

Study of catalytic processes for biodiesel production wastewater treatment

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Abstract: The study of the possibility of removing organic compounds from wastewater originating from the biodiesel purification stage by two catalytic processes, HSO_5^- /transition metal and Fenton method has been presented. The source of the ion HSO_5^- is potassium monopersulphate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) (Oxone) that may be decomposed into radicals (OH^\cdot , $\text{SO}_4^{\cdot-}$, $\text{SO}_5^{\cdot-}$) by means of transition metal as Co(II). Different concentrations were used for both compounds and the combination ($[\text{Co}^{2+}] = 1.00 \mu\text{M}/[\text{HSO}_5^-] = 5.00 \cdot 10^{-2} \text{ M}$) achieved the highest COD removal (60%) and complete decomposition of the oxidant was verified for contact times of 45 min. This process has some advantages comparing to the conventional Fenton method such as the absence of the costly pH adjustment and the Fe(III) hydroxide sludge which characterize this treatment process. The Fenton process showed that the combination of $[\text{H}_2\text{O}_2] = 2.00 \text{ M}/[\text{Fe}^{2+}] = 0.70 \text{ M}$ was the best and archived COD removal of 80%. The treatments studied in this research have achieved high COD removal, but the wastewater from the biodiesel purification stage presents very high parametric values of Chemical Oxygen Demand (667,000 mgO_2/L), so the final COD concentration reached is still above the emission limit of discharge in surface water, according the Portuguese Law (Decree-Law 236/98). However, both treatments have proved to be feasible techniques for the pre-oxidation of the wastewater under study and can be considered as a suitable pre-treatment for this type of wastewaters. A rough economic analysis of both processes was, also, made.

Introduction

Biodiesel has become very attractive as a biofuel due to its environmental benefits in terms of reducing greenhouse gas emissions and it has been mainly produced from edible vegetable oils all over the world, which are easily available. The production of purified biodiesel includes the generation of a highly polluting wastewater that needs to be treated prior to environmental discharge. This type of effluent presents high values of Chemical Oxygen Demand (COD), much higher than allowed by the Portuguese legislation (Decree-Law 236/98) for wastewater discharges into surface water (150 mg/L).

Several strategies based on physical, chemical and biological treatments have been purposed to treat this type of effluent (Ayoola et al. 2016, Mozaffarikhaha et al. 2017, Pardal et al. 2014, Rattanapan et al. 2011), but, none of them reduced COD levels sufficiently to allow direct discharge.

Advanced Oxidation Processes (AOPs) may be a potent tool in the treatment of these effluents, due to the capacity of generating free radicals, which can attack and degrade complex organic molecules (Ebrahimi et al. 2017, Ríos et al. 2017, Thomas et al. 2017).

Fenton's reagents oxidation is a homogeneous catalytic advanced oxidation process based on the decomposition of

hydrogen peroxide by Iron (II) ions resulting in the generation of hydroxyl radicals (HO^\cdot) (Pignatello et al. 2006, Rivas et al. 2003a). These radicals are characterized by high reactivity, due to its significant oxidizing potential ($E^0=2.31\text{V}$) (Parson 2004).

Generally, Fenton's oxidation process consists in pH adjustment, oxidation reaction, neutralization and coagulation for precipitation. So, the organic substances are removed at two stages: oxidation and coagulation (Kange and Hwang 2000).

The use of persulphate salts ($\text{Na}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{S}_2\text{O}_8$ and KHSO_5), is an emerging technology in situ of chemical oxidation of organic compounds (Wei et al. 2015). These compounds can directly react with organic molecules with a redox potential comparable to hydrogen peroxide, but the reaction is slow at room temperature (Hussain et al. 2013, Solís 2017). However, they can be induced to form sulphate radicals, thereby providing mechanisms for reaction with free radicals like to the hydroxyl radicals.

Monopersulphate (HSO_5^-) is an active ingredient of a triple potassium salt, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (Oxone). At pH above the 8–9, monopersulphate, ($\text{pK}_a=9.13$), dissociates and the predominant specie is SO_5^{2-} , which, apparently, reacts with ionic forms of organic matter (Guan et al. 2011, Solís 2017). It also can be induced by photolytic, catalytic and/or photocatalytic processes to form sulphate radicals (Chen et al.

