Applying of Ecological Cost Accounting in a Dye Discoloring Process

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Abstract

This work sought to apply the Accounting of Complete Ecological Costs (ACEC) methodology in a textile segment company through the reutilization of colored wastewater, after treatment by advanced oxidation processes (POA) in reactors using hydrogen peroxide (H_2O_2) in a catalysis activated by ultraviolet light (UV). Facing the worries with the sustainable development and the difficulty in measuring environmental costs through the traditional accounting method, the proposed methodology tries to integrate costs, either internal or external ones, into a single dimension. At reducing the environmental impacts, the company shows a proactive position regarding the sustainability, becoming sustainable itself. The study presented the financial and ecological economy obtained, thus showing this process is efficient and may be used by companies in the textile sector for reutilizing water, reducing the financial and ecological costs, as well as the negative externalities.

Keywords: *advanced oxidation process, UV/H_2O_2, ecologic cost accounting, dye discoloring, sustainability.*

1 Introdução

According to Romanini (2007), the effect of global warming is one of the factors that have reignited discussions on sustainability by alerting society of the need for companies to adopt proper attitudes toward the environment. In order to express the concept of sustainability, a company must display environmental integrity, social equality and economic success (Bansal, 2005). Becoming a sustainable enterprise means reducing a company's impact in an economically feasible manner by using preventive approaches together with the principles of continuous improvement (Labodová, 2004). Rubestein (1994) states that a sustainable company should work in accordance with six guidelines: Qualitative growth, respecting human rights and the environment; Conservation and use of the environment and natural resources for the benefit of present and future generations; Maintenance of ecosystems and essential biospheric processes, preservation of biodiversity and fulfilment of the principle of optimised sustainable productivity; Establishment of environmental protection standards and supervision of all changes, publishing relevant data on the environment and the use of resources; Implementation of all changes in accordance with the environmental developments that arise; Periodic communication to everyone who may be significantly affected by forecast changes in business activities.

According to Romanini (2007), the discussion regarding sustainable companies does not only relate to large companies, which are pressured by their shareholders to demonstrate that their businesses are not running the risk of being devalued due to improper social and environmental attitudes. Small businesses are also now seen by society as offering possible risks to the environment in which they operate. However, it is difficult to measure and integrate the internal and external costs in such a way as to demonstrate the contribution made by these companies toward sustainability. The literature lists environmental cost accounting (ECA) as a way to calculate this contribution. As an example, Jimenéz (2006) successfully applied ECA to a Spanish transportation company based on the concepts of data reduction, data disclosure and verification/conclusion. Such initiatives have proven to offer adequate quality and efficiency and help maintain a company's good image in the eyes of society. Upon achieving self-sufficiency, such companies are rewarded for their practices with ISO 9001 and ISO 14001 certificates.

All industrial processes produce solid, liquid or gaseous effluents in different amounts, being their treatment of paramount importance so that the environmental standards established by law are fulfilled, more specifically the Conama Resolutions nº 357 from 2005 and nº 274 from 2000. For Conchon (1999), the textile industry represents an outstanding economic and social value, absorbing an expressive amount of manpower, generating exchange values. In Brazil, there are circa 5,000 textile industries distributed like this: 11% are large companies; 21% are small companies; and 68% are micro companies. The Brazilian textile sector occupies the 5th place in direct jobs and the 6th in turnover (Bastian, 2009).

The liquid effluents in the textile sector, when left untreated, are highly polluting, due to the presence of several chemicals used in the material composition. The main contaminants are the dyes used in coloring, once a great variety of dyes is used in these products for color diversification, generating a complexity of these effluents, ensuring a high biological demand for oxygen (DBO) and changes in the color of the receiving body.

Zanoni and Carneiro (2001) estimated that in the coloring process, at least 20% of textile dyes are discharges into effluents, due to the losses happened during the process for fixing the colors to the fibers. Removing these components from industrial waste is one of the major environmental problems faced by the textile sector, and the non-treatment of these effluents may cause serious risks to the environment and, consequently, to the whole productive chain; it is important for the control offices to have a permanent acting, avoiding thus problems for the population in contact with contaminated areas.

