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# Role of H<sub>2</sub>O<sub>2</sub> in the photo-transformation of phenol in artificial and natural seawater

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## Abstract

In previous works, it was observed that phenol photo-induced transformation in natural seawater (NSW) mediated by natural photosensitizers occurs and leads to the formation of numerous hydroxylated, condensed, halogenated and nitroderivatives. Irradiation of NSW added with phenol and iron species had provided the enhanced formation of several halophenols, suggesting a central role played by iron species on the phenol halogenation in marine water.

In this paper, we focus on hydrogen peroxide, another key photosensitizer, and its interaction with iron species. The ability of Fe(II)/Fe(III) and H<sub>2</sub>O<sub>2</sub> species to act as photo-sensitizers towards the transformation of organic compounds in seawater was investigated under simulated solar radiation.

Light activation is necessary to induce the transformation of phenol, as no degradation occurs in the dark when either H<sub>2</sub>O<sub>2</sub> or iron/H<sub>2</sub>O<sub>2</sub> are initially added to artificial seawater (ASW). Fe(II) is easily transformed into Fe(III), assessing that a Fenton reaction (dark, Fe(II)/H<sub>2</sub>O<sub>2</sub>) does not take place in marine environment, in favour of a photo-activated reaction involving Fe(III) and H<sub>2</sub>O<sub>2</sub>.

When NSW is spiked with H<sub>2</sub>O<sub>2</sub> and Fe(III), halophenols and nitrophenols concentration decreases and completely disappears at high hydrogen peroxide concentration. Since Fe(II) and Fe(III) in spiked seawater induce an enhanced formation of haloderivatives, an excess of hydrogen peroxide act as scavenger toward the photo-produced chloro/bromo radicals, so hindering halogenation process in seawater. Hence, even if hydrogen peroxide efficiently induces the •OH radical formation, and could then promote the phenol phototransformation, nevertheless it is negligibly involved in the production of the intermediates formed during phenol photolysis in seawater, whose formation is necessarily linked to other photosensitizer species.

**Keywords:** hydrogen peroxide, seawater, phototransformation, phenol, iron species

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## 1. Introduction

The photochemical degradation is likely to be an important loss mechanism for many pollutants in surface waters. Scarce investigation is reported at present for marine ecosystems on the role of natural photosensitizers and their effect on the possible abiotic transformation of anthropogenic compounds; proper designed laboratory and field experiments should help to determine direct and indirect photolysis rates and to identify photoproducts. Phenol was chosen as a model molecule to simulate organic matter transformation. Previous studies showed that its photo-induced transformation in seawater proceeds through the formation of a wide range of intermediate compounds including mono and dichlorophenols, nitrophenols, bromophenols and bisphenols (Calza et al., 2008). The contribution of different photosensitizers, e.g. Dissolved Organic Matter, the direct photolysis of sunlight-absorbing molecules and the reaction with transient species, like OH radicals produced by irradiation of diverse photoactive species (Boule et al., 2005), is invoked. In an attempt to discriminate the role played by the different photo-activators (dissolved organic matter itself, nitrate, nitrite, H<sub>2</sub>O<sub>2</sub>, Fe(III)) in producing these transformation products, each photosensitizer has been separately investigated. This paper is the second of a set on which the link among the natural photosensitizers and the secondary pollutants formed is for the first time evidenced. Firstly, the ability of iron species to act as photo-sensitizers in seawater was examined (Calza et al, 2012). In this work, we aimed to clarify the role played by hydrogen peroxide in the organic matter transformation and its interaction with iron species.

Hydrogen peroxide is assumed to play an important role in the redox reactions (Santana-Casiano et al., 2006) and in photochemical processes occurring in the oceans (Petasne and Zika, 1987). In surface waters, it is mainly produced by abiotic photochemical processes through the disproportionation of the O<sub>2</sub><sup>·-</sup> radical, formed by a light induced electron transfer process involving oxygen, metal ions and organic chromophores, e.g. humic acids (Baxter and Carey, 1983).



Hydrogen peroxide could also be produced through heterogeneous photocatalyzed processes (Cooper et al, 1988), photolysis reactions of organic compounds e.g. aldehydes and ketones, or photolysis of Fe(III)-oxalate complexes (Pelizzetti and Calza, 2002). The formation of H<sub>2</sub>O<sub>2</sub> is larger in coastal waters with higher humic concentrations than in oligotrophic waters, and the production rate seems to be directly related to the humic concentration, as assessed by absorbance measured at 300 nm (Zika et al., 1982).

Hydrogen peroxide is a source of  $\cdot\text{OH}$  radical and could then induce the transformation of organic matter; as it is a weak absorber of visible light,  $\cdot\text{OH}$  radicals formation slowly occurs (Price et al. 1992). Enhanced OH radical production should occur by a synergic reaction with iron species; reactions between Fe(II) and  $\text{H}_2\text{O}_2$  (Fenton reaction) (Rodriguez et al., 2002) or Fe(III) and  $\text{H}_2\text{O}_2$  (photo-Fenton reaction) (Zepp et al., 1992) are surely primary reactions for  $\cdot\text{OH}$  radical production in seawater.

The goal is obtained in two steps. Firstly, we planned a set of runs at typical pHs of the marine environment where iron species and hydrogen peroxide are contemporaneously present, in ratios similar to those found in marine water. Steady-state levels of  $\text{H}_2\text{O}_2$  in surface water are found at 10-200  $\text{nmolL}^{-1}$  (Price et al. 1992), while the total dissolved iron concentration (Fe(II) and Fe(III)) ranges from 0.01 to 10  $\text{nmolL}^{-1}$  (Rose and Waite, 2002), so that an excess of hydrogen peroxide is expected (Joseph et al., 2001). The overall process was studied by evaluating the phenol disappearance rate and the intermediates formation as a function of the irradiation time by varying:

- 1) iron and hydrogen peroxide concentration;
- 2) iron and hydrogen peroxide ratios;
- 3) type of salts, i.e. chloride and carbonate species, that could affect iron speciation and, consequently, the photo-activity of iron;
- 4) pH in the range 6.5-8, representative of estuarine water and seawater, respectively.

Secondly, results achieved in the marine water simulations were compared with those found in the natural seawater samples (NSW) spiked with increasing concentrations of  $\text{H}_2\text{O}_2$  or Fe(III)/ $\text{H}_2\text{O}_2$ ; this approach will permit to elucidate effect of hydrogen peroxide and its interaction with iron species in the organic matter transformation.

