REMEDIATION OF TEXTILE DYES MIXTURES USING TIO_2/VIS PHOTOCATALYSIS AND FENTON FE^{2+}/H_2O_2

P. M. Andrade[1], M. A. F. Carvalho[1], A. S. Miranda[2], H. R.Marques[2], S. R. Campos[2] e N. N. Brito[1*]

[1] UFG - Univ Federal de Goiás, Instituto de Química, (Industrial Chemistry/ Chemistry Institute - Goiás Federal University), Goiânia, GO, Brasil
[2] CEJA - Colégio Estadual Jardim América (Jardim America State School), Goiânia, GO, Brasil

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ABSTRACT

This study aimed to use the following treatment technology: TiO_2 photocatalysis and Fenton reaction for the remediation of mixture of textile dyes. For the photocatalytic treatment it was obtained a reduction in color of 80% and Chemical Oxygen Demand of 60% using for this 600 mg L^{-1} of TiO_2, 1500 mL min^{-1} recirculation flow, temperature 40 ^oC/45 ^oC and pH = 6.3 for 60 minutes of treatment. By Fenton reaction it was reached color reduction at 95% and Chemical Oxygen Demand reduction at 75% employing 60 mg L^{-1} H_2O_2, 50 mg L^{-1} de Fe^{2+} and pH = 4.0 for 62 minutes of treatment.

Keywords: treatment technology, textile industry, remediation.

REMEDIAÇÃO DE MISTURA DE CORANTES TÊXTEIS UTILIZANDO FOTOCATÁLISE TIO_2/VIS E FENTON FE^{2+}/H_2O_2

RESUMO

Este trabalho teve como objetivo utilizar as tecnologias de tratamento: fotocatálise com TiO_2 e reação de Fenton para remediação da mistura de corantes têxteis. Para o tratamento fotocatalítico obteve-se redução da coloração de 80% e Demanda Química de Oxigênio 60% utilizando para isto 600 mg L^{-1} de TiO_2, vazão de recirculação 1500 mL.min^{-1}, temperatura 40 ^oC/45 ^oC e pH= 6,3 durante 60 minutos de tratamento. Com a reação de Fenton alcançou-se redução da coloração de 95% e redução da Demanda Química de Oxigênio de 75% empregando 60 mg L^{-1} H_2O_2, 50 mg L^{-1} de Fe^{2+} e pH= 4,0 durante 62 minutos de tratamento.

Palavras-chave*:* tecnologia de tratamento, indústria têxtil, remediação.

* nubiabrito@ufg.br

INTRODUCTION

Among oxidative methods there is the oxidation via TiO_2/vis photocatalysis and the Fe^{2+}/H_2O_2 Fenton reaction. The photocatalytic degradation is obtained with the aid of a catalyst (a semiconductor). Some semiconductors are able to convert radiation into another type of energy, and in this case the radiation energy absorbed by the semiconductor results in the generation of electron/gaps pairs (e^-/ h^+) that will produce reactive radicals. These radicals are hydroxyl type (•OH) and can oxidize and mineralize organic compounds according to equations 1 and 2 (LIMA et al., 2014):

$$TiO_2 + hv \rightarrow TiO_2 (e^- / h^+) \quad \text{(eq 1)}$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \quad \text{(eq 2)}$$

The Fenton reaction has been extensively studied by many researchers for the treatment of wastewater with refractory / xenobiotic organic compounds (SOON and HAMEED, 2011; BIANCO et al., 2011; WU et al., 2011). Reactions 3 and 4 show the sequences of the oxidation possible stages of organic compounds (KARTHIKEYAN et al., 2011; SOUZA et al., 2010).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\cdot \quad K=70\ L.mol^{-1}.s^{-1} \quad \text{(eq 3)}$$

$$OH^\cdot + RH \rightarrow CO_2 + H_2O \quad \text{(eq 4)}$$

Given the above, this study was to evaluate the potential of the process via TiO_2 /vis photocatalysis and Fenton reaction (Fe^{2+}/H_2O_2) in the treatment of mixture containing three textile dyes: a reactive textile dye (Orange Indosol 2GL 250), a dispersive textile dye (Shiny Red Foron E-2BL 200) and a direct textile dye (Yellow Optisal 2RL).