2012, Chi et al. 2016, Wang and Chu 2012) thereby providing mechanisms for reaction with some advantages comparing to hydroxyl radicals (Hu and Long 2016, Oh et al. 2016). Oxone can also be decomposed into radicals by means of transition metals, such as Co (II), Ru (II) and Mn (II) (Rivas et al. 2012), according Eqs. 1, 2 and 3:



M = Co (II), Ru (II) or Mn (II)

Co (II) has been reported as one of the most effective metal catalysts for the activation of HSO_5^- promoting a radical sulphate complex mechanism (Rivas et al. 2012, Sun et al. 2009).

So, the main objective of this study was to evaluate the performance of two catalytic treatments based in advanced oxidation processes; the traditional Fenton process and the emerging treatment that uses the compound monopersulphate (HSO_5^-) on the removal of wastewater COD from the biodiesel purification stage. Several combinations of the amounts of oxidant/catalyst have been investigated and optimum conditions assessed.

Materials and methods

Materials and chemical reagents

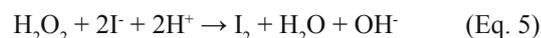
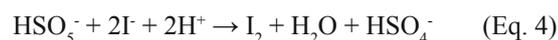
Table 1 summarises the physicochemical characteristics of the biodiesel wastewater used, provided by PRIO (Prio Energy Co).

The reagents used in this work were: sulfuric acid, H_2SO_4 , 95–98%, (Panreac); ultrapure water, Mili-Q. Resistivity 10 M Ω cm; sodium hydroxide, NaOH, 98%, (Panreac); potassium iodate, KIO_3 , (Panreac); potassium iodide, KI, 99.0–100.5%, (Panreac); ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4 \cdot 4\text{H}_2\text{O}$, 93.1–101.0% (Panreac); Oxone, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, 99.9%, (Sigma Aldrich); cobalt(II) sulphate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, (Sigma Aldrich); sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, 98–102%, (Panreac); hydrochloric acid, HCl, 36% (Panreac); barium chloride, $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ (Panreac); hydrogen peroxide, H_2O_2 , 30% w/w, (Scharlab); iron(II) sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, (Sigma Aldrich); potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, (Panreac) and silver nitrate, AgNO_3 , (Panreac). All reagents used were analytical grade.

Analytical method

Different physico-chemical parameters such as pH, Conductivity, Redox potential, Turbidity, Chemical Oxygen Demand (COD), Oil and grease and Chlorides were analysed for the sample characterization. The characterization was performed according to Standardized Water and Wastewater Methods (APHA 2012). The pH and Redox Potential were determined by the potentiometer pH – Metron 654 pH meter and WTW – Inolab potentiometer respectively, while Conductivity was measured by the conductivity meter Methohm, and the Turbidity using a WTW Turb.550 turbidimeter. In the determination of sulphates the furnace, Thermo – Heraeus, model K 114 was used.

For both catalytic treatments ($\text{HSO}_5^-/\text{Co}^{2+}$ and Fenton process) several concentrations of Oxone and hydrogen peroxide were tested and its evolution over time of reaction was monitored using the iodometric method. This method consists in adding to the sample an excess of iodide which is titrated with sodium thiosulphate solution. Thus, 5 mL of sample was taken, 10 mL of H_2SO_4 , 2.0 N, 25 mL of KI (20 g/L) and a few drops of saturated ammonium molybdate solution were added, which acted as a catalyst. The reaction that occurs is:



Then it is titrated with sodium thiosulfate, previously measured with KIO_3 and the desired concentration is obtained by:

$$C = (\text{V}_{\text{S}_{203}^{2-}} \cdot \text{C}_{\text{S}_{203}^{2-}}) / 2 \cdot \text{V}_{\text{sample}} \quad (\text{Eq. 6})$$

where $\text{V}_{\text{S}_{203}^{2-}}$ is the volume of thiosulphate spent in the titration, $\text{C}_{\text{S}_{203}^{2-}}$ is the concentration of the thiosulphate solution used and V_{sample} is the volume of the sample.

At the end of the treatments organic matter degradation was carried out by COD determination (APHA 2012). The sulphates were determined by using the gravimetric method (APHA 2012) and the chlorides with the Mohr method (APHA 2012).

