Photo-Fenton oxidation of pesticides

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Abstract The photo-Fenton process is becoming a practical treatment option for waters contaminated with pesticides and other organic compounds that are poorly biodegradable. This process can potentially be integrated into an existing water treatment process to enhance organic compound removal. It can operate at low concentrations of contaminant and can often completely mineralise the compound or convert it into a less toxic form. The process is most efficient at around pH 2.8; however, it has been found that with the addition of suitable complexing agents for Fe(III), the process can be operated at close to neutral pH. This study used citric acid as a complexing agent, 2,4-dichlorophenol (DCP) as a model contaminant and investigated the extension of the feasible pH range of the process from pH 5 to pH 8. The study involved synthetic solutions and light from a mercury arc lamp, with a bandpass filter used to isolate the emission band at around 360 nm. Low concentrations of DCP (12 µM) and Fe(II) (10 µM) were used to simulate conditions possible in the environment. In this work, no H₂O₂ was added, however, a relatively high concentration of citrate (100 µM) was used. Citrate is itself degraded in the process, and since it is highly biodegradable any excess could be consumed in a subsequent biological treatment process. The extent of degradation of DCP after 2 hours was found to be 91% at pH 5, 73% at pH 6, 74% at pH 7, and 59% at pH 8.

Keywords 2,4-dichlorophenol; advanced oxidation; citric acid; pesticides; photo-Fenton process

Introduction

Many treatment technologies are available for the removal of organic contaminants from water. However most of these processes (for example, adsorption and membrane separation) do not result in destruction of the organic chemical, but merely transfer it into another phase. Most destructive processes have limitations, for example, air stripping followed by incineration is usually precluded due to its high cost (especially for dilute wastes) and concern about atmospheric emissions, while biodegradation is usually slow and many chemicals are resistant to it (Huang et al., 1993). Hence, it is clear that processes which lead to the destruction of the contaminant or its conversion into a less toxic form are required to treat certain types of waters and wastewaters. Advanced oxidation processes show promise as treatment alternatives (Andreozzi et al., 1999). These processes involve the use of chemical oxidants (usually hydrogen peroxide, oxygen or ozone) and frequent catalysts (such as iron or manganese salts or oxides and titanium dioxide) and may require irradiation with ultraviolet or visible light (Huang et al., 1993).

In this paper the treatment of pesticide-contaminated water by a type of photo-Fenton process is discussed. The Fenton process involves the addition of one or more oxidising agents (oxygen or hydrogen peroxide) and a catalyst (a soluble iron salt), while the photo-Fenton process (also called the photo-assisted Fenton process) also involves irradation with sunlight or an artificial light source, which increases the rate of reaction by promoting reactions which reduce Fe(III) to Fe(II), thus completing the catalytic cycle. The reactions produce a range of free radicals, which can react with any organic compounds present, including pesticides. Reactions involving the highly reactive hydroxyl radical (·OH) are the most important, and are characteristic of all advanced oxidation processes. Other processes which may occur during the photo-Fenton process are direct photolysis
especially if ultraviolet light with a wavelength below 300 nm is used) and hydrolysis of the organic compound (especially at very high or low pH).

The photo-Fenton process is less expensive to operate than most other advanced oxidation processes. For example, ozonation requires expensive generators for on-site ozone production, while the titanium dioxide (TiO₂) used for photocatalysis is expensive and difficult to separate from the solution at the end of the treatment (Ormad et al., 2001). The photo-Fenton process requires relatively inexpensive and easily transported chemicals (iron salts and hydrogen peroxide), as well as a light source, which can often be the Sun. Hence, the photo-Fenton process may be suitable for on-site treatment processes.

This oxidation technology may be integrated into an existing water or wastewater treatment process to enhance organic compound removal (see example in Figure 1). The photo-Fenton process may be used to treat the concentrate from a membrane or adsorption process or to pre-treat water that will be subjected to biological treatment. The iron used in the process may also be used to replace some of the ferric iron that is dosed during coagulation (Dolejs et al., 1994). The process also has application in the augmentation of the natural degradation rates of pesticides in retention ponds on farms. Addition of iron salts and/or hydrogen peroxide to relatively shallow sunlit ponds may increase the rate of formation of radicals, which react with the pesticide residues. This assists with water management and recycling because water may not be released into natural waterways while it still contains high levels of pesticides. Application of this type of technology to soils and groundwater that are contaminated by pesticides is also possible.

