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Role of H_2O_2 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_2O_2 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_2O_2 or iron/H_2O_2 are initially added to artificial seawater (ASW). Fe(II) is easily transformed into Fe(III), assessing that a Fenton reaction (dark, Fe(II)/H_2O_2) does not take place in marine environment, in favour of a photo-activated reaction involving Fe(III) and H_2O_2.

When NSW is spiked with H_2O_2 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_2O_2, 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 disproportion of the $O_2\cdot^-$ radical, formed by a light induced electron transfer process involving oxygen, metal ions and organic chromophores, e.g. humic acids (Baxter and Carey, 1983).

$$2O_2\cdot^- + 2H^+ \rightarrow H_2O_2 + O_2 \tag{1}$$

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_2O_2 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 $\cdot OH$ radical and could then induce the transformation of organic matter; as it is a weak absorber of visible light, $\cdot OH$ 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 H_2O_2 (Fenton reaction) (Rodriguez et al., 2002) or Fe(III) and H_2O_2 (photo-Fenton reaction) (Zepp et al., 1992) are surely primary reactions for $\cdot OH$ 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 H_2O_2 in surface water are found at 10-200 $nmolL^{-1}$ (Price et al. 1992), while the total dissolved iron concentration (Fe(II) and Fe(III)) ranges from 0.01 to 10 $nmolL^{-1}$ (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 disapperance 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 H_2O_2 or Fe(III)/H_2O_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 $mmolL^{-1}$) photo-induced transformation has been investigated in solutions added with H_2O_2 10 $mmolL^{-1}$, Fe(II) (0.1 $mmolL^{-1}$) or Fe(III) (0.1 $mmolL^{-1}$) ions at pH 8 in 0.7 $molL^{-1}$ 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 μm 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 (1×10^{-2} molL^{-1}) at pH 2.8 at a flow rate of 1 mL/min.

Iron (II)/(III) and H_2O_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 5×10^{-6} μmol L^{-1}.

Fe(II) formation has been followed through colorimetry, complexing Fe^{2+} with 1,10-phenanthroline. The absorbance of the complex $[(C_{12}H_{18}N_2)_3Fe]^{2+}$ was measured at 511 nm. The detection limit was 1×10^{-6} μmol 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 Fe(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 H_2O_2 10 mmolL^{-1} were carried out at pH 8 in pure water, in NaCl 0.7 molL^{-1} or artificial seawater (ASW). In the considered times, negligible phenol disappearance occurs in the dark, so excluding a direct phenol oxidation by H_2O_2 and under illumination without H_2O_2 . Conversely, under illumination in the presence of hydrogen peroxide phenol transformation takes place (see Figure 1a), promoted by the ·OH radicals produced through reaction 2.

$$H_2O_2 \xrightarrow{\ h\nu\ } 2 \cdot OH \tag{2}$$

The phenol disappearance as a function of the irradiation time approximated a pseudo-first order law and a rate of 5.63×10^{-7}, 6.03×10^{-7} and 2.17×10^{-7} molL^{-1} min^{-1} in pure water, 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 ·OH radicals by the carbonate ions (King and Farlow, 2000; Calza et al, 2012).

3.1.2 Fe(II)/Fe(III) and H_2O_2

Irradiation of aqueous solution containing phenol and Fe(II) or Fe(III)/H_2O_2 were carried out on: 1) filtered or unfiltered solutions, aimed to discriminate the role of the precipitate iron on the process. At pH>6, Fe(III) is chiefly in the insoluble 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 Fe(II)/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 Fe(II) or Fe(III) and of stirring, with a marginal increase of the rate in unfiltered solutions in the presence of 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 $Fe(II)/H_2O_2$ nor with $Fe(III)/H_2O_2$, 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_2O_2

Table 2 summarises the phenol disappearance rates evaluated in the case of different H_2O_2/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_2O_2 concentration is lower (rates passes from 7.38×10^{-7} $molL^{-1}$ min^{-1} (H_2O_2 0.4 $mmolL^{-1}$) to 4.40×10^{-7} $molL^{-1}min^{-1}$ (H_2O_2 0.1 $mmolL^{-1}$)). A similar trend was followed at pH 8. Conversely, in ASW the phenol disapperance rates are minima and scarcely modified by variation in iron/H_2O_2 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).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad\qquad k_1 \qquad\qquad (3)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + \cdot O_2^- \qquad\qquad k = 13\ (mol^{-1}L\ s^{-1}) \quad (4)$$

$$Fe^{2+} + \cdot O_2^- \xrightarrow{2H+} Fe^{3+} + H_2O_2 \qquad\qquad k = 1.0 \times 10^7 (mol^{-1}Ls^{-1})\ (5)$$

