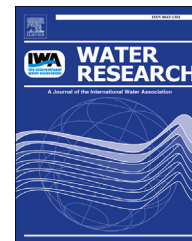




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Sulfate radical-based water treatment in presence of chloride: Formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and influence of bicarbonate

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ABSTRACT

Sulfate radical ($\text{SO}_4^{\bullet-}$) based oxidation is discussed as a potential water treatment option and is already used in ground water remediation. However, the complex $\text{SO}_4^{\bullet-}$ chemistry in various matrices is poorly understood. In that regard, the fast reaction of $\text{SO}_4^{\bullet-}$ with Cl^- is of high importance since Cl^- belongs to the main constituents in aqueous environments. This reaction yields chlorine atoms (Cl^\bullet) as primary products. Cl^\bullet initiate a cascade of subsequent reactions with a pH dependent product pattern. At low pH (<5) formation of chlorine derived oxidation products such as chlorate (ClO_3^-) is favoured. This is undesired because ClO_3^- may reveal adverse effects on the environment and human health. At pH > 5 Cl^\bullet mainly react with water yielding hydroxyl radicals. Thus, at moderate Cl^- concentrations (mM range) the $\text{SO}_4^{\bullet-}$ -based process may be converted into a conventional (hydroxyl radical -based) advanced oxidation process. The conversion of $\text{SO}_4^{\bullet-}$ into $^\bullet\text{OH}$, however, is interrupted in presence of bicarbonate by scavenging of Cl^\bullet .

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1. Introduction

Highly reactive sulfate radicals ($\text{SO}_4^{\bullet-}$) are principally capable of oxidizing pollutants such as trichloroethene (Liang et al., 2008), tert-butylmethylether (George et al., 2001), chlorinated ethenes (Waldemer et al., 2007), and pharmaceuticals such as endosulfan (Shah et al., 2013) and different derivatives of phenol

(Anipsitakis et al., 2006; Fang et al., 2013; Lin et al., 2011). Thus, $\text{SO}_4^{\bullet-}$ based oxidation is frequently discussed as an alternative oxidative treatment option for pollutant control in water treatment. Conventional radical-based processes rely on nonselective hydroxyl radicals ($^\bullet\text{OH}$) (advanced oxidation process (AOP)). Due to the different nature of $^\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, $\text{SO}_4^{\bullet-}$ may have the potential to overcome limitations of a conventional AOP. A case in point are perfluorinated

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compounds which are inert towards $\bullet\text{OH}$ (Hori et al., 2004; Schröder and Meesters, 2005) but slightly reactive towards $\text{SO}_4^{\bullet-}$ (Hori et al., 2004).

$\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ can be formed in an analogous way by using H_2O_2 (for $\bullet\text{OH}$) and $\text{S}_2\text{O}_8^{2-}$ (for $\text{SO}_4^{\bullet-}$) as radical precursors. For example, the chemical reduction of H_2O_2 by Fe^{2+} yields $\bullet\text{OH}$, which works in a similar way in the reaction of $\text{S}_2\text{O}_8^{2-}$ with Fe^{2+} (Siegrist et al., 2011). The same applies for UVC-photolysis, either of H_2O_2 (UV/ H_2O_2) yielding $\bullet\text{OH}$ or of $\text{S}_2\text{O}_8^{2-}$ (UV/ $\text{S}_2\text{O}_8^{2-}$) yielding $\text{SO}_4^{\bullet-}$ (Herrmann, 2007) (absorption coefficients and quantum yields see results and discussion). Thus, water treatment and remediation processes based on H_2O_2 could be retrofitted to a $\text{SO}_4^{\bullet-}$ -based process by addition of $\text{S}_2\text{O}_8^{2-}$ instead of H_2O_2 . In case of photochemical processes, UV/ $\text{S}_2\text{O}_8^{2-}$ might reveal some advantages over UV/ H_2O_2 due to higher quantum yields of radical formation (see result and discussion). Furthermore handling of $\text{S}_2\text{O}_8^{2-}$ (powder) might be easier than that of H_2O_2 (solution).

An important aspect in radical-based processes is related to the main water matrix constituents. In advanced oxidation processes these compounds typically comprise dissolved organic carbon (DOC) and HCO_3^- (von Gunten, 2003a). In that regard, Méndez-Díaz et al. described a remarkably different behaviour of $\text{SO}_4^{\bullet-}$ compared with $\bullet\text{OH}$ in presence of DOC. The authors indicated that in presence of fulvic acids as representative for organic matter, dodecylbenzenesulfonate is degraded faster in UV/ $\text{S}_2\text{O}_8^{2-}$ than in UV/ H_2O_2 , which has been explained by a weaker scavenging of $\text{SO}_4^{\bullet-}$ than $\bullet\text{OH}$ by fulvic acids (Méndez-Díaz et al., 2010). Another important reaction in $\text{SO}_4^{\bullet-}$ -based processes is $\text{SO}_4^{\bullet-}$ with Cl^- ($k = 2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (McElroy, 1990)). The Cl^- concentration in natural waters displays a large range from very low levels (e.g., several Canadian lakes and rivers 0.8–10 mg L^{-1} (0.024–0.3 mM) (Canada, 1978), to concentrations in the mM level (e.g., rivers in the UK 11–42 mg L^{-1} (0.32–1.5 mM) (Fawell et al., 2003). The 95% quantil of chloride concentration in >600 environmental samples from different German ground-drinking- and surface waters was determined by Kowal et al., to be 1.69 mM (Kowal et al., 2012). As a rough approach the fraction of $\text{SO}_4^{\bullet-}$ reacting with Cl^- can be calculated by Equation (1) if the kinetic constants for reactions with other main constituents are known (i.e., DOC and HCO_3^- (Schwarzenbach et al., 2003)).

