Electrochemical oxidation of 2-chloroaniline in single and divided electrochemical flow cells using boron doped diamond anodes

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ABSTRACT

Electrochemical oxidation (EO) using boron-doped diamond (BDD) electrodes attracted increasing interests due to its high efficiency in mineralizing chlorinated organic pollutants in water. However, it produces hazardous disinfection by-products (DBPs) including chloramines, chlorate and perchlorate ions and discharges acidic streams. In this work, an attempt to neutralize the acidic effluent and reduce the production of DBPs was developed. To do that, the EO of 2-chloroaniline (2-CA) in single and divided electrochemical flow cells using BDD anode and stainless steel cathode was investigated. The results showed that complete degradation of 2-CA and high mineralization yields were achieved using single and divided compartment cells. The separation of anolyte and catholyte by anion exchange membrane (AEM) in divided electrochemical configuration enhanced the efficiency of the electrochemical treatment and reduced the energy consumption; while, higher concentrations of free chlorine, nitrate, chlorate, and perchlorate ions were generated in the anolyte. A post-treatment of the treated solution in the cathodic compartment at low current density was effective in reducing the amount of free chlorine and chlorate ions, transferring chloride and nitrate ions to the anodic compartment by electro-dialysis, and neutralizing the anolyte and catholyte. Divided electrochemical cell configuration has the potential to achieve more efficient treatment of 2-CA for the recovery of valuable by-products (which can be considered as a powerful synthetic tool, from an environmental point of view; to produce high-added value products).

1. Introduction

Aniline and its derivatives constitute a class of organic molecules frequently detected in industrial discharges [2,80]. In fact, aniline, chloroanilines and nitroanilines constitute the raw material for the synthesis of isocyanate phenyls [58], which are intermediates used in the manufacture of polyurethanes [75]. Other main uses of aniline and its derivatives include the manufacture of polymers including conductive polymers [1,17,22,38] and rubbers [71], the synthesis of herbicide and pesticides [11,70], the production of dyes and paints [51]. These substances are also used in the manufacture of pharmaceutical products [9,30], resins [31], perfumes [46], products used in the photographic field (hydroquinone) [64], diphenylamine [29] and other phenolic and cyclic products [27]. A deep literature survey confirmed that aqueous effluents containing these aromatic amines constitute a hazard to human health and the environment [18,34,73]. These substances are recognized by their recalcitrance and bio-resistance [54]. Several methods were proposed to treat aniline-contaminated wastewaters. Among these methods can be cited biodegradation [76,81], photocatalytic degradation [13,26], wet air catalytic oxidation [55,59], ultrasonic degradation [15], decomposition in supercritical conditions [41], ozonation [21,69,77], advanced oxidation processes (AOPs) [8,14,39,45,78], and electrochemical techniques [4,12,42–43,68]. Although promising success was obtained related to the degradation of aniline and its derivatives, the efficiency of these processes depends on several factors (composition, concentration, pH, temperature, etc.), the costs and energy requirements are high, and pre- and/or post-treatments are needed in many cases.

EO using non-active electrodes has attracted a growing attention as potential technology to treat water and wastewater contaminated with recalcitrant pollutants [50,56,72]. This technology use electrons as the only reactants to degrade organic pollutants and then can be easily
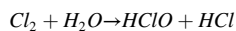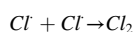
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integrated with renewable energy sources qualifying it to be a sustainable and green technology [25,23]. Especially, thin film boron-doped diamond (BDD) anode has been distinguished from other active electrodes by the chemical and electrochemical stability and the competency to electrogenerate large quantity of free hydroxyl (HO$^\bullet$) radicals from water oxidation at BDD anode (Eq. (1)) [35,47,53]. Being weakly adsorbed on BDD electrode surface, unstable and powerful oxidizing agents, the electrogenerated HO$^\bullet$ radicals are able to immediately and non-selectively attack pollutants in water and decompose them into biocompatible substances[28,48,60].

$$H_2O \xrightarrow{BDD} BDD(HO^.) + 1e + H^+ \tag{1}$$

Further to the electrogeneration of HO$^.$ radicals, EO using BDD anode can produce other oxidizing radical species among them hydroperoxyl (HO$_2$) and sulfate (SO$_4^{-.}$) radicals [16,24,36]and strong oxidants (persulfate [20,52] peroxodiphosphate [67], and percarbonate [66] ions, free chlorine [63], O$_3$ [53], H$_2$O$_2$ [32], ferrate [6] from the oxidation of water and supporting electrolyte (Eqs. (2)–(10)). It was demonstrated that these oxidizing reagents contribute effectively in the degradation of organic pollutants by EO using BDD anodes [6,32].

