Role of ferric and ferrous ions in the enhancement of the heterogeneous solar photocatalytic degradation of combined mixture of chlorophenols

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ABSTRACT

The solar photocatalytic degradation of 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) was investigated individually and combined in the presence of Fe^{2+} and Fe^{3+} ions. The results revealed that both Fe^{2+} and Fe^{3+} ions enhanced the heterogeneous photocatalytic degradation. Fe^{3+} ions rapidly converted to Fe^{2+} ions as soon as the irradiation started. The intermediates formed during the degradation of 4-CP/2,4-DCP were also monitored and identified. Three main intermediates were observed, hydroquinone, phenol, and 4-chlorocatechol with traces of benzoquinone. The results support a new trend of research by utilising other cheap iron ion sources in the photocatalytic degradation.

INTRODUCTION

Chlorophenols have been categorised as highly nonbiodegradable toxic compounds which can be extremely dangerous to human and aquatic life. These pollutants are produced in the environment by chlorination of monoaromatic and polyaromatic compounds present in water (Ahmed et al. 2010). The toxicity of these pollutants comes from the C–Cl bond which is highly stable and has been reported as a main reason for their toxicity (Ba-Abbad et al. 2013). Among these pollutant compounds, 4-chlorophenol (4-CP) has been recognised as a threat to human health by both the EU and the US Environmental Protection Agency (USEPA) (Bandara et al. 2001; Hou et al. 2008). Another chlorinated phenolic compound, 2,4-dichlorophenol (2,4-DCP), has been listed as a very toxic pollutant by USEPA since 1976 (USEPA 2014). Chlorophenols are used or generated by many chemical industries including textile, pharmaceutical, plastic, and petroleum refineries (Czaplicka 2004; Pino & Encinas 2012).

These refractory toxic contaminants present in water need to be effectively treated using efficient methods. Different biological and chemical methods have been used to dispose of such pollutants. The advanced oxidation processes (AOPs) have been widely applied as an effective method to destroy organic pollutants and mineralise them into CO_{2} and H_{2}O (Salaices et al. 2004; Chong et al. 2010; Clament et al. 2013). Among the AOPs, the photocatalytic degradation using TiO_{2} and UV light has been reported to be a useful method for mineralising most organic contaminants present in water without significant drawbacks except the cost of energy (Jia et al. 2012). However, using solar light instead of UV light can effectively reduce the operating cost, making this method economically feasible (Abeish et al. 2015a). To enhance the efficiency of solar photocatalytic degradation different oxidants have been used in order to reduce the e^{-}/h^{+} recombination (Chen et al. 1998; Cornish et al. 2000; Pirkanniemi & Sillanpää 2002; Rodríguez et al. 2011). Among these oxidants iron has shown a significant positive effect on the photocatalytic degradation efficiency for organic compounds (Rodríguez et al. 2009, 2011; Zhen et al. 2012).

