

## Alkydic resin wastewaters treatment by fenton and photo-Fenton processes

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Available online 20 April 2007

### Abstract

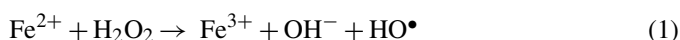
Advanced oxidation processes are an emerging option to treatment of the painting industry effluents. The aim of this study was to compare the effectiveness of the Fenton and photo-Fenton processes in chemical oxygen demand (COD), total organic carbon (TOC) and phenolic compounds removal from wastewaters generated during alkydic resins manufacture. The optimized treatment conditions are the following: pH 3.0,  $15.15 \times 10^{-3} \text{ mol L}^{-1}$   $\text{FeSO}_4$  and  $0.30 \text{ mol L}^{-1}$   $\text{H}_2\text{O}_2$  for a reaction time of 6 h. photo-Fenton experiments were carried out in the presence of sunlight or artificial radiation and complementary additions of  $\text{H}_2\text{O}_2$  were made for all experiments. The best results were obtained with photo-Fenton process assisted with solar radiation, with reductions of 99.5 and 99.1% of COD and TOC levels, respectively. Fenton and photo-Fenton (with artificial irradiation) processes presented lower but not insignificant removals, within 60–80% reduction for both COD and TOC. In addition, an excellent removal (95%) of total phenols was obtained using photo-Fenton process assisted with artificial irradiation. This study demonstrated that the use of photo-Fenton process on alkydic resins wastewater treatment is very promising especially when solar light is used.

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**Keywords:** Photo-Fenton; Fenton; Painting industry effluent; Phenolic compounds

### 1. Introduction

The increasing concern about the environmental impacts caused by the industrial development has stimulated the development of new technologies to effluents treatment. The toxic effluents containing recalcitrant compounds (for example phenols) are found in industrial wastewaters, especially in the production of the pesticides, herbicides, pharmaceuticals, paints and dyes [1]. The advanced oxidation processes (AOP), based on the generation of the hydroxyl radical, have attracted great interest in the last years [2,3] due to their ability to destroy a large variety of organic compounds [4]. Among AOP processes, Fenton reaction has been widely studied because is an important source of hydroxyl radicals, generated from the reaction between hydrogen peroxide and ferrous ions in acid medium, as following:



The efficiency of the Fenton reaction depends on the sample characteristics, pH, iron concentration,  $\text{H}_2\text{O}_2$  dosage and the reaction time.

The Fenton process in combination with the UV–vis radiation (photo-Fenton) increases the hydroxyl radical generation by the photoreduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions which produces new  $\text{HO}^\bullet$  radicals, in addition to peroxide photolysis, according to the following mechanism [3,5,6].



The choice of iron source is crucial for an efficient wastewater treatment process and it should be chosen according to the chemical structure of the target compounds [3,4]. In Fenton “like” processes, ferric salts and complexes or iron powder are used as sources of catalytic iron [7–9]. Ferrioxalate is the oldest and best-known photoactive example of  $\text{Fe}^{3+}$ –polycarboxylate complexes which have a broad absorption range (up to 450 nm) thus utilizing more efficiently the UV–vis radiation when compared to  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system (Eq. (2,3)). The irradiation of ferrioxalate in acidic solution generates carbon dioxide and ferrous ions free

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or complexed with oxalate [10,11], which in combination with  $\text{H}_2\text{O}_2$  provides a continuous source of Fenton's reagent. Despite of this beneficial effect the addition of oxalate has been considered as disadvantageous due to the increase of carbon load in the system, if a complete conversion of oxalate to  $\text{CO}_2$  is not attained [7].

The aim of this study was to evaluate the efficiency of the Fenton and photo-Fenton processes in chemical oxygen demand (COD), total organic carbon (TOC) and phenolic compounds removal from wastewaters generated during alkydic resins manufacture that are used in paints formulations in a Brazilian facility. The results obtained in this work will add the enterprise to choose the most suitable technology to treat this effluent.

