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Modeling the Removal of Indigo Dye from Aqueous Media in a Sonoelectrochemical Flow Reactor

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Several processes in the textile industry require large amounts of water that inevitably are contaminated. Major pollutants are dyes, such as the indigo blue used in the denim textile industry. Therefore, specific wastewater treatment is used to eliminate dyes before being discharged into the sewage collection system. Conventional treatments have several main drawbacks such as, large consumption of reagents, generation of large quantities of sludge, prolonged treatment times, and low removal efficiency. In this research work, electrochemical and sonoelectrochemical treatments were evaluated as alternative methods to remove dyestuff from textile industry wastewater. The electrochemical treatment consists of passing a continuous current through the wastewater by using metallic electrodes, and for the sonoelectrochemical treatment, an ultrasonic irradiation is added within the reactor. Carbon steel, stainless steel and aluminum electrodes were used to evaluate their efficiency. When the sonoelectrochemical process was applied using carbon steel electrodes, it was possible to remove up to 90% of the indigo dye. The main dye removing processes were electroflotation and electrocoagulation. The electrochemical and sonoelectrochemical processes were implemented using flow reactors. The hydrodynamics of the tubular flow reactor were modeled in non-steady state.

Keywords: Modeling; ultrasonic; irradiation; electrochemical; indigo dye; wastewater.

1. INTRODUCTION

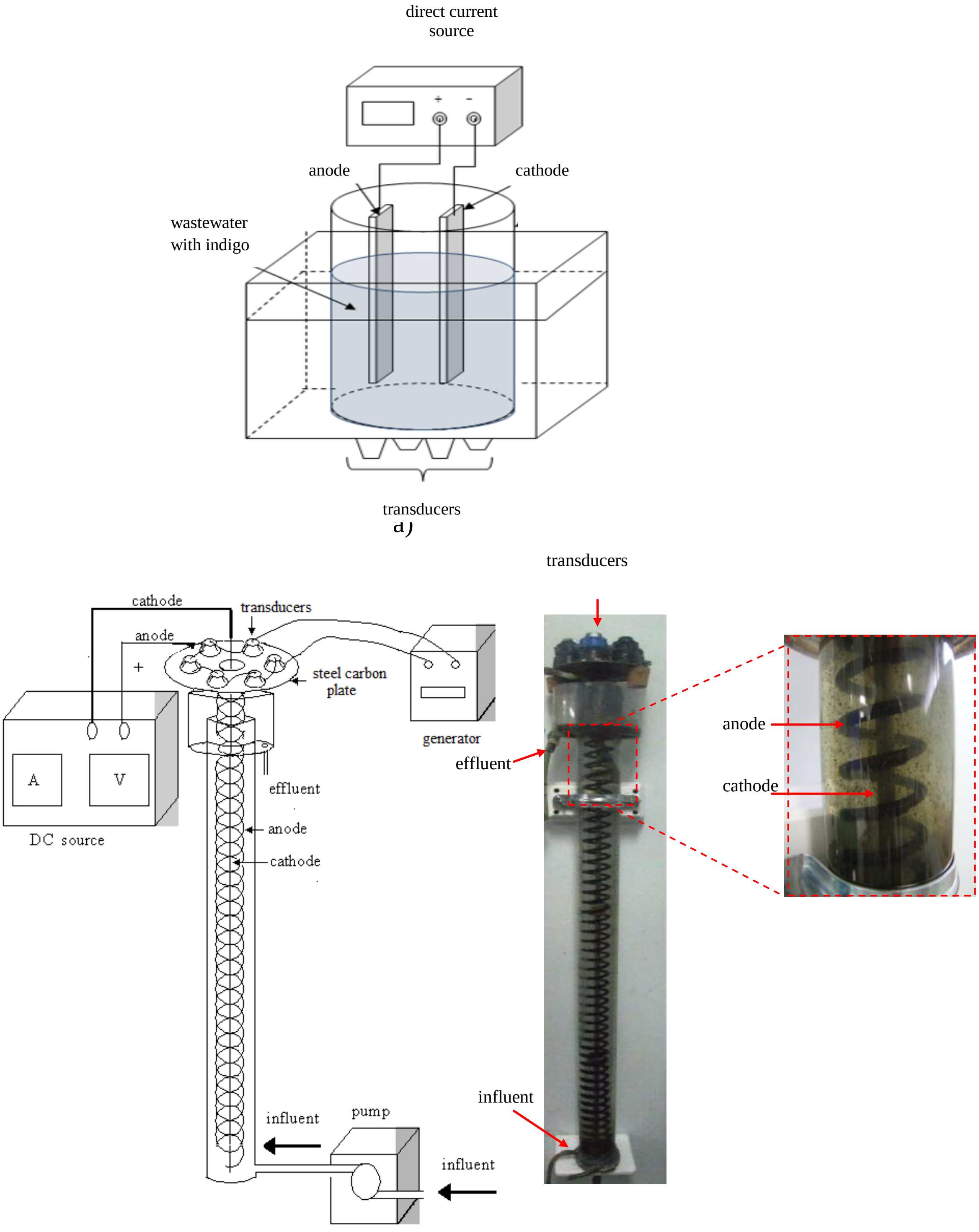
Effluents from textile facilities contain several different pollutants that can be measured as chemical oxygen (COD) or biochemical oxygen demand (BOD), pH and so on. Nevertheless, the most evident pollutant, even at low concentration levels, is color [1]. It is worth noting that color reduces water transparency, affects photosynthetic process, and solubility of gases in the body of the water [2]. Mexico is the leading Latin American textile exporter to the North American Market. The Mexican textile industry of denim consumes large amounts of water that get contaminated with colorants. In order to avoid pollution and to comply with the environmental regulations, the wastewater must be treated before being discharged into the sewage collection system.

