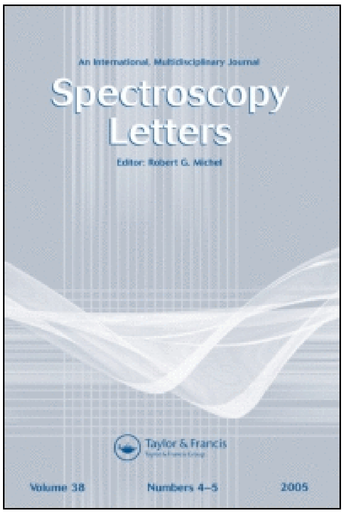

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Kinetic of Copper(III)/(II) Tetraglycine Reactions with Sulfite. Analytical Potentialities

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KINETIC OF COPPER(III)/(II) TETRAGLYCINE REACTIONS WITH SULFITE. ANALYTICAL POTENTIALITIES.

KEYWORDS: Cu(II)/(III) tetraglycine, sulfite, formaldehyde, flow injection analysis

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ABSTRACT

The oxidation of Cu(II)/tetraglycine complex in borate buffer (pH=9.2) in aqueous medium, by dissolved oxygen is strongly accelerated by S(IV). The reaction is adequate for S(IV) determination as the concentration of

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$[Cu(H_{-3}G_4)]^-$ formed is proportional to SO_3^{2-} concentration. The $[Cu(H_{-3}G_4)]^-$ presents a maximum absorbance at 365 nm (ε = 7400 $mol^{-1}.L.cm^{-1}$) and it was followed spectrophotometrically by flow injection analysis procedure. The detection limit was $7x10^{-6}$ $mol.L^{-1}$ and the linear regression showed a standard deviation of 0.02% (n=5). Kinetics studies showed the catalytic effect of some transition metal ions, which can be present in environmental samples, in the oxidation of S(IV). The pseudo-first-order rate constants were determined in the presence of formaldehyde.

INTRODUCTION

The oxidation of S(IV) oxides, by dissolved oxygen, catalyzed by transition metal ions in aqueous solution has been the subject of a large number of experimental studies[1-6]. Most of these have focused on the catalysis of Mn(II), Fe(II)/Fe(III), Cu(II), Ni(II) and Co(II) ions, of which manganese and iron have shown to be the most effective.

Many studies have dealt with the effect of the aquated metal ions, whereas some have investigated the effect of chelated metal complexes[7-11]. In general chelates such as polyaminecarboxylate, phtalocianine and polyglycine, can stabilize the metal ion in the higher oxidation state and higher pH. Such metal ions and complexes in the trivalent state can react with S(IV) to initiate a radical chain reaction in where S(IV) is oxidized to sulfate by dissolved oxygen and the metal is reduced to the divalent state[12-16]. The reduced metal can be re-oxidized to the trivalent state by strong sulphur oxidant generated during the chain reaction. A redox-cycling of metal ions was reported, and a crucial control over the S(IV) and O_2 concentrations will determine which oxidation state the metal ion species are present[14, 15, 17, 18]. Thus, the trivalent metal ion, or complex, is the real catalyst in the oxidation process and will be produced during an induction period, when it is not present in the solution at the start of the reaction.

The oxidation of Co(II) complexes in tris(hidroxymethyl)aminomethane or azide buffers in aqueous medium, by dissolved oxygen, is strongly accelerated by S(IV). The process is still faster in the presence of Mn(II)[19-23]. The reaction is adequate for S(IV) determination, as the concentration of Co(III) formed is proportional the initial sulfite concentration and can be followed spectrophotometrically.

The complex Cu(II)/tetraglycine, $[Cu(H_{-3}G_4)]^{2-}$, in the presence of dissolved oxygen and sulfite is slowly oxidized to Cu(III), with the simultaneous formation of S(VI) . The Cu(III) complex can be followed at 365 nm (ε = 7400 $mol^{-1}.L.cm^{-1}$). A detailed kinetic study was done by Anast and Margerum[24]. It was observed an autocatalytic mechanism and the rate constant depends on the initial Cu(III), which reacts with $SO_3^{2-}$with formation of $SO_3^{-\bullet}$ radical (equation 1), which reacts with O_2 giving $SO_5^{-\bullet}$ (equation 2). The initiation in absence of Cu(III) may be whether due to disproportionation of Cu(II) to Cu(I) and Cu(III) or formation of peroxomonosulfate by the reaction (3). The peroxomonosulfate can then oxidizes Cu(II) to Cu(III) (equations 4 and 5).

