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SHORT COMMUNICATION

Combining Chemical and Photo-Fenton Solar Coagulation Processes in the Treatment of Real Wastewater from Paint Industry

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Abstract:

In this work are presented and discussed the results related to the obtaining of the best conditions for the treatment of a real paint wastewater by combining the chemical coagulation methods and solar photo-Fenton process. The best conditions for the coagulation-flocculation process involved the use of 8 mL of chemical coagulant (ferric chloride) for every 1.0 L of wastewater. At this condition, total removal of turbidity and color (visual inspection) of the wastewater were achieved. For the solar photo-Fenton process, the concentration of Fe^{2+} and H_2O_2 at 105 mg L^{-1} and 2.0 g L^{-1}, respectively, resulted in the complete removal of organic matter and odor (olfactory perception). Therefore, the combined use of these techniques in the treatment of the real paint wastewater presented quite relevant results from the environmental standpoint, as evidenced by the reduction/elimination of important environmental parameters, with the real possibility of disposal and/or reuse proposals of treated water.

Keywords: chemical coagulation; real paint wastewater; ferric chloride; solar photo-Fenton; advanced oxidation process; wastewater treatment.

1. Introduction

Scientific research related to the investigation of new processes for treatment of industrial effluents has become quite frequent, given that the problems regarding the quality and availability of water in the world [1]. In this sense, the search for new treatment processes that can achieve the necessary conditions and norms for their final disposal in water bodies becomes essential [2].

Paint industries are among those that raise great concern about the environmental impact, by being one of the major water consumers and by the wide variety of chemicals present in their processes [3]. Despite the pollution generated in the paint production process reaches the three states of matter, water residues have a noticeably greater impact, mainly due to the use of dyes, which are mostly very toxic and difficult to degrade [4, 5]. These effluents are characterized by high color, turbidity, odor, and high concentrations of chemicals. Thus, releasing them into water bodies without previous treatment can causes serious ecological problems, because the process of photosynthesis carried out by aquatic plants is impaired by the presence of color in the water, which prevents the passage of light. Consequently, dissolved oxygen is depleted, causing the death of living beings [2-5].

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Considering the high turbidity and coloration of this type of effluent, the choice of coagulation/flocculation technique is very interesting, since it allows the removal of colloidal suspension or dispersed materials in the solution, which are not removed by conventional physical processes, such as filtration [6]. This technique consists in the addition of salts (usually aluminum or iron salts) which in the presence of water hydrolyze, forming multi-charged polynuclear complexes that interact with impurities. Depending on the concentration of these coagulant salts and the medium pH, destabilized particles are formed and collide with each other to form larger aggregates, which can be removed by sedimentation, flotation or filtration [6, 7]. However, although satisfactory results are obtained regarding the removal of suspended solids and staining, this type of treatment alone does not solve the problems related to parameters such as toxicity, odor, and organic load, evidencing the need for additional or combined treatment [8]. In this sense, advanced oxidative processes (AOP) are a very promising option to solve this problem, considering that these processes are widely used in the treatment of effluents containing high concentrations of organic matter, besides presenting a relatively low cost. POAs are based on photocatalytic production of hydroxyl radicals (•OH), a strongly oxidizing species capable of oxidizing a great variety of organic compounds to CO_2 and H_2O, with low or no selectivity [9-12]. This strongly oxidizing character is a result of its high standard reduction potential.

The photo-Fenton process consists in the combination of UV-Vis radiation with the Fenton reaction, proposed by Henry J. H. Fenton. In this process, catalytic decomposition of hydrogen peroxide by Fe^{2+} ions in acid media promotes the generation of hydroxyl radicals (Eq. 1) and their combination with UV-Vis radiation allows to increase •OH production (Eq. 2). This provides advantages to the process, given the possibility of using solar radiation as a source of UV-Vis radiation, thus reducing the cost of the process with the use of free and clean energy [10-12].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + \bullet OH \quad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH \quad (2)$$

In recent years, our research group has investigated new processes for treatment of wastewater from paint industry by combining coagulation methods with the electrochemical technique [13, 14], which have proved to be quite efficient. The quality of the treated water met the requirements both for its final disposal in water bodies and for its reuse, as well as for the production of a new paint. Thus, with a view to expanding and improving the processes for treatment of this kind of residue, the present work presents and discusses the results obtained in the investigation of the combination of chemical coagulation methods (ferric chloride) with advanced oxidative processes (photo-Fenton Solar) in the treatment of the same wastewater previously described (from paint industry).

