Full Paper

Fenton Coagulation/Oxidation Using Fe^{2+} and Fe^{3+} Íons and Peracetic Acid for the Treatment of Wastewater

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Abstract: The Fenton coagulation/oxidation process is divided into two steps: coagulation, in alkaline pH and oxidation, in acid pH. This configuration provides a reduction in oxidant concentration, due to the pretreatment conducted in the coagulation step. This study proposes the substitution of hydrogen peroxide (HP) by peracetic acid (PAA) in a Fenton coagulation process to treat sanitary sewage and provide its disinfection. The new combination is proposed in a single step and presented good results in removing turbidity (98.5%), apparent color (95.4%), phosphorus (100%) and COD (58.2%) even at the effluent natural pH, besides demonstrating higher reduction in *E. coli* when compared with the process that employs hydrogen peroxide. The formation of Fe^{3+} ions was shown to be responsible for the removal of the particulate material.

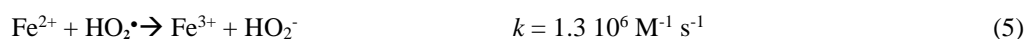**Keywords:** fenton coagulation/oxidation; peracetic acids; removing particulate matter; disinfection
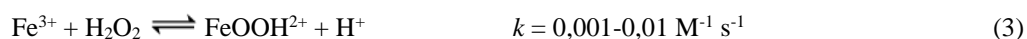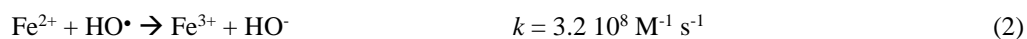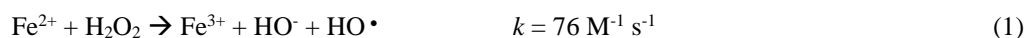
1. INTRODUCTION

Although conventional processes of sanitary effluent treatment, in most cases, are sufficient to ensure current legislation concerning the quality of the effluent discharged into water bodies, the increase of the demand of water encourages the use of new technologies that can lead these effluents for nobler purposes, such as reuse. Another important factor to consider is that effluents discharged in a region may be the affluent of drinking water treatment plant of another region, so one form of indirect reuse.
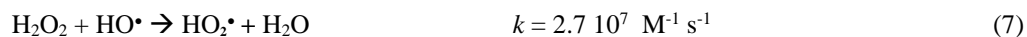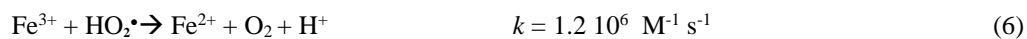
Among the latest technologies for wastewater treatment are the advanced oxidation processes (AOPs) as the process Feton. The Fenton process stand out for being applicable to various types of effluents, such as: COD and color removal from UASB used to treated poultry manure wastewater [1] pretreatment on the biodegradability of surfactants [2], and destruction of disperse dyes in textile wastewater [3].

The Fenton's reagent consists in reaction between ions iron and hydrogen peroxide (HP), which generates hydroxyl and hydroperoxyl radicals with high oxidation-reduction potential (2.8 V vs. SHE), losing only to fluorine (3.03 V vs. SHE). According to the reactions [4]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \qquad k = 76 \ M^{-1} \ s^{-1} \qquad (1)$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^- \qquad k = 3.2 \ 10^8 \ M^{-1} \ s^{-1} \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightleftharpoons FeOOH^{2+} + H^+ \qquad k = 0,001\text{-}0,01 \ M^{-1} \ s^{-1} \qquad (3)$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \qquad (4)$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \qquad k = 1.3 \ 10^6 \ M^{-1} \ s^{-1} \qquad (5)$$

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$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad k = 1.2\ 10^6\ M^{-1}\ s^{-1} \qquad (6)$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \qquad k = 2.7\ 10^7\ M^{-1}\ s^{-1} \qquad (7)$$

These radicals attack indiscriminately all species present in the reaction, oxidizing organic compounds by abstraction of hydrogen or engaging in double bonds and aromatic rings (hydroxylation), causing reactions such as demethoxylation, dehalogenation, dealkylation, denitration, deamination and decarboxylation [5, 6]. These reactions contribute to refractory organic contaminants become biodegradable, which makes the process Fenton an excellent pretreatment for biological processes [2].

The main drawbacks of Fenton process is related to the wastage of oxidants due to the radical scavenging effect of hydrogen peroxide, its selfdecomposition and the loss of iron ions and the formation of solid sludge [7].

Some authors propose the use of ferrous sulfate (FS), ferric chloride or polyferric sulfate to provide previous coagulation at alkaline pH, and then apply the hydrogen peroxide (HP) in the sobrenatant, at acid pH, which reacts with soluble residual iron in the sobrenatant generating hydroxyl radicals [8-10]. In this process, called Fenton coagulation, reduction in the HP occurs due to the removal of contaminants through coagulation. Fenton coagulation is also proposed simultaneously, that is, in one phase only, in which pHs between 3 and 6 are used throughout the process [11].

