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To cite this article: Ronal Morales-Lame *et al* 2018 *J. Phys.: Conf. Ser.* **1119** 012024

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Improvement of the quality of wastewater in a printing industry by physicochemical methods and Fenton treatment.

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Abstract.

Wastewater samples from flexographic printing machines, characterized by high coloration, low pH, high chemical oxygen demand, and low biodegradability, were subjected to primary physicochemical treatments and a subsequent Fenton process to decrease the chemical oxygen demand (COD). The primary treatment consisted of coagulation with aluminium polychloride or ferric chloride followed by filtration over activated carbon. The Fenton process was optimized by varying pH, and the iron and hydrogen peroxide concentrations. Upon primary treatment, aluminium polychloride was the better coagulation agent. After one hour of treatment with the Fenton process at pH: 4.0; 40 mgL⁻¹ ferric chloride, 200 mgL⁻¹ hydrogen peroxide, COD removal of up to 92% was achieved. Thus, coupling of physicochemical treatments with the Fenton process yields wastewater of low environmental impact

1. Introduction

The wastewater treatment systems have evolved according to the nature, type and load of the effluent, in order to improve the quality of the treated water [1]. The most advanced treatments consist of couplings of primary processes (such as physicochemical treatment for the removal of suspended solids and floating materials) [2] and secondary processes, which are either biological or advanced oxidation processes (AOPs).

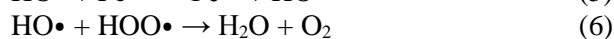
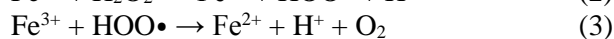
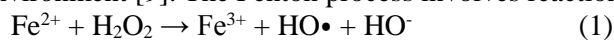
Primary treatment involves the use of coagulants, among which, pre-polymerized aluminum polychloride (APC), aluminum chlorhydrate (ACH) and aluminum polysulfate (APS) perform better than more conventional coagulants such as aluminum sulfate, or ferric chloride, which are widely used in the treatment of domestic and industrial wastewater worldwide [3].

The waste from the graphics industry, flexography, for instance, is composed of pigments, resins, additives, ink levelers, and surfactants and other effluents from the washing processes. The discharge is characterized by high coloration, low pH levels, high chemical oxygen demand (COD) and high biochemical oxygen demand (BOD) [4].

The AOP processes allow for the degradation of organic components in wastewater. Two useful AOPs for the treatment of wastewater from the graphics industry and tanneries are the Fenton process and electrocoagulation [5], [6], [7]. The Fenton reaction is a homogeneous catalytic oxidation process in which a mixture of hydrogen peroxide and iron ions (Fe²⁺) in an acidic medium produces highly active hydroxyl radicals (HO•) [8]. In recent decades, the Fenton reaction has been used for the treatment



of wastewater, allowing for the effective degradation of persistent organic compounds without releasing toxic substances to the environment [9]. The Fenton process involves reactions (1) through (6) [10].



In this work, physicochemical processes of flocculant and filtration with activated carbon are coupled with Fenton treatment, this one optimizes the ferrous iron and hydrogen peroxide concentrations and medium pH required for efficient COD removal from the wastewater of a graphics industry [11].

2. Methodology

2.1. Effluent sample

Liquid waste from water-based inks with dark pigments of various colors (black, red, blue or orange), with residues of resins, additives and butyl glycol, low pH (4-5), high COD (>15000mgL⁻¹), BOD₅ (>7000 mgL⁻¹) and total solids (>425 mgL⁻¹) were studied for wastes in batches during 13 weeks.

2.2. Optimization of the primary-physical-chemical treatment

The samples were alkalized with NaOH (Merck) (10%) to achieve pH values in the range 6.0 and 9.0. Aluminum polychloride coagulant (APC) (Environmental Chemical Industry IQA) was then added slowly under stirring (100 rpm), (10 % and 25 %). After one minute rest, the filtrate was separated with activated carbon (Panamerican Chemicals PQP). The optimum pH was determined according to the greatest discoloration and highest COD reduction, obtained in the sample. The previous procedure was repeated with 10% ferric chloride. Once the conditions that improve coagulation were selected, the recommended resting time was established. The samples are different each time since they depend on the process undertaken in the factory. For this reason, the organic load is variable from week to week.

2.3. Fenton process

The test variables with the Fenton process were: pH (2.00 to 6.50) adjusted with 10% HCl (Merck) and measured by the method SM 4500-H + B of the Standard Methods for the Examination of Water and Wastewater; iron concentration (0 to 70 mgL⁻¹) and hydrogen peroxide (Chemi) (0 to 500 mgL⁻¹). The amount of residual water sample worked was 40 mL in constant agitation at 200 rpm for one hour. At the end of the trial, COD was determined (method (USEPA 410.4) of the EPA Environmental Protection Agency).

