A comparison between different advanced oxidation processes for the remediation of PCP contaminated wastewaters

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Abstract

In this paper a comparison between different advanced oxidation processes (AOP), for the remediation of a wastewater contaminated with 100 mg/l of pentachlorophenol (PCP), is proposed. The AOP chosen were: Fenton or Fenton-like reactions in which the soluble iron catalyst salt was added as Fe(II) or Fe(III) or a mixture of Fe(II) and Fe(III), and ozonation. In the latter case the effects of the presence of a solid iron oxide (hematite) were also evaluated. For the Fenton's reactions, the investigated parameters were: pH (from pH=1.5 to pH=5), reaction time, H_2O_2/PCP ratio (from 5/1 to 20/1), Fe/H_2O_2 ratio (from 0 to 2/1) and the effect of a H_2O_2 stabilizer: KH_2PO_4. The highest TOC removal (75%) was reached, using stabilized H_2O_2 and Fe(II), when H_2O_2/PCP=5/1 and Fe/H_2O_2=1/1; in this case, dechlorination was 96% and KH_2PO_4 increased H_2O_2 lifetime significantly. Fe(III) or the mixture of Fe(II) and Fe(III), proved to be more efficient than Fe(II) when H_2O_2/PCP<15/1 and Fe/H_2O_2<1/1. For ozonation the effects of pH and of the ratio between airflow and the solution's volume, were investigated. The highest efficiencies (TOC removal=35%, Cl^- release=80%) were reached when O_3=0.24 mg/l at pH=11; however diminishing the volume of treated solution, 47% TOC removal and stoichiometric Cl^- release were observed. The addition of hematite resulted in a slight increase of TOC removal and Cl^- release. By comparing the experimental results, among the tested AOP systems, Fenton's reaction proved to be the most effective for PCP remediation.

Keywords: Fenton, Fenton-like, PCP, AOP, ozone, iron oxide, hydrogen peroxide.

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1 Introduction

Advanced oxidation processes (AOP) can be considered as possible pre-treatment steps to either achieve complete mineralization of organic contaminants to CO_2 and H_2O, or transform them into more biodegradable intermediates. In effect, the toxicity of the pollutants can inhibit successive biological steps. One of the most commonly used oxidizing agents is hydrogen peroxide (H_2O_2), which acts as a source of free radicals when a metal catalyst is added. The effectiveness of H_2O_2 when in contact with a transition metal catalyst added as a soluble salt or as a solid, in Fenton or Fenton-like reactions, has been proven in the treatment of hazardous compounds in the aqueous phase [1–3]. In particular, when $FeSO_4$ is added to a H_2O_2 solution in Fenton systems, reactions that lead to the formation of hydroxyl radical ($OH^\bullet$), and numerous other competing reactions occur. Among these reactions are the production of hydroperoxyl radicals, the cycling of Fe(III) to Fe(II) and the quenching of $OH^\bullet$ by Fe(II) and H_2O_2 [4, 5].

Ozonation has been widely used for drinking water disinfection, and thanks to the high oxidation power of ozone, it can achieve high efficiencies avoiding the addition of other compounds. The degradation of organic compounds may proceed via direct reaction with O_3 or via free radicals formation such as $OH^\bullet$, or via the both mechanisms concurrently [6]. The pH of the solution strongly influences ozone decomposition [7]. In particular at $pH<4$, dissolved O_3 reacts directly with the substrate, while at $pH>9$ the $OH^\bullet$ formation, which is catalyzed by OH^- prevails, and at $4<pH<9$ both the mechanisms are present [8]. Ozone's oxidation efficiency may also be enhanced through the addition of transition metals cations [7, 8]. In this work air was utilized for ozone production thus limiting the cost of oxygen supply, although introducing CO_2.

This paper presents a comparison between different AOP for the treatment of a wastewater contaminated with 100 mg/l of pentachlorophenol (PCP). PCP is a preservative agent for woods, vegetable fibres, leathers and a pesticide. It is listed by the US EPA as a priority pollutant because it is toxic, hardly biodegradable and highly persistent in the environment. It was therefore chosen as a model compound because it is very difficult to oxidize and the available literature concerning water treatments generally focuses on other chlorophenols or really dissimilar concentrations, making it very difficult to compare the different treatments.