MATERIALS AND METHODS

Reagents Used

At the photocatalytic treatment process it was used Titanium Dioxide - Degussa P25 (TiO_2) 75% anatase and 25% rutile, acquired from Degussa SA Industry in São Paulo city.

For the Fenton reaction it was used heptahydrate ferrous sulfate (Cinética química) at 1000 mg L^{-1} (stock solution) concentration and hydrogen peroxide (Lafan-Química Fina company) 10% m/m per standardized by permanganometric titration.

The textile dyes used in this study were: Orange Reactive dye Indosol 2GL 250, shiny red dispersive dye Foron E-2BL 200 and yellow direct dye Optisal 2RL, all of them were acquired in solid form and provided by the Daneto company (São Paulo)

The simulated wastewater with the mixture of those three dyes was prepared with distilled water and contained a total concentration of 50 mg L^{-1} and at pH = 6.30, this is the natural pH of the solution.

Photocatalytic treatment

The photocatalytic treatment was carried out in a borosilicate glass reactor with 2.0 L volumetric capacity (90 mm internal diameter, 130 mm outside diameter and 150 mm total height), and polychromatic radiation source at visible and ultraviolet range, provided by a high pressure mercury vapor light bulb of 250 W power (Osram HQL). The bulb was supported by a borosilicate glass tube, which was immersed in the reactor allowing irradiation of the inside uniformly at the visible range.

The stirring process was maintained continuously through the textile dyes solution recirculation by means of a hydraulic pump (Invensys Bav 1115-02U 220 V 60 Hz 34 W). The cooling system

consisted of a spiral condenser, which allowed to maintain the temperature inside the reactor between 25–55°C. The sample volume added in the reactor for the tests was 2.0L and the treatment time was 60 minutes.

The oxygen supply for the photocatalytic process was maintained by bubbling air through a hose placed at the bottom of the reactor, using a compressor with air pump and electric drive with a maximum air flow rate of 8,0 $L.min^{-1}$ (Inalar Compact) (Figure 1).

A: Photochemical reaction chamber; B: Borosilicate or quartz tube for light bulb; C: Condenser cooling water; D: Capacitor for gas output; E: Hydraulic pump for recirculation; F: Tap for sampling; G: Recirculation flow regulator; H: Wastewater output for recirculation; I: Entry of wastewater; L: Light bulb; S: Wastewater movement direction inside the reactor

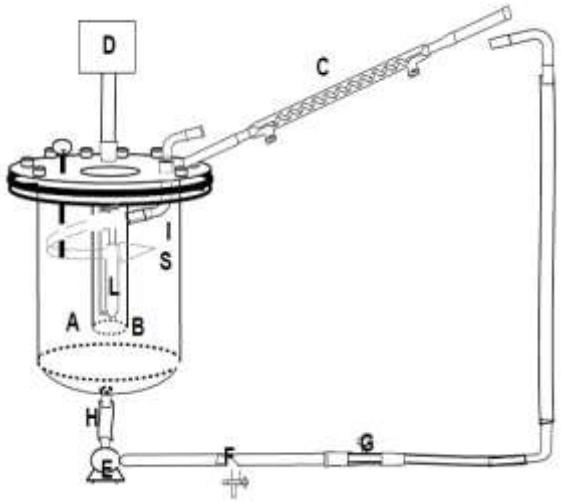

Figure 1: Scheme of the photocatalytic reactor used in the treatment.

For the oxidative process via photocatalysis, initially it was conducted a 2^2 factorial design (two variables and two levels) tested to levels: a lower (-) and higher (+) levels for the variables: the TiO_2 concentration and recirculation flow of the dyes solution.

