

# Influence of variables of the combined coagulation–Fenton-sedimentation process in the treatment of trifluraline effluent

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## Abstract

The effluent stream from the industrial production of the herbicide trifluraline (amination water) was submitted to a combined treatment of a physical–chemical process (coagulation) with an advanced oxidation process (Fenton). The recovering of the residual sludge was performed. The combined coagulation–Fenton-sedimentation process proved to be very suitable for wastewater color reduction (91.6%), promoting considerable abatement of the organic load (63.4% COD reduction). According to the fractionary factorial design, the main effects of pH (A) and Fenton sludge (B) variables were considered statistical fluctuations of the process (and not decisive), while the main effects of  $\text{Fe}^{3+}$  (C),  $\text{Fe}^{2+}$  (D) and  $\text{H}_2\text{O}_2$  (E), as well as the interactions between variables A and B, A and E, C and D and C and E were considered significant. The obtained results suggest that the combined process can be advantageous for the treatment of recalcitrant industrial effluents, such as the amination water from the trifluraline production.

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**Keywords:** Recovery of Fenton sludge; Coagulation; Sedimentation; Factorial design

## 1. Introduction

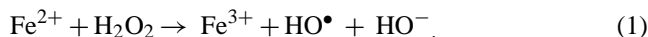
The trifluraline herbicide is still widely used in plantations of soy bean and cotton in Brazil and, according to the USEPA, it is classified as group C, a possible human carcinogen [1]. During the industrial production of this herbicide, an effluent stream called amination water (AW) is generated, which is recalcitrant to conventional treatments, causing problems of management and final disposal [2].

In wastewater handling, in general, coagulation precedes chemical or biological processes, is a pretreatment for the removal of suspended solids, foam and high molecular weight compounds. Coagulation is also used for the removal of turbidity, water clarification and organic load abatement (COD, BDOC) [3].

Metallic compounds, such as iron ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) and aluminum ( $\text{Al}^{3+}$ ) salts, are largely used as coagulants. Compared to aluminum sulfate, ferric chloride coagulates in a wider pH range, forms heavier flocs and is less harmful in the event of an overdose. The ferric ion, in general, is more advantageous and effective in the removal of color, turbidity and total carbon and presents no problems of toxicity [4,5].

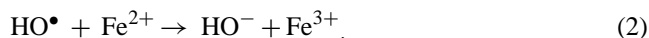
Advanced oxidation processes (AOPs) are emergent technologies for wastewater treatment, mostly taking advantage of the strong oxidant power of the generated hydroxyl radical ( $\text{HO}^\bullet$ ) [6]. It can partially or even completely degrade a large spectrum of organic and inorganic compounds [7,8], recalcitrant to conventional processes.

The Fenton reagent, a combination of the ferrous ion and hydrogen peroxide, can generate hydroxyl radicals in a complex sequence of reactions in an aqueous solution:



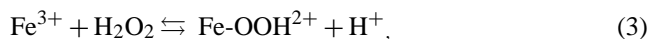
$$k_1 \approx 70 \text{ M}^{-1} \text{ s}^{-1} \text{ (Rigg et al. [9])}$$

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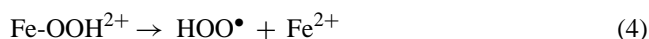


$$k_2 = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ (Walling [10])}$$

The ferric ion catalyzes peroxide decomposition, forming the complex  $[\text{Fe-O}_2\text{H}]^{2+}$  (Reaction (3)), which is later decomposed to  $\text{HO}_2^\bullet$  and  $\text{Fe}^{2+}$  (Reaction (4)), restarting the reaction chain of hydroxyl radical generation. Reactions (3) and (4) are known as *Fenton-like oxidation reactions* [11].



$$k_3 = 0.001\text{--}0.01 \text{ M}^{-1} \text{ s}^{-1}$$



Different kinds of combinations have been well investigated, as for instance, coagulation/Fenton oxidation and coagulation/photooxidation for the treatment of sanitary landfill leachates [12–14]. The combination of coagulation and electrooxidation for the treatment of textile wastewater using a fluidized biofilm stream bed has been reported [15]. Furthermore, flocculation/coagulation has been associated with photochemical degradation, in the treatment of effluents from pulp and paper industries [16].

Therefore, the aim of this study was to investigate both the influence of physical–chemical variables on the combined process (coagulation/Fenton) as well as the reuse of the residual sludge to assist in coagulation. Additionally, we intended to contribute to the mitigation of the environmental problem related to the final disposal of the residual sludge in landfills.

## 2. Experimental

### 2.1. Effluent sample

AW effluent samples (300L) were collected in March 2003 at the dump point of the amination reactor, before derivation of the wastewater treatment system of the participating industry. Due to their proven high stability, samples were stored in 50 L plastic containers at room temperature, in a dark and dry place. Some characteristics of the effluent can be seen in Table 1.