## 2. EXPERIMENTAL SECTION

### 2.1. Irradiation procedures

The irradiation experiments were carried out in Pyrex glass cells, containing 5 mL of the samples. The illuminations were performed using a 1500 watt Xenon lamp (CO.FO.MEGRA, Milan, Italy) equipped with a 340 nm cut-off filter simulating AM1 solar light. Temperature reached during the irradiation is 38° C. Phenol ( $0.2 \text{ mmolL}^{-1}$ ) photo-induced transformation has been investigated in solutions added with  $\text{H}_2\text{O}_2$   $10 \text{ mmolL}^{-1}$ , Fe(II) ( $0.1 \text{ mmolL}^{-1}$ ) or Fe(III) ( $0.1 \text{ mmolL}^{-1}$ ) ions at pH 8 in  $0.7 \text{ molL}^{-1}$  NaCl solution, artificial seawater (ASW) or natural seawater (NSW). Natural seawater (NSW) was sampled in June 2007 in the Gulf of Trieste, northern Adriatic

Sea, Italy under the project in acknowledgement (see [Calza et al. 2012](#) for NSW analysis). Experiments reported below in 3.3. were performed just after the sampling.

## **2.2. Analytical determinations**

The disappearance of the primary compound and the intermediates evaluation were followed using an HPLC system (Merck-Hitachi L-6200 pumps), equipped with a Rheodyne injector, a RP C18 column (Lichrochart, Merck, 12.5 cm x 0.4 cm, 5  $\mu\text{m}$  packing) and a UV-Vis detector (Merck Hitachi L-4200). The disappearance of phenol is followed at 220 nm, using as eluant acetonitrile and phosphate buffer ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ) at pH 2.8 at a flow rate of 1 mL/min.

Iron (II)/(III) and  $\text{H}_2\text{O}_2$  concentrations have been measured by using a spectrophotometer (Varian Cary 100 Scan). Hydrogen peroxide was quantified by the peroxidase-catalysed oxidation of phenol/4-aminoantipyrine protocol ([Frew et al., 1983](#)). Measurements were made at 505 nm. The detection limit  $5 \times 10^{-6} \mu\text{mol L}^{-1}$ .

Fe(II) formation has been followed through colorimetry, complexing  $\text{Fe}^{2+}$  with 1,10-phenanthroline. The absorbance of the complex  $[(\text{C}_{12}\text{H}_{18}\text{N}_2)_3\text{Fe}]^{2+}$  was measured at 511 nm. The detection limit was  $1 \times 10^{-6} \mu\text{mol L}^{-1}$ .

## **2.3. Material and reagents**

Phenol, catechol, hydroquinone, 1,3-dihydroxybenzene, 1,4-benzoquinone, 1,3,5-trihydroxybenzene, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2-bromophenol, 4-bromophenol, 2,6-dichlorophenol, 3,5-dichlorophenol, 3,4-dichlorophenol, 2,2'-bisphenol, 4,4'-bisphenol, Fe(III)perchlorate and 4-aminoantipyrine were all purchased by Aldrich and were used as received. 2,3-Dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol were purchased by Fluka, while  $\text{Fe}(\text{SO}_4)$  by Carlo Erba. Acetonitrile was purchased from Scharlau (AC0331, Supergradient HPLC grade).

Eluents have been prepared in MilliQ water and degassed before utilization. Artificial seawater (ASW) has been prepared in milliQ water containing the 11 major salts, in the amounts indicated elsewhere ([Calza et al., 2008](#)).

## **3. Results and discussion**

### **3.1. Phenol photo-induced disappearance in NaCl and ASW**

#### **3.1.1 Hydrogen peroxide**

Experiments on aqueous solution containing phenol and  $\text{H}_2\text{O}_2$   $10 \text{ mmolL}^{-1}$  were carried out at pH 8 in pure water, in  $\text{NaCl}$   $0.7 \text{ molL}^{-1}$  or artificial seawater (ASW). In the considered times, negligible phenol disappearance occurs in the dark, so excluding a direct phenol oxidation by  $\text{H}_2\text{O}_2$  and under illumination without  $\text{H}_2\text{O}_2$ . Conversely, under illumination in the presence of hydrogen peroxide phenol transformation takes place (see Figure 1a), promoted by the  $\cdot\text{OH}$  radicals produced through reaction 2.



The phenol disappearance as a function of the irradiation time approximated a pseudo-first order law and a rate of  $5.63 \times 10^{-7}$ ,  $6.03 \times 10^{-7}$  and  $2.17 \times 10^{-7} \text{ molL}^{-1} \text{ min}^{-1}$  in pure water,  $\text{NaCl}$  and ASW, respectively. Chloride ions show a negligible effect on phenol disappearance rate, while in ASW  $t_{1/2}$  increases from 5h (pH 8) to 13 h (ASW), most likely due to scavenging of  $\cdot\text{OH}$  radicals by the carbonate ions (King and Farlow, 2000; Calza et al, 2012).

### 3.1.2 *Fe(II)/Fe(III) and $\text{H}_2\text{O}_2$*

Irradiation of aqueous solution containing phenol and  $\text{Fe(II)}$  or  $\text{Fe(III)}/\text{H}_2\text{O}_2$  were carried out on: 1) filtered or unfiltered solutions, aimed to discriminate the role of the precipitate iron on the process. At  $\text{pH} > 6$ ,  $\text{Fe(III)}$  is chiefly in the insoluble  $\text{Fe(OH)}_3$  (ferrihydrite) form, so that the photo-degradation process could occur at the water/solid interface (Calza, et al. 2005) as already observed in seawater (Kuma, et al. 1992 and 1996); 2) stirred (for 96h) or unstirred solutions, in order to evaluate if the equilibrium among the different species is easily (or not) reached.

A study performed on solutions spiked with  $\text{Fe(II)}/\text{Fe(III)}$  had shown that phenol disappearance rate was scarcely influenced by the presence/absence of precipitate iron (Calza et al., 2012). Similar considerations arose from the analysis of the data summarised in Table 1, which collects the rates evaluated following the decrease with time of phenol for runs performed in the different conditions. Phenol degradation rates are similar under the different experimental conditions irrespective of adding  $\text{Fe(II)}$  or  $\text{Fe(III)}$  and of stirring, with a marginal increase of the rate in unfiltered solutions in the presence of  $\text{Fe(II)}$ . Since the presence of precipitate seems not to modify the photo-activity of iron(II)/(III) species, all the presented experiments have been performed on unfiltered and unstirred solutions.

No reaction takes place in the dark, neither with Fe(II)/H<sub>2</sub>O<sub>2</sub> nor with Fe(III)/H<sub>2</sub>O<sub>2</sub>, in analogy with the cases with hydrogen peroxide or Fe(II)/Fe(III) alone (Calza et al., 2012; Pelizzetti and Calza, 2002). Again, it implies that light absorption is needed to promote the phenol transformation.