Treatment via Fenton reaction

The Fenton tests performed in Jar Test equipment (Alfakit, Model 403) which contains 6 jars each with 2 L volumetric capacity of mixture dyes. The stirring process was continuous by the rotating blades for a fast mixing of 100 rpm during 2 minutes followed by slow mixing for 30 minutes at 50 rpm and a subsequent 30-minute sedimentation, which is an operational parameter, used in water treatment plants. The procedures were performed at room temperature.

These operating physical parameters of the jar equipment and the initial Fe^{2+} concentration were the same as those recommended by the Goiânia Sewage Treatment Plant.

For oxidative process via Fenton reaction, it was initially carried out a 2^2 factorial design with central point with 3 level experimentation: a lower (-), an intermediate (0) and a higher (+) levels for the variables: concentration of H_2O_2 and Fe^{2+}.

Experimental Procedure

In the evaluation of efficiency treatments (photocatalysis and Fenton) the following parameters were used: pH, total iron, conductivity, chemical oxygen

demand (COD) and total phenols, according to Standard Methods for the Examination of Water and Wastewater, 20 ^{h} Edition (APHA, 1998) (9).

The true color (color analysis accomplished after spinnin / filtration) of textile dyes was determined according to the maximum absorbance wavelength at the visible region and ultraviolet using a spectrophotometer (alpha-plus 700).

The residual hydrogen peroxide was determined according to procedure adapted from the OLIVEIRA et al., (2001), based on the reaction between hydrogen peroxide and vanadate ion (VO_3^-) in acidic medium. The reaction leads to the formation of reddish peroxovanadium ion (VO_2^{3+}) which strongly absorbs at 446 nm.

RESULTS AND DISCUSSION

Optimization of TiO_2/Vis photocatalytic treatment

The "gross" mixture of the three textile dyes in this study showed an average: pH = 6.30; absorbance 1.13 UA (400 nm) and COD of 136.24 mg O_2 L^{-1}.

The first experiments were performed using only TiO_2 in order to check the adsorption potential of the semiconductor used, the parameters studied were concentration of TiO_2 600 e 300 mg L^{-1} and the recirculation flow of textile dye solution of 1000 and 1500 $mLmin^{-1}$

TiO_2 has character, i.e., dependent species on pH, then, pH with zero load, 6.8 TiO_2 occurs as TiOH in acid medium (pH <6.8) has a positive charge ($TiOH_2^+$) and in basic medium (pH> 6.8) has a negative charge (TiO^-) according to equations 5 and 6 (ALMEIDA, 2011):

$$TiOH + H^+ \rightleftharpoons TiOH_2^+ \quad \text{(eq.5)}$$
$$TiOH + OH^- \rightleftharpoons TiO^- + H_2O \quad \text{(eq.6)}$$

At this study, it was used the natural solution pH of the dyes mixture (pH = 6.30) in this manner, color removal occurred in an acidic medium, where TiO_2 occurs as $TiOH_2^+$ (pH<6,8). In this medium, the sulfonic groups of the dyes can be ionized by promoting adsorption of the negatively charged dye on the surface of the catalyst in the $TiOH_2^+$ positive form (CLAUSEN and TAKASHIMA, 2007).

Another explanation would be that the azo groups (-N = N-) have electron densities that can interact with the $TiOH_2^+$ surface (CLAUSEN and TAKASHIMA, 2007).

In this work, TiO_2 used refers to the proportion of 75% anatase and 25% rutile, the phase anatase, has a higher specific surface area and pore volume which interferes in a better adsorption (DA SILVA et al., (2013)

The highest concentration of TiO_2 (600 mg L^{-1}) and recirculation flow (1000 mL min^{-1}) demonstrate an adsorption of the dyes mixture with a removal of the absorbance at 7.22%.

After the adsorption the experiments were conducted via photolysis treatment on textile dyes solutions, according to the data obtained, the bleaching efficiency achieved is negligible (10.38%) indicating that only the radiation is insufficient for degradation of the pollutant matrix under investigation.