The treatment of effluents on the textile industries gets more complicated with the common use of several other chemicals with diverse composition, like, for instance: moisturizers, defoamers, electrolytes, dispersers, pH controllers, stabilizers, among others, during the coloring process. The VS-type reactive dyes are used mainly for coloring cellulosic fibers, except CA (cellulose acetate) and CT (cellulose tri-acetate). The fact that these dyes react not only with the substrate but also with water, make them major components in dry-cleaners effluents. After the coloring process, the substrate undergoes washing for eliminating the hydrolyzed dye from the fiber surface. The process of coloring cellulose with this kind of dye happens with an alkali presence and due to this fact the effluent generated also has an alkaline pH (Oliveira et al., 2009; Rosa et al, 2010).

This work tried to apply the Accounting of Ecological Costs methodology in a company on the textile sector through the reutilization of the colored wastewater after treatment by advanced oxidation processes (POA) in reactors using hydrogen peroxide (H_2O_2) in a catalysis activated by ultraviolet light (UV). By the environmental problems, seeking to treat the effluents from the textile companies, the goal of this work is to check the effects of pH (9 and 11) over the kinetics of photochemical degradation in VS-type chromogenous systems, using the irradiation of ultraviolet waves in the presence of Hydrogen Peroxide.

2. Material and Methods

2.1 Materials

For performing the advanced oxidation process (POA), we used: Gehaka AG 200 analytical scale; a reactor with twin UVC, 6W Philips bulbs; a magnetic agitator; spectrophotometer UV-VIS, Datacolor SF-600 Plus; HT Alt-1 Mathis; Quimis pH meter; the reagents used were: solution of 1.0 mol dm-3 acetic acid/sodium acetate; solution of 1.0 mol dm-3 bicarbonate/sodium carbonate; C.I. Reactive Black 19 dye, sodium chloride and carbonate; surfactant; disperser; 35% hydrogen peroxide; 50°Bé sodium hydroxide; sodium metasilicate; bi-filtered water for preparing the solutions and the material was half knitted, 100% cotton, and 30:1 Ne combed thread.

2.2 Preparation of the effluent

Seeking to produce a coloring effluent for a later photochemical treatment, we performed a coloring with the antraquinine dye or C.I. RB19 Reactive Black 19 reactive dye in a 100% cotton mesh previously bleached. The recipes and phases of the whole coloring process are proposed by the dye manufacturer, as it follows. We used 15 g of substrate paste for a bath ratio of 1:10 in a volume of 150 cm^3. For obtaining the effluent, the recipes and procedures described below were followed:

Recipe and previous treatment procedure: 1.0 $g.dm^3$ of nonionic surfactant; 1.0 $g.dm^3$ of Sodium metasilicate; 3.0 $cm^3.dm^{-3}$ of H_2O_2 and 2.0 $cm^3.dm^{-3}$ of NaOH 50°Bé. Add all ingredients and heat them up to 80°C, keeping for 20 minutes; cool down to 70°C, release the bath; fill it up, heat up to 60°C, keeping for 10 minutes, release the bath; cold wash for 5 minutes, release the bath (Rosa, 2008).

Coloring recipe: 2% of C.I Reactive Black 5; 40.0 $g.dm^{-3}$ of Sodium Chloride; 12.0 $g.dm^{-3}$ of Sodium Carbonate. Add the salt, keep cold for 10 minutes, add the dye and keep cold for extra 10 minutes, add the carbonate mixed with the soda and, 4 times, with 5-minute intervals between dosages. Heat up to 40°C, keep for 60 minutes, and release the bath (Rosa, 2008).

Recipe for the posterior treatment: 1.0 $cm^3.dm^{-3}$ of Acetic acid; 1.0 $g.dm^{-3}$ of Disperser. Add the acetic acid, wash for 5 minutes and release the bath. Cold wash twice for 5 minutes each. Add the disperser, heat up to 80°C, keep for 10 minutes, cool down to 70°C and release the bath. Wash at 60°C and cold-wash for 5 minutes each (Rosa, 2008).

