



# HOMOGENEOUS OXIDATION OF PHENOLS IN AQUEOUS SOLUTION WITH HYDROGEN PEROXIDE AND FERRIC IONS

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## ABSTRACT

The chemical oxidation of phenol and chlorophenols with hydrogen peroxide in the presence of soluble iron can be economically attractive at low oxidant consumption, leading then to intermediates that are more easily biodegradable. The homogeneous oxidation of phenol and chlorophenols in aqueous solutions with hydrogen peroxide is studied at oxidant : phenol ratio of about 4:1 and 16:1 (mol/mol) at various catalyst concentrations, at ambient temperature without pH control. Ferric chloride, ferric and ferrous sulphate and ferrous ammonium sulphate are used as oxidation catalysts. Ferric salts induce higher oxidation rates than ferrous ones and the nature of the anions present does not affect reaction rate. 4-Chlorophenol is found to be most resistant to oxidation and 2,4,6-Trichlorophenol is not attacked by hydrogen peroxide in the presence of ferric ions at the experimental conditions studied. © 1997 IAWQ. Published by Elsevier Science Ltd

## KEYWORDS

Phenols oxidation; hydrogen peroxide; ferric catalyst.

## INTRODUCTION

A large amount of chlorinated compounds is produced industrially and some of them are discharged into the environment. These compounds are known to be toxic, inhibitory and/or non-biodegradable (Bridgewater *et al.*, 1979). Their recommended destruction to a level of 0.1-1 mg/l is not easy. Chemical treatment of wastewaters containing such compounds is often the only solution, nevertheless a costly one. The chemical oxidation can be economically attractive at low consumption of chemicals, leading then to intermediate products that are less toxic and/or biodegradable.

Most common oxidants are chlorine, ferrate, permanganate, ozone and hydrogen peroxide (Bowers *et al.*, 1988; Eckenfelder, 1989). Chlorine and permanganate always lead to contamination of the water with other toxic pollutants. Ozonation and wet-air oxidation are energy consuming. Treatment with hydrogen peroxide is effective, but it is not used in industry because of the high cost of hydrogen peroxide.

Oxidation of phenol-bearing wastewaters with hydrogen peroxide in the presence of ferrous or ferric salts has been widely studied for excess quantities of oxidant (Eisenhauer, 1964; Bishop *et al.*, 1968; Kibbel *et al.*, 1972; Al Hayek *et al.*, 1982; Koyama *et al.*, 1994; Preis *et al.*, 1994). Hydrogen peroxide has also been

shown to effectively reduce the refractory load of wastewaters containing 2,4-Dichlorophenol when applied at 4:1 total molar ratio (Bowers *et al.*, 1989).

In the present work, the oxidation of phenol (Ph), 2-Chlorophenol (2-CP), 3-Chlorophenol (3-CP), 4-Chlorophenol (4-CP), 2,4-Dichlorophenol (2,4-DCP), 2,6-Dichlorophenol (2,6-DCP) and 2,4,6-Trichlorophenol (2,4,6-TCP) with hydrogen peroxide ( $H_2O_2$ ) is studied at oxidant : phenol ratios of about 4:1 and 16:1 at various catalyst concentrations and ambient temperature.

## METHODS

All reagents (FLUKA) were used as received.  $H_2O_2$  solution 28% w/w was used as oxidant. Ferric and ferrous salts were used as catalysts at ambient temperatures in a mechanically agitated batch system at 500 rpm, without air bubbling and without pH control. Samples were withdrawn from the reactor and reaction was blocked by adding catalase. Phenols concentration was determined with the 4-aminoantipyrine method. Analysis of non-reacted  $H_2O_2$  and Chemical Oxygen Demand (COD) of the samples was performed according to the Standard Methods procedures (sodium thiosulphate and potassium dichromate respectively).

## RESULTS AND DISCUSSION

The oxidation of phenol with excess hydrogen peroxide, in the presence of ferric chloride, at 30°C is shown in Fig. 1, with the respective COD reduction and hydrogen peroxide consumption. As can be seen, the stoichiometry of the reaction (expressed as phenolics oxidation) changes with time, and excess hydrogen peroxide does not attack all intermediate products.

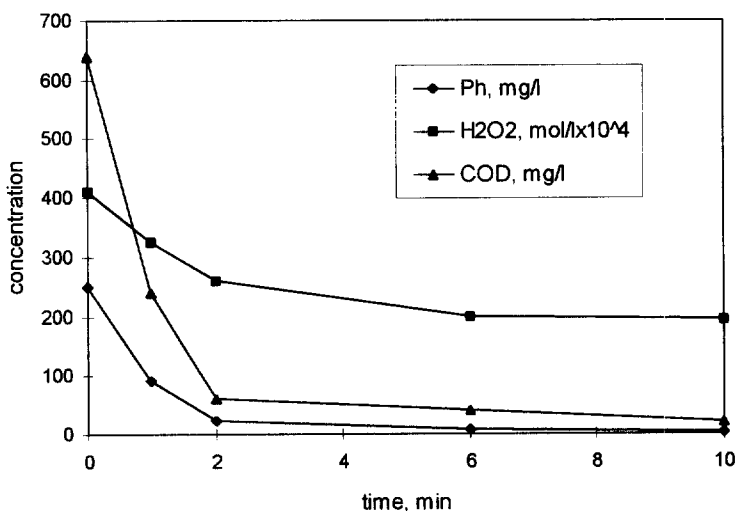


Figure 1. Phenol oxidation with 37 mg  $Fe^{3+}/l$  at 30°C, with excess hydrogen peroxide.