### Fe(II)/H<sub>2</sub>O<sub>2</sub>

Table 2 summarises the phenol disappearance rates evaluated in the case of different H<sub>2</sub>O<sub>2</sub>/Fe(II) ratios, aimed to recreate the large variability existing in surface seawater. The rates are enhanced as the hydrogen peroxide concentration is increased (high ratios) and are larger at pH 6.5.

The phenol disappearance rate diminishes when pH increases from 6.5 to 8. In particular, the decrease is larger at lower ratios (when ratio is 100 rate is halved, while at ratio 4 rate is 6 times lower). Closer inspections of data at pH 6.5 shows that rates are more influenced by the variation in hydrogen peroxide concentration rather than iron concentration. In NaCl solution, the rate is higher at the lowest ratio (4) than when ratio is higher (10) but H<sub>2</sub>O<sub>2</sub> concentration is lower (rates passes from 7.38x10<sup>-7</sup> molL<sup>-1</sup> min<sup>-1</sup> (H<sub>2</sub>O<sub>2</sub> 0.4 mmolL<sup>-1</sup>) to 4.40x10<sup>-7</sup> molL<sup>-1</sup>min<sup>-1</sup> (H<sub>2</sub>O<sub>2</sub> 0.1 mmolL<sup>-1</sup>)). A similar trend was followed at pH 8. Conversely, in ASW the phenol disappearance rates are minima and scarcely modified by variation in iron/H<sub>2</sub>O<sub>2</sub> concentrations.

Fe(II) is rapidly oxidised to Fe(III) and, already before illumination, only 15% of the initial iron is still present as Fe(II) (data not shown). Its rapid oxidation could be due to the reaction with hydrogen peroxide or dissolved oxygen, according to reactions 3-5 (Santana-Casiano et al., 2005; Gonzalez-Davila et al., 2005 and 2006).



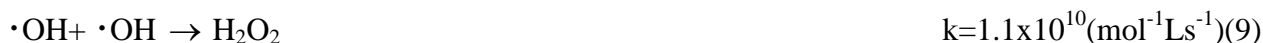
Bautista et al. 2008 report a  $k_1=76 \text{ mol}^{-1}\text{L s}^{-1}$ , while the kinetic constants calculated by Santana-Casiano et al. 2005 in sea water, at pH 8 and ionic strength 0.7 M is higher ( $k_1=3.1 \times 10^4 \text{ (mol}^{-1}\text{L s}^{-1}\text{)}$ ). The formed  $\cdot\text{OH}$  radicals could then react with iron(II) or hydrogen peroxide (Neta et al., 1988; Buxton et al., 1988) (eq. 6-8):







Hydrogen peroxide concentration as a function of the irradiation time is kept almost constant (Figure 2A), suggesting that it could be back-formed according to reaction 9 and undergo a sequence of disappearance/formation reactions. High concentration of hydrogen peroxide are still measured at long irradiation times, so guarantying a continuous  $\cdot\text{OH}$  radical production.



In ASW these radical species ( $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals) could not only react with phenol, but also be reactive for other species, such as  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  (see reaction 11-13) (Petasne and Zika, 1987).



At pH 8, Fe(II) is mostly present as  $\text{Fe}(\text{CO}_3)_2^{2-}$ , a species slowly oxidised by  $\text{H}_2\text{O}_2$ ; as the  $\cdot\text{OH}$  radical production is inhibited (Joseph et al., 2001; King and Farlow, 2000), a consequent lower phenol disappearance rate was observed in ASW.

### Fe(III)/H<sub>2</sub>O<sub>2</sub>

Same experiments were carried out in solutions spiked with Fe(III) ions. The calculated rates are reported in Table 2, while the hydrogen peroxide profile as a function of the irradiation time is plotted in Figure 2B. The measured  $\text{H}_2\text{O}_2$  concentration ranges from 5 to 10  $\text{mmolL}^{-1}$ ; again, it follows a sequence of formation/consumption reactions, so keeping an almost constant concentration.

When Fe(III) is initially added, only a slight amount is reduced to Fe(II) (maxima Fe(II) concentration is 1  $\mu\text{M}$ ). Fe(III) is present under different forms, i.e. colloidal and precipitate forms, here indicated as Fe(III)-L, and leads to the  $\cdot\text{OH}$  radicals production according to reactions 3 and 14.



In analogy with Fe(II), analysis of the data collected in Table 2 shows that:

- (1) at pH 8 rates are slower in ASW than in NaCl, due to the formation of carbonate radicals (Calza et al., 2012).
- (2) at pH 6.5 the reaction quickly proceeds, favoured by an acidic pH (Gallard et al., 1998), and phenol is completely disappeared within 4h of irradiation.

The overall data described permit to conclude that, independently from the initial addition of Fe(II) or Fe(III), iron(III) species are predominant in solution: a photo-Fenton reaction rather than a Fenton reaction seems then to occur in the marine water. The close analogy between the disappearance rates in the presence of Fe(II) or Fe(III) suggest a key role played by Fe(III) colloidal species; under illumination Fe(II) can be oxidized to goethite, with an involvement in photo-assisted phenol degradation of Fe(III) colloidal species, rather than Fe(II) species.

The concurrent addition of Fe(III) and H<sub>2</sub>O<sub>2</sub> shows a synergic effect. Particularly interesting is the case where Fe(III) is in excess (Fe(III) 0.1 mM/H<sub>2</sub>O<sub>2</sub> 0.01 mM). In this case, despite the low hydrogen peroxide concentration, the rate is 10 times higher than with Fe(III) alone, so underlining the importance of hydrogen peroxide in the production of photoactive species. For the highest ratio (100), the rate constant is 80 (pH 8) or 40 (ASW) times higher than with Fe(III) alone and 2 times higher than with hydrogen peroxide alone (ASW).

### 3.2. Intermediate compounds

Along with the phenol disappearance, the formation of several transformation products occurs. The time evolution of intermediates in all cases as a function of time was recorded. For sake of brevity, in Figure 1b are only plotted the phenol transformation products formed in the presence of H<sub>2</sub>O<sub>2</sub>, while in Table 3 are summarized the maximal concentration of the intermediate compounds formed in solutions spiked with different Fe(II)/Fe(III) and H<sub>2</sub>O<sub>2</sub> concentrations, together with their irradiation time formation.

