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ELECTROCHEMICAL REDUCTION-ADSORPTION PROCEDURE FOR THE REMOVAL OF NITROPHENOL CONTAMINANTS FROM AQUEOUS MEDIA

MIHAELA-CLAUDIA TERTIS[a], MARIA JITARU[a], VIRGINIA COMAN[b], MIUTA FILIP[b], DANIEL A. LOWY[c]

ABSTRACT. Work reported here was performed with the goal of reducing the concentration of 4-nitrophenol (4-NP) and 2,6-dinitrophenol (2,6-DNP), present in synthetic solutions to values below 0.5 mg L^{-1}, the maximum concentration level tolerated by international environmental regulations [1, 2]. In the electrochemical reduction of 4-NP the final product was 4-aminophenol, as assessed by HPLC. Three methods were used for decreasing 4-NP and 2,6-DNP concentrations: electrochemical reduction, adsorption on active carbon, and the combined electrochemical reduction-adsorption. Best results were obtained by applying the combined procedure, which employed as the cathode granular activated carbon in fluidized bed. In these experiments 95-97% removal of 4-NP and 2,6-DNP from solutions occurred within the first 20 min.

Keywords: nitrophenol removal, electrochemical reduction, removal by adsorption, activated carbon, fluidized bed cathode.

INTRODUCTION

Nitrophenols (NPs) are important and versatile organic compounds used in industrial, agricultural, and defense applications. They serve frequently as intermediates in the manufacturing of explosives, pharmaceuticals, pesticides, pigments, dyes, and rubber chemicals [3]. Because they are very toxic to humans and animals, their monitoring is essential in environmental pollution control. In order to avoid environmental water pollution, the European Council Directive "Dangerous Substances Directive 67/548/EEC" of 2006 [2] enforces low concentrations of nitrophenols (below 0.5 mg L^{-1}).

A variety of treatment technologies are being explored or already used for the removal of nitrophenols from wastewater. These methods belong to several types, such as *physical procedures*, such as adsorption on solid

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[a] *Research Center LAF-INT-ECOL, Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, 11 Arany Janos Street, 400028; e-mail mjitaru@chem.ubbcluj.ro*

[b] *Chemical Research Center (ICCRR), "Babes-Bolyai" University, 30 Fantanele Street, Cluj-Napoca, Romania, e-mail v.coman@iccrr.ro*

[c] *Davia Corporation, 13255 Revilo Loop, Woodbridge, VA 22191, USA, e-mail: daniellowy@davia.biz*

adsorbents, including non-porous carbon blacks [4], granular activated carbon and hyper-cross-linked polymer resins [5, 6], methacrylate based adsorbents [7], anion-cation modified palygorskites [8], or natural linear polysaccharides, e.g., alginate extracted from marine brown algae [9]. As of today, activated carbon is the most widely used adsorbent in wastewater treatment [10, 11]. Given that it is an expensive material for large-scale application, search is directed toward identifying low-cost and widely available adsorbents, such as zeolites, biosorbents, and clays [12-16]. Next one has c*atalytic* and *photocatalytic* procedures, ranging from photocatalytic ozonation, ozonation, and catalytic ozonation to photocatalysis and photolysis, all conducted on TiO_2 in the presence of visible/UV light [17]. Photocatalytic degradation of NPs yielded improved results on TiO_2 modified with a thin layer of molecular imprinted polymer, where the polymer provides molecular recognition ability toward the template molecules [18], a process, which has been shown to occur via a charge-transfer-complex-mediated pathway [19]. A group of *biological* methods typically consist in biodegradations conducted in an aerobic sequencing batch reactor [20, 21], while *electrical* techniques showed useful upon applying various types of pulsed electrical discharges, the most efficient being the pulsed corona discharge in humid air above the water [22]. Several electrochemical methods belong to oxidations and reductions, which can be driven as a direct or mediated process. Examples include, but are not limited to electro-oxidation of nitrophenols on tantalum substrate born-doped diamond electrode [23, 24-26], degradation by electrochemical oxidation on lead oxide/ titanium modified anodes [27]. Electrochemical treatment is promising for waste waters containing organics that are not biodegradable, where, in most cases, total mineralization of the organic compounds can be accomplished [26, 28]. For example, by the electrochemical reduction of NP, the aromatic nitro group undergoes conversion to aromatic biodegradable amines [29]. Finally, reported in the literature is a limited number of *combined procedures*, which exploit the synergic effect of applying two procedures in an integrated device; for example oxidation and adsorption were utilized simultaneously in a device performing ozonation and adsorption on activated carbon [30].

