Toluene gas treatment by combination of ionic liquid absorption and photocatalytic oxidation

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ABSTRACT

Toluene exhaust gas is a nuisance to the environment and human beings. In this study, 1-dodecyl-3-methylimidazolium chloride (DDMIM Cl) was selected as the absorbent solution and was combined with photocatalytic oxidation (PCO) for the treatment of toluene gas. The effects of toluene concentration, UV lamp power, catalyst dosage, coexisting ions and pH on the toluene removal ratio by PCO were investigated. Changes to the absorbent structure after four reuses were compared according to the UV–vis absorption spectrum, and the anti-oxidation ability of the absorbent was evaluated. The results showed that the absorbent concentration was an important factor in the absorption of toluene. At the absorbent concentration of 5%, the initial absorptivity reached 96.79%, and the saturated absorption capacity was 43.8 mg/L. With a toluene concentration of 13.1 mg/L, an 18-W UV lamp, a photo catalyst dosage of 400 mg/L, and a reaction time of 80 min, the removal ratio of toluene reached 91.3%. The PCO of toluene followed pseudo-first-order kinetics. The main intermediates of toluene oxidation were benzoic acid and benzaldehyde, while traces of cresol and benzyl alcohol were also found. After four reuses, the absorption capacity of the absorbent was not weakened, and the molecular structure of DDMIM Cl remained stable, reflecting its oxidation resistance. Therefore, the use of an ionic liquid as an absorption solution combined with PCO for the treatment of toluene waste gas is theoretically feasible.

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1. Introduction

Toluene exhaust gas emitted during production processes in the chemical, ceramic, paint, electroplating, and other industries greatly harms employee health [1–3]. Currently, combustion and adsorption methods are used to treat toluene gas [4]. Of these, the combustion method has a greater temperature requirement for the exhausted gas, with a direct combustion that should occur at temperatures above 1100 °C. The investment and operation costs of this method are also great [5]. The adsorption method has a better removal ratio of toluene exhaust gas at low concentrations, although it has some problems, such as adsorbent regeneration and the inability to reduce contaminants to harmless levels [6]. Photocatalytic oxidation (PCO) is considered a promising method for the treatment of toluene exhaust gas owing to its powerful catalytic activity, mild working conditions, and safe environment [7–9]. However, the removal ratio of the exhaust gas is restricted by

the contact reaction time and the toluene concentration on the surface area of the photo catalyst [10]. By adding absorbents that enhance the solubilization of toluene in the solution, absorption can make up for the shortcomings of PCO [11]. Thus, absorption combined with PCO should be feasible for the treatment of toluene exhaust gas.

Ionic liquids (ILs), composed of an organic cation and an organic or inorganic anion, are molten salts at room temperature, and imidazoles are the most common cations [12]. They have many unusual properties, such as high thermal and chemical stability and excellent solvability for inorganic and organic compounds [13]. In recent years, many researchers have reported treating inorganic and organic gases using ILs [14–18], but rarely treating toluene exhaust gas. By analyzing Henry's constant of toluene over 272 types of ILs using the COSMO-RS method, Bedia et al. [19] found that imidazole ionic liquid with long-chain alkanes in the imidazolium cations had better toluene absorption capabilities. Stepnowski et al. [20] noted that elongating the substituent length in the imidazolium cations could significantly decrease degradability. Siedlecka et al. [21] observed that Cl⁻ was able to compete

for hydroxyl radicals with $BMIM^+$, and the degradation of ionic liquids by PCO could be inhibited.

Therefore, in this study, 3-methyl, 1-dodecyl imidazole chloride (DDMIM Cl) was selected as an absorbent to treat simulated toluene gas, and the influence of its concentration on absorption was assessed. Further, the effects of toluene concentration, UV lamp power, photo catalyst amount, system pH, and coexisting ions on the PCO process were investigated. Oxidation mechanisms of toluene were determined based on the identification of intermediates. The oxidation resistance of the absorbent was also investigated.

2. Experimental design and methods

2.1. Materials

Toluene (purity: 99.8%) was purchased from Sigma-Aldrich, DDMIM Cl (purity: 97–98%), was purchased from Shanghai Chengjie Chemical Co. without further purification, and the photo catalyst (80% anatase TiO_2, particle diameter ≈ 15–20 nm, surface area ≈ 60–100 m^2/g) was purchased from Hangzhou Wan Jing New Material Company.

2.2. Experimental device

A schematic diagram of the absorption and PCO processes is depicted in Fig. 1. The inner diameter of the reaction vessel was 4.5 cm; its height, 30 cm; and working volume, 300 mL. An 18-W ultraviolet (UV) lamp with a radiation peak at 254 nm (Fujitsu, Japan) was placed in the middle of the vessel for illumination. The reaction vessel was shielded with tinfoil for protection against UV rays. The reaction temperature was controlled at $25 \pm 1\,°C$ via a water bath.