$$[Cu(H_{-3}G_4)]^- + SO_3^{2-} \rightarrow [Cu(H_{-3}G_4)]^{2-} + SO_3^{-\bullet} \qquad (1)$$

$$SO_3^{-\bullet} + O_2 \rightarrow SO_5^{-\bullet} \qquad \text{or} \qquad (2)$$

$$SO_3^{2-} + O_2 \rightarrow SO_5^{2-} \qquad (3)$$

$$[Cu(H_{-3}G_4)]^{2-} + SO_5^{-\bullet} \rightarrow [Cu(H_{-3}G_4)]^- + SO_5^{2-} \qquad (4)$$

$$2[Cu(H_{-3}G_4)]^{2-} + SO_5^{2-} + H_2O \rightarrow 2[Cu(H_{-3}G_4)]^- + SO_4^{2-} + 2OH^- \qquad (5)$$

In the present work it was studied the influence of formaldehyde, which has been used to stabilize S(IV) in aqueous solutions due to hydroxymethene sulfonic acid formation. Formaldehyde has been considered a good stabilizer in the absence of metal ions, in a non complex medium[25]. A flow injection analysis system was also used to develop a analytical method for S(IV) determination as the Cu(III) formation is a linear function of the initial S(IV) concentration.

EXPERIMENTAL

REAGENTS

All reagents were from AR specification (Merck or Sigma).

Deionized water was used to prepare all solutions. All solutions were air saturated.

Copper(II) perchlorate 0.2 mol.L^{-1} stock solution was prepared from the direct reaction of excess carbonate with perchloric acid and standardized with EDTA by conventional procedure. Stock solutions of

Mn(II), Ni(II), Co(II), Fe(II), Fe(III) and Cr(III) were prepared by the same procedure.

Borate 0.05 mol.L^{-1} and 0.1 mol.L^{-1} (pH = 9.2) and acetate 0.02 mol.L^{-1} (pH = 4.7) buffer solutions were prepared as described elsewhere[26].

Cu(II)/tetraglycine complex solution, $[Cu(H_{-3}G_4)]^{2-}$, was freshly prepared dissolving 0.0124 g of tetraglycine in 12 mL of deionized water in the presence of 8 mL of borate buffer solution and 0.22 mL of copper(II) perchlorate in order to obtain the final concentration 2.2x10^{-3} mol.L^{-1}.

S(IV) 2x10^{-3} mol.L^{-1} solution was prepared by dissolving $Na_2S_2O_5$ salt in deionized water just before use. When necessary it was iodometrically standardized as described in the literature[23].

Formaldehyde 8.8x10^{-2} mol.L^{-1} stock solution was prepared from dilution of concentrated reagent in deionized water. Standardization was carried out as follow: in a 100 mL flask, over a cold bath, were transferred 5.00 mL of formaldehyde solution and 10.0 mL of I_2 0.05 mol.L^{-1} standardized solution. After 2 minutes 2.5 mL of NaOH 10% solution was slowly added. After 20 minutes 10 mL of HCl 10% was added and it was titrated with $Na_2S_2O_3$ 0.05 mol.L^{-1} standardized solution, using starch as indicator.

Tris(hydroxymethyl)aminomethane (TRIS), triethanolamine (TEA), monoethanolamine (MEA), Na_3PO_4 and Na_2CO_3 0.2 mol.L^{-1} solutions were prepared without further standardization.

STOPPED FLOW SYSTEM

A stopped flow arrangement was initially used to follow the Cu(III) formation as a function of added [S(IV)]. It was built fixing two 10 mL hypodermic syringe in a plastic body. In the outlet of each syringe there was a polyethylene tubing that leads each solution to a Teflon mixing chamber. After mixing the solutions in a 1:1 proportion, the final solution was driven through the quartz flow placed inside the spectrophotometer.