(Dogliotti, 1967; Huie and Clifton, 1990), $k(\text{CO}_3^{2-}) = 4.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Padmaja et al., 1993)). It can be assumed that the second order reaction rate constant of the reaction of $\text{SO}_4^{\bullet-}$ with DOC is somewhat similar if not smaller than $k(\bullet\text{OH} + \text{DOC})$ as indicated by Méndez-Díaz et al. (see above) (Méndez-Díaz et al., 2010). The reaction rate for $\bullet\text{OH}$ with natural DOC was determined for several surface waters ranging between $1.4 \times 10^4 \text{ L mg}^{-1} \text{ s}^{-1}$ and $6.8 \times 10^4 \text{ L mg}^{-1} \text{ s}^{-1}$ (Brezonik and Fulkerson-Brekken, 1998 and references therein). Based on such literature data, Schwarzenbach et al. suggest a value of $k(\text{DOC} + \bullet\text{OH}) \approx 2.5 \times 10^4 \text{ L mg}^{-1} \text{ s}^{-1}$ (Schwarzenbach et al., 2003)). Using this reaction rate for the reaction of $\text{SO}_4^{\bullet-}$ with DOC seems sufficient for a rough estimation of the minimal fraction of $\text{SO}_4^{\bullet-}$ reacting with Cl^- .

As will be shown in the experimental part, a sample from River Ruhr, which is used for drinking water production contained 1.9 mg L^{-1} DOC, 1.57 mM HCO_3^- and 0.78 mM Cl^- (Results and Discussion). Equation (1) reveals that in this water $\approx 77\%$ of $\text{SO}_4^{\bullet-}$ react with Cl^- , thus direct reactions of $\text{SO}_4^{\bullet-}$ with pollutants are strongly diminished. However, this reaction gives rise to chlorine atoms ($\text{Cl}\bullet$) as primary products that induce a sequence of reactions involving water and Cl^- as main reactants. In the literature one can find basically three different results with regard to the influence of Cl^- on $\text{SO}_4^{\bullet-}$ -based oxidation: (1) Formation of $\bullet\text{OH}$ (Buxton et al., 1998a, 1999; McElroy, 1990), (2) loss of oxidation strength in the reaction of $\text{SO}_4^{\bullet-}$ with Cl^- (Gu et al., 2012; McKenna and Doering, 1995), and (3) formation of halogen radicals or $\bullet\text{OH}$ (Bennedsen et al., 2012; Fang et al., 2012). In that regard, the formation of $\bullet\text{OH}$ has been reported to become important at high pH values (≥ 9) (Fang et al., 2012). In all reaction systems $\text{Cl}\bullet$ are primary products which also reveal a fast reaction with HCO_3^- ($k = 2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) (Mertens and von Sonntag, 1995). However this reaction is hardly addressed in the current literature. The oxidation of Cl^- might also yield ClO_3^- especially at acidic conditions. The presence of ClO_3^- is undesired, since it is classified as being harmful to human health and ecosystems (EU regulation, 1907/2006; note that Switzerland established a drinking water standard of 200 $\mu\text{g L}^{-1}$ (von Gunten, 2003b) and WHO recommends a maximum value of 700 $\mu\text{g L}^{-1}$ (WHO/SDE/WSH/05.08/86)).

In $\text{SO}_4^{\bullet-}$ -based processes such as UV/ $\text{S}_2\text{O}_8^{2-}$ the influence of Cl^- is a very important issue and has to be carefully investi-

$$f_{\text{chloride}} = \frac{[\text{Cl}^-] \times k(\text{Cl}^-)}{[\text{Cl}^-] \times k(\text{Cl}^-) + [\text{DOC}] \times k(\text{DOC}) + [\text{HCO}_3^-] \times k(\text{HCO}_3^-) + [\text{CO}_3^{2-}] \times k(\text{CO}_3^{2-})} \quad (1)$$

With: f_{chloride} = fraction of $\text{SO}_4^{\bullet-}$ reacting with Cl^- , $[\text{Cl}^-]$ = concentration of Cl^- , $[\text{DOC}]$ = concentration of DOC, $[\text{HCO}_3^-]$ = concentration of HCO_3^- , $k(\text{Cl}^-)$ = second order reaction rate constant of the reaction $\text{SO}_4^{\bullet-}$ with Cl^- , $k(\text{DOC})$ = second order reaction rate constant of the reaction of $\text{SO}_4^{\bullet-}$ with DOC, and $k(\text{HCO}_3^-)$ = second order reaction rate constant of the reaction of $\text{SO}_4^{\bullet-}$ with HCO_3^- .

The second order reaction rate constants of HCO_3^- and CO_3^{2-} have already been determined ($k(\text{HCO}_3^-) = 2.8\text{--}9.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$

gated. In the present study formation of ClO_3^- in UV/ $\text{S}_2\text{O}_8^{2-}$ has been studied in pure water. Furthermore, the influence of Cl^- and alkalinity in UV/ $\text{S}_2\text{O}_8^{2-}$ treatment of surface waters was characterized with regard to degradation of recalcitrant pollutants. To that end, the degradation of a set of model compounds with different second order reaction rates towards $\text{SO}_4^{\bullet-}$ was used: atrazine (herbicide) ($k(\text{SO}_4^{\bullet-} + \text{atrazine}) = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Manoj et al., 2007), 4-nitrobenzoic acid (pNBA, $k(\text{SO}_4^{\bullet-} + \text{pNBA}) < 10^6 \text{ M}^{-1} \text{ s}^{-1}$

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