2.3 Photochemical treatment of the effluent

The effluent generated in the coloring process of cotton mesh was divided into three samples, A, B and C, containing 1.0 liter each. The pH values were corrected for 9 (Sample A) and 11 (Sample B). Then, 1.0 cm^3 of H_2O_2 was added to each of the samples for a posterior reactor treatment for 90 minutes, with 10 cm^3 samples gathered in 10-minute intervals and posterior UV/VIS spectrophotometric analysis (Rosa, 2008 and 2010; Rosa et al., 2009 and 2010).

2.4 Effluent Analysis

We used absorption spectra in the visible region on a wavelength with maximum dye absorption (λ_{max}), for determining the efficiency percentage at the effluent discoloring. The data reading was done by the spectrophotometer Datacolor SF-600 Plus, using acrylic cubes with 1.0 cm of optical pathway. The wavelength used for this work and for all the calculations was 580 nm (Zollinger, 1991).

For determining the pH influence, we performed initial (Abs_o) and final (Abs_f) absorbance readings of the three samples, adopting λ_{max} = 580 nm. From these data, the efficiency was calculated according to the Eq. 1 (Oliveira et al., 2009; Rosa, 2010a):

$$\text{Efficiency}\,(\%) = \frac{\text{Abs}_o\,(\lambda_{max}) - \text{Abs}_f\,(\lambda_{max})}{\text{Abs}_o\,(\lambda_{max})}\ \text{x}\,100 \quad (1)$$

However, it is important to highlight that there are still many phases to be developed, because this is just the study of a certain dye, of a certain class or type, in 100% cotton and under certain circumstances.

2.5. Environmental cost accounting strategies

The steps suggested for an eco-friendly solution for discarding frying oils are presented below. These steps are commonly illustrated in a table and represent the following stages (Burritt and Saka, 2004; Chulián, 2006; Fresner and Engelhardt, 2004; Jimenéz, 2006):

Stage 1 – the current stage of a company in an unsustainable position. At this stage, many of the environmental impacts result from process feedstock and waste production, not including the costs of this production. Stage 2 – a more sustainable position in which a company is taking steps to reduce its impact on the environment. Stage 3 – a position in which operations should have no impact on the environment. Stage 4 – a position in which a company is self-sustainable, whereby the environmental accounting balance of its operations results in credits for the company.

For Bebbington (2001), the Accounting of Complete Ecological Costs (ACEC) may happen in four different phase when implemented as a tool: a) Definition of the cost object; b) Specification of the analysis scope; c) Identification and measurement of externalities, phase in which the author suggests eco-balance techniques, life cycle analysis or ecological impact and d) Calculation of external costs.

The present work will focus phase 3, where the externalities are identified and measured; for so, we will have as parameter information from a textile company located in São Paulo, Brazil, presented on Table 1.

Table 1. Information on the company

Type of company	Textile
Size	Medium
Main activity	Cotton and viscose fabric production
Production	250 tons/month
Current water use	1.7 m³/h
Cost of water	R$ 24,920.64*/month
Approximate flow	1.0 m³/h
Contaminants	High load of inorganic salts, mainly chlorides and sulfates, dyes, besides several polyacrylate-based organic compounds, aliphatic glycol polyether and sulfated nitrobenzene

*Source: Rosa (2008)

For a company with this profile, there is the need for implementing six units. The implementation cost for the new system will be approximately R$ 5,983.79 per unit, according to Table 2, supposing it may lose value as the UV lights fade with time, normally in 12 months, the monthly depreciation value to be deduced is R$ 498.65 per unit. With the implementation of the new system, the cost with water and contaminant effluent emission will be zero, once the company becomes sustainable by treating and reusing water in its productive process.