Bautista et al. 2008 report a $k_1 = 76$ $mol^{-1}L$ 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 ($k_1 = 3.1 \times 10^4$ ($mol^{-1}L$ s^{-1}). The formed $\cdot OH$ radicals could then react with iron(II) or hydrogen peroxide (Neta et al., 1988; Buxton et al., 1988) (eq. 6-8):

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \qquad\qquad k = 5.0 \times 10^8 (mol^{-1}Ls^{-1})\ (6)$$

$$\cdot OH + H_2O_2 \rightarrow \cdot HO_2 + H_2O \qquad\qquad k = 2.7 \times 10^7 (mol^{-1}Ls^{-1})\ (7)$$

$$Fe^{2+} + \cdot HO_2 + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad\qquad k=1.2x10^6(mol^{-1}Ls^{-1})\ (8)$$
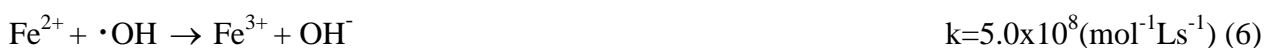
Hydrogen peroxide concentration as a function of the irradiation time is kept almost constant (Figure 2A), suggesting that it could be back-formed according to reaction 9 and undergo a sequence of disappearance/formation reactions. High concentration of hydrogen peroxide are still measured at long irradiation times, so guarantying a continuous $\cdot OH$ radical production.

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \qquad\qquad k=1.1x10^{10}(mol^{-1}Ls^{-1})(9)$$

$$\cdot OH + HO_2^- \rightarrow H_2O + O_2\cdot^- \qquad\qquad k=6.8x10^9(mol^{-1}Ls^{-1})(10)$$
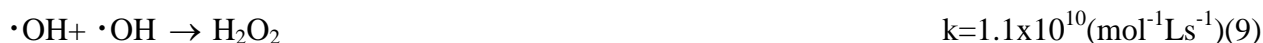
In ASW these radical species ($\cdot O_2^-$ and $\cdot OH$ radicals) could not only react with phenol, but also be reactive for other species, such as Br^-, Cl^- and HCO_3^- (see reaction 11-13) (Petasne and Zika, 1987).

$$\cdot OH + HCO_3^- \rightarrow H_2O + CO_3\cdot^- \qquad\qquad k=8.5x10^6(mol^{-1}Ls^{-1})(11)$$

$$CO_3\cdot^- + H_2O_2 \rightarrow HCO_3^- + HO_2\cdot \qquad\qquad k=8.0x10^5(mol^{-1}Ls^{-1})(12)$$

$$CO_3\cdot^- + HO_2\cdot \rightarrow HCO_3^- + \cdot O_2^- \qquad\qquad k=3.0x10^7(mol^{-1}Ls^{-1})(13)$$

At pH 8, Fe(II) is mostly present as $Fe(CO_3)_2^{2-}$, a species slowly oxidised by H_2O_2; as the $\cdot OH$ 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$_2$O$_2$

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 H_2O_2 concentration ranges from 5 to 10 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 μM). Fe(III) is present under different forms, i.e. colloidal and precipitate forms, here indicated as Fe(III)-L, and leads to the $\cdot OH$ radicals production according to reactions 3 and 14.

$$Fe^{3+}L + h\nu \rightarrow Fe^{2+} + L^+ \tag{14}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{3}$$

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_2O_2 shows a synergic effect. Particularly interesting is the case where Fe(III) is in excess (Fe(III) 0.1 mM/H_2O_2 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_2O_2, 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_2O_2 concentrations , together with their irradiation time formation.

In solution spiked with H_2O_2, hydroquinone and 1,4-benzoquinone are formed as major products and resorcinol (1,3-dihydroxybenzene) at lower amount (maximum at 0.3 mgL^{-1}). Hydroxyl radical quickly reacts with phenol (k=1.4x10^{10} mol^{-1}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_2O_2 produces OH radicals that fast reacts with Cl^- leading to $\cdot Cl$. At high chloride concentration $\cdot Cl$ forms dichloro radical $\cdot Cl_2^-$ (see eq. 15-17 reported below) that should be the predominant radical species (Pelizzetti and Calza, 2002, Santana-Casiano et al., 2005).