3. Analysis of results

3.1. Physicochemical treatment

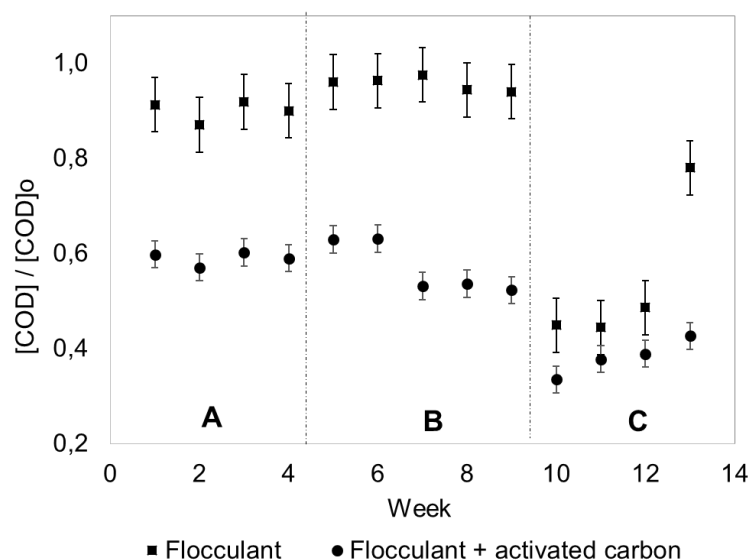
Ensuring the formation of small flocs, which later form agglomerates easily separated by gravity or sedimentation is of great importance in the efficiency of the coagulation /flocculation processes [12], [13]. In particular, iron chloride and aluminum polychloride depend mainly on the homogenization time and the pH of the sample to improve its performance. Table 1 illustrate the scope of these tests in different discharges.

The experimental results of the first week did not show differences in COD with the two flocculants at 10% concentration. However, when the concentration of APC was increased to 25%, the flocculation time decreases to 30% at the same sample. Samples are different every week. For the APC, better results are observed at pH close to 6.0, where the pKa value of APC became relevant. The characteristics of the sample are significant in flocculation, the samples of higher COD require longer flocculation time at identical pH conditions.

Table 1. Determination of coagulant, optimal pH and flocculation time in physicochemical treatment

Coagulant	pH ($\pm 0,01$)	Flocculation time ($\pm 0,01$ minutes)		
		Week 1*	Week 2	Week 3
FeCl ₃	8.0	4,15	7,39	16,64
	7.0	4,02	7,14	15,62
	6.0	4,12	6,48	15,60
APC	8.0	12,00	4,22	8,01
	7.0	12,00	4,10	6,91
	6.0	12,00	4,03	6,26

*FeCl₃ and APC 10%, in week 1. Next week APC 25%

**Figure 1.** Reduction of COD after physicochemical treatments.

APC 25%. Coagulation time 10 minutes. Activated carbon 1.5 g. L⁻¹.

A. [COD]_o > 15000 mgL⁻¹ **B.** [COD]_o ≈ 10000 mgL⁻¹ **C.** [COD]_o < 5000 mgL⁻¹

The pH was also a determining variable in the reduction of the COD in the shedding. Table 1 shows the results of COD obtained in a sample with 25% coagulant supplied at different pH, values close to 6.00 generate higher removals. The aluminum polychloride [Al₂(OH)₅Cl₂·5H₂O] being an inorganic multinuclear aluminum salt is preferred since it form more quickly and perfectly flocs of better sedimentation and clarifying power at pH close to neutrality, achieving more efficient removals of turbidity, color, COD, and are easier to filtrate. In this adsorption, an interparticle bridge link is formed as a complex particle-polymer-particle [14]. Previous works indicate that ferric chloride has good performance at pH between 5.00 and 9.00 [15]. Our results agree with was reported. We found that samples with COD greater than 10000 mgL⁻¹ (Figures 1A, 1B) give low efficiency in flocculation, which are compensated with activated carbon. On the other hand, samples with COD close to 5000 mgL⁻¹ show good coagulation results (Figure 1C).

The use of activated carbon as a filtering medium generates reductions in COD close to 50%, which is important since this process can be coupled to the coagulation-flocculation process to obtain reductions of up to 60%. The characteristics of the water show high absorptivity in the particulate material, after the filtration process, in addition to removing the floccules, the coloration of the sample is diminished.