### 2.2. Materials used

All reagents were of analytical degree and were used without any additional purification process. The absorptiometric color reduction was measured with the aid of a spectrophotometer Shimadzu Multispec-1501 ([www.shimadzu.com](http://www.shimadzu.com)). The coagulation–Fenton reactor consisted of a 600 mL polyethylene bottle provided with a magnetic stirrer Hanna Instruments HI 190M ([www.hannainst.com](http://www.hannainst.com)). A centrifuge Sigma 3K30 ([www.sigma-zentrifugen.de](http://www.sigma-zentrifugen.de)), a Bertel bolter ([www.bertel.com.br](http://www.bertel.com.br)), a Quimis digital pHme-

Table 1  
Characteristics of AW effluent stream

Parameter	Value
pH	14
Color	Abs ~ 11
COT (mg CL <sup>-1</sup> )	500
COD (mg O <sub>2</sub> L <sup>-1</sup> )	2032
Cl <sup>-</sup> (mg L <sup>-1</sup> )	121,000
F <sup>-</sup> (mg L <sup>-1</sup> )	96
Nitrate (mg L <sup>-1</sup> )	0.75
Nitrite (mg L <sup>-1</sup> )	16
Carbonate (mg L <sup>-1</sup> )	2800
Trifluraline (μg L <sup>-1</sup> )	5958
<i>p</i> -Chlortoluene (μg L <sup>-1</sup> )	5.9
3,4-Dichlor-trifluorbenzene (μg L <sup>-1</sup> )	3.0
Di- <i>n</i> -Propyl-nitrosamine (μg L <sup>-1</sup> )	306
Nitro-chlortoluene (μg L <sup>-1</sup> )	43.5
Dinitro-chlortoluene (μg L <sup>-1</sup> )	11.7
Diethyl-phthalate (μg L <sup>-1</sup> )	0.58

ter ([www.quimis.com.br](http://www.quimis.com.br)) and a Marconi sample digester ([www.marconi.com.br](http://www.marconi.com.br)) were also used.

### 2.3. Combined coagulation–Fenton process

The coagulation–Fenton experiments were performed in a 600 mL stirred tank reactor, evaluating the influence of process variables by factorial design. Firstly, the wastewater sample was diluted with distilled-deionized water to close to 500 mL 25% and then adjusted to desired pH (3 or 9) with a 1:3 H<sub>2</sub>SO<sub>4</sub> (98%) solution. After this the sample solution was completed to exactly 500 mL. In the sequence, the coagulation was performed by adding weighed amounts of ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O) and Fenton sludge, in the solid state, mixing vigorously for 5 min, then decreasing the stirring speed, for another 30 min. Later, the Fenton reagent (FeSO<sub>4</sub>·7H<sub>2</sub>O + H<sub>2</sub>O<sub>2</sub> 60%) was dosed and the experiment proceeded for a total of 60 min running time. For monitoring purposes, samples were removed at determined time intervals.

### 2.4. Residual sludge recovery

At the end of the combined process (coagulation–Fenton), the pH of samples was adjusted to 8–9 and left to decant the iron hydroxide precipitate. Then, the samples were filtered and the solid residue dried at 100–110 °C. After this, the residue was ground and sifted, collecting the 0.074 mm particle diameter fraction. To eliminate any organic contamination, the residue was finally calcined at 500 °C, for 3 h.

### 2.5. Wastewater monitoring

The monitoring of the combined process was measured both in the 200–800 nm absorptiometric spectrum of the effluent samples (25%, v/v; pH 5) as well as the maximal absorbance of 420 nm. The COD was determined according to the Standard Methods [17], using the correction for high salt content samples [18].

Samples, removed during the experiment, were basified to precipitate iron, being then centrifuged at 6000 rpm, during 20 min, and finally filtered. Residual peroxide of the samples was eliminated with the addition of 5 drops of catalase 1:10 (v/v) and stirred for 10 min. The contributing value of residual peroxide for the COD was abated by means of blank readings.

Sample aliquots were picked up along the Fenton process for accompaniment of the peroxide concentration decay (due to generation of hydroxyl radicals) by means of permanganimetry.

## 2.6. Factorial design

In this study, a fractional factorial design was employed and the interactions among the experimental factors and same confounding relations are taken into account by using the proper defining relations. With this, the obtained experimental results by this approach will be in good agreement with those obtained by the full factorial design. Usually, the effect analysis is conducted for the result obtained from the fractional factorial design to determinate which factor has the main effect. The main effects in the fractional factorial design,  $2\sqrt{5-1}$ , are mixed with the interactions with four factors, whereas the interactions with two factors are mixed with the interactions with three factors [19,20].

With the aid of a fractionary factorial design [20], the five process variables shown in Table 2 were tested, on two levels, where the parameter used was absorptiometric color reduction at 420 nm. The experiments were carried randomly to

avoid atypical errors associated with the chosen combination of levels. In order to evaluate wastewater degradation, four indicators of performance were used: absorptiometric color reduction (420 nm, pH 5), disappearance of the peak attributed to the AW (200–550 nm, pH 5),  $H_2O_2$  decay and COD reduction. Room temperature, effluent concentration (25%, v/v) and a 60 min reaction period were taken as constants.

The variables chosen were pH and the following reagent concentrations:  $Fe^{3+}$ , Fenton sludge,  $H_2O_2$  and  $Fe^{2+}$ . As recommended in the literature [21], a 5:1 relation for the concentrations  $H_2O_2:Fe^{2+}$  was used.