The inlet gas feed was provided via bubbling a bottle of compressed dry air through liquid toluene in the glass cylinder. The air flux containing toluene was mixed with air, forming a simulated gas with the desired toluene concentration. It was then fed into the reaction vessel, which was filled with 200 mL of absorption solution, through a gas disperser. In this study, the total flow ratio of gas measured and controlled with rotary flow meters was fixed to 100 mL/min, and the toluene concentration of the inlet gas was approximately 1000 mg/m^3.

2.3. Toluene absorption experiments

The absorption solutions were prepared according to varying weight ratios of DDMIM Cl to water (0, 0.01%, 0.02%, 0.05%, 0.1%, 0.2%, 0.5%, 1%, 2%, and 5%). During the experiment, the UV lamp was turned off. The toluene concentrations of the inlet and outlet gas were measured once every 10 min by a ppbRAE monitor (PGM 7340, RAE Systems, USA) [22,23]. When the toluene concentration of outlet gas was equal to that of the inlet gas, the absorption solution reaches its saturation toluene absorption, its toluene concentration was determined from the absorbance of the peak maximum at 261 nm on a Lambda 850 UV–vis spectrophotometer [24]. Repetition experiments were performed 3 times.

Toluene absorptivity (A, %) at a certain absorption time was calculated as follows:

$$A = \frac{Y_0 - Y_g}{Y_0} \times 100\% \tag{1}$$

where Y_0 (mg/m^3) and Y_g (mg/m^3) are toluene concentrations of the inlet and outlet gas, respectively.

2.4. PCO of toluene in absorption solution

The two rotary flow meters were turned off, and a certain amount of photo catalyst was added to the saturated toluene absorption solution. Prior to the PCO experiments, the suspension was stirred for more than 1 h in the dark, ensuring full adsorption of toluene on the photo catalyst [25]. When the UV lamp was switched on, air was bubbled continuously into the suspension at low speed (20 mL/min) by opening rotary flow meter 1 during the runs. Aliquots of 10 mL were collected every 20 min and were centrifuged before being analyzed by the ultraviolet absorption method. Each analyzed sample was returned to the reaction vessel after the test [26]. Blank tests were performed in the absence of the photo catalyst and illumination by the UV lamp.

After their extraction by dichloromethane, the intermediate oxidation products of toluene were analyzed by GC–MS (Agilent 7890A) equipped with a DB-WAX column (30 m × 0.25 μm × 0.25 mm) and a flame ionization detector. The primary temperature of 40 °C was maintained for 1 min, after which the temperature was increased by 10 °C/min to 200 °C. The temperature was again raised by 8 °C/min to a final temperature of 240 °C. The sample was held at the final temperature for 5 min. The MS operating conditions included an ion source at 200 °C, full scan mode, and the MS mass range of m/z 35–450 with an acquisition ratio of 200 spectra per second. The electron impact (EI) ionization source at −70 eV was used after a 4-min solvent delay. Intermediates were identified using a program of the NIST Library.
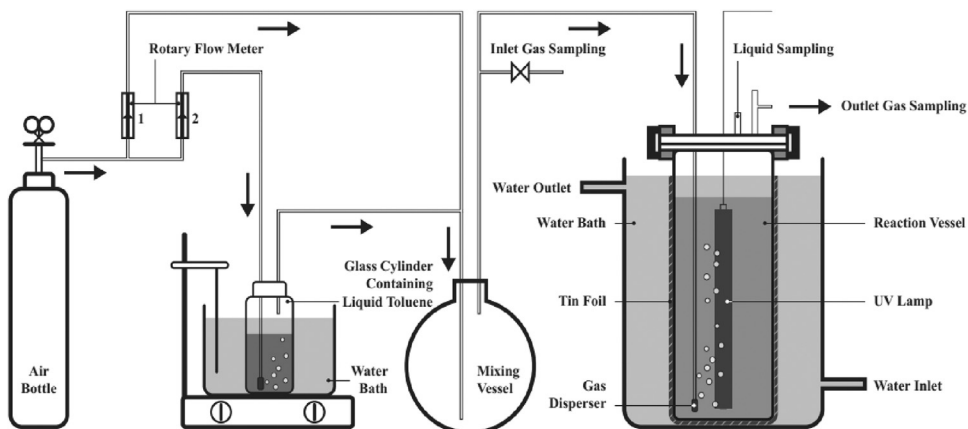

Fig. 1. A sketch map showing the lab-scale set-up.