Organic peroxide (RO$_2$H) is also decomposed by the iron ion, forming the alcoxyl (RO•) and organic peroxyl (RO$_2$•) radicals [6]. According to the proposed reactions:

$$Fe^{2+} + CH_3OCO_2H \rightarrow Fe^{3+} + CH_3OCO\bullet + HO^- \qquad (8)$$

$$Fe^{3+} + CH_3OCO\bullet \rightarrow Fe^{3+} + CH_3O^- \qquad (9)$$

$$Fe^{3+} + CH_3OCO_2H \rightleftharpoons FeOOCOCH_3{}^{2+} + H^+ \qquad (10)$$

$$FeOOCOCH_3{}^{2+} \rightarrow Fe^{2+} + CH_3OCO_2\bullet \qquad (11)$$

The peracetic acid (PAA) is an organic peracide used as disinfectant of hospital materials, food industry equipment and has been widely studied as a disinfectant of wastewater [12, 13]. PAA is a quaternary mixture in equilibrium, commercially available in the composition of PAA (15%), HP (23%), acetic acid (16%) and water (CH$_3$COOH + H$_2$O$_2$ $\rightleftharpoons$ CH$_3$COOOH + H$_2$O), and presents higher disinfectant potential when compared with HP. Aslari *et al*. compared the bactericidal potential PAA and HP, for the inactivation of *E. coli* in water. They observed that PAA 12 mg L^{-1} presented same inactivation efficiency than 3125 mg L^{-1} of HP, 260 times greater than the concentration of PAA [14].

This study investigated the substitution of HP from the Fenton reagent by PAA as well as the simultaneous coagulation/oxidation with the combination FS/PAA instead of a two-phase process.

2. MATERIAL AND METHODS

Coagulation tests were carried out in *Jar-test* equipment using upflow anaerobic sludge blanket (UASB) reactor effluent. 120 combinations were provided, varying pH (3 to 9), FS concentration (40 to 320 mg L^{-1}), HP (150 to 350 mg L^{-1}) 1 and PAA (5 to 150 mg L^{-1}), in fixed coagulation operational conditions: Fast mixture gradient 320 s^{-1}, for 1 minute; Slow mixture gradient 18 s^{-1}, for 10 minutes. In sedimentation tests, times up to 30 minutes were set. For filtration simulation tests, sedimentation was substituted by filtration with medium speed qualitative filter paper porosity 8 µm (Figure 1).

Figure 1. *Jar test* equipment and filtration system of the effluent after coagulation.

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This phase was adapted from the method proposed by Di Bernado *et a* [15]. In the solution preparation, heptahydrated ferrous sulfate (FS), hexahydrated ferric chloride (FC) 33% HP and 15% PAA (composition 15% PAA, 23% HP and 16% acetic acid) were employed. The sample pH was adjusted with sodium hydroxide and sulfuric acid solutions whenever necessary. For the FS and FC doses, the reagent total mass was considered rather than the HP and acetic masses in the mixture. PAA residual was determined through the DPD method [16]. The tests were performed on the same day of collection, with an operating temperature of 18°C ±1°C.

The minimum and maximum values for turbity 95 to 147 NTU, apparent color 803 to 1308 uC, pH 7,1 a 7,57 e COD 158 a 347mg L^{-1}.

Methodologies adopted for the effluent characterization follow the Standard Methods for the Examination of Water and Wastewater description [17] and Standards CETESB [18] (Tab. 1). Statistical analyses were carried out through the Programs Statgraphics Plus 5.1 (Factorial analysis) and Statistica 7 (response surface methodology).

Table 1. Parameters analyzed in raw effluent and later the treatment.

Physico-chemical parameters	Method
Absorbance 254 nm	Spectrophotometric 5910 B
Residual peracetic acid (PAA) (mg L^{-1})	Spectrophotometric (DPD)
Apparent color (uC)	Spectrophotometric 2120C
Chemical oxygen demand (COD) (mg L^{-1})	Spectrophotometric 5220D
Total Iron (mg L^{-1})	Spectrophotometric (Ortofenatroline)
Total Phosphorous (mg L^{-1})	Spectrophotometric 4500-P E
Dissolved oxygen (DO) (mg L^{-1})	Oximetric 4500-O G
pH	Potentiometric 4500-H^+B
Total Suspended Solids (TSS)	Gravimetric 2540D
Total Solids (TS)	Gravimetric 2540B
Turbity (NTU)	Nephelometric 2130B
Microbiological parameters	Method
Total Coliform (TC) (CFU/100 mL)	Membrane Filter 9222B
E. coli (CFU/100 mL)	Membrane Filter 9222B
Coliphage (UFP/100mL^{-1})	CETESB, 1990 - L5.225
Clostridium perfringens (MPN/100mL^{-1})	Multiple tubes (CETESB, 1993 - L5.213)

3. RESULTS AND DISCUSSION

In order to limit the doses to be applied to the effluent, several FS concentrations at pH 8 were evaluated; this pH band was based on the studies of Perdigón-Melón et al.[9], who obtained good coagulation results with FS in industrial effluent.

The FS concentrations evaluated ranged from 40 to 320 mg L^{-1} and the efficacy in removing the effluent apparent color, COD and turbidity was assessed. The best results obtained were observed between 150 and 280 mg L^{-1} FS, with the removal of 75 to 85% COD, 11 to 22% apparent color and 42 to 62% turbidity. The results are shown in Figure 2.
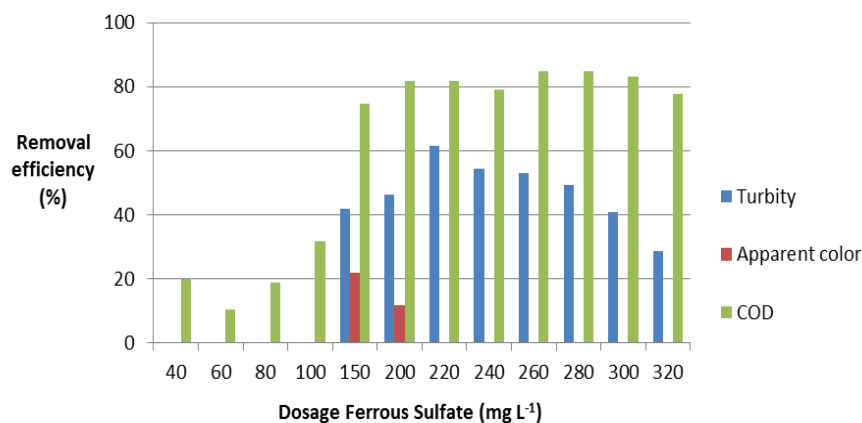

Figure 2. Efficiency by FS for removal of turbidity, apparent color and COD in the effluent, at pH 8, varying coagulant concentration.

