Macrothink Institute™

Journal of Environment and Ecology
ISSN 2157-6092
2013, Vol. 4, No. 2

Photo Electrolytic Process in A Simulated Textile Effluent Treatment and Its Cost for Application

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Received: August 14, 2013 Accepted: September 5, 2013 Published: October 25, 2013

doi:10.5296/jee.v4i2.4460 URL: http://dx.doi.org/10.5296/jee.v4i2.4460

Abstract

A textile effluent treatment (Remazol Dark Blue HR dye - CI Reactive Blue 89) was realizaed to investigate the effect of electrolysis associated with photochemical process. It was used a reactor containing a 70% TiO_2/30% RuO_2 electrode (dimensionally stable anode – DSA) and an ultraviolet lamp. Experiments parameters were: 125 $mA.cm^{-2}$ of current density and solution composition as 10,000 $mg.L^{-1}$ NaCl, 1,320 $mg.L^{-1}$ Na_2CO_3 and 200 $mg.L^{-1}$ dye. The influence of flow-rate, initial pH and UV radiation were determined by absorbance, color, toxicity, monochloroamine, pH and conductivity analyses. In conclusion, the treatment proved to be very efficient and it promoted total color removal in 5 minutes.

Keywords: DSA electrode, Dye, Electrochemical treatment, Photochemical process

1. Introduction

The increasing technological advances and the raised demand in chemical industry are promoting an increase in the number of new formulations every year. These chemical structures are made for being resistant to discoloration and chemical agents. Consequently, the textile effluents are becoming more difficult to degrade physico-chemically or biologically. Therefore, their hazardous to the environment is also increasing due to high coloration, high Chemical Oxygen Demand (COD) and high stability in rivers and streams (Chiang et al., 1997).

World production of dyes and pigments is higher than 800,000 ton per year and 12% of organic dyes are lost in effluent during the manufacture processes. Thus, a large amount of dyes is released daily on water bodies (Georgiou et al., 2002). Furthermore, some textile dyes and their byproducts are mutagenic and/or carcinogenic and they generally present heavy metals in significantly levels (Akyol & Bayramoglu, 2005; Catanho et al., 2006). Therefore, new methods aiming to the degradation of these compounds are necessary.

Many methodologies and products can be applied to remove color as adsorption, coagulation, biological processes and chemical oxidation (Comninellis & Platner, 1986; Comninellis & Pulgarin, 1993). Thereby, the common methods actually adopted are biodegradation, chemical degradation using O_3 and Cl_2 and physical treatments as adsorption and filtration (Kunz et al., 2002.). Such methodologies produce a large amount of sludge and use oxidant agents which can be dangerous to the environment (Rajeshwar et al., 1994).

Newer processes as electrochemical (Inazaki et al., 2008) and photochemical are considered promissory for treating organic effluents. They present efficient results for textile effluents (Sousa et al., 2011) and can contribute as alternative or complementary treatment. Therefore, the purpose of the study was verify the photoelectrolytic system efficiency attached to an electrochemical reactor in simulated textile effluent treatment containing the reactive dye Remazol Navy Blue HR. It was investigated the optimization of the treatment, evaluating flow, initial pH, UVC lamp application and treatment time.

2. Material and Methods

2.1 Photoelectrolytic System

The photoelectrolytic system was composed by: stainless steel chamber; UVC lamp (Germetec model GPJ-MP 1,600 W); flow meter; PVC reservoir; pump; electrodes (70%TiO_2/30%RuO_2 with 40 cm^2 and rectangular cathode with 50 cm^2 arranged at 3.0 mm distance). A power supply (Instrutherm FA-2030) was used for electrodes polarization and it is known that the DSA electrode presented a high mechanical resistance and chemical stability and it is able for work in a long time. Current density was obtained with the relation between current (I) and anode area (A), i.e., J = I/A. The system also had a high overpotential for oxygen evolution that extended oxidation range of organic compounds and its dimensions were 80 x 40 x 130 cm (Figure 1).