The removal ratio of toluene (R, %), characterizing the removal effect of PCO, was calculated as follows:

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (2)$$

where C_0 (mg/L) is the initial toluene concentration in the absorption solution, and C_t (mg/L) is the toluene concentration at reaction time t.

2.5. Reuse of absorption solution

The absorption solution was treated by centrifugation and filtration for removal of the photo catalyst and then by abstersion and separation with 50 mL of dichloromethane for reduction of intermediate interference. The experimental process detailed in sections 2.3 and 2.4 (including absorption and PCO) was repeated four times for evaluation of the effects of reuse of the absorption solution.

UV-vis was utilized for analysis of changes in the absorption spectra of the absorbent through reuse [27]. After each reaction, the treated absorption solutions were sampled, diluted, and scanned with a UV–vis spectrophotometer at 195–400 nm.

3. Results and discussion

3.1. Absorption capacity of the absorbent

The toluene absorption capacity of absorbent was investigated for different concentrations of the simulated exhaust gas. Fig. 2 presents the absorption curves and clearly shows the differences in absorptivity and duration among the absorption solutions. When the concentration of the absorption solution increased from 0% to 5%, the absorption time extended from 20 min to 120 min, and the initial toluene absorptivity increased from 27.3% to 96.79%. These findings indicate that the concentration of the absorption solution plays an important role in the absorption capacity.

As shown in Fig. 3, with increased absorbent concentration, the saturation toluene concentration in the solution increased by a factor of 19 from 2.3 mg/L to 43.8 mg/L. It is remarkable that the increase of toluene was so distinguishable at different absorbent concentration ranges. Toluene concentrations increased significantly and then slowly as the absorbent concentration increased from 0 to 0.5% and then 0.5% to 5%, respectively. This is because when the concentration of the absorbent is equal to or greater than the critical micelle concentration (CMC), a large number of
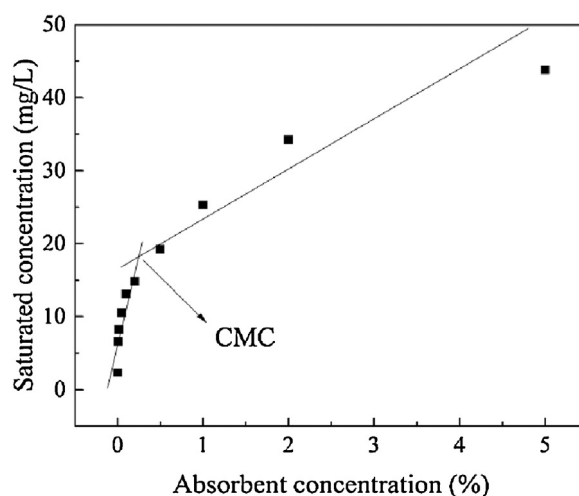
Fig. 3. Changes in saturation toluene concentration of the absorption solutions.

micelles form [28]. The surface tension of the solution decreases rapidly, which may promote the solubilization of toluene molecules in micelles. As the concentration continues to increase, the micelles may swell to their limit, reducing the toluene concentration growth rate in the solution [29].

3.2. Removal of toluene by PCO

3.2.1. Effect of toluene concentration

Four absorption solutions at concentrations of 0.1%, 0.5%, 2% and 5% and saturated with toluene via the absorption of toluene gas were used for investigation of the effect of toluene concentration on removal by PCO. All experiments were performed with the 18-W UV lamp, a dosage of 400 mg/L of photo catalyst, a pH of 7 and an 80-min reaction time. As shown in Fig. 4, the blank test revealed that the loss of toluene via gas exposure was less than 1%.

Photocatalytic oxidation kinetics of organic compounds can be successfully modeled using the Langmuir–Hinshelwood (L–H) equation to describe a correlation between degradation rate constants and initial concentrations [30]:
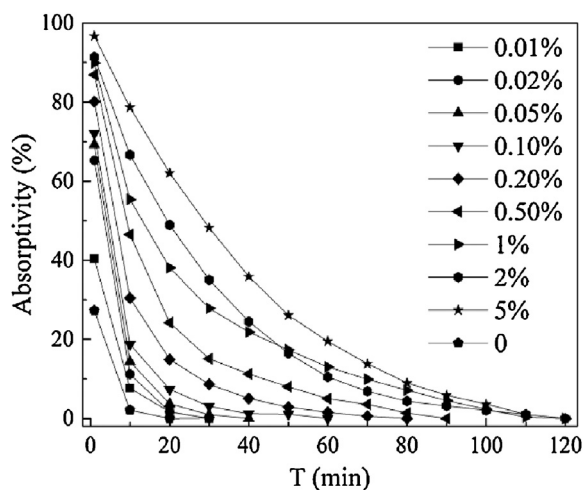
$$-\frac{dC}{dt} = kC \qquad (I)$$