2 Experimental

PCP (99% pure) was obtained from Aldrich. The contaminated solution was prepared by dissolving 100 mg of PCP in 1l of distilled water and alkalinising to pH=11 with NaOH to help PCP dissolution. H_2O_2 (30% w/w unstabilized) was from Merck, Fe(II) and Fe(III) sulphate ACS, were from Carlo Erba Reagenti. Total organic carbon (TOC) was monitored using a ShimadzuTOC-5000 analyser after alkalinising the samples with NaOH to ensure complete dissolution of residual PCP, Cl^- release was determined by ionic chromatography using a DionexDX120 ion chromatograph equipped with a IONPAC AS 12A column (20 cm, 4 mm i.d.) and guard column (5cm, 4mm i.d.).

Fenton's reactions were conducted using Fe(II), Fe(III) or a mixture 50% w/w of the two salts, on 50 ml samples in 100 ml beakers covered with parafilm. The Fe catalyst was added first, and the pH was adjusted with H_2SO_4. H_2O_2 was then added to the solution and the samples were stirred at 750 rpm with a magnetic stirrer. The pH was manually monitored and kept constant. A first series of tests was performed to investigate pH, using Fe(II) as a catalyst and the following reagents' ratios: H_2O_2/PCP=5/1 and Fe/H_2O_2=1/1. At the optimised pH value, other experiments were performed using H_2O_2/PCP=5/1, 10/1 and 15/1, for different Fe/H_2O_2 ratios (1/10, 1/5, 1/1, 2/1). A further series of tests was realized to evaluate the influence of the addition of 16 g/l KH_2PO_4 to the 30% stock H_2O_2 solution, using Fe(II) as a catalyst. Initial tests were performed to investigate the optimal pH, for the following reagents' ratios: H_2O_2/PCP=5/1 and Fe/H_2O_2=1/1. At the optimised pH value, other experiments were performed using H_2O_2/PCP=5/1, 10/1 and 15/1, for different Fe/H_2O_2 ratios (1/3, 1/2, 1/1, 2/1). Dissolved oxygen was monitored with an Aqualytic OX 22 O_2-meter. Hydrogen peroxide was determined by a colorimetric method using a Merk RQ-flex reflectometer.

Ozonation experiments were conducted on 1l samples in a covered glass reactor. Mixing was provided by a magnetic stirring bar. Ozone was produced using an ozone generator INO3MAX-04 functioning with air, and was bubbled in the solution trough a porous media. The gas flow was 3.5l per minute and the O_3 concentration in the gas was 0.24 mg/l. The pH of the solution was manually controlled, and kept constant or not. The investigated pH values were pH=11, 9 and 7. Hematite when added, weighed 0.5g. Other experiments were conducted on 75 ml of solution with the same flux and ozone concentration.

3 Results and discussion

3.1 Fenton's reaction

3.1.1 Influence of pH

The optimal pH range for Fenton's reaction is between pH=2 and pH=4. In effect, at low pH, the solubility of the Fe(II) increases and H_2O_2 decomposition decreases [9]. Results presented in Figure 1. indicated pH=2.5 as the best operating pH for TOC removal and Cl^- release. The reduced efficiency observed at pH<2.5 was probably due to the concurrent effects of: the quenching of $OH^\bullet$ by the excess of H^+, the presence of PCP as an insoluble particulate [10, 11], and the transformation of H_2O_2 in the $H_3O_2^+$ ion, which is electrophillic and therefore does not react well with Fe(II) [12]. At higher pH, Fe(II) may be present in a colloidal form less reactive with H_2O_2 and in addition, the oxidation potential of $OH^\bullet$ decreases [12]. In experiments whose pH was not controlled, we observed a decrease of its value, from pH=7 to pH=3 and from pH=2.5 to pH=1.9, which could be associated with the formation of acid species that are usual in oxidation treatments [8, 13, 14].