## 2. Materials and methods

### 2.1. Reagents

All chemicals were at least of reagent grade (Merck) and used without purification. Iron solutions were prepared using three different reagents:  $\text{Fe}(\text{NO}_3)_3$  and  $\text{FeSO}_4$  in concentration of  $0.25 \text{ mol L}^{-1}$  with  $\text{H}_2\text{SO}_4$  10% (v/v); and potassium ferrioxalate ( $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ )  $0.1875 \text{ mol L}^{-1}$  made by mixture (1:3) of  $\text{Fe}(\text{NO}_3)_3$  and  $\text{K}_2\text{C}_2\text{O}_4$  solutions [4]. The  $\text{H}_2\text{O}_2$  solution (30% w/w) had its content determined for titration with potassium permanganate in acid solution [12]. Deionized water (MilliQPlus, Millipore) was used in the preparation of all solutions.

### 2.2. Hydrogen peroxide determination

The residual concentration of  $\text{H}_2\text{O}_2$  was monitored during samples treatment using a metavanadate method [13]. This method is based on the reaction of the  $\text{H}_2\text{O}_2$  with ammonium metavanadate in acid medium, resulting in the formation of the red-orange color ion, which presents an intense absorbance at 450 nm. An external calibration was made using  $\text{NH}_4\text{VO}_3$  (across) solutions ( $0.06 \text{ mol L}^{-1}$  prepared in  $\text{H}_2\text{SO}_4$   $0.4 \text{ mol L}^{-1}$ ) and  $\text{H}_2\text{O}_2$  30% (w/w) diluted to required concentration ( $0.5\text{--}5.0 \times 10^{-3} \text{ mol L}^{-1}$ ).

### 2.3. Degradation procedures

The wastewaters degradation conducted without UV radiation (Fenton process) was started when  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  solutions were added to glass reactor (0.200 L capacity) containing 0.150 L of effluent. The solutions had been kept under magnetic agitation in the dark and the temperature was monitored periodically.

In the photo-Fenton process using artificial radiation, the solution was illuminated from the top using a high-pressure 60 W mercury lamp (Philips R-UVA 60W/10R) which was centered at a distance of 25 cm from the liquid surface. A radiometer provided global lamp radiation (irradiance of  $14.8 \pm 1.2 \text{ W m}^{-2}$ ). Photodegradation with natural sunlight, was carried out in Porto Alegre-RS, South Brazil ( $30^\circ 21' \text{ S}$  and  $51^\circ 14' \text{ W}$ ) under clear sky conditions from 10 a.m. to 4 p.m. (more intense solar period). Both artificial and solar photo-Fenton processes were conducted

in the apparatus described above. Some tests were performed at different acidities and NaOH solution (40%, w/v) was added for pH adjustment between 2.5 and 3.5 to stay within optimal conditions [10].

### 2.4. Analyses

The chemical characteristics of the samples, before and after the treatments, were made according to Standard Methods [12]. The efficiency of the processes was evaluated by measuring the COD and TOC decays. Typical wastewater samples presented initial pH 2.02, conductivity  $3.19 \mu\text{S cm}^{-1}$ , total phenols  $63.4 \text{ mg L}^{-1}$  and high values of COD  $80.750 \text{ mg O}_2 \text{ L}^{-1}$  and TOC  $33,600 \text{ mg L}^{-1}$ . The artifacts on COD determination of the treated samples, due to the presence of the residual  $\text{H}_2\text{O}_2$  [14] and oxalate ( $\text{FeO}_x$  tests) [7], were estimated and used in the correction of the presented values.

