

Use of EAF dust as heterogeneous catalyst in Fenton oxidation of PCP contaminated wastewaters

R. Mecozzi, L. Di Palma*, D. Pilone, L. Cerboni

*Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia,
Università di Roma "La Sapienza", via Eudossiana 18, 00184 Rome, Italy*

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Abstract

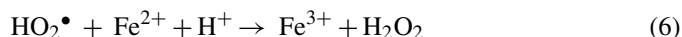
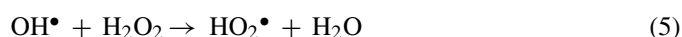
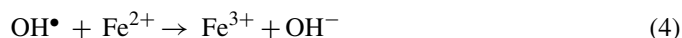
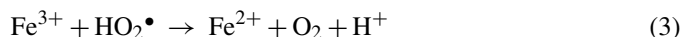
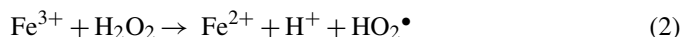
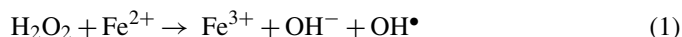
In this study, chemical oxidation tests using H_2O_2 were performed on a solution contaminated with 100 mg l^{-1} of pentachlorophenol (PCP). The effectiveness of electric arc furnace dust and hematite as heterogeneous catalysts was evaluated. Reactions were conducted at pH 2 for 24 h. Either H_2O_2 stabilized with KH_2PO_4 or un-stabilized H_2O_2 was used. Total organic carbon (T.O.C.) removal and chloride release from PCP molecule were monitored. Results showed that the maximum removal yields for electric arc furnace (EAF) dust (49.2% T.O.C., 56.7% Cl) were achieved when H_2O_2 :PCP ratio was 10:1 and $\text{Fe}:\text{H}_2\text{O}_2 = 1:5$ for un-stabilized H_2O_2 and when H_2O_2 :PCP = 10:1 and $\text{Fe}:\text{H}_2\text{O}_2 = 1:1$ for stabilized H_2O_2 (48% T.O.C., 60.6% Cl). The maximum yield using hematite (45.2% T.O.C., 55.2% Cl) was obtained when H_2O_2 :PCP ratio was 10:1 and $\text{Fe}:\text{H}_2\text{O}_2$ was 1:2. When EAF dust was used and $\text{Fe}:\text{H}_2\text{O}_2 > 1:5$, Cl release was higher than the one expected from T.O.C. removal.
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1. Introduction

The increasing amounts of toxic and recalcitrant compounds in several industrial wastewaters focus the attention on chemical oxidation as initial step to achieve their complete treatment. Chemical oxidation offers the advantage of being insensitive to the toxicity of the pollutants and the possibility of fast treatments. In effect it can either achieve a complete mineralization of the organic contaminants to CO_2 and H_2O or transform them into less harmful or more biodegradable intermediates. Chemical oxidation becomes then a pre-treatment step that can be followed, if necessary, by a successive biological step [1,2]. 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 [3–8]. In particular, when ferrous sulphate is added to a H_2O_2 solu-

tion in Fenton systems, reactions that lead to the formation of hydroxyl radical (OH^\bullet) and numerous other competing reactions occur. Among these reactions, the production of hydroperoxyl radicals, the cycling of iron(III) to iron(II) and the quenching of OH^\bullet by iron(II) and H_2O_2 , occur, as summarised below [9].



In addition the reaction of OH^\bullet with organic substrates can lead to the formation of organic radicals, which might also be oxidised by Fe^{3+} , thus regenerating Fe^{2+} [5].

Homogeneous systems generally offer effective contaminant removal at high rates [10,11]. The metal catalyst added as soluble salt however, dissolves in water and cannot be retained in

* Corresponding author. Tel.: +39 06 44585571.

E-mail address: luca.di.palma@ingchim.ing.uniroma1.it (L. Di Palma).

the process. This adds other pollutants to the water, which can be treated in a subsequent precipitation stage. Heterogeneous catalysis offers significant advantages in separation since in this case, the catalyst can be easily recovered by sedimentation or filtration and further used.

Different types of solids can be used as heterogeneous catalysts. Among them iron powder and different iron oxides have been tested [4,6,7,12]. Solid catalysts can also be constituted by iron dispersed on different supports such as alumina [13], zeolite [14,15], cation exchange resins [16] and clay [17].

