Scale-up of an electrochemical reactor for treatment of industrial wastewater with an electrochemically generated redox mediator

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Abstract

This paper presents the results of a study on the scale-up, from a batch to a continuous flow unit, of an electrochemical reactor applied for the treatment of textile wastewater. Decolourisation of the wastewater bearing a reactive dye Red Procion H-EXGL proceeded via indirect electro-oxidation, mediated by "active chlorine". The kinetics of decolourisation in a single-cell reactor under different operating conditions were second order, with the highest apparent rate constant ($k = 0.523$ l mol^{-1} s^{-1}) achieved at 40 °C. A low Hatta number (Ha = 0.03) indicated that the reaction occurred totally in the bulk solution, hence homogeneous reaction kinetics were used successively to scale-up a continuous flow electrochemical unit: a once-through filter-press reactor. Its hydrodynamic characteristics were defined by the residence time distribution ($E(t)$) function using a pulse injection method. The decolourisation efficiency experimentally determined in a continuous flow reactor was further compared with that predicted on the basis of the knowledge of the $E(t)$ of the reactor and the homogeneous phase kinetic expression, obtained from the batch study and corrected for the geometric parameters of the reactors. A complete segregation of the fluid inside the flow reactor was assumed. For different applied flow rates, the experimentally defined conversion of the dye was close to the calculated value.

1. Introduction

One of the most important technological problems related to the treatment of industrial wastewater is the removal of colour. The dye present at a concentration as low as 1 mg l^{-1} can impart colour to the wastewater and the dye molecules, regardless of their chemical structure, are difficult to treat by biological processes. Considering the above, elimination of colour from textile wastewater can often be accomplished only via chemical oxidation or reduction, and the oxidation of dyes by hypochlorite is conventionally used. This method requires careful control of the pH and a massive dose of hypochlorite, which causes increased salinity of the wastewater. Electrochemical processes offer an excellent alternative for the removal of colour from dye containing effluents, as documented in a vast literature on this topic [1, 2]. When sodium chloride is present in the electrolyte, decolourisation proceeds at high rates with low electric power consumption (e.g., 1.84 kWh were needed to treat one m^3 an indigo polluted solution [2]), showing that electrochemical decolourisation is an economically interesting method of treatment and that chlorine-mediated electrooxidation can be efficient in removing several types of pollutants from industrial wastewater [3–6].

However, despite the fact that electrochemical oxidation mediated by an electrochemically generated redox mediator proved an efficient and cost effective way of the treatment of many hazardous compounds, a full-scale application of this process has yet to be achieved. The main problem in the practical implementation of electrochemical reactors for the treatment of industrial wastewater is related to the difficulty in scaling-up the reactor from the laboratory, usually a batch scale, to a continuous flow unit. The situation is very complex in case of mediated electro-oxidation, as anodic generation of the mediator (that can be mass or charge transport controlled, in function of the applied conditions) is simultaneous to a series of parallel and/or consecutive reactions that occur in the homogeneous phase between the mediator itself, pollutants and the intermediate products of their transformation. This implies that to model the performance of a continuous flow reactor a wide set of values of the kinetic constants and the mass transport coefficients would be necessary. Despite the fact that such a detailed approach is in principle possible, as shown, e.g., for an ethylene chlorination reaction [7] and for an indirect electro-oxidation of aromatic hydrocarbons [8], the complexity of such a model would probably be too high to be applied for the

treatment of wastewater which is a non profit operation. In fact, attempts to find simplified but reliable design procedures for electrochemical reactors treating polluted water were recently envisaged [9]. In particular when the reactions between the electro-generated mediator and pollutants proceed at a rate significantly lower than the transport of the mediator through the diffusive layer near the anode and the homogenous phase reaction can occur mostly, if not totally, in the bulk of the solution, it is possible to neglect the portion of the reaction that takes place in the reaction layer near the anode, and to disregard the mass transfer to and from the electrode in analogy to some fluid–fluid reactions [10]. This leads to a noteworthy simplification of the model and exploring if such a possibility exists when treating polluted effluents is worth undertaking.