## 3. Results and discussion

### 3.1. Evaluation of $\text{H}_2\text{O}_2$ residual and its influence on COD measurements

The amount of residual hydrogen peroxide is an important parameter in the Fenton and photo-Fenton processes. When  $\text{H}_2\text{O}_2$  is completely consumed, the rate of the degradation decreases, making new additions of the oxidant necessary. On the other hand, excessive  $\text{H}_2\text{O}_2$  reacts with hydroxyl radicals competing with organic pollutants and consequently reducing treatment efficiency [13]. The residual concentration of  $\text{H}_2\text{O}_2$  was monitored spectrophotometrically by forming the peroxovanadium cation that has a maximum of absorbance in 450 nm, as illustrated in the Fig. 1.

From the spectrophotometric study an analytical curve was constructed ( $\lambda_{\text{max}}$  450 nm) for the determination of the residual  $\text{H}_2\text{O}_2$  in the concentration range of  $0.5\text{--}5.0 \times 10^{-3} \text{ mol L}^{-1}$  (Fig. 2). This procedure was used in all subsequent degradation tests and the results were used to make supplementary additions of  $\text{H}_2\text{O}_2$  during the sample treatment.

The presence of residual amounts of hydrogen peroxide provokes an artifact on the COD determination [14]. However, if the peroxide concentration on treated effluent is known, it is possible to deduct its contribution on global COD value. For this purpose an analytical curve of the COD values in function of the

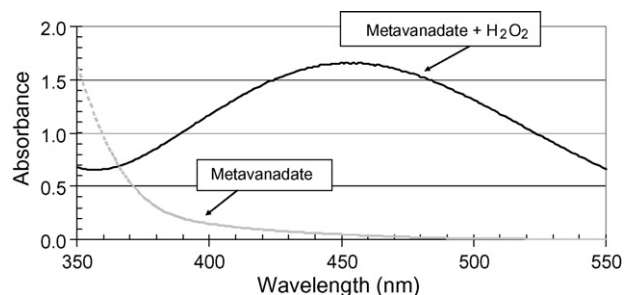


Fig. 1. Absorbance spectra of metavanadate ( $0.06 \text{ mol L}^{-1}$  in  $\text{H}_2\text{SO}_4$   $0.4 \text{ mol L}^{-1}$ ) and metavanadate in the presence of  $\text{H}_2\text{O}_2$   $5.0 \times 10^{-3} \text{ mol L}^{-1}$ .

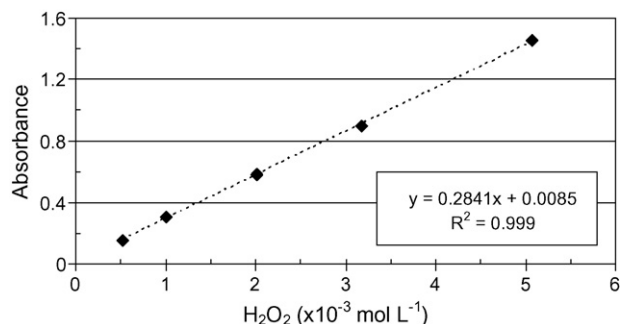


Fig. 2. Analytical curve for spectrophotometric determination of  $\text{H}_2\text{O}_2$  with metavanadate at 450 nm.

peroxide concentration was constructed (Fig. 3). The obtained curve showed good linearity ( $R^2 = 0.992$ ) in the  $\text{H}_2\text{O}_2$  concentration range studied ( $0.05\text{--}0.55\text{ mol L}^{-1}$ ). The observed artifact in treated samples showed a significant contribution in COD value (up to 10%). If the proposed correction is not taken in account, the COD values will present a poor precision. In function of that, all subsequent COD measurements were corrected considering the contribution of residual  $\text{H}_2\text{O}_2$  on the original COD value.

### 3.2. Optimization of the photo-Fenton process assisted by artificial radiation

#### 3.2.1. Iron sources

Preliminary tests were performed to compare the efficiency in the mediation of the photo-Fenton process by ferrous or ferric ions. Two different sources of ferric ions were tested: ferric nitrate ( $\text{Fe}^{3+}$ ) and potassium ferrioxalate ( $\text{FeO}_x$ ). For a fixed reaction time of the 3 h, iron concentrations of  $11 \times 10^{-3}\text{ mol L}^{-1}$  and in samples natural pH (2.02), the best results were obtained for  $\text{H}_2\text{O}_2$  concentration of the  $0.30\text{ mol L}^{-1}$ . COD reductions of 40, 18 and 17% were observed using  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{FeO}_x$  solutions, respectively.