There are several different biological and physicochemical conventional treatments for removing dyestuff. Unfortunately, indigo color is a very stable molecule that is difficult to eliminate using conventional biological treatments, and it must be removed using physicochemical treatments. However, those treatments have significant drawbacks, namely, the need of reagents and the generation of large quantities of sludge that subsequently increment costs due to its handling, treatment and disposal [3] Although chemical methods are lengthy processes, which use oxidizing agents (e. g. ozone); they are not efficient in removing insoluble disperse dyes [4].

Treatments based on electrochemical techniques have been applied to remove different pollutants in aqueous media [5, 6, 7]. Textile dyes [8], and specifically the indigo dye [9], have been removed from wastewater using electrochemical treatments. These techniques produce very low amounts of sludge, which gives them an important advantage over other treatments. However, the electrode materials used are expensive; the process requires longer treatment times, as well as high temperatures. Cheaper electrode materials, such as aluminum and iron, have been applied [10, 11, 12], yet electrode passivation can be present due to the formation of oxide on the anode, which in turn reduces process efficiency and increases energy consumption. Electrochemical process has been complemented with ultrasonic irradiation (UI) to improve its performance [13, 14].

The effect of the UI is to produce acoustic cavitations that cause the formation, growth, and rapid recompression of vapor bubbles in the liquid. The bubbles are unstable and collapse generating microscopic shock waves that produce a micro-stirring effect and pyrolytic pathways [15, 16]. The ultrasonic irradiation increases the micro-mixing near the electrodes surface, which in turn increases the mass transfer and cleans the electrodes by reducing the passivation effect. In addition, hydroxyl free radicals are generated, which can affect the structure of the organic compounds [17, 18, 19]. Most of the previously cited studies were carried out in batch reactors and only a few were conducted in flow reactors. In this research, the removal of indigo by combining electrochemical and UI in aqueous media using batch and tubular flow reactors was evaluated. Three low cost materials were tested for the construction of the electrodes: carbon steel, stainless steel and aluminum. Finally, the hydrodynamics of the process were modeled for the tubular flow reactor, and the model was validated, in non-steady state, with experimental results.

2. MATERIALS AND METHODS



b)

Figure 1. Sonelectrochemical reactors; a) batch and b) flow reactor.

Both batch and flow reactor experiments were performed in two conditions: a) applying only a direct current (electrochemical treatment) and b) applying a direct current and ultrasonic irradiation (sonoelectrochemical treatment). For both reactors, a DC power source was used to supply and control the current density at 67.3 A/m^2. Batch reactor tests were performed in a glass reactor with an operation volume of 1.5 L.

The electrode area was 0.0779X10^{-2} m^2. Stainless steel, aluminum, and carbon steel were used to manufacture the electrodes. The results for all three electrode materials are shown in Figure 1a. The flow reactor tests were carried out in a tubular reactor of Plexiglas with tangential inlet and operation volume of 2.540 L, as shown in Figure 1b. In this case, a central polished carbon steel rod measuring 1.07 m was used as cathode; a helical electrode of the same material and cross section, as anode.

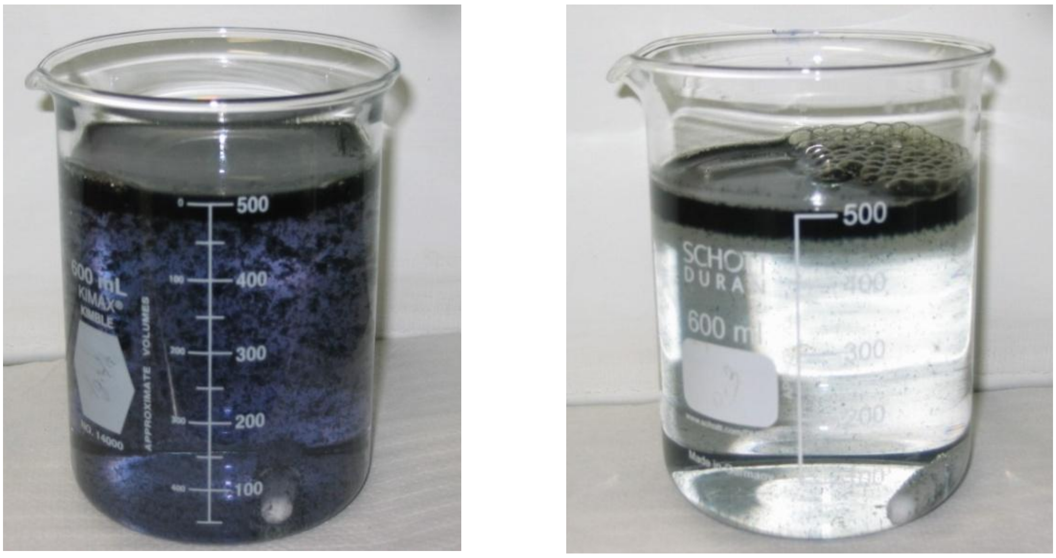
The helical electrode area was 0.101 m^2. The anode and cathode were isolated using rubber gaskets. Six standard piezo-composite transducers having a resonance frequency of 40 kHz were driven by an ultrasonic generator of 300 W. In order to create the ultrasonic field inside the reactor, the transducers were bonded to a carbon steel plate attached to the anode (fig. 1b). An evaluation of the flow patterns of the electrochemical flow reactor (ER) and the sonoelectrochemical reactor (SER) was performed by instantaneously adding an input pulse of a non reactive tracer (KCl) to the influent while recording the conductivity of the effluent. The concentrations of tracer in the reactor effluent were recorded using a conductivity meter. The experiments were performed to obtain the exit age distribution function (**E**). This method is reliable when the dispersion number ($N_d = \frac{D}{uL}$) < 1.0 [20]; where D is the dispersion coefficient (m^2 s^{-1}), u is flow velocity (m s^{-1}) and L is the length of the reactor (m). In these tests, tap water was used. Synthetic wastewater was prepared using pure indigo textile dye, and its concentration was adjusted to 450 mg/L. Due to the low conductivity of the aqueous media, 100 mg/L of NaCl was added; which is lower than the 250 mg/L concentration reported in other studies [13]. The fluctuations of indigo concentration were measured in different times during the treatment process by monitoring the optical absorbance (597 nm) of the solution using a UV-VIS spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Batch test