Initially, 4.0 L of simulated effluent in the reservoir was pumped through the whole system.

The flow started in the vertical direction for the electrolytic reactor and then the chamber UVC. All assays was prepared as batch with recirculation.

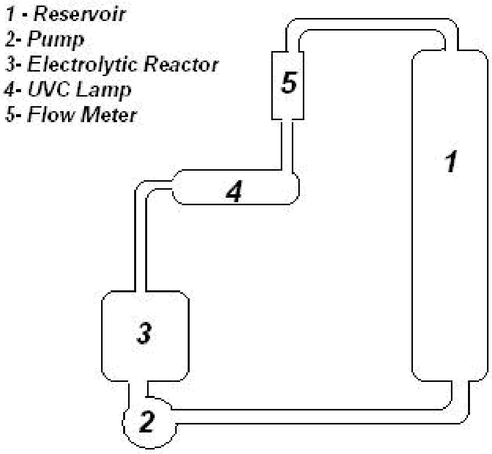

Figure 1. Scheme of the photoelectrolytic system

2.2 Experimental Procedures

Textile effluent treatment investigated was performed using a solution composited by: Remazol Dark Blue HR dye (CI Reactive Blue 89) and support electrolytes. NaCl e Na_2CO_3 was used once these salts are commonly used on textile industry during dyeing process. Their initial concentrations were 10,000 mg.L^{-1}, 1,320 mg.L^{-1} and 90 mg.L^{-1} for NaCl, Na_2CO_3 and the dye respectively. The initial pH in solution was 2.73.

In relation to UVC lamp, its use for a long time can damage the system due to overheating since the system operates in batch with recirculation. Thus, it wass applied for 3 minutes in beginning or final of the treatment.

Experiments were performed using flows of 200 L.h $^{-1}$ and 500 L.h^{-1} and current density of 125 mA.cm^{-2}. Samples were obtained in predetermined times for measuring of absorbance, pH, toxicity, monochloramine and conductivity.

2.3 Analytic Methods

Absorbance measures were obtained in UV-Visible Spectrophotometer (Shimadzu® model 2401PC) and they were converted to concentration values from data in 599 nm wavelength. Conductivity and pH were determined by Tecnopon® CA150 conductivimeter and Digimed® pHmeter DMPH-2 respectively. Toxicity, monochloramine and Chemical Oxigen Demand (COD) were evaluated by methods and equipaments by Hach® Company: ToxTrack method (Hach® 10017). indophenol colorimetric method (Hach® 10172), Hach® digester DR2500 and

Hach® colorimeter DB200. All the reagents used were analytic (APHA, 1998).

3. Results and Discussion

Firstly, it was observed that the flow did not represent a significant influence on color removal. For a complete color removal it was necessary 5 minutes of treatment which leads to an energetic consumption of 15.71 kWh.m^{-3} (0.71 kWh.m^{-3} for electrolysis and 15.00 kWh.m^{-3} for UVC lamp). Therefore, the system can be operated using a 500 L.h^{-1} flow that enables a bigger volume of effluent treated.

The influence of initial pH using a 500 L.h^{-1} flow is demonstrated in Figure 2. Photolysis was applied just from 0 to 3 minutes and electrolysis was always in operation until 60 min of treatment. It was observed an increase of color removal when the solution was in lower pH. According to this, Sauer et al. (2002) revealed that the zero charge point (pcz) of the titanium electrodes is 6.8. Therefore, it would probably work better in acid conditions.

