Electro-Fenton decoloration of dyes in a continuous reactor: A promising technology in colored wastewater treatment

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ABSTRACT

This study focuses on the application of Electro-Fenton technique for the remediation of wastewater contaminated with synthetic dyes. A bubble reactor was designed to develop this treatment operating in continuous mode. In order to increase the efficiency of Electro-Fenton treatment, the effect of key parameters (iron dosage and pH) that play an important role in this process was investigated for Lissamine Green B decoloration in batch mode. Operating at the optimal conditions, determined for Lissamine Green B, several dyes (Methyl Orange, Reactive Black 5 and Fuchsin Acid) were decolorized by using Electro-Fenton process. A first-order kinetic model was used to simulate the experimental results operating at different pH, and iron concentration of 150 mg L^{-1}. This kinetic model for Lissamine Green, Methyl Orange and Reactive Black 5 was successfully used in the progression of the process from batch to continuous mode. About 80% color removal was achieved for Lissamine Green and Methyl Orange with a residence time of 21 h. The decoloration for Reactive Black 5 was lower, reached a value around 60% at the same residence time. Nevertheless in all assays a good agreement between experimental results and proposed model in a continuous bubble reactor was detected. In addition a continuous treatment with a mixture of dyes was carried out. Operating with a residence time of 21 h the obtained decoloration was close to 43% which is squared with a TOC reduction around 46%. Therefore, the results provide fundamental knowledge for the treatment of a real wastewater stream.

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1. Introduction

Synthetic dyes are used to color many different products such as textiles, paper, cosmetics and drugs [1]. The discharge of these colored compounds in the environment causes considerable non-aesthetic pollution and serious health-risk factors [2]. Conventional wastewater treatment plants cannot degrade the majority of these pollutants and generating large volumes of sludge, thus causing secondary loading of environmental pollutants [3,4].

Advanced oxidation processes (AOPs) offer effective and rapid alternative treatments for various contaminants. The AOPs are based on the *in situ* generation of hydroxyl radicals (•OH), a highly powerful oxidizing agent, and are effective in treatment of persistent organic pollutants aqueous solutions until their overall mineralization [5]. Among these AOPs, the Fenton reaction with hydrogen peroxide and transitional metals, especially the ferrous ion, in an acidic aqueous system has been investigated in numerous studies [6]. However, this system generally offers effective contaminant removal only at high rates of hydrogen peroxide

and soluble iron consumption due to the stoichiometric reaction [7].

Currently, some research groups have reported Electro-Fenton oxidation offering significant advantages as well as solving problems, without requirement for special equipment, and high efficiency in organic pollutants removal [8–10]. Electro-Fenton process consists of treating wastewater *in situ* with H_2O_2 electro-generated in the presence of catalytic amounts of Fe(II) [11]. According to Fenton's reaction (Eq. (1)), hydroxyl radicals (•OH) are formed. These radicals are high oxidant species, they attack most organic molecules with rate constants usually in the order of 10^6–10^9 L mol^{-1} s^{-1} [12]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + \text{•OH} \tag{1}$$
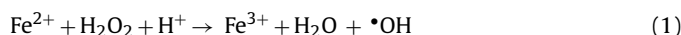
This new hybrid technology employs the electricity which is a clean energy source so the overall process does not create secondary pollutants and is compatible with the environment [13].

Furthermore, *in situ* generation of H_2O_2 avoids the need for transport and storage of this hazardous substance, offers safer operation by virtue of providing diluted H_2O_2 solutions, enhances the mixing of solution [11].

There are many reports on Electro-Fenton process application for the degradation of phenol [14], aniline [15] and azo dyes [10,16]. Nevertheless to our knowledge there is no application of this hybrid

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technology in continuous mode. Industrial activities constantly produce colored wastewaters that need to be treated. Therefore, it is necessary to validate an adequate technique to remediate colored streams continuously.

The aim of this work is to design an Electro-Fenton bubble reactor to treat colored effluents in continuous mode at bench scale. In order to analyze the technique capacity, different dye solutions are used as model samples. The influence of several key parameters that play an important role in the Electro-Fenton process were investigated. In a first stage the electrode material, iron dosage and pH were evaluated to determine the best treatment conditions. From the kinetic studies in batch mode a bubble continuous reactor could be simulated. Finally, the Electro-Fenton bubble reactor was used to validate the treatment of different dyes in continuous flow.

