

56 (2015) 1793–1801 November

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Photocatalytic degradation of Kraft Lignin using the $S_2O_8^{2-}/Fe^0/UV$ process: optimization with multivariate analysis

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Received 27 December 2013; Accepted 1 August 2014

ABSTRACT

The combination of persulfate, zerovalent iron, and UV radiation is an advanced oxidation process which allows for the degradation of high concentrations of organic dyes. This process is based on the generation of transient species with high oxidizing power, mainly the hydroxyl radical (HO') and the sulfate radical (SO₄⁻). The reaction was carried out in a cylindrical glass reactor using potassium peroxydisulfate as an oxidant and zerovalent iron as a catalyst. The reaction was performed in a radiation chamber using a Philips HP-120 W lamp ($\lambda \ge 254$ nm). A Box–Behnken design and response surface methodology were employed to evaluate the effect of persulfate dosage (0.01 (-1)–0.05 (+1) g L⁻¹), iron dosage (0.01 (-1)–0.05 (+1) g L⁻¹), pH (2 (-1)–11 (+1)), and reaction time (10 (-1)–120 (+1) min) on the reduction of 100 mg L⁻¹ of Kraft Lignin. Optimization of the process determined that optimal experimental conditions were acidic pH (3.5), a persulfate concentration of 0.05 g L⁻¹, a zerovalent iron concentration of 0.01 g L⁻¹, and 60 min of reaction time, which resulted in 92% removal of Kraft Lignin, 96% chemical oxygen demand, 94% phenols, and 61.1% total organic carbon. The results indicate that the photocatalytic system was efficient in degrading a high concentration Kraft Lignin, and experimental design allowed determination of the maximum efficiency, with a 95% confidence interval.

Keywords: Advanced oxidation process; Biodegradation; Experimental design; Zerovalent iron; Persulfate; Sulfate radical

1. Introduction

In recent years, advanced oxidation processes (AOPs) have been developed as effective tools for the treatment of contaminated water. AOPs are particularly useful in the treatment of industrial effluents containing mainly organic matter that is difficult to degrade by natural or conventional methods. AOP processes are based on the *in situ* generation of highly reactive species, such as the hydroxyl radical (HO· E° ,

which varies between +1.8 and +2.7 V vs. NHE) [1], which is able to more quickly degrade organic matter through hydrogen abstraction [2]. The degradation of organic compounds using persulfate has recently emerged as a new AOP, and is used for *in situ* degradation of effluents with a high organic load. The decomposition of the persulfate anion $(S_2O_8^{2-} E^\circ = +2.01 \text{ V})$ [3], activated by UV radiation, generates the sulfate radical, which is a powerful oxidant $(SO_4^{-} E^\circ)$ between +2.5 and +3.1 V vs. NHE) [4], able to propagate the chain degradation of organic matter,

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generating radical species. Simultaneously, the sulfate radical can generate additional a hydroxyl radical *in situ*, which has as a short half life, but is able to abstract hydrogen from organic compounds, generating organic radicals that initiate the chain degradation of organic matter [5] (Eqs. (1)–(3)).

Aromatic electrophilic addition

$$OH + ArX \rightarrow HOArX$$
(1)

Electron transfer

$$\cdot OH + RX \to RX^{\cdot +} + OH^{-}$$
⁽²⁾

Hydrogen abstraction

$$OH + RH \rightarrow R' + H_2O \tag{3}$$

The key to the oxidation of organic compounds by persulfate is the generation of sulfate radicals (SO_4^-), which can be accomplished thermally [6–8], by photolysis (Eq. (4)) [9–12], as well as by an activated metal (Eq. (5)) [13–17], or by radiolysis (Eq. (6)) [18].

$$S_2 O_8^{2-} + hv \to 2SO_4^{-} \tag{4}$$

$$S_2O_8^{2-} + M^{n+} \to SO_4^{\cdot -} + M^{(n+1)+} + SO_4^{2-}$$
 (5)

$$S_2O_8^{2-} + e^- \to SO_4^{2-} + SO_4^{--}$$
 (6)

