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Rapid oxidation of paracetamol by Cobalt(II) catalyzed sulfite at alkaline pH

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ABSTRACT

In this study we have investigated the efficiency Cobalt (II) (Co(II)) for the activation of sulfite ions following the oxidation of paracetamol used as model contaminants. Physico-chemical parameters that can impact the paracetamol degradation (pH, initial paracetamol concentration, Co(II)/S(IV) molar ratio, oxygen concentration) and contribution of various radicals were investigated in order to elucidate the chemical mechanism. Main results show that the pH is a key factor controlling the efficiency in the system Co(II)/Sulfite. Higher efficiency is observed for pH between 9.0 and 10.0. Increasing S(IV) concentrations, until 1 mM, slightly promoted the degradation of paracetamol. In fact, an excess of sulfite ions inhibits the reaction through the scavenging of $SO_4^{\cdot -}$ and $SO_5^{\cdot -}$. Moreover, degradation efficiency drastically decreases from ~ 85% to less than 5% in absence of oxygen. $SO_4^{\cdot -}$ was confirmed to be the main oxidant responsible for the paracetamol degradation. For the first time we determined the second order rate constant between $SO_4^{\cdot -}$ and paracetamol ($1.33 \pm 0.79 \times 10^9\,M^{-1}\,s^{-1}$ (at pH 5) and $6.14 \pm 0.99 \times 10^8\,M^{-1}\,s^{-1}$ (at pH 11.0)). Moreover, radical-scavenging experiments also suggest the possible implication of $SO_5^{\cdot -}$. Hence, this work provides a precise understanding of the overall mechanism and a new promising strategy by using sulfite and transition metal such as Co(II) to promote organic compounds degradation in water under neutral and alkaline pH conditions.

1. Introduction

Advanced oxidation processes based on sulfate radical (SR-AOPs) have emerged as a promising method in the field of oxidative decontamination of polluted water and soil [1–3]. Sulfate radical ($SO_4^{\cdot -}$), a strong one-electron oxidant, has relatively high standard redox potential ($E^0 = 2.6$ V *vs* NHE) with an oxidation potential comparable to or even higher than that of hydroxyl radical [4]. Moreover, $SO_4^{\cdot -}$ can react *via* electron transfer, by addition to C=C double bonds and H-abstraction [5,6], thus, it is able to oxidize a large number of pollutants such as phenol derivatives and aniline in water [7–9]. $SO_4^{\cdot -}$ can be generated in homogeneous or heterogeneous systems *via* photolysis, thermolysis and radiolysis [10,11] or *via* transition metal activation of persulfate ($S_2O_8^{2-}$, PS) [[7–9],12–15] and peroxymonosulfate (SO_5^{2-}, PMS) [16,17].

In fact, PMS can be activated by various transition metals such as Fe, Mn, Ni and Co in the homogenous systems [[19],18]. Among them, Co and Fe are the most commonly used metal to promote radical formation due to their occurrence in natural media and low cost. Huang and Huang investigated the ability of Co(II) and PMS system to degrade Bisphenol A at pH 7, and achieved an efficient detoxification and mineralization method [19]. A process based on the sulfate radicals generation through iron (Fe(II), Fe(III)) activation of PMS or PS was studied for polychlorinated biphenyls degradation in aqueous system [20]. The high oxidation efficiency and slow rate of consumption of the oxidants make metal-mediated activation system a feasible strategy for degradation of recalcitrant organic compounds. Furthermore, PMS activation using cobalt oxide or cobalt-metal oxide as heterogeneous catalysts also gains significant relevance in water treatment applications [21]. The cobalt oxides such as CoO, CoO_2, CoO(OH), Co_2O_3 and Co_3O_4, Fe–Co mixed oxide nanocatalysts, cobalt oxide supported on MgO (Co/MgO), on TiO_2 (Co/TiO_2) and Co_3O_4/TiO_2 and combined with other metals were used as efficient heterogeneous catalysts for activation of PMS [22–25]. The most advantage of heterogeneous catalyst is that solid particles can be easily removed from liquid phase and, in some cases, reused.

Recently, sulfite ions were found to react with transition metals such as Fe(II), Fe(III) and Cr(VI) to generate $SO_4^{\cdot -}$ and application for the azo dyes and amine compounds decontamination was tested [17,26–30].