2. Materials and methods

2.1. Dyes solutions

In this work several dye solutions were used to evaluate the Electro-Fenton treatment. The dyes characteristics and their concentrations are described in Table 1. Sodium sulfate 0.01 M was used as inert electrolyte, furthermore the presence of this compound is well-known in the wastewater from dyeing processes [17]. When a

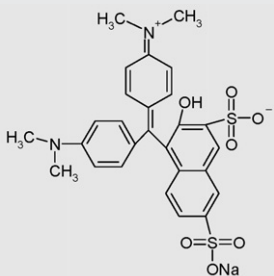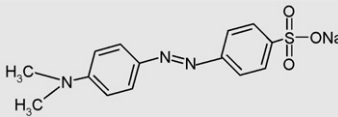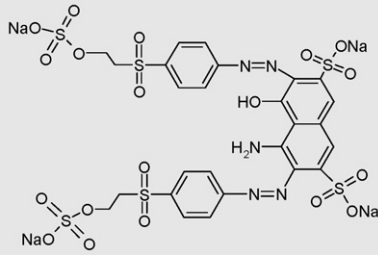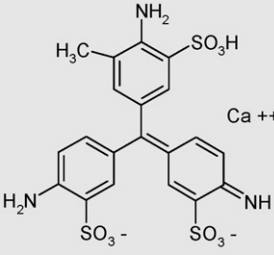mixture of dyes was used the electrolyte concentration was raised proportionally (0.04 M).

2.2. Electro-Fenton bubble reactor

A glass cylindrical reactor with two electrode bars connected to a direct current (DC) power supply was used (Fig. 1). The Electro-Fenton bubble reactor had working volume of 0.675 L, and was operated in batch mode with total reflux or continuous mode (at 5.5, 16 and 21 h of residence time). The cathode and anode bars were placed 30 mm and 270 mm above the bottom of the cell, respectively. The distance between electrodes bars was fixed at 240.4 mm. Steel or graphite bars were employed. Each bar was 100 mm high with a diameter of 6.35 mm for graphite and 10 mm for stainless steel, resulting in a total contact surface area of 1.27 cm^2 to graphite and 3.14 cm^2 to stainless steel. A constant potential difference (15 V) was applied with a power supply (HP model 3662) and the process was monitored with a multimetre (Fluke 175).

In the Electro-Fenton process H_2O_2 is produced electrochemically via oxygen reduction on the cathode. For this purpose, continuous saturation of air at atmospheric pressure was ensured by bubbling compressed air near the cathode at about 1 L min^{-1}, starting 10 min before electrolysis to reach a stationary O_2 concentration [18]. Iron dosage was added as $FeSO_4 \cdot 7H_2O$ at different

Table 1
Dye class, chemical structures, wavelength at maximum absorbance and concentration used of the different dyes employed.

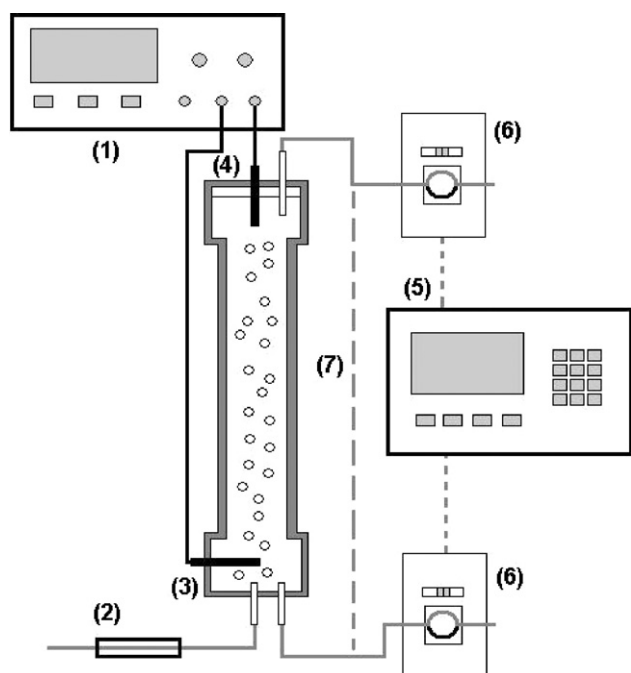| Dye	Type	C.I.	Structure	λ_{max} (nm)	Concentration (mg L^{-1})
Lissamine Green B (LGB)	Diphenylnaphthyl-methane	44,090		633	8.5
Methyl Orange (MO)	Mono-azo	13,025		466	1.5
Reactive Black 5 (RB5)	Di-azo	20,505		597	70
Fuchsin Acid (FA)	Triarylmethane	42,685		546	15