Potassium persulfate is less expensive than other oxidants, such as hydrogen peroxide or ozone, is easy to handle, and is soluble in water, which makes it a good additive for wastewater treatment [9,12]. When the persulfate anion is submitted to thermal activity or photolysis, sulfate radicals are generated. These radicals react with the aqueous medium generating hydroxyl radicals (Eq. (7)). The sulfate radicals predominate in neutral and acidic solutions [19,20], reacting with many organic compounds, especially aromatics, and are an effective oxidant given that oxidation is more efficient [4].

$$\mathrm{SO}_4^{-} + \mathrm{H}_2\mathrm{O} \to \mathrm{OH} + \mathrm{SO}_4^{2-} + \mathrm{H}^+ \tag{7}$$

Zerovalent iron is oxidized in an acid medium to form ferrous ions (Fe^{2+}). Simultaneously, the persulfate reacts with iron, generating sulfate anion and ferrous ions and subsequently sulfate radicals (Eqs. (8)–(11)) [14,21–23].

$$Fe^0 + hv \rightarrow Fe^{2+} + 2e^- \tag{8}$$

$$Fe^0 + S_2O_8^{2-} \to Fe^{2+} + 2SO_4^{2-}$$
 (9)

$$Fe^{2+} + S_2O_8^{2-} \to Fe^{3+} + 2SO_4^{--}$$
 (10)

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH$$
(11)

In general, the photolysis of various oxidant species generates strongly oxidizing radicals *in situ*, which together contribute to the overall efficiency of the process. Therefore, this research is based on the generation of the sulfate radical, catalyzed by zerovalent iron, to degrade Kraft Lignin as a model compound. This compound is the main component of the effluents generated in the process to obtain Kraft pulp, accounting for the elevated color and high organic charge present in the effluents [24].

2. Materials and methods

2.1. Reagents

Persulfate and zerovalent iron were acquired from Merck. Kraft Lignin $M_{\rm w}$ (molecular weight) 28,000 g mol⁻¹ was acquired from Aldrich.

2.2. Chemical oxygen demand

Chemical oxygen demand (COD) determination (mg O_2L^{-1}) was performed using the Merck Spectroquant kit. The range of measurement used in each treatment was 25–1,500 mg O_2L^{-1} . The measurement was performed by submitting the samples to closed reflux for 2 h in a thermoreactor (Spectroquant TR620), and COD was subsequently determined photometrically in a Spectroquant[®] NOVA 60 Merck using the EPA 410.4 and ISO 15705 methods.

2.3. Total organic carbon

Total organic carbon (TOC) (mg C L⁻¹) determination was performed using Merck Spectroquant kit (range 50–800 mg C L⁻¹). The samples were submitted to closed reflux for 2 h in a thermoreactor (Spectroquant TR620), and then allowed to cool to room temperature before TOC was determined photometrically in a Spectroquant[®] NOVA 60 Merck using ISO 84661-1 and DIN-38402 A51 methods.

2.4. Total phenol determination

Total phenol was determined using a test kit (Spectroquant Merck). The measurement range used was from 0.02 to 5.00 mg L⁻¹. We added 10 mL of sample, 5 mL of reagent pH 1 containing sodium hydroxide, one micro-spoonful of reagent pH 2 containing 4-amino-2, 3-dimethyl-1-phenyl-3-pyrazolin-5-one, and one micro-spoonful of reagent pH 3 containing peroxodisulfate. The mixture was then left to stand for 10 min. Phenol in the buffer solution and its ortho and meta substituted compounds react in the presence of an oxidant with 4-amino-antipyrine, resulting in a red compound, which can be determined photometrically in a Spectroquant[®] NOVA 60 Merck using ISO 8466-1 and DIN 38 402 A 51 methods.

2.5. Toxicity test

Toxicity was evaluated with *Pseudomonas aeruginosa* bacterial strains, using the serial dilution method, which was standardized with the McFarland standard. The bacterial culture inocula were incubated for 24 h at 37° C. Viable *P. aeruginosa* bacterial colonies were counted each 24 h for 120 h, recording the number of colony forming units (CFUs). All of the experiments were performed under sterile conditions.