In all the three cases, the most important mechanism of indigo dye removal was electrocoagulation and electroflotation. The insoluble metal hydroxides flocs (photograph 1a) have a large surface area that is favorable for a rapid adsorption and trapping of colloidal particles of the indigo dye particles, which are removed easily from aqueous medium by electroflotation [21], to the liquid surface(photograph 1b). Figure 2 shows the experimental results for the sonoelectrochemical process corresponding to each electrode material.

As seen, the best performance was achieved using carbon steel electrodes. Figure 3 shows that the Fe concentration reached with the carbon steel electrodes in the batch reactor is the highest and it is closer to the theoretical Fe concentration, calculated using Faraday´s constant. The Fe concentration obtained with the stainless steel anode is significantly smaller.



a) b)

Photograph 1. a) flocs formation and b) indigo removed by eletroflotation (on the liquid surface).

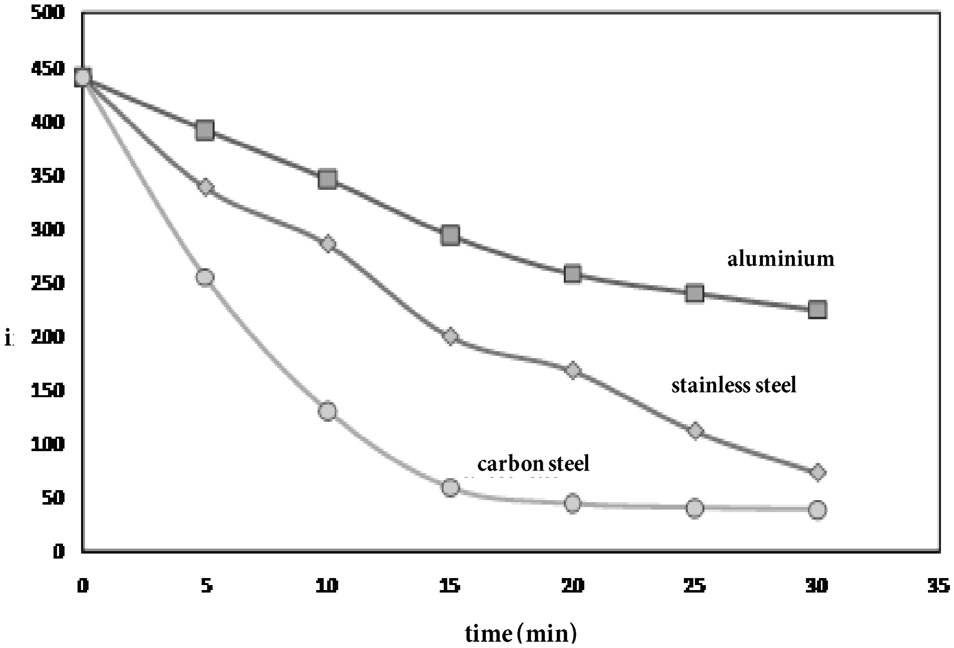


Figure 2. Removal of indigo dye using different electrode materials.

The quantity of aluminum, released from the anode during the experimental test, is the same as the one calculated by Faraday´s constant, and then the values of current efficiency are higher in comparison with the other tested materials. On the other hand, the aluminum is released at lower rate and reached a lower concentration than the one obtained from Fe electrodes. Therefore, a lower Al coagulant concentration is available to remove the indigo dye. This is because, to release a mol of the coagulant Al(III), three electrons are required while in the case of the Fe(II) ion, only two electrons are required. Hence, a higher quantity of coagulant is released from the carbon steel electrodes compared to that of the Al electrodes. It can be concluded that, the highest indigo removal rate of all three electrode materials is achieved with carbon steel electrodes. Moreover, the coagulants with ferrous ions are considered among the most efficient coagulants [4]. Other advantage of carbon steel comes from a much lower cost, when compared to that of stainless steel and aluminum.