The catalytic activity can be related to the activation of hydrogen peroxide by iron ions leached from the solid material and acting as homogeneous catalysts [1,4]. The main advantage in comparison with homogeneous catalysis is the slow release of metal ions that limits undesired reactions (3), (4) and (6). Other authors [15,18] associated the catalytic activity to the combined and pH dependent effects of metal leaching and direct heterogeneous catalysis. In the latter case, the initiation step involves H_2O_2 adsorbed on the iron oxide surface [19].

Electric arc furnace (EAF) dusts are an industrial by-product, which could be an interesting heterogeneous catalyst. These dusts are recovered in gas cleaning units during the production of steel in electric arc furnaces, which are fed with scrap metal. EAF dust composition can vary greatly depending on the scrap metal composition, furnace additives, operating conditions, degree of recycling of dusts in the steelmaking process and on the type of steel produced. The high temperature of the EAF process results in the volatilization of iron and zinc, which is predominantly used as a corrosion inhibiting coating on steel products.

Over the last decade, the amount of heavy metals in EAF dusts has increased due to large increase in the quantity of automotive scrap. As much as 10–20 kg of EAF dust are generated per ton of steel produced. The increasing dust dumping costs and liabilities constitute a driving force for the adoption of new treatments and disposal methods. Hydrometallurgical, pyrometallurgical or hybrid processes can be used for the recovery of valuable metals [20,21], however, stabilization followed by landfilling is currently the common practice [22,23].

To test the effectiveness of this particular catalyst, pentachlorophenol (PCP) was chosen as a model compound. PCP is a preservative agent for woods and leathers and is also a pesticide. It is listed by the U.S. Environmental Protection Agency as a priority pollutant because it is toxic, hardly biodegradable and highly persistent in the environment [1,24]. The treatment of PCP in contaminated soils and sands is discussed in literature [12,16,25,26]. However, the available literature concerning water treatments of chlorophenols either focuses on chlorophenols other than PCP or different oxidation processes [4,10,27–32].

The main purpose of this study is to assess EAF dust efficiency as a heterogeneous catalyst in the Fenton remediation of PCP contaminated water. In fact, using as a catalyst what is commonly considered as a waste, would be of economic interest considering the high costs required for its disposal. In addition the efficiency of EAF dust is compared to the one of hematite a common iron oxide.

2. Materials and methods

2.1. Solid characterisation

Pelletized EAF dust was supplied by an Italian steelmaking company producing carbon steel and pure hematite was provided by the faculty of Geology of the University of Rome “La Sapienza”.

Both EAF dust and hematite were characterized by means of SEM/EDS analysis using a S-2500 Hitachi microscope equipped with a Thermo Noran System Six apparatus. The sample's powder particles were separated using ultrasounds and metallised to allow SEM observation.

The two solids were initially crushed and sieved. The collected fraction was $0.5 < d < 1$ mm.

The pH of the two solids was determined using a Crison GLP21 pH-meter after 2 h stirring at 175 rpm and 15 min sedimentation of a mixture of 100 g of solid in 250 ml of distilled water [33].

The chemical oxygen demand (C.O.D.) was determined by back-titration with ferrous ammonium sulphate of residual potassium dichromate [33].

Leaching experiments were conducted with bi-distilled water or with a HNO_3 1 M solution. Two grams of solid were placed in 30 ml centrifuge glass tubes with Teflon caps. Twenty milliliter of solution were added and the tubes were shaken, then centrifuged in an ALC 4929 centrifuge for 10 min at 4000 rpm. The supernatant was analysed by atomic adsorption for Pb, Mn, Fe and Zn while Cl^- and SO_4^{2-} were determined by ionic chromatography on a Dionex DX 120 ion chromatograph equipped with a IONPAC AS12A column (200 mm, 4 mm i.d.) and guard column (50 mm, 4 mm i.d.) (only when bi-distilled water was used). The supernatant was then replaced with unused solution. The chosen solid-solution contact times were: 4, 24, 48 and 72 h.

