



Influence of chloride and carbonates on the reactivity of activated persulfate

Lars R. Bennedsen^{a,b}, Jens Muff^a, Erik G. Søgaard^{a,*}

^a Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Niels Bohrs Vej 8, DK-6700 Esbjerg, Denmark

^b Rambøll Denmark A/S, Lystholt Allé 10, DK-7100 Vejle, Denmark

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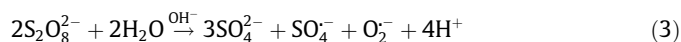
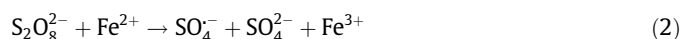
ABSTRACT

Chloride and carbonates have the potential to impact pathway, kinetics, and efficiency of oxidation reactions, both as radical scavengers and as metal complexing agents. Traditionally, it is assumed that they have an overall negative impact on the activated persulfate performance. This study investigated the influence of carbonates and chloride on the reactivity of persulfate for three different activation techniques to produce reactive free sulfate radicals; heat, alkaline and iron activation. By using *p*-nitrosodimethylaniline as model target compound, it was demonstrated that iron activation at neutral pH was not affected by Cl^- or HCO_3^- , alkaline activation was enhanced by Cl^- and even more by CO_3^{2-} , and heat activation was enhanced by Cl^- , and no effect from HCO_3^- was observed. At pH 2 destruction of perchloroethylene by iron activated persulfate was significantly affected by chloride. Reaction rates decreased, but the overall oxidation efficiency was unaffected up to 28 mM Cl^- . The effect of chloride and carbonates is caused by direct attack of produced reactive chlorine, or carbonate species or by catalysis of the propagation reactions resulting in more sulfate radicals. These results show that carbonate and chloride might play an important role in activated persulfate applications and should not strictly be considered as scavengers.

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1. Introduction

Peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$) is a novel oxidant used widely for remediation of organic contaminants in soil and groundwater with in situ chemical oxidation (ISCO) (Tsitonaki et al., 2010). To enhance the oxidation strength, peroxodisulfate (E° 2.01 V) needs to be activated in order to produce free sulfate radicals ($\text{SO}_4^{\cdot-}$) with a standard reduction potential of 2.6 V (Huie et al., 1991). This process is referred to as activated persulfate. As with hydroxyl radicals, sulfate radicals are short lived (Banerjee and Konar, 1984) and highly reactive. Activation of persulfate can be accomplished by heat (reaction (1)) (House, 1962; Huang et al., 2002, 2005; Liang et al., 2003), metals (reaction (2)) (Kolthoff and Miller, 1951; Anipsitakis and Dionysiou, 2004), or ultraviolet light (Neta et al., 1977). These mechanisms are well described. In full scale ISCO applications more recent activation methods include strong alkaline pH (reaction (3)) (Buxton et al., 1988) or addition of hydrogen peroxide (Crimi and Taylor, 2007). At high pH sulfate radicals will form hydroxyl radicals according to reaction (4) (Peyton, 1993).



The primary limitation of activated persulfate for ISCO is the minimal knowledge of its reaction pathways in the subsurface (Furman et al., 2010). One factor resulting in reduced reaction efficiency and effectiveness is reactions between the produced radicals and naturally occurring and anthropogenic non-target chemical species present in soil and aquifer material. These reactions are often referred to as scavenging reactions. Scavenger ions are one of the most common factors limiting the oxidation efficiency in ISCO and especially chloride and carbonates (carbonate and hydrogen carbonate anions) have the potential to impact pathway, kinetics, and efficiency of oxidation reactions both as radical scavengers and as metal complexing agents (Lipczynskakochany et al., 1995; Beltran et al., 1998; Valentine and Wang, 1998; De Laat et al., 2004). Carbonates and chloride are also believed to adsorb and inactivate catalytic and scavenging sites such as iron oxides (Miller, 1995) and form aqueous complexes or solid precipitates with metals or mineral surfaces (Valentine and Wang, 1998; De Laat et al., 2004).