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The optimal pH band for this coagulant was confirmed by the scanning of the interval 150 to 280 mg L[1] FS at six different pH values (5; 6; 7; 8; 8,5 and 9), according to Figure 3.
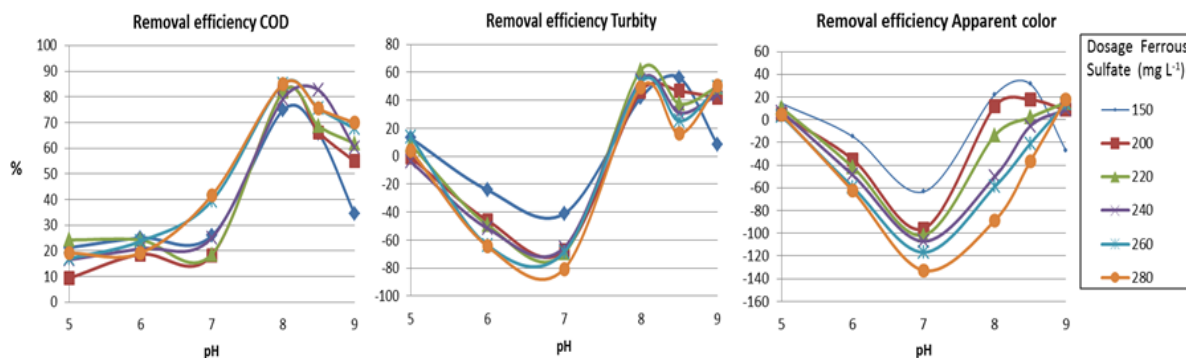

Figure 3. Efficiency by FS for removal of turbidity, apparent color and COD in the effluent, varying pH and coagulant concentration.

The coagulant best efficacy was observed at pH 8 in most of the doses applied to the effluent under study, confirming the pH band used to limit the FS dosage. The FS dose selected for the combined PAA test was 150 mg L^{-1} prioritizing a lower FS dose.

The PAA dose (50 mg L^{-1}) was adopted taken into consideration the HP dose employed by De Julio et. al. [19], who obtained good results in terms of coagulation in water, using the stoichiometry 1 mol Fe for 1 to 3 mol HP, in acid pH. The theoretically,

1000 mg L^{-1} removal 470.6 mg L^{-1} of COD [9, 11].The dosages tested were FS 150 mg L^{-1}/HP 150 mg L^{-1} and FS 220 mg L^{-1}/HP 350 mg L[1].

As the PAA 15% has 23 % HP in its composition, a 50 mg L^{-1} PAA solution also has 75 mg L^{-1} HP, for this reason a lower dose of PAA was used for the FS coagulation, aiming to compare it with the oxidant higher equivalence.

Table 2 presents results of the comparison test between FS coagulation with HP and PAA.

Table 2. Comparison between SF/HP and FS/PAA coagulation.

pH	FS (mg L^{-1})	Oxidant (mg L^{-1})	Turbidity (NTU)	Apparent color (UC)	COD (mg L^{-1})	Sed. speed (cm min^{-1})	E. coli (CFU 100mL^{-1})	TC (CFU 100mL^{-1})	Coliphage (UFP/ 100mL^{-1})	*Clostridium perfringens* (MPN/ 100mL^{-1})
3	150	PAA 50	32.7	367	68	1.2	> 1.0	5	> 1.0	$8.0x10^3$
3	150	HP 150	40	405	37	0.6	$3.0x10^1$	6	> 1.0	$8.0x10^3$
3	220	PAA 50	21.5	260	62	1.2	-	-	-	-
3	220	HP 350	39.5	363	86	0.6	-	-	-	-
7.1*	-	-	124*	1190*	236*	-	$4.80x10^5$	$1.42x10^6$	$1.52x10^3$	$3.50x10^5$

CFU= Colony Forming Unit; MPN= Most Probable Number; PFU= Plate Forming Unit. * Values obtained from the raw effluent.

Increase in the concentration of HP resulted in higher COD values. HP in excess acts as a hydroxyl radical scavenger, forming the hydroperoxyl radical ($HO_2\bullet$), which presents lower reduction potential ($E° = 1,42$ V *vs.* SHE) than $HO^\bullet$. Besides that, the Fe^{2+} concentration in the medium is low in relation to Fe^{3+}, and as a reaction between Fe^{3+} and HP is much slower than the HP decomposition in the presence of Fe^{2+} the degradation process is hampered [20].

In this test (Tab. 2) the slow mixture gradient was 50 s^{-1} for 30 minutes, in order to have a longer oxidation time. The pH 3 recommended for the Fenton reaction was adopted [21]. The basic pH efficacy reduction is ascribed to the hydrated ferrous ion iron transition into a colloidal ferric species, in the latter form, the iron decomposes catalytically the HP into oxygen and water, without forming hydroxyl radicals [22].