All reagents were ACS grade and supplied by Carlo Erba Reagents, Milano, Italy. The SEM micrograph reported in Fig. 1 shows that EAF dust particles have spherical shape and different sizes. Pure hematite, after crushing, was characterized by platelets having different sizes and a thickness ranging from 12 to 20 μm (Fig. 2). EDS analyses were carried out on several samples of both solids to determine their mean composition, which

Table 1
Selected properties and mean composition of EAF dust and hematite

	pH	COD (gO ₂ /kg)	Cl (%)	Zn (%)	Fe (%)	K (%)	Pb (%)	Ca (%)	Mn (%)
EAF dust	8.57	25.4	41	21	19.4	11.6	3	2.3	1.7
Hematite	7.73	19.61	0	0	66	0	0	0	0

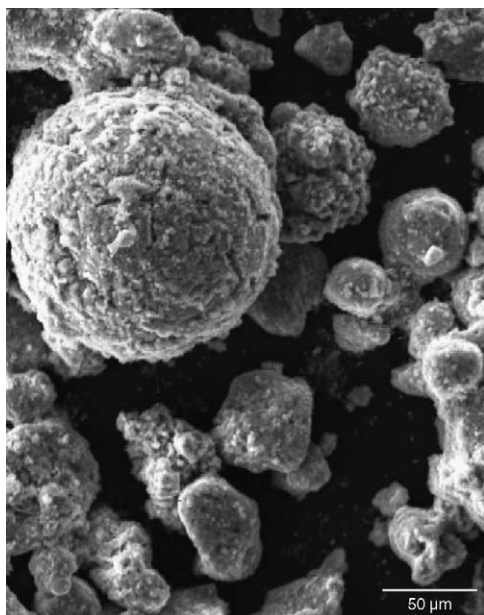


Fig. 1. SEM micrograph of EAF dust.

is reported in Table 1 together with COD and pH values. The concentrations of Zn, Cl^- and SO_4^{2-} in the leaching solutions are reported in Table 2 while Pb, Fe and Mn were not as they were only detected in traces.

2.2. Catalyst preparation

EAF dust was washed four times with bi-distilled water, using the same liquid solid ratio selected for the leaching experiments. This was done to reduce its chloride release, which could interfere with the determination of PCP dechlorination. Hematite was used without any preparation.

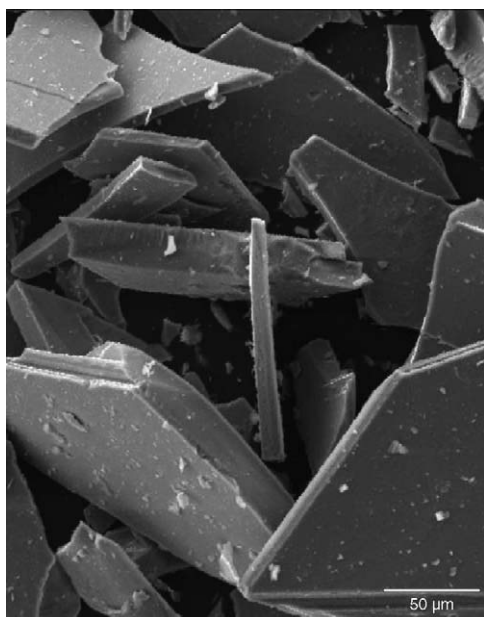


Fig. 2. SEM micrograph of hematite.

Table 2
Leaching experiments results

Leaching experiments	4 h	24 h	48 h	72 h
EAF dust distilled water				
Zn (mg/l)	0.5	0.12	0.08	0.05
Cl^- (mg/l)	3495.2	716.4	474	151.2
SO_4^{2-} (mg/l)	1371.4	501.7	364.13	118.6
EAF dust HNO_3 1 M				
Zn (mg/l)	3.52	0.95	0.33	0.12

2.3. Reaction conditions, sample analysis

Pentachlorophenol (99% pure) was obtained from Aldrich. The contaminated solution was prepared by dissolving 100 g of PCP in 1 l of distilled water and alkalizing the solution to pH 11 with NaOH to help PCP dissolution. Reactions were conducted using 50 ml samples in 100 ml beakers covered with parafilm. The catalyst was added to the solution in the selected quantities and the pH was adjusted with sulphuric acid (Carlo Erba Reagents) to pH 2. Unstabilized H_2O_2 (30% supplied by Merck) or stabilized H_2O_2 with KH_2PO_4 (16 g/l), was then added. The pH was monitored and kept in a limited range (pH 2–2.5) with H_2SO_4 . After, NaOH was added to stop the reaction and allow all the PCP to solubilize again. The solution was then vacuum filtered using 0.45 μm Whatman filters and analysed.