2.6. Procedure

To optimize the degradation of 100 mg L⁻¹ of Kraft Lignin, we generated an experimental design, where the effects of four experimental variables were studied: pH, time of reaction (min), persulfate dosage, and zerovalent iron dosage. By applying the 2^{*n*} experimental design we obtained a Box–Behnken matrix of 27 experiments. The ranges of the values associated with the variables are shown in Table 1. The range for each variable was entered in an experimental design program, obtaining as the response the percentage of Lignin removed.

Before each photochemical treatment, the pH was adjusted accordingly as indicated by the experimental design, for which it was used a pH meter (model pH 2.11, with a dual-function electrode, provided by Sen Tix Inolab WTW). The samples were irradiated with UV-C HPLN-Lamp (125 W, $\lambda \ge 254 nm$). All of the

Table 1

Ranges of experimental variables studied for Kraft Lignin removal (coded and uncoded values)

Variables	Ranges
$ {S_2O_8^{2-} (g L^{-1})} Fe^0 (g L^{-1}) pH Time (min) $	0.01 (-1)-0.05 (+1) 0.01 (-1)-0.05 (+1) 2.0 (-1)-11.0 (+1) 10.0 (-1)-120.0 (+1)

experiments were carried out at a constant temperature of 20 °C. Subsequently, the samples were analyzed using a spectrophotometer (Pharo 300 Spectroquant Merck).

2.7. Reaction kinetics

After obtaining the values of the variables that attained the greatest Kraft Lignin removal (100 mg L^{-1}), we performed the kinetics of the degradation in order to verify the degradation of the compound over time.

3. Results and discussion

3.1. Multivariate analysis

To optimize the Kraft Lignin degradation we worked with four experimental variables, pH, persulfate (g L^{-1}), zerovalent iron (g L^{-1}), and reaction time (min), resulting in a matrix of 27 experiments. Table 2 shows the observed response for the removal of organic compounds.

The experimentally obtained responses were entered in the design to obtain the response surface (Fig. 1). The red area indicates the maximum synergism achieved by the experimental variables in removal of Kraft Ligin from a 100 mg L^{-1} sample. As is observed, Lignin removal is higher in acidic pH given that the sulfate radicals predominate under acidic conditions [25,26], and the iron is oxidized in an acid medium, resulting in ferrous ions, which act as a catalyst to the reaction [27].

The three-dimensional representation, or response surface, for the removal of Kraft Lignin is shown in Fig. 2, where it can be observed that maximum removal is obtained with 0.05 g L^{-1} of persulfate and 0.01 g L^{-1} of iron, independent of reaction time, suggesting that iron acts as a catalyst, increasing persulfate radical formation [28].

The influence of each variable on the obtained response is plotted in Fig. 3, where it can clearly be observed that at a higher iron concentration and pH greater than 6.0 the response decreases. This observation corroborates the persulfate and iron concentrations obtained from experimental design, which determined a pH of 3.5 as the optimum value for greatest removal of the compound by the $S_2O_8^{2-}/Fe^0/UV$ system.

The effect of each factor and combined factor effects on Lignin removal are shown in Fig. 4, where it can be highlighted that the variable persulfate has a positive influence on removal, and iron and pH have a negative influence, meaning that at a higher pH and iron dosage, removal is lower, supporting the idea that the influence of iron is directly related to the pH, Table 2