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The combination FS(150)/APA(50) presented the best efficacy to remove turbidity, apparent color and *E. coli,* however, SF(150)/HP(150) showed higher efficacy to remove COD which is explained by the PAA organic load. A 50 mg L^{-1} PAA solution presents 140 mg L^{-1} theoretical COD.

Regarding sedimentation time of the flakes formed during coagulation, it was seen that SF(150)/APA(50) presented sedimentation speed higher than SF(150)/HP(150), 1.2 cm min^{-1} and 0.6 cm min^{-1}, respectively. These results indicate that with SF(150)/APA(50) the flakes that formed were denser, which might be ascribed to the formation of iron organic complexes [23]. According to Kwon et al. ferrous and ferric metals in water promptly form stable complexes with organic substances [24]. Thus, part of the effluent organic acids and other organic products might complex with iron species stopping the redox cycle (Fe^{2+} / Fe^{3+}).

In order to evaluate the optimum pH at which coagulation occurs, different pH bands were tested for the FS/PAA reaction, using the doses 150 mg L^{-1} and 50 mg L^{-1}, respectively.

The best results obtained were in the pH band ranging between 3 to 5, where the efficacy in the removal of turbidity was 75 to 89%, apparent color 69 to 86%, COD 61 to 69% and phosphorus 64 to 68%, with the highest values obtained at pH 3 and the lowest at pH 5. In lower pH bands the FS/PAA efficacy was higher and can be compared to the Fenton reaction. The Fenton reaction optimum pH band is between 2.5 and 3, as in pH bands above 3 the Fe^{3+} precipitation occurs. The interaction between the oxidant and the Fe^{3+} ions decreases with the pH increase and the formation of $HO^{\bullet}$ reduces; in pH bands below 2.5 the degradation speed also decreases, due to the high H^+ concentration, which might kidnap hydroxyl radicals generated and form water [20].

Kang and Hwang removed organic substances by oxidation and coagulation in treatment of the non-biodegradable landfill leachate (COD 1200 a 1500 mg L^{-1}) by Fenton's reagents. The authors used FS 1310 mg L^{-1} and HP 1600 mg L^{-1}, for removal 70% of COD [11].

Reduction from 50 mg L^{-1} to 20 mg L^{-1} in the concentration of the PAA applied resulted in 10 to 20% lower removal efficacy in all parameters under evaluation (turbidity, color, COD and total phosphorus), confirming the PAA contribution to the effluent coagulation process.

Another important fact to be observed, is that even reducing the PAA dose in 60% ($COD_{theoretichal}$=84 mg L^{-1}) a COD value lower than that obtained by the 50 mg L^{-1} PAA dose was not obtained, demonstrating the PAA participation in the organic matter as well.