Total organic carbon (T.O.C.) was monitored with a Shimadzu TOC-5000 analyzer, chloride release was determined by ionic chromatography as previously described.

The $\text{H}_2\text{O}_2/\text{PCP}$ and $\text{Fe}/\text{H}_2\text{O}_2$ ratios were expressed as weight ratios. The catalyst was weighed in order to obtain the desired $\text{Fe}/\text{H}_2\text{O}_2$ ratio, considering its iron content. To estimate correctly the efficiency of T.O.C. removal and chloride release from PCP molecule, parallel experiments were conducted adding distilled water instead of H_2O_2 .

3. Results and discussion

3.1. pH monitoring experiments

In Fig. 3 the results of pH monitoring experiments are shown. The tests were conducted with different EAF dust quantities. The initial pH value was pH 2 and there was not any further pH adjustment. As a result of the basicity of EAF dust, an increase

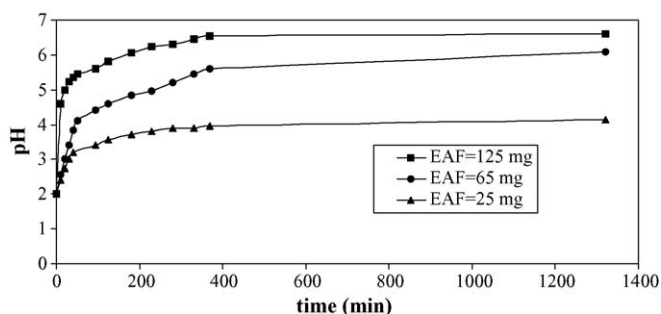


Fig. 3. Results of pH monitoring experiments with EAF dust. All solutions were initially at pH 2 and there was not any further pH adjustment.

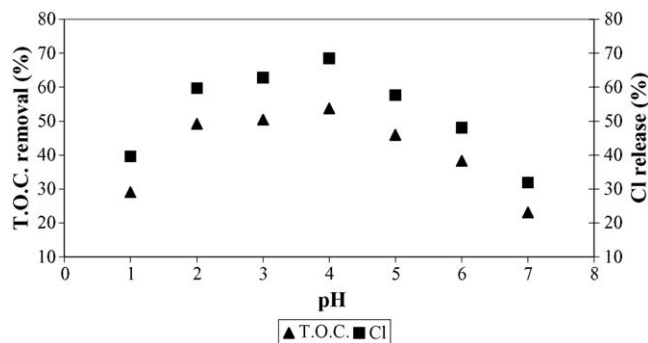


Fig. 4. Results of T.O.C. removal and chloride release at different pH for H_2O_2 :PCP = 10:1 and $\text{Fe}:\text{H}_2\text{O}_2 = 1:5$.

of the pH of the solution was observed, depending on the catalyst amount. A stable value was reached only after 3 h, thus emphasizing the necessity of a continuous pH adjustment to maintain the pH in a limited range (pH from 2 to 2.5).

The presence of hematite or oxidant did not alter the solution pH (data not shown) after the initial adjustment.

3.2. Effect of the reaction's pH on contaminant removal and chloride release

Fig. 4 illustrates the effect of pH on T.O.C. removal and chloride release due to PCP degradation after 24 h for different reactions conducted with a H_2O_2 :PCP ratio equal to 10:1 and $\text{Fe}:\text{H}_2\text{O}_2 = 1:5$. The optimal reaction pH was found to be pH 4, however due to difficulties in maintaining this pH in a limited range, the reactions were carried out at pH 2, given that this strong acid condition provided a high removal efficiency coupled with an easier control of the solution pH.

3.3. Effect of reaction time on contaminant removal

In Fig. 5 the T.O.C. removal versus time is detailed for a reaction conducted with a H_2O_2 :PCP ratio of 10:1, $\text{Fe}:\text{H}_2\text{O}_2 = 1:5$ and pH from 2 to 2.5. A high removal yield was observed in the first 6 h, while after 24 h the reaction rate was negligible. From this data, a parallel monitoring of H_2O_2 concentration in the solution showed a 75% reduction of its concentration after 6 h and 93% after 1 day (data not shown). The chosen reaction time for the following sets of reactions was 24 h, as no significant removal was expected after this lapse of time.