An equal volume of $[Cu(H_{-3}G_4)]^{2-}$ 2.2×10^{-3} mol.L^{-1} in borate buffer 0.1 mol.L^{-1} (pH=9.2) solution *(solution 1)* was mixed with a solution containing S(IV) 1.0×10^{-4} mol.L^{-1} and formaldehyde $(0\text{-}8.8) \times 10^{-4}$ mol.L^{-1} *(solution 2)*. The absorbance measurements at 365 nm were recorded on a HP8452A Diode array spectrophotometer.

FIA SYSTEM

A reverse flow injection analysis system was also used to study the Cu(III) formation as a function of [S(IV)], as shown in Figure 3. A borate buffer solution 0.05 mol.L^{-1} (pH=9.2) and S(IV) solution $(0.10\text{-}10) \times 10^{-4}$ mol.L^{-1} were mixed in a flow system (0.4 mL.min^{-1}) in which 0.59 ml of $[Cu(H_{-3}G_4)]^{2-}$ 2.2×10^{-3} mol.L^{-1} (in buffer borate) was introduced into the stream by a manual injection valve. A reactor consisting of one tube of 200 cm length was necessary. A Gilson Minipuls 3 peristaltic pump was used to drive the reagents into the polyethylene tubing (i.d. 0.8 mm.) through the quartz flow cell. The absorbance at 365 nm, due to Cu(III) complex, was continuously measured by Micronal B342-II spectrophotometer.

The influence tests were performed by adding appropriate aliquots of Mn(II), Ni(II), Co(II), Fe(II), Fe(III), Cr(III), TRIS, TEA, MEA, PO_4^{3-} and CO_3^{2-} in the S(IV) $9x10^{-5}$ $mol.L^{-1}$ standardized solution prior to the injection.

RESULTS AND DISCUSSION

PSEUDO-FIRST-ORDER KINETICS IN THE PRESENCE OF FORMALDEHYDE.

The S(IV) induced oxidation of $[Cu(H_{-3}G_4)]^{2-}$, in air saturated solutions, was studied under pseudo-first order conditions where $[Cu(H_{-3}G_4)]^{2-}$ was always in a large excess compared to S(IV).

In the experiments, freshly prepared solutions were mixed in a stopped flow system. An equal volume of S(IV) and formaldehyde solution was mixed with $[Cu(H_{-3}G_4)]^{2-}$ solution in borate buffer. The absorbance changes at 365 nm, showed a induction period, an evidence of autocatalytic behaviour, very well defined for higher concentration of aldehyde. In the Figure 1 it is indicated the final solution after the mixture.

In the presence of formaldehyde, due to the adduct formation, the S(IV) reacts slower as the aldehyde concentration increases. The absorbance limit reached was almost independent on the aldehyde concentration.

The Olis Kinfit set of programs[27] was employed to fit the absorbance-time traces according to the first order behaviour.

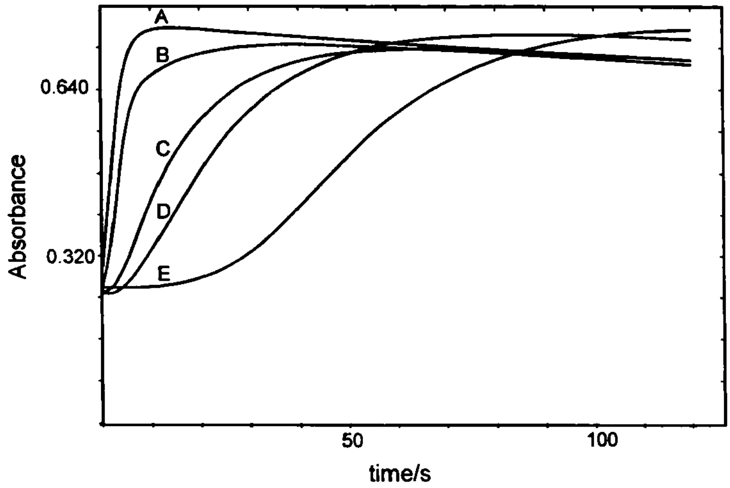

FIG. 1 - Absorbance changes at 365 nm. Influence of formaldehyde on the Cu(II) formation. $[[Cu(H_{-3}G_4)]^{2-}] = 1.1 \times 10^{-3}$ mol.L^{-1} in borate buffer 0.05 mol.L^{-1} (pH=9.2), [S(IV)] = 5×10^{-5} mol.L^{-1} and formaldehyde A) zero; B) 0.881×10^{-5} ; C) 4.41×10^{-5}; D) 17.6×10^{-5} and E) 44.1×10^{-5} mol.L^{-1}(T=25 ^{0}C).