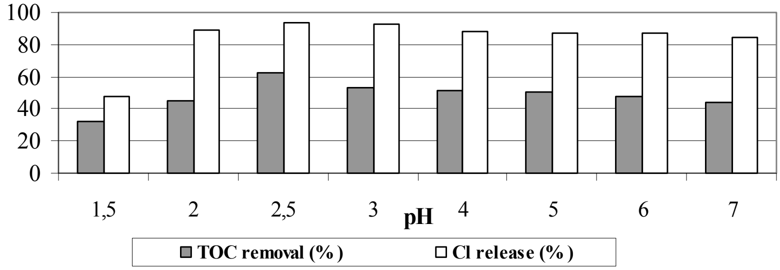

Figure 1: Effect of pH variation on TOC removal and chloride release.

3.1.2 Catalyst evaluation

Once pH value was fixed at pH=2.5, the three types of iron catalyst were compared in terms of TOC removal and chloride release (Figure 2).

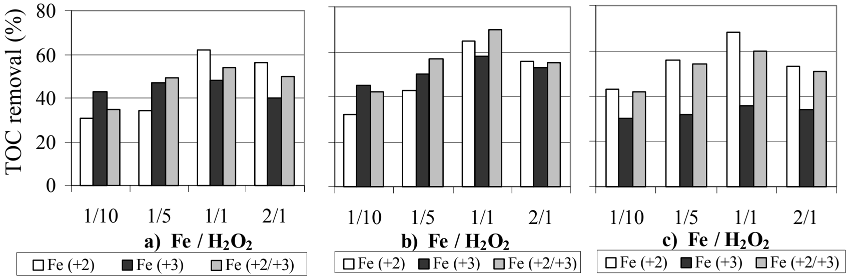

Figure 2: TOC removal: a) H_2O_2/PCP=5/1, b) H_2O_2/PCP=10/1, c) H_2O_2/PCP=15/1.

When no iron was added, no TOC removal was observed. When H_2O_2/PCP<15/1 and Fe/H_2O_2<1/1, Fe(III) or the mixture of the two irons proved to be more efficient than Fe(II). Increasing the H_2O_2/PCP ratio up to 15/1 augmented TOC removal when Fe(II) was used. Further experiments, conducted with H_2O_2/PCP=20/1, showed indeed a significant efficiency decrease (data not shown). This could be attributed to the quenching of radical species operated by H_2O_2. An increase in the Fe/H_2O_2 ratio up to 1/1, showed similar behaviour for the three Fe species: the maximum removal efficiency was reached when Fe/H_2O_2=1/1, and a further addition of iron (Fe/H_2O_2=2/1) resulted inefficient probably because undesired reactions, between Fe(II) and the radical species, became predominant. When H_2O_2/PCP=15/1, the dosage of Fe(III) appeared to be irrelevant leading to quasi-similar TOC removals and, in general, it was not really affected by the variation of experimental conditions. The performance of the mixture of Fe(II) and Fe(III) was more comparable to the one of Fe(II).

To explain these results some considerations must be made. First Fe(III) is less soluble than Fe(II) and possibly takes part mostly as a precipitate to the reaction, explaining the little differences between the removal efficiencies. Then, PCP is not completely soluble at acidic pH and, therefore, takes also part as a particulate to the reaction. Problems related to the difficulties in the radical attack on PCP particulates have been discussed [10]. Partitioning might segregate PCP from the $OH^{\bullet}$ that is presumably generated in the aqueous phase [15]. Since PCP degradation products are more soluble than the parent compound, they could be oxidized more easily as soon as they were formed [16]. In addition, the soluble PCP undergoes acid-base equilibrium with pK_a=4.7 [6]. At pH=2.5 it is mostly present in the undissociated form and therefore, it is less easily attacked by the $OH^{\bullet}$ radical. $OH^{\bullet}$ is a strong electrophilic compound, which reacts rapidly with alkenes and aromatic compounds in a non-selective way. Some authors [17] evidenced, as possible reaction pathway of PCP with $OH^{\bullet}$, an ipso-addition followed by an electron transfer reaction. However steric hindrance must be taken into account and, as the 5 electron withdrawing chlorine atoms decrease the electron density of the aromatic ring and deactivate it [6, 16], the radical attack could also be of nucleophilic nature. A study [18], has evidenced the reactivity of the superoxide radical anion $O_2^{\bullet -}$, which is a strong nucleophile. The simultaneous presence of $OH^{\bullet}$, $O_2^{\bullet -}$,$HO_2^{\bullet}$ and HO_2^- could then provide a pool of oxidants of enhanced reactivity capable to partially mineralize PCP and to achieve nearly complete dechlorination.