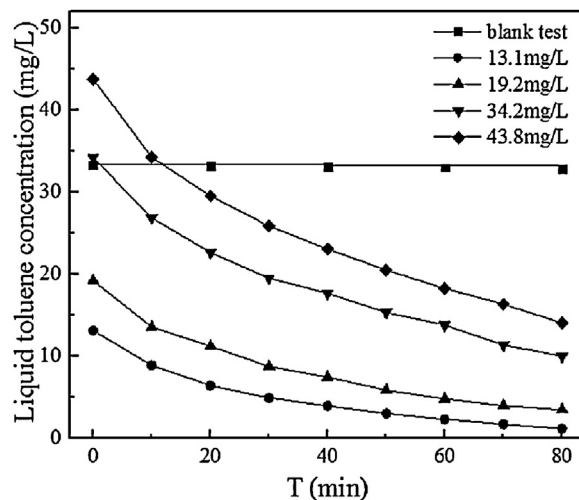**Fig. 2.** Absorption curves of the absorption solutions.

Fig. 4. Effect of toluene concentration on toluene removal.
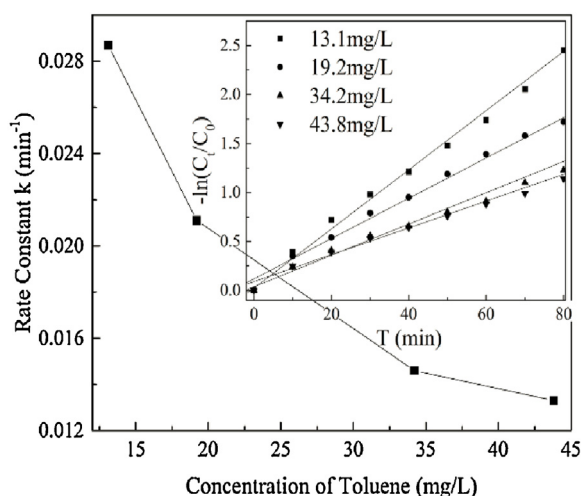
Fig. 5. Effect of toluene concentration on the rate constants.

where k is the rate constant in min^{-1}.

A satisfactory linear correlation ($R^2 > 0.98$) between k and initial concentration was given in Fig. 5 (inset of Fig. 5). It shows that the rate constant of toluene decreased when the initial concentrations of toluene increased from 13.1 to 43.8 mg/L. Within 80 min of reactions, more than 90% of toluene at concentration of 13.1 mg/L was degraded, whereas at concentration of 43.8 mg/L, less than 70% of toluene was removed, and the rate constants decreased from 0.0287 min^{-1} to 0.0133 min^{-1}. At a higher initial concentration, two factors could hinder the degradation of toluene. Firstly, increased amount of toluene may occupy a greater number of TiO_2 active sites, which subsequently inhibits generation of the oxidants and results in lower degradation rates. Secondly, a higher toluene concentration absorbs more photons, which consequently decreases available photons to TiO_2. Hence, the overall reaction rates were lowered with the higher initial toluene concentration, which has been observed in many photochemical reactions [31].

3.2.2. Effect of lamp power

The effect of different powers of the UV lamp (4, 8, 12, and 18 W) on removal of toluene by PCO was assessed. As shown in Fig. 6, it should be noted that UVC (254 nm) radiation with low power (4W) can degrade an unnegligible amount of toluene (approximately 20%). By contrast, with UVA (365 nm) radiation (4W), the
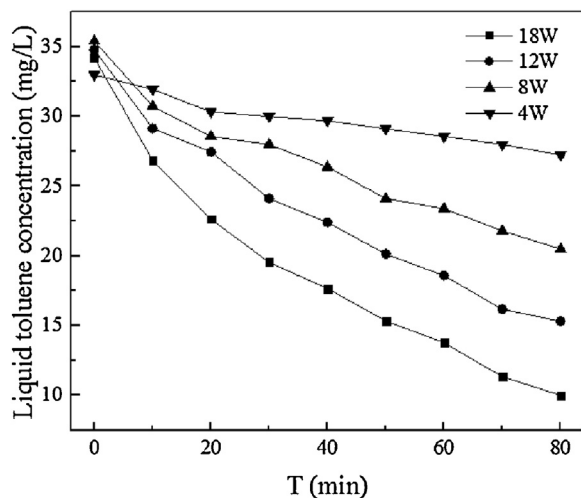
degradation is less than 10% [32]. Some reports have shown that UVC radiation irradiation could generate a great number of a reactive species like hydroxyls radical, hence it could efficiently excite the TiO_2 catalys [33].