$\cdot OH + Cl^- \rightarrow HOCl^-$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $k=4.3 \times 10^9 (mol^{-1}Ls^{-1})$ (15)

$HOCl^- + H^+ \rightarrow Cl\cdot + H_2O$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (16)

$Cl\cdot + Cl^- \leftrightarrow Cl_2\cdot^-$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $k=7.8 \times 10^9 (mol^{-1}Ls^{-1})$ (17)

$Cl_2\cdot^- + Cl_2\cdot^- \rightarrow Cl_3^- + Cl^-$ $\qquad\qquad\qquad\qquad\qquad\qquad$ $k=6.5 \times 10^9 (mol^{-1}Ls^{-1})$ (18)

Two different pathways for phenol transformation are proposed in Scheme 1, involving $Cl_2\cdot^-$ or the $\cdot OH$ radical attack. Both $Cl_2\cdot^-$ and $\cdot OH$ concur for *ortho/para* positions on the aromatic ring of phenol. When $Cl_2\cdot^-$ attacks the ring, chloroderivatives are expected. 3-Chlorophenol (3-CP) is formed through a second $Cl_2\cdot^-$ addition and HCl elimination, while the $\cdot OH$ addition could evolve into 4-chlorophenol or 1,3-dihydroxybenzene (through H_2O 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 OH radical attack, hydroquinone is formed by OH addition followed by H_2O elimination, while the further addition of $Cl_2 \cdot^-$ and H_2O loss leads to the formation of 3-chlorophenol.

Analysing the data of Table 3 shows that with Fe(II)/(III) and H_2O_2 spiked solution only hydroxylated compounds are formed, similarly to the case with H_2O_2 alone but in contrast with the results obtained on solutions spiked with only 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^{-1} and 0.1 mmolL^{-1}, 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_2O_2 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$\cdot$ and Cl$_2\cdot^-$ radicals are strong oxidants (E$°$ $_{Cl\cdot/Cl^-}$ =2.41 V, E$°$ $_{Cl2^-/2Cl^-}$= 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$\cdot$ can rapidly react with phenol, H_2O_2 or Fe(II) (see reactions 21, 25, 27), while for Cl$_2\cdot^-$ the reaction rates are lower, above all toward H_2O_2 (reaction 22) and Fe(II) (reaction 26) (Neta et al., 1988).

$$HOCl + Fe^{2+} \rightarrow Fe(OH)^{3+} + Cl^- \qquad (19)$$

$$Fe(OH)^{3+} + Fe^{2+} \rightarrow 2Fe(OH)^{2+} \qquad (20)$$

$$Cl\cdot + H_2O_2 \rightarrow HO_2\cdot^- + Cl^- + H^+ \qquad k=1.0 \times 10^9 (mol^{-1}L^1s^{-1})(21)$$

$$Cl_2\cdot^- + H_2O_2 \rightarrow HO_2\cdot^- + 2Cl^- + H^+ \qquad k=1.4 \times 10^5 (mol^{-1}Ls^{-1})(22)$$

$$Cl_2\cdot^- + HO_2\cdot^- \rightarrow 2Cl^- + H^+ + O_2 \qquad k=3.1 \times 10^9 (mol^{-1}Ls^{-1})(23)$$

$$Cl_2\cdot^- + O_2\cdot^- \rightarrow 2Cl^- + O_2 \qquad k=2.0 \times 10^9 (mol^{-1}Ls^{-1}) (24)$$

$$Cl\cdot + Fe^{2+} \rightarrow Cl^- + Fe^{3+} \qquad k=5.9 \times 10^9 (mol^{-1}L^1s^{-1})(25)$$

$$Cl_2\cdot^- + Fe^{2+} \rightarrow 2Cl^- + Fe^{3+} \qquad k=5.0 \times 10^6 (mol^{-1}Ls^{-1})(26)$$

$$\Phi\text{-OH} + \cdot Cl \rightarrow C_6H_5O\cdot + HCl \qquad k=2.5 \times 10^{10} (mol^{-1}Ls^{-1})(27)$$

$$\Phi\text{-OH} + Cl_2\cdot^- \rightarrow C_6H_5O\cdot + 2 Cl^- + H^+ \qquad k=3.2 \times 10^8 (mol^{-1}Ls^{-1}) (28)$$
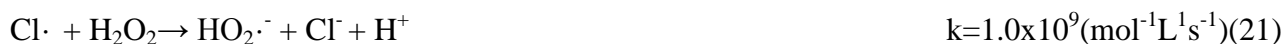
Although the reactivity of ·Cl/ Cl_2·$^-$ toward phenol is high (Neta et al., 1988), the Cl· radical should be rapidly captured by H_2O_2 and Fe(II), preventing the phenolic ring chlorination; the excess of H_2O_2 and its high reactivity toward chlorine radical hinders the Cl_2·$^-$ formation through 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 H_2O_2 no significant amount of halogenated compounds is expected. However, if the formation of Cl· indeed occurs through the reactions 15-16, the absence of halophenols in the presence of high concentration of OH radicals is rather surprising and suggest that, when initially only Fe(II) or Fe(III) are added, halogenation may be induced by a different path, i.e. mediated by iron species.