Fig. 1. Schematic diagram of Electro-Fenton experimental set-up: (1) power supply, (2) air compressor, (3) cathode, (4) anode, (5) control unit, (6) pumps, and (7) reflux (only in batch conditions).

concentrations. The pH was adjusted to working value with sodium hydroxide or sulfuric acid to promote the formation of hydroxyl radicals in the Fenton process when it was required.

Samples were taken periodically from the electrochemical reactor to be analyzed for pH, dye concentration and decoloration, and the electric parameters recorded.

2.3. Dye decoloration

For analytical determinations, aliquots were taken at convenient times. The absorption spectrum showed in all cases a single peak with a strong absorption in the visible region at the wavelength indicated in Table 1. For all experiments, the residual dye concentration was measured spectrophotometrically (Unicam Helios β, Thermo Electron Corp.) at the maximum visible wavelength. The assays were done twice, the experimental error was calculated as standard deviation (SD) and in all cases the SD was below 3%. The decoloration, expressed in terms of percentage, was calculated from these curves following the diminution of the area under the curve when mixtures of dyes were used (Eq. (2)):

$$D = \frac{A_i - A_t}{A_i} \times 100 \qquad (2)$$

where D, decoloration (%); A_i and A_t, area under curve of dyes at the initial and through time, respectively.

2.4. Decoloration rate

The concentration of each dye throughout the experiments was calculated from the absorbance value at the corresponding wavelength (Table 1) using a calibration curve. The concentration profiles were fitted by a suitable kinetic equation and the rate constants were calculated by using SigmaPlot 4.00 (1997) software. The SigmaPlot curve fitter uses an iterative procedure, based on the Marquardt–Levenberg algorithm, which seeks the values of the parameters that minimize the sum of the squared differences

between the observed and predicted values of the dependent variable.

2.5. TOC analysis

Total organic content (TOC) was determined by using a Lange cuvette test (LCK 380) in a Hach Lange DR 2800. The sample was introduced in the Lange cuvette. Under the conditions of the test, the carbon forms carbon dioxide, which diffuses through a membrane into an indicator solution. The change of color of the indicator solution is evaluated photometrically.

2.6. Residence time distribution (RTD) curves

The RTD curves can be obtained from tracer stimulus–response technique, whereby the response of the system to a certain perturbation (stimulus) is studied. These curves can indicate the hydrodynamic behaviour of the bubble reactor described above. The reactor was fed with distilled water at different residence times. The RTD curves were obtained by perturbation via a pulse injection with a syringe of 1 mL concentrated LGB solution at the inlet of the bubble reactor without direct current. Then, the changes in dye concentration were measured along time in the outlet stream.

3. Results and discussion

3.1. Effect of the electrode materials

Different configurations can be used for the application of electrochemical remediation techniques and the electrodes can be made of different materials. A significant interest in the effectiveness of different electrode materials has recently arisen, with the use of stainless steel, graphite, platinum, PbO_2, titanium compounds, boron doped diamond, and ceramics. In an electrochemical cell, hydrogen peroxide is yielded as a result of redox reactions and in particular by the reduction of O_2 from air at the cathode. The hydrogen peroxide production is closely related to cathode material. Thus, the selection of an appropriate electrode plays an important role on the efficiency of the electrochemical process. In this work, bars of graphite and stainless steel have been selected as electrode materials. In Fig. 2 the decoloration profiles obtained operating in batch mode with total reflux and different electrode materials are shown. It was observed that the graphite electrodes led to the highest LGB decoloration rate, with total decoloration
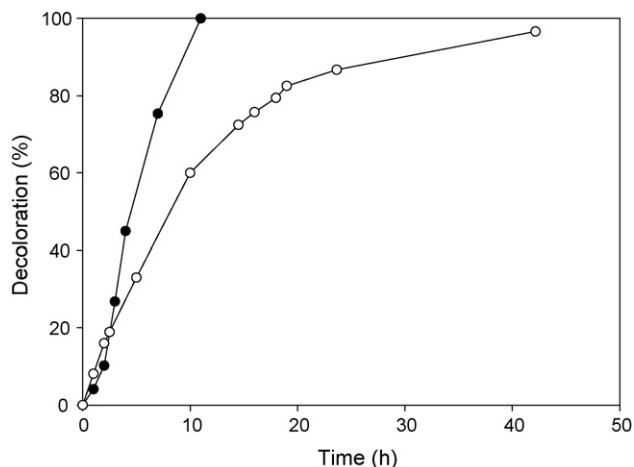