Ma and Xia used SF and HP and observed that the COD removal was high in a broad pH band from 1 to 6 [25].
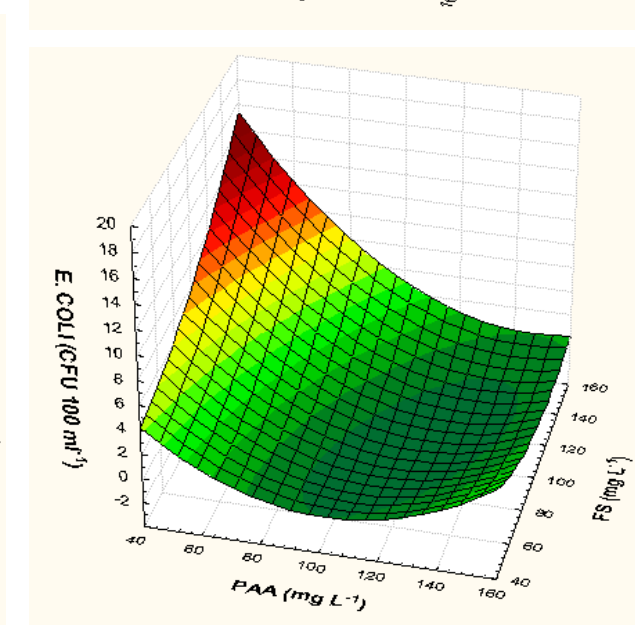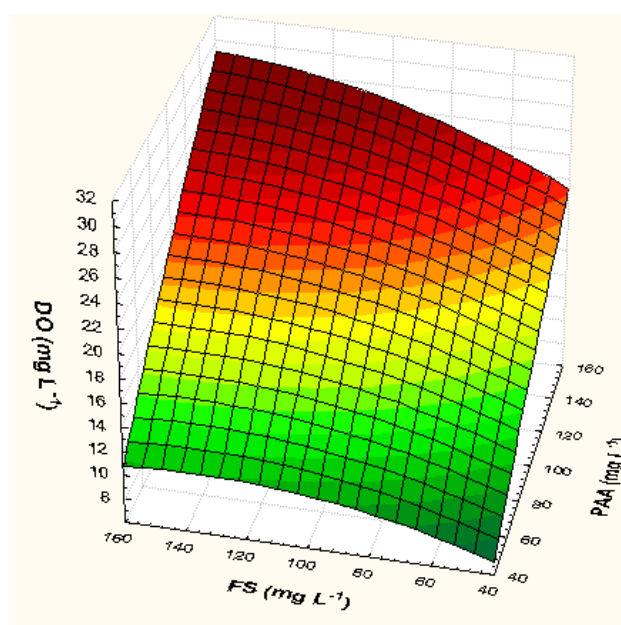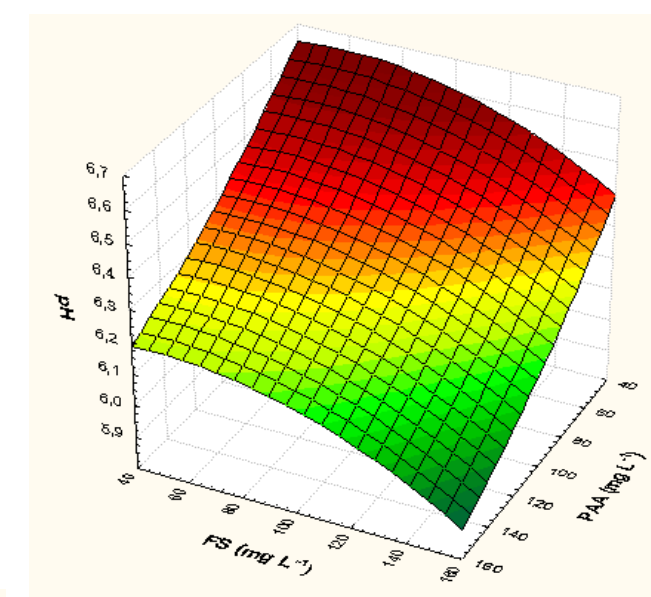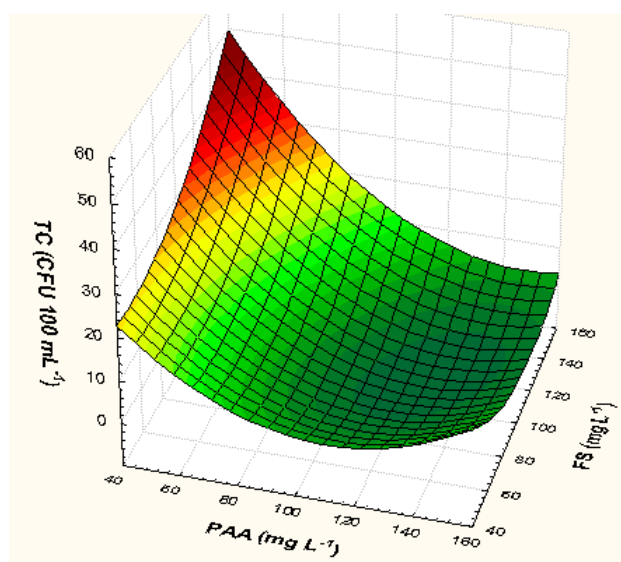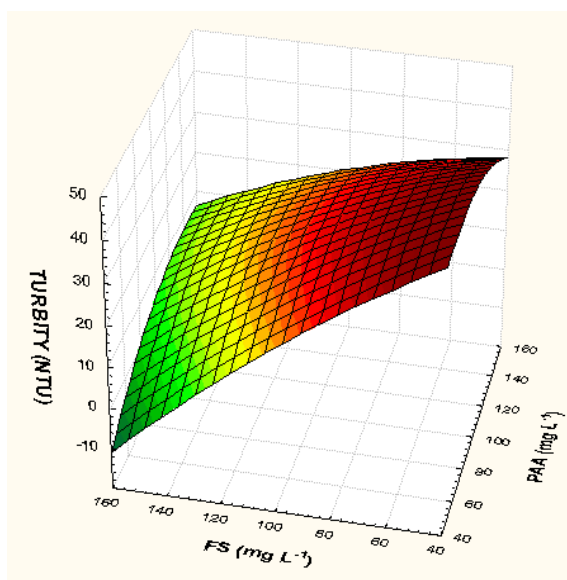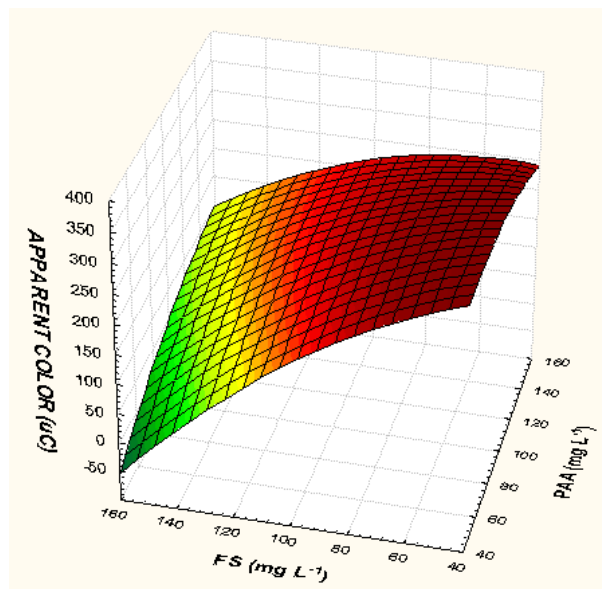
Comparing the best conditions of the three treatments: FS (150 mg L^{-1}) at pH 8.5; FS (150 mg L^{-1})/PAA (50 mg L^{-1}) at pH 4, and FS (150 mg L^{-1})/HP (150 mg L^{-1}) at pH 3, it was observed that FS/PAA presented the best results for turbidity and apparent color, however, regarding COD it presented efficacy close to that of FS and 13% lower than FS/HP. However, the increase in PAA concentration did not raise the COD value, for this reason tests with higher PAA doses were carried out.
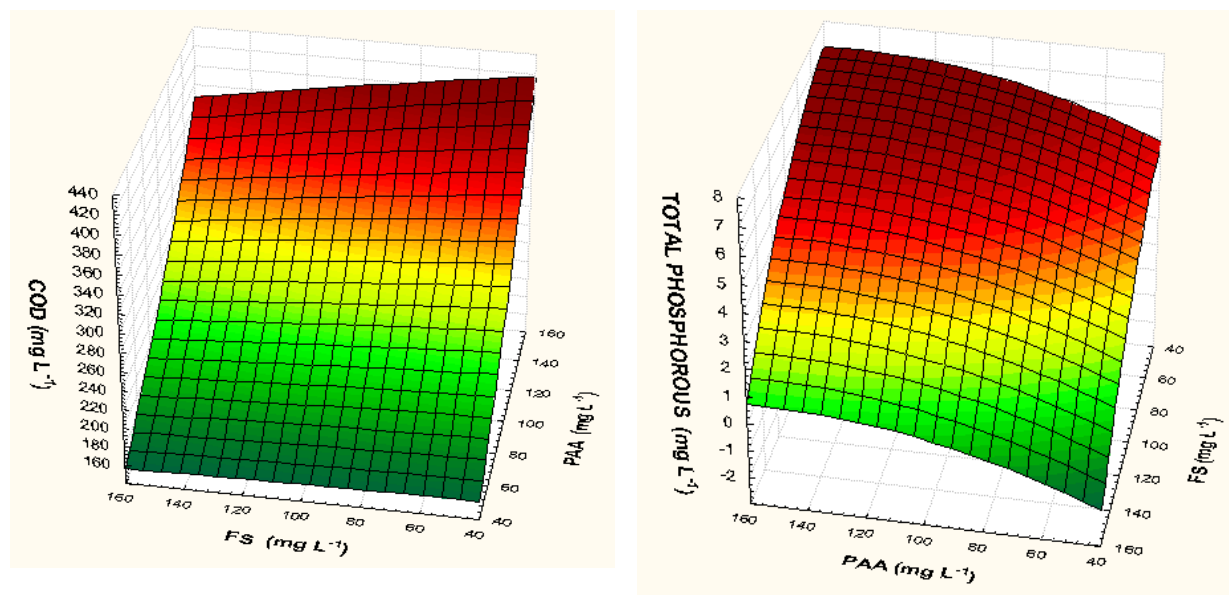
Results obtained through the coagulation tests followed by filtration simulation

