Effect of Fe Composition

The effect of Fe loading to the degradation efficiency of [bmim]Cl is depicted in figure 4. The percentage of degradation increased as the amount of dopant increase.

![Figure 4. Efficiency [bmim]Cl degradation system for different amount of Fe at \([\text{IL}_0]\) = 5 mM, pH = 8 and [photocatalyst] = 1 g/L.](image)

3.2.2. Effect of Extrinsic Factor: Initial Concentration of [bmim]Cl \([\text{IL}_0]\)
Figure 5. Efficiency of [bmim]Cl degradation system at different [ILo]

Figure 5 presents the effect of initial concentration of [bmim]Cl [ILo] to the overall performance of the system. The study was conducted by keeping other parameters constant i.e 0.2 wt% Fe, pH 8 and 1 g/L of photocatalyst. As the [ILo] was reduced, the total percentage degradation recorded increased.

3.2.3. Effect of Extrinsic Factor: pH of [bmim]Cl solution

Pursuant to section 3.2.2, optimum [ILo] was observed at 1 mM. Hence, this [ILo] has been selected to study the effect of initial pH of [bmim]Cl solution while keeping other parameters constant i.e 0.2 wt%Fe, [ILo] at 1 mM and 1 g/L of photocatalyst. Figure 6 depicts the comparative study pH of [bmim]Cl solution. As the initial solution pH increased, the total removal of [bmim]Cl increased up to the optimum point, then decreased.
3.2.4. Effect of Extrinsic Factor: Dosage of Photocatalyst

Figure 7. Efficiency of \([\text{bmim}]\text{Cl}\) degradation system at different \([\text{photocatalyst}]\)

The effect of photocatalyst dosage, \([\text{photocatalyst}]\) to the efficiency of the system was evaluated by keeping other factors constant i.e 0.2 wt% Fe, \([\text{IL}]\) at 1 mM and initial pH 10. Figure 7 summarizes the removal efficiency at different \([\text{photocatalyst}]\). as can be observed from the figure, \([\text{photocatalyst}]\) has significant effect to the total removal of \([\text{bmim}]\text{Cl}\).

4. Discussion

4.1 Fourier Transform Infrared (FTIR)

From Figure 1, the first broader peak recorded at at 766 cm\(^{-1}\), could be ascribed to the titania framework that has been deposited onto AC such as Ti—O—Ti [13, 17, 18]. The vibration peak recorded at 1390 cm\(^{-1}\) represent the C=O stretching related to carboxylic groups and carboxylate moieties [19, 20] while the presence of C=O stretching could be due to the oxidation treatment of AC with nitric acid. The usage of acid as treatment agent was also stated that it could produce homogenous distribution of titania with complex structure [19]. This can be supported with vibration peak around 766 cm\(^{-1}\) which shows strong vibration of Ti—O proving that TiO\(_2\) is well distributed on the surface of AC [21].

The small and sharp vibration peaks of C-H have been detected in IR spectra at wavenumber 1390 and 1478 cm\(^{-1}\). These peaks show that the dissociation of precursor TiO\(_2\)/AC may occur leaving behind the substrate such as O, Ti and C. The presence of C—H bond is also stated to be chemisorbed [22]. Meanwhile, peak at 1640 cm\(^{-1}\) represents the vibration of O—H that may comes from adsorption of H\(_2\)O onto surface of photocatalyst [13, 21, 22]. Small peak detected at 2412 cm\(^{-1}\) represents the double bond that may present on surface of photocatalyst such as C=O [22]. Two close vibration peaks at 2956 and 2974 cm\(^{-1}\) also represent the O—H stretching. Broader peak at 3454 cm\(^{-1}\) represent the O-H group [13, 21, 22]. The presence of this broader peak shows high vibration of O-H that exist on AC’s surface that has been oxidized with nitric acid. This is in line with the purpose of oxidation treatment which is to obtain more hydrophilic surface of photocatalyst with oxygen-containing functionalize group on surface of AC such as O—H group [19]. In adsorption study of hydrophobic ILs, the presence of O—H is important as it could act as pollutant concentrator for the composite photocatalyst. The O—H group that present on the surface of photocatalyst were able to promote the H-bonding interactions with anion of hydrophobic ILs [23, 24].
4.2. Optical Property (UV-Vis)

Significant shift of the absorbance edge at 400 nm wavelength could be observed for all photocatalysts containing Fe. This shift could be ascribed to the excitation of electron ($e_{CB}$) from valence band (VB) of TiO$_2$ as described by equation (1-3) [25]. The $h_{VB}^+$ and trapped electron ($et$) refer to hole form at VB after excitation of $e_{CB}$ and electron that has been trapped on surface AC and dopant respectively.