Figure 3 presents the results of the Cl^- release analyses. When no iron was added, little Cl^- release was observed (max 10% when H_2O_2/PCP=15/1). Between the Cl^- release and the previously illustrated TOC removal data, a considerable difference exists. In fact, almost independently from the Fe/H_2O_2 ratio and slightly from the H_2O_2/PCP ratio, nearly complete dechlorinations were always achieved. A trend similar to the one of TOC was observed only when Fe(III) was used and H_2O_2/PCP=15/1.

The maximum release efficiency was reached when Fe/H_2O_2=1/1 and a further addition of Fe (Fe/H_2O_2=2/1) resulted inefficient, as previously observed.

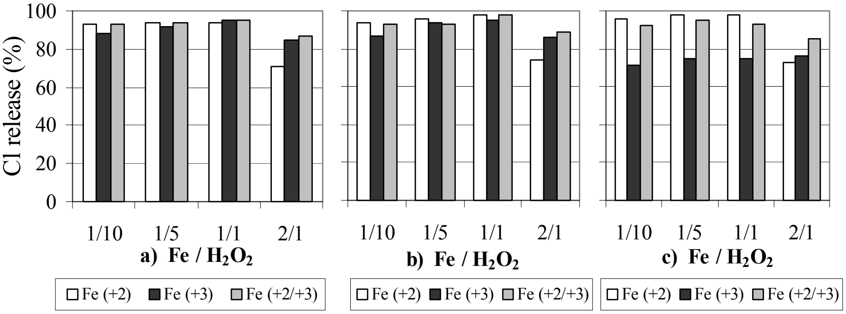

Figure 3: Cl release: a) H_2O_2/PCP=5/1, b) H_2O_2/PCP=10/1, c) H_2O_2/PCP=15/1.

Considering that the removal of six atoms of organic C must be accompanied by removal of five atoms of Cl, we calculated the MCR (Minimum Chloride Release) [19]. When the Cl^- release of the treated solution is approaching MCR value, we can assume that a certain selectivity of the reaction did occur. The comparison between the Cl^- release and the MCR value, showed a decrease of their difference with increasing Fe/H_2O_2 ratios, when Fe(II) or Fe(II)/Fe(III) were used, indicating a more selective reaction pathway. A little decrease was also observed with increasing H_2O_2/PCP ratios. The results obtained using Fe(III) were only a little affected by the variation of these parameters, as previously discussed. It can be concluded that for low Fe dosages, the reactions were slightly selective while, for high dosages, reactions proved to be highly selective especially in the case of Fe(II). The abundance of Fe(II) in effect, may enhance reactions that end with the formation of reactive species other than $OH^{\bullet}$.

3.1.3 Influence of KH_2PO_4

Results of tests performed to evaluate the influence of pH, are presented in Figure 4a). They indicated pH=2.5 as the best operating pH for TOC removal and Cl^- release, with marked differences between the reactions conducted with and without stabilizer (compare with Figure 1.)

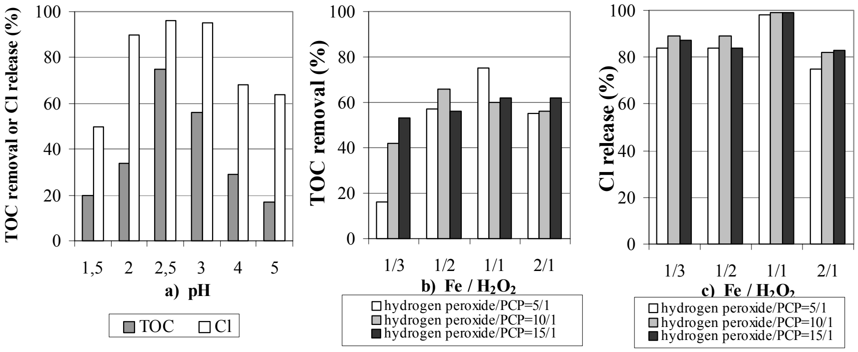

Figure 4: a) pH variation H_2O_2 /PCP=5/1 b) TOC removal %, c) Cl release %.