The photo-Fenton process can mineralise many pesticides completely, converting them to CO₂, H₂O and inorganic ions. However, this would usually involve a large excess of chemicals, often preventing the process from being cost effective, hence only partial degradation usually occurs (Huston and Pignatello, 1999). Partial degradation usually reduces the toxicity and increases the biodegradability of the pesticide residue. However, it is possible for the process to generate products with the same or higher toxicity than the parent compound.

One of the main limitations of the photo-Fenton process is its inefficiency in the pH range of natural waters (pH 5–9). The photo-Fenton process is usually most efficient at
around pH 2.8 (Pignatello, 1992). However, it has been found that addition of certain organic ligands that can complex Fe(III) enable the process to be carried out at higher pH (Balmer and Sulzberger, 1999). This occurs both because complexation limits the loss of Fe(III) by hydroxide precipitation and because organically complexed Fe(III) is more efficiently photolysed than hydrated or inorganically bound Fe(III) (Andreozzi et al., 1999). The higher the concentration of the organic complexant, the more the Fe(III) is complexed. Hence at higher organic complexant concentrations, higher pH can be attained without precipitation of the Fe(III). However, since most organic compounds also react with radicals and other oxidants, increasing the concentration of these organic complexing agents can also lead to a decrease in the rate of oxidation of the pesticide.

The use of organic compounds that can complex Fe(III) is an important modification of the process because the addition of large amounts of acid, followed by base to neutralise the water, makes the process less suitable for most applications as this would usually increase the salinity of the water. The organic ligands that can be used are usually consumed at least partially in the process and are biodegradable. Possible ligands should bind Fe(III) strongly resulting in the formation of a photosensitive complex which undergoes ligand to metal charge transfer (LMCT) induced reduction of the metal centre. Ligands that have been used for this purpose include oxalic and citric acids. Some of these compounds are naturally occurring in water or may be added from natural sources. In this study, citric acid was used. It is a low cost chemical, which can be obtained as a by-product of food processing.

**Chemistry of the photo-Fenton process**

Addition of Fe(II) salts to a water containing hydrogen peroxide leads to the oxidation of the Fe(II) to Fe(III) and the formation of the hydroxyl radical (\(^\cdot\)OH) in a spontaneous reaction which occurs without the influence of light (Reaction 1).

\[
\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \cdot\text{OH} + \text{OH}^- \quad (1)
\]

This reaction is often known as the Fenton reaction, after H.J.H. Fenton who first described the process, but is actually the Haber–Weiss reaction, which is a specific example of the Fenton reaction. The hydroxyl radical can be scavenged by reaction with another Fe(II) species, producing more Fe(III) (Reaction 2).

\[
\cdot\text{OH} + \text{Fe(II)} \rightarrow \text{OH}^- + \text{Fe(III)} \quad (2)
\]

When irradiated with light of suitable wavelength (180–400 nm), i.e. ultraviolet light, Fe(III) can catalyse the formation of hydroxyl radicals (Reaction 3).

\[
\text{Fe(III)} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{Fe(II)} + \text{H}^+ + \cdot\text{OH} \quad (3)
\]

This is called the photo-Fenton reaction and, since it is followed by Reaction 1, iron becomes cycled between the +II and +III oxidation states. The \(^\cdot\)OH production is determined by the availability of light of suitable wavelength and \(\text{H}_2\text{O}_2\). In theory, by combination of Reactions 1 and 3, two moles of \(^\cdot\)OH should be produced per mole of \(\text{H}_2\text{O}_2\) consumed.

If the pH becomes too high, precipitation of Fe(III) salts occurs and Reaction 3 cannot occur. The actual reaction pathway is more complicated that that shown above due to the large number of ionic species and radicals that may form in the solution. For solutions at pH > 3, Gallard et al. (1998) have questioned the existence of \(^\cdot\)OH itself. For the pH range 5–8, Hug et al. (2001) found that photolysis of dissolved organic Fe(III) species or surface...
Fe(III) complexes provide the most efficient pathways in the Fe(III)-mediated oxidation of pollutants. Citrate is a strong complexant of Fe(III) and was found to greatly improve photoproduction of Fe(II) in the pH range 5–8.