The removal ratio and rate constants of toluene in the absorption solution by PCO increased with increasing UV lamp power (Fig. 7). This was likely because greater UV lamp power produced more photons and free radicals in the system, which may have improved the removal of toluene by PCO [34].

3.2.3. Effect of photo catalyst dosage

The effect of different dosages of the photo catalyst (100, 200, 300, 400 and 500 mg/L) on removal of toluene by PCO was also investigated. As shown in Figs. 8 and 9, when the photo catalyst dosage increased from 100 to 400 mg/L, the removal ratio and rate constants increased from 33.33% and 0.0053 min^{-1} to 70.76% and 0.0146 min^{-1}, respectively. With the further increase of the photo catalyst dosage, the removal ratio and rate constants decreased. When the dosage of the photo catalyst is lower than the optimal, more of the catalyst will be excited by the UV lamp; therefore, more H^+, hydroxyl radicals, and other active substances will be produced by the addition of the catalyst, accelerating the reaction ratio. When the photo catalyst is overdosed, the existence of excessive particles may cause unfavorable light scattering, reduce the penetration of light into the solution and increase the recombination ratio of electron-hole pairs, thus weakening toluene removal [35].

3.2.4. Effect of pH

The pH of an aqueous environment plays an significant role on the PCO of organic contaminant since it determines the surface charge of the photo catalyst and the size of aggregates it forms. To elucidate the role of pH, five experiments were performed in sequence at every pH (3, 5, 7, 9, and 11). The pH was adjusted using NaOH and HCl.

As shown in Fig. 10 and 11, pH clearly had a significant effect on the PCO of toluene. The removal ratio and rate constants were greatest at a pH of 6–7 and less in acidic or alkaline conditions. The surface charge of photo catalyst can be profoundly affected by the solution pH, and the ionization state of the surface can be protonated and deprotonated under acidic and alkaline conditions respectively as shown in the following reactions:
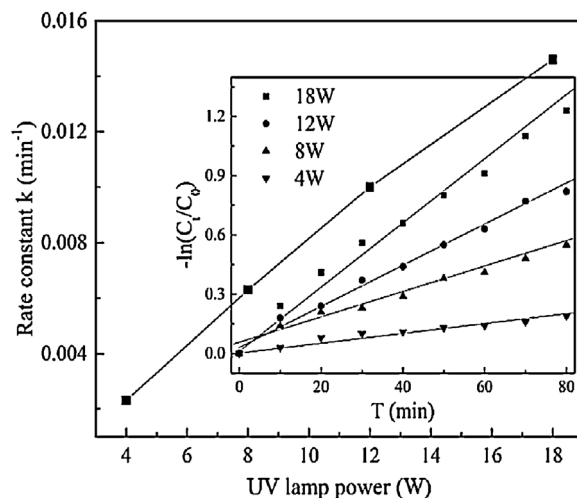
$$pH < P_{ZC} TiOH + H^+ \rightarrow TiOH_2^+ \qquad (II)$$

Fig. 6. Effect of UV lamp power on toluene removal.

Fig. 7. Effect of UV lamp power on the rate constants.
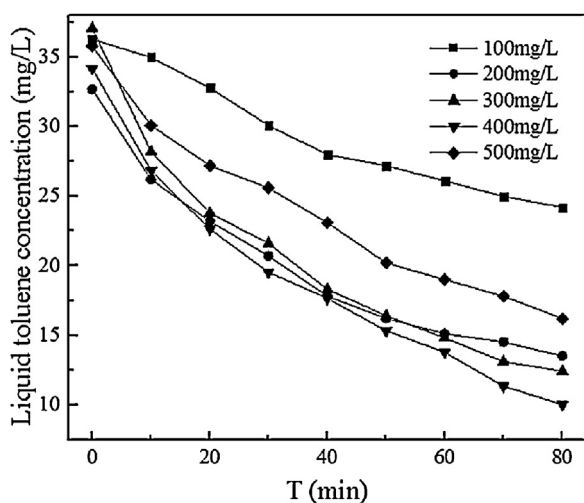
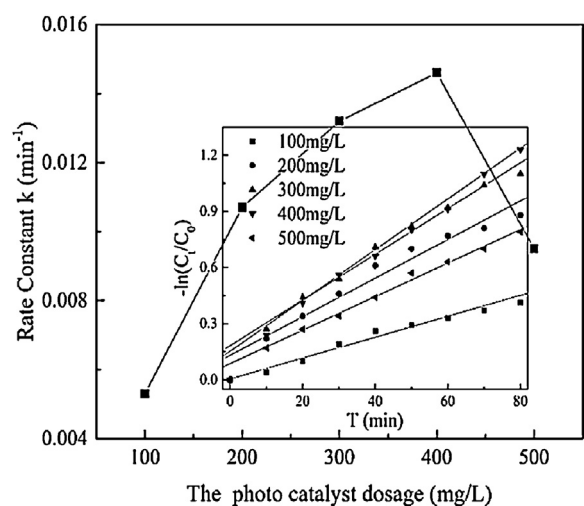**Fig. 8.** Effect of photo catalyst dosage on toluene removal.
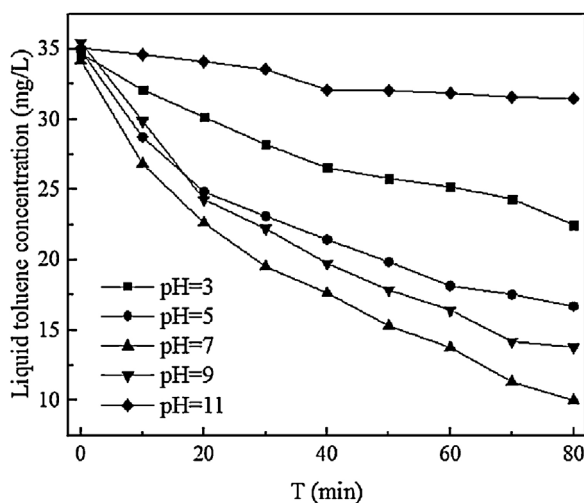