Fig. 2. Decoloration profiles of LGB by Electro-Fenton process using as electrodes bars of graphite (●) and stainless steel (○).

after 10 h. Moreover, gradual corrosion of stainless steel electrodes was detected.

These results are in accordance with Sudoh et al. [19]. They reported that graphite was the best cathode material for electro-generation of H_2O_2 while metal cathodes such as copper, stainless steel, lead and nickel were likely to decompose H_2O_2. Currently, Da Pozzo et al. [20] found that on graphite cathode the H_2O_2 generation rate was 15 mg L^{-1} h^{-1} cm^{-2}, while Qiang et al. [21] also with graphite electrode, detected a rate 10-fold lower. Recently, Zhou et al. [10] noticed a high H_2O_2 generation rate (around 45 mg L^{-1} h^{-1} cm^{-2}) when graphite–polytetrafluoroethylene cathode was employed.

Therefore, all subsequent experiments were carried out with graphite bar electrodes; this set-up has been demonstrated to favour the LGB decoloration rate at low power consumption.

3.2. Effect of pH

The efficiency of the Fenton reactions depends on pH, iron and H_2O_2 concentration, current intensity, the length of the treatment, etc. In order to optimize the Electro-Fenton process, batch experiments were carried out with LGB solutions, as model dye. Initially, it was determined that 150 mg L^{-1} is the optimal iron concentration that corresponds with the value reported by Da Pozzo et al. [22].

At that iron dosage, the influence of the initial pH in the degradation of LGB was studied. Several Electro-Fenton experiments, operating in batch mode, were conducted by varying pH (2–5). Fig. 3 shows the decoloration grade along the time for all pH conditions studied. At pH above 3, decoloration degree significantly decreases, mainly because the dissolved fraction of iron species diminishes [23]. Actually, at high pH values Fe(III) precipitates, and the dissolved Fe(III) concentration is reduced. Consequently, the concentration of Fe(II) species also decreases because Fe(III) hydroxides are much less reactive than dissolved Fe(III) species towards H_2O_2 [24]. In this system the highest decoloration rate was found when pH was maintained at a value around 2. Some researches indicated that at pH < 3 the Fenton process becomes less effective because the regeneration of Fe(II), through reaction between Fe(III) and H_2O_2, is inhibited [24,25]. Nevertheless, this fact did not happen during the Electro-Fenton process since the Fe(II) is continuously regenerated from the reduction of Fe(III) upon the cathode surface [2].
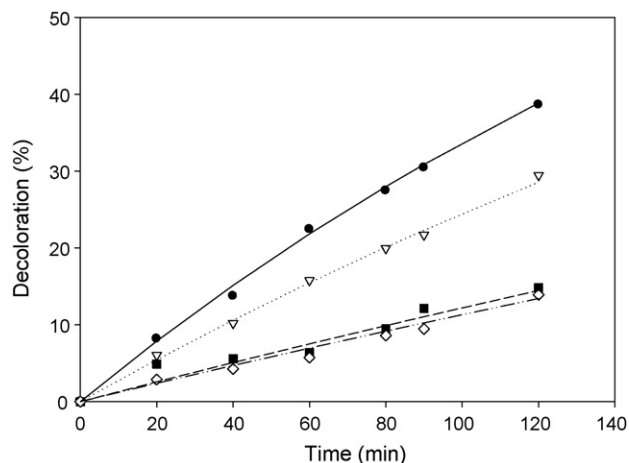

Fig. 3. Influence of pH in the decoloration of LGB: (●) pH = 2; (▽) pH = 3; (■) pH = 4; (◇) pH = 5. Lines represent the first-order kinetic (Eq. (3)).