The observed difference may be explained by the combined effects of the lower solubility of Fe(II) and of this decreased availability. The KH_2PO_4 stabilizer lowers dissolved metal concentrations through either precipitation reactions or, in the presence of excess phosphate, conversion to relatively stable complexes [9]. As a result Fe(II) activity as Fenton catalyst decreases as it becomes less reactive with H_2O_2. Phosphate may also function as a radical scavenger quenching $OH^{\bullet}$ and finishing the chain decomposition reactions [9]. The results, in terms of TOC removal and Cl^- release, of experiments conducted at pH=2.5 are presented in Figure 4b) and 4c). The best TOC removal was achieved when H_2O_2/PCP=5/1 and Fe/H_2O_2=1/1. A comparison between data obtained in the same conditions without stabilizer, showed that KH_2PO_4 enhanced to some extent the TOC removal efficiency only when H_2O_2/PCP=5/1 and Fe/H_2O_2=1/1. In this particular condition, also Cl^- release was a little enhanced. For higher Fe concentrations, although the presence of KH_2PO_4 did not produce any modification in TOC removal, it augmented the Cl release. In addition, for H_2O_2/PCP=5/1 and Fe/H_2O_2>1/3, the stabilizer lowered the differences between the Cl^- release and the MRC value, indicating a different reaction pathway.

Analyses of H_2O_2 and dissolved oxygen concentrations, in the presence or not of the stabilizer when H_2O_2/PCP=5/1 and Fe/H_2O_2=1/1, showed lower H_2O_2 depletion rates and a lower oxygen production when KH_2PO_4 was used (data not shown). In Fenton's systems, oxygen is generated by undesired quenching reactions between H_2O_2 and the radical species, or between the radical species themselves [8]. In this case, the stabilizer proved to be effective in lowering H_2O_2 consumption and in increasing TOC removal.

3.2 Ozonation experiments

These experiments were conducted fluxing ozonized air. The pH value was consequently expected to decrease because of the introduction of CO_2 in the reaction vessel, and this was confirmed by our experimental data in which we observed a decrease from pH=9 down to pH=3. The formation of acid by-products [8, 13] was proven by the decrease of pH measured during the reaction of PCP solutions that was greater than the one of control experiments conducted without any substrate. In addition, during the experiments, a strong solution's coloration, which disappeared by the end of reaction, was observed. The colouration that was associated with the presence of quinone and ketone compounds [6], depended upon pH value and was pink at controlled pH=11 and 9, while at pH=7 and at initial pH=11 and 9, it was yellow.

As prevalent reaction pathway, Weavers et al. [20] reported an $OH^\bullet$ addition at the ortho and para position, while Hong and Zeng [6], the nucleophilic attack of dissolved ozone with PCP, which could be followed by a subsequent radical degradation of the reaction intermediates, and would be independent from the solution's pH.

3.2.1 Influence of pH control

Results of tests performed to evaluate the influence of the control of the pH value, are presented in Figure 5.

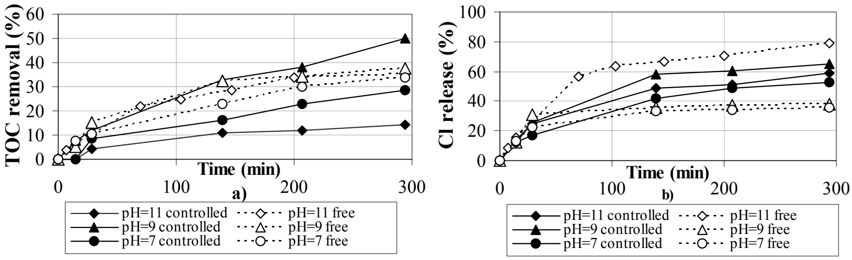

Figure 5: a) TOC removal (%), b) Cl release (%).