In our previous work (Abeish et al. 2014) we investigated the influence of ferric ions on the solar photocatalytic degradation of a chlorophenols mixture and the results showed that the degradation efficiency of 4-CP and 2,4-DCP significantly increased to reach 91% and 81% respectively. Furthermore, the complete degradation time was reduced from 240 min without Fe^{3+} to 150 min with 10 mg/L Fe^{3+}. In fact iron ions used in photocatalytic degradation processes can be either ferrous (Fe^{2+}) or ferric (Fe^{3+}). Despite the use of ferrous ion in AOPs as reagent in Fenton-like or in photo-Fenton processes, a few studies have used it as additives for the photocatalytic degradation of organic...
pollutants and their intermediates (Sclafani et al. 1991; Selvam et al. 2005). The role of Fe$^{2+}$/Fe$^{3+}$ ions in solar photocatalytic degradation processes strongly depends on several key parameters such as oxidation state, pH and type of metallic salt used as a source of iron as well as the presence of other oxidants like H$_2$O$_2$ and O$_2$ (Kavitha & Palanivelu 2004). For instance, Nogueira et al. (2005) investigated the influence of two different iron sources, Fe(NO$_3$)$_3$ and complexed ferrioxalate (FeOx), on the solar photocatalytic degradation of organic compounds. They found that the efficiency of Fe(NO$_3$)$_3$ is less than that of FeOx due to the presence of nitrogen leading to low quantum yield of Fe$^{2+}$ generation. Generally, the presence of iron ions (Fe$^{2+}$ or Fe$^{3+}$) can effectively enhance the photocatalytic degradation efficiency of organic compounds. However, there is a need to determine the residual iron at the end of degradation processes because the excess concentrations might negatively affect aquatic life. Thus, minimum amounts of iron should be used in this kind of degradation or alternatively the residual amounts might be recovered and used again in the treatment system. Muthuvel & Swaminathan (2007) stated that there are no negative impacts on the catalytic activity when using recovered iron in the degradation processes. There has been strong debate about the role of iron ions in photocatalytic degradation processes and which one of them gives better degradation efficiency. As a result further investigations and clarifications are needed to see if there is a significant difference between using Fe$^{2+}$ and Fe$^{3+}$ in the oxidation processes. Therefore, the aim of this study is to investigate the influence of ferrous and ferric ions on the solar photocatalytic degradation of a chlorophenols mixture consisting of 4-CP and 2,4-DCP and their intermediates. Furthermore, the role and mechanism of Fe$^{2+}$ and Fe$^{3+}$ ions during the solar degradation are also discussed.

**MATERIALS AND METHODS**

**Materials**

4-CP (99%), 2,4-DCP (98%), hydroquinone (HQ, 98%), 4-chlorocatechol (4-cCat, 99%), phenol (Ph, 99%), benzoquinone (BQ, 98%), ferrous sulphate hydrate (FeSO$_4$, 7H$_2$O), and iron(III) chloride hexahydrate (FeCl$_3$,6H$_2$O) were purchased from Sigma-Aldrich. Titanium(IV) oxide Aeroxide P25 was purchased from Acros Organics (99.5%, New Jersey, USA); the powder is 80% anatase and 20% rutile, with a primary particle size of 21 nm. All chemicals were used as received without further purification. Hydrochloric acid (HCl, 32%) was used to adjust the pH of the reacting mixture. All solutions were prepared with deionised and ultra-pure water.

**Photocatalytic degradation experiments**

A combined chlorophenols mixture (50 mg/L of both 4-CP and 2,4-DCP) was degraded under solar light using TiO$_2$, Fe$^{3+}$, Fe$^{2+}$, FeSO$_4$,7H$_2$O or FeCl$_3$,6H$_2$O. A Pyrex glass beaker of 15.5 cm height and 11 cm diameter was employed as a reactor, equipped with a magnetic stirrer; the volume of suspension used was 1 L. The experiments were carried out using a solar simulator (Sun 2000 210 × 210 mm, Abet Technologies Model 11044) to irradiate the reactor. The light intensity of the solar simulator was 1,000 mW/cm$^2$. The pH value of the solution was monitored using a pH meter (SP-701LI 120). The mixture was dissolved in distilled water and transferred to the photoreactor before adding TiO$_2$. Then, 0.5 g/L of photocatalyst TiO$_2$ and the desired amounts of ferrous ions (FeSO$_4$,7H$_2$O) or ferric ions (FeCl$_3$,6H$_2$O) were suspended in 200 mL and then added to the mixture. All suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between chemical components and TiO$_2$. After that, the lamp was turned on and the timer set to zero to start measuring the reaction time. All experiments were carried out at room temperature (26 ± 1 °C). At specific time intervals of 30 min, 5 mL was withdrawn and filtered by polytetrafluoroethylene 0.45 µm membrane filters to separate the catalyst particles from the liquid phase; then the composition of the liquid phase was analysed by high-performance liquid chromatography (HPLC). The photocatalytic degradation efficiency of each compound at different irradiation times was calculated using Equation (1)

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100$$  \hspace{1cm} (1)

where $\eta$ is the degradation efficiency, $C_0$ is the initial concentration and $C_t$ the concentration of the compound at any irradiation time. Furthermore, samples of 1 mL and 25 mL were withdrawn each 60 min to measure the chemical oxygen demand (COD) and iron ions respectively.