This paper presents the results of a study on the application of indirect electro-oxidation, performed in batch and continuous flow reactors, for the treatment of synthetic textile wastewater bearing a reactive dye Red Procion H-EXGL. Previous investigations comparing voltammetric experiments with several electrode materials [11] proved a Ti/Pt-Ir anode, used in the present study, electrocatalytic towards the chlorine evolution reaction under typical experimental conditions characterising textile wastewater and demonstrated a lack of a direct discharge of the studied dye molecule on this material. It was shown that under the conditions adopted here, chlorine-mediated oxidation is responsible for the degradation of the dye.

The present study concerns the kinetics of decolourisation, which was chosen as a priority for electrochemical treatment. It was carried out under different operating conditions in the batch reactor, in order to determine whether the reaction was kinetically or mass transfer controlled, and to define the expression for the scale-up of the reactor. The conversion of the dye in a continuous flow reactor, predicted on the basis of the knowledge of its residence time distribution function $E(t)$ and the kinetic expression obtained in the batch study (corrected for differences in the geometric parameters of the two reactors), is compared with the experimental performance.

2. Experimental

In order to define the best conditions of treatment of the simulated textile wastewater, batch exhaustive electrolysis was carried out in an electrochemical reactor of 0.6 l working volume, equipped with a Ti/Pt-Ir anode and a stainless steel cathode (both 10^{-2} m^2 surface area), at different temperatures and agitation rates. Details of the experimental set-up have been reported previously [11] and the procedure for the preparation of the material used as an anode was described in Ref. 12. The composition of the coating: 70% Pt + 30% of Ir (molar percentage) was chosen considering that for lower quantities of Ir the electrocatalytic properties of the electrode diminish while the higher quantities result in a deterioration of the mechanical properties (in particular the adherence of the coating). An addition of a certain amount of Ir (literature indicates 20% as the minimum quantity) prevents passivation of Pt and ensures that chlorine evolution proceeds at a constant potential for a long electrolysis time.

As a model pollutant a reactive di-azo dye H-EXGL (Dystar) was used due to its low biodegradability and due to the need to propose an alternative efficient method of treatment for the spent dyeing baths. The simulated textile wastewater had the following composition: 0.6 g l^{-1} of the reactive dye Red Procion H-EXGL, 16.25 g l^{-1} NaCl, 2.5 g l^{-1} Na$_2$CO$_3$ and 0.25 g l^{-1} NaOH. The performance of the batch reactor was followed by analysis of pH, total organic carbon (TOC, Shimadzu 5050A Analyser) and colour (absorbency at 535 nm) of the samples withdrawn at regular time intervals.

The batch reactor was under galvanostatic control and the current density was 260 A m^{-2}. The anode potential was measured against a home-made saturated calomel reference electrode (SCE), in a Luggin capillary probe, using a high impedance voltmeter (Keithley 169 Multimeter). The SCE reference electrode has an electrode potential of $+0.245$ V vs standard hydrogen electrode (SHE). The experiments were performed varying the temperature in the range 10–40 °C $\pm$ 1 °C. Isothermal conditions were obtained by using a thermostatic bath (Thermo Haake DC30).

Different hydrodynamic conditions in the batch reactor were provided by pumping by means of a peristaltic pump (Watson Marlow Mod. 313 F/D), and complete recycle of the flow to the reactor. The mean mass transfer coefficient during pumping at the rates of 54 and 108 cm^3 min^{-1} and at quasi-stagnant conditions was equal to 2.3×10^{-5} m s^{-1}, 2.45×10^{-5} m s^{-1} and 2.2×10^{-5} m s^{-1}, respectively (values obtained from the limiting current density of potassium ferricyanide reduction).