The pseudo-first-order constants, k_{obs}, were calculated from the absorbance-time traces, neglecting the induction period elapsing some initial seconds. The results showed that k_{obs} decreases drastically as the aldehyde concentrations increase. For $[CH_2O]:[S(IV)] > 1$, k_{obs} is almost constant (Figure 2).

In previous studies this induction period was showed to be dependent on the initial Cu(III) complex. Similar induction period and autocatalytic

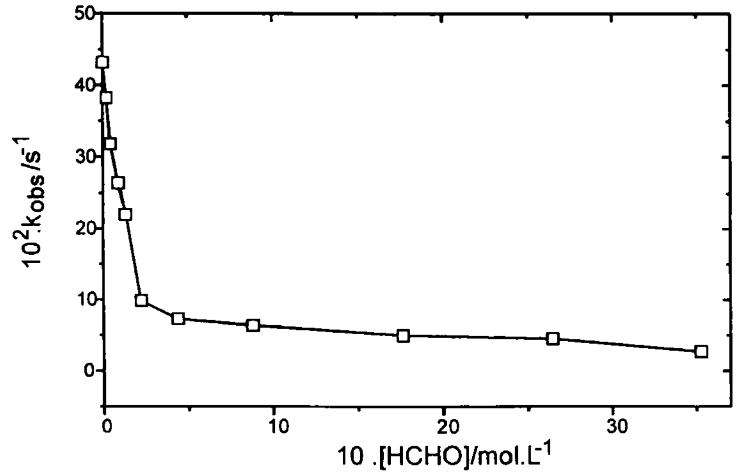

FIG. 2 - Pseudo-first-order constant as function of formaldehyde concentration. Conditions are indicated in the Figure 1.

behaviour have been reported for the Co(II)/Co(III)/N_3^-[12], Mn(II)/Mn(III)/N_3^-[13], Fe(II)/Fe(III)/H_2O [8,15,28] and Mn(II)/Mn(III)/H_2O[29] systems. These studies have also shown that due of the nature of the autocalytic process, the rate and the concentration of the trivalent metal ion depend on the employed S(IV) concentration.

The interference of formaldehyde, at higher concentrations, in the determination of S(IV) by FIA procedure it is important to consider the change in the reaction time.

FLOW ANALYSIS OF S(IV)

Using the experimental conditions described in the Figure 3, the absorbance, due to Cu(III) complex, was continuously measured. A

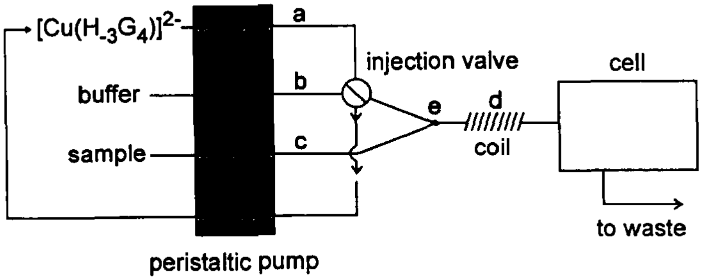

FIG. 3 - FIA arrangement used for the S(IV) spectrophotometric determination: *a*, *b* and *c* = polyethylene tubes (*a* = *b* = 19.4 cm; *c* = 27.5 cm), *d* = mixing coil (200 cm) and *e* = confluence point.

calibration graphic with six points showed a linear dependence between the maximum absorbance, A, and the initial [S(IV)] ((0.1-1.2) 10^{-4} mol.L^{-1}). The line of regression was A = 0.02535 + 0.04657x10^{-5} [S(IV)] and the correlation coefficient was 0.998. The detection limit was 0.07x10^{-4} mol.L^{-1} and the relative standard deviation was 0.02% for five determination of [S(IV)] = 7x10^{-5} mol.L^{-1}. This method can be used as an alternative analytical method for S(IV) determination in environmental samples as rain water.