**Analytical methods**

4-CP, 2,4-DCP and their intermediates were identified and quantified by HPLC analysis. Detection of 4-CP and
2,4-DCP was conducted at 265 nm and 275 respectively, using a Varian Prostar 210 chromatograph with a UV-visible detector and a C18 reverse phase column (25 cm × 4.6 mm × 5 μm). The mobile phase was a mixture of 30% acetonitrile and 70% water with a flow rate of 1 mL/min. The temperature of the column was kept at 25 °C throughout all the analysis. Injection volume for all samples was 5 μL. The identification of the intermediates by HPLC was performed by the comparison of the retention time of the peak in the discharged sample with that in the standard sample. The concentrations of compounds were calculated by using the equations derived from the calibration measurements for standard samples.

A DR/2400 Hach spectrophotometer was used to measure COD, following the standard procedure of sample digestion. This equipment was also used to determine the concentration of ferric and ferrous ions (phenanthroline method) in the solution at different irradiation times.

RESULTS AND DISCUSSION

Effect of ferrous and ferric ions

It is well known that the photocatalytic degradation of chlorophenols is more efficient in acidic medium than in basic medium; therefore all experiments were conducted at pH 3 (Selvam et al. 2007; Dhir et al. 2012). The initial concentration of both 4-CP and 2,4-DCP used in all solar photocatalytic degradation experiments was 50 mg/L with 0.5 g/L of TiO₂. To investigate the optimum value of ferrous ions, different concentrations of Fe²⁺ were used. Figure 1 illustrates the effect of Fe²⁺ on the solar photocatalytic degradations of 4-CP and 2,4-DCP; it is clear that the maximum degradation occurred at a Fe²⁺ concentration of 7 mg/L, for both the contaminants. This result should be clarified by the fact that the recombination of the e⁻/h⁺ pairs increases at high metal ion doses, leading to reduce d hydroxyl radicals (‘OH) (Arslan et al. 2000).
The influence of Fe$^{3+}$ on the photocatalytic degradation of the same contaminants was also investigated under the same conditions (0.5 g/L TiO$_2$, 1,000 mW/cm$^2$ light intensity). The results in Figure 2 show that the best Fe$^{3+}$ concentration was 10 mg/L, which is in agreement with our previous work (Abeish et al. 2014). Kim et al. (2005) investigated the effect of ferric ion on the photocatalytic degradation of alachlor in the presence of TiO$_2$ and UV radiation and found that the degradation efficiency was enhanced by 80% when 7.5 mg/L of Fe$^{3+}$ applied.

The degradation efficiency of 4-CP and 2,4-DCP at different Fe$^{2+}$ or Fe$^{3+}$ doses was determined. Figure 3(a) shows the influence of ferrous ions on the degradation efficiency of both compounds. It can be seen that the maximum degradation values of 4-CP and 2,4-DCP were 93% and 87% respectively, at 7 mg/L Fe$^{2+}$. These percentages were

![Graph showing the influence of ferrous ions on the degradation efficiency of 4-CP and 2,4-DCP](image)

![Graph showing the influence of ferric ions on the degradation efficiency of 4-CP and 2,4-DCP](image)

**Figure 3** | Effect of iron ions on the degradation efficiency of 4-CP and 2,4-DCP at 150 min (0.5 g/L TiO$_2$, 1,000 mW/cm$^2$ light intensity): (a) Fe$^{2+}$ = 7 mg/L; (b) Fe$^{3+}$ = 10 mg/L.
achieved at 150 min, when most of the intermediates formed had been degraded. The difference in the efficiency between 4-CP and 2,4-DCP can be due to the increase of Cl atoms in 2,4-DCP, which need more irradiation time to be degraded.