## 3. Results and discussion

### 3.1. Absorptiometric color reduction

The best condition for the Fenton process was defined in a preliminary factorial design. For the coagulation process, a mass ratio of 1:1 for the Fenton sludge and  $Fe^{3+}$  salt was used. Samples were diluted (5%, v/v) and adjusted exactly to pH 5 to prevent eventual peak displacement. After this, spectrophotometric measurements at 200–800 nm were performed and the absorbance decrement along this interval was evaluated. Table 2 shows the absorptiometric color reduction at 420 nm.

Table 2 shows the absorptiometric color reduction after the first 30 min of coagulation reaction. In Table 2 the color reduction attributed to the Fenton process can be seen in the

Table 2

Factorial design of resolution  $2\sqrt{5-1}$  for the AW degradation and the absorptiometric color reduction by the combined coagulation–Fenton–sedimentation process

Symbol	Experimental factors			Level (-)	Level (+)
A	pH			3	9
B	Fenton sludge (mg)			100	500
C	$Fe^{3+}$ ( $mg L^{-1}$ )			100	500
D	$Fe^{2+}$ ( $mg L^{-1}$ )			100	600
E	$H_2O_2$ ( $mg L^{-1}$ )			500	3000

Experiments	A	B	C	Average color reduction for coagulation (%)	D	E	Average color reduction for Fenton process (%)	Total color reduction for combined process (%)
1	-	-	-	14.2	-	+	35.1	49.3
2	+	-	-	14.9	-	-	29.2	44.1
3	-	+	-	14.6	-	-	20.4	35.0
4	+	+	-	13.7	-	+	28.9	42.5
5	-	-	+	28.8	-	-	14.2	42.9
6	+	-	+	34.1	-	+	55.3	89.4
7	-	+	+	29.4	-	+	62.2	91.6
8	+	+	+	34.8	-	-	8.9	43.7
9	-	-	-	13.4	+	-	38.9	52.3
10	+	-	-	17	+	+	68	85.0
11	-	+	-	15.2	+	+	76.4	91.6
12	+	+	-	16	+	-	38.7	54.7
13	-	-	+	26	+	+	63.8	89.8
14	+	-	+	30.3	+	-	25.3	55.5
15	-	+	+	24.5	+	-	31.1	54.8
16	+	+	+	35.8	+	+	50.9	86.7

Conditions: AW 25% (v/v), 500 mL; 60 min; 420 nm.

last 30 min of treatment. The highest coagulation efficiency was observed at pH 9 with the maximum addition of Fenton sludge and ferric chloride; absorptiometric color reduction was close to 36% and the greatest influence was exerted by the ferric chloride variable.

This can be explained by the presence of negative charges in the AW sample at pH 9, and by the fact that ferric chloride, as a cationic coagulant, can react with negative ions [22].

Dependence between the variables  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  was observed; therefore, with the maximum amounts of both reagents added, a higher absorptiometric color reduction (~76%) was achieved, whereas for the maximum amount of  $\text{Fe}^{2+}$  added and the minimum amount of peroxide added, a lower absorptiometric color reduction was verified (38%). Moreover, with the maximum amount of  $\text{H}_2\text{O}_2$  added and the minimum amount of  $\text{Fe}^{2+}$  added, the color reduction was about 62% (Table 2), which led us to infer that  $\text{H}_2\text{O}_2$  exerts greater influence in the process than  $\text{Fe}^{2+}$ .

Looking at Fig. 1, a relatively fast kinetic color reduction is evidenced for the coagulation process. After 30 min of treatment, no additional considerable color reduction was obtained. Subsequently, a slow stirring period is necessary for obtaining bigger aggregates for easier sedimentation, and consequently, to promote the decrease of the wastewater color.

By the Fenton process, the same phenomenon occurred, causing a very quick (1 min) reduction of the absorptiometric color. Then, the system seemed to reach a stable condition, and no other significant variation was observed in the curve profile of the degradation process. This can also be explained by the intensive generation of  $\text{HO}^\bullet$  radicals verified by the electron transfer reaction  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  (Reaction (1)). When an almost total consumption of  $\text{Fe}^{2+}$  occurs, an accumulation of  $\text{Fe}^{3+}$  in the system is observed, since the regeneration of  $\text{Fe}^{2+}$  (Reactions (3) and (4)) is slow compared to the formation of  $\text{Fe}^{3+}$ . There is also formation of hydroperoxide

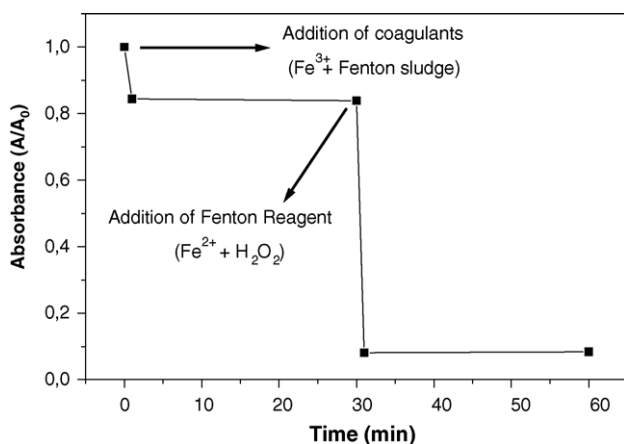


Fig. 1. The color reduction of AW subject to coagulation–Fenton–sedimentation process. Conditions: Exp. 11 (pH 3, 500 mg of Fenton sludge, 100 mg of  $\text{Fe}^{3+}$   $\text{L}^{-1}$ , 600 mg of  $\text{Fe}^{2+}$   $\text{L}^{-1}$  and 3000 mg of  $\text{H}_2\text{O}_2$   $\text{L}^{-1}$ ), AW 25% (v/v), 500 mL; 60 min; 420 nm.