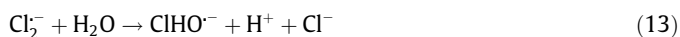
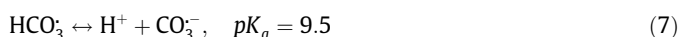
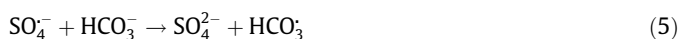
Experiments with modified Fenton's reagent showed that these complexation processes decreased the rate of contaminant degradation as well as oxidant decomposition and effectively inhibited the reaction (Sung and Morgan, 1980; Lipczynskakochany et al., 1995; Beltran et al., 1998; De Laat et al., 2004), whereas it was shown that

* Corresponding author. Tel.: +45 99407622; fax: +45 99407710.

E-mail address: egs@bio.aau.dk (E.G. Søgaard).

the overall efficiency was not decreased even though the reaction rate was decreased (Valentine and Wang, 1998). Carbonates have also been showed to reduce rates of contaminant degradation and oxidant decomposition for activated persulfate (Peyton, 1993; Huang et al., 2002; Liang et al., 2003). The adverse impact of the carbonates on activated persulfate systems increases with increasing pH (Peyton, 1993; Liang et al., 2006).

Besides the complexation processes, chloride and hydrogen carbonate can also form radicals through reactions with reactive species in activated persulfate systems (Buxton et al., 1988; Huie et al., 1991; Zuo et al., 1999; Kiwi et al., 2000; Yu and Barker, 2003; Liang et al., 2006):



The reactivity of these radicals with organic contaminants or participation in chain propagation reactions is not well understood, but it is traditionally assumed that they have an overall negative impact on the activated persulfate performance (Huang et al., 2002; Liang et al., 2006). The carbonate radical ($\text{CO}_3^{\cdot-}$) generated by the reaction (6) is reported to yield a reduction potential E° ($\text{CO}_3^{\cdot-}$, $\text{H}^+/\text{HCO}_3^-$) of 1.63 V at pH 8.4 and 1.59 V at pH 12 (Zuo et al., 1999). They was shown to be strong enough to degrade PAHs (Umschlag and Herrmann, 1999). It has also been suggested that chloride radicals can participate in propagation reactions with oxidants and thereby not be entirely unproductive (Yu et al., 2004). These findings indicate that carbonate and chloride radicals might play an important role in activated persulfate applications and should not strictly be considered as a scavenger.

The concentration of chloride needed to decrease the oxidation efficiency of heat activated persulfate at 130 °C was shown to be more than 20 mM Cl^- (Aiken, 1992). Other studies with persulfate at 20 °C at neutral pH showed that only chloride levels above 200 mM affected the degradation of trichloroethylene and that hydrogen carbonate up to 9.2 mM had no influence (Liang et al., 2006). High concentrations (>100 mM) of chloride have also been reported to result in formation of halogenated by-products (Aiken, 1992). Even hexachloroethane has been observed to be formed during treatment of perchloroethylene (PCE) as a result of the reactive chloride species (Waldemer et al., 2007).

The objective of the present study was to investigate and compare the influence of chloride and hydrogen carbonate on the reactivity of peroxodisulfate for three different activation methods; heat, iron and alkaline (reactions (1)–(3)). The organic dyestuff *p*-nitrosodimethylaniline (RNO) has been chosen as the primary contaminant model compound. RNO has been widely used as an easily detectable probe compound for detection of particular hydroxyl radicals in aqueous oxidation studies since the second order rate constant for reactions between RNO and hydroxyl radicals is $1.25 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Baxendale and Khan, 1969). That will make

the reaction become controlled by diffusion (rate constant for diffusion is about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$). RNO is also bleached through reaction with other strong oxidants (Muff et al., 2009) including sulfate radicals (Simonsen et al., 2010), but does not react with singlet oxygen, superoxide anions or other peroxy compounds (Kraljic and Trumbore, 1965; Comninellis, 1994; Holt et al., 2003). The influence of chloride on degradation of PCE by chelated iron activated persulfate was also tested, since this is a compound often treated by ISCO, and high concentrations of chloride can be produced through the oxidation of high concentrations of PCE, which might inhibit the oxidation.