Měšťánková et al. (2005)) investigated the effect of ferrous ions on the photocatalytic degradation of monuron (3-(4-chlorophenyl)-1,1-dimethylurea) and found that the positive effect of ferrous was in the range of 2 to 15.19 mg/L.

Figure 3(b) represents the effect of ferric ions on the degradation efficiency of 4-CP and 2,4-DCP. At 150 min irradiation time, the maximum degradation efficiencies of 4-CP and 2,4-DCP were 91% and 81% respectively. It can be seen that there is a difference between the efficiencies of the compounds which is very close to that achieved when using ferrous ions (Figure 3(a)).

Solar photocatalytic degradation of the combined mixture

In the presence of the optimal concentrations of Fe$^{2+}$ (7 mg/L) or Fe$^{3+}$ (10 mg/L), the solar photocatalytic degradation of the chlorophenols mixture generated three main intermediates, namely HQ, Ph, and 4-cCat as shown in Figure 4. It can be seen from Figure 4(a) that all the formed intermediates have the maximum concentrations at around 60 min before they degraded at 120 min solar irradiation time. These results indicate that there is a significant enhancement of the degradation time compared with our previous work (Abeish et al. 2015b) where no ferrous ions were used and the complete degradation was obtained at 240 min. Figure 4(b) shows similar results on the influence of Fe$^{3+}$ ions. It is clear that there is no considerable difference in terms of the types of intermediates formed compared to Fe$^{2+}$. However, the complete degradation time was reduced from 150 min to 120 min. This difference in the degradation time may indicate that ferrous ion is more active with TiO$_2$ than ferric ion. This activity might be achieved by at least two ways including: (i) efficiently trapping the photogenerated electron e$^-$ by Fe$^{2+}$ leading to reduced e$^-$/h$^+$ recombination rate; and (ii) the reaction of Fe$^{2+}$ with hydrogen peroxide generated from TiO$_2$ during solar irradiation time according to Equations (2)–(6) (Arslan et al. 2000).

\[
\begin{align*}
\text{TiO}_2 + h_v & \rightarrow h^+ + e^- \quad (2) \\
h^+ + OH^- & \rightarrow \text{•OH} \quad (3) \\
O_2 + e^- & \rightarrow O_2^- \quad (4) \\
\end{align*}
\]

\[
2O_2^- + H_2O \rightarrow H_2O_2 + 2O_2 \quad (5)
\]

\[
\text{Fe}^{2+} + H_2O_2 \rightarrow \text{Fe}^{3+} + \text{•OH} + OH^- \quad (6)
\]

However, when ferric salts are used instead of ferrous ions in the oxidation process, the •OH radical is produced in two stages with the slow reaction between ferric ion and H$_2$O$_2$ generated from TiO$_2$ making ferric ions slightly less active than ferrous. The reaction mechanism of ferric ions can be represented by Equations (7) and (8) (Nidheesh et al. 2013).

\[
\begin{align*}
\text{Fe}^{3+} + H_2O_2 & \rightarrow \text{FeO}_2H^2^+ + H^+ \quad (7) \\
\text{FeO}_2H^2^+ & \rightarrow \text{HO}_2^* + \text{Fe}^{2+} \quad (8)
\end{align*}
\]

To monitor the total removal efficiency of the combined mixture, COD was continuously measured during the course of the reaction. Figure 5 illustrates the COD reduction of the...
mixture at the optimal conditions of Fe²⁺ = 7 mg/L, and Fe³⁺ = 10 mg/L. It can be seen from Figure 5(a), for Fe²⁺, that significant reduction of COD started after 60 min. The low reduction rate during the first 60 min of the solar irradiation might be attributed to the formed intermediates (HQ, Ph, 4-cCat) that make the solution rich in organic compounds (Figure 4).