Methodology of research

Both experiments were carried out in a discontinuous way using 300 mL of wastewater with stirring at a constant speed of 250 rpm to avoid concentration gradients. The assays started

Table 1. Biodiesel wastewater physicochemical characteristics and the respective Limit Emission Values (LEV) of wastewater discharges in surface water according Decree-Law 236/98 (Portuguese legislation)

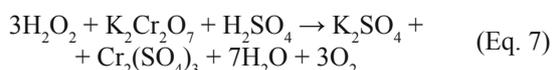
Parameter	Biodiesel wastewater	Decree-Law 236/98 (LEV)
pH	3.0	6.0–9.0
Redox Potential (mV)	360	–
Conductivity ($\mu\text{S}/\text{cm}$)	190	–
Turbidity (NTU)	0.36	–
COD (mgO_2/L)	667,000	150
Oil and grease (mg/L)	17	15
Chlorides (mg/L)	1065	–

after the addition of different dosages of (i) Oxone and Co^{2+} and (ii) H_2O_2 and Fe^{2+} depending on the type of test (catalytic oxidation of Oxone or Fenton process, respectively). Sodium hydroxide had been added to maintain the pH ($9 \leq \text{pH} \leq 10$) along the assays of catalytic treatment with Oxone.

Samples were withdrawn over time to analyze the evolution of the concentration of (i) Oxone and pH and (ii) hydrogen peroxide and pH according to the type of treatment to be performed (catalytic treatment with Oxone or Fenton process, respectively).

COD was analyzed at the end of each treatment, to assess the respective removal efficiency. For Fenton's assays the samples were previously filtered to remove the formed Fe(III) hydroxide.

According to previous studies, the residual amounts of H_2O_2 consume $\text{K}_2\text{Cr}_2\text{O}_7$, according to Eq.7, leading to an increase in COD measured (Lee et al. 2011, Pieczykolan et al. 2012). It is mostly due to the Cr^{3+} ions formed by the reduction of potassium dichromate (Kang et al. 1999).



This interference of H_2O_2 in COD analysis depends on the type of pollutants (Wu and Englehardt 2012) and may be avoided by using a calibration curve calculated specifically for the type of effluent (Rivas et al. 2003a).

So an experimental correlation was adopted deducing the empirical correlation by mixing different known amounts of H_2O_2 into the wastewater and measuring the total COD of the mixture. By subtracting the COD concentration without the addition of hydrogen peroxide the expression was obtained:

$$C_{\text{COD}} = C_{\text{CODm}} - 0.48 \cdot C_{\text{H}_2\text{O}_2} \quad (\text{Eq. 8})$$

In this equation all concentrations are given in mg/L and COD is the COD before reaction, COD_m is the COD measured after the reaction and $C_{\text{H}_2\text{O}_2}$ is the concentration of residual H_2O_2 . The COD measured on the samples after reaction time was converted to prevent the interference of H_2O_2 in COD analysis using the Eq. 8.

All the experiments were carried out in triplicate and the values presented are the average of the results and the obtained standard deviation.

Results and discussion

Fenton treatments

In the application of Fenton treatment, there were tested two oxidant concentrations: 1.50 M and 2.00 M with several doses of Fe (II) sulphate. Experiments with higher concentrations could not be carried out because in those cases a violent reaction with a quick boiling of the sample was observed. Figure 1 shows the evolution of the hydrogen peroxide concentration over time for different concentrations of Fe (II).

For all tested $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ combinations, the reaction has a very rapid kinetics, with the disappearance of approximately 96% of H_2O_2 at the initial time for concentration of 1.50 M (Figure 1.A) and 97% for 2.00 M H_2O_2 (Figure 1.B), with virtually no decomposition beyond this time. This result is supported by the literature that, also, reports short oxidation times (Kang et al. 2002, Martínez et al. 2003).

In figure 2, the COD removals obtained for both tests are presented.

As we can see, the COD removals for the tests performed with the initial H_2O_2 concentration of 1.50 M (Figure 2.A), were low and ranged from 23% to 49%. For the 2.00 M H_2O_2 tests, lower parametric values of COD were obtained and increasing removals rates were achieved up to the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ combination of 2.00 M/0.70 M (Figure 2.B). The highest percentage reaching 80% was obtained. It seems, therefore, that this combination of reactants is optimal. This result is corroborated by Gonçalves et al. 2014, who reported COD removal percentages in the order of 70 to 80%. The COD value obtained was 133,400 mgO_2/L . For the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ combination, 2.00 M/0.80 M, the removal obtained was already lower, which may indicate that the Fe (II) ion added was already excessive, causing inhibition of the oxidative process. In fact, the scavenging effect of Fe^{2+} on the hydroxyl radicals generated, may contribute to the decrease in COD removal, according to the Eq. 9 (Buxton et al. 1988):