INTERFERENCE IN THE S(IV) DETERMINATION

Interference in the determination of S(IV) by FIA procedure, were observed when the interfering species were added to a S(IV) standard solution S(IV) (9x10^{-5} mol.L^{-1}) prior to the mixture.

In the present work, TRIS, PO_4^{3-} and TEA ($2x10^{-3}$ mol.L^{-1}), MEA (0.2 mol.L^{-1}) and formaldehyde ($9x10^{-3}$ mol.L^{-1}), at these concentration levels, suppressed completely the peak. Carbonate and MEA ($2x10^{-3}$ mol.L^{-1}) had almost no influence.

These studies are important since the presence of MEA, TEA and TRIS at 0.05-0.2 mol.L^{-1} range have shown a remarkable stabilizing effect of S(IV) at pH values higher than 10.5[30]. In the present work, MEA could be used at lower concentration ($2x10^{-3}$ mol.L^{-1}) without interference.

The rate constants for the reactions of $[Cu(H_{-2}G_3)]^-$ and $[Ni(H_{-2}G_3)]^-$ with TRIS, H_3O^+, HCO_3^-, HPO_4^-, are reported in the literature[31], so these species interact with the Cu(II) ion displacing the peptide. However if these species are present at low concentration, as in environmental samples, the interference can be neglected.

The Mn(II), Ni(II), Co(II), Cr(III) and Fe(II)/Fe(III) metal ions when at the same $[Cu(H_{-3}G_4)]^{2-}$ level concentration (10^{-3} mol.L^{-1}) can complex with the peptide or hydrolyze at high pH and then act as interfering species.

KINETIC OF TRACE-METAL- CATALYZED OXIDATION OF S(IV)

The studies of the influence of metal ions, such as Mn(II), Ni(II), Co(II), Cr(III), Fe(II) and Fe(III) at 10^{-4} mol.L^{-1} level, when initially mixed to the S(IV) solution ($9.0x10^{-5}$ mol.L^{-1}), showed that these metal ions (except Ni(II)) catalyze the autoxidation of S(IV). After two hours, no S(IV) remained in solution. Besides the Fe(II)/(III) ions, at this level, interfere since there is a strong hydrolysis.

It is important to note that the trace-metal-catalyzed autoxidation of sulfite is much slower than any of the reactions observed with copper peptide complex[24] (see Figure 1*(A)*), and that in the working solutions the peptide was kept in 10% molar excess to the Cu(II) ion. This ligand is a strong chelator for some trace metals.

In this way, to follow the kinetic of the S(IV) catalyzed autoxidation, it was possible to use the Cu(III) formation in a FIA system, as an indicator of S(IV) concentration in a acetate 0.02 $mol.L^{-1}$ buffer solution (pH= 4.7) and metal ions at 10^{-5} $mol.L^{-1}$solution. These studies were carried out by using one constant flow of the buffer sample solution containing S(IV) ($9x10^{-5}$ $mol.L^{-1}$) and metal ion ($1x10^{-5}$ $mol.L^{-1}$) and introducing, every 100 seconds, a new volume of $[Cu(H_{-3}\ G_4\ )]^{2-}$ solution, in the flow stream. The absorbance change, considering the calibration graphic, allowed to calculate the S(IV) concentration as the solution aged.

In the Figure 4, the catalytic effects of Mn(II) and Fe(II)/Fe(III) ions are showed. It can be seen that Mn(II) is more effective than Fe(III) and Fe(II) for the same concentration. For $1x10^{-5}$ $mol.L^{-1}$ in Fe(II) it was also clear an induction period. In approximately 20 minutes the limit absorbance was reached. This time is very long compared to the short time spent during the Cu(II) complex injection, so the relative error is small. During this time Co(II), Ni(II), Cu(II) and Cr(III) ($1x10^{-5}$ $mol.L^{-1}$) have showed no influence.