Table 2
Kinetic coefficients for a first-order decoloration reaction of different dyes.

Dye	pH	k (min^{-1})	R^2
Lissamine Green B	2	0.0041	0.9979
	3	0.0028	0.9968
	4	0.0013	0.9477
	5	0.0012	0.9821
Methyl Orange	2	0.0038	0.9978
Reactive Black 5	2	0.0011	0.9919
Fuchsin Acid	2	0.0018	0.9959

3.3. Kinetic studies

The dye concentration profiles permit to evaluate the kinetic behaviour of this reaction. In these experiments the reaction kinetics was researched and the regression coefficients for zero, first and second-order reactions were calculated. The results indicated that the decoloration of LGB at different pH could be quantitatively described by a first-order kinetic equation (Eq. (3)) with respect to the dye concentration:

$$\frac{dC}{dt} = -kC \tag{3}$$

where C, concentration of dye (mg L^{-1}); t, reaction time (min); k, kinetic coefficient for the first-order reaction (min^{-1}). The rate constant values and the statistical correlation parameters are shown in Table 2.

Moreover, at the optimal conditions obtained for LGB, the decoloration of other dyes with different chromophore groups (Table 1) was tested in order to evaluate the suitability of the technology developed. The results indicate that the decoloration pattern of the studied dyes is different, and each dye presents a behaviour according to its chemical structure and substituents. The decoloration kinetics can also be quantitatively described as a first-order with respect to the dye concentration. The rate constant values and the statistical correlation parameters are shown in Table 2. LGB showed a decoloration percentage of about 40% after 2 h of treatment followed by MO with rate constant values of 0.0041 and 0.0038 min^{-1}, respectively. This fact could be related with their chromophore groups and the ease to be broken. These results are in accordance with the results obtained by Sanromán et al. [26]. They found that the electrochemical decoloration rate largely depended on the chemical structure, especially the phenyl groups substituents. Besides, their research determined that the indirect oxidation by a redox mediator (e.g. Fe^{2+}/Fe^{3+}) favours the degradation of the mixture dyes into simpler compounds, even reaches a complete mineralization to CO_2 and water.

3.4. Continuous operation

Most industrial applications operate in continuous mode; therefore continuously polluted colored streams are generated. Consequently, the development of a continuous reactor for the treatment of those streams is necessary. For this reason a continuous bubble Electro-Fenton reactor was developed in order to validate this hybrid technique in dyes aqueous solutions at bench scale.

Initially, tracer experiments were carried out at different flow rates to confirm that the reactor used in this work closely matches ideal mixing conditions. In bubble reactor configuration, operating at high air flow, its hydrodynamic behaviour is close to continuous stirred tank (CSTR). In these experiments the RTD curves had a profile similar to ideal CSTR. Therefore to describe the blend time, it can be assumed that the reactor behaves ideally, which means that the concentration everywhere in the reactor is equal to the outlet concentration and the fluid has a mean residence time equal to
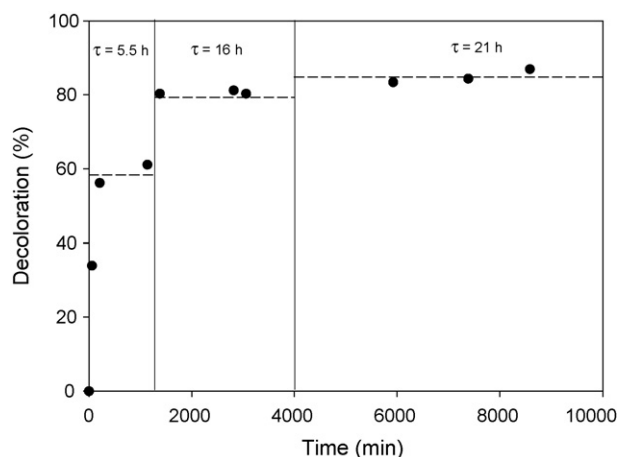
Fig. 4. Decoloration profile in continuous reactor of LGB at different residence times: (●) experimental data and (– –) model predictions.

the reactor volume divided by the volumetric flow rate through the tank. Then, the results were compared with those obtained based on the design equation for ideal CSTR (Eq. (4)):

$$\frac{C(t)}{C_0} = \exp\left(-\frac{t}{\tau}\right) \tag{4}$$

where $C(t)$, dye concentration along the time (mg L^{-1}); C_0, initial dye concentration (mg L^{-1}); t, time (min); τ, residence time (min).

