### **ORIGINAL ARTICLE**



# Neutral pH, multioxidants Fenton oxidation of dimethyl sulfoxide and acetamidophenol as water pollutant models

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### Abstract

Organic water pollution is calling for advanced remediation methods such as the Fenton process, yet actual procedures involve transition metals at acidic pH, and generate only one oxidant, the hydroxyl radical. Here we used a solution of magnesium ions, bicarbonate ions, and hydrogen peroxide at pH 7.4 to generate reactive oxygen species for degrading dimethyl sulfoxide and acetamidophenol, as models of water pollutants. The performance and the identification of degradation products were assessed by nuclear magnetic resonance and high-performance liquid chromatography. Results show the generation of several oxidizing agents such as hydroxyl radical, carbonate anion radical, and superoxide. The novel aspect is that the Fenton-like process can be achieved with Mg<sup>2+</sup> serving only as a template to facilitate redox reactions rather than participating directly. The mechanisms for generating oxidizing radicals suggests potential applications in both environmental cleanup and biological processes.

**Keywords** Advanced oxidation processes · Biology · Carbonate-anion-radical · Environmental Fenton-like-reactions · Magnesium

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# Introduction

The growing accumulation of waste in freshwater systems is increasingly threatening both planetary health and societal sustainability [1]. Currently, there is a sharp increase in waste and pollution due to shifts in human activities following the pandemic. There are growing concerns about the disposal of unused pharmaceuticals and their metabolites, which are often inadequately treated by wastewater treatment plants and could potentially lead to a global health crisis [2]. Researchers are continually developing newer and greener strategies to address the challenge of cleaning water contaminated with pharmaceuticals [3, 4]. The major focus has been on innovating existing technologies to address the current challenges in water purification.

The Fenton and Fenton-like reactions, e.g.,  $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^-$ , have been investigated for several decades due to their potential to generate highly reactive hydroxyl radical (OH) in biological systems [5–7], in environmental processes [8, 9] and in advanced oxidation processes/technologies, AOPs [10–12]. Fenton and Fenton-like reactions are primarily conducted using Fe<sup>2+</sup> and occasion-ally involve other transition metal complexes. Transition-metal-based Fenton reactions, often involve the formation

of metal complexes and the precipitation of metal oxides/ hydroxides, e.g.,  $Fe(OH)_3$  [13], which poses treatment efficiency, water quality, and sludge generation challenges.

Researchers have been exploring replacing transition metal complexes with other metals (M) like beryllium and aluminum to carry out Fenton-like processes to produce OH<sup>•</sup> through reaction (1) [14–17]. However, reaction (1) typically occurs only in organic solvents with minimal water and requires very high concentrations of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to proceed. Additionally, an acidic environment must be maintained for the reaction. These stringent conditions make reaction (1) impractical for treating polluted water directly. This study thus aims to provide a greener solution for depolluting water. The solutions containing  $Mg(H_2O)_6^{2+}$ ,  $HCO_3^-$ , and  $H_2O_2$  could carry the Fenton-like processes effectively. Experiments focused on the oxidation of dimethyl sulfoxide (DMSO) and acetamidophenol were performed to demonstrate a new Fenton-like greener process to de-contaminate water. These chosen model reactions serve as representative systems to investigate the intricate mechanisms and dynamics involved in Fenton-like processes in the studied solutions. The implications of these findings in biological processes and the potential for alternative advanced oxidation processes without transition-metal complexes are briefly discussed.

$$(H_2O)_k M^n(^{\circ}OOH)(H_2O_2)^{(n-1)+} \rightarrow (H_2O)_k M^n(^{\circ}OOH)(OH^{-})^{(n-1)+} + OH^{\circ} (M = Be, Al)$$

$$\tag{1}$$

We stride out to achieve reaction (1) possible for treating water under neutral conditions. This stems from consideration of the similarity in the redox potentials of the couples  $((^{\circ}OOH + e^{-} + H^{+})/(H_2O_2) = 1.46 \text{ V}$  versus NHE [18] and  $(CO_3^{\circ -} + e^{-})/CO_3^{2-}$  1.57 V versus NHE [18], and thus it seemed reasonable to expect the feasibility of the occurrence of reaction (2).

## **Results and discussion**

The experimental procedures are detailed in the supplemental material (Text S1). In an initial experiment, the nature of the formed intermediate oxidizing agents in the reaction mixtures of  $Mg^{2+}$  and  $H_2O_2$  in the absence and presence of  $HCO_3^-$  was studied. Dimethylsulfoxide ((CH<sub>3</sub>)<sub>2</sub>SO) was

$$(H_2O)_k M^n (CO_3^{2-}) (H_2O_2)^{(n-2)+} \to (H_2O)_k M^n (OH) (OH^{-1)+} + CO_3^{--} / (H_2O)_{k+1} M^n (OH^{-1)+} + CO_3^{--} + OH^{-1}$$

$$(2)$$

Significantly, herein we provide evidence of the occurrence of a Fenton-like reaction in an aqueous environment by using magnesium ion (Mg<sup>2+</sup>), i.e., without the use of a transition metal complex. Magnesium ion (Mg<sup>2+</sup>) was intuitively chosen as the cation due to the following reasons: (i) it is a small cation and therefore expected to complex with  $H_2O_2$  better than Fe<sup>2+</sup>, (ii) magnesium salts are soluble in neutral solutions even in the presence of bicarbonate, (iii) magnesium ion plays several important roles in the environment due to its abundance and unique chemical properties [19, 20] and (iv) magnesium ions are present in most of the water bodies including tap water and seawater [21] and thus address the drawbacks of secondary contamination of conventional Fenton reaction processes to treat polluted water.