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 (e_{CB}) + \text{TiO}_2 (h_{VB}^+) \quad (1)
\]

\[
\text{TiO}_2 (h_{VB}^+) \xrightarrow{\text{organic groups}} \text{TiO}_2 \quad (2)
\]

\[
\text{TiO}_2 (e_{CB}) \rightarrow \text{TiO}_2 (et) \quad (3)
\]

The $h_{VB}^+$ will then be scavenged through interaction with organic groups that is present on AC surface which led to the formation of new trapped electron. This continuous phenomenon creates centers of excitons which then will cause the red shift and additional peak of the absorption onset [25]. The trapped electron could also occur from $e_{CB}$ to dopant on photocatalyst before the $et$ be excited again to the TiO$_2$ surface to undergo redox process as per equation (4-7). The $e^-$ refer to electron from dopant itself.

\[
\text{Fe}^{3+} + \text{TiO}_2 (e_{CB}) \rightarrow \text{Fe}^{2+} \quad (4)
\]

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{TiO}_2 (et) \quad (5)
\]

\[
\text{Fe}^{3+} \rightarrow \text{Fe}^{4+} + e^- \quad (6)
\]

\[
\text{Fe}^{4+} + \text{TiO}_2 (et) \rightarrow \text{Fe}^{3+} \quad (7)
\]

From Table 1, the estimated band gap energy of TiO$_2$ and P25 were approximately lower than reported [26] which could be due to the treatment procedure. It could be deduced that this reduction occurred due to: 1) when P25 and TiO$_2$ were calcined after the impregnation processes, the phase structure of photocatalyst increased hence reducing the band gap energy as reported from previous study [26, 27] and 2) transformation of anatase to rutile could occur which led to reduction in band gap energy [26, 28]. The band gap of TiO$_2$ doped with Fe also shows significant reduction with the increased amount of Fe (Table 1). This phenomenon could be explained when the excited $e_{CB}$ combine with Fe dopant as the mid band gap energy introduced by dopant is low compared to band gap of bare TiO$_2$. Then, the $e_{CB}$ can be excited again from dopant to CB of TiO$_2$. The reduction in band gap energy mean that the photocatalyst requires lower energy to generate more charge carrier to undergo redox process for degradation of [bmim]Cl [7].

4.3 Surface Charge ($pH_{pzc}$)

It was found that, the $pH_{pzc}$ of photocatalyst was 6.3 (Figure 3). On the other hand, the pH of [bmim]Cl solution was recorded around 8.2 ± 0.2 regardless of [bmim]Cl concentration.

Generally, when the pH of the solution is higher than $pH_{pzc}$ of photocatalyst, the surface of photocatalyst will be negatively charged. Different charges between the photocatalyst surface and its [bmim]Cl will attract each other, hence increase the diffusion rate of [bmim]Cl into TiO$_2$ [9]. On the other hand, similar charges between both entities reduce the ability for TiO$_2$ to attract [bmim]Cl compound towards its surface.

4.4. Effect of Fe Composition

Positive effect of increasing Fe amount could be observed in Figure 4. This is because, as the amount of Fe dopant increased, the band gap energy of TiO$_2$ decrease as proven in tauc plot analysis.
(Table 1). Consequently, lower energy is required to initiate the generation of charge carrier to proceed with redox process and consequently degrade [bmim]Cl compound. In theory, upon radiation of light energy at certain value, $e_{CB}^{-}$ could be excited to the covalence band of TiO$_2$ (CB). These electrons will be trapped by metallic dopant Fe$^{3+}$ with the value of redox potential 0.77 eV respect to flat band potential ($V_{fb}$) of TiO$_2$ and follow several redox reaction as in equation (4-7) [12].

Based on the classical field theory, the formation of Fe$^{2+}$ and Fe$^{4+}$ is very unstable. This is because in their molecular state 3d$^6$ configuration, it is only occupied with half-filled electron. Hence, the charge carrier can be migrated to the surface of TiO$_2$ to degrade the [bmim]Cl. The Fe$^{2+}$ can be returned back to Fe$^{3+}$ by donating one ($e_{CB}^{-}$) either directly to [bmim]Cl or to H$_2$O to undergo reduction process. H$_2$O will be reduced to form strong radical such as hydroxyl radical (OH$^\cdot$). These radicals are active species that could attack wide range of organic pollutants thus enhance the degradation rate of pollutants. Meanwhile Fe$^{4+}$ can be transformed to Fe$^{3+}$ by receiving an electron or lose a hole ($h_{VB}^+$). The ($h_{VB}^+$) will come in contact with the oxygen (O$_2$) that also has been adsorbed on surface of TiO$_2$ leading to the formation of superoxide radical ($O_2^{-}$) [12, 29]. During the degradation process of [bmim]Cl, the formed ($O_2^{-}$) will attack the C2, C4 and C5 of imidazolium ring and produce unstable by-product known as 1-alkyl-3-methyl-2,4,5-trioxoimidazolidine. The formation of these by-products means the first stage of the degradation process where the phenomenon opening ring of cation occurred [30].