The best efficiency of the ferrous ion, compared to  $\text{FeO}_x$  and ferric ions reagents, was not expected. However some studies [4,7,9,15–16] demonstrated that photo-Fenton process efficiency depends not only of the iron source but also of the sample composition. Kusic et al. [9] studied the phenol degradation by photo-Fenton using  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  as iron sources and

observed a best TOC removal in the presence of  $\text{Fe}^{2+}$ . Nogueira et al. [7] observed that oxidation of 4-chlorophenol is favored by the use of  $\text{Fe}^{3+}$  compared to  $\text{FeO}_x$ , while for other compounds (such as dichloroacetic acid and herbicides) ferrioxalate is more efficient in the degradation. During the photodegradation of highly concentrated phenol solutions Araña et al. [15] observed the formation  $\text{Fe}^{3+}$  complex and the correspondent diminution of iron ion in solution. Other authors [4,7] also suggested that the complex formation involving  $\text{Fe}^{3+}$  ions could be related to photo-Fenton activity decrease.

In this work the composition of the wastewater is complex and the presence of organic compounds capable to form photo-stable complex with  $\text{Fe}^{3+}$  could be possible. Furthermore,  $\text{Fe}^{2+}$  is very efficient in odor removal while treatment mediated by  $\text{Fe}^{3+}$  and  $\text{FeO}_x$  did not promote significant reduction in the odor of the samples. In function of these, ferrous ions were used in all subsequent tests.

#### 3.2.2. Influence of reagent concentrations and reaction time

To optimize the process conditions, a series of experiments was performed with different initial concentrations of  $\text{H}_2\text{O}_2$  (in the range  $0.30\text{--}0.55\text{ mol L}^{-1}$ ) at  $11\text{ mol L}^{-1}\text{ Fe}^{2+}$  concentration, extending irradiation time from 3 to 6 h. The increase of  $\text{H}_2\text{O}_2$  initial concentration had an inhibition effect on COD removal. The best result (90.5% COD removal) was obtained at lowest peroxide concentration ( $0.30\text{ mol L}^{-1}$ ). As commented before, this behavior could be explained because excessive  $\text{H}_2\text{O}_2$  reacts with hydroxyl radicals reducing treatment efficiency [3]. In complementary studies were verified that successive peroxide additions promote better degradation compared to single addition made in the beginning of the process (not shown). Therefore, consecutive additions of hydrogen peroxide (30%) were realized when the reagent concentration had been reduced in 80% of the initial value.

In general, the optimal pH of the photo-Fenton reaction is in the range 2.5–3, because the main specie at this acidity,  $\text{Fe}(\text{OH})^{2+}$ , is the one with both largest light absorption and hydroxyl radical generation [2,3,10]. In addition, the decomposition of  $\text{H}_2\text{O}_2$  in acidic medium is very fast also contributing in  $\text{HO}^\bullet$  generation [17]. In function of that effect of pH on the degradation of samples was investigated over a narrow pH range 2.55–3.52, and the results are shown in Table 1. As expected the best result on COD removal (81.8%) was obtained at pH 3.08. The subsequent tests were performed in this acid concentration.

Table 1  
Influence of pH on COD reduction in photo-Fenton process assisted by artificial irradiation (6 h)

COD (mg $\text{O}_2/\text{L}$ )	After the treatment		
	2.55 <sup>a</sup>	3.08 <sup>a</sup>	3.52 <sup>a</sup>
Before the treatment	80.750	80.750	80.750
	23744	14730	18350
COD reduction (%)	71	82	77

[ $\text{Fe}^{2+}$ ] =  $15.15 \times 10^{-3}\text{ mol L}^{-1}$  and [ $\text{H}_2\text{O}_2$ ]<sub>0</sub> =  $0.30\text{ mol L}^{-1}$  with supplementary additions.

