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TRATAMENTO DE ÁGUA RESIDUAL PROVENIENTE DA PRODUÇÃO DE BODIESEL COM RECURSO AO OXIDANTE QUÍMICO IÃO PERSULFATO

WASTEWATER TREATMENT OF BODIESEL PRODUCTION USING PERSULPHATE ION AS AN OXIDANT

TRATAMIENTO DE AGUAS RESIDUALES DE LA PRODUCCIÓN DE BODIESEL UTILIZANDO ION PERSULFATO COMO OXIDANTE

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RESUMO

Introdução: A produção de biodiesel produz um efluente altamente poluente, apresentando altos valores de Carência Química de Oxigênio (CQO), óleos e gorduras, entre outros contaminantes.

O persulfato de sódio é um poderoso oxidante ($E^\circ = 2.1V$). Além da oxidação direta que é favorecida em meios alcalinos, ela pode ser induzida por processos fotolíticos, fotos catalíticos e / ou catalíticos formando radicais sulfato ($E^\circ = 2.6 V$), proporcionando mecanismos de reação com radicais livres como radicais hidróxilo.

Objetivos: Neste trabalho foi testado o efeito do composto monopersulfato de potássio ($2KHSO_5KHSO_4K_2SO_4$), (Oxone) na remoção da CQO em água residual da etapa de purificação do biodiesel.

Resultados: Os ensaios, oxidação direta a pH alcalino e oxidação catalítica com íons cobalto, Co (II), mostraram que os primeiros, para concentrações de Oxone de $1.00 \times 10^{-2} M$ e $4.00 \times 10^{-3} M$, não foram efetivos, pois não houve decomposição do mesmo, para tempos de reação de três horas, não tendo ocorrido, portanto, remoções da CQO. Nos ensaios catalíticos foram testadas combinações variando entre $5.00 \times 10^{-3} M$ e $7.50 \times 10^{-2} M$ para o oxidante e $0.10 \mu M$ e $1.00 \mu M$ para o catalisador.

A decomposição completa do oxidante foi sempre verificada entre 15 min. e 2 h.

Os testes com menor concentração de cobalto mostraram taxas de remoção de CQO em torno de 20% enquanto as maiores atingiram os 60%.

Conclusões: O ensaio mais favorável consegue remoções significativas da CQO, mas não o suficiente para que o efluente seja descarregado em meio hídrico, de acordo com a legislação portuguesa.

Palavras-chave: “Monopersulfato de potássio”, “Oxidação química”, “Carência Química de Oxigênio”, “Águas residuais da purificação do biodiesel”.

ABSTRACT

Introduction: The production of biodiesel produces a highly polluting effluent, because presents high values of Chemical Oxygen Demand (COD), oils and fats, among other contaminants.

Sodium persulphate is a powerful oxidant ($E^\circ = 2.1V$). In addition to the direct oxidation that is favored in alkaline media, it can be induced by photolytic processes, catalytic and / or catalytic photos forming sulphate radicals ($E^\circ = 2.6 V$) thus providing reaction mechanisms with free radicals like hydroxyl radicals.

Methods: In this work the effect of the potassium monopersulphate compound ($2KHSO_5.KHSO_4K_2SO_4$), (Oxone) on the removal of COD in residual water from the biodiesel purification step was tested.

Results: The tests, direct oxidation at alkaline pH and catalytic oxidation with cobalt ions, Co(II), showed that the former, for Oxone concentrations of $1.00 \times 10^{-2} M$ and $4.00 \times 10^{-3} M$, were not effective because no decomposition occurred, for reaction times over three hours, thus not occurring removal of COD. In the catalytic assays combinations were tested, varying between $5.00 \times 10^{-3} M$ and $7.50 \times 10^{-2} M$ for the oxidant and $0.10 \mu M$ and $1.00 \mu M$ for the catalyst.

The complete decomposition of the oxidant was always verified between 15 min. and 2 h.

The tests with the lowest concentration of cobalt showed COD removal rates around 20% and the highest one reached 60%.

Conclusions: The most favorable assay achieves significant COD removals, but not enough for the effluent to be discharged in the hydric medium according the portuguese legislation.

Keywords: “Potassium monopersulphate”, “Chemical oxidation”, “Chemical Oxygen Demand”, “Wastewater from biodiesel purification”.

RESUMEN

Introducción: La producción de biodiesel produce un efluente altamente contaminante, presentando altos valores de Demanda Química de Oxígeno (DQO), aceites y grasas, entre otros contaminantes.