The highest TOC removal (50%) was achieved at the fixed pH=9 value, while when pH=11, the pH control caused a decrease of the removal efficiency. The experiments conducted without any pH adjustment, generally reached higher efficiencies. To explain the observed data, the presence of HCO_3^- and CO_3^{2-} ions in the solution must be considered. These ions are known to be $OH^\bullet$

scavengers [21] and were produced by the fluxing of CO_2 into the alkaline solution. The results obtained at pH=9 were consistent with other results [8] where the rate of oxidation of chlorophenol at pH=9 was related to the high rate of reaction between the phenolate ion and the dissolved ozone. At neutral or alkaline pHs, PCP was expected to exist in the deprotonated form that could react more easily with the oxidant species. The highest Cl^- release was observed at non-controlled pH=11, but generally the pH-controlled experiments, guaranteed greater dechlorinations. This could be explained by the higher $OH^\bullet$ formation rate in alkaline conditions. In effect, although PCP seems to react preferentially with O_3, its degradation products could be degraded by free radicals and the impact of different reaction's pH could become relevant [6].

Results of tests conducted fluxing the same gas in a littler reactor without hematite addition indicated, for all pHs after 90 min of reaction, higher TOC removals and Cl^- release (data not shown). Stoichiometric dechlorination was obtained at pH=11.

3.2.2 Influence of hematite

To increase TOC removal and Cl^- release, hematite was added as solid catalyst. This Fe oxide proved to be efficient in catalyzing the Fenton-like degradation of PCP [19]. Results presented in Figure 6 evidenced an increase of approx 15% TOC removal for the reactions conducted without pH control and, apart from the one at pH=9, also for the pH controlled ones.

Also the Cl^- release was increased, up to 74% at pH=11, and the same trend than in the absence of hematite was observed. The activity of metal oxides is mainly based on the catalytic decomposition of O_3 and the enhanced generation of $OH^\bullet$. These can be affected by changes in the catalyst surface properties due to different solution's pH. The proposed mechanism generally assumes that ozone is adsorbed on the catalyst's surface and subsequently leads to surface bond oxygen radicals or to $OH^\bullet$ [7]. In our case, owing to the low concentration of solid hematite used (0.5 g/l), we can assume that the heterogeneous catalysis occurred together with the homogeneous one.

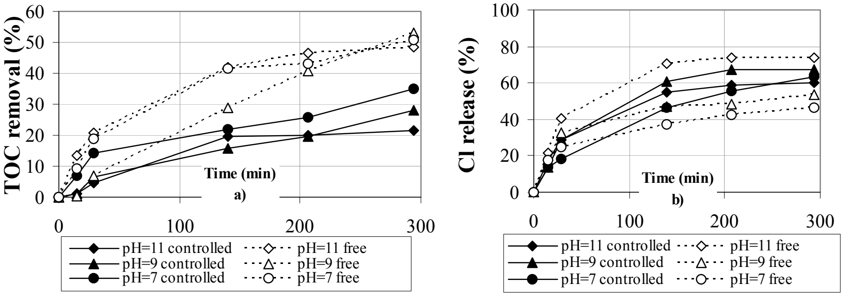

Figure 6: a) TOC removal (%), b) Cl release (%).

4 Conclusions

In this paper, a comparison between the Fenton's reaction catalyzed with Fe(II), Fe(III) or a mixture 50%(w/w) of the two species and ozonation was described.

Results indicated Fe (II) as the most efficient catalyst when high doses of hydrogen peroxide were employed. The highest TOC removal (75%) was reached using stabilized H_2O_2 when H_2O_2/PCP=5/1 and Fe/H_2O_2=1/1; dechlorination was 98% and KH_2PO_4 increased H_2O_2 lifetime significantly. Without stabilizer TOC removal reached 68% and Cl release 98% when H_2O_2/PCP=15/1 and Fe/H_2O_2=1/1.

Ozonation experiments resulted in lower TOC removals but in stoichiometric dechlorination at pH=11 in the littler reactor. These results demonstrate the difficulties in utilizing air as gas feed for the ozonator instead of oxygen, due to the excessive increase of the concentration of powerful hydroxyl radical scavengers. Hematite proved to increase the reaction's yield and seems promising due to its low cost.

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