The differences between the data obtained from the fit to experimental tracer data and the formula value (Eq. (4)) are between 4% and 10%. Therefore, it has been confirmed that the hydrodynamic behaviour of this reactor is such as a CSTR.

The efficiency of the continuous bubble Electro-Fenton reactor designed in this work was evaluated operating with different dyes and flow rates. Two dyes, LGB and MO, were degraded in continuous mode at different residence times (5.5, 16 and 21 h) in order to determine the adequate operational conditions.

Figs. 4–6 show the decoloration degree at different residence times to LGB, MO and RB5, respectively. It is clear the relationship between residence time and decoloration. The higher decolorations were obtained when the residence time was increased. As it is shown, LGB and MO decoloration degree profiles were very similar. Around 80% decoloration degree was reached when residence time was 21 h in both dyes. On the other hand, the color removal for RB5 was lower, reaching a value around 60% at the same residence time. This fact is due to the kinetic behaviour which has been deter-
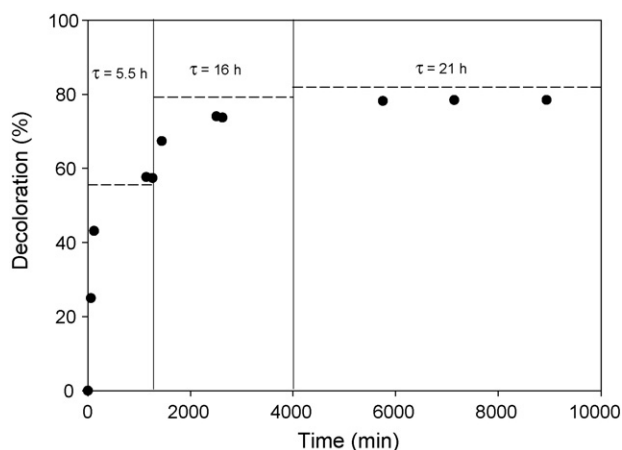

Fig. 5. Decoloration profile in continuous reactor of MO at different residence times: (●) experimental data and (– –) model predictions.
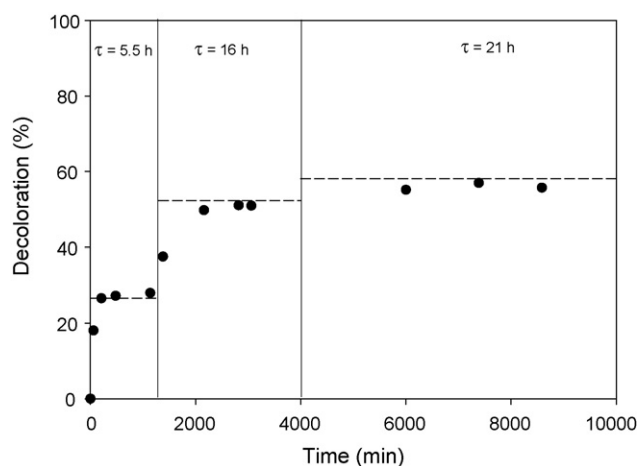

Fig. 6. Decoloration profile in continuous reactor of RB5 at different residence times: (●) experimental data and (– –) model predictions.

mined previously. In order to predict the dye decoloration along the time, it was postulated the equation of an ideal CSTR in steady-state (Eq. (5)):

$$D = \frac{k \cdot \tau}{1 + k \cdot \tau} \times 100 \tag{5}$$

where D, decoloration of dye (%); τ, residence time (min); k, kinetic coefficient for the first-order reaction (min^{-1}), the value considered was obtained from Table 2.