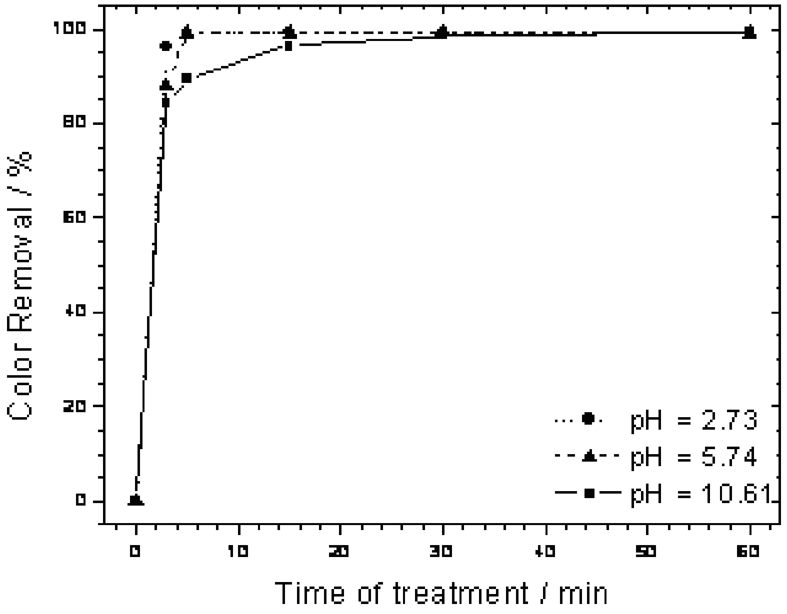

Figure 2. Color removal of Remazol Navy Blue HR dye during treatment by different pH initial. J = 125 mA cm^{-2}, Q = 500 L h^{-1}, [NaCl] = 10.000 mg L^{-1}, [Na_2CO_3] = 1320 mg L^{-1}, C_{dye} = 190 mg L^{-1}

In Table 1, the treatment cost was calculated according to industrial kWh price in Brazil as USD 0.117 (www.aneel.gov.br) and it was considered the cost per liter of H_2SO_4 (USD 5.43). It was not considered the salt costs (NaCl and Na_2CO_3) once they are normally present in real textile effluent.

It was revealed that it would be necessary 3 minutes of photolysis and 60 minutes of electrolysis without H_2SO_4 for 99.4% color removal and 40% COD decrease in initial pH of 10.61. These conditions reached a total cost of USD 2.64 (USD 1.76 for UVC lamp and USD 0.88 for electrolytic reactor). In same parameters except of electrolysis for 30 minutes, the color removal was 98.5% and the total cost would be USD 2.23 (USD 1.76 for UVC lamp and USD 0.47 for electrolytic reactor).

In 3 minutes of electrolysis and 2 minutes of photolysis, monochloramine concentration reduced from 8.88 to 0.50 mg.L^{-1} and the toxicity decreased from 60% to 0%. According to Table 1, it was verified that H_2SO_4 addition increased the color removal, but also the final cost for a 5 min treatment.

Table 1. Treatment cost for Remazol Navy Blue dye in 5 minutes treatment in different initial pH

pH	Color removal (%)	Lamp cost (USD.m^{-3})	Electrolysis cost (USD.m^{-3})	H_2SO_4 (USD.m^{-3})	Total Costs$^{(1)}$ (USD/m^{-3})	K (m.min^{-1} mg.L^{-1})
2.73	99.3	1.76	0.08	3.39	5.23	0.991
5.74	99.2	1.76	0.08	2.58	4.42	0.947
10.61	89.3	1.76	0.08	0.00	1.84	0.011

(1)Not considering pump consumption.

Also, the influence of UVC lamp (photolysis) applied in beginning and in end of treatment was determined. The initial pH chosen was 2.73 owing to results showed in Figure 2. It was observed that the color removal was faster when UVC lamp is applied in the beginning than when in the end of treatment, i.e., in the last 3 min (Figure 3).