The filtration procedure was adopted so that the formation of colloids could be more clearly observed, since not all the colloids formed might have enough mass to sediment. In order to force the formation of colloids, pH 6 was used [22].

Figure 4 presents results obtained through the coagulation followed by the filtration using higher PAA doses.

Through the response surface graphs, it was possible to observe similar behavior between the removal of turbidity and apparent color from the effluent, as well as between the *E. coli* and TC inactivation according to each combination. Equations obtained through the modeling of results of each parameter allowed the prediction of results with other combinations within the concentration band under evaluation. The models generated are described by a quadratic function, which demonstrated better data fit, evaluated by the R^2. Through the variance analysis (ANOVA), it was seen that all combinations presented results with significant differences among them, that is, the combination of different PAA and SF doses influenced the results obtained. The interaction between PAA and SF occurred in all parameters under evaluation, except for pH, which confirms that PAA and SF do not act separately.

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Apparent color (uC) = 349,5185+0,2389*x-1,0067*y-0,0071*x*x+0,0152*x*y-0,0132*y*y (R^2 = 0,98)
Turbidity (NTU) = 53,587+0,1342*x-0,3594*y-0,0018*x*x+0,0023*x*y-0,001*y*y (R^2 = 0,98)
E. coli (UFC 100mL^{-1}) = 11,1111-0,2333*x+0,0267*y+0,0013*x*x-0,001*x*y+0,0005*y*y (R^2 = 0,79)
TC (UFC 100mL^{-1}) = 53,2963-0,7744*x-0,1356*y+0,004*x*x-0,0025*x*y+0,0023*y*y (R^2 = 0,85)
DO (mg L^{-1}) = -2,5174+0,1512*x+0,1023*y-0,0002*x*x+0,0003*x*y-0,0004*y*y (R^2 = 0,99)
COD (mg L^{-1}) = 91,7407+1,53*x+0,1622*y+0,0038*x*x-0,0033*x*y-0,0003*y*y (R^2 = 0,98)
Total Phosphorous (mg L^{-1}) = 2,8937+0,0557*x+0,0124*y-0,0002*x*x+8E-6*x*y-0,0003*y*y (R^2 = 0,99)
pH = 6,8074-0,006*x+0,0027*y+1,1556E-5*x*x-3E-6*x*y-2,3111E-5*y*y (R^2 = 0,96)

Figure 4. Graphs and equations of the response surfaces in the combinations PAA / FS for parameters Apparent color, turbidity, phosphorous, COD, DO, E. coli, TC and pH.

The best results obtained were observed in the combination PAA(50)/FS(150), in which there was 96.6% turbidity, 90% apparent color and 95.6 % total phosphorus removal from the effluent, however, COD had an increase of 28.6%, because a 50 mg L^{-1} PAA solution presents 140 mg L^{-1} theoretical COD, making it possible to increase the effluent COD. Both the coagulation and the oxidation at neutral pH were less effective. The treated effluent COD was higher than the raw one in all combinations.

Regarding the effluent disinfection, it was observed that at higher PAA and FS concentrations there was total inactivation of the microorganisms under evaluation, however, the effluent COD was practically tripled, which makes this combination unsuitable.

The highest PAA consumption was observed when higher doses of FS were applied. Zhao et al. ascribed the PAA decomposition to the presence of metals in the effluent, with acetic acid and oxygen as possible products formed [26]. The increase in dissolved oxygen (DO) in the effluent was also observed in Figure 4, where it is seen that both the increase in PAA and FS contributed to the increase in DO.

