

# Formation of halogenated disinfection by-products in sulphate radical based oxidation processes

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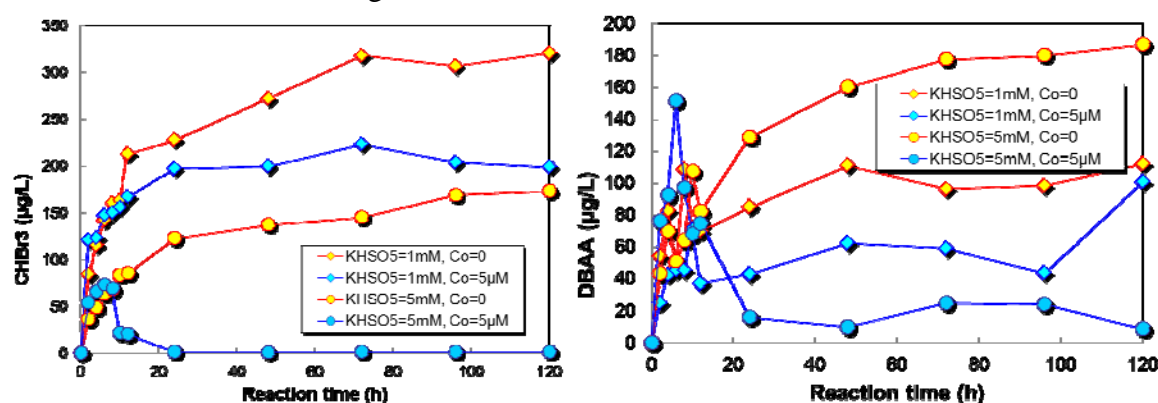
## Abstract

Cobalt catalysed decomposition of peroxymonosulfate (PMS) generates highly reactive sulfate radical, making it a viable way to degrade a broad range of contaminants. The high oxidation potential of  $\text{SO}_4^{\cdot-}$  ( $E^0=2.5\text{-}3.1\text{V}$ ) also enables it to react with inorganic halides (Fang and Shang 2012, Lutze et al. 2014). For instance,  $\text{SO}_4^{\cdot-}$  oxidizes  $\text{Cl}^-$  to chlorine radicals ( $\text{Cl}\cdot$ ).  $\text{Cl}\cdot$  further reacts with  $\text{Cl}^-$  yielding dichloride radicals ( $\text{Cl}_2^{\cdot-}$ ) which reacts with additional  $\text{Cl}^-$  or couples to each other to form free chlorine ( $\text{Cl}_2$ ) (Anipsitakis et al. 2005, Bennedsen et al. 2012, Yu et al. 2003).  $\text{Br}^-$  is theoretically more readily oxidized and expected to follow a similar reaction scheme upon contacting  $\text{SO}_4^{\cdot-}$ . Generation of the reactive halogen species, especially free halogen is of particular concern because halogen can react with natural organic matter (NOM) leading to the formation of halogenated by-products (DBPs). Such process has been well recognized in drinking water treatment processes. This research was designed to investigate formation of halogenated DBPs in  $\text{Co}^{2+}$ /PMS process in the presence of halides and NOM.

It was revealed that no DBPs were formed in the presence of  $\text{Cl}^-$  as the only halide species in the reaction solutions. When  $\text{Br}^-$  was present, bromoform and dibromoacetic acid (DBAA) were formed as illustrated in Figure 1. However, no other DBP species were detected. Formation of bromoform and DBAA increased monotonically and their concentrations reached 198.9 and 100.7  $\mu\text{g/L}$ , respectively, after 120 h when 0.1 mM  $\text{Br}^-$  and 1.0 mM PMS were present initially. Formation of brominated DBPs implies the activation of  $\text{Br}^-$  in  $\text{SO}_4^{\cdot-}$  based oxidation process.  $\text{SO}_4^{\cdot-}$  mediates a one-electron oxidation of  $\text{Br}^-$  to form bromine radical ( $\text{Br}\cdot$ ) with a second-order rate constant of  $3.5\times 10^9\text{ M}^{-1}\text{s}^{-1}$ .  $\text{Br}\cdot$  can react rapidly with  $\text{Br}^-$  and  $\text{OH}^-$  to form  $\text{Br}_2^{\cdot-}$  and  $\text{BrOH}^{\cdot-}$ . Kinetic analysis revealed that the equilibrium concentration of these bromine radicals could exceed that of  $\text{SO}_4^{\cdot-}$  by several orders of magnitude in the presence of trace level of  $\text{Br}^-$  in  $\text{SO}_4^{\cdot-}$  based oxidation processes. Bromine radicals are good nucleophiles and can selectively attack electron-rich compounds. NOM molecule contains phenolic moieties which can serve as the targets of bromine radical attack, resulting in bromination and formation of brominated products. In addition to the bromine radicals, free bromine could also be generated via the coupling of the radical species. Time-dependent formation of Br-DBPs showed quite different profiles in the reaction solution dosed with 5.0 mM PMS. Both bromoform and DBAA underwent an increasing phase during the first 6 h and reached temporal maximum of 72.7 and 151.5  $\mu\text{g/L}$ , respectively. After that, their concentrations decreased drastically. Such a time-dependent formation trend implies the degradation of Br-DBPs in the presence of excessive  $\text{SO}_4^{\cdot-}$ .

Formation of DBPs was also found in the absence of  $\text{Co}^{2+}$ , suggesting the formation of reactive bromine species (RBS) in the solution as well. Because activation of PMS without catalysis by metals or photon was negligible, bromine

radical species was not likely formed in the absence of  $\text{SO}_4^{\bullet-}$ . Activation of  $\text{Br}^-$  in this case was most likely due to the oxidation potential of PMS *per se*. PMS is a stronger oxidant ( $E_{\text{HSO}_5^-/\text{HSO}_4^-}^0 = +1.82\text{V}$ ) than hydrogen peroxide ( $E_{\text{H}_2\text{O}_2/\text{H}_2\text{O}}^0 = +1.76\text{V}$ ) (Rastogi et al. 2009). Based on the redox potentials, PMS is capable to oxidize  $\text{Br}^-$  ( $E_{\text{HOBr}/\text{Br}^-}^0 = +1.338\text{V}$ ) (Benjamin 2002) to free bromine which can attack NOM subsequently. Nonetheless, the DBPs thus formed could not be further degraded in the absence of  $\text{SO}_4^{\bullet-}$ . Thus, formation of Br-DBPs increased monotonically with the reaction time as shown in Figure 1.



**Figure 1** Time dependent formation of bromoform and DBAA in  $\text{Co}^{2+}$ /PMS oxidation process.

More DBPs including chlorinated species were detected in the presence of both  $\text{Cl}^-$  and  $\text{Br}^-$ . However, the total DBPs yield decreased with the increase of  $\text{Cl}^-$  content when total halides kept constant and more brominated species produced than chlorinate ones in general. This study demonstrates the formation of halogenated DBPs in sulphate radical based reaction systems, which shall be taken into consideration when such technologies were used to eliminate contamination in real practice.

**Keywords:** peroxymonosulfate; cobalt, halogenated disinfection-by products

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