Exp.	Order	$[S_2O_8^{2-}] g L^{-1}$	$[Fe^0]$ g L^{-1}	pН	Time (min)	Total phenols removed (%)
N1	15	0.01 (-1)	0.01 (-1)	6.5 (0)	65 (0)	60.1
N2	2	0.05 (+1)	0.01 (-1)	6.5 (0)	65 (0)	92.0
N3	9	0.01 (-1)	0.05 (+1)	6.5 (0)	65 (0)	58.0
N4	22	0.05 (+1)	0.05 (+1)	6.5 (0)	65 (0)	42.7
N5	13	0.03 (0)	0.03 (0)	2.0 (-1)	10 (-1)	63.2
N6	11	0.03 (0)	0.03 (0)	11 (+1)	10 (-1)	0
N7	23	0.03 (0)	0.03 (0)	2.0 (-1)	120 (+1)	21.7
N8	10	0.03 (0)	0.03 (0)	11 (+1)	120 (+1)	0
N9	1	0.01 (-1)	0.03 (0)	6.5 (0)	10 (-1)	49.9
N10	21	0.05 (+1)	0.03 (0)	6.5 (0)	10 (-1)	55.2
N11	25	0.01 (-1)	0.03 (0)	6.5 (0)	120 (+1)	24.9
N12	27	0.05 (+1)	0.03 (0)	6.5 (0)	120 (+1)	67.0
N13	5	0.03 (0)	0.01 (-1)	2.0 (-1)	65 (0)	80.1
N14	18	0.03 (0)	0.05 (+1)	2.0 (-1)	65 (0)	25.4
N15	16	0.03 (0)	0.01 (-1)	11 (+1)	65 (0)	0
N16	8	0.03 (0)	0.05 (+1)	11 (+1)	65 (0)	0
N17	14	0.01 (-1)	0.03 (0)	2.0 (-1)	65 (0)	42.8
N18	19	0.05 (+1)	0.03 (0)	2.0 (-1)	65 (0)	60.1
N19	3	0.01 (-1)	0.03 (0)	11 (+1)	65 (0)	13.3
N20	6	0.05 (+1)	0.03 (0)	11 (+1)	65 (0)	0
N21	4	0.03 (0)	0.01 (-1)	6.5 (0)	10 (-1)	69.0
N22	26	0.03 (0)	0.05 (+1)	6.5 (0)	10 (-1)	64.9
N23	12	0.03 (0)	0.01 (-1)	6.5 (0)	120 (+1)	61.8
N24	7	0.03 (0)	0.05 (+1)	6.5 (0)	120 (+1)	80.6
N25	24	0.03 (0)	0.03 (0)	6.5 (0)	65 (0)	40.6
N26	17	0.03 (0)	0.03 (0)	6.5 (0)	65 (0)	47.6
N27	20	0.03 (0)	0.03 (0)	6.5 (0)	65 (0)	34.3

Experimental matrix with the response expressed as the percentage of Lignin removal

all of which, once again, confirms that the optimum values obtained for each variable are correct.

3.2. Reaction kinetics

According to the studied model, using the values of the experimental parameters that resulted in the greatest amount of Kraft Lignin degradation, we followed the kinetics of reaction time. Fig. 5 shows that with 0.01 g L⁻¹ of Fe⁰, 0.05 g L⁻¹ of persulfate and pH 3.5, the study system is more efficient, achieving 100% removal. This indicates that the Fe⁰ is acting as a catalyst, since it promotes the additional generation of hydroxyl radicals [4,16].

Fig. 6 shows that color removal from 100 mg L⁻¹ of Kraft Ligin solution is fastest with the $S_2O_8^{2-}/Fe^0/UV$ system, removing 80% of color in 15 min of treatment. The $S_2O_8^{2-}/UV$ system takes longer to remove 80% of the color, which corroborates our observation that the *in situ* generation of sulfate and hydroxyl radicals enhances organic matter degradation.

To corroborate the efficiency of the photochemical degradation of Kraft Lignin (100 mg L^{-1}), total phenol and COD were determined at the kinetics point where

maximum removal was achieved. As shown in Fig. 7, the removal of both parameters is more efficient with the $S_2O_8^{2-}/Fe^0/UV$ system, reaching 96% for COD, and 94% for total phenols.

Previous research investigated the bleaching effluents of Kraft pulp with TiO2, using Cu(II) as an electron acceptor [29], which achieved 70% of COD removal and 100% of total phenols. Saien et al. [19] analyzed the AOPs for the degradation of Triton X-100 in aqueous medium through persulfate activated by UV irradiation, and was able to remove 61.2% COD after 60 min of radiation. Kavitha and Palanivelu [30] studied the degradation of 2-chlorophenol via the Fenton process (non-photochemical treatment), removing only 39% of COD after 120 min of irradiation. These studies demonstrate that AOPs are efficient in degrading organic matter, and that the efficiency achieved depends on the characteristics of the compounds to be treated, where the chosen treatment should be suitable according to the characteristics of the sample.