Table 2. Approximate cost with materials and manpower per unit

Item	Value (R$*)
Concrete	372.10
Piping	15.70
Circuit breaker/cables	55.54
Concrete mixer rent	5.75
Manpower and basic social rates	48.62
UV Lamps	5,417.33
Mirrors	68.75

Source: Sinduscon (2009); *1 U$ = 1.84 R$ (Folha de São Paulo, 2009);

3 Results and Discussion

3.1. Effluent treatment and water reuse

Figure 1 shows the efficiency of discoloration of dye effluent for the experiments performed in pH values 9 and 11, respectively. We notice through this figure that the intensity of light absorption is reducing as exposed to UV light in the reactor used for the photochemical decomposition. By the end of the process, the absorbance within the range λ_{max} = 600 nm is reduced to insignificant values. Based on data obtained by the photometric measurements of samples for the three analyzed systems (on pH 9 and 11), we reached the efficiency results in the process of effluent photochemical treatment. Table 3 shows the results obtained by substituting the initial and final absorbance in **Eq. 1**.

Table 3. Efficiencies of dye discoloring after 90 min of process.

Parameter	pH 9	pH11
Abs_o	0.0848	0.0837
Abs_f	0.0059	0.0066
% Eficiêncy	93.04	92.11

As the goal was obtaining reuse water to be used in new processes, allied to the fact that the pH 9 is the one used as starting pH in all improvement processes, it is proven fact that the best treatment was obtained with the pH 9. This fact may also be proved on the transmittance graph Figure 2, on the left), where we showed the similarity between the transmittance indexes between the effluent at pH 9 and bi-filtered water in the whole visible spectrum. This treated effluent was reused more than ten times and its efficiencies of dye discoloring were higher.

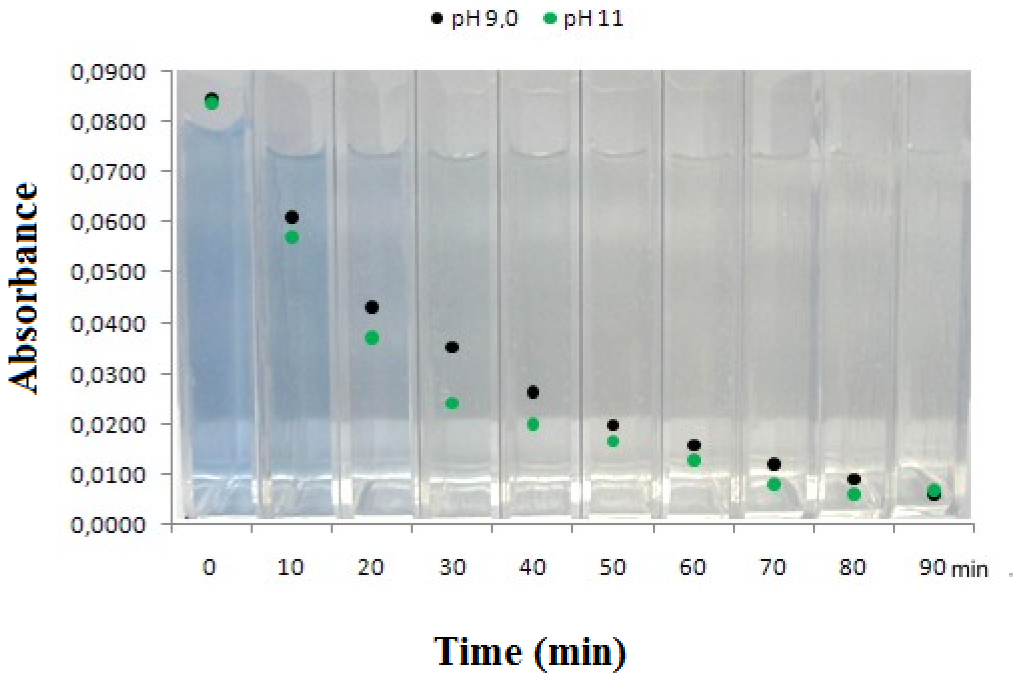

Fig. 1. Dye discoloring on action of H_2O_2 and UV at pH 9 and 11.