Owing to its high surface area, low specificity, and fast adsorption kinetics, activated carbon remains the most effective adsorbent for organic contaminants [31]. Therefore, when designing our combined procedure, we built on the favorable properties of activated carbon, exploiting not only its adsorptive capacity, but also its good electric conductivity, which enables its use as an electrode in an electrochemical cell. When activated carbon is introduced in an electrochemical reactor, operated in the fluidized mode, the reactor becomes a fluidized electrochemical reactor in which electrochemical conversions (reduction or oxidation) and adsorption are integrated in one combined procedure.

There are only a few reports in the literature on the treatment by combined electrochemical and adsorption methods of biorefractory nitrophenol derivatives. Papers published so far refer exclusively to the combined treatment of 4-nitrophenol, a procedure, which consists of adsorption associated with electrochemical oxidation [32-34].

Work described here discloses preliminary results obtained in the removal of nitrophenols from solutions, by utilizing the combined procedure of adsorption-electrochemical reduction (Ads+ER) on activated carbon. The goal of the research was to reduce 4-NP and 2,6-DNP concentrations in synthetic solutions to the low values enforced by environmental legislation. Also, we assessed the advantages of using the combined procedure as compared to the individual techniques of electrochemical reduction (ER) or adsorption on active carbon (Ads).

RESULTS AND DISCUSSION

1. Preliminary determinations

1.1. UV-Visible spectrophotommetry

We determined spectral and calibration data for treated nitrophenol derivatives in water by UV-visible spectrophotometry. Results were reported in a previous paper [35]. Optimal ranges of nitrophenols concentrations for UV-vis spectrophotometry are:

0.15 ÷ 15 mg L^{-1} for 4-NP (maximum accepted level 0.33 mg L^{-1});
0.2 ÷ 20 mg L^{-1} for 2,6-DNP (maximum accepted level 0.5 mg L^{-1}).

1.2. Cyclic voltammetry

Voltammetric properties and calibration data of treated nitrophenols were determined by cyclic voltammetry (CV). The supporting electrolyte was 1 mol L^{-1} aqueous sodium phosphate buffer (pH 4). For 4-nitrophenol we found a linear relationship between I_p and concentration, in the range from 0.001 to 1.5 mg L^{-1}, with the regression coefficient 0.9935. Statistical treatment of ten CV scans yielded standard deviations of 3.20% and a relative error of 3.05%. In the case of 2,6-dinitrophenol, we found a linear relationship of I_P vs. concentration for both peaks; the linear range encompassed 0.002 ÷ 2 mg L^{-1}, with excellent regression coefficients (0.976 respective 0.9912). The relative standard deviation calculated for ten scans was 2.8%, while the relative error was 1.85%.

The electrochemical reduction of both nitro group in the case of 2,6-DNP takes place easier ($E_{P,1}$ = -0.37 V vs. Ag/AgCl,KCl; $E_{P,2}$ = -0.55 V vs. Ag/AgCl,KCl*)* comparing to 4-NP (E_P = -0.65 V vs. Ag/AgCl,KCl).

1.3. High performance liquid chromatography (HPLC)

HPLC determinations are important, as they allow for determining the final composition of the solutions yielded by the electrochemical process. The HPLC diagram of 4-NP and the corresponding amine is shown in Figure 1, while Figure 2 displays the HPLC diagram of 2,6-DNP. Retention times indicate that the mixture components are well resolved; we found 2.503 min for 4-aminophenol, 3.670 min for 2,6-DNPl; 11.89 min for 4-NP. Consequently, HPLC can be used for determining the composition of solutions obtained in the electrochemical treatment of nitrophenol derivatives.