When Fe(III) is initially added, the intermediates summarized in Table 3 were detected. Similarly to the case with H_2O_2 alone and Fe(II)/H_2O_2, no chlorophenols are formed; again, a scavenging effect by hydrogen peroxide toward 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 H_2O_2/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 H_2O_2

NSW was spiked with phenol, Fe(III) and/or H_2O_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 Fe(III) ($t_{1/2}$ passes from 192 to 38 h) or H_2O_2 ($t_{1/2}$ 7h); when Fe(III) 0.1 mmolL^{-1} and H_2O_2 10 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 H_2O_2, r_{0ASW}=2.17x10^{-7} molL^{-1}min^{-1} and r_{0NSW} = 4.1x10^{-7} molL^{-1}min^{-1}) probably due to the presence of chromophores. i.e. fulvic and humic acids or 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, Fe(II) or Fe(III), an enhanced formation of halophenols was evidenced (Calza et al., 2012). Conversely, when NSW is spiked with 10 mmolL^{-1} H_2O_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 •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 H_2O_2. At low concentration (Fe(III) 0.1 $\mu molL^{-1}$ and H_2O_2 2 $\mu molL^{-1}$) 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 mg L^{-1}). At higher concentrations (Fe(III) 0.1 $mmolL^{-1}$ and H_2O_2 0.1 $mmolL^{-1}$ or 10 $mmolL^{-1}$), 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)/H_2O_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 H_2O_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 •Cl and •Cl_2^- radicals, able to oxidize both H_2O_2 and Fe(II). Fe(II) and hydrogen peroxide act as the main scavengers for chloro radicals; both species are easily oxidised by Cl•, while can slowly react with $Cl_2•^-$. This implies that with a high concentration of

H_2O_2 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^{-1} solution and in artificial seawater (ASW) in the presence of Fe(II)[0.1 mmolL^{-1}] (or Fe(III)[0.1 mmolL^{-1}]) and H$_2$O$_2$ [10 mmolL^{-1}] on stirred (96h) or unstirred solution, filtered (0.45 µm) or unfiltered solution.

		r_0(molL^{-1}min^{-1})	Unstirred	Stirred
Fe(II)	**NaCl 0.7 molL^{-1}**	**Filtered**	8.72×10^{-7}	1.05×10^{-6}
		Unfiltered	1.02×10^{-6}	1.23×10^{-6}
	ASW	**Filtered**	3.32×10^{-7}	2.55×10^{-7}
		Unfiltered	3.67×10^{-7}	3.57×10^{-7}
Fe(III)	**NaCl 0.7 molL^{-1}**	**Filtered**	9.95×10^{-7}	1.24×10^{-6}
		Unfiltered	1.07×10^{-6}	1.19×10^{-6}
	ASW	**Filtered**	3.72×10^{-7}	3.55×10^{-7}
		Unfiltered	3.97×10^{-7}	4.07×10^{-7}

Table 2. Phenol transformation rate in the presence of Fe(II) or Fe(III) and H$_2$O$_2$ (unfiltered and unstirred condition) at pH 8 and 6.5.

	Ratio	**molL^{-1}**	r_0 (molL^{-1} min^{-1})			
			NaCl pH 6.5	**NaCl pH 8**	**ASW**	**NSW**
none	-	-	-	-	-	1.40×10^{-8}
H$_2$O$_2$	-	1×10^{-2}	-	-	2.17×10^{-7}	4.11×10^{-7}
Fe(II)	-	1×10^{-4}	-	1.20×10^{-8}	1.04×10^{-8}	-
Fe(III)	-	1×10^{-4}	-	1.01×10^{-8}	9.20×10^{-9}	2.40×10^{-8}
H$_2$O$_2$/Fe(III)	100	1×10^{-2} /1×10^{-4}	2.57×10^{-6}	1.07×10^{-6}	3.97×10^{-7}	5.20×10^{-7}
	10	1×10^{-6} /1×10^{-7}	-	-	-	4.70×10^{-8}
	0.1	1×10^{-5} / 1×10^{-4}	-	-	8.70×10^{-8}	-
H$_2$O$_2$/Fe(II)	100	1×10^{-2} / 1×10^{-4}	1.93×10^{-6}	1.02×10^{-6}	3.67×10^{-7}	-
	57	4×10^{-3}/ 7×10^{-5}	1.16×10^{-6}	2.86×10^{-7}	-	-
	20	1×10^{-3} / 5×10^{-5}	9.42×10^{-7}	1.76×10^{-7}	1.68×10^{-7}	-
	10	1×10^{-4}/ 1×10^{-5}	4.40×10^{-7}	-	-	-
	4	2×10^{-4}/ 5×10^{-5}	1.02×10^{-6}	1.62×10^{-7}	-	-
	4	4×10^{-4} / 1×10^{-4}	7.38×10^{-7}	-	-	-