The color TP 181346, on the "Inspirations and Tendencies for Fashion Design Notebook" (SENAI, 2008), was selected to be developed in four colorings. In one of them, bi-filtered water was used and in the other three, the treated effluents. The process is described in Rosa (2008) and the coloring done with bi-filtered water (AB) was classified as standard. The deviations were obtained through **Eq. 2** described in Zollinger (1991) and are represented on Table 4.

$$\Delta E = \sqrt{(\Delta H)^2 + (\Delta C)^2 + (\Delta L)^2} \quad (2)$$

Where: ΔE = total color deviation; ΔH = saturation deviation; ΔC = chromaticity deviation and ΔL = luminosity deviation.

Lucas *et al.* (2008) mentioned that "the contamination of natural waters has been a major problem in modern society. Thus, saving water in productive processes has gained special attention due to the aggregated value attributed to this commodity, through principles like "paying consumer" and "paying polluter", recently incorporated into our legislation". With the results presented in this work, we may prove that the method used for degrading the dye is fast and efficient. The photo-chemically treated samples may be reused both in coloring processes and in cleaning, in discharge systems and plant irrigation.

The results for the deviations of coloring for the effluent samples treated with ultraviolet light are shown on Table 4; meanwhile, on Figure 1, the colorings are shown in a graph where we may notice the similarity between all of them.

Table 4. Coloring deviations

Color Deviation	Average
$\Delta E_{AB/pH\ 9}$	0.51
$\Delta E_{AB/pH\ 11}$	0.68

The results showed that for any pH used in this work, the efficiency of the dye decomposition within the range λ_{max} = 600 nm via photo-catalysis with H_2O_2 and UV light was 100%, showing that the pH does not interfere in this range. The three effluents obtained may be used as reuse water for coloring dark shades, as we observed in the deviations $\Delta E_{AB/pH7}$ = 0.16; $\Delta E_{AB/pH9}$ = 0.51 and $\Delta E_{AB/pH11}$ = 0.68; perfectly acceptable for the current standards, which is ΔE = 1.0. Besides, as the visual aspect of the effluent treated in pH 7 was better than the others, it is advisable to use it in the process of photo-decomposition of the dye C.I. RB19.

3.2 Use of ecologic cost accounting in the textile process

As one phase of the industrial bath generally has a flow of 1 m³/h, if this company has 6 baths (which is common for a medium-sized textile company), the outflow (Q) of 6 m³/h. Thus, as the bioreactors generally need a residence gap of 48 h by Equation 3 we notice that the volume of this reactor will be 288 m³, or the company may build 6 bioreactors with a volume of 48 m³ each. This construction will obviously occupy a certain space in the company and, generally, the treatment efficiency does not overcome 90%, besides the treated liquid cannot be reutilized for having microorganisms and a high turbidity (Correia et al., 2004; Oliveira et al., 2009).

$$Q(m^3/h) = \frac{Volume(m^3)}{Residence \quad time(h)} \tag{3}$$

Now, for the effluent treated by the new process, using advanced oxidation (POA) – UV/H_2O_2, the residence time for the total decomposition of the dye is one hour. Thus, using Equation 3, we find that the capacity of the reactor would be reduced to 1m³ once the UV reactor needs only one hour for processing, as **Fig. 3** illustrates, optimizing the physical space and the fact that there is the possibility for the reactor to be built underground, thus, not occupying space in the company.