In our previous work, we reported some novel AOPs using Fe(II)-sulfite, Fe(III)-sulfite, photo-Fe(II)-sulfite system able to produce oxysulfur radicals (including $SO_3^{\cdot -}$, $SO_4^{\cdot -}$ and $SO_5^{\cdot -}$). Combined with the work conducted by other researchers [31–33], the basic chain

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oxidation mechanisms of oxysulfur radicals generation has been investigated.

In this work, Co(II)-sulfite ions (S(IV)) system has been investigated to promote the paracetamol degradation in water. Paracetamol (PARA) is a widely used analgesic and antipyretic drug and an important material for the manufacturing of azo dyes. PARA was chosen as a target contaminant in this work due to its presence in the environment from several emissions from manufacturing facilities, consumer use and disposal, and hospital waste [34,35]. The effect of pH, initial PARA concentration, Co(II)/S(IV) molar ratio, the presence of oxygen were investigated. Moreover, the activation mechanism and contribution of reactive oxygen and sulfur species were elucidated by using different kinds of radical scavengers and transient absorption spectroscopy.

2. Materials and methods

2.1. Chemicals

Cobalt(II) sulfate ($CoSO_4 \cdot 7H_2O$, analytical reagent grade), Cobalt(II) oxide (CoO) and Paracetamol ($C_8H_9NO_2$), were purchased from Sinopharm Chemical Reagent Co., Ltd. Sulfite solutions (from Na_2SO_3, Sinopharm Chemical Reagent Co., Ltd) were prepared just prior to measurements. The radical scavengers *tert*-butyl alcohol (TBA), ethanol (EtOH) as well as NaOH and H_2SO_4 which were used to adjust the pH of the solutions, were obtained from Sinopharm Chemical Reagent Co., Ltd. Methanol was HPLC grade and purchased from Fisher Corporation. Ammonium thiocyanate (NH_4SCN) and Methyl isobutyl ketone (MIK) used to determine the concentration of Co(II), were obtained from Sigma, France. All chemicals were used without further purification. Ultrapure water with 18.2 MΩ cm resistivity used in this work was obtained through a water purification system.

2.2. Degradation experiments

All experiments were conducted in a 250 mL open cylindrical reactor cooled by an external jacket water circulation at a constant temperature of 25 °C. Appropriate amounts of the PARA, scavengers and Na_2SO_3 were mixed in the solution and the pH was adjusted using a pHS-3C pH meter by adding dilute NaOH and H_2SO_4 until desired value. Each solution was constantly stirred with a Polytetrafluoroethylene (PTFE)-coated magnetic stirrer and purged with air with a fixed flow of 0.8 L min^{-1}.

Each experiment was initialed spiking with Co(II) or CoO into the solution. Samples were withdrawn at fixed interval times and analyzed immediately to determine the remaining concentration of PARA and Co (II). For radical-scavenging experiments, specific concentrations of TBA or EtOH were added to the solutions before Co(II) addition. In order to assess the role of oxygen during Co(II)-sulfite solution were purged by bubbling N_2 (99.99%) or O_2 (99.99%) for 30 min before and throughout the experiment. A dissolved oxygen (DO) meter (8403, AZ Instrument Co. Ltd.) was used to determine the oxygen concentration in solution. During anoxic reaction, the DO was 0.01 mg L^{-1} while for O_2 saturated solution a concentration of 20 mg L^{-1} was determined. All experiments were carried at least two times.

2.3. Chemical analysis

The concentration of PARA was determined using a high-performance liquid chromatography (HPLC) Shimadzu LC-10A system equipped with UV–vis detector (SPD-10AV; Shimadzu) and an ODS-C18 column (25 cm × 4.6 mm, 5 μm; Shimadzu, Kyoto, Japan). The separation was warried out using methanol:water (25:75 v/v) as isocratic mobile phase at a flow rate of 1.0 mL min^{-1}. The detector was set at 241 nm. The concentration of Co(II) in solution was determined by Methyl isobutyl ketone and Ammonium thiocyanate (see Supplementary material for the method description and Fig. S1) [36]. An optical-fiber coupled to a spectrophotometer (UV-1601 Shimadzu, Japan) was used to scan the UV–vis absorption spectra of Co(II)-SO_3^{2-} complex.