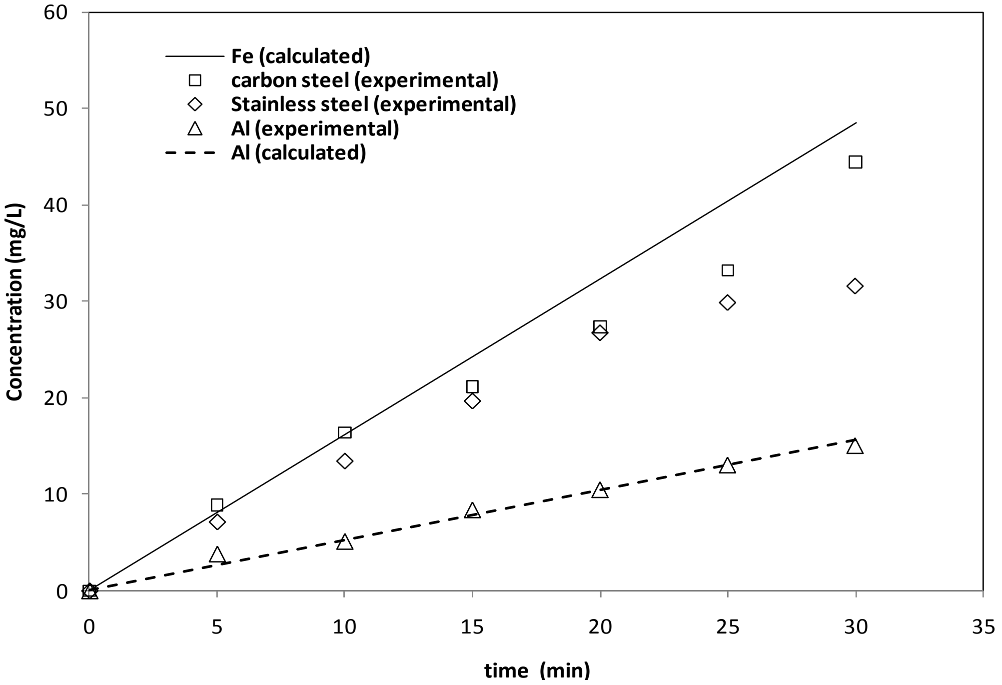


Figure 3. Fe and Al released as a function of time.

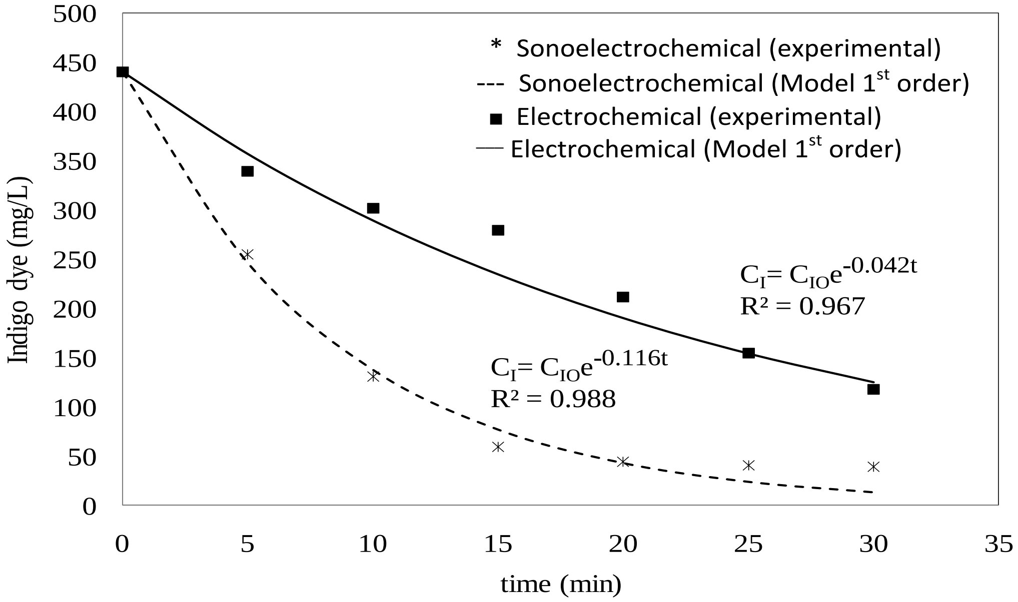


Figure 4. Experimental data and kinetic model of the indigo dye concentration with electrochemical and sonoelectrochemical treatments.

Based on these results, the carbon steel electrodes were chosen to carry out the experiments. These tests were performed to evaluate the indigo kinetic removal in the batch reactor. As shown in Figure 4, indigo dye removal exhibits a first order kinetics for both electrochemical and sonoelectrochemical treatments.

For the electrochemical process, the kinetic coefficient is 0.042 min^{-1}, which is in good agreement with other studies [2], where a coefficient of 0.049 min^{-1} was obtained. The noteworthy feature of the sonoelectrochemical process is that the kinetic coefficient increases by more than twice, reaching 0.116 min^{-1}. This behavior is due to the enhanced mass transfer from electrode to electrolyte induced by the micro stirring effect of the UI that reaches the electrode surface and deters electrode passivation. Then, as passivation is decreased, another positive effect of UI is to reduce electrical power consumption. Figure 5 shows that UI improves Fe(II) generation by about 60%. It is worth mentioning that, UI can produce H_2O_2 [18], which could also improve the indigo removal rate.