Fig. 11. Effect of pH on the rate constants.

$$pH > P_{ZC} \quad TiOH + OH^- \rightarrow TiO^- + H_2O \tag{III}$$

The point of zero charge (Pzc) of the TiO$_2$ is widely reported at approximately 7 [36]. Some organic contaminants are reported to be favourable in acidic and neutral solutions [37], while others are found to undergo degradation at a faster rate at higher pH values [38]. All these effects can be attributed to the nature of the pollutant to be degraded. In this study, the stability of nanoparticles is the most important factor. When the pH value was beyond the range of 6–7, the aggregation of nanoparticles can be observed, especially in strongly alkaline medium, which reduced solution permeability and the adsorption of toluene on the surface of the photo catalyst.

3.2.5. Influence of inorganic coexisting ions

It is well-known that PCO occurs at the surface of the catalyst particle. Thus, adsorption of specific ions may affect system performance by competing with the adsorption of organic molecules. The effect of the presence of common anions, including nitrate, sulfate, carbonate and chloride, was studied using the corresponding sodium. All the experiments were performed using 0.1-mol/L solutions.

As shown in Fig. 12, different anions had different levels of influence on the PCO of toluene. The effects of Cl$^-$ and CO$_3$$^{2-}$ were so pronounced that the toluene removal ratio was reduced from

Fig. 9. Effect of photo catalyst dosage on the rate constants.

Fig. 10. Effect of pH on toluene removal.

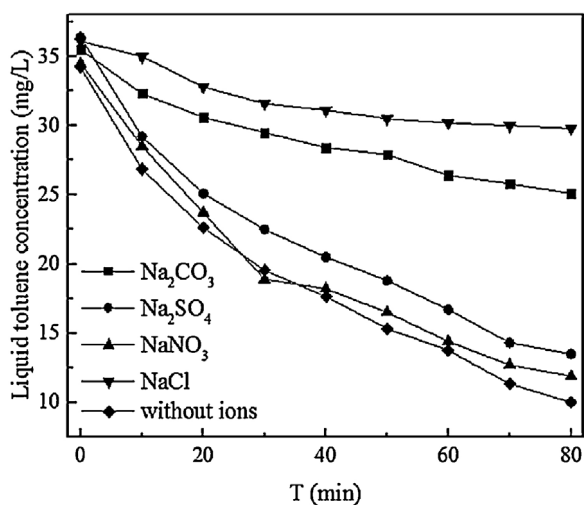**Fig. 12.** Removal of toluene with the present of coexisting ions.

70.76% to 17.45% and 29.3%, respectively, while SO_4^{2-} and NO_3^- exerted comparatively less influence on adsorption and, consequently, on the PCO. In general, the presence of anions in the system was adverse to the photocatalytic reaction. This is because, firstly, anions can not only affect toluene adsorption on the surface of the photo catalyst by blocking the active sites but also act as scavengers of the hydroxyl radical[39]. Secondly, the presence of anions reduces the diffusion characteristics of the matrix and the dissolved oxygen adhered to the surface of the photo catalyst [40].