LGB, MO and RB5 model predictions, in terms of dye decoloration, are reported in Figs. 4–6, respectively. The differences between the dye decoloration obtained from the fit to experimental tracer data and formula value (Eq. (4)) for different flow rates are between 1.8% and 5.9% in the case of LGB, 3% and 7.5% in the case of MO and 2.5 and 3.2% in the case of RB5. This behaviour can be related with a total segregation model [27]; which assumes that all fluid elements having the same age (residence time) "travel together" in the reactor and do not mix with elements of different ages, until they exit the reactor [24].

In order to analyze the viability of an industrial application, a continuous treatment with a mixture of dyes was carried out. The four studied dyes (LGB, MO, RB5 and FA) were mixed and introduced in the bubble reactor. The initial concentrations were the same used in previous experiments (Table 1). The electrolyte concentration and iron dosage were proportionally increased according to the amount of treated dyes (0.04 M sodium sulfate and 600 mg L^{-1} iron dosage). Similar to previous experiments, the pH was adjusted at a value of 2. The results of the continuous treatment at different residence time are shown in Table 3. Operating with a residence time of 21 h the decoloration was closed to 43%. Although the removal color is lower than that obtained previously this fact could be due to the high amount of organic compounds present in the system. The reduction in TOC was evaluated in order to verify the Electro-Fenton dye degradation (Table 3). The results demonstrated that color removal is closely related with the reduction of TOC. Daneshvar et al. [28] reported that the Electro-Fenton process can degrade

Table 3
Decoloration and TOC reduction at different residence times for a mixture of four dyes (LGB, MO, RB5 and FA) operating in the optimized conditions.

Residence time (h)	Decoloration (%)	TOC reduction (%)
0	0	0
5.5	11.15	5.71
16	27.60	28.79
21	42.68	46.57

and finally mineralize organic pollutants to less toxic and non-toxic compounds. By reacting with hydroxyl radicals, the dye is degraded step-by-step, and eventually mineralized.

These results suggest that decoloration of dyes in continuous reactor can be achieved by Electro-Fenton process. Furthermore, dyes decoloration can also be rationalized by using the model described in this manuscript. It is remarkable the good agreement between experimental and model results that permits to predict the behaviour of this reactor to several dyes operating at different residence times. In addition the bubble Electro-Fenton reactor was able to operate in a continuous flow mode. Different kinds of dyes were treated without operational problems and attaining high decoloration percentages without the addition of other oxidant agents. This indicates the suitability of this system to treat colored effluents.

4. Conclusions

The results obtained in this work demonstrate that the dyes studied can be effectively decolorized by Electro-Fenton process. Batch experiments in saturated air conditions determined that the optimal values for the degradation of LGB are $150 \, \text{mg L}^{-1}$ Fe(II) and pH 2. Operating at the optimized conditions several dyes showed a first-order reaction. Besides, the degradation of different dyes by Electro-Fenton oxidation was carried out successfully in a continuous reactor. This reactor follows an ideal CSTR behaviour. Based on the kinetic and hydrodynamic studies a model prediction was developed. The experimental data showed a good fit to the theoretical model and verified the utility of this model to scale-up the process. It is noticeable that the continuous bubble Electro-Fenton reactor was able to operate without operational problems, and attaining high decoloration percentages depended on the residence time without the addition of other oxidant agents. It points out the relevance as well as the novelty of the results obtained in the present work.

Acknowledgements

References

[1] H. Zollinger, Colour Chemistry—Synthesis, Properties and Applications of Organic Dyes Pigments, VCH Publishers, New York, 1987.

[2] C.A. Martínez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, Appl. Catal. B: Environ. 87 (2009) 105–145.

[3] F. Herrera, A. Lopez, G. Mascolo, P. Albers, J. Kiwi, Catalytic decomposition of the reactive dye Uniblue A on hematite. Modeling of the reactive surface, Water Res. 35 (2001) 750–760.

[4] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters: a review, Environ. Int. 30 (2004) 953–971.

[5] S. Hammami, N. Bellakhal, N. Oturan, M.A. Oturan, M. Dachraoui, Degradation of Acid Orange 7 by electrochemically generated $^\bullet$OH radicals in acidic aqueous medium using a boron-doped diamond or platinum anode: a mechanistic study, Chemosphere 73 (2008) 678–684.

[6] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.