Table 3. Intermediates maxima concentration and corresponding irradiation time when Fe(II)/Fe(III) and H_2O_2 are initially added (ND= not detected).

	Ratio, (molL^{-1})	Intermediates	max. concentration (mgL^{-1}) and t_{max} (min.)		
			NaCl pH 6.5	NaCl pH 8	ASW
H_2O_2/Fe(III)	100, 1x10^{-2} /1x10^{-4}	Hydroquinone	1.15 (30')	1.06 (15')	0.86 (60')
		1,4-benzoquinone	3.71 (45')	2.08 (60')	0.52 (120')
		1,3,5-trihydroxybenzene	0.90 (60')	0.92 (120')	0.11 (120')
		1,3-dihydroxybenzene	0.20 (60')	0.16 (120')	ND
	0.1, 1x10^{-5} /1x10^{-4}	Hydroquinone	-	-	0.77 (5')
		1,4-benzoquinone	-	-	0.11 (10')
		4,4'-bisphenol	-	-	0.61 (120')
H_2O_2/Fe(II)	100, 1x10^{-2} /1x10^{-4}	Hydroquinone	0.51 (15')	1.27 (30')	1.13 (30')
		1,4-benzoquinone	3.20 (30')	1.50 (60')	0.11 (180')
		1,3,5-trihydroxybenzene	ND	ND	0.13 (120')
		1,3-dihydroxybenzene	0.13 (60')	0.92 (120')	ND
	57, 4x10^{-3}/7x10^{-5}	Hydroquinone	0.78 (15')	0.89 (45')	-
		1,4-benzoquinone	0.56 (30')	0.68 (60')	-
		1,3,5-trihydroxybenzene	ND	0.48 (120')	-
		1,3-dihydroxybenzene	ND	0.11 (120')	-
	20, 1x10^{-3} /5x10^{-5}	Hydroquinone	0.66 (20')	0.44 (30')	0.38 (60')
		1,4-benzoquinone	0.16 (30')	0.12 (60')	ND
		1,3,5-trihydroxybenzene	ND	ND	0.44 (120')
		1,3-dihydroxybenzene	ND	ND	ND
	10, 1x10^{-4}/1x10^{-5}	Hydroquinone	0.44 (10')	-	-
		1,4- benzoquinone	0.37 (30')	-	-
		1,3,5-trihydroxybenzene	0.51 (60')	-	-
		1,3-dihydroxybenzene	0.17 (30')	-	-
	4, 2x10^{-4}/5x10^{-5}	Hydroquinone	0.32 (15')	0.41 (30')	-
		1,4-benzoquinone	0.15 (30')	0.20 (120')	-
		1,3,5-trihydroxybenzene	ND	ND	-
		4,4'-bisphenol	ND	0.65 (240')	-
	4, 4x10^{-4} /1x10^{-4}	Hydroquinone	0.38 (15')	-	-
		1,4-benzoquinone	0.17 (60')	-	-

Fig. 1. Phenol disapperance at pH 8 under a variety of conditions as a function of the irradiation time in the presence of H_2O_2 [10 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. H_2O_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 m molL^{-1}] and H_2O_2 [10 mmolL^{-1}]; (B) added with Fe(III) [0.1 mmolL^{-1}] and H_2O_2 [10 mmolL^{-1}].

Fig. 3. Intermediate compounds formed during phenol photo-transformation in natural seawater: (A) spiked with H_2O_2 10 mmolL^{-1}; (B) spiked with H_2O_2 2 μmolL^{-1} and Fe(III) 0.1 μmolL^{-1}; (C) spiked with H_2O_2 10 mmolL^{-1} and Fe(III) 0.1 mmolL^{-1}.

Figure 1

Figure 2

Figure 3