In metal contaminated effluents the PAA decomposition is catalyzed, for this reason, complexant agents are many times added to the commercial PAA in order to stop reactions between peroxide and metallic ions, and the diethyltriaminepentacetic (DTPA) is one of the most efficient complexants to reduce free metallic ions and smooth the oxidant decomposition, which might justify the formation of flakes in the SF/PAA combination.

Although the values obtained in the combination PAA(50)/FS(150) have optimized the effluent particle removal, regarding turbidity and apparent color removal, a more thorough analysis was adopted with the aim to obtain some guidelines for new combinations that might improve results obtained in relation to the effluent COD. For that, the results of Figure 4 were interpreted employing a multivariate statistical method called factorial analysis. The kind of factoring adopted was the main components, with two extracted factors. The objective

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of this analysis was to obtain factors which are responsible for the greatest variability of all the variables under investigation. In this test, two factors were extracted, which represented 86.653% of the variability of the data obtained, these factors were selected following the Kaiser criterion (eingenvalue > 1) [27]. These factors were latent variables which represent the set of results of all parameters evaluated, and it was possible to originate an equation where the weights of each parameter were attributed as .

coefficients, thus forming the factors, for this reason they can better represent the tests under study.

When the main component method is applied the communality estimates are defined to assume that all data variability is due to common factors. Through these factors it was possible to evaluate which parameters were influenced by the PAA dose and which were influenced by the FS dose, which can be seen in Figure 5
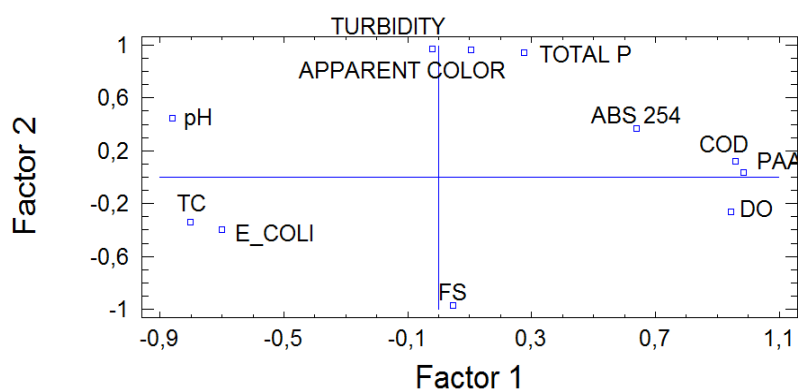

Figure 5. Influence of PAA and FS concentrations for removal values of Apparent color, turbidity, Total Phosphorus, COD, DO, E. coli, TC, Absorbance (254 nm) and pH.

According to Figure 5, the increase in the FS concentration is responsible for the apparent color, Turbidity and total phosphorus removal from the effluent, that is why they appear opposite to the FS position in the Y axis.

The increase in PAA concentration is directly proportional to the increase in COD and DO, once they are grouped in the same direction in the axis x. On the other hand, the microorganisms *E. coli* and TC as well as the pH decreased with the PAA increase.

The absorbance in 254 nm, which corresponds to the organic matter, suffered PAA influence at higher concentrations, that is why it is farther in relation to the axis x, but also demonstrated to be directly proportional do the PAA increase.

Results obtained with increasing concentrations of FS and PAA

After evaluating these results, new combinations could be directed to higher FS concentrations, once the increase in the coagulant

concentrations always presented improvement, while the increase in PAA concentration did not result in higher organic matter oxidation.

According to Kang and Hwang [11] the Fenton oxidation process is usually composed of four phases: pH adjustment, oxidation reaction, neutralization/coagulation and precipitation. Thus, the organic substances are removed into two phases, oxidation and coagulation, and the COD removal efficacy is higher through coagulation with the formation of iron hydroxide complexes than through oxidation with HP reaction.

This study employed PAA (0, 5, 10, 20, 30, 40 and 50 mg L^{-1}) and FS doses (100, 200 and 250 mg L^{-1}) totaling 18 combinations, at the effluent natural pH (7.5). The use of lower PAA doses is also justified by the presence of residual PAA in the tests using 50 mg L^{-1} PAA.

PAA participation in the suspended solids removal was observed mainly through the apparent color and turbidity values, due to the removal low percentages obtained in the free PAA conditions,

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where with FS above 150 mg L^{-1} the effluent turbidity and apparent color became worse in the presence of the coagulant. The average *E.coli* and TC inactivation was 3 logs.

The best results were obtained with FS 200 mg L^{-1} /PAA 10 mg L^{-1} and FS 250 mg L^{-1}/PAA 30 mg L^{-1} doses. The best results are shown in Table 3 with the triplicate standard deviation values (*sd*).

Table 3. Comparison between FS and FC in the removal of P, COD, Turbidity, apparent color and DO.