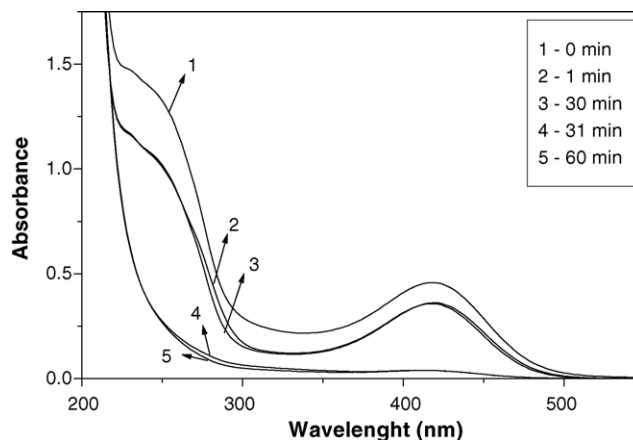


Fig. 2. UV–visible absorbance spectra of AW subject to coagulation–Fenton–sedimentation process. Conditions: Exp. 11 (pH 3, 500 mg of Fenton sludge, 100 mg of  $\text{Fe}^{3+}$   $\text{L}^{-1}$ , 600 mg of  $\text{Fe}^{3+}$   $\text{L}^{-1}$  and 3000 mg of  $\text{H}_2\text{O}_2$   $\text{L}^{-1}$ ), AW 25% (v/v), 500 mL; 60 min.

radicals, which have less oxidation power, contributing to a decrease in the efficiency of the process.

As well in the UV region, a gradual reduction of absorbance in the visible part of the electromagnetic spectrum was also observed (Fig. 2). The band decrease below 300 nm can be considered an indication of the degradation of aromatic compounds.

### 3.2. COD reduction

According to Fig. 3, in the coagulation process, as in absorptiometric color reduction, a fast decrease of organic load of the AW effluent is observed. In acidic conditions, about 20% of the COD is reduced in only 1 min of treatment; but almost 40% of the COD is reduced at alkaline conditions,

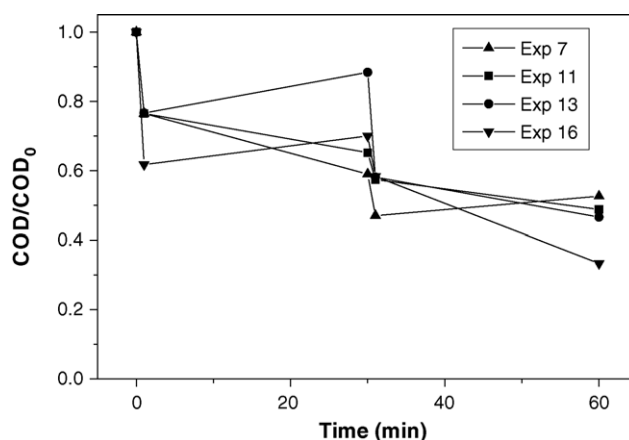


Fig. 3. Accompaniment of the COD reduction of AW by the coagulation–Fenton–sedimentation process. Conditions: AW 25% (v/v), 500 mL; 60 min. (▲) pH 3,  $\text{Fe}^{3+}$ : 500 mg  $\text{L}^{-1}$ , Fenton sludge: 500 mg,  $\text{Fe}^{2+}$ : 100 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 3.0 g  $\text{L}^{-1}$ ; (■) pH 3,  $\text{Fe}^{3+}$ : 100 mg  $\text{L}^{-1}$ , Fenton sludge: 500 mg,  $\text{Fe}^{2+}$ : 600 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 3.0 g  $\text{L}^{-1}$ ; (●) pH 3,  $\text{Fe}^{3+}$ : 500 mg  $\text{L}^{-1}$ , Fenton sludge: 100 mg,  $\text{Fe}^{2+}$ : 600 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 3.0 g  $\text{L}^{-1}$ ; (▼) pH 9,  $\text{Fe}^{3+}$ : 500 mg  $\text{L}^{-1}$ , Fenton sludge: 500 mg,  $\text{Fe}^{2+}$ : 600 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 3.0 g  $\text{L}^{-1}$ .

which agrees with the description above (Section 3.1). The same occurs in the Fenton treatment.

The fast removal of the organic load is due to the formation of substances with functional groups that can react with specific sites of the colloidal coagulants, giving rise not only to insoluble complexes with  $Fe^{3+}$ , but also to the adsorption into Fenton sludge particles. Therefore, neutral compounds are adsorbed, originating heavier and more voluminous flocs, improving the abatement of organic load, agreeing with Stephenson and Duff [4].

In Fig. 3, it can be observed that the reduction of COD by coagulation at pH 9 (level +) is higher than at pH 3 (level –), which may be due to the formation of iron hydroxides and adsorption of organic substances. In acidic conditions, the anionic organic molecules react forming insoluble complex and, thus lower the COD reduction.