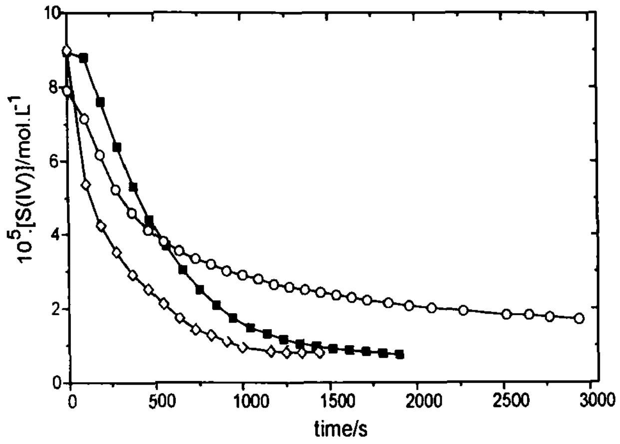

FIG. 4 - Catalytic effect of some transition metals (1.5×10^{-5} mol.L^{-1}) in the S(IV) autoxidation ([S(IV)] = 9×10^{-5} mol.L^{-1}, acetate buffer = 0.02 mol.L^{-1}, pH = 4.7; ■ =Fe(II);○ = Fe(III) and ◇ = Mn(II) (T=25 ^{0}C).

Figure 5 shows the catalytic effect of Mn(II), at different concentrations, on the autoxidation of S(IV) and the synergistic effect of Fe(III).

The trivalent metal ion is the catalyst in the autoxidation process, which can react with SO_3^{2-} to initiate the radical chain reaction (similar to equation (1)). If Fe(III) is present it reacts with S(IV), which rapidly forms peroxomonosulfate radical by reaction with oxygen (equation 3).

$$Fe^{3+} + SO_3^{2-} \rightarrow Fe^{2+} + SO_3^{-\bullet} \qquad (6)$$

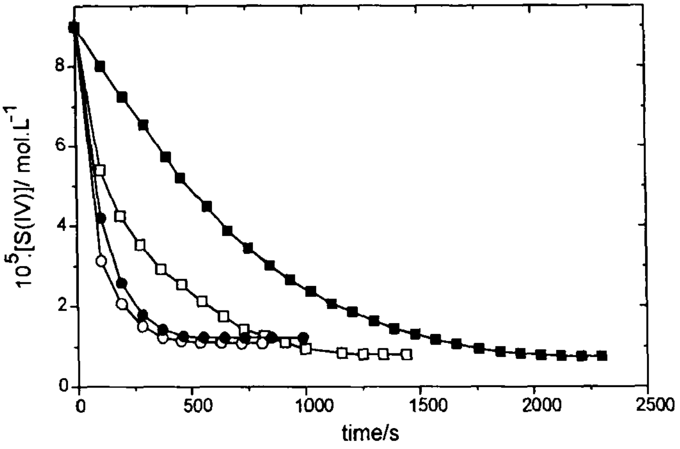

Figure 5 - Catalytic effect of Mn(II) and the synergistic effect of Fe(III) on the S(IV) autoxidation. [S(IV)] = 9×10^{-5} mol.L^{-1}, ■ = [Mn(II)] = 1.0×10^{-5} mol.L^{-1}; □ = [Mn(II)] = 1.5×10^{-5} mol.L^{-1}; O = [Mn(II)] = 2.5×10^{-5} mol.L^{-1} and ● = mixture of [Mn(II)] = 1.0×10^{-5} mol.L^{-1} and [Fe(III)] = 1×10^{-7} mol.L^{-1}; acetate buffer = 0.02 mol.L^{-1} (pH = 4.7) T = 25^{0}C.

Then $SO_5^{-\bullet}$ can oxidize Mn(II) to Mn(III). The subsequent reactions involve the reduction of Mn(III) by SO_3^{2-}. Fe(III) is present as unavoidable impurities in the chemicals. It is difficult to exclude Fe(III) even in a highly purified water where it may be present at concentration of 8×10^{-8} mol.L^{-1}[29].

It must be noted that these level concentrations of S(IV) and catalyst, are very close to the environmental conditions. Other methods proposed to study this phenomenon were not sensitive enough to follow low S(IV) concentration in presence of trace metal ions, since they have worked at 10^{-4} to 10^{-3} mol.L^{-1} level[8,28,29].

The order of catalytic activity varies significantly dependening on the selected experimental conditions, specially the oxidation state of the metal ion, the concentration range, pH and complex medium.

All the published data lead to predictions that Fe(III) and Mn(II) catalyzed autoxidation reactions can represent up to 80% of the overall oxidation process in the pH range 4 to 7 in the aqueous phase [2, 3, 18].

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