Investigation on the scale-up from the batch to a continuous flow reactor comprised the use of a once-through filter-press reactor of which the cross section is shown in Figure 1. The reactor consisted of two discs (external diameter 20.5 cm and 1.5 cm thickness), inside which the electrodes (13.1 cm $\times$ 7.1 cm) were held by internal discs (diameter 18.3 cm and 0.5 cm thickness). The anode and cathode were of the same materials as in the batch reactor. The distance between the electrodes was 1 cm and the liquid volume 93 ml.

A study of the hydraulic characteristics of the reactor comprised a determination of the residence time distribution function ($E(t)$) at three different flow rates. Hydrodynamic tests were carried out using a pulse injection of a tracer and defining the $E(t)$ curve from the concentration curve $c(t)$ [13]:

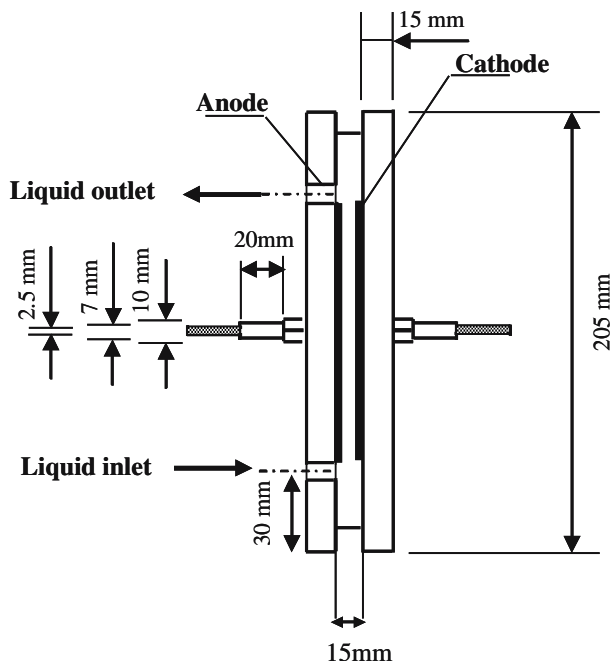$$E(t) = \frac{c(t)}{\int_0^\infty c(t)\mathrm{d}t} \tag{1}$$

Fig. 1. Scheme of the continuous flow electrochemical reactor.

The $E(t)$ function was then used to predict the conversion in the flow reactor.

3. Results and discussion

3.1. Batch reactor studies

Under all experimental conditions no variation of solution pH was observed during the electrolysis and the pH maintained its initial alkaline value (pH $\approx$ 11.5). Regarding TOC, whose initial value was 156 mg l^{-1}, the differences when decolourisation was completed were insignificant and were in the range 2.5–3% at the most. It can be concluded that for the electrolysis conducted at short times, as in the experiments described here, the process does not lead to mineralisation of the dye.

3.1.1. Influence of temperature on the kinetics of decolourisation

Figure 2 shows the decolourisation performance obtained at four different temperatures, ranging from 10 °C to 40 °C. The reactor performance varied with temperature and was best at the highest temperature. Kinetics of decolourisation for all the temperatures were second order, according to

$$\frac{d(abs)}{dt} = -k(abs)C_{Cl_2} \tag{2}$$

where k – second-order rate constant (mol^{-1} l s^{-1}), abs – measured absorbency, C_{Cl2} – concentration of dissolved chlorine (mol l^{-1}). Assuming that the rates of chlorine loss reactions due to the cathodic reduction of "active chlorine", anodic oxidation to ClO$_3^-$ and the quantity
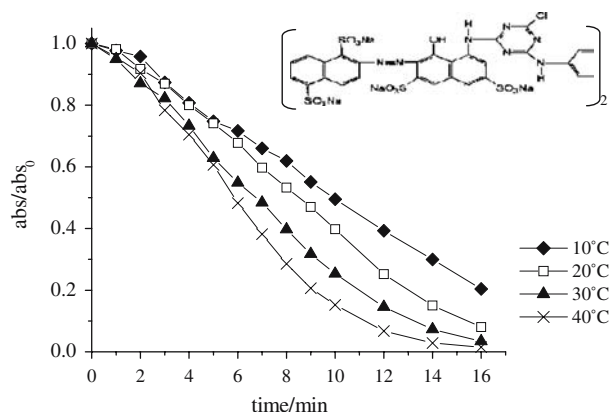