Importantly, reaction (2) directly forms two strong oxidizing radicals:  $OH^{\bullet}$  and carbonate anion radical  $(CO_3^{\bullet-})$ , resulting in a multi-oxidant system. The  $CO_3^{\bullet-}$  as an oxidant is of tremendous interest due to its involvement in various catalytic oxidation processes [22, 23], some of which are major biological [24, 25] and water remediation importance [22, 26]. Significantly,  $CO_3^{\bullet-}$  anion radicals, despite their lower reactivity compared to  $OH^{\bullet}$  radicals, exhibit a specific reactivity towards active moieties of pollutants, establishing their significant role in AOPs [27]. introduced into the reaction mixtures, and the identification of dimethylsulfone (DMSO<sub>2</sub>) as a product was established through the analysis of <sup>1</sup>H NMR spectra. The results are presented in Fig. 1. The formation of DMSO<sub>2</sub> was not seen in any solution mixtures except in which both  $Mg^{2+}$  and  $HCO_3^-$  were present together in the solution.

The results in Fig. 1 indicate the oxidation of DMSO by OH<sup>•</sup> and CO<sub>3</sub><sup>•-</sup> and by HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>. These reactions have been reported to yield CH<sub>3</sub><sup>•</sup> radicals [28]. In this system, the production of radicals is very slow, and therefore CO<sub>3</sub><sup>•-</sup> and O<sub>2</sub><sup>•-</sup> are long-lived and enable their reactions with DMSO [28] and with H<sub>2</sub>O<sub>2</sub>,  $k(CO_3^{\bullet-} + H_2O_2)$ ~ 4.0 × 10<sup>5</sup> M<sup>-1</sup>s<sup>-1</sup> [29]. The CH<sub>3</sub><sup>•</sup> radicals formed react with H<sub>2</sub>O<sub>2</sub>,  $k(CH_3^{\bullet} + H_2O_2 \rightarrow CH_4 + HO_2^{\bullet}/(O_2^{\bullet-} + H^+))$ = 2.70 × 10<sup>5</sup> M<sup>-1</sup>s<sup>-1</sup> [30]. Thus all the radicals formed in reaction (2) are transformed into HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup> radicals that are expected to react with DMSO to yield CH<sub>3</sub><sup>•</sup> and CH<sub>3</sub>S(O) OOH [28]. This explains the observed oxidation products in Fig. 1.

The oxidizing properties of a solution containing a mixture of  $Mg^{2+}$ ,  $HCO_3^-$ , and  $H_2O_2$  were further tested to oxidize a well-known micropollutant, acetamidophenol (ACP). The results are presented in Fig. 2, which clearly shows the efficient oxidation of ACP when all

**Fig. 1** <sup>1</sup>H nuclear magnetic resonance (NMR) spectra of the products of the reactions of  $Mg^{2+} + H_2O_2$  with dimethylsulfoxide (DMSO) at pH 7.40 with and without HCO<sub>3</sub><sup>-</sup>. Measured one week after preparation of samples, deaerated solutions. Experimental conditions:  $[H_2O_2] = 5.0 \text{ mM},$  $[HCO_3^{-}] = 5.0 \text{ mM},$  $[Mg^{2+}] = 1.0$  mM, and [DMSO] = 25.0 mM. The results show that DMSO is oxidized by both OH• and CO3• radicals, as well as by  $HO_2^{\bullet}/$  $O_2^{\bullet-}$  species. These reactive species contribute to the oxidation processes observed





**Fig. 2** Removal efficiency of acetamidophenol (ACP) was obtained for the systems:  $HCO_3^- + ACP$ ,  $Mg^{2+} + ACP$ ,  $H_2O_2 + ACP$ ,  $H_2O_2 + ACP$ ,  $Mg^{2+} + H_2O_2 + ACP$ , and  $Mg^{2+} + H_2O_2 + HCO_3^- + ACP$ . ( $[HCO_3^-]$ ,  $[H_2O_2]$ , and  $[MgCl_2GH_2O] = 10.0$  mM, [ACP = acetamidophenol] = 0.25 mM). All samples were at pH 7.40, de-aerated, and analyzed by HPLC after one week of preparation. The results indicate that the removal efficiency of ACP was evaluated in various systems, including  $HCO_3^-$ ,  $Mg^{2+}$ ,  $H_2O_2$ , and their combinations with ACP. HPLC analysis revealed varying levels of ACP removal for each system, with the most complex system ( $Mg^{2+} + H_2O_2 + HCO_3^- + ACP$ ) showing significant removal efficiency