For $SO_4^{\cdot -}$ reactivity a laser flash photolysis (LFP) system was used with 266 nm excitation following the procedure reported by Wu at al. [15]. Analysis of transient decay and second order rate constant determination (using PARA concentrations from 0 to 0.1 mM) were determined at 470 nm corresponding to the maximum absorption of $SO_4^{\cdot -}$. The second order rate constants were determined at pH 5.0 and 11.0 corresponding to the molecular and deprotonated forms respectively of PARA (pKa = 9.5).

3. Results and discussion

3.1. Effect of initial pH on paracetamol degradation

The effect of the initial pH on the Co(II) + S(IV) system oxidation of PARA was investigated from 3.0 to 11.0. The initial concentrations of Co(II) and SO_3^{2-} were 0.1 mM and 1.0 mM, respectively and during the reaction, air (otherwise stated) was constantly bubbled at a flow rate of 0.8 L min^{-1}. The PARA degradation shows a strong pH-dependence as illustrated in Fig. 1A. Despite a negligible degradation at relatively acidic values (pH 3.0–5.0), PARA degradation is enhanced from pH 5.0 to pH 10.0 while a decrease is observed at pH 11.0. It is interesting to observe that degradation efficiency between pH 3.0 and 10 is strongly correlated to the HSO_3^{-}/SO_3^{2-} speciation in solution (pKa = 7.2) as shown in Fig. 1B in which degradation of PARA after 30 min at different pH values is correlated to the concentration of SO_3^{2-} in solution. However, at pH 11, the inhibition of PARA degradation can be attributed to the formation of insoluble Cobalt-hydroxide ($Co(OH)_2$) complex that is expected to precipitate in solution [37].

Moreover, it has been reported that deprotonated complexes (Co (II) − OH), which is more reactive toward SO_3^{2-} compared to HSO_3^{-} would be formed at alkaline pH values (R1) leading to the formation of a Co(II) − SO_3 complex [27]. Co(II) − SO_3 could be oxidized to Co (III) − SO_3^{+} complex in the presence of dissolved oxygen as reported in different works (R2 and R3) [38]. $SO_3^{\cdot -}$ could be generated during the redox reaction between the Co(III)-SO_3^{+} complex and SO_3^{2-} (R4).

UV–vis absorption spectra of Co(II), S(IV), Co(II) and S(IV) during the reaction (Fig. S1) were acquired to investigate the complexation between Co(II) and S(IV). The result showed that: only Co(II) or S(IV) at pH 9.0 did not show absorption in the range 250–600 nm. However, when S(IV) was added to the solution containing 0.1 mM Co(II) an absorption band absorbing up to ~ 600 nm is present. The presence of this new absorption band demonstrates that the Co(II)-S(IV) complex could be formed and decreasing in the absorption during time proved the reaction between Co(II) and S(IV), and corresponding depletion of S (IV).

$$Co(II) + H_2O \rightarrow Co(II) - OH \quad \text{alkaline pH} \qquad \text{(R1)}$$

$$Co(II) - OH + SO_3^{2-} \rightarrow Co(II) - SO_3 + H_2O \qquad \text{(R2)}$$

$$Co(II) - SO_3 + O_2 \rightarrow Co(III) - SO_3^{+} \qquad \text{(R3)}$$

$$Co(III) - SO_3^{+} + SO_3^{2-} \rightarrow Co(II) - SO_3 + SO_3^{\circ -} \qquad \text{(R4)}$$

The pH represents also a key factor influencing the $SO_3^{\cdot -}$ reactivity in water. In fact, the primary step is the oxygen-mediated oxidation of $SO_3^{\cdot -}$ to $SO_5^{\cdot -}$ (R5), this latter can react with HSO_3^{-}/SO_3^{2-} leading to the formation of $SO_3^{\cdot -}$ and $SO_4^{\cdot -}$ (R6-R9).

As reported in R6 and R8, $SO_5^{\cdot -}$ could react with SO_3^{2-} to generate $SO_3^{\cdot -}$ and $SO_4^{\cdot -}$ at a rate constant around $10^5 - 10^6$. $SO_4^{\cdot -}$ could react with PARA or with SO_3^{2-} leading to the generation $SO_3^{\cdot -}$ (R10), then a $SO_x^{\cdot -}$ ($SO_3^{\cdot -}$, $SO_4^{\cdot -}$ and $SO_5^{\cdot -}$) cycle can be achieved. However, in the presence of HSO_3^{-} (acidic conditions), $SO_5^{\cdot -}$ reacts with HSO_3^{-} to generate $SO_4^{\cdot -}/SO_3^{\cdot -}$ with a relatively