2. Materials and methods

2.1. Chemicals

Analytical grades of ferrous iron sulfate heptahydrate (>99%), citric acid (>99%), sodium peroxodisulfate (>99% $\text{Na}_2\text{S}_2\text{O}_8$), potassium iodide (>99.5%), extra pure n-pentane (95%), RNO (>95% $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$), PCE (>99%), sodium hydrogen carbonate (100%), disodium hydrogen phosphate (>99%), sodium dihydrogen phosphate monohydrate (>99%), sodium hydroxide (100%) and sodium chloride (>99.5%) were purchased from Merck; Fluka or Sigma Aldrich. Demineralized water was used for all tests.

Stock solutions of 0.05 mM RNO solutions were prepared by dissolving 0.150 g RNO in 2000 mL demineralized water. 14.2 g of Na_2HPO_4 and 13.8 g $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was added (pH 6.72) to solutions used for heat and iron activation.

2.2. Analytical methods

Absorbance of RNO was measured continuously using a UV/Vis spectrophotometer (Varian Cary 50 Conc) at a wavelength of 440 nm. The calibration curve at 440 nm was linear in the investigated area from 0 to 0.050 mM. PCE was extracted from 3 mL water samples into 3 mL pentane with an internal standard and analyzed by gas chromatography (Varian 3800) equipped with Mass Spectrometer (Varian Saturn 2000 GC/MS/MS) which use a Varian factor Four capillary column (VF-5 ms 20m \times 0.15 mm id DF = 0.15). Peroxodisulfate was determined by a spectrophotometric method proposed by Liang et al. (2008) using a UV/Vis spectrophotometer (Varian Cary 50 Conc). Monitoring of pH was performed using a Radiometer PHM210 pH meter.

2.3. Test setup RNO (heat, alkaline and iron activation)

All tests were performed in a 150 mL continuously stirred glass reactor placed on a heating element. All temperatures was measured and regulated automatically and kept constant at ± 0.2 °C. 100 mL RNO stock solution was heated to the desired temperature. NaCl , NaHCO_3 or Na_2CO_3 was dissolved into the solution and for the alkaline activation 0.220 mL 9 M NaOH was added to obtain a concentration of 20 mM and a pH of 12. At last 0.250 mL 2 M persulfate was added to obtain a concentration of 5 mM in the reactor and the timing was started. For the iron activated reactors 2.5 mL of pre mixed 16 mM citric acid and 80 mM iron sulfate was added after the persulfate to initiate reactions. Absorbance at 440 nm or spectra from 200 to 600 nm was recorded and logged automatically as a function of time by recirculating a small side stream through a quartz flow cuvette placed in the spectrophotometer.

2.4. Test setup PCE (iron activation)

These tests were performed in closed 100 mL volumetric flasks. Each flask received 8.0 mL 50 mM $\text{Na}_2\text{S}_2\text{O}_8$, a known volume of

1.410 mM NaCl solution, 40 mL 0.5 mM PCE solution and then filled with water to 95 mL. Reaction and timing was started by adding 5 mL of chelated iron catalyst containing 8 mM citric acid and 40 mM FeSO_4 . The resulting concentrations were (in mM) 0.2 PCE, 0.4 citric acid, 2 FeSO_4 and 4 $\text{Na}_2\text{S}_2\text{O}_8$, and different concentrations of chloride mixed in demineralized water. After 60 min of reaction a 3 mL sample was collected and immediately put into pentane to stop further degradation of PCE and residual persulfate concentration was measured.

3. Results and discussion

3.1. RNO as model compound

Heating the 0.05 mM RNO stock solution to 80 °C for 120 min did not change the absorbance as a function of temperature and time, and RNO is therefore considered thermally stable. Also, the absorbance of RNO was constant in the presence of persulfate at 20 °C, indicating that activation is needed to bleach RNO. When the buffered RNO stock solution was heated in the presence of persulfate, the absorbance decreased significantly with time due to the heat activation, with an increasing rate at increasing temperature as presented in Fig. 1a. pH remained constant at 6.72 throughout the tests and less than 5% decrease in persulfate concentration was observed and is considered constant. The rate of reaction seems very close to zero order with small deviations in the beginning, which might be explained by an autocatalytic effect increasing the rate of reaction/bleaching over time or by a matrix effect in the analytical method due to intermediates absorbing light at the analytical wavelength. At the end of the runs the data approached a first order reaction (data not shown). Fig. 1b shows an example of the absorbance spectrum of RNO over time. It is clearly seen that the maximum absorbance peak of RNO at 440 nm, caused by a system of conjugated double bonds in the molecule, decreases over time. This is ascribed to an oxidation of the nitroso group to a nitro group fixing the conjugated double bond structure. RNO is considered an applicable model compound, since increased sulfate radical production increased the rate of bleaching and the absorbance of RNO without persulfate was unaffected by high temperatures and high pH. At pH below 6, the absorbance of RNO at 440 nm decreased significantly due to protonation.