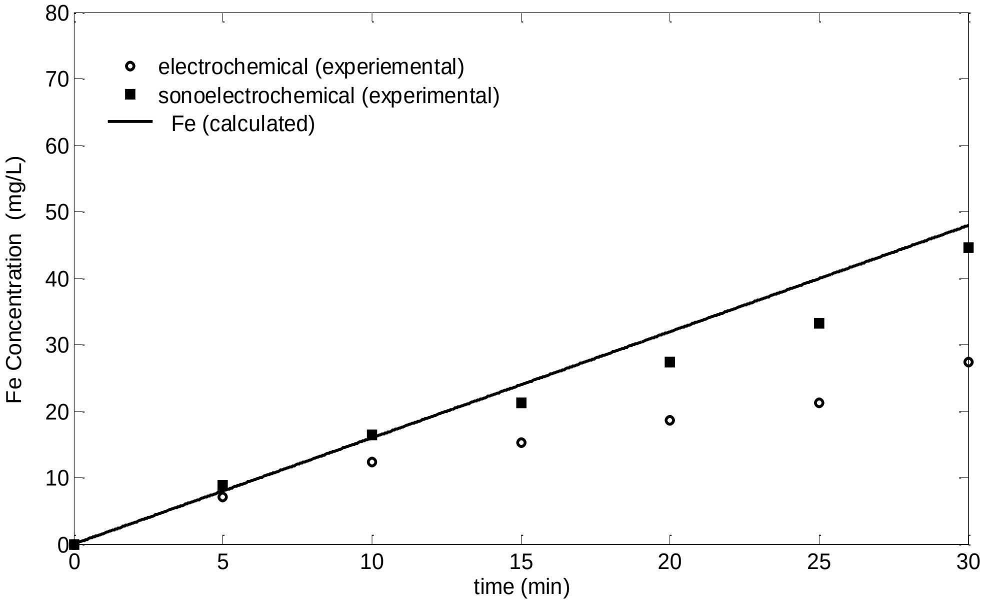


Figure 5. Comparisons between the Fe concentrations of the electrochemical and sonoelectrochemical processes.

3.2 Tracer tests in flow reactors

In order to evaluate the flow patterns during the operation of the flow reactor, tracer tests were performed with tap water for both electrochemical reactor (ER) and sonoelectrochemical reactor (SER). Figure 6 shows the experimental data and the model for the tracer concentration at the reactor effluent as a function of the time. As can be seen, the ER behaved as a plug flow reactor with N_d=0.025 [20]. The dispersion effect is included in the model for the indigo concentration (C_I) as shown in equation 1.

The conventional boundary conditions [22] are established in equations 2 and 3.

at $z = 0$

$$\mathrm{th} \cdot \frac{\partial C_I}{\partial t} = \frac{D}{uL} \cdot \frac{\partial^2 C_I}{\partial z^2} - \frac{\partial C_I}{\partial z} - \mathrm{th} \cdot k_1 \cdot C_I \qquad (1)$$

at *z = 1*

$$C_I - \frac{D}{uL} \cdot \frac{\partial C_I}{\partial z} - C_{IO} = 0 \qquad (2)$$

$$\frac{\partial C_I}{\partial z} = 0 \qquad (3)$$

Where: C_{IO} = influent indigo concentration, k_1 = first order rate constant (min^{-1}), th= hydraulic time (min), D = dispersion coefficient (m^2/s), u = flow velocity (m/s), L = reactor length (m), x = lagoon length (m), z = x/L (dimensionless), t =time (min).

On the other hand, Figure 6 shows the results of the tracer tests, for both ER and SER. As can be seen, the SER behaved as a plug flow reactor followed by a stirred tank flow reactor (PF-STR). The flow pattern model for the SER is shown in Figure 7, where Q = influent flow rate (L/min), V_{PF} = plug flow reactor volume (L), V_{STR}= stirred tank flow reactor volume (L) and V_T = the total reactor volume (L) = V_{PF} + V_{STR}.