With the addition of the Fenton reagent, organic compounds are quickly removed in consequence of the formation of  $HO^\bullet$  radicals (Reaction (1)). The oxidation continues throughout the reaction, and this may be attributed to the regeneration of the ferrous ion, since *Fenton-like reactions* renew the oxidation capability (Reactions (3) and (4)).

The formation of radical species with lower oxidation power, such as  $HOO^\bullet$  radicals, can also be considered to retard the oxidation of organic compounds. The maximum COD reduction was around 50–60%, and looking at the decay profile of the Fenton process curve, a higher COD reduction can be predicted if more than 60 min of reaction is performed.

### 3.3. Effect of the variables

The fractionary factorial design can only estimate the effect of each variable.

The results obtained after applying analysis of variance (ANOVA) are shown, as a Pareto chart of effects, in Fig. 4 together with a line for probability  $P=0.05$  that points out

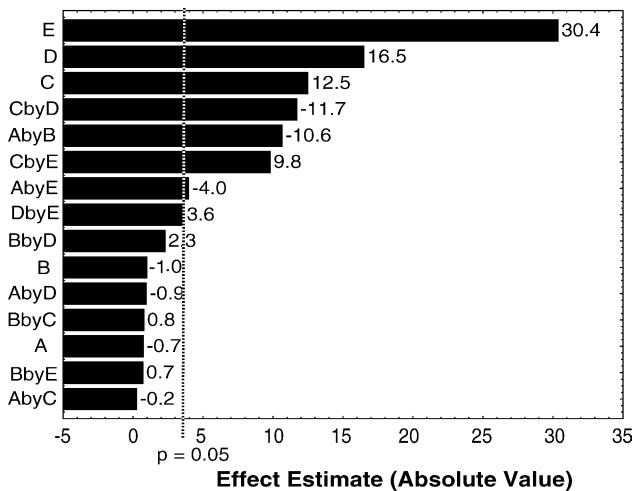


Fig. 4. Pareto chart of effects obtained from two level  $2v^{5-1}$  fractionary factorial design.

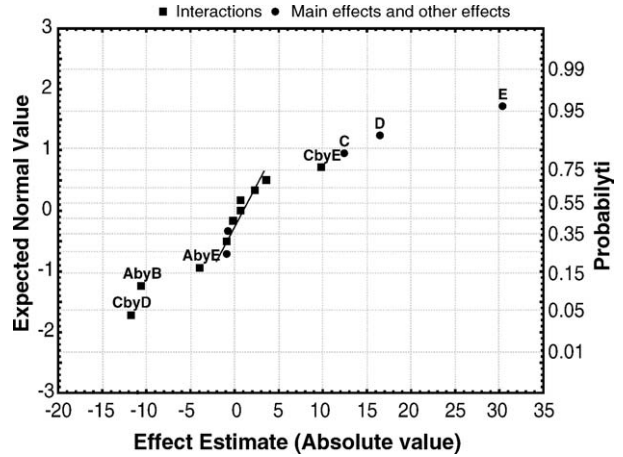


Fig. 5. Estimate of the effect factorial design  $2v^{5-1}$  in chart of cumulative normal probability. C =  $Fe^{3+}$ , D =  $Fe^{2+}$ , E =  $H_2O_2$ , AbyB = pH and Fenton sludge, AbyE = pH and  $H_2O_2$ , CbyD =  $Fe^{3+}$  and  $Fe^{2+}$ , CbyE =  $Fe^{3+}$  and  $H_2O_2$ .

which effects can be considered significant. With a reliability of 95%, it can be affirmed that the effects of values over 3.6% are statistically significant; therefore, simple effects of the variables  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $H_2O_2$  are considered significant to the process and also to the interactions between the variables pH and Fenton sludge, pH and  $H_2O_2$ ,  $Fe^{3+}$  and  $Fe^{2+}$ ,  $Fe^{3+}$  and  $H_2O_2$  (Fig. 4). The simple effects of the pH and Fenton sludge variables can be considered fluctuations in the process.

Fig. 5 allows us to evaluate the veracity of simple and combined interactions of each factor (significance) in a chart of normal accumulated probability. A value of accumulated probability is associated for each effect in Fig. 4. It can be observed that the central points of the figure adjust very well to a straight line, whose intersection with the accumulated probability near to 50% occurs at point zero of the estimate axle of the effects. Thus, we must consider that these points have no practical meaning related to the effects in the combined coagulation–Fenton–sedimentation process. This strengthens the affirmation that the effects related to the factors below 3.6% are the same that are represented on the straight line, and the other points, more distant from the curve center, are considered significant.

#### 3.3.1. Effect of pH

The pH proved to be a statistical fluctuation of the combined coagulation–Fenton–sedimentation process and this can be explained by the addition of  $FeCl_3 \cdot 6H_2O$ , an acid salt that reacts with  $HO^-$  ions, forming  $Fe(OH)_3$ . In the first minute of the reaction, the pH of the sample, both acid and alkaline (two levels studied), decreased, as can be seen in Fig. 6.