El persulfato de sodio es un poderoso oxidante ($E^\circ = 2.1V$). Además de la oxidación directa que es favorecida en medios alcalinos, puede ser inducida por procesos foto líticos, fotocatalíticos y/o catalíticas formando radicales sulfato ($E^\circ = 2.6 V$), proporcionando mecanismos de reacción con radicales libres como los radicales hidroxilo.

Objetivos: En este trabajo se probó el efecto del compuesto monopersulfato de potasio ($2KHSO_5KHSO_4K_2SO_4$), (Oxone) en la remoción de la CQO en agua residual de la etapa de purificación del biodiesel.

Resultados: En los ensayos catalíticos se probaron combinaciones que oscilan entre $5.00 \times 10^{-3} M$ y $7.50 \times 10^{-2} M$ para el oxidante y $0.10 \mu M$ y $1.00 \mu M$ para el catalizador. La descomposición completa del oxidante ha sido siempre comprobada entre 15 min. y 2 h.

Los ensayos, oxidación directa a pH alcalino y oxidación catalítica con iones cobalto, Co (II), mostraron que los primeros, para concentraciones de Oxone de $1.00 \times 10^{-2} M$ y $4.00 \times 10^{-3} M$, no fueron efectivos, pues no hubo descomposición de este, para

tiempos de reacción de tres horas, no habiendo ocurrido, por lo tanto, remociones de la CQO. En los ensayos catalíticos se probaron combinaciones que oscilan entre 5.00×10^{-3} M y 7.50×10^{-2} M para el oxidante y $0.10 \mu\text{M}$ y $1.00 \mu\text{M}$ para el catalizador. La descomposición completa del oxidante ha sido siempre comprobada entre 15 min. y 2 h.

Las pruebas con menor concentración de cobalto mostraron tasas de remoción de DQO en torno al 20% mientras que las mayores alcanzaron el 60%.

Conclusiones: La prueba más favorable logró una importante eliminación de DQO, pero no lo suficiente para que el efluente se descarga en el medio acuático, de acuerdo con la ley portuguesa.

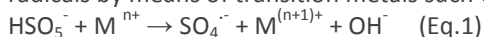
Palabras clave: "Monopersulfato de potasio", "Oxidación química", "Demanda Química de Oxígeno", "Aguas residuales de depuración de biodiesel".

1. STATE OF ART

The untreated biodiesel contains several impurities, which will impact on the performance and durability of the diesel engine. Therefore, the purification stage is essential. The more traditional purification method is wet washing. However, the inclusion of additional water to the process offers many disadvantages, including the generation of a highly polluting wastewater that needs to be treated prior to environmental discharge and the significant loss of biodiesel into the wastewater phase. This type of effluent has quality parameters much higher than allowed by the portuguese legislation, Decree Law 236/98 of 1st August.

Several strategies based on physical, chemical and biological treatments have been purposed to treat this type of effluent (Rattanapan, Sawain, Suksaroj & Suksaroj, 2011; Pardal *et al*, 2014; Borrvalho, Pardal, Carvalho, Almeida & Baltazar, 2015). However, none of the processes reduced the Chemical Oxygen Demand (COD) levels sufficiently to allow direct discharge. 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). This compound can directly react with organic molecules with a redox potencial comparable to hydrogen peroxid (Hussain, Green & Ahmed, 2013; Solís, 2017). In addition to direct oxidation, the persulphate can be induced to form sulphate radicals, thereby providing mechanisms for reaction with free radicals like to the hydroxyl radicals. Activation of persulphate to form sulphate radicals is a potent remediation tool for a wide variety of contaminants (Rivas, Gimeno & Borrvalho, 2012).

Monopersulphate (HSO_5^-) is the 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 (Solís, 2017). It also can be induced by photolytic, catalytic and /or photocatalytic processes to form sulphate radicals (Chen *et al*, 2012; Wang & Chu, 2012; Chi *et al*, 2016) thereby providing mechanisms for reaction with some advantages comparing to hydroxyl radicals (Hu & Long, 2016; Oh, Dong & Lim, 2016). Oxone can also be decomposed into radicals by means of transition metals such Co(II), Ru(II) and Mn(II) (Rodriguez- Chueca *et al*, 2017), according Eq.1:



M= Co(II); Co(III), Ru(II) and Mn (II)

Moreover, Oxone is relatively stable at room temperature and easy to handle since is available in powder form (Rodriguez-Chueca *et al*, 2017).

So, this work was intended to study the effect of the potassium monopersulphate compound in the removal of chemical oxygen demand (COD) of wastewater from the biodiesel purification stage. Two types of tests were performed; direct oxidation and oxidation using the metal catalyst Co (II).