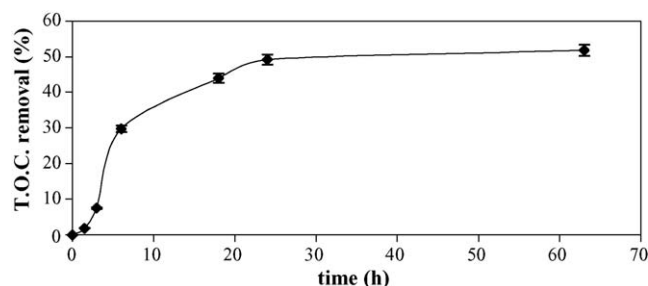


Fig. 5. T.O.C. removal vs. time for H_2O_2 :PCP = 10:1 and $\text{Fe}:\text{H}_2\text{O}_2 = 1:5$.

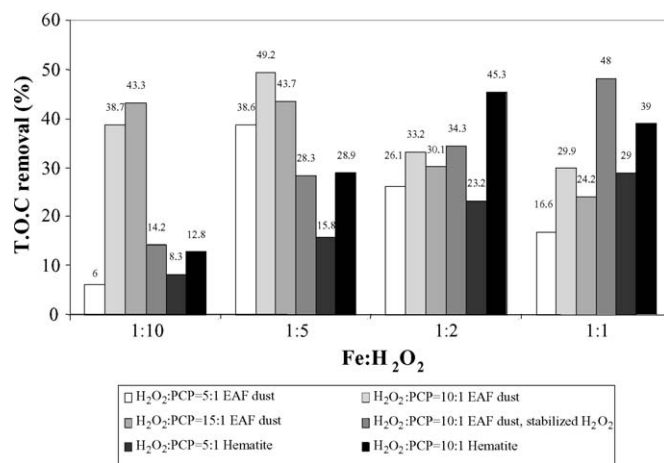


Fig. 6. T.O.C. removal after 24 h for different H_2O_2 :PCP and $\text{Fe}:\text{H}_2\text{O}_2$ ratios.

3.4. Influence of H_2O_2 :PCP and $\text{Fe}:\text{H}_2\text{O}_2$ ratios on contaminant removal

When H_2O_2 was not stabilized, the maximum removal of T.O.C. with EAF dust was achieved when $\text{Fe}:\text{H}_2\text{O}_2 = 1:5$, independently from H_2O_2 :PCP ratio (Fig. 6). The H_2O_2 :PCP ratio that produced the highest removal yield was H_2O_2 :PCP = 10:1. When the $\text{Fe}:\text{H}_2\text{O}_2$ ratio was increased, an initial increase in the removal efficiency was followed by a successive decrease ($\text{Fe}:\text{H}_2\text{O}_2 > 1:5$). In fact, this behaviour could be clarified on the basis of undesired reactions (2), (4) and (6); both the quenching of reactive species and H_2O_2 decomposition could occur easily when the dissolved metals' concentration was higher. In addition, a similar behaviour was seen as H_2O_2 :PCP ratio increased. In this case reactions (2) and (5) could be involved leading to the formation of less reactive radicals.

In the same conditions that led to the highest removal yield (H_2O_2 :PCP = 10:1), a new set of reactions was conducted using hydrogen peroxide stabilized with KH_2PO_4 . The KH_2PO_4 stabilizer lowers dissolved metal concentrations through reactions of precipitation or complexation [34]. As a result, their activity as Fenton catalyst decreases as they become non reactive with H_2O_2 . The presence of stabilizer enhanced the reaction yield when higher quantities of EAF dust were used, hindering the unfavourable reactions (2), (4) and (6) and explaining why in this case T.O.C. removal increases with larger amounts of solid catalyst. In effect phosphate appeared to inhibit the decomposition of H_2O_2 when catalysed by mineral surfaces, possibly by affecting the surface charge or redox potential at the mineral surface [34].