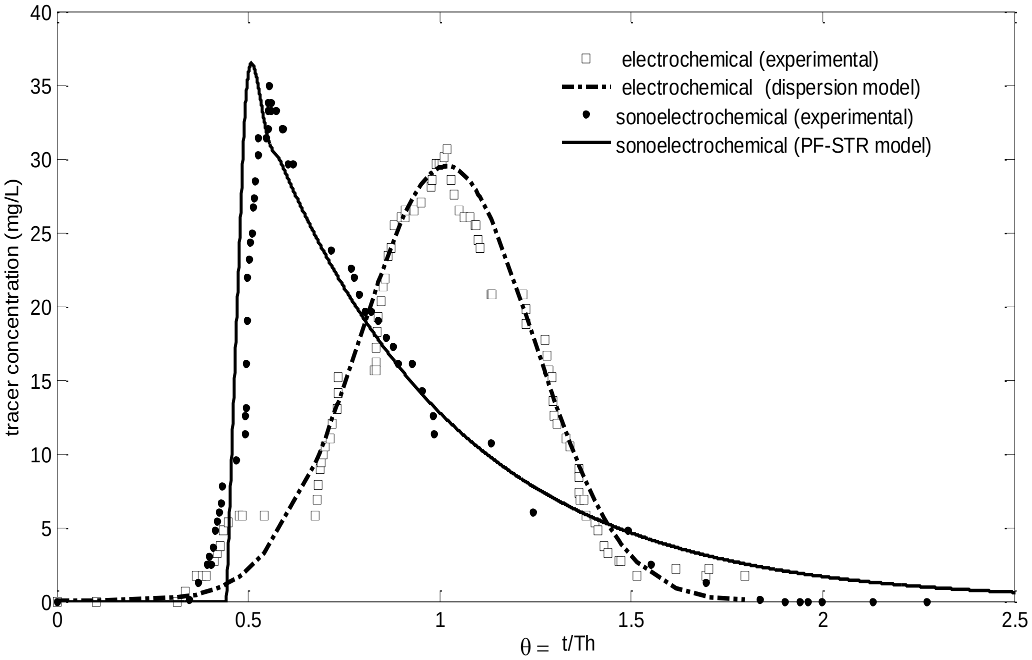


Figure 6. Experimental data and model obtained from the tracer tests in the SER and the ER.

This result implies that the cavitation produced by the ultrasonic irradiation provides a mixing effect which affects the flow pattern inside the reactor. Therefore, in the SER, only the first part of the reactor, about 35% (0.9L) of the total volume, has a plug flow behavior, but the last part, 65% (1.64L) of the reactor volume, behaves as stirred tank reactor. Clearly, the UI affects the flow pattern in the SER.

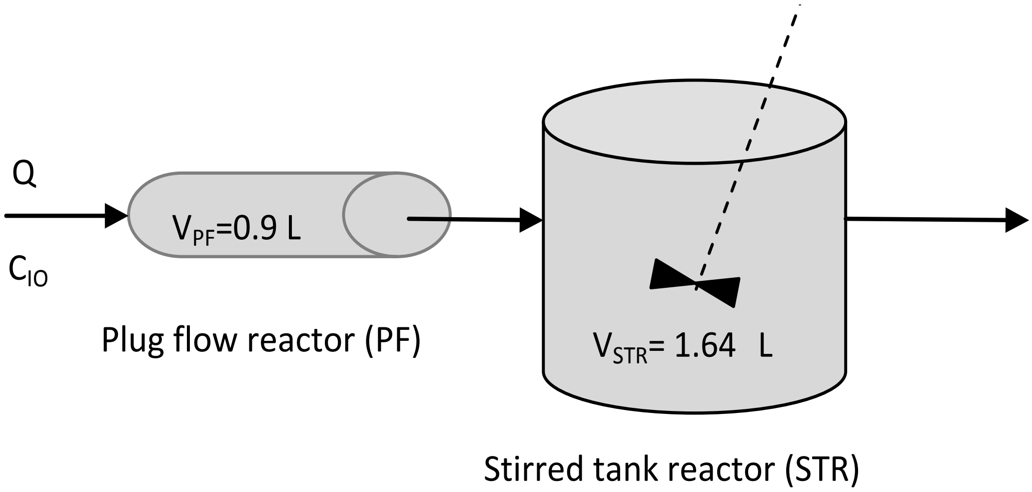


Figure 7. Flow pattern model for the sonoelectrochemical reactor (SER).

3.3 Model validation in flow reactors

During the experimental tests with the electrochemical and sonoelectrochemical flow reactors, the influent concentration was 450 mg/L, and the current density applied was 6.73x10^{-3} A/cm^2. The experimental results and models for both reactors are shown in Figure 8.