components of the mixture are present. Experiments using four mixtures,  $HCO_3^- + ACP$ ,  $Mg^{2+} + ACP$ ,  $H_2O_2 + ACP$ , and  $Mg^{2+} + H_2O_2 + ACP$  have no oxidation capacity to degrade ACP. The results are adequately explained by the lack of formation of radicals in these reaction media. The observation that the mixture of  $Mg^{2+}$  and  $H_2O_2$  does not oxidize the ACP points out that the Shul'pin mechanism [14–17] is not operating in aqueous solutions and at low



**Fig. 3** High performance liquid chromatography-ultraviolet detection (HPLC-UV) chromatograms were obtained for the acetamidophenol (ACP) degradation in the systems: ACP (green),  $H_2O_2 + HCO_3^- + ACP$  (purple), and  $Mg^{2+} + H_2O_2 + HCO_3^- + ACP$  (orange). The lines are shifted horizontally for better vision. The figure indicates the HPLC chromatogram of the major oxidized product (OP) of ACP. ACP eluted at a retention time of 5.50 min, while the oxidized product was observed at 6.70 min, indicating successful oxidation

 $H_2O_2$  concentrations. Whereas  $H_2O_2 + HCO_3^- + ACP$ and  $Mg^{2+} + H_2O_2 + HCO_3^- + ACP$  systems showed 25 and 60 percent acetamidophenol degradation respectively. The chromatogram of the major oxidized product (OP) analyzed by HPLC is shown in Fig. 3. The acetamidophenol was eluted at a retention time of 5.50 and the oxidized product at 6.70. The pH values mentioned throughout the manuscript refer to the final pH measured after the completion of the reaction.

The results point out that oxidizing reactive species are formed in a neutral aqueous solution containing  $Mg^{2+}$ ,  $H_2O_2$ , and  $HCO_3^{-}$ . This suggests that  $OH^{\bullet}$  and  $CO_3^{\bullet-}$  anion radicals are indeed formed via reaction (2) or  $CO_3^{\bullet-}$  and  $HO_2^{\bullet/}O_2^{\bullet-}$  via reactions (3)–(6) that are analogous to the proposed mechanism for an analogous system containing  $Co_{aq}^{II}$  [31].

$$(CO_3)Mg^{II}(H_2O)_5 + HO_2^- \approx (CO_3)Mg^{II}(HO_2)(H_2O)_4^- + H_2O$$
(3)

$$(CO_3) Mg^{II} (HO_2) (H_2O)_4^- \rightarrow (CO_4) Mg^{II} (OH) (H_2O)_3^- + H_2O$$
(4)

$$(CO_4) Mg^{II}(OH) (H_2O)_3^- + H_2O_2 \rightarrow (CO_4) Mg^{II} (HO_2) (H_2O)_3^- + H_2O$$

$$(5)$$

The results demonstrate that indeed  $CO_3^{\bullet-}$  are formed via one of these mechanisms. It should be noted that the observed process is considerably slower than the Fenton reaction.

# Conclusion

The results clearly show that the solutions of  $Mg^{2+}$ ,  $H_2O_2$ and HCO<sub>3</sub><sup>-</sup> generate reactive oxygen species, OH<sup>•</sup> and  $CO_3^{\bullet-}$ , or  $CO_3^{\bullet-}$  and  $HO_2^{\bullet}/O_2^{\bullet-}$  under neutral pH conditions. In these systems, the central cation acts only as a template for a redox process between its ligands. Hence, the presented Fenton-lie reaction system without transition metal ions opens the door to new advantageous AOPs. The results point out that carbonate anion radicals are formed also, via the mechanism reported herein, in oceans and other natural waters that contain high concentrations of Mg<sup>2+</sup> and  $HCO_3^{-}$  (Mg<sup>2+</sup> is present in high concentrations in oceans). Furthermore, the presence of Mg<sup>2+</sup> in biological systems, where it typically acts as an antioxidant due to complex biological mechanisms, raises intriguing questions. The possibility that the Fenton-like processes reported herein may have been overlooked in biological systems is a noteworthy point. This opens avenues for further research into the role of Mg<sup>2+</sup> in biological processes and whether it contributes to radical-induced degradation in living organisms. MgCO<sub>3</sub> is a common additive in pharmacological preparations and foods. Thus it has to be investigated whether the new Fenton-like process reported herein plays a role in the radical-induced degradation of pharmaceuticals and foods.

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Further studies are crucial to gain a better understanding of the phenomena and their implications. Overall, the findings lead to the development of new advanced oxidation processes that do not require transition metal complexes as catalysts. The advantage of bicarbonate as a co-catalyst in the process is that it does not decompose in the catalytic oxidation processes.

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#### Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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