The last two sets of reactions used hematite as a solid catalyst instead of EAF dust and non stabilized hydrogen peroxide with the ratios H_2O_2 :PCP = 5:1 and 10:1. A lower removal yield than with EAF dust was observed (in the same conditions) and the maximum T.O.C. removal occurred when $\text{Fe}:\text{H}_2\text{O}_2 = 1:2$ and H_2O_2 :PCP = 10:1. This maximum yield variation could be explained by the presence of Mn in the EAF dust. When larger quantities of EAF dust were used, a larger quantity of Mn was present into the solution. This may have enhanced the decomposition of hydrogen peroxide, which can occur faster when

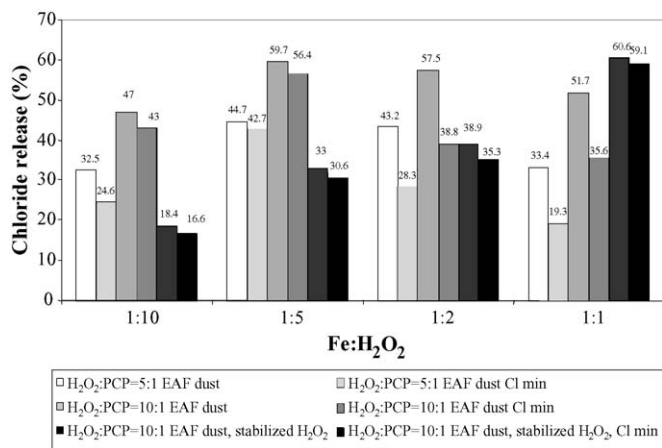


Fig. 7. Cl⁻ release after 24 h reaction with EAF dust and different H₂O₂:PCP and Fe:H₂O₂ ratios.

inorganic compounds such as Mn are present, and may also have enhanced the scavenging of OH• radicals [35–37] thus lowering the oxidant's concentration. Using a stabilizer substance such as KH₂PO₄ when EAF dust was employed, could limit these undesired effects explaining why in this case we observed a similar behaviour.

3.5. Influence of H₂O₂:PCP and Fe:H₂O₂ ratios on chloride release

Preliminary tests were performed to evaluate the influence of H₂O₂ on chloride release from the EAF dust. The results (data not shown) indicated that the oxidant presence did not affect chloride release.

In Figs. 7 and 8 the results of chloride release are reported. For every set of reactions two values are given: the actual chloride release (ACR) in the solution and a value calculated from the T.O.C. removal data, in the following way.

$$\text{MCR}(\%) = \frac{((\text{T.O.C.}_{\text{blank}} - \text{T.O.C.}_{\text{actual}}) \times 5 \times 35.45) / 6 \times 12.01}{66.56} \times 100$$

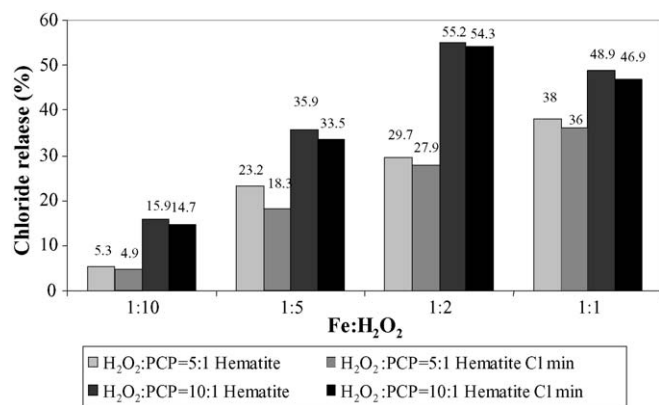


Fig. 8. Cl⁻ release after 24 h reaction with hematite and different H₂O₂:PCP and Fe:H₂O₂ ratios.