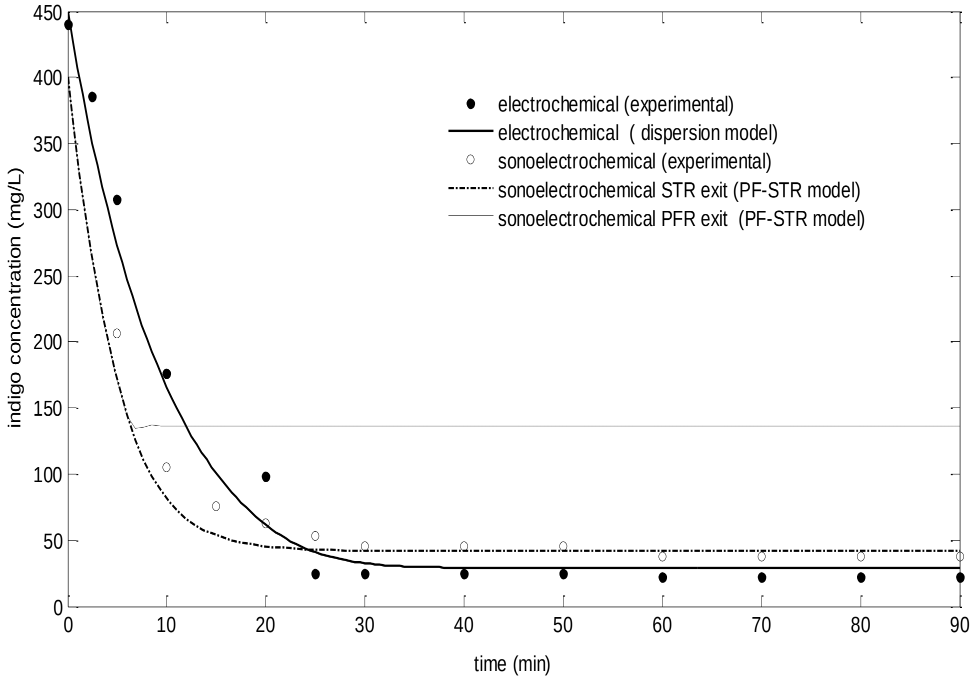


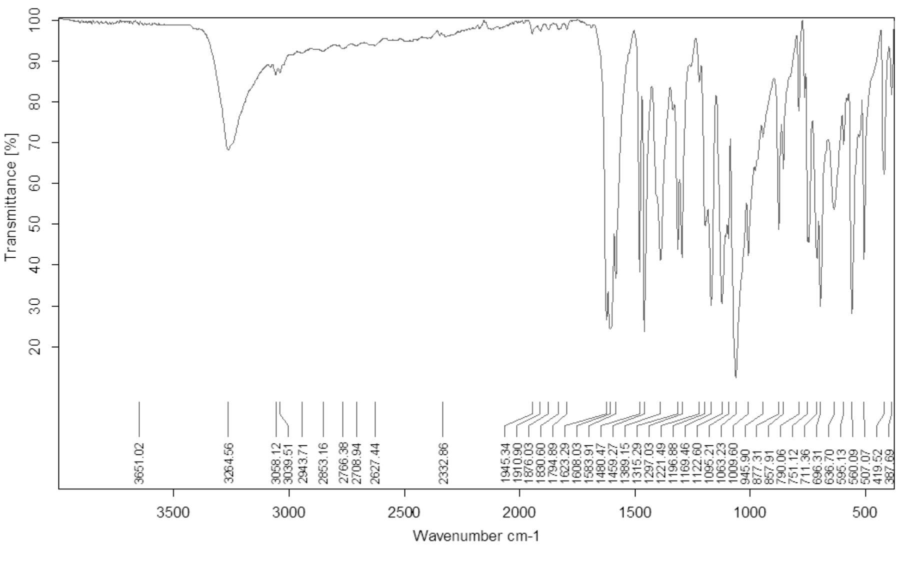
Figure 8. Experimental results and models for the ER andthe SER.

The models describe, with a confidence of 95%, the actual behavior of both flow reactors in non steady conditions. For the ER the residence time was 29.8 minutes, the dispersion number was 0.025, presenting a first order kinetic coefficient of 0.1 min^{-1}. In the case of the SER as a PF-STR, the global residence time was 15 minutes, and the first order kinetic coefficient was 0.17 min^{-1}. The increased kinetic coefficients, in both cases, were due to the larger electrodes area in the flow reactors compared to the batch reactors. The results show that removal of colorant using a sonoelectrochemical process is faster than the electrochemical process by itself. In both cases, almost the same effluent concentration of indigo dye is reached, but the residence time for the electrochemical treatment (29.8 min) is twice as long as the time of the sonoelectrochemical process (15 min). The UI improves the mass transfer in the reactor and generates H_2O_2 [13, 18] during the process. Both phenomena increase the indigo removal rate comparing to the electrochemical treatment alone. Therefore, the first order kinetic coefficient of the SER (0.17 min^{-1}) is higher than the one of the ER (0.1 min^{-1}).

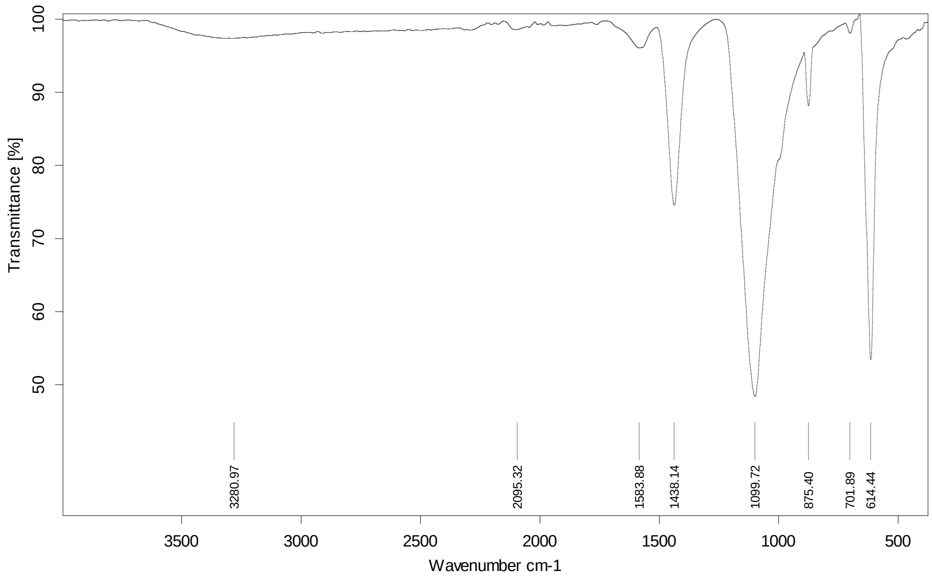
3.4 IR spectra for the indigo before and after treatment

The IR spectra for the indigo before (Figure 9a) and after treatment (Figure 9b) show that indigo-related bands disappeared ,3300 cm^{-1} (NH stretch) and 1630 cm^{-1} (C=O stretch), indicating that the structure of this compound could have undergone significant changes [23, 24] due to the sonoelectrochemical treatment.