TSS (mg L^{-1})	Coagulant (mg L^{-1})	pH ±sd	P (mg. L^{-1}) ±sd	COD (mg L^{-1}) ±sd	Turbidity (NTU) ±sd	Apparent Color (UC) ±sd	DO (18ºC) (mg L^{-1}) ±sd
	FS 200/PAA 10	6.82 ±0.01	0.45 ±0.11	69 ±2.5	5.50 ±1.11	90.67 ±15.63	2.73 ±0.07
	FS 200/PAA 30	6.65 ±0.05	0.35 ±0.32	110 ±2.0	5.66 ±0.23	84.67 ±1.53	8.27 ±0.19
87	FS 250/PAA 10	6.73 ±0.01	< 0.1 0	66 ±7.5	1.96 ±0.26	43.67 ±2.52	2.39 ±0.26
	FS 250/PAA 30	6.59 ±0.01	0.1 ±0.10	98 ±8.1	1.72 ±0.55	36.67 ±9.07	7.50 ±0.22
	RAW	7.47	6.2	158	121	803	1.66
	FC 258/PAA 10	5.7 ±0.08	< 0.1 0	49 ±1.5	0.49 ±0.03	8 ±0.6	1.59 ±0.08
	FC 258	5.7 ±0.005	< 0.1 0	47 ±1	1.27 ±0.33	19 ±3.5	1.87 ±0.13
168	FS 250/ PAA 10	6.8 ±0.011	0.3 ±0.1	74 ±2.5	50.3 ±7.3	792 ±79	1.34 ±0.11
	FS 250	6.99 ±0.017	1.9 ±0.17	81 ±12	137 0	1950 ±225	1.00 ±0.02
	FS 250/HP 10	6.9 ±0.006	0.37 ±0.13	69 ±5	135 ±5.03	1798 ±92	1.44 ±0.01
	FS 250/HP 25	6.7 ±0.01	< 0.1 0	59 ±5	43 ±2.85	606 ±25	1.67 ±0.07
	RAW	7.1	6.1	258	95	825	1.61

With the increase in FS concentration and decrease in PAA concentration it was possible to increase the efficacy of apparent color, turbidity, total phosphorus and COD removal from the effluent, as it had been foreseen by the statistical analysis applied to the results of Figure 5.

Residual concentrations were determined with FS 250 mg L^{-1} with PAA 10 and 30 mg L^{-1} dose in the composed sample, and presented, respectively, Fe 0.83 mg L^{-1} / PAA < 0,4 mg L^{-1} and Fe 0.75 mg L^{-1} / PAA 2.81 mg L^{-1}. In both combinations the total iron residual concentrations were below the maximum limit established [28]. The Fe^{3+} ions are more easily removed through filtration when compared with the Fe^{2+} ions which are more soluble in water [29]. The variation of effluent characteristics such as TSS revealed great influence in the results obtained after treatment.

In general, all results obtained with the use of FS indicate that the PAA participation in the coagulation/oxidation process is mainly in the oxidation of Fe^{2+} into Fe^{3+}. In order to evaluate this hypothesis, tests were carried out with ferric chloride (FC), with equivalent concentrations of iron in relation to the FS. In this test the effluent presented COD values higher than those in the previous tests, for this reason the PAA combinations with HP were also compared again.

Both combinations with HP and PAA presented lower efficacy with the increase in the effluent COD, demonstrating the consumption of oxidants by the effluent organic matter.

From the results obtained with FC it was seen that in such pH conditions FC presented better results when compared with FS, supposedly due to the higher Fe^{3+} concentration. However, the addition of PAA in FC presented even better results suggesting that the oxidant participates in the formation of colloids, for this reason the coagulation phase should not be carried out separated from the oxidation.

A negative factor in the use of FC was the reduction in the effluent final pH. Aiming to minimize this effect PAA was applied to the FS solution provoking Fe^{2+} oxidation into Fe^{3+}, and then this mixture was applied to the effluent.

By altering the sequence of application, the main aim of the PAA in the process was highlighted, since when this oxidant was exclusively available for iron oxidation (PAA applied to the FS solution) higher removal of turbidity and apparent color was obtained. Unlikely the sequence in which the PAA was applied directly to the effluent, where the oxidant concentration was partially consumed by the effluent organic matter, reducing the formation of Fe^{3+} ions, resulting in the reduction of coagulation efficacy in

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the raw effluent. According to Xing and Sun ferric ion, in general, is more advantageous and efficient to remove color, turbidity and total carbon, besides not presenting toxicity problems [10].

It is also important to emphasize that this test also justifies why at higher concentrations of the oxidant, even in the presence of organic matter, the removal efficacy was higher. The 10 mg L^{-1} PAA

4. CONCLUSION

The coagulation/oxidation of wastewater, at neutral pH, can be used since the oxidant is employed mainly to the oxidation of Fe^{2+} into Fe^{3+}. With the use of PAA as oxidant the oxidation/coagulation process might be carried out in one phase only, once its greater contribution is in the coagulant action and the Fe^{3+} coagulation can occur at neutral pH. Therefore, the PAA dose can be applied as a function of the FS concentration, and thus, lower doses can be used, when the PAA is applied to the FS solution rather than directly to the effluent.

The oxidant participation in the coagulating phase contributes to the formation of colloids, becoming useful for treatment processes that involve coagulation followed by filtration (for example), and the oxidant can be applied even to ferric coagulants (Fe^{3+}) in order to optimize their efficacy.

The effluent disinfection becomes less effective with the presence of FS, however the microorganisms *E. coli* and TC inactivation was 100 times higher than that expected with the use of ferric chloride.

Considering the higher coagulant action of the Fe^{3+} ions and that the reaction between these ions and the oxidant enable the removal of color from the effluent, it was observed that before the use of a two-phase process, employing FS and HP, the use of FC/PAA (or HP) should be tested, since this combination presented 99% color removal at pH around 6.

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concentration is enough to oxide 250 mg L^{-1} FS stoichiometrically, and the concentrations of PAA, HP and dissolved oxygen present during the reaction must be considered. FC results were better when compared with the SF ones due to the pH difference in the samples, since with more acid pH the coagulant effect of Fe^{3+} is higher.

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