3.2.6. Intermediate analysis

Reaction intermediates were identified by GC/MS with 5% of the absorption solution saturated with toluene, an 18-W UV lamp, 400 mg/L of the photo catalyst, a pH of 7 and an 80-min reaction time for elucidation of the toluene oxidation mechanisms. As shown in Fig. 13, based on the mass spectrum of the structure in the NIST05 database, dichloromethane and siloxane were determined to be the solvent and residue in the column, respectively. The main intermediates of toluene oxidation were benzoic acid and benzaldehyde, while traces of cresol and benzyl alcohol were also detected.

Fig. 14 presents a tentative reaction mechanism for the PCO of toluene in the absorption solution. The reaction is mainly initiated via the transfer of an electron from toluene to TiO_2 or the reaction between the toluene molecule and a hydroxyl free radical directly alongside the formation of a benzyl radical and hydrogen radical. The benzyl radical then reacts with O_2 to form a benzylperoxy radical, which can couple to form a tetroxide. The tetroxide is unstable and subsequently decomposes into benzaldehyde and benzyl alcohol, which can be further oxidized easily into benzoic acid in the system. With the side-chain oxidation pathway directly attacking CH_3, the electron density on the benzene ring is reduced by the conjugated effect of the carbonyl group, which reduces the activity and toxicity of toluene [41]. The generation of the cresol may be attributable to the addition of a hydroxyl radical on the aromatic ring of toluene in the presence of O_2 and UV irradiation [42].

3.3. Reuse of absorption solution

Experiments were conducted on the effects of the reuse of the solution with an absorbent concentration of 2%. The shapes of five absorption curves produced after four reuses were nearly identical
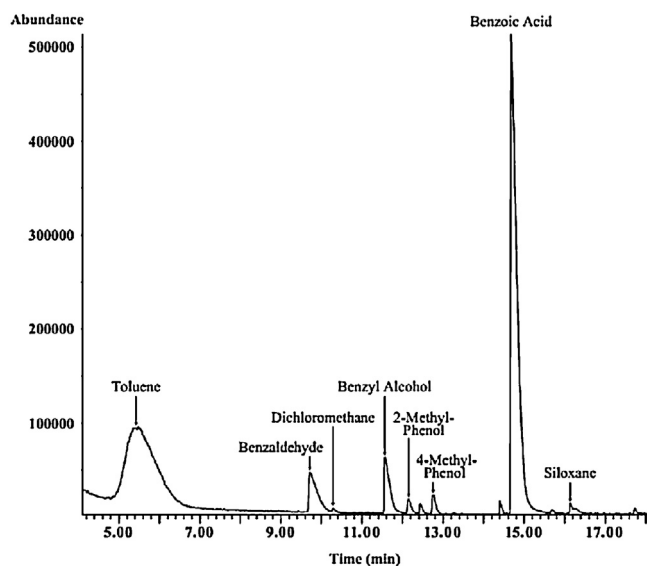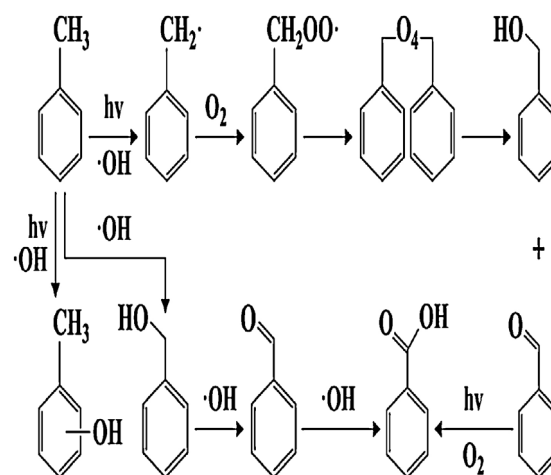
Fig. 14. Mechanism of oxidation toluene by PCO.

(Fig. 15). The initial removal ratio remained between 85% and 90%, and the absorption time for saturation was approximately the same. The toluene saturation concentration was maintained at 34–37 mg/L and did not decrease with increasing number of uses (Fig. 16). Therefore, the process of PCO did not affect the absorption capacity of the absorbent.

It is evident from Fig. 17 that the absorption spectrum of DDMIM Cl in water is characterized by a main band in the ultraviolet region located at 204–206 nm, which is associated with the imidazolium ring [27]. With increasing uses, the band was essentially the same. This finding indicates that the molecular structure of DDMIM Cl remained stable through the process of reuse, reflecting its oxidation resistance. In comparison, the presence of tetradecyldimethylamino-oxide was found beneficial for photocatalytic oxidation of toluene in liquid–solid regime, but it was also completely degraded and could not be reused [43].