**Degradation of 2,4-dichlorophenol**

An investigation has been carried out into the photo-Fenton degradation of 2,4-dichlorophenol (DCP). DCP was used as a model compound because it is highly toxic and is not readily biodegradable. It is also a degradation product of some chlorinated herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D), as well as being an intermediate in the industrial synthesis of these herbicides (Ormad et al., 2001). It mineralises relatively easily under photo-Fenton conditions, but does not degrade significantly by photolysis at wavelengths above 300 nm (in the absence of dissolved iron). It can be analysed without derivatisation by HPLC with ultraviolet detection.

Most photo-Fenton studies on DCP have been carried out in the pH range 2–3 (Nogueira and Guimaraes, 2000; Benitez et al., 2001; Ormad et al., 2001). The investigation described here was carried out in the pH range 5–8 and, as such, significant differences between the results reported here and those of other workers are to be expected.

DCP does not appear to form significant quantities of any one organic degradation product, and its degradation pathway is not clear. Ormad et al. (2001) carried out experiments at high DCP concentration (2.8 mM) at pH 3. They found that less than 10% of the total organic carbon existed as degradation products at any time during the process. Over 20 degradation products were found, consisting mainly of aromatic and aliphatic carboxylic acids, most of which had a higher number of carbons than DCP itself, suggesting that polymerisation took place. Benzoic acid was the major product identified.

Brillas et al. (2000) carried out experiments on 2,4-D at pH 3 using electrogenerated \( \text{H}_2\text{O}_2 \) and Fe(II). In their proposed reaction pathway, DCP was formed by reaction of the hydroxyl radical with 2,4-D. DCP then reacted further with the hydroxyl radical to produce 4,6-dichlororesorcinol and chlorohydroquinone (which reacted further to produce chlorobenzoquinone). Subsequent ring breaking and dechlorination was proposed leading to the formation of small aliphatic carboxylic acids such as maleic, fumaric and oxalic acids, followed by complete mineralisation of the organic compounds.

**Experimental**

Experiments were performed using the set-up shown in Figure 2. The solution to be treated (1 L) was placed in the glass water-jacketed reactor, and was irradiated through a quartz window using an Oriel 200 W Hg arc lamp (set to 160 W). The reactor was of inner diameter 94 mm and the quartz window was attached to a side chamber of length 27 mm, giving a total light path length of 121 mm. A band pass filter with maximum transmission at 360 nm was used to isolate a major peak in the spectrum of the mercury lamp. The reactor contents were stirred using a magnetic stirrer bar. To control the temperature of the reactor contents, a thermostatic water-bath was used to circulate water through the reactor’s water-jacket (set at 25°C). The pH of the solution was monitored and controlled by manual addition of 0.1 M KOH when required.

Solutions were prepared using ultrapure (Milli-Q) water and analytical reagent grade chemicals. Most experiments were carried out using the following standard concentrations of chemicals, listed in the order in which they were added: 12 \( \mu \)M DCP, 1 mM KNO\(_3\) (used to maintain the ionic strength of the solution at an approximately constant value), 100 \( \mu \)M citrate (from a 10 mM citric acid solution), and 10 \( \mu \)M Fe(II) (from a 1 mM Fe(NH\(_4\))\(_2\)(SO\(_4\))\(_2\).6H\(_2\)O solution in 1 mM H\(_2\)SO\(_4\), pH 3). After addition of DCP and KNO\(_3\), the solution was stirred in the dark, open to the atmosphere for about 30 minutes to allow...
thermal equilibration and to ensure equilibration with atmospheric oxygen. The pH was
adjusted by addition of 0.1 M KOH before and after addition of the Fe(II). The reaction was
monitored over a period of 2 hours or more, during which time significant degradation
occurred in most cases.

Analysis of DCP and its degradation products was carried out by high-pressure liquid
chromatography (HPLC; Hewlett-Packard, 1100 series) equipped with diode array detec-
tor, using ChemStation Software. Absorbance was measured at 198 nm and the identifica-
tion spectrum was recorded from 190–360 nm. Analysis of DCP itself was performed using
isocratic elution at 1 mL/min using a C18 column (Alltech Econosphere, 5 µm, 150 mm
length, 4.6 mm diameter). The eluant consisted of 30% acetonitrile, 70% buffer solution
(5 mM KH₂PO₄, 0.1% acetic acid, at pH 4.2). The end time was 3 minutes, and DCP was
eluted at 2.6 minutes. For a sample injection of 20 µL, the detection limit for DCP was
0.1 µM. A gradient elution method was also used to separate the degradation products of
DCP. Methanol (100 µL) was added to each sample (1 mL) to scavenge excess radicals and
hence stop the reaction. Samples were analysed within 1 hour of sampling.