3.2. Heat activated persulfate

From the results presented in Fig. 1, it was decided to use 65 °C for activation of persulfate to investigate the effects of hydrogen carbonate and chloride. Bleaching of the phosphate buffered RNO solutions treated with 5 mM $\text{S}_2\text{O}_8^{2-}$ at 65 °C after additions of hydrogen carbonate and chloride are shown in Figs. 2 and 3. Hydrogen carbonate up to 100 mM did not affect the bleaching process or absorbance spectra of the process compared to the control with no hydrogen carbonate. On the contrary, chloride affected the bleaching process by significantly enhancing the initial reaction rate compared to the control reactor with no chloride (Fig. 3a). Some optimum exists in the chloride concentrations between 1 and 50 mM since the time to obtain a 50% reduction in RNO concentration increased in the following sequence 10, 50, 1, 0, 200, 400 mM Cl^- . This shows that higher concentrations of chloride will increase the bleaching rate, but at too high concentrations the NaCl will have an inhibiting effect. These results show that chloride cannot be considered purely as a scavenger. Different scenarios can explain this; reactive chlorine species capable of bleaching RNO are produced through reactions with sulfate radicals (reactions (8)–(13)) or produced chlorine radicals can participate in propagation reactions with persulfate and increase the overall

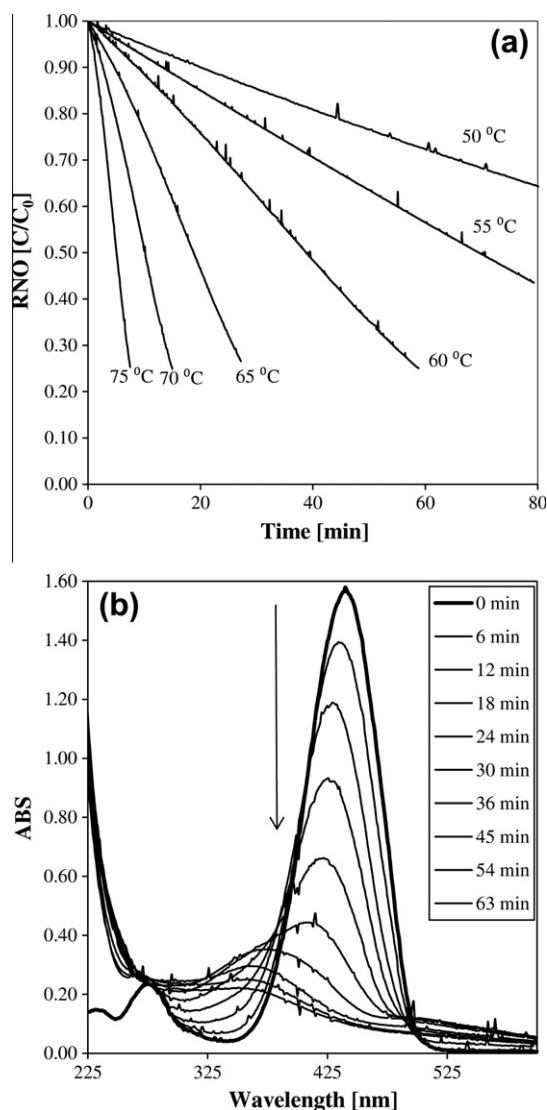


Fig. 1. (a) Bleaching of a phosphate buffered 0.05 mM RNO solution measured as absorption at 440 nm as a function of temperature and time with initial concentrations of 5 mM $\text{S}_2\text{O}_8^{2-}$. The minor divergences seen on some of the curves are due to small bubbles in the analytical system. (b) Absorbance spectra for the test conducted at 65 °C as a function of time.