In the coagulation process, when the reaction started at pH 9 and  $100 \text{ mg of } Fe^{3+} \text{ L}^{-1}$  were added, the decrease of the pH was lower, remaining around pH 6. With the addition of  $500 \text{ mg of } Fe^{3+} \text{ L}^{-1}$ , after 5 min, the pH was around 2–4, remaining there for the rest of the coagulation process. This

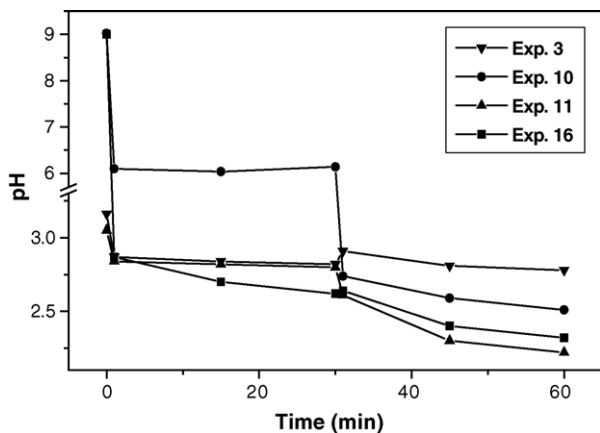


Fig. 6. Change of pH during the coagulation–Fenton–sedimentation process. Conditions: AW 25% (v/v), 500 mL; 60 min. (▼) pH 3,  $\text{Fe}^{3+}$ : 100 mg  $\text{L}^{-1}$ , Fenton sludge: 500 mg,  $\text{Fe}^{2+}$ : 100 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 500 mg  $\text{L}^{-1}$ ; (●) pH 9,  $\text{Fe}^{3+}$ : 100 mg  $\text{L}^{-1}$ , Fenton sludge: 100 mg,  $\text{Fe}^{2+}$ : 600 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 3.0 g  $\text{L}^{-1}$ ; (▲) pH 3,  $\text{Fe}^{3+}$ : 100 mg  $\text{L}^{-1}$ , Fenton sludge: 500 mg,  $\text{Fe}^{2+}$ : 600 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 3.0 g  $\text{L}^{-1}$ ; (■) pH 9,  $\text{Fe}^{3+}$ : 500 mg  $\text{L}^{-1}$ , Fenton sludge: 500 mg,  $\text{Fe}^{2+}$ : 600 mg  $\text{L}^{-1}$ ,  $\text{H}_2\text{O}_2$ : 3.0 g  $\text{L}^{-1}$ .

range is considered best for the generation of hydroxyl radicals through the Fenton reaction [6], initiated soon after the initial 30 min of the reaction.

In the coagulation process, the pH acts on the nature of the polymeric metal species, soon after the salt is dissolved in wastewater. The influence of the pH is generally due to two competitive forces: (1) the  $\text{H}_3\text{O}^+$  ion and metal hydrolysis products competing for the organic compounds and (2) hydroxide and organic anions competing for the products of metal hydrolysis. At a lower pH,  $\text{H}_3\text{O}^+$  ions compete with the products of metal hydrolysis for organic ligands [23]. Table 2 shows that higher absorptiometric color reduction occurred when basic pH and 500 mg of  $\text{Fe}^{3+}$   $\text{L}^{-1}$  were used.

The effect of pH on the Fenton process is complex. The acid medium (pH  $\sim$  3) is the most important variable to obtain a more efficient Fenton reaction [24]. At this pH the formation of the  $[\text{FeH}_2\text{O}_2]^{2+}$  complex can occur as an intermediate by Reaction (1), which can further decompose, generating hydroxyl radicals. At a pH below 2, the decomposition of hydrogen peroxide by  $\text{Fe}^{2+}$  is inhibited and the complex  $[\text{Fe}^{\text{III}}\text{HO}_2]^{2+}$  is not formed. Furthermore, the reaction chain of regeneration of  $\text{Fe}^{2+}$  is affected according to Reactions (3) and (4). Another explanation is the formation of some complexes such as  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , which react slowly with peroxide, delaying the formation of  $\text{HO}^\bullet$  radicals. At a higher pH (pH 6), the formation and precipitation of  $\text{Fe}(\text{OH})_3$  can occur, which possesses less activity. In agreement with Buxton et al. [25], at a pH around 2–3, the oxidation potential of the  $\text{HO}^\bullet$  radical is 2.8 V, whereas, at a pH next to 7, it is 1.9 V, decreasing the capacity of degradation of organic substances.

After adding the Fenton reagent, the pH decreased, remaining between 2.8 and 2.2, probably due to the formation of carboxylic and other acids, as well as of  $\text{H}_3\text{O}^+$  ions, in agreement with Reactions (3), (7)–(9).

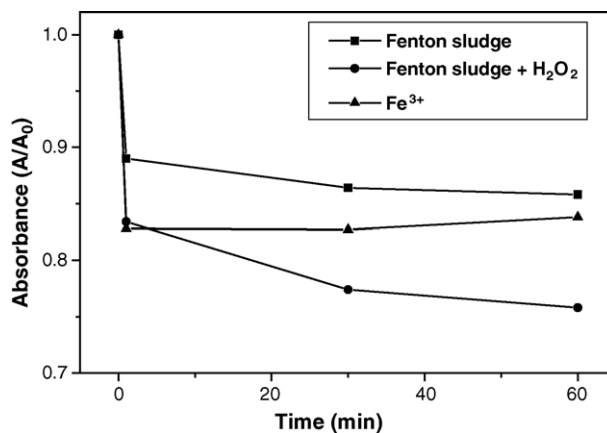


Fig. 7. Comparison of the AW absorptiometric color reduction using only Fenton sludge, Fenton sludge and  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$  in separate assays. Conditions: AW 25% (v/v), pH 3, 500 mL; 420 nm, 60 min. (■) 500 mg of Fenton sludge. (●) 500 mg of Fenton sludge plus 3.0 g  $\text{H}_2\text{O}_2$  of  $\text{L}^{-1}$ . (▲) 100 mg of  $\text{Fe}^{3+}$   $\text{L}^{-1}$ .