The data of the treatment carried out with solar radiation show the discoloration efficiency enhance by increasing concentration of TiO_2 to about 600 mg L^{-1}; according to SOUSAS et al., (2010), this behavior can be attributed to the increase of sites for dye adsorption on the catalyst surface and with the free generation of more hydroxyl radicals.

According CLAUSEN and TAKASHIMA (2007), the increase of discoloration rate of the azo dye depends on the semiconductor mass enhance indicating the increasing production for the electron-pair gap under irradiation, simultaneously promoting the oxidation

and reduction processes on the surface. However, TiO_2 concentrations above 600 mg L^{-1} diminish the efficiency of this discoloration. This is because of the radiation scattering due to the increase of particles in suspension.

In addition to this solar radiation is a promissory option, considering its no-pollutant nature, its permanent readiness and its zero cost (ROMÁN et al., 2008).

The optimized concentration was 600 mg L^{-1}, which reached 30.00% removal of color, 41, 00% removal of organic matter and pH: 5.66 under 8 UV index, temperature solution 36^0C and 3 hours of treatment time.

In order to improve the treatment, it was decided to conduct an experiment using a reactor and artificial light (250 watt light bulb at the visible range) (Table 1):

Table 1- Factorial design 2^3. Volume 1.8 L, for 60 minutes of treatment, pH= 6.30 with artificial radiation – Photocatalysis

Parameters	**Variables**	
	(+)	**(-)**
TiO_2 Concentration (mg L^{-1})	600	300
Recirculation Flow (mL.min^{-1})	1500	1000
Temperature (°C)	50 °C/ 55 °C	40°C/45 °C

Tests	**TiO_2**	**Flow**	**Temperature**	**Colour Removal (400nm)**
1	**+**	**-**	**-**	73.00%
2	+	-	+	54.00%
3	**+**	**+**	**-**	**80.00%**
4	+	+	+	75.00%
5	-	-	-	57.00%
6	-	-	+	69.00%
7	-	+	-	23.00%
8	-	+	+	52.00%

Parameters	**Variables**	
	(+)	**(-)**
TiO_2 Concentration (mg L^{-1})	600	300
Recirculation Flow (mL.min^{-1})	1500	1000
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Tests	**TiO_2**	**Flow**	**Temperature**	**Colour Removal (400nm)**
1	**+**	**-**	**-**	73.00%
2	+	-	+	54.00%
3	**+**	**+**	**-**	**80.00%**
4	+	+	+	75.00%
5	-	-	-	57.00%
6	-	-	+	69.00%
7	-	+	-	23.00%
8	-	+	+	52.00%

With treatment using the maximum TiO_2 concentration (600 mg L^{-1}) recirculation flow of 1500 mL.min^{-1} and a maximum temperature of 40 ^{o}C/ 45 ^{o}C, it was possible to obtain 80% for color removal, a greater semiconductor concentration up to certain limits makes the most efficient treatment technology.

Where according to TEKIN (2014), the first step is the adsorption of the dye on the surface of the catalyst embodying the adsorption / desorption equilibrium. A pair electron / gap is generated when the focused radiation has energy greater than or equal to the band gap energy of the semiconductor. The electron is transferred from the conduction band to the valence band, if any, there is e^-/h^+ pair recombination, and there will be deactivation of the system with heat release.

This proposed mechanism starts with the irradiation of the catalyst followed by formation of hydroxyl and superoxide radicals. The superoxide radical and hydroxyl radical attack the coloring dyes structure (TEKIN, 2014).

The recirculation flow of the dye mixture at 1500 mL.min^{-1} makes possible larger turbulence that could increase the contact between oxygen and TiO_2 favoring the transfer of electrons of the conduction band of the semiconductor for the oxygen benefitting the photocatalysis.

With relationship the temperature in a photocatalytic process, when it is increased from 23 ° C to 45° C, for example, a synergistic effect on the degradation of organic matter may occur, favoring the combination with the hydroxyl radical (•OH) produced during the photocatalysis (BRITO et al., 2011).