production of sulfate radicals. Another possible influence by the presence of chloride is a decrease in recombination frequency of the sulfate radicals (reverse of reaction (1)) through reaction (8). This reaction produces chlorine radicals potentially capable of RNO bleaching. This influence might be dominant at low chloride concentration, whereas an overall inhibitory influence is seen at higher concentrations where the chlorine radicals may react further on with chloride (reaction (9)) producing presumed less bleaching efficient Cl_2^- . Only the reactor containing 10 mM chloride was more effective compared to the control over the entire 60 min, which is because of the observed increase in bleaching rate over time when chloride was not present. When the absorbance spectra for the control (Fig. 1b) and the reactor containing 10 mM chloride (Fig. 3b) are compared, it can be seen that the presence of chloride inhibits the formation of products absorbing in the 350–400 nm range. Formation of these products is also the reason why the absorbance maximum is shifting towards lower wavelengths in the control. This difference in reaction products indicates that the reactive species bleaching RNO are different.

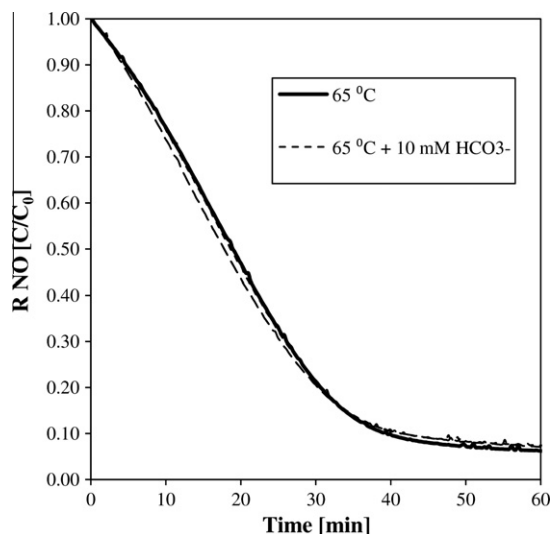


Fig. 2. Bleaching of a phosphate buffered 0.05 mM RNO solution measured as absorption at 440 nm as a function of hydrogen carbonate concentration and time with initial concentrations of 5 mM $S_2O_8^{2-}$ at 65 °C.

3.3. Alkaline activated persulfate

RNO bleaching was obtained by raising pH to 12.4 by adding 20 mM NaOH, which will activate the persulfate according to reaction (3). pH in the reactor containing 100 mM Na_2CO_3 only reached 12.2 after NaOH addition. The results are presented in Fig. 4 and showed that chloride at concentrations from 1 to 400 mM enhanced the bleaching of RNO and that presence of carbonate in concentrations from 10 to 100 mM enhanced the rate of bleaching even more. Again, the persulfate concentration can be assumed constant, since no significant changes (<5%) could be measured over the 4 h reaction period. For the alkaline activation, there were no differences in absorption spectra with time for the control and the reactors with chloride (data not shown), indicating that the reactive species involved in the bleaching could be the same. Because of the high pH, hydroxyl radicals will play a significant role, according to reaction (4). The same applied for carbonate. Therefore, chloride and carbonate will not act as a scavenger during alkaline persulfate activation, but will both enhance the bleaching rate of RNO through production or reactive chlorine or carbonate species as presented in reactions (5)–(13) or via an enhancement of the propagation reactions. This only applies to RNO and more studies with other contaminants needs to be performed to evaluate how chloride and carbonate affect degradation of these compounds.