2. METHODS

In this work the effect of the potassium monopersulphate compound ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), (Oxone) on the removal of COD in residual water from the biodiesel purification step was tested.

2.1. Sample

Table 1 summarises the physicochemical characteristics of the biodiesel wastewater (BWP) used, that it was supplied by PRIO (Prio Energy Co).

Table 1. Biodiesel wastewater physicochemical characteristics.

Parameter	Biodiesel wastewater
pH	3.0
Redox Potential (mV)	360
Conductivity (μS/cm)	190
Turbidity (NTU)	0.36
COD (g O ₂ /L)	667
Fats (mg/L)	17

2.2 Data collection instruments

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. The absorbance at 254nm was measured using a UV/Visible espectrofotometer Pharmacia Biotech Ultraspec 2000. In the determination of Sulphates it was used the furnace, Thermo – Heraeus, model K 114.

The reagents used in this work were:

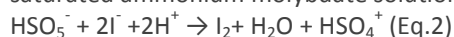
Sulfuric acid, H₂SO₄, 95-98%, (Panreac); Ultrapure water, Mili-Q. Resistivity 10 MΩ cm; Sodium hydroxide, NaOH, 98%, (Panreac); Potassium iodate, KIO₃, (Panreac); Potassium iodide, KI, 99.0-100.5%, (Panreac); Ammonium molybdate, (NH₄)₂MoO₄.4H₂O, 93.1-101.0% (Panreac); Oxone, 2KHSO₅.KHSO₄.K₂SO₄, 99.9%, (Sigma Aldrich) ; Cobalt sulphate, CoSO₄ 7H₂O, (Sigma Aldrich); Sodium thiosulphate, Na₂S₂O₃, 98-102%, (Panreac); Cloridric acid, HCl, 36% (Panreac); Barium chloride, BaCl₂.H₂O (Panreac).

All reagents used were analytical grade.

2.3 Analytical determinations

The experiments were carried out in alkaline medium, so the pH was maintained (9≤pH≤10) with addition of NaOH. For both treatments (direct oxidation and catalytic oxidation) several concentrations of Oxone were tested and its evolution over time of reaction was monitored using the iodometric method. This method consists of 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 H₂SO₄, 2.0 N, 25 mL of KI (20 g/L) and a few drops of saturated ammonium molybdate solution were added, which acts as a catalyst. The reaction that occurs is:



Then it is titrated with sodium thiosulfate, previously measured with KIO₃ and the desired concentration is obtained by:

$$C_{\text{HSO}_5^-} = (\text{Vs}_2\text{O}_3^{2-} \cdot \text{Cs}_2\text{O}_3^{2-}) / 2V_{\text{sample}} \quad (\text{Eq.3})$$

Where $\text{Vs}_2\text{O}_3^{2-}$ is the volume of thiosulphate spent in the titration, $\text{Cs}_2\text{O}_3^{2-}$ is the concentration of the thiosulphate solution used and V_{sample} is the volume of the sample.

The evolution of the organic matter degradation was carried out by COD determination (APHA 2012).

The sulphates were determined using the gravimetric method (APHA 2012).

2.4 Procedures

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

The observed standard deviation was always less than 5% of the reported value.

Different physic-chemical parameters such as pH, Conductivity, Redox potential, Turbidity and COD were analyzed for the sample characterization.

Both experiments were carried out in a discontinuous way using 300 mL of BWP with stirring. The assays started after the addition of different dosages of (i) Oxone and (ii) Oxone and Co (II) depending of the type of test (direct oxidation or catalytic oxidation, respectively). Sodium hydroxide had been added to maintain the pH (9≤pH≤10) along the assays.

Samples were withdrawn over time of the assay to analyze the evolution of the concentration of Oxone and the pH.

COD was analyzed at the end of each treatment, to assess the respective removal efficiency.

Finally, for the assay that reached the best removal of COD were measured the absorbance at 254 nm and the sulphates.

3. RESULTS

Direct oxidation results are shown in figure 1:

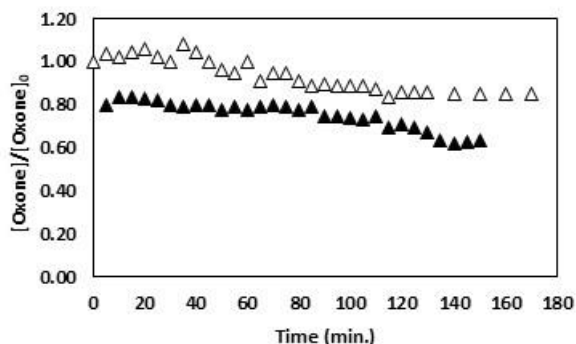


Figure 1 – Evolution of normalised concentration of Oxone in direct oxidation.