Fig. 2. Influence of temperature on the process rates in a batch reactor (inset-The H-EXGL dye molecular structure).

consumed in the homogeneous reaction with the dye were much lower than the production rate and thus can be considered insignificant, the variation of chlorine concentration with time (till saturation value is reached) can be described by equation:

$$\frac{dC_{Cl_2}}{dt} = \frac{\Phi jA}{nFV} \tag{3}$$

which, after integration, and substituting for Cl$_2$ in the integrated form of Equation 2 gives

$$\ln\frac{(abs)_t}{(abs)_o} = -\frac{k\Phi jAt^2}{4nFV} = -k't^2 \tag{4}$$

with the rate constant k':

$$k' = k\frac{\Phi jA}{4nFV} \tag{5}$$

Values of k' were derived for different temperatures from the slopes of the logarithms of abs$_t$/abs$_0$ vs the square of the time of electrolysis and were used to calculate the second order rate constant k, using Equation 5. Table 1 shows the obtained values of k.

Figure 3 shows the Arrhenius plot of the kinetic rate constant k. The plot indicates an exponential increase in the k value with temperature and suggests that the same reaction mechanism was responsible for the destruction of the dye over the whole temperature range. The high value of the activation energy, $E = 24.13$ kJ mol^{-1}, obtained from the slope of the plot in Figure 3, indicates that decolourisation is highly temperature sensitive and suggests that a correct placement of the electrochemical reactor in the textile industry should be immediately close to the dyeing vessel. As during the Cl$_2$ mediated oxidation the temperature can affect both the homogeneous phase reaction rate constant k and concentration of chlorine (this last decreases due to the decrease in solubility with temperature), it can be expected that the higher the homogeneous rate constant, the more positive the increase in temperature, as under these conditions the quantity of dissolved chlorine used in the reaction will be higher, with the chlorine saturation concentration

Table 1. Values of the kinetic rate constant k and the Hatta number for the batch electrochemical reactor at different temperatures of operation

Temperature/°C	Kinetic rate constant mol^{-1} l s^{-1}	Hatta
10	0.186	0.01
20	0.297	0.02
30	0.399	0.03
40	0.523	0.03

being reached later with respect to the case with a low reaction rate constant. Thus the decrease in solubility of Cl_2 with temperature influences the reaction rate to a minor degree, as has probably been experienced in the present study.

3.1.2. *Location of the reaction zone in the homogeneous phase*

Figure 4 depicts the time-trends of decolourization observed at different pumping rates and a temperature of 30 °C. Similar graphs were obtained for other temperatures, showing that the process rates were essentially independent of the reactor hydrodynamics, in the range of flow and current conditions used.

To define the regime which controls the reaction of decolourization, the Hatta number (Ha) was calculated from [10]:

$$Ha = \frac{\sqrt{k[R]D_{Cl_2}}}{k_m} \qquad (6)$$

where: k – the derived second-order decolourization rate constant (mol^{-1} l s^{-1}); $[R]$ – initial dye concentration (mol L^{-1}); D_{Cl2} – diffusivity of chlorine (m^2 s^{-1}) [14]; k_m – mass transport rate coefficient (m s^{-1}). The values of Ha obtained for operation at different temperatures, given in Table 1, indicate that the reactor was under kinetic control as the homogeneous reaction proved slow by comparison to the rate of transfer of chlorine
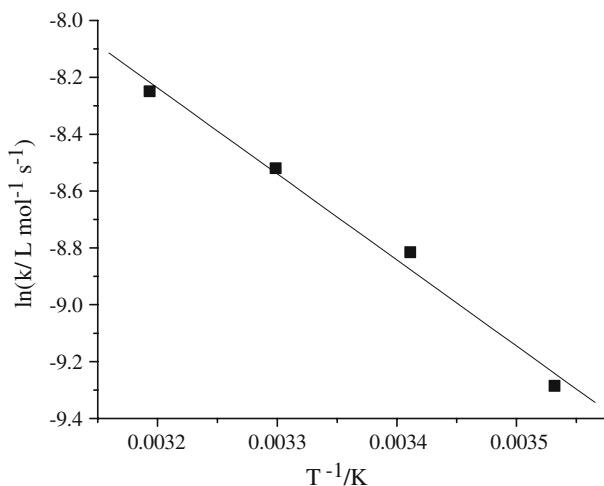

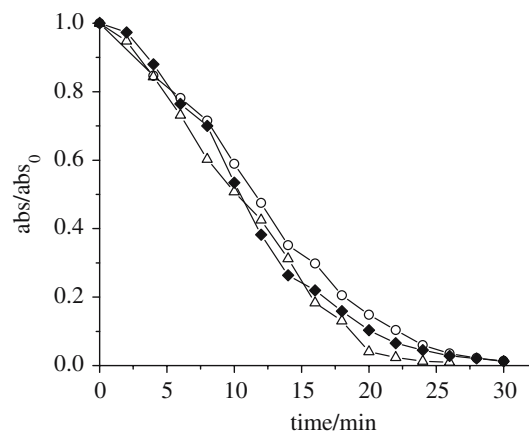*Fig. 3.* The Arrhenius plot of the kinetic rate constant of decolourisation.

Fig. 4. Influence of mixing on the process rates in a batch reactor, recycle rate: $\triangle$ 54 cm^3 min^{-1}; $\bigcirc$ 108 cm^3 min^{-1}; $\blacklozenge$ no recycle.

species from the anode to the bulk solution. Thus, with the reaction occurring mainly in the bulk and not near the electrode, enhancing mass-transport rates in the reactor is not advantageous, as also shown experimentally. These results are in line with the conclusions drawn in previous studies on the chlorine-mediated electro-oxidation of disperse dyes [15].

On the basis of the above results it can be concluded that the reactor can be modelled using homogeneous kinetics.

3.2. *Continuous flow reactor*

3.2.1. *Residence time distribution function*

The knowledge of fluid flow conditions in real reactors is fundamental, as their hydrodynamic behaviour rarely corresponds to ideal plug-flow or perfect mixing. Generally a filter-press reactor is modelled as a plug-flow (PFR) and a continuously stirred tank reactor (CSTR) in series, the latter accounting for the inlet and outlet effects [16, 17]. Such an approach assumes that the observable dispersion occurs only in the direction of the fluid flow with no radial dispersion. Considering that the reactor used in the present study was characterized by the length $L = 7.1$ cm and with $B = 13.1$ cm ($L < B$), so its geometry was far from the ideal PFR, other defects of the flow pattern could be envisaged and the reactor $E(t)$ function was defined experimentally using a pulse injection method. The values of the tracer concentration were analysed at the outlet of the reactor with a sampling frequency of 30 s. Using Equation 1, the $E(t)$ function was calculated for the flow rates of 6.8, 13.6 and 17.3 cm^3 min^{-1}. The $E(t)$ function was then modelled using a parametric curve:

$$E(t) = \frac{1}{\bar{t}} \cdot f \cdot \frac{N^N}{(N-1)!} \cdot \beta^N \cdot \left(\frac{t}{\bar{t}}\right)^{N-1} \cdot e^{-N\cdot\beta\cdot\frac{t}{\bar{t}}} + \frac{1}{\bar{t}} \cdot (1-f)$$

$$\cdot \frac{M^M}{(M-1)!} \cdot \left(\frac{\beta}{\alpha}\right)^M \cdot \left(\frac{t}{\bar{t}}\right)^{M-1} \cdot e-M\cdot\frac{\beta}{\alpha}\cdot\frac{t}{\bar{t}} \qquad (7)$$

with N, f and β being a function of the flow rate. Examples of the experimental and modelled RTD ($E(t)$) curves are shown in Figure 5 for the different flow rates.