In the coagulation–Fenton–sedimentation process, the maximum addition of ferric chloride and peroxide always led to better results, regardless of the pH.

### 3.3.2. Effect of the Fenton sludge

The Fenton sludge variable can be seen as a fluctuation of the process, having a rather small contribution to the efficiency of the process. As demonstrated in Fig. 7 and Table 2, the contribution of the Fenton sludge is around 15% of the total absorptiometric color reduction.

The Fenton sludge precipitation with NaOH led to  $\text{Fe}(\text{OH})_3$  formation. The small influence of the Fenton sludge in the coagulation process can be explained by the formation of iron oxide (e.g.  $\text{Fe}_2\text{O}_3$ ) during the calcination at 500 °C, which is less efficient compared to ferric chloride and ferrous sulfate.

With the addition of 100 mg of  $\text{Fe}^{3+}$   $\text{L}^{-1}$  and 100 or 500 mg Fenton sludge, a colloid formation occurred at both pH 5 and 9. When the Fenton reagent was added, the pH continued to decrease. This colloidal compound (e.g.  $\text{FeOH}$ ), which can be considered a Lewis base, is able to react with  $\text{H}_3\text{O}^+$ , forming  $\text{FeOH}^{2+}$  on the colloidal surface [26]. Therefore, it contributes to decrease the amount of free  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ , reducing the degradation of the organic load of the effluent, and thus, the efficiency of the process.

According to Fig. 7, it can be observed that coagulation happened quickly (1 min, by fast stirring), due not only to the generation of insoluble agglomerates through the reaction of ionic iron species with opposite charged colloidal particles, but also to the adsorption phenomena [27]. The next step was the flocculation of the colloidal species, after which there was no more color reduction of AW effluent sample, even far beyond 60 min of treatment.

However, when the Fenton sludge was employed in the presence of  $\text{H}_2\text{O}_2$ , this phenomenon occurred after only 30 min of treatment. This profile of absorptiometric color

abatement can be explained by  $\text{H}_2\text{O}_2$  decomposition by  $\text{Fe}^{3+}$  ions from the Fenton sludge, in accordance with Reactions (3) and (4). Other possible explanations could be the occurrence of iron oxides that decompose  $\text{H}_2\text{O}_2$ , generating  $\text{HO}^\bullet$  radicals, or, at a lower pH, a reductive dissolution of the iron sludge could generate a homogeneous catalytic reaction (Fenton) [28].

### 3.3.3. Effect of ferric iron

The  $\text{Fe}^{3+}$  variable increased the efficiency of the combined coagulation–Fenton–sedimentation process by 12.5%, considering that the increase of the amount of  $\text{Fe}^{3+}$  from a (–) level to a (+) level led to greater efficiency. This influence can be observed in Table 2, in that, when 500 mg of  $\text{Fe}^{3+} \text{ L}^{-1}$  were used, the absorptiometric color reduction was higher compared to the reduction obtained at the minimum added amount (100 mg  $\text{Fe}^{3+} \text{ L}^{-1}$ ).

In Table 2, it can be seen that the best results are reached at pH 9, with the highest concentration of  $\text{Fe}^{3+}$ , since the organic molecules reacted directly with the  $\text{Fe}^{3+}$ , forming insoluble complexes at a higher pH.

The most probable mechanisms involved were adsorption and charge neutralization, leading, at slow agitation, to the formation of flocculates of organic compounds adsorbed by colloidal ferric hydroxide, formed in alkaline conditions, agreeing with Cheng and Chi [27]. Because  $\text{FeCl}_3$  hydrolysis is not regular, forming different mono and polymeric ferric species, the effluent receives a great cationic charge, undergoing neutralization and generating colloidal agglomerates of macroscopic particles, highly dependent on the pH, which can be easily removed by sedimentation [26].

As observed in Fig. 7, this phenomenon occurred due to the combination of  $\text{Fe}^{3+}$  and the Fenton sludge, where the coagulation quickly elapsed (1 min) with formation of  $\text{Fe}(\text{OH})_3$ , which acted through adsorption and the neutralization of charges, especially at an alkaline pH [27].

Another factor of great influence is the reduction of  $\text{Fe}^{3+}$  by  $\text{H}_2\text{O}_2$  in accordance to the so called *Fenton-like reactions*. It can be seen in Fig. 7 that both coagulation processes involving the Fenton sludge alone, and those involving only  $\text{Fe}^{3+}$  under the same conditions, demonstrated similar results in absorptiometric color abatement.

### 3.3.4. Effect of hydrogen peroxide

$\text{H}_2\text{O}_2$  exerts great influence on the coagulation–Fenton–sedimentation process, because increasing its concentration from a (–) level to a (+) level, increased the efficiency by around 30%. This can be explained by the high relation  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  (1:5) used. A sharp decrease of the  $\text{H}_2\text{O}_2$  concentration was also observed during the last 30 min of treatment.