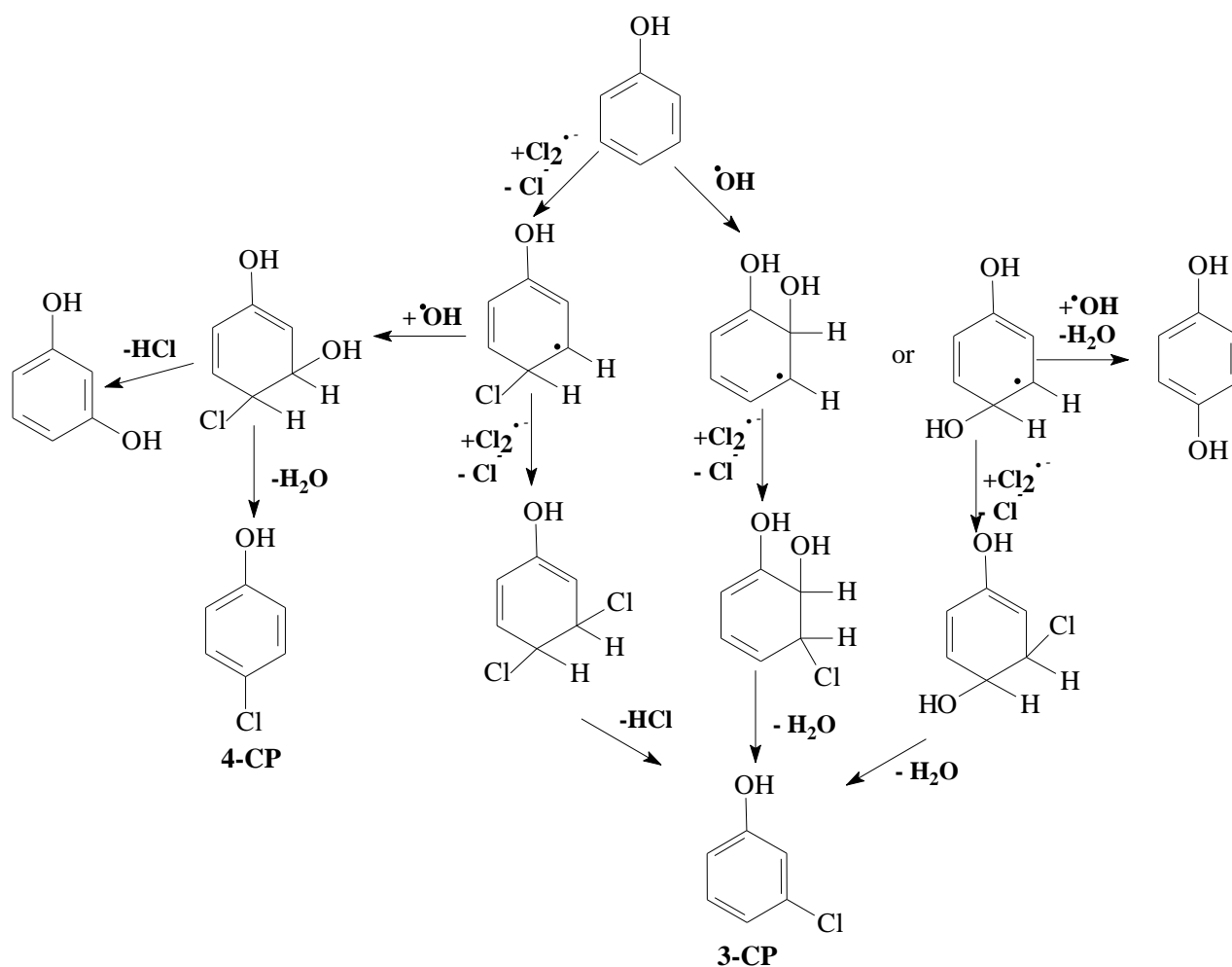
In solution spiked with H<sub>2</sub>O<sub>2</sub>, hydroquinone and 1,4-benzoquinone are formed as major products and resorcinol (1,3-dihydroxybenzene) at lower amount (maximum at 0.3 mgL<sup>-1</sup>). Hydroxyl radical quickly reacts with phenol ( $k=1.4 \times 10^{10} \text{ mol}^{-1}\text{Lsec}^{-1}$ ) (Alfassi et al., 1990),

producing typical primary products of the hydroxyl radical attack to the aromatic moiety. In addition, chlorination will most likely occur.

From eq. 2, photochemical scission of H<sub>2</sub>O<sub>2</sub> produces OH radicals that fast reacts with Cl<sup>-</sup> leading to ·Cl. At high chloride concentration ·Cl forms dichloro radical ·Cl<sub>2</sub><sup>-</sup> (see eq. 15-17 reported below) that should be the predominant radical species (Pelizzetti and Calza, 2002, Santana-Casiano et al., 2005).



Two different pathways for phenol transformation are proposed in Scheme 1, involving Cl<sub>2</sub><sup>-</sup> or the ·OH radical attack. Both Cl<sub>2</sub><sup>-</sup> and ·OH concur for *ortho/para* positions on the aromatic ring of phenol. When Cl<sub>2</sub><sup>-</sup> attacks the ring, chloroderivatives are expected. 3-Chlorophenol (3-CP) is formed through a second Cl<sub>2</sub><sup>-</sup> addition and HCl elimination, while the ·OH addition could evolve into 4-chlorophenol or 1,3-dihydroxybenzene (through H<sub>2</sub>O or HCl loss, respectively).



**Scheme 1.** Proposed mechanisms for the formation of hydroquinone, 1,3-dihydroxybenzene and 3 and 4-chlorophenol.

In the case of  $\text{OH}$  radical attack, hydroquinone is formed by  $\text{OH}$  addition followed by  $\text{H}_2\text{O}$  elimination, while the further addition of  $\text{Cl}_2^{\cdot-}$  and  $\text{H}_2\text{O}$  loss leads to the formation of 3-chlorophenol.

Analysing the data of Table 3 shows that with  $\text{Fe(II)/(III)}$  and  $\text{H}_2\text{O}_2$  spiked solution only hydroxylated compounds are formed, similarly to the case with  $\text{H}_2\text{O}_2$  alone but in contrast with the results obtained on solutions spiked with only  $\text{Fe(II)/Fe(III)}$  (Calza et al., 2012), where chloroderivatives were detected.