3.2.2. *Performance of the filter-press reactor and its modelling*

The continuous filter-press reactor was used at 40 °C and 200 A m^{-2} current density, as at higher currents development of gas bubbles caused an interruption of the flow. The performance of the reactor for decolourisation at the three flow rates is depicted in Figure 6.

For each flow rate the dye conversion was calculated on the basis of the information gained from the relative $E(t)$ function. For this modelling purpose the first and second moment of the experimental $E(t)$ curves were calculated respectively, from [13]:

$$M_1 = \tau = \int_0^\infty tE(t)\mathrm{d}t \qquad (8)$$

$$M_2 = \sigma^2 = \int_0^\infty (t-\tau)^2 E(t)\mathrm{d}t \qquad (9)$$

The reactor was treated as a closed–closed vessel and the Pe$_r$ number was calculated [13] from:

$$\frac{\sigma^2}{t_m^2} = \frac{2}{\mathrm{Pe}_r} = \frac{2}{\mathrm{Pe}_r^2}(1 - e^{-\mathrm{Pe}_r}) \qquad (10)$$

using a "trial and error" method. The values of Pe$_r$ were 6.7, 5.7 and 3.9, respectively, for flow rates of 6.8, 13.6 and 17.3 cm^3 min^{-1}.

The conversion X of the dye was calculated, for each flow rate, on the basis of the Pe$_r$ value determined above, from [13]:

$$X = 1 - \frac{4q\,\exp(\mathrm{Pe}_r/2)}{(1+q^2)\exp(\mathrm{Pe}_r q/2)(1-q^2)\exp(-\mathrm{Pe}_r q/2)} \qquad (11)$$

where: $q = \sqrt{1 + 4D_a/\mathrm{Pe}_r}$ and D_a(Damköhler number) $= k[R]\tau$.

The values of the kinetic rate constant in Equation 11 were taken from the batch experiment and were corrected to consider the difference in specific area of the anode in the batch and filter-press reactors, which was equal to 0.167 and 1 cm^{-1}, respectively, for the two reactors.