In this equation, 66.56 ppm Cl is the chloride concentration that can be released from 100 ppm of PCP, T.O.C._{blank} is the T.O.C. of a parallel experiment where no H₂O₂ was added and T.O.C._{actual} is the T.O.C. of the treated solution. MCR is the minimum chloride release that must be obtained considering that the removal of six atoms of organic C must be accompanied by a removal of five atoms of Cl. When the chloride release of the treated solution is approaching MCR value, it can be assumed that certain reaction selectivity did occur. In this case, it is probable that the molecules that underwent through dechlorination were the same where the oxidation continued, from ring opening to the final conversion to CO₂ (this conversion is responsible for the loss of T.O.C.). Some studies [38,39] suggested in fact that chlorinated aliphatic intermediates could be formed after the rupture of the aromatic ring and that these compounds would be further oxidised. When the two values ACR and MCR were slightly different, the molecules reached a higher degree of dechlorination indicating the possibility of a non-selective radical attack and the presence of numerous other species. In fact Hirvonen et al. found as intermediates in the oxidation of PCP using UV/H₂O₂ and O₃, chlorobenzenediols and other products [39]. The difference between the two values could therefore suggest a different reaction mechanism. Fig. 7 presents the results for reactions conducted with EAF dust. According to the T.O.C. data (Fig. 6), with unstabilized H₂O₂, the highest dechlorination was obtained when Fe:H₂O₂ = 1:5. A significant difference between the ARC and MRC values was observed when Fe:H₂O₂ ≥ 1:2, while when Fe:H₂O₂ < 1:2, these two values were almost comparable. This was observed independently from the H₂O₂:PCP ratio and it suggests that the reaction went through a different mechanism and was more selective when the Fe:H₂O₂ ratio was ≥ 1:2. When KH₂PO₄ was present, by increasing EAF quantities an increase in chloride removal was observed. In this case the ACR and MCR values were almost similar independently from the Fe:H₂O₂ ratio. This behaviour could be reasonably attributed to the effect of the stabilizing agent, which limits the undesired effects of Mn. When hematite was used as a solid catalyst, the maximum chloride release was observed when Fe:H₂O₂ = 1:2 and the ACR and MCR values matched. This could be attributed to the absence of Mn, which enhances the decomposition of hydrogen peroxide.

To explain the different behaviours described in the above text, some additional factors must be considered. Firstly, the concentration of chloride and sulphate ions, which was higher using greater quantities of EAF dust. In fact because of EAF dust composition and basicity, a higher level of Cl was observed than with hematite and a greater quantity of sulphuric acid was employed to acidify the solution. In a study [40] the effects of chloride and sulphate ions were investigated. These two ions could interfere through scavenging reactions and formation of the less reactive radicals Cl•, Cl₂• and SO₄•⁻, or of Fe³⁺ complexes, especially in the Fe³⁺/H₂O₂ system [40]. In addition, when EAF dust was used, the overall ionic strength of the solution was greater due to the dissolution of Cl⁻ and to the added SO₄²⁻. Kuznetsova et al. [18], showed that when the ionic strength of the solution increased, the rate constant of reaction (2) decreased. This influence became negligible when KH₂PO₄ was present [18],

explaining why in our experiments we had only a slight difference between the ACR and MCR values in presence of stabilized H_2O_2 . Furthermore at the low pH used in our experiments, PCP shows a low solubility and takes part also as a particulate to the first phases of the reaction. Problems related to the difficulties in the radical attack on PCP particulates have been discussed elsewhere [41]. Since PCP degradation products are more soluble [38], these products were oxidised as soon as they were formed and consequently the two values ARC and MRC were close.

As the reaction proceeded, H_2O_2 and PCP were consumed so PCP became completely soluble and Fe: H_2O_2 ratio increased. This effect was more evident with increasing quantities of EAF dust. In these conditions the effects of H_2O_2 decomposition catalysed by Mn, could be stronger and the radical attack could lose selectivity giving a further explanation of the differences between ACR and MCR values.

4. Conclusions

In this study EAF dust and hematite were used as Fenton catalyst.

The results showed that:

- The best removal efficiencies were achieved when H_2O_2 :PCP ratio was 10:1.
- EAF dust can be used as catalyst and the maximum removals achieved were 49.17% T.O.C. and 56.68% Cl release when Fe: H_2O_2 ratio was 1:5 and 48% T.O.C. and 60,6% Cl when Fe: H_2O_2 ratio was 1:1 and H_2O_2 was stabilized.
- Using hematite a maximum T.O.C. removal of 45.23% and Cl release of 55.15% was achieved when Fe: H_2O_2 ratio was 1:2.
- When Fe: H_2O_2 > 1:5, for unstabilized H_2O_2 , EAF dust showed a different reaction mechanism with a Cl release higher than expected from T.O.C. removal data.
- EAF dust was responsible for Cl and Zn release in the solution and this must be taken into account in developing the process.

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