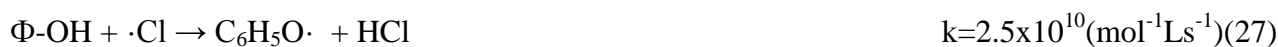
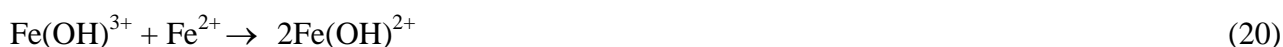
Catechol was not experimentally observed as already reported (Calza et al., 2012). Relevant amounts of resorcinol are detected. The concentrations of intermediates are correlated with the reactant amount and show similar variation when changing hydrogen peroxide or iron concentrations. Hydroquinone and 1,4-benzoquinone concentrations are maxima at pH 6.5 (1,4-benzoquinone 3.71 mg/L, hydroquinone 1.15 mg/L), when also the phenol disappearance rate is

high (Table 2), i.e. when elevated concentration of either hydrogen peroxide or iron are added (10 mmolL<sup>-1</sup> and 0.1 mmolL<sup>-1</sup>, respectively).

Hydroquinone is the earliest formed intermediate, then easily oxidized to 1,4-benzoquinone; the time at which the maximum of 1,3-dihydroxybenzene and 1,3,5-trihydroxybenzene appears is larger than that of the other degradation compounds due to the consecutive pathways depicted in Scheme 1.

At pH 8, a similar trend exists both in NaCl or ASW solution when increasing the concentration of iron or hydrogen peroxide; the rates are lower and also the intermediates concentrations are reduced. 1,3-Dihydroxybenzene concentration improves at the increasing of the reactant concentrations but it is not detected in ASW, in analogy with the case of Fe(II) alone (Calza et al., 2012).

Despite the high chloride (and bromide) concentrations, no halogenated compounds have been identified; they in fact are only observed in the presence of very low H<sub>2</sub>O<sub>2</sub> concentration (see section 3.3). The absence of chlorinated compound under these experimental conditions could be linked to a scavenging effect of hydrogen peroxide toward Cl radicals, that would be produced accordingly to reactions 15-17. Cl<sup>•</sup> and Cl<sub>2</sub><sup>•-</sup> radicals are strong oxidants (E°<sub>Cl<sup>•</sup>/Cl<sup>-</sup></sub> = 2.41 V, E°<sub>Cl<sub>2</sub><sup>•-</sup>/2Cl<sup>-</sup></sub> = 2.09 V) (Schwarz et al., 1984; De Laat et al., 2006), able to oxidise either hydrogen peroxide or Fe(II). The presence of hydrogen peroxide and the reactions induced by its photolysis can result in the depletion of the reactive species for phenol photochlorination. Cl<sup>•</sup> can rapidly react with phenol, H<sub>2</sub>O<sub>2</sub> or Fe(II) (see reactions 21, 25, 27), while for Cl<sub>2</sub><sup>•-</sup> the reaction rates are lower, above all toward H<sub>2</sub>O<sub>2</sub> (reaction 22) and Fe(II) (reaction 26) (Neta et al., 1988).



Although the reactivity of  $\cdot\text{Cl}/\text{Cl}_2\cdot^-$  toward phenol is high (Neta et al., 1988), the  $\text{Cl}\cdot$  radical should be rapidly captured by  $\text{H}_2\text{O}_2$  and  $\text{Fe(II)}$ , preventing the phenolic ring chlorination; the excess of  $\text{H}_2\text{O}_2$  and its high reactivity toward chlorine radical hinders the  $\text{Cl}_2\cdot^-$  formation through reaction 17.

Similarly, bromine radicals can be formed and scavenged by the hydrogen peroxide, so preventing the formation of bromoderivatives. This implies that with a high concentration of  $\text{H}_2\text{O}_2$  no significant amount of halogenated compounds is expected. However, if the formation of  $\text{Cl}\cdot$  indeed occurs through the reactions 15-16, the absence of halophenols in the presence of high concentration of  $\text{OH}$  radicals is rather surprising and suggest that, when initially only  $\text{Fe(II)}$  or  $\text{Fe(III)}$  are added, halogenation may be induced by a different path, i.e. mediated by iron species.

When  $\text{Fe(III)}$  is initially added, the intermediates summarized in Table 3 were detected. Similarly to the case with  $\text{H}_2\text{O}_2$  alone and  $\text{Fe(II)/H}_2\text{O}_2$ , no chlorophenols are formed; again, a scavenging effect by hydrogen peroxide toward  $\text{Cl/Br}$  radicals should occur. In ASW, hydroquinone and 1,4-benzoquinone are still the main intermediates, even if formed at a lower rate. When the  $\text{H}_2\text{O}_2/\text{iron}$  ratio is low, 4,4'-bisphenol was also identified. Its formation is likely to pass through the abstraction of an hydrogen from phenol with the formation of phenoxyl radical, in equilibrium with its tautomeric form. Through a dimerization reaction the formation of 4,4'-bisphenol is then obtained. This reaction is kinetically hampered and occurs at slower rates (5 to 10 times lower).

### **3.3. Phenol transformation in natural seawater added with iron and/or $\text{H}_2\text{O}_2$**

NSW was spiked with phenol,  $\text{Fe(III)}$  and/or  $\text{H}_2\text{O}_2$  and irradiated as described above. Upon light exposure, phenol disappearance occurs and the calculated rates are summarized in Table 2. When only phenol was added, its photo-transformation slowly occurred ( $t_{1/2}=192$  h). The phenol disappearance rate in natural seawater increases after addition of  $\text{Fe(III)}$  ( $t_{1/2}$  passes from 192 to 38 h) or  $\text{H}_2\text{O}_2$  ( $t_{1/2}$  7h); when  $\text{Fe(III)}$   $0.1\text{ mmolL}^{-1}$  and  $\text{H}_2\text{O}_2$   $10\text{ mmolL}^{-1}$  are contemporaneously added, the rate is further increased ( $t_{1/2}$  3h). In all cases, the disappearance rates are higher in NSW than in ASW (i.e., with only  $\text{H}_2\text{O}_2$ ,  $r_{0\text{ASW}}=2.17\times 10^{-7}\text{ molL}^{-1}\text{min}^{-1}$  and  $r_{0\text{NSW}} = 4.1\times 10^{-7}\text{ molL}^{-1}\text{min}^{-1}$ ) probably due to the presence of chromophores. i.e. fulvic and humic acids or  $\text{Fe(III)}$  species, as already described (Gonzalez-Davila et al., 2006, Calza et al, 2012).