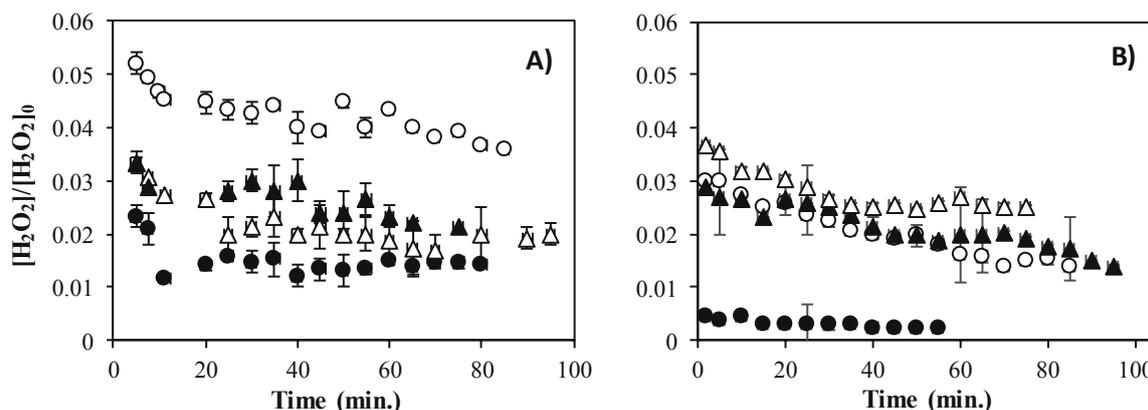
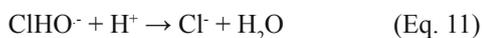


Fig. 1. Evolution of normalized concentration of H_2O_2 with time in presence of Fe^{2+} . Experimental conditions:
A) $[\text{H}_2\text{O}_2]_0 = 1.50 \text{ M}$; $[\text{Fe}^{2+}]_0 (\text{M})$: ● – 0.20 M; △ – 0.40 M; ○ – 0.60 M; ▲ – 0.70 M; $\text{pH}_i = 2.98$; $T = 25^\circ\text{C}$.
B) $[\text{H}_2\text{O}_2]_0 = 2.00 \text{ M}$; $[\text{Fe}^{2+}]_0 (\text{M})$: ○ – 0.50 M; ▲ – 0.60 M; △ – 0.70 M; ● – 0.80 M; $\text{pH}_i = 2.98$; $T_i = 25^\circ\text{C}$

The wastewater contains a great amount of chlorides, so they can have interfered in the efficacy of Fenton treatment, because they destroy hydroxyl radicals by means showed in Eq. 10 and Eq. 11 (Kumar 2011):



HSO_5^-/Co (II) treatments

To avoid the disadvantage of the generation of iron (III) hydroxide sludge of Fenton's reagent, the effect of the combination of Oxone with the transition metal Co^{2+} was tested. The results are presented in Figure 3. However, it is necessary to consider the residual metal concentration in the treated effluent, as well as the accumulation of sulphates in the solution.

All assays had run at alkaline pH and started with cobalt concentrations of $0.10 \mu\text{M}$ (Figure 3.A), but the difficulty in dosing the compound led to its increase to $1.00 \mu\text{M}$ which significantly increased the rate of Oxone decomposition (Figure 3.B). All catalytic assays showed total decomposition of the oxidant for contact times ranging from 45 min. to

2 hours depending of the initial concentration. Figure 4 shows COD removal rates variable and assumed values between 17% and 60%. The most effective test was the combination of $[\text{Oxone}]_0 = 5.00 \cdot 10^{-2} \text{ M}$; $[\text{Co}^{2+}] = 1.00 \mu\text{M}$ that reached a COD removal near 60%, assuming the parametric value of $260,000 \text{ mgO}_2/\text{L}$. As this reaction process generates sulphates these were measured for this assay and the parametric value obtained was 2000 mg/L SO_4 . Although elevated, they are still within the values allowed by the Portuguese legislation for discharge (2000 mg/L SO_4).

As rule of thumb we can say that an increase in the initial Oxone concentration exerts a positive effect on COD removal reaching an optimum value after which it slightly starts to be negative. This result was also mentioned by (Solís 2017). The scavenging effects of $\text{SO}_4^{\cdot-}$ in catalyst, according to Eq. 12, (Rivas et al. 2012) and/or the SO_5^{2-} on hydroxyl radicals (Solís 2017) may contribute to the decrease of COD.