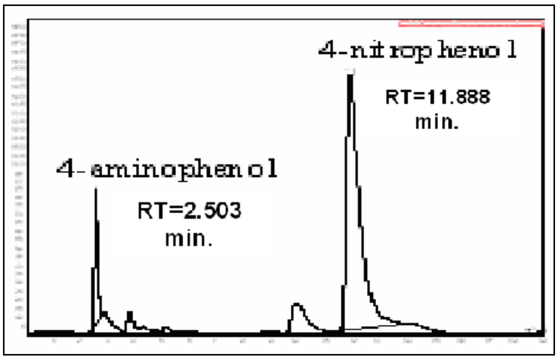


Figure 1. HPLC of the mixture of 4-aminophenol and 4-nitrophenol (1:1, v/v)

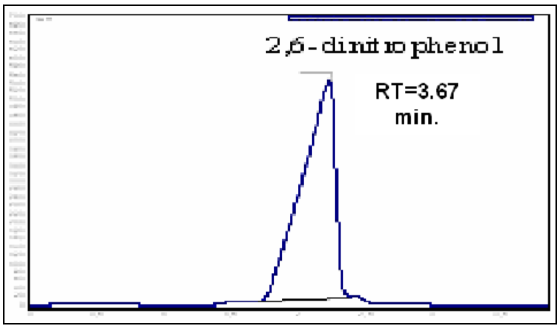


Figure 2. HPLC of 2,6-DNP (0.25 mg mL^{-1}).

2. Electrochemical reduction experiments

Electrochemical reduction experiments of nitrophenols were performed in 3 different electrochemical reactors, under various hydrodynamic conditions, and in dissimilar supporting electrolytes. Most results were discussed in detail in our previous publications [36-38]. Results are summarized in Figure 3.

Best results for electrochemical reduction of 4-NP were obtained in an electrochemical micro-flow cell (experimental setup A), on nickel cathode (98% of 4-NP removal). In the case of 2,6-DNP satisfactory results were obtained at low concentrations only (experimental setup C; 99% of 2,6-DNP removal). The experimental setups characteristics are presented in experimental section.

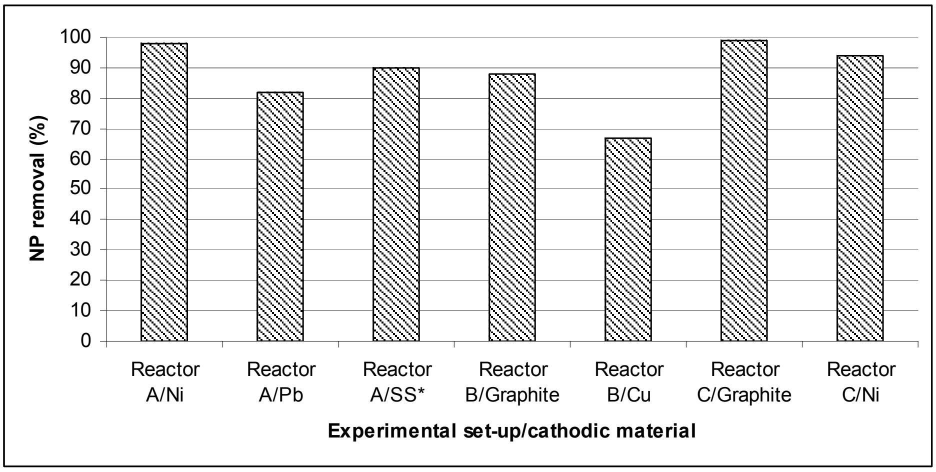


Figure 3. Synoptic presentation of nitrophenols (NP) removal experiments by the mean of electrochemical reduction in different electrochemical reactors.
* SS – stainless steel.