In the process of PCO, carbon atoms on the imidazole ring are easily attacked by free radicals when the absorbent molecules are adsorbed onto the surface of the photo catalyst. The spatial configuration of the absorbent molecule, in which the non-polar substituted alkyl on the imidazole ring points to the surface of the photo catalyst and the imidazole ring with a positive charge points in the opposite direction, protects it from attack by the steric effect [20].
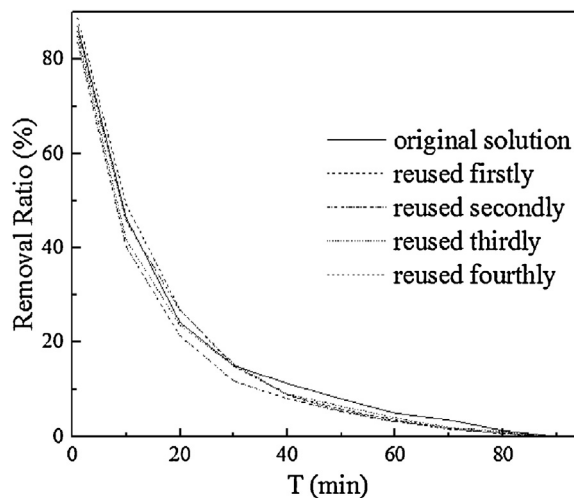
Fig. 13. GC/MS spectrum of intermediate products of toluene by PCO.

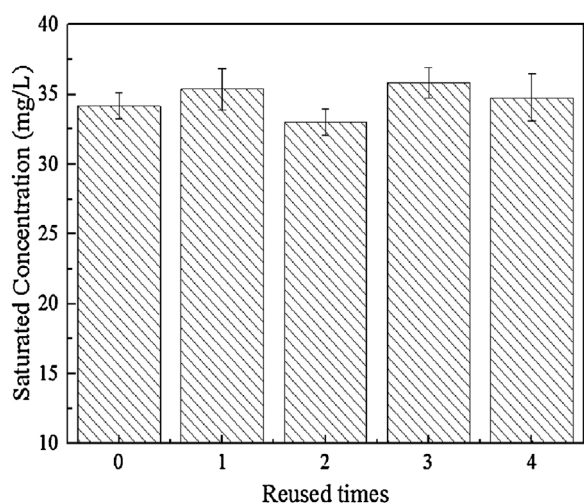**Fig. 15.** Toluene absorption curves of DDMIM Cl solution after reused.

Fig. 16. Changes in toluene saturation absorption concentration during the reuse of the studied absorbent solution.
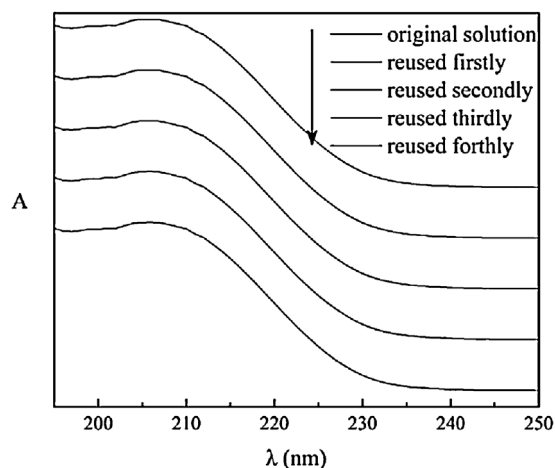

Fig. 17. UV spectra of the absorption solution after reused.

4. Conclusion

The treatment of toluene gas by combination of ionic liquid absorption and photocatalytic oxidation has been investigated. The heterogeneous gas–liquid photocatalytic oxidation of toluene gas involves gas–liquid mass transfer with simultaneous reaction. By adding ionic liquid that enhance the solubilization of toluene in the solution, absorption can make up for the shortcomings of PCO. When the concentration of absorbent was 5%, the initial removal ratio of toluene reached approximately 96.79%, and the toluene saturation concentration was 43.8 mg/L.

The rate of toluene degradation may be influenced by toluene concentration, UV lamp power, dosage of photo catalyst, pH and inorganic coexisting ions. With an initial toluene concentration of 13.1 mg/L, an 18-W UV lamp, 400 mg/L of the, and a reaction time of 80 min, the toluene removal ratio by PCO was 91.3%. The PCO of toluene followed pseudo-first-order kinetics. The reuse test revealed that the molecular structure of DDMIM Cl remained stable and the toluene absorption capacity did not decrease after four reuses. Transformation products formed during the PCO were shown to mainly follow the side-chain oxidation pathway (i.e., toluene → benzyl alcohol → benzaldehyde→ benzoic acid).

This study has confirmed the potential of the combination of absorption and PCO for the treatment of harmful toluene emissions. Future systematic studies are required to elucidate the detailed processes involved in this treatment method and especially the accumulation of the intermediate and the durability of the reaction system.

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