According to FERREIRA and DANIEL (2004) the degradation rate increases with the increase of the temperature, without this parameter interferes significantly in the photocatalytic process. However although the energy of activation of the photocatalytic reaction is affected lightly by temperature, the reaction redox can be quite affected by the same, influencing the frequency of collision of the molecules so much as the balance of adsorption.

Important to point also is that the solubility of the gases in aqueous medium decreases with the increase of the temperature. The decrease of the solubility of oxygen inserted in the photocatalytic process it will interfere directly in removing of the semiconductor electrons what will reduce the generation of the hydroxyl radical consequently the efficiency in the chemical oxidation (equation 7) (BRITO et al., 2011).

$$TiO_2 + H_2O + O_2 + \lambda vis \rightarrow {}^{\cdot}OH + O_2^{\cdot -} + H^+ + TiO_2 \qquad \text{(eq.7)}$$

DAMODAR and YOU (2010), using 50 mg L^{-1} Reactive Black 5 dye in a photocatalytic treatment (TiO_2 P-25 0,5gL^{-1}), coupled to a membrane filtration treatment, obtained color removal at 95% and matter organic removal at 79% for 90 minutes of treatment.

In this study, the parameters obtained (600 mg L^{-1} TiO_2, 1500 mL.min^{-1} recirculation flow and a maximum temperature of 40° C/45° C), it was possible to achieve 80.00% removal of color, 60.00% removal of organic matter and final pH of 5.66 during 60 minutes of treatment.

Process optimization via the Fenton reaction Fe^{2+}/H_2O_2

In figure 2, it is seen the absorbance values and Chemical Oxygen Demand graphically displayed as a percentage order. It can be seen that for the COD values reduction ranged between 35 and 75% and the absorbance reduction values ranged between 60 and 95%.

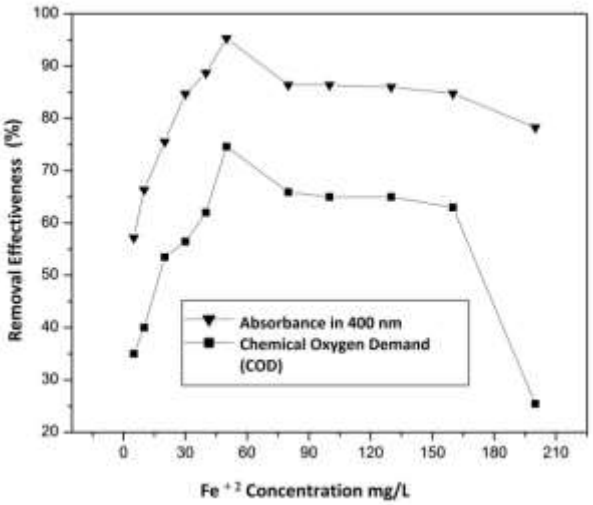

Figure 2- Effect of Fe^{+2} concentration on the absorbance removal and COD at the treatment with FENTON reagent (H_2O_2 = 60 mg L^{-1} ; pH 4,0).

The 50 mg L^{-1} concentration of iron, with a 75% COD reduction, 95% absorbance value might be considered the best result.

It is also possible to observe that an increase in iron concentration causes a decrease in the removal of the COD parameter values. MA and XIA (2009) reported that a high concentration of iron causes the interaction of ferrous ions with hydroxyl radical, acting as radical sequestrants, which decreases the Fenton reaction efficiency as shown in equation 8.

$Fe^{+2} + \bullet OH \rightarrow Fe^{+3} + OH^-$
$K = 2{,}8x10^8\ L.mol^{-1}.s^{-1}$ (eq.8)

It is also possible to observe a marked decrease in absorbance removal efficiency with increasing Fe^{2+} concentrations such behavior can be explained by the action of complexes formed by the hydrolysis of ferric and ferrous ions in the system (MA and XIA, 2009).