A rough economic analysis of both processes was made based on the costs of oxidants. The value of mg oxidant/mg COD degraded for the best experiment of both treatments

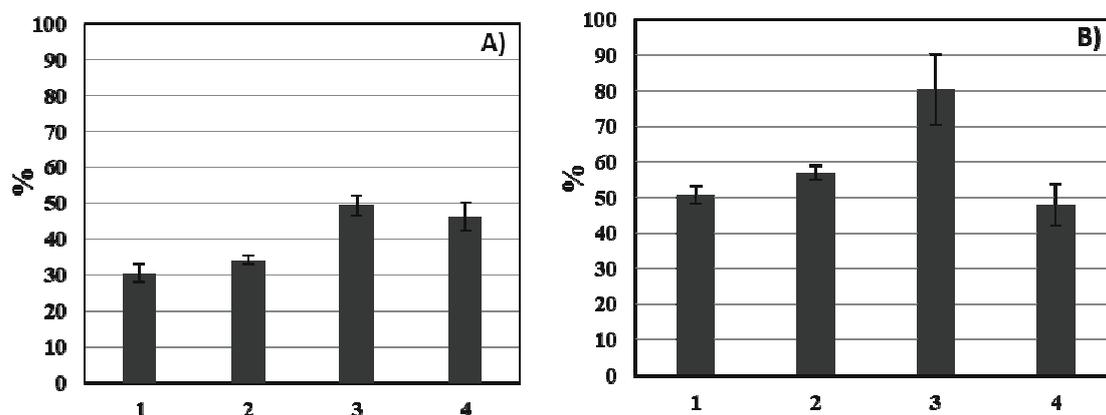


Fig. 2. COD removal for the different catalytic assays of Fenton's reaction: Experimental conditions:

A) $[\text{H}_2\text{O}_2]_0 = 1.50 \text{ M}$; $[\text{Fe}^{2+}] \text{ (M)}$: 1 – 0.20; 2 – 0.40; 3 – 0.60; 4 – 0.70.

B) $[\text{H}_2\text{O}_2]_0 = 2.00 \text{ M}$; $[\text{Fe}^{2+}] \text{ (M)}$: 1 – 0.50; 2 – 0.60; 3 – 0.70; 4 – 0.80

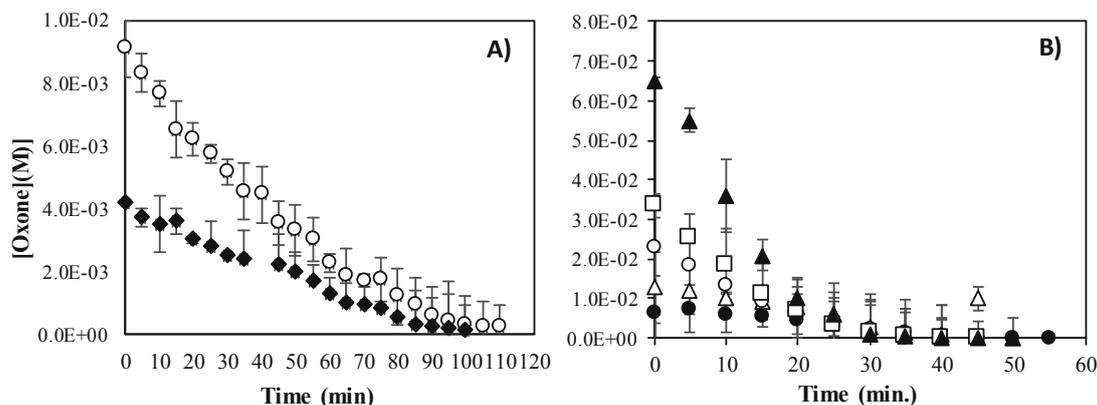


Fig. 3. Evolution of the concentration of Oxone for catalytic assays. Experimental conditions: A) $[\text{Oxone}]_0/[\text{Co}^{2+}]_0 \text{ (M}/\mu\text{M)}$:

◆ – $5.00 \cdot 10^{-3}/0.10$; ○ – $1.00 \cdot 10^{-2}/0.10$; $9 < \text{pH} < 10$; $T = 25^\circ\text{C}$. B) $[\text{Oxone}]_0/[\text{Co}^{2+}]_0 \text{ (M}/\mu\text{M)}$: ● – $1.00 \cdot 10^{-2}/1.00$; △ – $2.00 \cdot 10^{-2}/1.00$; ○ – $3.00 \cdot 10^{-2}/1.00$; □ – $5.00 \cdot 10^{-2}/1.00$; ▲ – $7.50 \cdot 10^{-2}/1.00$; $9 < \text{pH} < 10$; $T = 25^\circ\text{C}$

was calculated, the price of H₂O₂ and Oxone on the market was considered, and the cost associated with H₂O₂ and Oxone consumption was estimated (Table 2).