Experimental conditions: Empty symbols- $[Oxone]_0 = 4.00 \times 10^{-3} M$; Full symbols- $[Oxone]_0 = 1.00 \times 10^{-2} M$; $9 < pH < 10$; $T = 25^\circ C$.

Next, it was studied the effect of the catalyst Co (II) into the process of decomposition of Oxone and were made different combinations of oxidant and catalyst.

Figure 2 shows the results obtained:

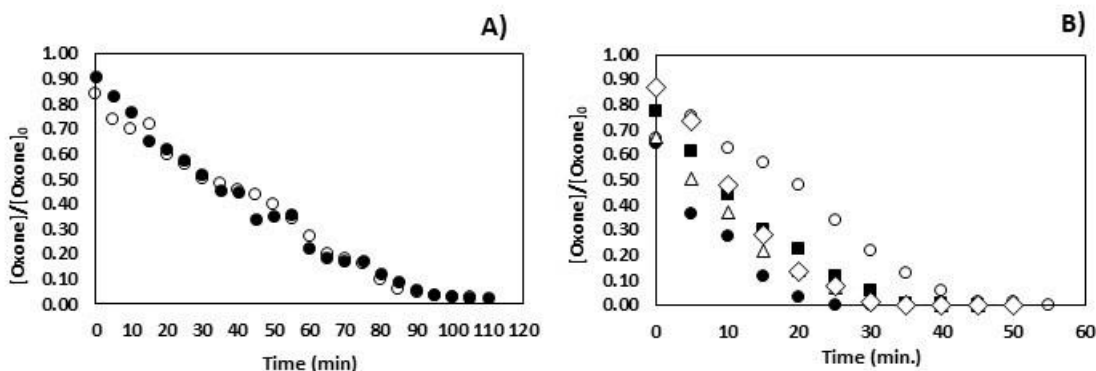


Figure 2 – Evolution of normalized concentration of Oxone for catalytic assays. Experimental conditions at A:

●- $[Oxone]_0 = 1.00 \times 10^{-2} M$; $[Co(II)] = 0.1 \mu M$; ○- $[Oxone]_0 = 5.00 \times 10^{-3} M$; $[Co(II)] = 0.1 \mu M$. Experimental conditions at B:
 ○- $[Oxone]_0 = 1.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; ●- $[Oxone]_0 = 2.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; *- $[Oxone]_0 = 3.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$;
 Δ- $[Oxone]_0 = 5.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; ◊- $[Oxone]_0 = 7.50 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; $9 < pH < 10$; $T = 25^\circ C$.

The results of COD removal for all experiments are in figure 3.

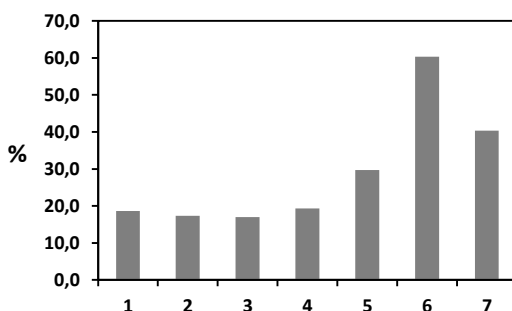


Figure 3 – COD removal rates for the different catalytic assays. Experimental conditions; 1- $[Oxone]_0 = 5.00 \times 10^{-3} M$; $[Co(II)] = 0.1 \mu M$;

2- $[Oxone]_0 = 1.00 \times 10^{-2} M$; $[Co(II)] = 0.1 \mu M$; 3- $[Oxone]_0 = 1.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; 4- $[Oxone]_0 = 2.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; 5- $[Oxone]_0 = 3.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; 6- $[Oxone]_0 = 5.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; 7- $[Oxone]_0 = 7.50 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$; $9 < pH < 10$; $T = 25^\circ C$.

At 254 nm the aromatic and, in general, the unsaturated compounds have a high molar extinction coefficient and consequently high absorbance. Thus, given the proportionality between this and the concentration, it can be said that the measurement obtained at this wavelength is indicative of the total amount of aromatic and unsaturated compounds present.

So, for the best assay, ($[Oxone]_0 = 5.00 \times 10^{-2} M$ and $[Co(II)] = 1.00 \mu M$), the absorbance at $\lambda = 254 \text{ nm}$ was measured. The results are in figure 4.