In NSW, along with the phenol disappearance, the formation of numerous hydroxylated, condensed, halogenated and nitroderivatives was observed (Calza et al., 2008). When NSW was spiked with iron oxides,  $\text{Fe(II)}$  or  $\text{Fe(III)}$ , an enhanced formation of halophenols was evidenced (Calza et al., 2012). Conversely, when NSW is spiked with  $10\text{ mmolL}^{-1}\text{ H}_2\text{O}_2$ , only hydroxylated

compound are formed (Figure 3), in a close analogy with the experiment performed in chloride rich solution (see Figure 1). Hydrogen peroxide seems to hinder the formation of haloradicals, nitroradicals and the formation of condensed products. Therefore, even if hydrogen peroxide is able to effectively produce  $\bullet\text{OH}$  radical, and could then promote the phenol phototransformation, it is negligibly involved in the production of intermediates formed during phenol photolysis in seawater, the formation of which is necessarily linked to the presence of other photo-sensitizer species.

NSW has been then spiked with increasing concentrations of Fe(III) and  $\text{H}_2\text{O}_2$ . At low concentration (Fe(III)  $0.1 \mu\text{molL}^{-1}$  and  $\text{H}_2\text{O}_2$   $2 \mu\text{molL}^{-1}$ ) in “almost” natural seawater, the degradation rate slightly increases and the haloderivatives concentrations decrease (i.e. 3-chlorophenol passes from  $0.015$  to  $0.008 \text{ mg L}^{-1}$ ). At higher concentrations (Fe(III)  $0.1 \text{ mmolL}^{-1}$  and  $\text{H}_2\text{O}_2$   $0.1 \text{ mmolL}^{-1}$  or  $10 \text{ mmolL}^{-1}$ ), no more haloderivatives are formed. These results prove the scavenging effect of hydrogen peroxide described above, pointing out that the inhibition in the chlorophenols formation is directly related to the hydrogen peroxide concentration.

## Conclusions

Phenol was taken as model molecule to investigate the role of hydrogen peroxide on the degradation of the organic compounds in seawater. The overall data described permit to conclude that, independently from the initial addition of Fe(II) or Fe(III), iron(III) species are predominant in solution. The system Fe(III)/ $\text{H}_2\text{O}_2$  favourably acts in the transformation of organic matter upon activation with UV/vis radiation, while no reaction occurs in the dark. This imply that in seawater a photo-Fenton reaction rather than a Fenton reaction seems then to occur in the marine water.. This reaction takes place by means of colloidal Fe(III) species, while the Fe(III) precipitate scarcely affects the photo-transformation. The rate of disappearance of phenol is larger at pH 6.5 and depends on the concentration of hydrogen peroxide and iron concentration and, above all, the efficiency of the process increases to high concentrations of hydrogen peroxide.

Despite the formation of several halophenols during photo-induced transformation of phenol in seawater, the addition of increasing concentrations of  $\text{H}_2\text{O}_2$  to NSW had shown to hinder the formation of halophenols and only hydroxyderivatives were detected. This appears to be related to the high oxidation potential of  $\bullet\text{Cl}$  and  $\bullet\text{Cl}_2^-$  radicals, able to oxidize both  $\text{H}_2\text{O}_2$  and Fe(II). Fe(II) and hydrogen peroxide act as the main scavengers for chloro radicals; both species are easily oxidised by  $\text{Cl}\cdot$ , while can slowly react with  $\text{Cl}_2\cdot^-$ . This implies that with a high concentration of

H<sub>2</sub>O<sub>2</sub> no significant amount of halogenated compounds is expected; halophenols formation is necessary reduced in marine water rich in hydrogen peroxide.

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**Table 1.** Phenol disappearance rate in NaCl 0.7 molL<sup>-1</sup> solution and in artificial seawater (ASW) in the presence of Fe(II)[0.1 mmolL<sup>-1</sup>] (or Fe(III)[0.1 mmolL<sup>-1</sup>]) and H<sub>2</sub>O<sub>2</sub> [10 mmolL<sup>-1</sup>] on stirred (96h) or unstirred solution, filtered (0.45 μm) or unfiltered solution.

	<b>r<sub>0</sub>(molL<sup>-1</sup>min<sup>-1</sup>)</b>		<b>Unstirred</b>	<b>Stirred</b>
<b>Fe(II)</b>	<b>NaCl 0.7 molL<sup>-1</sup></b>	<b>Filtered</b>	8.72x10 <sup>-7</sup>	1.05x10 <sup>-6</sup>
		<b>Unfiltered</b>	1.02x10 <sup>-6</sup>	1.23x10 <sup>-6</sup>
	<b>ASW</b>	<b>Filtered</b>	3.32x10 <sup>-7</sup>	2.55x10 <sup>-7</sup>
		<b>Unfiltered</b>	3.67x10 <sup>-7</sup>	3.57x10 <sup>-7</sup>
<b>Fe(III)</b>	<b>NaCl 0.7 molL<sup>-1</sup></b>	<b>Filtered</b>	9.95x10 <sup>-7</sup>	1.24x10 <sup>-6</sup>
		<b>Unfiltered</b>	1.07x10 <sup>-6</sup>	1.19x10 <sup>-6</sup>
	<b>ASW</b>	<b>Filtered</b>	3.72x10 <sup>-7</sup>	3.55x10 <sup>-7</sup>
		<b>Unfiltered</b>	3.97x10 <sup>-7</sup>	4.07x10 <sup>-7</sup>

**Table 2.** Phenol transformation rate in the presence of Fe(II) or Fe(III) and H<sub>2</sub>O<sub>2</sub> (unfiltered and unstirred condition) at pH 8 and 6.5.