Although the amounts of Oxone used, compared to hydrogen peroxide are much smaller, the Fenton process seems to be more attractive. It is estimated that the cost of the reactant is 75% of the total of the operation (Rivas et al. 2003b).

Summarizing, both treatments are efficient on the removal of organic matter. The Fenton process showed a higher capacity to remove COD but HSO₅⁻/Co²⁺ has some advantages such as it does not generate Fe (III) hydroxide sludge and it is much easier to store and handle in comparison to hydrogen peroxide. However, it is, also, necessary to consider the environmental impact of the residual metal, as well as the accumulation of sulphates in the solution.

Conclusions

- Biodiesel wastewater has higher COD parametric values than allowed by the Portuguese Law for wastewater discharge in surface waters. It is therefore imperative to treat it before being discharged.
- The carried-out studies showed the possibility of using the two catalytic processes: the Fenton process and the potassium monopersulphate compound activated by cobalt ion into removing the COD from the biodiesel wastewater.
- From the results of this study, the following order of treatment efficiency was obtained: Fenton Process > HSO₅⁻/Co²⁺.
- For Fenton's reaction the optimal value of hydrogen peroxide and Fe(II) concentrations were 2.00 M and

0.70 M, respectively and an COD reduction of 80% was obtained.

- The combination of [Oxone]₀ = 5.00·10⁻² M; [Co (II)] = 1.00 μM, reached the best COD removal (near 60%) assuming the parametric value of 260,000 mgO₂/L.
- Both treatments showed to be effective into oxidation of wastewater under study. However, the final COD concentration reached is still above the emission limit value of discharge of wastewater in surface water, according to the Portuguese Law.
- The two treatments can be considered as a suitable pre-treatment for this type of wastewater, although a rough economic analysis of the processes indicates that the Fenton's process could be more interesting to deal with this type of effluent.
- In the future, it is necessary to know the mineralization obtained for both processes and make a deeper study of the best operational conditions of the process HSO₅⁻/Co²⁺.

Acknowledgement

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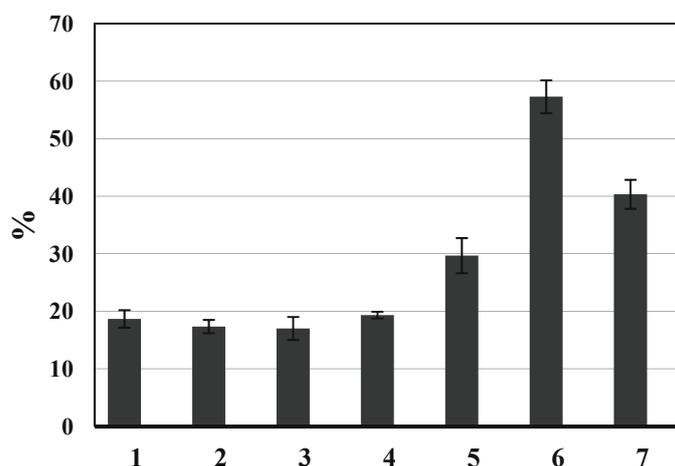


Fig. 4. COD removal rates for different catalytic assays of Oxone and Co²⁺.

Experimental conditions: [Oxone]/[Co²⁺] (M/μM): 1 – 5.00·10⁻³/0.10; 2 – 1.00·10⁻²/0.10; 3 – 1.00·10⁻²/1.00; 4 – 2.00·10⁻²/1.00; 5 – 3.00·10⁻²/1.00; 6 – 5.00·10⁻²/1.00; 7 – 7.50·10⁻²/1.00

Table 2. Economic analysis of the Fenton process and Oxone/Co²⁺ process

Parameter	Fenton Process	Oxone/Co ²⁺ Process
	H ₂ O ₂ (Solution 50%)	Oxone
mg H ₂ O ₂ /mg COD	7.80	–
mg Oxone/mg COD	–	0.08
Price (USA\$)	750/ton	65.5/kg
Price/m ³ (USA\$/m ³ .ppm COD)	0.012	0.052

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