Another important analytical parameter that should be analyzed is the mineralization of organic matter by analyzing TOC. As shown in Fig. 8, the greatest TOC removal (61.2%) was achieved using the



Fig. 1. Contour plot used to optimize Kraft Lignin removal by the photocatalytic $S_2O_8^{2-}/Fe^0/UV$ system.



Fig. 2. Response surface used to optimize Kraft Lignin removal by the photocatalytic $S_2O_8^{2-}/Fe^0/UV$ system.

 $S_2O_8^{2-}/Fe^0/UV$ system, demonstrating that the study system was efficient in organic matter degradation, achieving its mineralization.

Catalkaya and Kargi [31] studied TOC removal in pulp and paper effluents using AOPs, reaching 56.8% removal at pH 3.0 in 30 min of treatment with the photo Fenton system. Pelegrini et al. [32] studied Lignin degradation with a photoelectrochemical system, obtaining 70% color removal, 51% TOC removal, and 83% total phenols removal in 6 h of treatment.

Table 3 shows the rate constant and the electrical energy per order (EE/O) for the photochemical systems studied. The EE/O was determined as the electrical energy in kilowatt hours (kWh) required to remove the TOC contained in 1 m³ in 60 min of treatment, at pH 3.5. As can be observed, for the $S_2O_8^{2-}/Fe^0/UV$ system, the reaction rate is higher compared with the two other studied systems, achieving a higher mineralization, which leads to a higher energy cost. However, such values are consistent with those obtained by Sahoo et al. [33] in the degradation of an anionic azo compound, where higher mineralization was observed using persulfate in acidic pH, achieving an EE/O of 437.59 (kWh/m³). Therefore, it can be confirmed that energy consumption depends on the degree of mineralization that is reached.

In order to observe whether the residual organic matter is biodegradable and non-toxic following chemical treatment, a biological treatment was performed, using the bacterial strain *P. aeruginosa*, which was subjected to growth under each of the five treatments: $S_2O_8^{2-}/Fe^0/UV$, Fe^0/UV , $S_2O_8^{2-}/UV$, Lignin 100 mg L⁻¹ (control), and distilled water (blank). Each treatment was adjusted



Fig. 3. Graphic representation of the contour surface for Kraft Lignin removal with the $S_2O_8^{2-}/Fe^0/UV$ system.



Fig. 4. Influence of different variables and variable combinations on Kraft Lignin removal by the $S_2O_8^{2-}/Fe^0/UV$ system.

to pH 7.0 since most species of this kind do not grow in acidic conditions (i.e. pH 4.5 or lower).

As observed in Fig. 9, bacterial growth was the greatest in the Lignin treatment; therefore, the bacteria were able to grow in a medium containing high concentrations of Lignin, and incorporate it into its metabolism as a sole carbon source. There are reports

on bacteria having the ability to use low molecular weight fragments for their metabolism [34]. Lignin is biodegradable without treatment but after 5 d of incubation, we achieved only 20% of solution discoloration, which is not acceptable, considering that color is an environmental issue [35]. However, the photochemical system $S_2O_8^{2-}/Fe^0/UV$ achieved color



Fig. 5. Kraft Lignin (100 mg L⁻¹) removal with the photochemical $S_2O_8^{2-}/Fe^0/UV$, Fe^0/UV , and $S_2O_8^{2-}/UV$ systems under optimal experimental conditions, as given by the model: $[Fe^0] = 0.01 \text{ g L}^{-1}$, $[S_2O_8^{2-}] = 0.05 \text{ g L}^{-1}$ and pH 3.5.