After carrying out the optimization for iron concentration, the next step was to optimize pH. In figure 3, it is seen the absorbance values and Chemical Oxygen Demand displayed graphically as a percentage order. For COD, maximum reduction values were around 75 -77% and for the absorbance maximum values were around 95%; these reductions have been achieved using pH 3.0; 3.5 and 4.0.

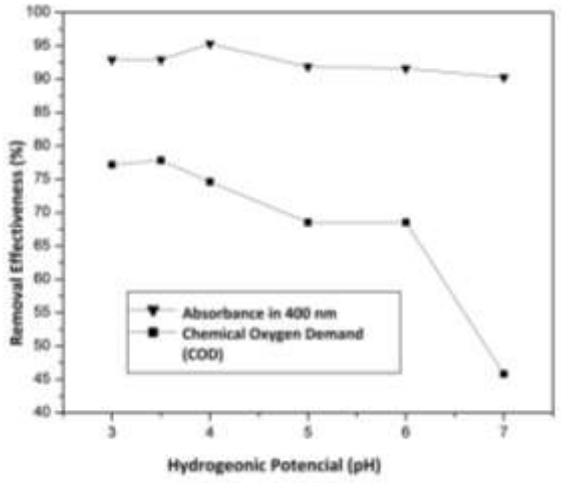

Figure 3- Effect of pH value on the absorbance removal and COD at the treatment with FENTON reagent (H_2O_2 = 60 mg L^{-1} ; Fe^{+2} = 50 mg L^{-1}).

As a suitable pH for the wastewater discharge the range is 5.0 to 9.0, the appropriate for the treatment to be carried out is the pH=4.0 in order to obtain a treatment as close as possible to the discharge conditions (CONAMA, 2011).

Setting the "optimal" pH value for the treatment with Fenton reagent, the next analyzed variable was the H_2O_2 concentration, which, together with Fe^{2+} and pH led to the application and effectiveness of the treatment (BORBA et al., 2008). For this assay, the Fe^{2+} concentration was kept constant at 50 mg L^{-1} and the pH at 4.0.

By analyzing figure 4, it was found that with the 60 mg L^{-1} concentration of H_2O_2 the COD showed a reduction in efficiency of around 75% and 95% absorbance. At concentrations from 80 to 100 mg L^{-1} of H_2O_2 for the COD, the reduction values showed, if higher, on average at 12% compared to the percentage removal in the 60 mg L^{-1} concentration of H_2O_2. This does not justify the use of more highly oxidizing chemical reagents to the medium.

It is important to point out the possible negative effect that the high concentration of hydrogen peroxide can cause when it reacts with the hydroxyl radical forming hydroperoxyl radical (equation 9) (DIA, 2008).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$$
$$K = 1{,}2x10^{7}\ L.mol^{-1}.s^{-1} \qquad \text{(eq. 9)}$$

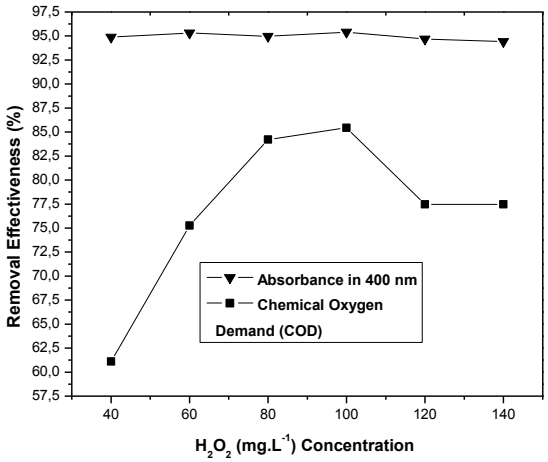

Figure 4- Effect of H_2O_2 concentration on the absorbance removal and COD at the treatment with FENTON reagent (Fe^{+2} = 50 mg L^{-1}; pH 4.0).

