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Transition metal catalyzed mineralization of Calcon and bioassay of the mineralized solutions by *Escherichia coli* colony forming unit assay

M.K. Sahoo [a,*], B. Sinha [a], M. Marbaniang [a], D.B. Naik [b], R.N. Sharan [c]

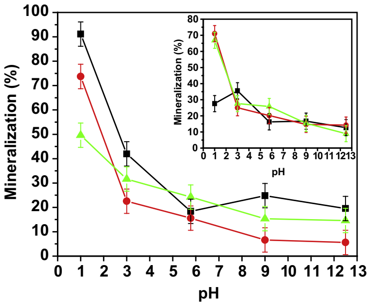
[a] *Department of Chemistry, North-Eastern Hill University, Shillong 793 022, India*
[b] *Radiation and Photochemistry Division, BARC, Trombay, Mumbai 400 085, India*
[c] *Radiation and Molecular Biology Unit, Department of Biochemistry, North-Eastern Hill University, Shillong 793 022, India*

HIGHLIGHTS

- Calcon resists mineralization by Fenton process.
- Metal ions display maximum catalytic activity in acidic media and lowest in basic media.
- Efficiency of the systems is in the order: $Fe^{2+}/APS > Ag^{+}/APS \approx Ag^{+}/HP > Co^{2+}/HP > Co^{2+}/APS > Fe^{2+}/HP$.
- Metal catalyzed AOPs are not environmentally benign as the treated solutions are more toxic to the microorganism, *Escherichia coli*.
- pH as well as the presence of metal ions is responsible for the toxicity of the treated solutions.

GRAPHICAL ABSTRACT

Effect of pH on the mineralization of Calcon in different metal/APS systems. Inset: Effect of pH on the mineralization of Calcon in different metal/HP systems. [Calcon] = 0.05 mM; [metal] = 0.05 mM; [oxidant] = 0.35 mM; time = 120 min. ■ Fe^{2+}, ●, Ag^{+}, ▲Co^{2+}.



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ABSTRACT

Mineralization of Calcon was studied by Fenton and Fenton like processes in a wide range of pH with hydrogen peroxide (HP) and ammonium persulphate (APS) as oxidants and catalyzed by transition metal catalysts such as Fe^{2+}, Ag^{+} and Co^{2+}. Maximum mineralization for Fenton and other processes was achieved at pH 3 and 1, respectively. Although mineralization was negligible in alkaline media, the catalytic activity of metal ions on HP is found to be similar, while that on APS was in the order: $Fe^{2+} > Co^{2+} > Ag^{+}$. The study reveals that Calcon resisted mineralization by Fenton process (35.6% in 120 min) and the efficiency of other systems followed the order: $Fe^{2+}/APS > Ag^{+}/APS \approx Ag^{+}/HP > Co^{2+}/HP > Co^{2+}/APS$ and a maximum of 91.1% and 73.7% mineralization were achieved with Fe^{2+}/APS and Ag^{+}/APS systems, respectively, at pH 1. To understand the impact of these processes operating at low pH, biotoxicity of the treated solutions was evaluated on the basis of *Escherichia coli* (*E. coli*) growth inhibition bioassay. It was observed that the treated solutions were still more toxic to *E. coli* than the original dye solution. Thus, metal catalyzed Fenton and Fenton like processes are not environmentally benign under the specified conditions of our study.

1. Introduction

Advanced oxidation processes (AOPs) which involve the generation of highly reactive hydroxyl and sulphate radicals are of particular interest for the destruction of a wide variety of recalcitrant organic pollutants present in wastewater. The oldest among the

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* Corresponding author. Tel.: +91 364 2722632, mobile: +91 9436706767; fax: +91 364 2551634.
E-mail addresses: mksahoo@nehu.ac.in, mihir.nehu@gmail.com (M.K. Sahoo).

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AOPs is the Fenton oxidation process (Fe^{2+}/HP) [1], which involves the iron catalyzed decomposition of HP, used as an oxidant, into hydroxyl radicals (Eq. (1)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \quad (1)$$

Since this reaction takes place in acidic medium, it can alternatively be written as:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + HO^{\cdot} \quad (2)$$

It has been demonstrated that Fenton oxidation is more efficient if the contaminated solution is within the pH range of 2.8–3.0. One important advantage of this process is that only a catalytic amount of Fe^{2+} is required as it is regenerated from the Fe^{3+} ion in a process called Fenton-like reaction (Eq. (3)) [2]. Fe^{2+} can also be regenerated from Fe^{3+} by reduction with $HO_2^{\cdot}$, and/or superoxide radical ($O_2^{\cdot -}$), which is generated by the decomposition of the hydroperoxyl radical (Eqs. (4)–(6)) [3,4].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (3)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad (4)$$

$$HO_2^{\cdot} \rightarrow O_2^{\cdot -} + H^+ \quad (5)$$

$$Fe^{3+} + O_2^{\cdot -} \rightarrow Fe^{2+} + O_2 \quad (6)$$

Thus, the regeneration of Fe^{2+} constitute a redox cycle of reactions ($Fe^{2+} \rightleftarrows Fe^{3+}$) and provides a constant source of hydroxyl radicals. Being the second strongest oxidizing agent after fluorine with a standard oxidation potential of E^0 ($HO^{\cdot}/H_2O$) = 2.8 *vs.* NHE, the $HO^{\cdot}$ acts in a nonselective oxidation way onto organic compounds and destroys them until total mineralization, i.e., conversion into CO_2, H_2O and inorganic ions. The factors, e.g. pH of the medium, concentration of iron, HP and the target contaminant, affecting the efficiency of the Fenton process have been reported in various publications [5,6] and need not be detailed here. In addition to Fe^{2+}, Co^{2+} has been reported to react with HP in a way similar to Fenton's reagent constituting a source of hydroxyl radical production [7,8].