$$SO_4^{2-} \xrightarrow{BDD} BDD(SO_4^{-.}) + 1e \tag{2}$$

$$SO_4^{2-} + HO^. \rightarrow SO_4^{-.} + HO^- \tag{3}$$

$$2SO_4^{2-} \xrightarrow{BDD} S_2O_8^{2-} + 2e \tag{4}$$

$$2HO^. \rightarrow H_2O_2 \tag{5}$$

$$2H_2O \xrightarrow{BDD} O_2 + 4e + 4H^+ \tag{6}$$

$$3H_2O \xrightarrow{BDD} O_3 + 6e + 6H^+ \tag{7}$$

$$Cl^- \xrightarrow{BDD} BDD(Cl^.) + 1e \tag{8}$$

$$Cl^. + Cl^. \rightarrow Cl_2$$

$$Cl_2 + H_2O \rightarrow HClO + HCl$$

$$2PO_4^{2-} \xrightarrow{BDD} P_2O_8^{2-} + 2e \tag{9}$$

$$2CO_3^{2-} \xrightarrow{BDD} C_2O_6^{2-} + 2e \tag{10}$$

Several challenges including the production of hazardous by-products and the high costs of manufacturing BDD electrodes still to be overcame to reach the commercialization of BDD-based electrochemical technologies for water treatment in large scale [50]. The focus on searching alternative electrode materials could solve the drawbacks of BDD-based electrochemical technologies. Another important approach related to the separation of the electrochemical cell by ion exchange membranes is not well explored. This approach can enhance the efficiency of the treatment by minimizing the loss of electrogenerated oxidants, reduce the costs by decreasing the specific energy consumption, and improve the quality of treated water through better selectivity.

This work aims to investigate the EO of 2-chloroaniline (2-CA) in sulfate medium using single and divided compartment cells. The extent of 2-CA degradation was measured by the decrease of chemical oxygen demand (COD), total organic carbon (TOC) and the increase of organic (2-CA, oxalic, maleic, oxamic acids) and inorganic ions (chloride, nitrate, ammonium) concentrations. The effect of introducing an anion exchange membrane to separate the anodic and cathodic compartments on the EO of 2-CA aqueous solutions and the formation of by-product were evaluated.

2. Materials and chemicals.

2.1. Chemicals.

2-chloroaniline (2-CA, C$_6$H$_4$NH$_2$Cl) was received in analytical grade (≥99.5%) from Sigma Aldrich. Oxalic, oxamic, and maleic acid were VWR analytical chemicals. Analytical grade sodium salts of chloride, sulfate, nitrate, chlorate, and perchlorate were obtained from BDH. All the other chemicals used were received from Fluka or Sigma Aldrich in the highest analytical grade. Aqueous solution were prepared with deionized water obtained from Millipore Milli-Q equipment (resistivity = 18.2 MΩ cm and TOC content ≤ 5 ppb).

2.2. Analytical methods

Total organic carbon (TOC) and Total Nitrogen (TN) analysis was conducted using Skalar Formacs^{HT} TOC/TN analyzer. UV–Visible spectrophotometer (Perkin Elmer Lambda 5) was used for UV–visible spectra plotting using a 1 cm-quartz cells. COD was performed using HACH DR 2000 spectrophotometer after digestion of the samples (2 mL of the electrolyzed solution at certain time intervals) mixed in a glass tube filled with an oxidizing solution purchased from HACH (the concentration of Cl$^-$ in samples was kept below 2 g/L, as recommended). Free chlorine was monitored using DPD (N,N-diethyl-p-phenylenediamine) method [65]. The analysis of chloride, nitrate, chlorate, and perchlorate ions was performed by ion chromatograph (Dionex ICS 2000) using Ion Pac AS 19 column. DS6 conductometric cell was used as detector in parallel with ASRS 300 mm-4 mm suppressor. The analysis of ammonium ions was performed using ion-selective electrode for ammonium ion (ELIT 8051 PVC membrane). 2-CA was analyzed by injecting 10 μL of each sample in C18 column (4.6 × 250 mm, 5 μm) of Shimadzu 20A Gradient LC chromatogram using UV–Visible detector. The separation was performed using a mobile phase composed of 30% water and 70% methanol at a fixed flow rate of 1.0 mL/min. The UV detector was set at a wavelength of 254 nm. The analysis of oxalic and maleic acids was performed using HPLC instrument equipped with Supelcogel H column. The mobile phase consists of 0.15% H$_3$PO$_4$ aqueous solution with a constant flow rate of 0.15 mL/min. The UV detector was set a wavelength of 210 nm. External standardization method was used for all the analytes in chromatography analysis. The pH was monitored using a pH-meter (Seven Compact S210, METTLER TOLEDO®).