3.2. Fenton process

After passing through the coagulation and filtration process described above, the samples were treated with Fenton process. Figure 2 shows the dependence of COD removal upon Fenton treatment of the sample as a function of pH at a constant H_2O_2 concentration. At pH 4.00, better performances were observed, with removals close to 14%. At pH above 5.00, the efficiency decreased to 8%, this can be explained due to the self-decomposition of hydrogen peroxide by the oxidation of Fe^{2+} to Fe^{3+} due to the presence of hydroxyl ions in the medium, and the conversion of the hydroxyl radicals to water (reaction 6), these results are in accordance with previous studies [2], [16].

The samples showed an average iron concentration of 0.77 mgL^{-1} after physicochemical treatment. The increase in the concentration of Fe^{2+} does not generate significant changes in the decrease of the organic load; however, a doping of 40 mgL^{-1} allow decreases that can be considered as contributors to the process. Concentrations close to these have been obtained in similar samples [17].

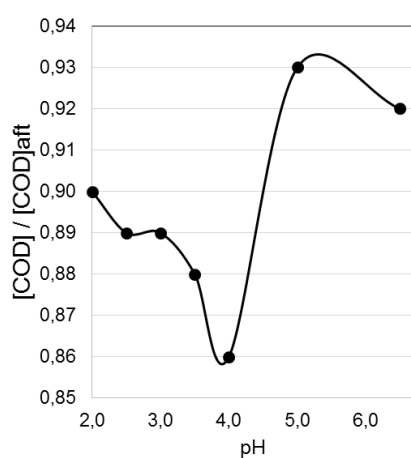


Figure 2. Reduction of COD vs. pH
COD after the physicochemical treatment
[COD]_{aft} 3320 mgL^{-1} , Fe^{2+} 40 mgL^{-1} , H_2O_2
 100 mgL^{-1} . 1 hour of reaction.

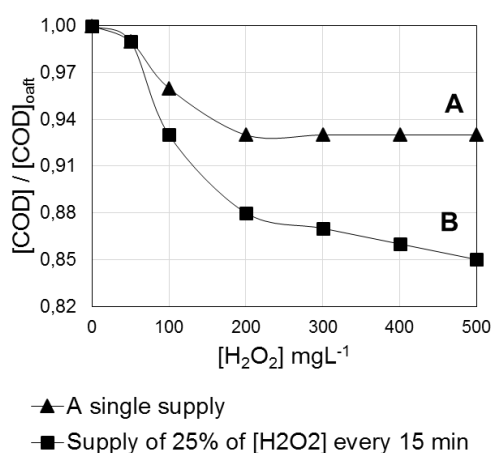


Figure 3. Reduction of COD vs. H_2O_2
[COD]_{aft} 3320 mgL^{-1} , Fe^{2+} 40 mgL^{-1} , pH
4.00, 1 hour of reaction.

Tests carried out at pH 4.00, iron of 40 mgL^{-1} and variable concentrations of hydrogen peroxide between 0 and 500 mgL^{-1} are reported in Figure 2A. An increase in the concentration of hydrogen peroxide in the Fenton treatment evidences reductions in the COD due to the generation of hydroxyl radicals that cause the oxidation of organic matter. Terminal reactions are observed (reactions 5 and 6) converting hydrogen peroxide and water to concentrations higher than 200 mgL^{-1} . Dosages spaced every 15 minutes of the reaction caused to improve the removals to 17% (Figure 3B).

Overall, the combined coagulation, filtration and Fenton yields COD removals greater than 92%. The results are encouraging, given the high organic load of the waste. But the final CODs are still higher than allowed by regulations for water discharge, it is necessary to establish other advanced oxidation methodologies such as photo Fenton that remit the use of light energy that optimize the process of formation of hydroxyl radicals.

4. Conclusion

The coupling of physicochemical processes with advanced oxidation methods shows encouraging results for the oxidation of organic material in samples with a high pollutant content. The optimization of the variables in each of the treatments is essential and are closely related to the characteristics of the sample. The APC as coagulant, imparts better conditions of flocculation. Filtration with activated carbon, in addition to allowing the separation of the floc's, contributes to the adsorption of soluble organic material, decreasing the color and the COD of the sample. The specific Fenton Treatment for the graphic industry samples containing surfactants, inks, levelers, among others, is favored at pH 4.00,

low iron concentrations and concentrations of hydrogen peroxide of 200 mgL^{-1} which must be added spaced to inhibit the self-reaction processes of hydroxyl ions.

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