3.4. Iron activated persulfate

Bleaching of RNO was also tested with iron activated persulfate and different concentrations of chloride and hydrogen carbonate. The phosphate buffer kept pH constant at 6.6 in all tests, except the reactor with 100 mM HCO_3^- where pH was 7.0. Measurements of persulfate with time in all reactors showed that the concentration was reduced by min 20–25% within the first 2 min of reaction, which was caused by a rapid oxidation of Fe(II), as shown in reaction (2). After this initial rapid reaction, persulfate concentrations were almost stable with only a small consumption of persulfate and in all reactors the concentrations after 60 min with a total consumption of persulfate of 25–30%, see Fig. 5b. Chloride was added in concentrations of 5 and 50 mM. Higher concentrations of chloride caused the solution to become turbid and absorbance could not be measured. The RNO measurements are presented in Fig. 5,

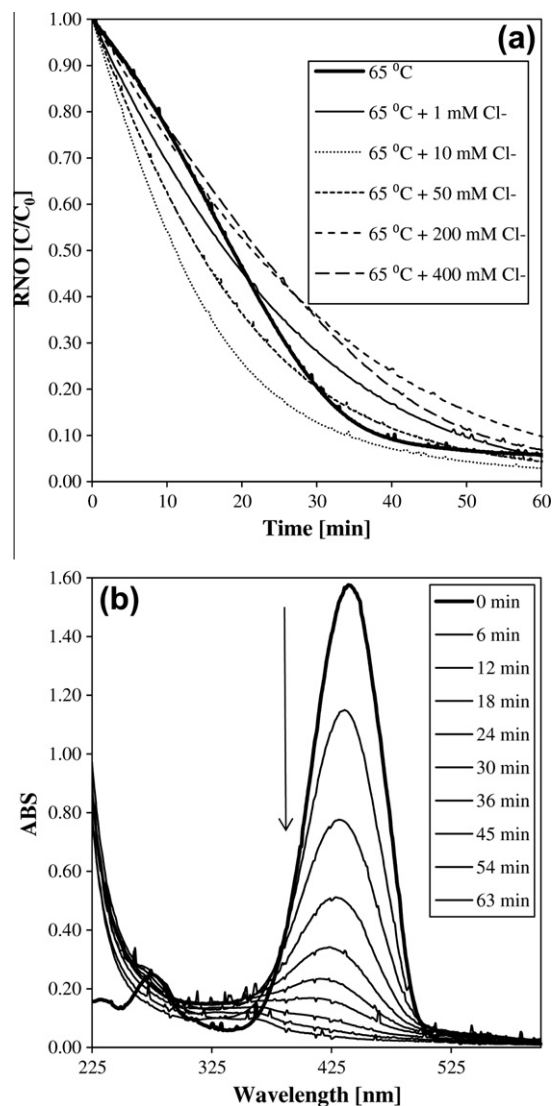


Fig. 3. (a) Bleaching of a phosphate buffered 0.05 mM RNO solution measured as absorption at 440 nm as a function of chloride concentration and time with initial concentrations of 5 mM $S_2O_8^{2-}$ at 65 °C. (b) Absorbance spectra for the solution containing 10 mM chloride as a function of time.

where it is seen that the initial fast consumption of persulfate also resulted in a very rapid bleaching rate within the first couple of minutes. Actually, 50% bleaching happened in 30 s, which is described to activation by easily accessible free Fe(II) (reaction (2)). The bleaching continued at a slower rate likely through activation by the chelated part of the added Fe(II). Chelated iron activation is assumed more effective with less scavenging by the Fe(II) (reaction (14)) compared to reactions happening within the first minutes where concentrations of sulfate radicals and soluble free Fe(II) were high:



The RNO bleaching and persulfate consumption show that chloride or hydrogen carbonate does not influence significantly on these processes, when iron activation is applied at neutral pH.

3.5. PCE degradation through iron activation

The above results have shown that chloride can affect the reaction rate for activated persulfate, but at neutral pH the iron activated