However, when the amount of Fe dopant exceeds the optimum, the overall efficiency of the system was significantly reduced. Even though higher amount of Fe further reduced the band gap energy of TiO$_2$ (Table 1), it also acts as the recombination center for the charge carriers. Furthermore, formation of ferum oxide (Fe$_2$O$_3$) on surface of photocatalyst during the synthesis process not only enhanced the system’s efficiency, excess amount of Fe$_2$O$_3$ will lead to the blockage of TiO$_2$ surface from harvesting the radiated light energy for chemical reaction. Hence, less charge carrier could be generated [29] leading to a reduced overall efficiency. The formation of oxygenated group on the surface of composite photocatalyst as proven by the IR spectra spectra (Figure 1) also plays an important role in the degradation of [bmim]Cl. The presence of functionalized groups such as O-H and –COOH is believed to able to increase the interaction of H-bonding between the surface of composite photocatalyst and the anion Cl-. Hence more [bmim]Cl will be attracted to the AC on the surface which then enhance the diffusion rate between [bmim]Cl and surface TiO$_2$ resulting in the significant increase of the total removal of [bmim]Cl [24].

4.2. Effect of Extrinsic Factor: Initial Concentration of [bmim]Cl (IL$_o$)

In Figure 5, it can be observed that the total degradation of [bmim]Cl decreased with the increasing of [IL$_o$]. As the amount of [bmim]Cl in the solution increase, the number of [bmim]Cl molecule increased and leading to poor adsorption and degradation rate of pollutant. On the other hand, at lower [IL$_o$], the accumulation of the pollutant on surface of TiO$_2$ reduced providing more active surface area to absorb photon and generate the charge carrier. As more charge carriers been generated, more [bmim]Cl can be degraded. This phenomenon follows the Lambert law where as concentration of organic molecules reduced, it will increase the path length taken by the photon to enter the solutions [31].

4.3. Effect of Extrinsic Factor: Initial pH of [bmim]Cl solution

The effect of varying initial pH of [bmim]Cl solution during the photodegradation process can be observed in Figure 6. The lowest [bmim]Cl degradation was recorded in acidic region at pH 3. In acidic region, the surface charges of photocatalyst and organic molecule were both protonated. Similar charges between both species make them repel each other causing less adsorbate to be adsorbed onto the surface of photocatalyst. Further, causing lower amount of [bmim]Cl being degraded by the charge carrier [32]. In addition, the photocatalyst was reported to be agglomerated in acidic condition thus reducing the availability of TiO$_2$ active site that can be used to absorb photon
and adsorb [bmim]Cl [33]. From the study, the best working pH for photodegradation of [bmim]Cl was recorded in alkaline condition at pH 10. In this condition, the OH\(^-\) interacted with h\(^{+}\)\(_{vb}\) leading to higher production of OH\(^•\) thus increased the degradation rate of [bmim]Cl. However, at even higher alkalinity, both organic molecule and surface of the photocatalyst were deprotonated. Similar charges of both species again repelled each other causing less [bmim]Cl been adsorbed on the surface of TiO\(_2\) hence reduced the total degradation [32]. This ionization of the surface charge photocatalyst in various pH conditions could be explained as in equation (8-9) [34].

\[
\text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}_2^+
\]  
\[
\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O}
\]  

4.4. Effect of Extrinsic Factor: Dosage of Photocatalyst [photocatalyst]

The effect of photocatalyst dosage, [photocatalyst] on the overall efficiency of photodegradation system of [bmim]Cl was studied by varying the [photocatalyst] between 0.0 to 8 g/L. From Figure 7, the total degradation of [bmim]Cl increased until the optimum [photocatalyst] was achieved. Insufficient amount of photocatalyst supplied to the system will cause blockage of the active site by [bmim]Cl hence poor efficiency of the system [35]. As the dosage increased, the active site available for photodegradation process increased leading to higher degradation rate. Beyond the optimum dosage (1 g/L), the overall efficiency of the system decreased despite larger amount of photocatalyst being used in the system. High amount of photocatalyst in the system lead the screening phenomenon of particles which will causes blockage of active site of photocatalyst. Furthermore, excess photocatalyst also lead to the agglomeration of the nanoparticles that will reduce the total surface area of photocatalyst. Hence less photon will be absorb and reduce the formation of generation charge carrier [36].

5. Conclusions

From the analysis study of composition Fe dope onto TiO\(_2\), it can be conclude that by doping metal with optimum amount on surface of TiO\(_2\) it can shift the performance of TiO\(_2\) into visible region and increase the performance of photocatalyst for removal of [bmim]Cl. By considering the effect of [IL\(_o\)], this factor highly influence the overall efficiency of the system. As excess [IL\(_o\)] was used, it will block the surface of TiO\(_2\) from harvesting the light. The pH synthetic of waste water also affect the overall efficiency of the systems where the most optimum pH conditions was recorded at pH 10. At this condition, the available OH\(^-\) will increase the production of OH\(^•\) as attacking agent that will increase the total degradation of bmimCl. Lastly, optimum dosage of Fe-TiO\(_2\)/AC was recorded with 1 g/L as excess of photocatalyst will agglomerate and reduce the availability of active site of photocatalyst.

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Conflicts of Interest: “The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results”.

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