The other popular iron catalyzed AOP is the Fenton-like reaction which involves the sulphate radicals. The persulphate, being the sulphate peroxide, $[SO_3—O—O—SO_3]^{2-}$, can be activated by transition metal ions such as Co^{2+}, Ag^+ and Fe^{2+} ions [9–17] by redox decomposition process (Eq. (7)). The $SO_4^{\cdot -}$ radical is a very strong oxidant (E_0 = 2.5–3.1 V *vs.* NHE) and is expected to degrade and mineralize contaminants more efficiently than $HO^{\cdot}$ [18].

$$M^{n+} + S_2O_8^{2-} \rightarrow M^{(n+1)+} + SO_4^{\cdot -} + SO_4^{2-} \quad (7)$$

Being environmentally benign in comparison to the other two metals, Fe^{2+} is commonly used as the catalyst for the activation of persulphate. However, the only disadvantage of using Fe^{2+} is that at high concentration it acts as a sulphate radical scavenger (Eq. (8)) [17,19,20]. Thus, maintaining desired concentration of Fe^{2+} is essential for the treatment process. An important advantage of this process over the Fenton process is that it can operate in alkaline medium by generating $HO^{\cdot}$ (Eq. (9)) [21]. The advantages of persulphate based AOP have been described in detail in our recent publication and is therefore, not discussed here [22].

$$Fe^{2+} + SO_4^{\cdot -} \rightarrow Fe^{3+} + SO_4^{2-} \quad (8)$$

$$SO_4^{\cdot -} + HO^- \rightarrow SO_4^{2-} + HO^{\cdot} \quad (9)$$

Degradation and mineralization Calcon, an azo dye, using UVC (λ = 254 nm) and UVA (λ = 365 nm) light in the presence of HP and APS has been studied in our laboratory [22,23]. It is established that greater mineralization is achieved at pH 1 in both the processes and UVC light is more efficient than UVA. Further, among the oxidants APS is more efficient than HP from both mineralization and detoxification efficiency point of view. The detoxification efficiencies of the treated solutions were determined on the basis of *Escherichia coli* colony forming unit (CFU) assay. In an effort to find the most suitable AOP and the corresponding optimal operational parameters, we have further exploited the oxidizing ability of $HO^{\cdot}$ and $SO_4^{\cdot -}$ radicals by generating them in two different processes, i.e. Fenton and Fenton-like processes. It may be mentioned that the optimal operational parameters mentioned throughout the text is obtained by analyzing each parameter at a time, keeping others constant and hence refer to a set of best suited parameters valid for a particular set of conditions for maximum mineralization. The transition metal catalysts used in this study are Fe^{2+}, Ag^+ and Co^{2+}, while the oxidants used are HP and APS. Although iron catalyzed Fenton and Fenton like reactions have been studied in detail, those catalyzed by Ag^+ and Co^{2+} are scarcely found in literature, even though it has been suggested that transition metals, particularly those possessing two or more valence states between which there is a suitable oxidation–reduction potential, can react with HP to produce $HO^{\cdot}$. It is worth to mention that optimization of various operational parameters has been done on the basis of degradation by most authors. But complete degradation does not guarantee complete removal of organic carbons, which are the main source of pollutants. As it is well known that the degradation of azo dyes may generate more toxic products than the original dye, various operational parameters such as pH and concentration of catalysts and oxidants in this experiment are optimized on the basis of mineralization. As the treated solution has to be released into the water bodies, it must be ensured that they are not toxic to the biotic components of the environment and detrimental to the eco-system, i.e. detrimental to the survival of the microorganisms. We expect that three practical problems may be encountered even after the treatment process. The first one is due to the high redox potentials of the oxidants, the treated solutions may show great biotoxicity and the other two, are due to the biotoxicity of the left over catalyst and the residual products of Calcon after the treatment process. To our knowledge, the biotoxicity of the resulting solutions generated by Fenton and Fenton-like processes using various transition metal catalysts has not been reported earlier. It is, therefore, planned to evaluate the biotoxicity of the treated solutions to understand the viability of the processes for their practical application. For this purpose *E. coli* has been taken as the target microorganism.

2. Materials and methods

2.1. Reagents

The azo dye, Calcon (Synonyms: Eriochrome Blue Black R, Palatine Chrome Black 6BN, Mordant Black 17; IUPAC name: 1-(2-Hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid sodium salt; C. I. Number: 15705; molecular formula: $C_{20}H_{13}N_2NaO_5S$; Molecular weight: 416.38 (g mol^{-1}); λ_{max} = 513 nm), used in this work was purchased from Sigma–Aldrich (Germany). Its molecular structure is shown as inset of Fig. 1. Ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$, GR), Cobalt nitrate ($Co(NO_3)_2 6H_2O$, purified), Silver nitrate ($AgNO_3$, GR), Hydrogen peroxide (H_2O_2, 30% w/w, Purified), sulfuric acid (H_2SO_4, GR), sodium hydroxide (NaOH, GR), ammonium persulphate ($(NH_4)_2S_2O_8$, extra pure) used in this work were acquired from Merck (India). Luria Bertoni (LB) agar, LB broth and ampicilin used in detoxification experiment were acquired from HiMedia (India). All the reagents were used without further purification.