[7] G.L. Truong, J. De Laat, B. Legube, Effects of chloride and sulfate on the rate of oxidation of ferrous ion by H_2O_2, Water Res. 38 (2004) 2383–2393.

[8] M. Faouzi, P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M.A. Rodrigo, C. Saez, Advanced oxidation processes for the treatment of wastes polluted with azoic dyes, Electrochim. Acta 52 (2006) 325–331.

[9] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigm. 71 (2006) 236–244.

[10] M. Zhou, Q. Yu, L. Lei, G. Barton, Electro-Fenton method for the removal of methyl red in an efficient electrochemical system, Sep. Purif. Technol. 57 (2007) 380–387.

[11] J. Casado, J. Fornaguera, Pilot-scale degradation of organic contaminants in a continuous-flow reactor by the Helielectro-Fenton method, Clean Soil Air Water 36 (2008) 53–58.

[12] S. Papić, D. Vujević, N. Koprivanac, D. Sinko, Decolourization and mineralization of commercial reactive dyes by using homogeneous and heterogeneous Fenton and UV/Fenton processes, J. Hazard. Mater. 164 (2009) 1137–1145.

[13] K. Jüttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, Electrochim. Acta 45 (2000) 2575–2594.

[14] E. Fockedey, A. Van Lierde, Coupling of anodic and cathodic reactions for phenol electro-oxidation using three-dimensional electrodes, Water Res. 36 (2002) 4169–4175.

[15] E. Brillas, J. Casado, Aniline degradation by Electro-Fenton and peroxicoagulation processes using a flow reactor for wastewater treatment, Chemosphere 47 (2002) 241–248.

[16] A. Lahkimi, M.A. Oturan, N. Oturan, M. Chaouch, Removal of textile dyes from water by the electro-Fenton process, Environ. Chem. Lett. 5 (2007) 35–39.

[17] V. López-Grimau, M.C. Gutiérrez, Decolourisation of simulated reactive dyebath effluents by electrochemical oxidation assisted by UV light, Chemosphere 62 (2006) 106–112.

[18] M.A. Oturan, I. Sirés, N. Oturan, S. Pérocheau, J.-L. Laborde, S. Trévin, Sonoelectro-Fenton process: a novel hybrid technique for the destruction of organic pollutants in water, J. Electroanal. Chem. 624 (2008) 329–332.

[19] M. Sudoh, H. Kitaguchi, K. Koide, Electrochemical production of hydrogen peroxide by reduction of oxygen, J. Chem. Eng. Jpn. 18 (1985) 409–414.

[20] A. Da Pozzo, L. Di Palma, C. Merli, E. Petrucci, An experimental comparison of a graphite electrode and a gas diffusion electrode for the cathodic production of hydrogen peroxide, J. Appl. Electrochem. 35 (2005) 413–419.

[21] Z. Qiang, J.-H. Chang, C.-P. Huang, Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions, Water Res. 36 (2002) 85–94.

[22] A. Da Pozzo, P. Ferrantelli, C. Merli, E. Petrucci, Oxidation efficiency in the electro-Fenton process, J. Appl. Electrochem. 35 (2005) 391–398.

[23] M. Pera-Titus, V. Garcia-Molina, M.A. Baños, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

[24] J.H. Ramirez, F.M. Duarte, F.G. Martins, C.A. Costa, L.M. Madeira, Modelling of the synthetic dye Orange II degradation using Fenton's reagent: from batch to continuous reactor operation, Chem. Eng. J. 148 (2008) 394–404.

[25] J.J. Pignatello, Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.

[26] M.A. Sanromán, M. Pazos, M.T. Ricart, C. Cameselle, Electrochemical decolourisation of structurally different dyes, Chemosphere 57 (2004) 233–239.

[27] A.E. Rodrigues, Theory of residence time distributions, in: A.E. Rodrigues, J.M. Calo, N.H. Sweed (Eds.), Multiphase Chemical Reactors, NATOASI Series, Sijthoff Noordhoff, 1981.

[28] N. Daneshvar, S. Aber, V. Vatanpour, M.H. Rasoulifard, Electro-Fenton treatment of dye solution containing Orange II: influence of operational parameters, J. Electroanal. Chem. 615 (2008) 165–174.