3. Combined procedure for the removal of nitrophenols

3.1. Batch tests

In order to evaluate the advantages of supplementing activated carbon to the electrochemical reactor, we used the same reactor for comparing the removal of nitrophenol derivatives by (i) adsorption, (ii) electrochemical reduction, and (iii) their combined process, respectively.

In Figure 4 the efficiency (η) of nitrophenol removal expressed in %, is plotted versus time. When utilizing the combined process, η reaches high values within significantly shorter time than in the individual processes. Thus, in the combined procedure, after 30 min 95% of 4-NP is removed from the solution, as compared to only 43% in adsorption and 21% in electrochemical reduction (see Figure 4a). The efficiency of removal for 2,6-DNP is of 97% in combined procedure, as compared to only 66% in adsorption and 27% in electrochemical reduction (Figure 4b).

Total organic carbon (TOC) determinations supported the results of spectrophotometric measurements. Variation of TOC values over time is displayed in Figure 5, for 4-NP, Figure 5 (a), and 2,6-DNP, Figure 5 (b). In both cases we compare removal processes by simple adsorption on active carbon, by electrochemical reduction on graphite cathode, and by the combined (Ads + ER) procedure.

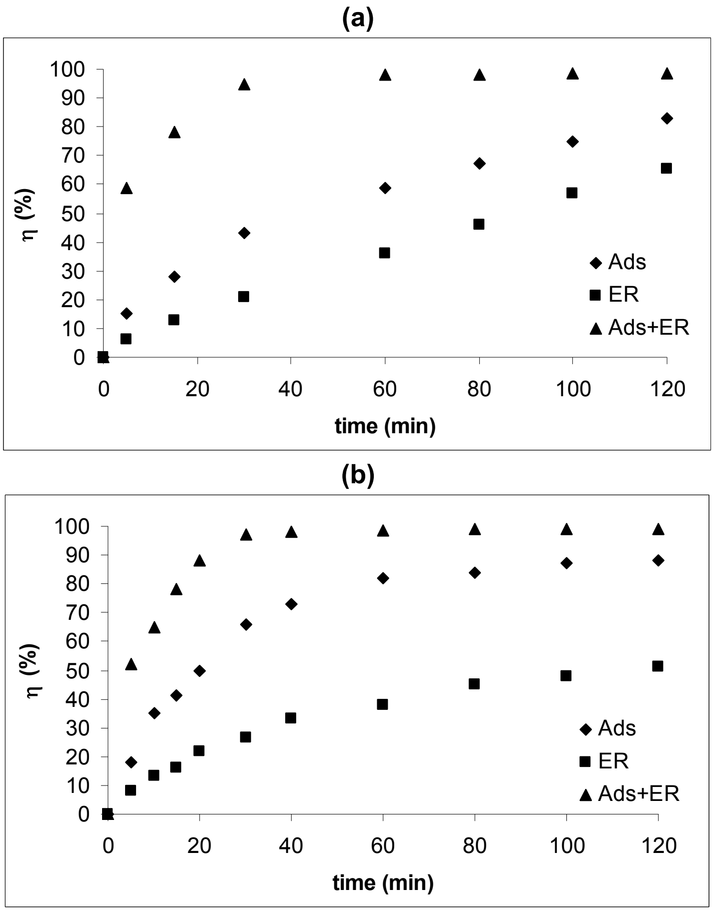


Figure 4. Comparison of the removal efficiency, η, by adsorption (Ads), electrochemical reduction (ER), and their combined process (Ads + ER) for (a) 4-NP and (b) 2,6-DNP

3.2. Electrochemical removal of nitrophenol on cathodes of activated carbon in fixed bed

After the batch tests, experiments were performed using electrochemical reactor type B, with fixed bed of activated carbon type NORIT ROW 0.8 mm pellets, employed as the cathode, while Ti plates were used as the anode.