When the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  relation is 0.2 (+ + or – – of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ) Reaction (1) occurs normally, and hydroxyl radicals are generated, which react with the organic load. An  $\text{H}_2\text{O}_2$  excess can react with hydroxyl radicals, producing  $\text{HO}_2^\bullet$ . These species show much lower oxidation power

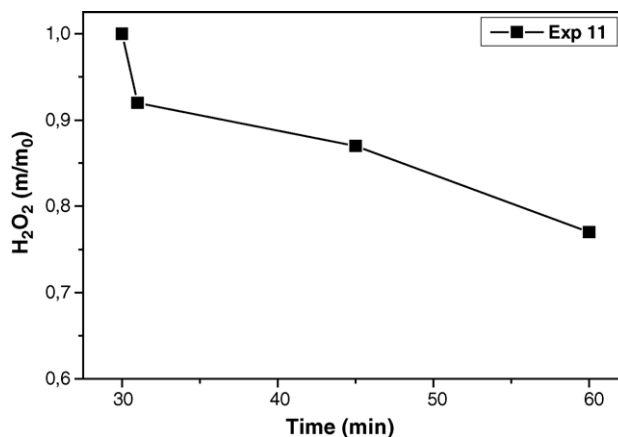
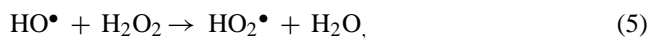
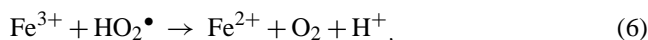


Fig. 8. Peroxide decay by the Fenton treatment in the combined coagulation–Fenton–sedimentation process. Conditions: Exp. 11 (pH 3, 500 mg of Fenton sludge, 100 mg  $\text{L}^{-1}$  of  $\text{Fe}^{3+}$ , 600 mg of  $\text{Fe}^{2+} \text{ L}^{-1}$  and 3.0 g of  $\text{H}_2\text{O}_2 \text{ L}^{-1}$ ), AW 25% (v/v), 500 mL; 30 min.

(Reaction (5)) and can reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , following Reaction (6) [29].



$$k = 3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

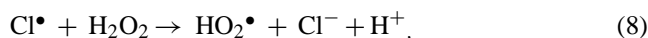


$$k = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

Another explanation for the fall in the concentration of  $\text{H}_2\text{O}_2$  during the coagulation–Fenton–sedimentation process may be the presence of high amounts of chloride ions in the AW effluent which decompose  $\text{H}_2\text{O}_2$  giving rise to  $\text{HO}_2^\bullet$  radicals, in accordance to Reactions (7) and (8). The chloride ion also acts as a scavenger (Reaction (9)), consuming hydroxyl radicals and reducing the degradation efficiency of the processes [30,31].



$$k = 9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$



$$k = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$



Fig. 8 presents the consumption of  $\text{H}_2\text{O}_2$  in experiment 11, revealing the existence of residual peroxide at the end of the experiments.

### 3.3.5. Effect of ferrous iron

Increasing the concentration of  $\text{Fe}^{2+}$  from a (–) to a (+) level, the reaction efficiency increased 16.5% (Fig. 4). At such concentrations, the formation of hydroxyl radicals is kinetically favored by higher peroxide doses [9].

However, when the two lowest levels, respectively, of hydrogen peroxide and ferrous ion concentration, were

used in a 1.2  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  relation, the reaction chain 1–4, which generates hydroxyl radicals, was quickly interrupted, decreasing the degradation rate.

The ferrous ion in excess can also act as a scavenger, reacting very quickly with hydroxyl radicals (Reaction (2)), being able to compete with organic compounds for the radicals. Therefore, when the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  relation from the Fenton process is 1.2, ferrous iron can act in two different ways: (1) generating hydroxyl radicals in accordance to the reaction chain 1–4, or/and (2) as a coagulant in the presence of organic compounds [29], mainly when pH is in the range 6–8. This occurred when the process was started at pH 9, and 100 mg of  $\text{Fe}^{3+} \text{ L}^{-1}$  and 100 or 500 mg of Fenton sludge were added (Fig. 7). There was a decrease in the generation of hydroxyl radicals because iron becomes partially complexed by organic substances, being no longer available for reaction with peroxide.

#### 4. Conclusion

The combined coagulation–Fenton–sedimentation process was efficient in the reduction of absorptometric color and COD of the effluent amination water, reaching values above 90 and 60%, respectively.

The influence of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  was shown to be significant for the combined process, since by the increase of these variables not only the efficiency of the color reduction was raised, but also the abatement of the organic load.

Moreover, the suggested reuse of the Fenton sludge was proved to be a fluctuation of the process and cannot be only considered as an alternative for sparing coagulant, but also as a factor in the reduction of around 15% of the total absorptometric color.

Considering the obtained results, the operational simplicity and the favorable cost/benefit relation, the employment of the here described coagulation–Fenton–sedimentation process can be advantageous for the treatment of the recalcitrant effluent stream amination water from the trifluraline production. Other similar industrial wastewater's can also take advantage of this combined process, especially, as a pre-treatment for posterior conventional treatments (such as activated sludge technology).

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