The values of conversion obtained from Equation 11 for the reactor operating at flow rates 6.8, 13.6 and 17.3 cm^3 min^{-1} and the mean observed conversions are
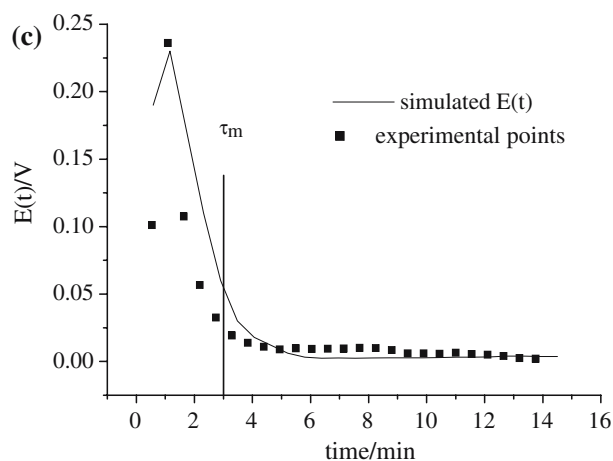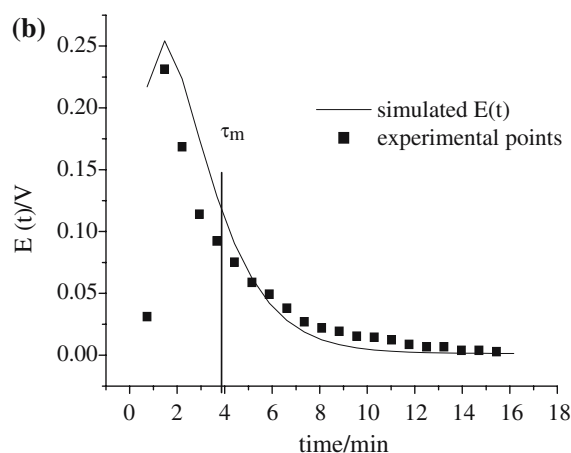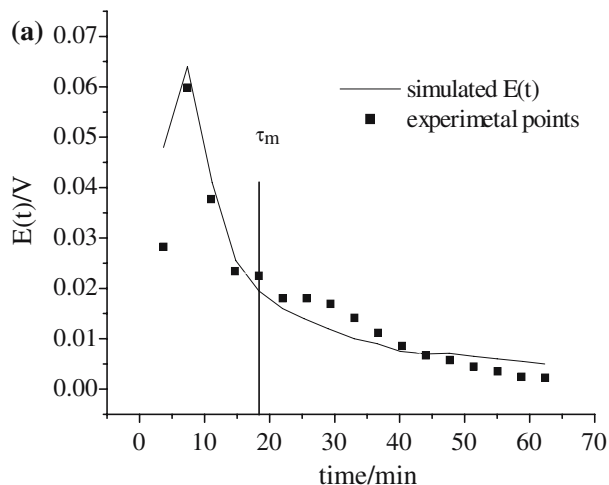
Fig. 5. Experimental and modelled RTD curves at different flow rates: (a) 6.8 cm^3 min^{-1}; (b) 13.6 cm^3 min^{-1}; (c) 17.3 cm^3 min^{-1}.
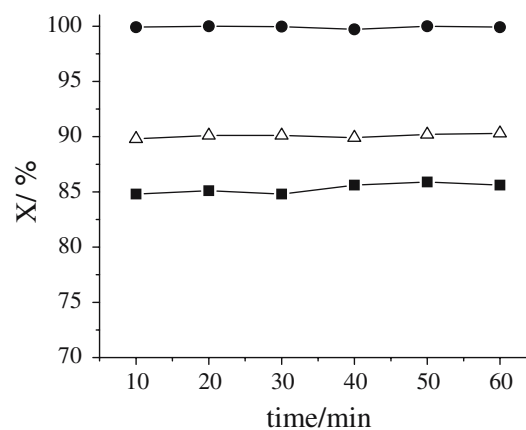
Fig. 6. Performance of the filter press reactor at different flow rates: ● 6.8 cm^3 min^{-1}; △ 13.6 cm^3 min^{-1}; ■ 17.3 cm^3 min^{-1}.

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Table 2. Calculated and mean observed conversion of the dye in the continuous flow reactor at different flow rates

Flow rate/cm^3 min^{-1}	X calc/%	$\bar{X}$obs/%
6.8	99.9	100
13.6	90.8	90.3
17.3	79.9	85.0

reported in Table 2. The experimental results and the performance of the reactor modelled using the $E(t)$ curve and homogeneous phase kinetics are reasonably close. Considering that for Ha^2 < 0.02 the fluid–fluid reactions can be regarded as infinitely slow, this approach would be valid for pseudo-first order reactions characterised by $k < 1 \times 10^{-3}$ s^{-1}, which is the case for the majority of environmental applications of electrochemical oxidation mediated by a Cl$^-$/Cl$_2$ redox couple.

4. Conclusions

This study shows that the performance of the electrochemical reactor treating industrial wastewater via the process based on Cl$^-$/Cl$_2$ mediated electro-oxidation can be quite accurately predicted using a model based on the residence time distribution of the fluid flow, provided the reactor performance is controlled by the homogeneous reaction kinetics. Considering that the removal of pollutants is generally characterised by slow kinetics and a low bulk concentration, this approach may often be valid when of electrochemical reactors are applied to environmental problems.

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