The Fe(II) concentration was determined using a ferrozine method. The sample (4 mL)
was added to the ferrozine reagent (0.4 mL) containing 0.01 M ferrozine [or 3-(2-Pyridyl)5,6-diphenyl-1,2,4-triazine-p,p-disulfonic acid, monosodium salt hydrate] and 0.1 M MES
[or 2-(N-morpholino)ethanesulphonic acid, hemisodium salt] at pH 6. The absorbance of
the mixture at 562 nm was then read after 1 minute using a 10 mm path length cuvette using
a Hach DR2000 spectrophotometer. The conversion of Fe(II) to Fe(III) is rapid when the
sample is removed from the reactor, hence the sample was added to a tube containing the
ferrozine reagent immediately after drawing it using an automatic pipette. However errors
in Fe(II) determination are possible, particularly at high pH.

Results and discussion
An initial experiment at a high concentration of DCP (100 µM) was carried out to deter-
mine whether any organic degradation products were formed (these would be difficult to
detect at lower initial concentration). At least four degradation products with similar ultra-
violet spectra to DCP were detected (see Figure 3 and note the use of two concentration
scales). If the detector response factors for each of these compounds were assumed to be the
same as for DCP, then these degradation products would all exist in concentrations below
10% of the initial DCP concentration. These compounds are believed to be chlorinated aro-
matic compounds of the types found by Brillas et al. (2000). Other organic degradation
products are also expected to be present but would not be detected using the HPLC method used here.

The effect of pH on the rate of photo-Fenton degradation of DCP was then investigated using the standard concentrations (see Figure 4). Analysis of the degradation products was not attempted. As expected, it was found that the rate of degradation of DCP decreased with increasing pH, except that at pH 6 some variation in curve shape occurred. Significant degradation of DCP still occurred at neutral and slightly basic pH, hence the process is expected to be effective in natural waters, provided sufficient citrate was present. It was found that the degradation of DCP under these conditions after 2 hours decreased from 91% at pH 5 to 73% at pH 6, 74% at pH 7 and 59% at pH 8. The pH of the system tended to decrease as the reaction proceeded, especially at higher pH (however, it increased slightly for the experiment at pH 6, possibly leading to the difference in curve shape for this experiment). Addition of KOH was used to maintain constant pH when required but the extent of the change in acidity or alkalinity of the solution was not determined.

The concentration of Fe(II) varied during these experiments (see Figure 5). The Fe(II) concentration tended to increase at the beginning of the experiment (as some of the Fe(II) that was oxidised before the lamp was switched on was reduced again), and then decrease again towards the end of the experiment (probably due to the fact that as the citrate was consumed, the Fe$^{III}$CitOH$^-$ complex decreased in concentration, leading to a decreased efficiency of the photolysis).

**Conclusions**

Relatively low concentrations of DCP (12 or 100 $\mu$M) can be degraded in low Fe(II)
concentration water (10 µM) in the presence of 100 µM citric acid and ultraviolet light of wavelength around 360 nm. Although no H$_2$O$_2$ was added to the system, this would be produced during the reactions. Although increasing the pH above pH 5 led to significant losses in the efficiency of degradation of the DCP, degradation still occurred at a feasible rate at the higher pHs. It remains to be established whether complete degradation of DCP could be achieved at high pH, because loss of dissolved Fe from the system as Fe(III) precipitates is expected.

Measurement of citrate and hydrogen peroxide concentrations were not carried out but are required for a complete kinetic analysis of the system. Future experiments should also involve the determination of the light intensity and calculation of the quantum efficiency of the process.

The results of this investigation will be used towards producing a kinetic model of this system, with the objective of understanding the mechanism of the photo-Fenton process, as well as finding suitable conditions for process operation. The model could then be extended to processes involving other organic compounds and pesticides.

**Acknowledgements**

This work was partially supported by the CRC for Waste Management and Pollution Control Limited, a centre established and supported under the Australian Government’s Co-operative Research Centres Program.

**References**