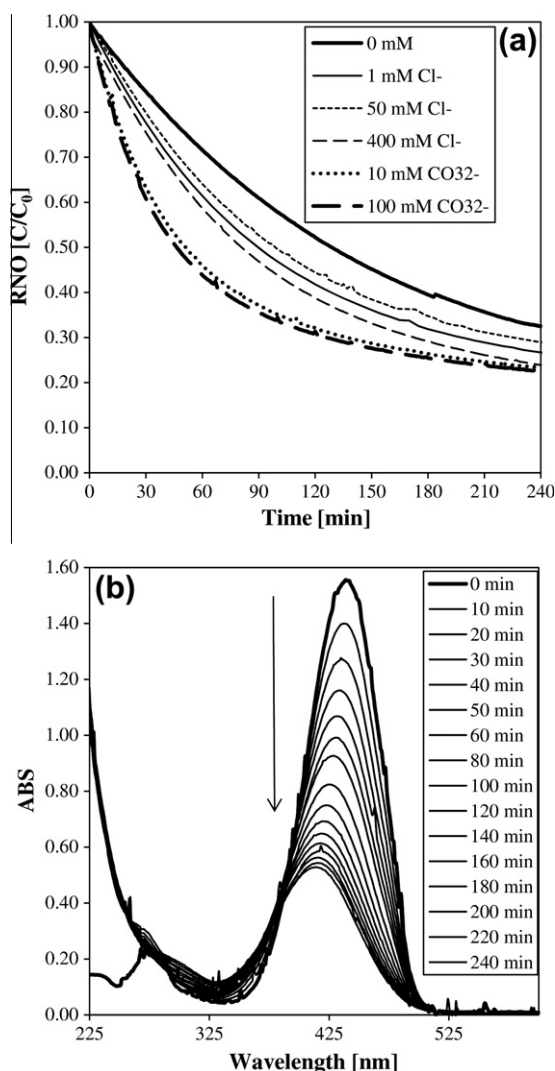


Fig. 4. (a) Bleaching of a 0.05 mM RNO solution measured as absorption at 440 nm as a function of chloride and hydrogen carbonate concentrations and time with initial concentrations of 5 mM $S_2O_8^{2-}$ and 20 mM NaOH at pH 12.4. (b) Absorbance spectra for the solution containing 400 mM as a function of time.

persulfate was not affected by chloride. The tests were repeated in un-buffered solutions containing PCE as a target compound instead of RNO. The concentrations of $S_2O_8^{2-}/Fe^{2+}/citric\ acid/PCE$ were 4/2/0.4/0.2 mM respectively in the reactors used for this test and results after 60 min of reaction are presented in Fig. 6. pH remained stable during reactions at 2.5–2.6 in all reactors. This enhanced the availability of iron compared to the neutral pH used for RNO bleaching in Section 3.4. From Fig. 6 it is seen that PCE was fully degraded, when no chloride was present and degradation decreased exponentially with increasing chloride concentrations. However, the consumption of persulfate also decreased and for 7, 14, 21 and 28 mM Cl^- the molar ratio between degraded PCE and consumed persulfate was constantly 8–9. Above 28 mM Cl^- , the results varied and no precise conclusion can be drawn. The constant ratio observed indicated that the chloride ions did not scavenge the produced reactive species (sulfate radicals) causing the degradation of PCE. The results documented that increasing concentrations of chloride will decrease the oxidation rate, but not affect the overall oxidation efficiency. The decreased oxidation rate is assumed to be caused by chloride acting as an iron complexing agent (De Laat et al., 2004) minimizing the availability of the already chelated iron (citrate-Fe) and the free Fe(II) in the solution. It has also been demonstrated by others that organic acids, such as citric acid, used for pH control and chelating