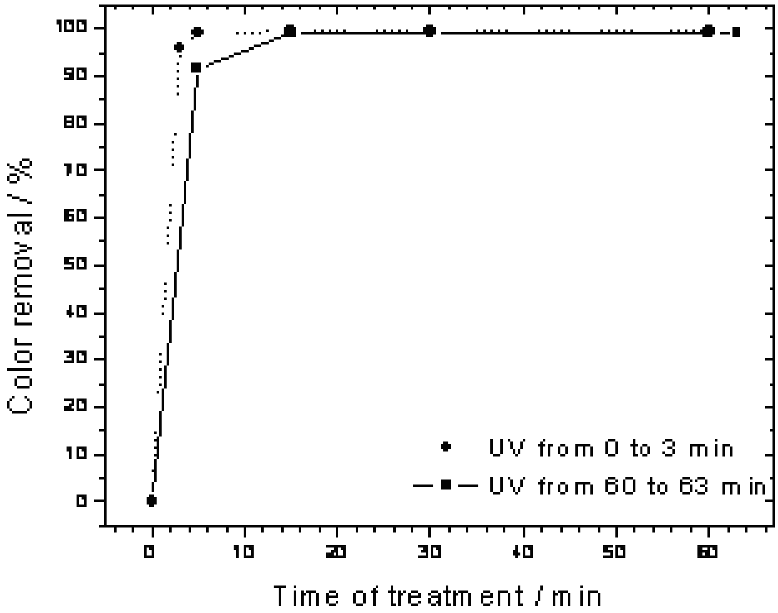

Figure 3. Color removal of Remazol Navy Blue HR dye during treatment by different times of UVC operation. J = 125 mA cm^{-2}, Q = 500 L h^{-1}, NaCl = 10,000 mg L^{-1} , Na_2CO_3 = 1,320 mg L^{-1}, C_{dye}= 190 mg L^{-1}

Figure 3 shows that the color removal was the same in both assays after 5 minutes of treatment. Moreover, it is not necessary a long treatment applying UVC lamp with a higher cost, when just 15 minutes are necessary to reach a great result.

Table 1. Treatment cost for Remazol Navy Blue dye in 5 minutes treatment in pH 2.73 with and without UVC lamp

UVC lamp application	Color removal (%)	Lamp cost (USD.m^{-3})	Electrolysis cost (USD.m^{-3})	H_2SO_4 (USD.m^{-3})	Total Costs$^{(1)}$ (USD/m^{-3})
Yes	99.3	1.76	0.08	3.39	5.23
No$^{(2)}$	92.0	0,00$^{(2)}$	0.08	3.39	3.47

$^{(1)}$Not considering pump consumption.
$^{(2)}$Considering the lamp will not be applied in 5 minutes.

Once the reservoir was a 4.0 L volume and the reactor volume was 0.015 L, a batch system of treatment was assumed for modeling. Thereby, the kinetic analysis for color removal was calculated (Equation 1).

$$\ln C_{(t)} - \ln C_{(t=0)} = -k\frac{A}{V_{(tot)}}t \qquad \text{(Equation 1)}$$

where: C(t) is the color rate in time t; C(t=0) is the initial color value; A is the anode area; V(tot) is the volume of solution; t is the treatment time; k is the apparent clearance rate constant (m.min-1 mg.L-1).

It was observed that results fit in a first order kinetic. Also, it was obtained the values of apparent constant rate of removal (k) which is a feature that depends of the electrode and the solution for each condition of flow and current. Thus, k = 0.991 for 3 minutes treatment of electrolysis and photolysis; k = 0.991 for 12 minutes of electrolysis (without photolysis); and k = 0.499 for 15 minutes of electrolysis (only).

4. Conclusion

Therefore, it was concluded that the system promoted an efficient treatment for simulated effluents with Remazol Navy Blue HR dye. The process promoted a complete color removal in a short treatment time. Furthermore, treatment system can be easily enlarged as all the components used are commercially available.

Acknowledgement

The authors acknowledge CNPq, FAPESP and the companies: Tigre Tubos e Conexões, Germetec and De Nora do Brasil for the support for this research.

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