Figure 6 (a) and 6 (b) present the variation of absorbance over time in 4-NP and 2,6-DNP removal, respectively. Results were obtained with the combined (Ads + ER) procedure. Removal of nitrophenols from the solutions was completed very fast. Hence, within the initial 20 min 94% of 4-NP 92% and of 2,6-DNP, respectively, were removed.

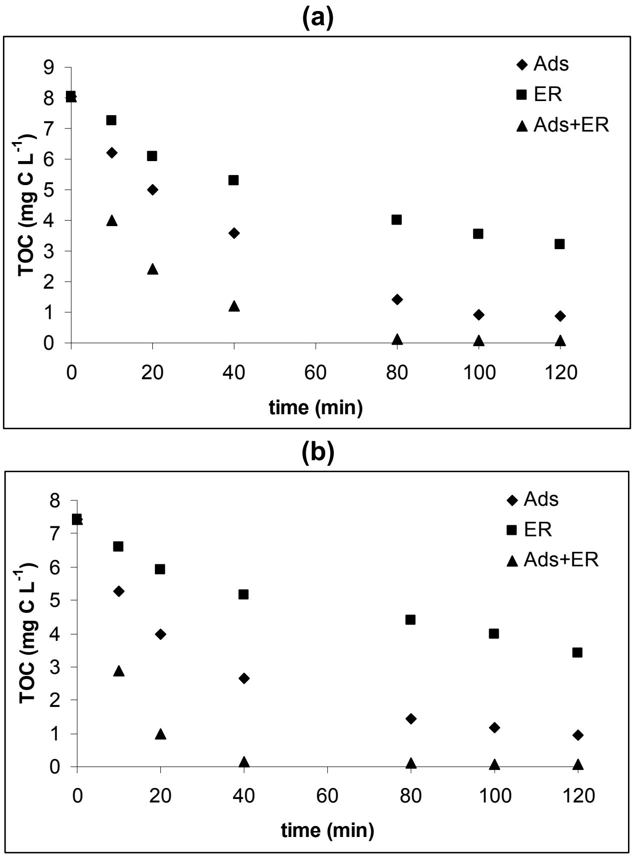
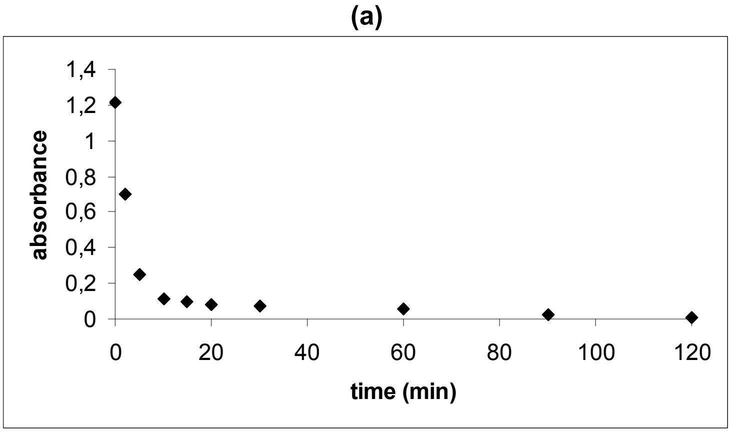


Figure 5. Comparison of TOC variation over time for: (a) 4-NP and (b) 2,6-DNP removal by adsorption, electrochemical reduction, and their combined process.



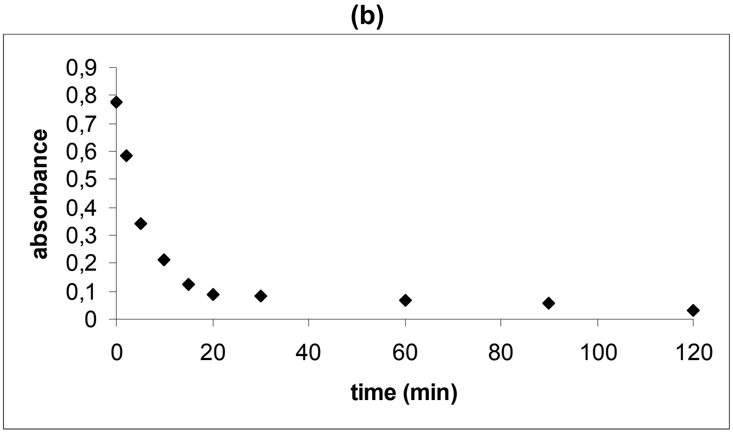


Figure 6. Absorbance variation over time for the removal of (a) 4-NP (λ = 317nm) and (b) 2,6-DNP (λ = 417nm) by the combined procedure of adsorption + electrochemical reduction on activated carbon fixed bed cathode.