Fig. 6. Color removal with the photochemical $S_2O_8^{2-}/Fe^0/UV$, Fe^0/UV and $S_2O_8^{2-}/UV$ systems under optimal experimental conditions, as given by the model: $[Fe^0] = 0.01$ g L^{-1} , $[S_2O_8^{2-}] = 0.05$ g L^{-1} and pH 3.5.

removal of 82% in 15 min of treatment and, as can be observed in Fig. 9, the oxidation products are not toxic for the bacteria, allowing them to grow. At the same time, we determined the degree of biodegradability of the remaining organic matter based on the bacterial growth methodology established by Sahoo et al. [36]. We found that for 100 ppm of Kraft Lignin, biodegradability reaches 100% with the $S_2O_8^{2-}/Fe^0/UV$ system and 93.5% with the $S_2O_8^{2-}/UV$ system. This result indicates that although the degree of mineralization is lower, the remaining organic matter is used by the bacteria to grow.

Chandra et al. [37] studied the ability of two bacterial strains to remove color from a pulp and paper



Fig. 7. COD and total phenols removal obtained with the photochemical $S_2O_8^{2-}/Fe^0/UV$, Fe^0/UV , and $S_2O_8^{2-}/UV$ systems, under optimal conditions: $[Fe^0] = 0.01 \text{ g L}^{-1}$, $[S_2O_8^{2-}] = 0.05 \text{ g L}^{-1}$, and pH 3.5.



Fig. 8. TOC removal with the photocatalytic $S_2O_8^{2-}/Fe^0/UV$, Fe^0/UV , and $S_2O_8^{2-}/UV$ systems, under optimal experimental conditions: $[Fe^0] = 0.01 \text{ g L}^{-1}$, $[S_2O_8^{2-}] = 0.05 \text{ g L}^{-1}$, and pH 3.5.

Table 3

Kraft Ligin (100 mg L⁻¹) mineralization compared with electrical energy per order of magnitude (EE/O), under optimal conditions: $[S_2O_8^{2-}] = 0.05 \text{ g L}^{-1}$, $[Fe^0] = 0.01 \text{ g L}^{-1}$

AOPs	Rate constant (min ⁻¹)	R^2	Mineralization (%)	EE/O (kWh/m ³)
$\frac{1}{S_2O_8^{2^-}/Fe^0/UV} \\ S_2O_8^{2^-}/UV \\ Fe^0/UV$	0.054	0.98	61.2	492.6
	0.023	0.93	48.0	340.8
	0.013	0.83	37.1	242.0



Fig. 9. Growth of *P. aeruginosa* bacteria (UFC mL^{-1}) in 100 ppm of Kraft Lignin and in the organic matter residual after the treatment with the photocatalytic systems studied.

effluent, observing a slow degradation given that biological degradation produces breaks in lignocellulosic compounds of high molecular weight, producing a higher concentration of compounds of lower molecular weight, which are directly responsible for the color. Moreover, in photochemical systems, bacterial growth is observed ($CFU mL^{-1}$), demonstrating that the remaining organic material is biodegradable and non-toxic. This is because the persulfate is used by the bacteria as a source of sulfur to synthesize amino acids (methionine and cysteine) as well as the sulfurcontaining vitamins (thiamine, biotin, and lipoic acid). With respect to iron, this element is required by most organisms as a macronutrient, and they are also capable of using the lignocellulosic compounds present in pulp and paper effluents as a carbon source [38].

4. Conclusions

Persulfate was used as an oxidant and iron zerovalent as catalyst in optimizing the advanced oxidation process of $S_2O_8^{2-}/Fe^0/UV$ to degrade Kraft Lignin, as a model compound of a real effluent of Kraft pulp. The influence of the experimental variables, such as pH, oxidant concentration and catalyst, were determined by experimental design. The results show that high concentrations of Kraft Lignin can be efficiently degraded under the optimal experimental conditions determined by the experimental design. Increased efficiency of Lignin degradation was obtained with the following values of the modeled variables:

 $[S_2O_8^{2-}] = 0.05 \text{ g L}^{-1}$, $[\text{Fe}^0] = 0.01 \text{ g L}^{-1}$, and pH 3.5. Color is one of the harmful parameters of the effluents, which contain colored compounds, given that they produce a direct impact on the environment, inhibiting photosynthesis and causing eutrophication in the bodies of water where they are discharged. In this study, we removed the solution's color in only a few minutes of treatment, and the remaining organic matter is biodegradable and non-toxic.

Acknowledgment

The author thanks the DIN-10-2011 grant for financial support.

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