Besides reacting with the hydrogen peroxide, as shown in equation 8, the hydroxyl radicals may react with each other, regenerating the hydrogen peroxide (eq. 10), lowering the concentration of radical in the medium and decreasing the efficiency for the Fenton reaction.

$$\bullet OH + \bullet OH \rightarrow H_2O_2$$
$$K = 5{,}3 \times 10^{9}\ L.mol^{-1}\ s^{-1} \qquad \text{(eq.10)}$$

Therefore, based on the optimization performed with the values set forth in the tables and figures, the "optimal" concentration, in the removal of both the COD as the absorbance, was 60 mg L^{-1} of hydrogen peroxide and 50 mg L^{-1} of Fe^{+2}. The pH was more efficient at 4.0.

The success of the treatment performed was due to chemical oxidation, but also to the coagulation / flocculation, a dual technology via Fenton reaction. The ferrous ions may be oxidized to ferric ions and Fe^{+3} hydroxyl complex which enable the coagulation the removal of suspended solids which are coagulated, flocculated and sedimented (MORAIS and BRITO, 2014).

It was observed that the COD, with 75% reduction, showed a high rate, although the legislation CONAMA 430 (2011) does not mention figures for the

COD. However, the law provides for the removal of Biochemical Oxygen Demand (BOD) a value of 60% removal. Therefore, paralleling, and assigning this value for COD, this fits to the treated wastewater, taking into account the current legislation.

The turbidity showed a very high reduction from 153 NTU for "gross" textile dyes mixture to 39 NTU for mixing the treated textile dyes, with a 75% removal. Regarding the total phenols analysis. it was observed that the final wastewater, after treatment, showed a 0,38 mg L^{-1} concentration of phenols. This final value meets the value limit set in the resolution CONAMA 430 (2011), which establishes 0.50 mg L^{-1}.

According to VILLOTA et al., (2014) turbidity can be regarded as a parameter representing the presence of oxidized intermediate species that are generated during the decomposition of recalcitrant species such as phenol. It is important to clarify that the presence of turbidity also has a linear dependence with the dosage of the catalyst which is determined by the initial concentration of contaminants.

For the absorbance analysis at 400 nm, the decrease was 95%; the decrease of the absorption band intensity, at a wavelength from 400 nm to about 700 nm, indicated a reduction of chromophoric groups, as evidenced by the decreased color. At the 347 nm wavelength, the major structures found are aromatic polycyclic compounds, at 386 nm carbohydrates, at 481 nm in humic acids, the absorption band of 487-500 nm refers mainly to the azo bond (-N = N-) (CAMPOS and BRITO, 2014).

For analysis of the residual H_2O_2, the value of 6.06 mg L^{-1} for residual hydrogen peroxide concentration being much lower than the present concentration, e.g. contact lenses detergents with 20 mg L^{-1} concentration (MATTOS et al., 2003).

It is small the concentration of remaining total iron in treated simulated wastewater. In the treated wastewater, the amount of total iron dissolved allowed in the legislation is 15 mg L^{-1}, and the textile dyes mixture showed total iron concentration of 2.82 mg L^{-1} (CONAMA, 2011).

CONCLUSIONS

Photocatalytic treatment for the TiO_2/Vis, the best results were achieved with the use of artificial radiation emitted at the visible range and catalyst; achieving reduction in color at 80%, 10% turbidity and 60% chemical oxygen demand using 600 mg L^{-1} of TiO_2, 1500 mL.min^{-1} recirculation flow, temperature at 40 ^oC/ 45 ^oC, and pH = 6.3 during 60 minutes of treatment.

For the treatment via Fenton reaction that combined Fe^{2+} with H_2O_2, the main results and most promising were: Optimized parameters: Fe^{2+} 50 mg L^{-1} concentration, H_2O_2 60 mg L^{-1} concentration and pH=4.0. The Fenton reaction is effective in reducing coloration around 95%, 75% turbidity and in achieving 75% reduction of the organic substance during 62 minutes of treatment.

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