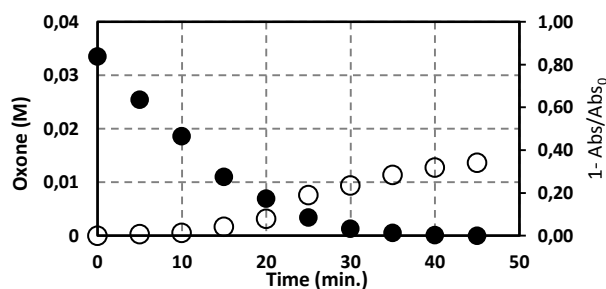


Figure 4 – Evolution of Oxone and absorbance ($\lambda = 254 \text{ nm}$) along de time.

Experimental conditions: Full Symbol- $[Oxone]_0 = 5.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \times 10^{-6} M$; Empty Symbol- Absorbance ($\lambda = 254 \text{ nm}$).

4. DISCUSSION

The results show that the direct oxidation tests for the potassium monopersulphate concentrations of $1.00 \times 10^{-2} M$ and $4.00 \times 10^{-3} M$ were not effective because there was no significant decomposition over more than three hours (Figure 1.), but after 2 days of reaction the monopersulphate suffered an abatement of 70% for the lower concentration tested.

The removal of COD was almost nonexistent, for these the assays (results not shown). The direct oxidation reported by some authors (Yu, Cui & Zhang, 2010; Rivas et al., 2012) and /or the initiation of the sulphate radical generation process by alkaline conditions (Guan, Ma, Li, Fang & Chen, 2011), seems to be a very slow process.

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

The reduction of Co(III) to Co(II) mediated by the oxidation of monopersulphate is thermodynamically feasible (0.82 V) and fast, and the process proceeds cyclically many times until monopersulphate is totally consumed (Rodríguez- Chueca et al., 2017). Actually, all catalytic assays showed total decomposition of the oxidant for contact times ranging from 15min. to 2 hours depending of the initial concentration (Figure2). The figure 3 shows the COD removal rates that were variable and assumed values between 17% and 60%.

The treatments were started with cobalt concentrations of $0.10 \mu M$, figure 2A, but the difficulty in dosing the compound led to its increase to $1.00 \mu M$ which significantly increased the rate of Oxone decomposition, Figure 2B. Obviously, for identical concentrations of Oxone tested ($1.00 \times 10^{-2} M$) COD removal was identical too (Figure 3).

An increase in the initial Oxone concentration had exert a positive effect on COD removal until reach an optimum value (60 %) after what it slightly started to be negative. This result was also mentioned by (Solís, 2017).

The most effective test in terms of removal of COD was the combination of $[Oxone]_0 = 5.00 \times 10^{-2} M$; $[Co(II)] = 1.00 \mu M$, that reached a COD removal near of 60%, assuming the value of 260 g /L . This result shows the efficacy of the monopersulphate into oxidate organic matter, but due to the large amount in the raw wastewater the final COD concentration is still above to the desired one. The Portuguese legislation, Decree-Law 236/98 of 1st August, indicates the parametric value of $150 \text{ mg O}_2/\text{L}$ as the discharge limit in a hydric medium. Anyway, the decrease of absorbance, (Figure 4), may indicate that the organic matter may be being decomposed into simpler molecules.

As monopersulphate is a source of sulphates they were measured ($2000 \text{ mg/L SO}_4^{2-}$) for the most favorable test. Although elevated, still are within the values allowed by the Portuguese legislation (2000 mg /LSO_4).

In summary, the direct oxidation $HSO_5^-/Co(II)$ treatment could be an interesting alternative for the treatment of this wastewater as a pre- or post-treatment process, alone or in combination with a biological system. In the latter case a biodegradation study should be recommended.

CONCLUSIONS

The BWP has COD values much higher than allowed by law. It is therefore imperative to treat them before being discharged into the hydric medium.

The direct oxidation with monopersulphate showed that decomposition was very slow, so there wasn't COD removal for the times of reaction monitorized. On the other hand, the use of Oxone with de catalyst cobalt seems to be a suitable alternative

to oxidize organic matter. Oxone improves catalytic oxidation of COD. The most effective test reached a COD removal rate near 60%, assuming the value of 260 g /L. This value is still far from the indicate for portuguese legislation as the discharge limit value in a hydric medium.

This treatment may to be a previous or post step to a treatment of this type of wastewater. The sulphates and cobalt must, also, be monitorized.

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