CONCLUSIONS

Work reported in this paper attempted reducing the concentration of 4-nitrophenol and 2,6-dinitrophenol present in synthetic solutions below 0.5 mg L^{-1}, which is the maximum concentration tolerated by international environmental regulations. UV-vis spectrophotometry, cyclic voltammetry, total organic carbon (TOC) determination, and HPLC were useful techniques for monitoring the removal of nitrophenols from aqueous solutions. In the electrochemical reduction of 4-NP the final product was 4-aminophenol. In HPLC, 4-aminophenol and 4-nitrophenol were well separated, yielding symmetrical peaks; hence this method is efficient for determining the two compounds in mixture, 4-aminophenol being the final product in the electrochemical reduction of 4-NP. Also, HPLC enables for detection limits of less than 3 ng L^{-1}.

Three avenues were explored toward decreasing the concentration of nitrophenols: electrochemical reduction, adsorption on active carbon, and the combined electrochemical reduction-adsorption. Best results were obtained by applying the combined procedure, which employed as the cathode granular activated carbon in fluidized bed. Experiments performed by this combined technique secured 95-97% removal of 4-nitrophenol and 2,6-dinitrophenol from solutions within the first 20 min.

EXPERIMENTAL SECTION

Reagents and solutions preparation

4-Nitrophenol (purity >98%, Merck, Germany) and 2, 6-DNP (purity >95%, calculated based on dry substance, moistened with 20% H_2O, Aldrich, Switzerland) were used to prepare the solutions of desired concentration.

Distilled water was used to prepare the aqueous solutions. All other reagents were analytical grade, and used without further purification.

Two adsorbents were used: granular activated carbon type NORIT GAC 1240W, (Netherlands) with the following characteristics: micropores volume: 0.38 cm^3 g^{-1}; specific area: 1062 m^2 g^{-1}; mesopores volume: 0.45 cm^3 g^{-1}; apparent density: 495 kg m^{-3}; and steam activated NORIT ROW 0.8 mm pellets. Prior to use, activated carbon was washed several times with deionized water, dried for 24 h to constant weight at 105 ^oC, and kept in a desiccator until it cooled to room temperature, so that re-adsorption of moisture before use was prevented.

Experimental setups

Electrochemical reduction experiments were carried out by means of three different experimental setups.

Experimental setup (**A**) consisted of a commercially available electrochemical filter press cell (Electrocell AB, Sweden). It was used as a micro-flow cell, being equipped with a DSA-O_2 anode (20 cm^2 area) and a cathode made of nickel, copper, lead, or stainless steel (20 cm^2 area). The compartments of the electrochemical cell were separated with a Nafion 117 Millipore proton-exchange membrane. This filter press cell was inserted into a hydraulic circuit, which comprised a GILSON MINIPULS 3 peristaltic pump for circulating the electrolyte in the compartments of the cell, at flow rates in the range from 1 x 10^{-6} to 3.3 x 10^{-3} L min^{-1}. In addition, experimental setup (**A**) had two glass reservoirs for the anolyte and catholyte, respectively.

Experimental set-up (**B**) was an undivided electrochemical reactor, with a volume of 1500 cm^3, equipped with a pump, which operated at the flow rate of 1.2 L min^{-1}. Two stainless steel anodes (212.3 cm^2 projected geometric surface area) and a graphite or copper cathode (185.7 cm^2) served for electrodes.