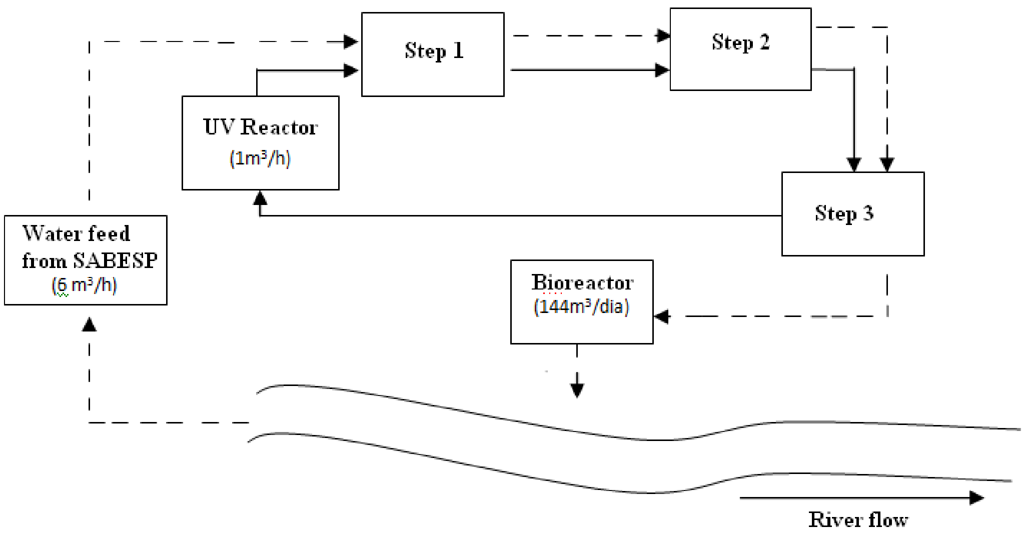

Fig. 3. Illustration of an unit of textile process (Bioreactor and UV Reactor), out of a total of 6 units. Where: (---------) current water flow and effluents, with biotreatment and (_______) flow after installing the UV/H_2O_2 reactor, in studied company.

With the new treatment, the phases start having a continuous flow so that the water returns to the process in approximately 1 h for treating each cubic meter; the whole amount of water can return to the coloring process with no need for external consumption and discharge effluents in the river, that is, the pollution level and/or contamination to the environment is zero. From this moment on, the company is plainly sustainable under the ecological point of view.

By treating the effluent, the company passes from unsustainable to sustainable in four stages, that is, besides not discharging highly polluting products, it also starts using water for its productive process through reutilization, having financial and ecological economy of R$ 21,908.75 per month, according to the SABESP consumption bills. The bills and the stages are presented on Tables 5 and 6.

Besides the financial economy, there is also the ecological and social economy, that is, in an unreachable level, with reduction to zero in the negative externalities, the company passes from polluting to sustainable, not causing environmental impacts, because there is no water consumption and no discharge of polluting effluent.

Table 5. Water supply and/or sewage bills for the industry.

m^3 / month	water bills (R$)	savage bills (R$)
0 - 10	26.21 / month	26.21 / month
11 - 20	5.09 / m^3	5.09 / m^3
21 - 50	9.78 / m^3	9.78 / m^3
Above 50	10.18 / m^3	10.18 / m^3

Source: Sabesp (2009)

Table 6. Stages for studied textile company to become sustainable

Factors	Stages			
	1	2	3	4
Ecological (Environmental)	Unsustainable	Adaptation	Zero net	Sustainable
	Effluent discharge out of CONAMA Law	Adaptation for UV/H_2O_2 methodology	Use of new method	Reuse total of the water
Financial (Costs)	Consumption of 6 m^3/h from SABESP	Investment in new equipment		Zero water consumption
	Value of consumption R$ 24,920.64 */ month	R$ 24,920.64/month Investment value R$ 2,991.89*/month		Savings of R$ 21,908.75*/month

*Source: Folha de São Paulo (2009) 1 U$ = 1.84 R$

4 Conclusions

The company, at implementing the new system, shows a proactive and compromised posture facing the environmental problems by measuring and eliminating its negative externalities, not causing impacts coming from its production process; at becoming sustainable there is no water consumption and discharge of polluting effluent.

With the simulation through experiments in laboratory for checking the quality of the water used and treated with advanced oxidation (POA) - H_2O_2 and its reutilization in the productive process of a textile company, along with the application of the ACEC, we can conclude that it is possible to reduce the financial and ecological costs, as well as the negative externalities at becoming sustainable.

By measuring the investment performed, we checked a monthly saving of around R$ 21,908.75, thus the study shows that the process and the application of the methodology are efficient and may be employed not only by textile companies but also by the others after the adaptations necessary in their processes.

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