Thus, samples after treatment do not exhibit the above mentioned vibrations, indicating indigo decomposition. Similarly, a decrease or the absence of the absorptions mainly attributed to C=O and C–C stretching vibrations of the aromatic ring around 1624, 1602, 1584,1480 and 1458 cm$^{−1}$ indicate the inexistence of indigo molecule [25]. As seen in Figure 9b, the shift of the band 3264 to longer wavelengths after treatment with the SER could be due to the OH absorption band at 3500 cm^{-1}. Usually the appearance of the OH band is considered as indicative of the presence of a hydrated compound whose OH is tightly bound to the molecular structure of the compound [26, 27].



a)



b)

Figure 9. IR spectra for the indigo:(a) before and (b)after treatment.

However, more studies are needed to quantify each effect separately and optimize the operating conditions to obtain higher removal efficiencies and reduce the treatment time. Moreover, studies have to be done in order to improve the ultrasonic effect by changing the reactor geometry.

4. CONCLUSIONS

As a result of this study, indigo dye was removed from wastewater up to 90.0%, using low cost carbon steel electrodes. The removal rate of the sonoelectrochemical process was faster than in the case of the electrochemical process alone. For both flow reactors, the process of indigo removal, exhibited a first order kinetics. The electrochemical and sonoelectrochemical treatments were operated and modeled as flow reactors and the models were validated experimentally. The effect of the ultrasonic irradiation on the flow patterns was evaluated and included in the SER model. It was shown that the indigo dye is removed by electrocoagulation, but it also could be decomposed by the sonoelectrochemical treatment.

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References

1. A. Lopes. *Portugaliae Electrochm. Acta*. (2004) 279.
2. M. Sanroman. M. Pazos, M. Ricart, and C. *Chemosphere.* 5 (2004) 233.
3. D. Doĝan and T. Haluk, *J. Chem. Techn. Biotech.* 80 (2005) 916.

4. A. Kumar, R. Roshan , P. Bhunia, *J. Environ. Manage*. 93 (2012) 154.
5. X. Chen, G.Chen, P.L.Yue, *Sep. Purif. Technol.* 19 (2000) 65.
6. C.Y Hu., S.L Lo., W.H. Kuan, *Water Res*. 37 (2003) 4513.
7. P.R. Kumar, S. Chaudhari, K.C. Khilar, S.P. Mahajan, *Chemosphere* 55 (2004) 1245.
8. N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar, *Sep. Purif. Technol.* 31 (2003) 153.
9. A. Roessler, D. Crettenand, O. Dossenbach, W. Marte, *Electrochm.Acta*. (2002) 1989.
10. S.A. Martiınez, M.G. Rodriguez and C. Barrera, *Water Sci. Technol.* 42 (2000) 55.
11. S.A. Martiınez, M.G. Rodriguez, R. Aguilar and G. Soto, *Water Sci. Technol.* 49 (2004) 115.
12. S.A. Martínez-Delgadillo, M.A. Morales-Mora, D. Barceló, *Sustain. Environ. Res.* 20 (2010) 227.
13. W. Chih-Ta, C.Wei-Lung, K. Yi-Ming, *J. Hazard. Mat.* 164 (2009) 81.
14. S. Martinez-Delgadillo, V. Mendoza, H. Mollinedo-Ponce, H. Puebla, J. Méndez-Contreras, *Ind. Eng. Chem. Res.* 50 (2011) 2501.
15. G. J. Price, M. Ashokkumar, F. J. Grieser, *Am. Chem. Soc.* 126 (2004) 2755.
16. G. J. Price, M. Ashokkumar, M. Hodnett, B. Zequiri, F.J. Grieser, *J. Phys. Chem. B.* 109 (2005) 1779.
17. G. Tezcanli-Guyer and N.H. Ince, *Ultrason. Sonochem.*10 (2003) 235.
18. V. Naddeo, V. Belgiorno, R. Napoli, *Desalination*. 1–3 (2007)**.** 175–182.
19. K. Zhang, N. Gao, Y. Deng, T. Lin, Y. Ma, L. Li, M. Sui, *J. Environ. Sci-China*, 23 (2011) 31.
20. O. Levenspiel, Chemical Reaction Engineering; John Wiley & Sons, New York (1999).
21. F. Jing-Wei, S. Ya-Bing, Z. Zheng, Z. Ji-Biao, L. Shu, T. Yuan-Chun, *J. Environ. Sci-China*. 19 (2007) 1409.
22. P. V. Danckwerts, *Chem. Eng. Sci*. 2 (1953) 1.
23. R. J. Clark, C.J. Cooksey, *New J. Chem.* 23 (1999) 323.
24. C. J. Cooksey, Molecules. 6 (2001) 736.
25. A. Fiedler, M. Baranska and H. Schulz, *J. Raman Spectrosc.* 42 (2011) 551.
26. A. Fernández-Jiménez, A. Palomo, T. Vasquez, R. Vallepu, T. Terai, K. Ikeda, *J. Am. Ceram. Soc.* 91 (2008) 1231.
27. T. Carvalho, D. Fungaro, C. Magdalena and P. Cunico, *J Radioanal. Nucl. Chem.* 289 (2011) 617.