In Fig. 2 the various forms of soluble iron catalysts are compared for their efficiency in phenol oxidation at 25°C at a hydrogen peroxide : phenol ratio of 4:1 and 7 mg  $Fe^{n+}/l$  ( $n=2,3$ ). Ferric salts are proved better than ferrous ones and the nature of the anions present does not affect reaction rate.

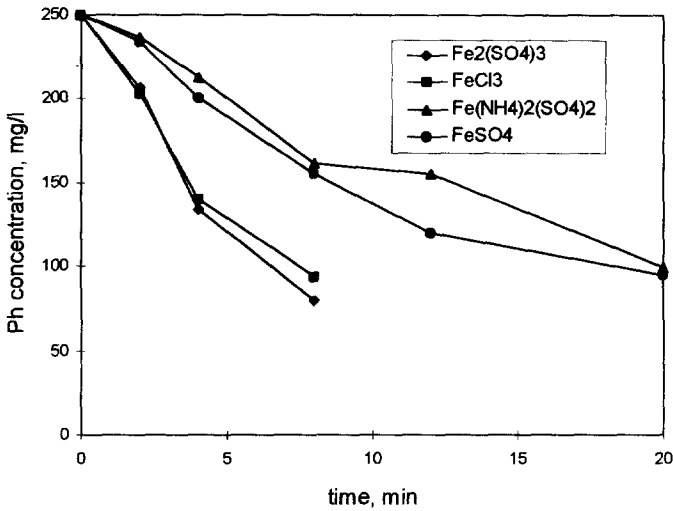


Figure 2. Efficiency of iron salts in the oxidation of phenol at 25°C.

Degradation efficiencies of Ph, 2-CP, 3-CP, 4-CP, 2,4-DCP and 2,6-DCP are compared at ambient temperature and for the same amount of catalyst at oxidant : phenol ratios of about 4:1 and 16:1 (Figs 3 and 4 respectively).

The lag phase observed for 2,6-DCP is not due to experimental error, since it is predicted by mechanisms proposed in the literature for phenols oxidation and was observed in the case of all phenols in experiences with smaller quantities of catalyst.

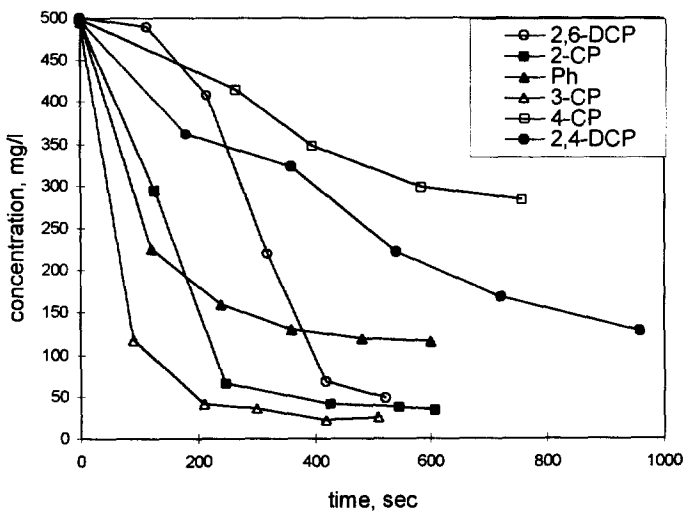


Figure 3. Oxidation of phenol and chlorophenols with 15.5 mg Fe<sup>3+</sup>/l at oxidant : phenol ratio 4:1.

4-CP is shown to be most resistant to oxidation in both cases, followed by 2,4-DCP. The presence of chloride in the para position seems thus to stabilize the aromatic ring. Finally, 2,4,6-TCP is not attacked by hydrogen peroxide in the presence of ferric ions at the experimental conditions mentioned above.

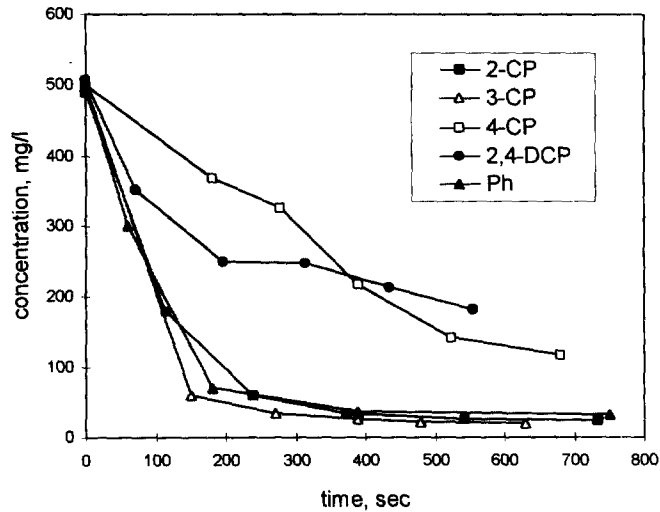


Figure 4. Oxidation of phenol and chlorophenols with 15.5 mg Fe<sup>3+</sup>/l at oxidant : phenol ratio 16:1.

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