However, when using Fe³⁺ instead of Fe²⁺ under the same conditions, the COD of the combined mixture decreased gradually as shown in Figure 5(b). The maximum COD reduction achieved at 240 min when using Fe³⁺ and Fe²⁺ was 79% and 88% respectively. These results might indicate that there are still other intermediates (undetected) that were not degraded, as the main pollutants were completely degraded at this irradiation time.

**Iron concentration analysis**

It is very important to follow the iron concentrations (Fe²⁺ and Fe³⁺) during the solar irradiation time. This can effectively help to understand the reaction mechanism of iron and the residual amount at the end of the degradation. Therefore, an accurate evaluation for the Fe²⁺ and Fe³⁺ concentrations during the solar photocatalytic degradation of the combined mixture was conducted as shown in Figure 6. It is obvious from Figure 6(a) that ferrous ions decrease gradually from 7 mg/L initial value to 1.9 mg/L at 240 min to generate *OH radicals (Equation (6)); furthermore, during the solar irradiation time some ferric ions were observed which might be due to the reaction between Fe²⁺ and H₂O₂ (Equation (6)) or the scavenging of *OH radicals by Fe²⁺ (Equation (9)) (Hasan et al. 2012).

Fe²⁺ + OH⁻ → Fe³⁺ + H₂O

However, it is clear from Figure 6(b) that most of the Fe³⁺ ions rapidly converted to Fe²⁺ due to photo-reduction of Fe³⁺ during the solar irradiation (Equations (10) and (11)) (Selvam & Muruganandham Swaminathan 2005).

Fe³⁺ + e⁻ → Fe²⁺

**Figure 5** | COD reduction of the combined mixture of 50 mg/L of both 4-CP and 2,4-DCP (7 mg/L) (0.5 g/L TiO₂, 1,000 mW/cm²) with the optimum values of (a) Fe²⁺ = 7 mg/L and (b) Fe³⁺ = 10 mg/L.

**Figure 6** | Evaluation of iron concentrations during solar photocatalytic degradation of the combined mixture of 50 mg/L of both 4-CP and 2,4-DCP (0.5 g/L TiO₂, 1,000 mW/cm²): (a) Fe²⁺ (Fe₀²⁺ = 7 mg/L); (b) Fe³⁺ (Fe₀³⁺ = 10 mg/L).
Fe$^{3+}$ + H$_2$O $\rightarrow$ $^{*}$OH + Fe$^{2+}$ + H$^+$  

These results indicate that Fe$^{2+}$ ions play a significant role in both solar photocatalytic degradation processes, as Fe$^{3+}$ is quickly reduced to Fe$^{2+}$. However, in terms of the reaction rate there is not much difference between using Fe$^{2+}$ or Fe$^{3+}$ because both lead to the same results. Similar findings have been reported in some studies that used Fe$^{2+}$ and Fe$^{3+}$ ions as a photocatalytic degradation enhancer (Martinez et al. 2007; Ortiz-Gomez et al. 2008).

**CONCLUSION**

The results of the present study indicated that there is no significant difference between using ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) ions as oxidants in the solar photocatalytic degradation of a chlorophenols mixture. However, the results obtained from this work showed that the Fe$^{2+}$ degradation efficiency was slightly higher than that of Fe$^{3+}$. In both cases, three intermediates, namely HQ, Ph, and 4-Cat, were detected during 240 min solar irradiation time and all of them completely degraded before the main compounds. COD measurements showed that there was no complete COD removal, which might be due to other undetected intermediates formed during the degradation. Iron concentration analysis clearly indicated that most of the ferric ions rapidly converted to ferrous as soon as the irradiation time started. This result shows that Fe$^{2+}$ plays an important role in both cases. In addition, small amounts of residual iron were detected, which could be recovered and reuse them again. As an interesting future work and for practical application, other cheap iron sources should be investigated and utilised instead of the costly source of Fe$^{3+}$ and Fe$^{2+}$ to enhance the heterogeneous solar photocatalytic degradation of chlorophenols combined mixture.

**REFERENCES**


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