	<b>Ratio</b>	<b>molL<sup>-1</sup></b>	<b>r<sub>0</sub> (molL<sup>-1</sup> min<sup>-1</sup>)</b>			
			<b>NaCl pH 6.5</b>	<b>NaCl pH 8</b>	<b>ASW</b>	<b>NSW</b>
<b>none</b>	-	-	-	-	-	1.40x10 <sup>-8</sup>
<b>H<sub>2</sub>O<sub>2</sub></b>	-	<b>1x10<sup>-2</sup></b>	-	-	2.17x 10 <sup>-7</sup>	4.11x10 <sup>-7</sup>
<b>Fe(II)</b>	-	<b>1x10<sup>-4</sup></b>	-	1.20x10 <sup>-8</sup>	1.04x10 <sup>-8</sup>	-
<b>Fe(III)</b>	-	<b>1x10<sup>-4</sup></b>	-	1.01x10 <sup>-8</sup>	9.20x10 <sup>-9</sup>	2.40x10 <sup>-8</sup>
<b>H<sub>2</sub>O<sub>2</sub>/Fe(III)</b>	<b>100</b>	<b>1x10<sup>-2</sup> / 1x10<sup>-4</sup></b>	2.57x10 <sup>-6</sup>	1.07x10 <sup>-6</sup>	3.97x10 <sup>-7</sup>	5.20x10 <sup>-7</sup>
	<b>10</b>	<b>1x10<sup>-6</sup> / 1x10<sup>-7</sup></b>	-	-	-	4.70x10 <sup>-8</sup>
	<b>0.1</b>	<b>1x10<sup>-5</sup> / 1x10<sup>-4</sup></b>	-	-	8.70x10 <sup>-8</sup>	-
<b>H<sub>2</sub>O<sub>2</sub>/Fe(II)</b>	<b>100</b>	<b>1x10<sup>-2</sup> / 1x10<sup>-4</sup></b>	1.93x10 <sup>-6</sup>	1.02x10 <sup>-6</sup>	3.67x10 <sup>-7</sup>	-
	<b>57</b>	<b>4x10<sup>-3</sup> / 7x10<sup>-5</sup></b>	1.16x10 <sup>-6</sup>	2.86x10 <sup>-7</sup>	-	-
	<b>20</b>	<b>1x10<sup>-3</sup> / 5x10<sup>-5</sup></b>	9.42x10 <sup>-7</sup>	1.76x10 <sup>-7</sup>	1.68x10 <sup>-7</sup>	-
	<b>10</b>	<b>1x10<sup>-4</sup> / 1x10<sup>-5</sup></b>	4.40x10 <sup>-7</sup>	-	-	-
	<b>4</b>	<b>2x10<sup>-4</sup> / 5x10<sup>-5</sup></b>	1.02x10 <sup>-6</sup>	1.62x10 <sup>-7</sup>	-	-
	<b>4</b>	<b>4x10<sup>-4</sup> / 1x10<sup>-4</sup></b>	7.38x10 <sup>-7</sup>	-	-	-

**Table 3.** Intermediates maxima concentration and corresponding irradiation time when Fe(II)/Fe(III) and H<sub>2</sub>O<sub>2</sub> are initially added (ND= not detected).

	Ratio, (molL <sup>-1</sup> )	Intermediates	max. concentration (mgL <sup>-1</sup> ) and t <sub>max</sub> (min.)		
			NaCl pH 6.5	NaCl pH 8	ASW
<b>H<sub>2</sub>O<sub>2</sub>/Fe(III)</b>	<b>100,</b> <b>1x10<sup>-2</sup> /1x10<sup>-4</sup></b>	<b>Hydroquinone</b>	1.15 (30')	1.06 (15')	0.86 (60')
		<b>1,4-benzoquinone</b>	3.71 (45')	2.08 (60')	0.52 (120')
		<b>1,3,5-trihydroxybenzene</b>	0.90 (60')	0.92 (120')	0.11 (120')
		<b>1,3-dihydroxybenzene</b>	0.20 (60')	0.16 (120')	ND
	<b>0.1,</b> <b>1x10<sup>-5</sup> /1x10<sup>-4</sup></b>	<b>Hydroquinone</b>	-	-	0.77 (5')
		<b>1,4-benzoquinone</b>	-	-	0.11 (10')
<b>4,4'-bisphenol</b>		-	-	0.61 (120')	
<b>H<sub>2</sub>O<sub>2</sub>/Fe(II)</b>	<b>100,</b> <b>1x10<sup>-2</sup> /1x10<sup>-4</sup></b>	<b>Hydroquinone</b>	0.51 (15')	1.27 (30')	1.13 (30')
		<b>1,4-benzoquinone</b>	3.20 (30')	1.50 (60')	0.11 (180')
		<b>1,3,5-trihydroxybenzene</b>	ND	ND	0.13 (120')
		<b>1,3-dihydroxybenzene</b>	0.13 (60')	0.92 (120')	ND
	<b>57,</b> <b>4x10<sup>-3</sup> /7x10<sup>-5</sup></b>	<b>Hydroquinone</b>	0.78 (15')	0.89 (45')	-
		<b>1,4-benzoquinone</b>	0.56 (30')	0.68 (60')	-
		<b>1,3,5-trihydroxybenzene</b>	ND	0.48 (120')	-
		<b>1,3-dihydroxybenzene</b>	ND	0.11 (120')	-
	<b>20,</b> <b>1x10<sup>-3</sup> /5x10<sup>-5</sup></b>	<b>Hydroquinone</b>	0.66 (20')	0.44 (30')	0.38 (60')
		<b>1,4-benzoquinone</b>	0.16 (30')	0.12 (60')	ND
		<b>1,3,5-trihydroxybenzene</b>	ND	ND	0.44 (120')
		<b>1,3-dihydroxybenzene</b>	ND	ND	ND
	<b>10,</b> <b>1x10<sup>-4</sup> /1x10<sup>-5</sup></b>	<b>Hydroquinone</b>	0.44 (10')	-	-
		<b>1,4- benzoquinone</b>	0.37 (30')	-	-
		<b>1,3,5-trihydroxybenzene</b>	0.51 (60')	-	-
		<b>1,3-dihydroxybenzene</b>	0.17 (30')	-	-
	<b>4,</b> <b>2x10<sup>-4</sup> /5x10<sup>-5</sup></b>	<b>Hydroquinone</b>	0.32 (15')	0.41 (30')	-
		<b>1,4-benzoquinone</b>	0.15 (30')	0.20 (120')	-
		<b>1,3,5-trihydroxybenzene</b>	ND	ND	-
		<b>4,4'-bisphenol</b>	ND	0.65 (240')	-
	<b>4,</b> <b>4x10<sup>-4</sup> /1x10<sup>-4</sup></b>	<b>Hydroquinone</b>	0.38 (15')	-	-
		<b>1,4-benzoquinone</b>	0.17 (60')	-	-

## Figure caption

**Fig. 1.** Phenol disappearance at pH 8 under a variety of conditions as a function of the irradiation time in the presence of  $\text{H}_2\text{O}_2$  [ $10 \text{ mmolL}^{-1}$ ]: a) disappearance curves in the diverse experimental conditions (dark, ultrapure water, NaCl 0.7 M, ASW); b) intermediates formation in NaCl 0.7 M.

**Fig. 2.**  $\text{H}_2\text{O}_2$  profiles in NaCl 0.7 M water at pH 8 and pH 6.5 and in ASW at pH 8 (A) added with Fe(II) [ $0.1 \text{ mmolL}^{-1}$ ] and  $\text{H}_2\text{O}_2$  [ $10 \text{ mmolL}^{-1}$ ]; (B) added with Fe(III) [ $0.1 \text{ mmolL}^{-1}$ ] and  $\text{H}_2\text{O}_2$  [ $10 \text{ mmolL}^{-1}$ ].