<sup>a</sup> pH.

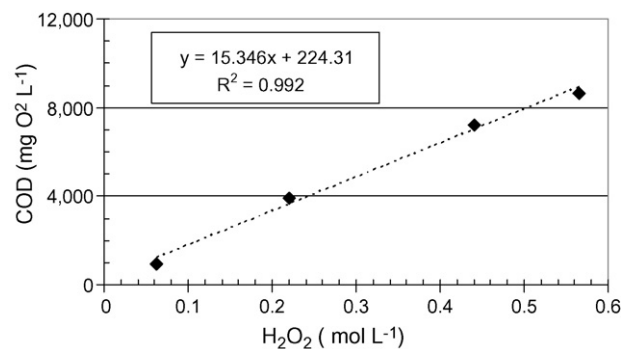


Fig. 3. Analytical curve of the COD values for different  $\text{H}_2\text{O}_2$  concentrations. The obtained curve (linear regression) was used to deduct the residual  $\text{H}_2\text{O}_2$  contribution to COD levels of treated wastewater.

Table 2  
COD and TOC variation during wastewater treatment by advanced oxidation processes

Processes	Reaction time (h)	pH	TOC		COD	
			(mg L <sup>-1</sup> )	Red. <sup>a</sup> (%)	(mg O <sub>2</sub> L <sup>-1</sup> )	Red.(%)
Initial conditions <sup>b</sup>	0	2.02	33600	0	80.750	0
Fenton	6	3.00	12800	61.9	19.990	75.2
Solar photo-Fenton	6	3.00	301	99.1	397	99.5
Artificial photo-Fenton	3	3.00	21800	35.1	46515	42.4
	6	3.08	9800	70.8	14730	81.8

<sup>a</sup> Percent reduction.

<sup>b</sup> [Fe<sup>2+</sup>]<sub>0</sub> = 15.15 × 10<sup>-3</sup> mol L<sup>-1</sup> and [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.30 mol L<sup>-1</sup> with supplementary additions.

The iron concentration is an important aspect when evaluating the efficiency of the degradation of organic compounds, since Fe<sup>2+</sup> catalyses the H<sub>2</sub>O<sub>2</sub> decomposition to generate reactive hydroxyl radicals. Further experiments were realized with different FeSO<sub>4</sub> concentrations (7.7–15.15 × 10<sup>-3</sup> mol L<sup>-1</sup>). The maximum COD removal (81.8%) was obtained in the biggest iron concentration used (15.15 × 10<sup>-3</sup> mol L<sup>-1</sup>) while low Fe<sup>2+</sup> concentration did not allow achieving satisfactory degradation (<10%). As photo-Fenton assisted by solar radiation tests (discussed below) indicated almost total COD removal for Fe<sup>2+</sup> concentration of the 15.15 × 10<sup>-3</sup> mol L<sup>-1</sup>, higher ferrous levels were not evaluated.

The irradiation time is a key parameter, which could be adjusted according to the conditions such as light intensity and sample composition. Preliminary tests showed low COD removal (<20%) for reaction times short than 2 h. In function of that longer irradiation times were tested. Extending reaction time from 3 to 6 h practically twice the COD (42.4–81.8%) and TOC (35.1–70.8%) removals (Table 2). These results indicated that a complete removal of the organic matter could be possible by just increasing irradiation time in this system. Even using a low intensity light source it was possible obtaining not only high organic matter degradation (low COD values) but also a very important mineralization (low TOC values) of the effluent.