2. Results and Discussion

In order to obtain the best chemical coagulant dosage condition (in mL L^{-1}), the parameters of turbidity, color and pH were evaluated. Table 1 shows the results of these measurements.

Table 1. Obtained results from the treatment of raw wastewater with different chemical coagulant dosages.

Dosage (mL L^{-1})	Turbidity NTU	Color	pH
0	> 1100	Present	8.13
2	> 1100	Present	7.69
4	945	Present	7.64
6	22	NO*	7.32
8	3	NO*	7.21
10	2	NO*	7.20
12	8	NO*	7.05

* Not observed

Table 1 shows that the coagulant dosage clearly plays an important role in removing turbidity and color from the wastewater. The increase in coagulant dosage promotes a significant improvement in solids removal (expressed as turbidity) at dosages ≥ 6 mL L^{-1}. The use of coagulant dosages higher than 10 mL L^{-1} did not present better turbidity results, which evidences the maximum capacity of coagulant activity. It is also possible to observe that the turbidity removal efficiency was decreased when the dosage was changed to 12 mL L^{-1}, which is the result of the precipitation of iron hydroxides that remain suspended in the treated effluent due to their saturation in the solution. In addition, Table 1 shows that the increase of coagulant dosages causes a decrease in pH due to the hydrolysis of Fe^{3+} ions, which result in the release of H^+ ions into the solution [6, 7].

Regarding the color of the wastewater, the obtained results obtained after coagulation process shows that dosages of 6 mL/L are already sufficient for apparent color elimination. Therefore, considering the turbidity and color removals, the dosage of 8 mL L^{-1} was considered the best condition for the treatment of paint wastewater by coagulation/flocculation process.

However, despite the elimination of color and turbidity parameters, the characteristic odor of the effluent (similar to the mineral turpentine) still remained very strong. This reinforces the need to proceed with additional treatment for the removal of remaining organic matter which was still very high (COD value was reduced from 1845 mg L^{-1} to 994 mg L^{-1}). Thus, the application of the solar photo-Fenton method is quite relevant for the treatment sequence of this wastewater. Figure 1 shows the obtained results from the assays carried out to evaluate the effect of the concentration of Fe^{2+} and H_2O_2 on the removal of organic matter.

According to Figure 1, it is clear that the Fe^{2+} and H_2O_2 concentrations play an important role in the kinetics of degradation of organic matter. The influence of the increase of ferrous ion concentration on organic matter degradation kinetics was observed in the first 40 min of the reaction (Figure 1a), due to the ferrous ion action which is the main catalyst in the Fenton reaction for hydroxyl radical generation [11, 12]. However, at the end of the process it was verified that the removal of 100% of organic matter was only possible in the concentration of Fe^{2+} of 105 mg L^{-1}. The percent removals of COD at concentrations of 65 mg L^{-1} and 150 mg L^{-1} were 85% and 93%, respectively. At the concentration of 65 mg/L it is quite evident that its lower performance is due to the lower concentration of hydroxyl radicals formed. The loss of the efficiency at the concentration of 150 mg L^{-1} can be attributed to the excess of iron in solution, which can affect the organic mineralization reaction especially due the hydroxyl radical sequestration (Eq. 3) [11,12].