**Fig. 3.** Intermediate compounds formed during phenol photo-transformation in natural seawater: (A) spiked with  $\text{H}_2\text{O}_2$   $10 \text{ mmolL}^{-1}$ ; (B) spiked with  $\text{H}_2\text{O}_2$   $2 \text{ }\mu\text{molL}^{-1}$  and Fe(III)  $0.1 \text{ }\mu\text{molL}^{-1}$ ; (C) spiked with  $\text{H}_2\text{O}_2$   $10 \text{ mmolL}^{-1}$  and Fe(III)  $0.1 \text{ mmolL}^{-1}$ .

Figure 1

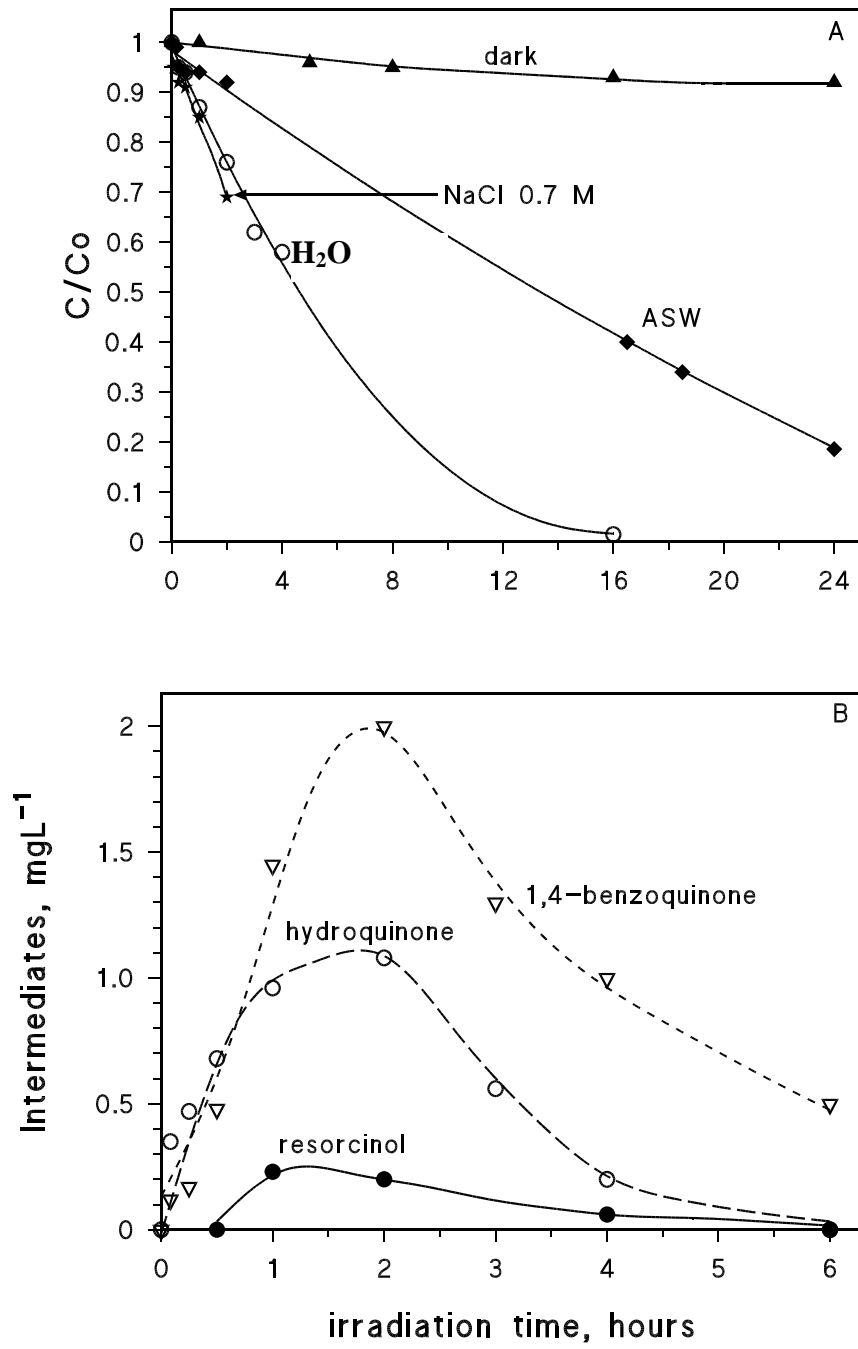
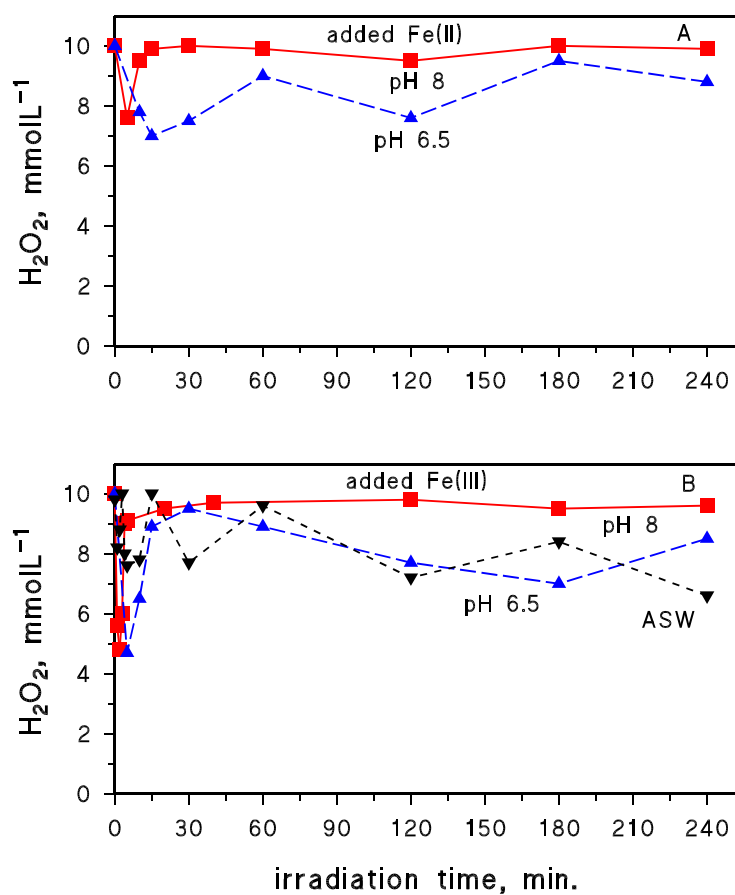


Figure 2



**Figure 3**