Experimental set-up (**C**) was an electrochemical reactor made of glass, and equipped with Ti/Pt-Ir anode and graphite or nickel cathode, each having a projected geometric surface area of 100 cm^2. A Nafion 117 Millipore cation exchange membrane was inserted between the half-cells. A WATSON MARLOW Mod.313 F/D peristaltic pump with two heads operated under conditions of full recycle, at flow rates in the range from 0.090 to 1.4 L min^{-1}. In all performed experiments Setups (**A**-**C**) described above were operated under galvanostatic conditions. Further details on the experimental equipment were reported in previous work [36].

The combined electrochemical reduction-adsorption procedure on activated carbon was first performed in a batch reactor, described in other work [37]. This reactor comprised a glass container (1 L volume), a titanium anode with oxide coating (grid; active surface: 47 mm x 65 mm) and a graphite cathode (active surface 47 mm x 65 mm). A known mass of activated carbon was introduced into the reactor before start up, and a magnetic stirrer allowed for maintaining the activated carbon in suspension (350 rpm). In each experiment we treated a volume of 0.5 L synthetic wastewater, containing 10^{-4} mol L^{-1} 4-NP or 2,6-DNP in sodium phosphate buffer solution, adjusted with H_3PO_4 to pH 4. Experiments were performed under galvanostatic conditions, at the current density of 20 mA cm^{-2}. Minor adjustments of the applied voltage (cell voltage was around 5 V) were needed for keeping the current density constant over the duration of experiment. At appropriate time, 3 mL of sample was taken for analysis. The stirring was stopped for 5 s during the sampling, and after measurements the sample was reintroduced into the batch reactor. All experiments were performed at constant temperature (20 ± 2 ^{o}C).

After completing preliminary batch experiments, the combined procedure was performed in experimental set-up (**B**), described above, but in this case the cathode was a fixed bed of activated carbon, type NORIT ROW 0.8 mm pellets.

Electrolysis efficiency was monitored by sampling the electrolyte over time, and analyzing the concentration of residual reagents by voltammetry, spectrophotometry, as well as by TOC and HPLC measurements.

Methods

Spectrophotometric measurement was carried out with a Unicam Helyos B spectrophotometer, with VISION 32 software, and a quartz vat of 2 mL, an optical path length of 1 cm, and a Direct Reading Spectrophotometer type DR/2800 HACH-LANGE with a quartz vat of 2 mL and an optical path length of 1 cm.

TOC determinations performed with a TOC-DR2800 HACH-LANGE spectrophotometer, using Lange TOC cuvette test type LCK 385 (in the concentration range from 0 to 30 mg L^{-1}) and LCK 386 (in the concentration range from 30 to 300 mg L^{-1}).

HPLC separations were accomplished with a JASCO 980 chromatograph equipped with Intelligent UV-VIS Detector JASCO UV-980-975, with specific software CHROMPASS; stationary phase: NUCLEOSIL 120C18 (5 μm, 25 x 0.46 cm) column; mobile phase: MeOH–H_2O–H_3PO_4 (30:70 ± 0.1, v/v); flow: 1 mL min^{-1}; detection at $\lambda = 280$ nm; the column temperature 21 °C.

Voltammetry was recorded with a Model 630C potentiostat-galvanostat system (CH Instruments, Austin, Texas), and data processed with the software of the instrument. Experiments were conducted in 3-electrode geometry, with glassy carbon working electrode (active surface of 0.0125 cm^2), a platinum plate auxiliary electrode, and Ag/AgCl, 3 M KCl electrode reference. All measurements were carried out in a glass cell, containing 5.0 mL of solution, without stirring. The supporting electrolyte was aqueous sodium phosphate buffer, adjusted to pH 4. Prior to each measurement the electrolyte was degassed with nitrogen for 15 min and the scans were recorded under N_2 blanket. The optimized parameters in cyclic voltammetry were found to be: scan rate of 0.1 V s^{-1} in the potential range from 0 and -1 V vs. Ag/AgCl, 3 M KCl.

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