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad (3)$$

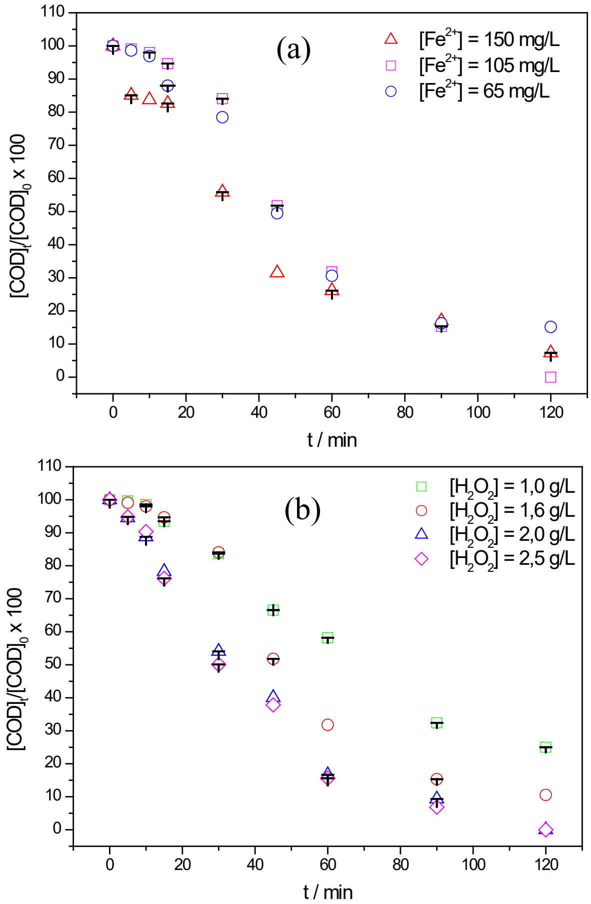

Figure 1. Influence of Fe^{2+} (a) and H_2O_2 (b) concentrations on COD removal mediated by the solar photo-Fenton process. (a) $[H_2O_2]_0$ = 1,6 g L^{-1} and (b) $[Fe^{2+}]_0$ = 105 mg L^{-1}. $[COD]_0$ = 994 mg/L.

As previously verified in the evaluation of the influence of the concentration of the catalyst, it is noticeable that the increase in H_2O_2 concentration promotes an increase in the organic matter degradation kinetics. Figure 1b shows that this phenomenon is observed until the concentration of 2.0 g L^{-1}. When the H_2O_2 concentration is increased to 2.5 g L^{-1} the performance was very similar, probably due to excess hydrogen peroxide, which can act as a hydroxyl radical scavenger (Eq. 4) or even self-decompose (Eq. 5) [11,12].

$$H_2O_2 + \bullet OH \rightarrow HO_2^\bullet + H_2O \quad (4)$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (5)$$

Therefore, it can be concluded that the best conditions obtained for the photo-Fenton process were with the addition of $[Fe^{2+}]$ and $[H_2O_2]$ at the concentrations of 105 mg L^{-1} and 2.0 g L^{-1}, respectively, and by the application of 2 h of solar radiation, which is equivalent to 30.2 J cm^{-2} of UV-A radiation. Under this condition, the organic matter and odor (sensory inspection) were completely removed.

3. Materials and Methods

The paint manufacturing wastewater was collected directly from the plant's wastewater reservoir (located in the municipality of Catalão-GO, Brazil) and used without any pretreatment. In order to preserve its characteristics, the effluent was stored at 5 °C. The initial COD of the effluent was 1845 mg L^{-1}.

3.1 Coagulation-flocculation

The coagulation-flocculation assays were carried out in a Jar Test device (Etik®), with 2 L vats. A rotation speed of 100 rpm was applied for 1 min, followed by slow mixing for 20 min at 40 rpm. At the end of the tests, the resulting flakes were allowed to stand for 30 min to ensure sedimentation. The experiments to obtain the best coagulant dosage conditions were perfomed by adding aliquots of 2 mL, 4 mL, 6 mL, 8 mL, 10 mL and 12 mL of ferric chloride solution (50 g L^{-1}) into 1 L of the raw wastewater. For this, analysis of turbidity parameters (HACH DR/890 photocolorimeter) and pH (Gehaka, PG 1800) were performed.

3.2. Photo-Fenton solar process

Solar photo-Fenton assays were carried out using a semi-pilot scale parabolic concentrator reactor [15-17] during 2 h, under flow regime. The volume of wastewater in reservoir was 7.5 L and a flow rate of 300 L/h was applied in the process.

The pH of the wastewater was adjusted with 1.0 mol L^{-1} sulfuric acid solution. Irradiance in the UV-A region was measured using a radiometer (Solar Light®, PMA 2100) with the sensor positioned at the same angle of incidence of radiation from the sun.

The concentrations of ferrous ion (65 mg L^{-1}, 105 mg L^{-1} and 150 mg L^{-1}) and hydrogen peroxide (1.0 g L^{-1}, 1.6 g L^{-1}, 2.0 g L^{-1}, and 2.5 g L^{-1}) by monitoring the chemical oxygen demand (HACH DR 2000, λ = 620 nm).

4. Conclusions

The optimum conditions for paint wastewater treatment by combining the chemical coagulation and photo-Fenton Solar methods involved the addition of $FeCl_3$ (50 g L^{-1}) at the dosage of 8 mL L^{-1} as well as the use of Fe^{2+} ions and H_2O_2 at concentrations of 105 mg L^{-1} and 2.0 g L^{-1}, respectively.

Under the best condition, the photo-Fenton Solar process resulted in the complete removal of the organic load, in addition to the noticeable odor removal.

Therefore, these results show that the combined use of the coagulation-flocculation method and the solar photo-Fenton process is very promising since important parameters of this class of effluent were significantly reduced/eliminated, which increases the real possibility for reuse and/or disposal of the water.

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