### 3.3. Comparison between advanced oxidation processes

The same operating parameters were applied in Fenton and photo-Fenton (solar and artificial light) processes in order to compare their efficiencies for the degradation of the effluent. All processes were carried out in pH 3.0; 15.15 × 10<sup>-3</sup> mol L<sup>-1</sup> FeSO<sub>4</sub> and 0.30 mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (with supplementary additions) during 6 h. The solar photo-Fenton was performed in a day with clean sky and a significant variation on solution temperature (20–40 °C) was observed during this treatment. For photo-Fenton artificial light assisted and Fenton processes less significant temperature variations were verified (20–30 °C). This behavior could be explained mainly by solar heating and a possible exothermic effect of the photo-Fenton reactions.

Table 2 shows a summary of the COD and TOC values for the samples submitted to three different treatment processes. The best result was observed for the photo-Fenton process assisted with solar radiation, with reductions of 99.5 and 99.0% for COD and TOC, respectively. Considering the high initial level of the

organic matter in the effluent, the obtained reductions of COD, and specially TOC, are very expressive. This fact could indicate photo-Fenton process as a promising technology for treating this kind of the wastewater.

The photo-Fenton artificial light assisted process also presented satisfactory degradation with reductions of 81.8 and 70.8% for COD and TOC values, respectively. The lower COD and TOC removal, compared with the solar radiation, could be related with the low radiation intensity of lamp used (irradiance of 14.8 Wm<sup>-2</sup>).

The lowest removal efficiency was observed for Fenton process, however the obtained TOC (61.9%) and COD (75.2%) reductions are not insignificant. In addition, industrial use of the photo-Fenton process (assisted with solar radiation) could be combined with Fenton process with further removal increasing. During day time higher efficient photo-Fenton process take place while at night period Fenton process promote the effluent degradation. Thus, the total time and/or reagent consumption in this combined treatment could be minimized.

The phenolic compounds are expected to be an important fraction of the effluent. The result of phenols analysis indicated that a significant reduction in their levels was obtained during photo-Fenton treatment. The excellent reduction of 95% in total phenols (from 63.4 to 3.0 mg L<sup>-1</sup>) was obtained for sample treated by process assisted by artificial light. These results suggest that reductions of this order are also possible using natural irradiation.

The COD removal obtained in this work are below of the Brazilian emission standards for this kind of the effluent (<300 mg O<sub>2</sub> L<sup>-1</sup>). On the other hand, a supplementary reduction of total phenols to 0.5 mg L<sup>-1</sup> is necessary to follow Brazilian emission standard for this parameter [18]. However, as discussed previously, the increase of the radiation intensity and/or the reaction time could be sufficient to attain this phenol removal level. Finally, the formation of iron sludge may cause waste disposal issues and its minimization must be considered in the use of the photo-Fenton processes.

## 4. Conclusion

The degradation of alkydic resins wastewater was investigated by Fenton and photo-Fenton processes, in the presence of sunlight or artificial radiation. The treatment was affected by many factors such as iron source and concentration,

sample pH, H<sub>2</sub>O<sub>2</sub> concentration and the type of radiation used.

The optimized treatment condition is the following: pH 3.0;  $15.15 \times 10^{-3} \text{ mol L}^{-1}$  FeSO<sub>4</sub> and  $0.30 \text{ mol L}^{-1}$  H<sub>2</sub>O<sub>2</sub> for a time of reaction of 6 h. Hydrogen peroxide was added successively when its concentrations had been reduced in 80%. The best results were obtained with photo-Fenton process assisted with solar radiation, with reductions of 99.5 and 99.0% of COD and TOC values, respectively. Fenton and photo-Fenton (with artificial irradiation) processes presented lower but not insignificant removal efficiencies, with reductions above 60% in both COD and TOC values. In addition, an excellent reduction (95%) of total phenols was observed in the sample treated with photo-Fenton with artificial irradiation.

This study suggests that the use of photo-Fenton process on alkydic resins wastewater treatment is very efficient when solar light is used. Finally, this process offers a promising technology for treating phenolic compounds in wastewater for tropical countries like Brazil, where solar energy is abundant.

### Acknowledgements

The authors thank Killing Tintas e Adesivos SA, CNPq and Fapergs for financial support.

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