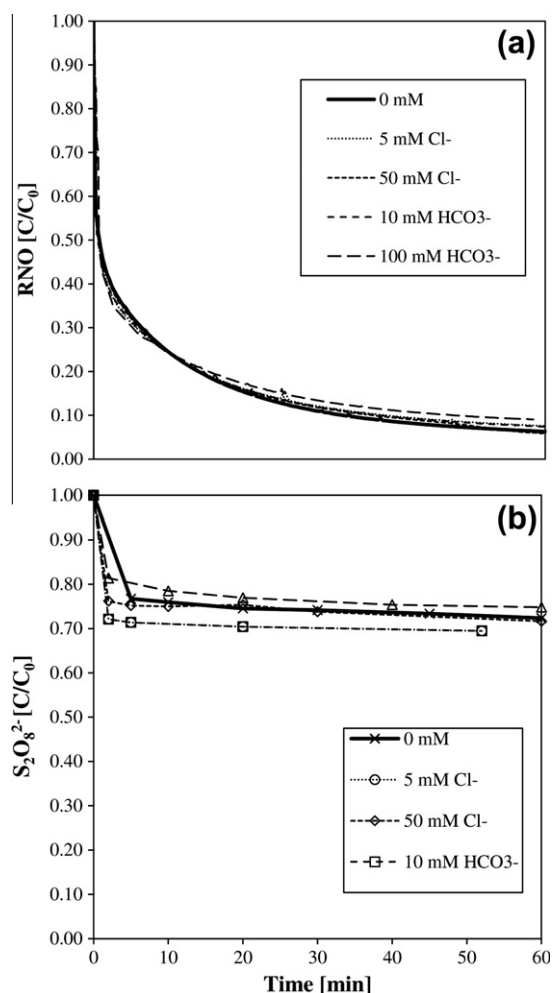


Fig. 5. (a) Bleaching of a phosphate buffered 0.05 mM RNO solution measured as absorption at 440 nm as a function of chloride and hydrogen carbonate concentrations and time with initial concentrations of 5 mM $S_2O_8^{2-}$, 2 mM Fe^{2+} and 0.4 mM citric acid. (b) Concentrations of persulfate.

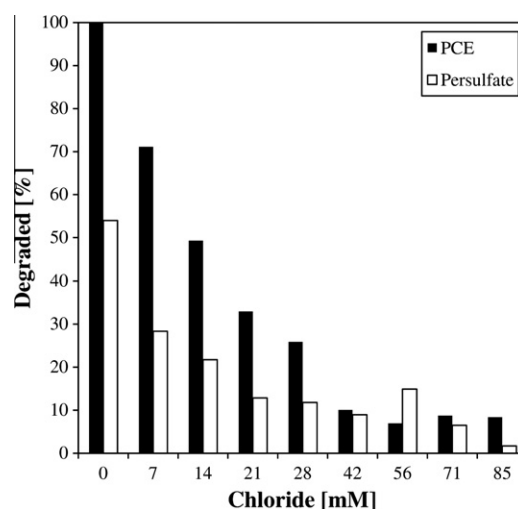


Fig. 6. Degradation of PCE by chelated iron activated persulfate as a function of chloride concentration after 60 min of reaction. Consumption of persulfate is also shown.

agent in chemical oxidation can inhibit organic compound decomposition by scavenging the radicals (Voelker and Sulzberger,

1996). This effect could not be observed in the present study. Results are different from the RNO results presented in Fig. 5, which is ascribed the low pH that will maintain iron in solution.

4. Conclusions

The influence of carbonates and chloride on the reactivity of activated persulfate was investigated and compared for three different activation techniques normally used to produced sulfate radicals; these were addition of heat, use alkaline conditions and activation by Fe(II). By using RNO and PCE as model target compounds, the following conclusions were drawn:

By increasing temperature to 65 °C at neutral pH we found no effects from adding hydrogen carbonate up to 100 mM. Contrary to this low concentrations of chloride (1 mM) could enhance the degradation rate of RNO. By alkaline activation 5–50 mM chloride and 10–100 mM carbonate could increase the rate of bleaching of RNO. By using iron activation no effect of chloride or hydrogen carbonate on the bleaching of RNO was observed at neutral pH. However, at pH 2.5 the rate of PCE degradation was significantly decreased at increasing chloride concentrations, but the overall oxidation efficiency was unaffected up to 28 mM of chloride.

Different activation mechanisms are affected differently by chloride and carbonates.

The effect enhanced bleaching observed when chloride or carbonates are present can be caused by direct attack of produced reactive chlorine or carbonate species produced by oxidation with sulfate radicals. It is also possible that the produced reactive chlorine or carbonate species can catalyze the propagation reactions resulting in more sulfate radicals.

Different activation mechanisms are affected differently by chloride and carbonates.

The effect enhanced bleaching observed when chloride or carbonates are present can be caused by direct attack of produced reactive chlorine or carbonate species produced by oxidation with sulfate radicals. It is also possible that the produced reactive chlorine or carbonate species can catalyze the propagation reactions resulting in more sulfate radicals.

These results show that carbonate and chloride might play an important role in activated persulfate applications and should not strictly be considered as a scavenger. Better understanding of the influence of chloride and carbonates might make it possible to minimize their negative impacts and maybe even enhance their potential positive aspects.

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