2.3. EO experiments

An electrochemical flow cell working in batch-operation mode was used to perform all experiments in single and divided compartment configurations (see Fig. 1). BDD anodes were purchased from Adamant Technologies (Neuchatel, Switzerland). These electrodes were fabricated by hot filament chemical vapor deposition (HF CVD) technique in which boron-doped diamond thin film deposited on single-crystal p-type Si (1 0 0) substrates (0.1 Ω cm Siltronix) was carried out as described elsewhere [57]. The BDD coating has a film thickness of 2 μm, a resistivity of 100 mΩ cm, and a boron concentration of 500 ppm, and the sp^3/sp^2 ratio is 150. Stainless steel (AISI 304) was used as cathode material in all the electrochemical experiments. Circular electrodes (100 mm diameter) with a geometric area of 78 cm^2 and separated by 9 mm to each other. A centrifugal pump was employed to circulate the electrolytic solution stored in a glass tank (600 mL in single and divided cell) through the electrolytic cell at a constant flow rate of 3.5 L/min (the capacity of the reactive chamber was 30 mL in single compartment and 15 mL in each compartment in divided cell). The temperature was maintained at 25 °C using a thermostatic bath/heat exchanger. All electrochemical experiments were performed under galvanostatic mode (constant current density). The electrodes were connected to a digital dc power supply (Monacor PS-430) providing current and voltage in the ranges 0–30 A and 0–20 V. In divided compartment configuration,
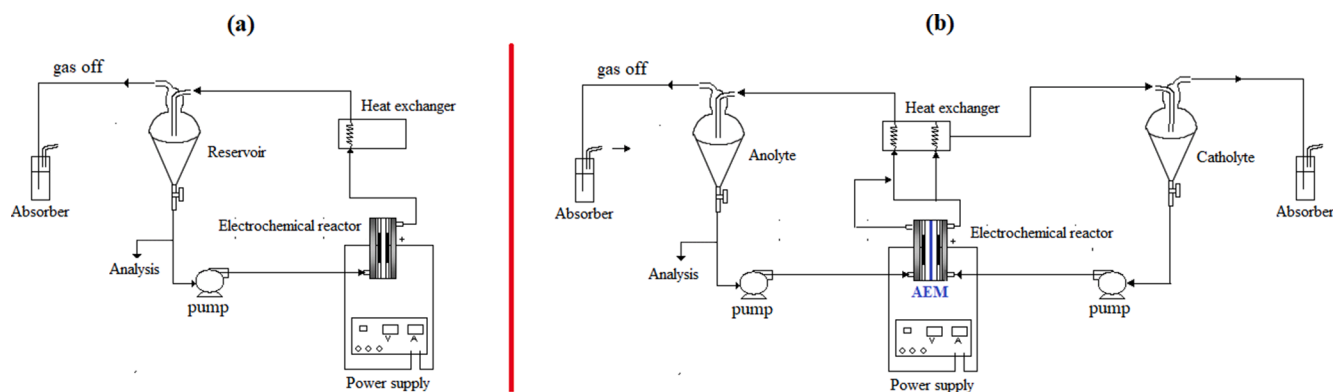
Fig. 1. Electrochemical set up: **(a)** Single compartment flow cell, **(b)** Divided compartment flow cell.

anodic and cathodic compartments were separated by an anion exchange membrane (AEM) (AMI 7001, Membrane International Inc. NJ, USA). The anolyte and catholyte have the same volumes and contain the same electrolyte (denoted anolyte 1 and catholyte 1). The organic pollutant was added only to the anolyte. The anolyte and catholyte were exchanged after electrochemical oxidation of 2-CA in order to improve the quality of the treated water.

3. Results and discussion

3.1. Degradation of 2-CA using single compartment flow electrochemical cell

2-CA is an aniline derivative in which the benzene ring is substituted with a mesomeric donating group ($-Cl$) at ortho position with amino ($-NH_2$) group. The degradation of this aniline derivative was performed by galvanostatic electrolysis in sulfate medium at neutral pH. The choice of sulfate medium was based on higher efficacy of the EO due to the generation of strong oxidants from the oxidation of sulfate ions on BDD surface or by hydroxyl radicals including sulfate radicals ($SO_4^{-\cdot}$) and persulfate ions ($S_2O_8^{2-}$) (Eqs. 2–4) inducing harsher degradation of organic pollutants [16,20,40,62].

Fig. 2a presents the effect of current density on COD changes with specific electrical charge (Q) during the EO of 2-CA (5 mM) aqueous solution containing 5000 mg/L Na_2SO_4 in single compartment cell using BDD anode and stainless steel cathode keeping pH = 7.0, T = 25 °C, and flow rate = 3.5 L/min in all experiments. A decrease of COD with Q was observed indicating a progressive degradation of the organic pollution for all current densities. It is remarkable that the lowest current density resulted in the highest efficiency in terms of COD removal as shown in Fig. 2a. The instantaneous current efficiency (ICE) and COD removal were estimated according to the following equations [5,49]:

$$CE(\%) = \frac{(COD_t - COD_{t+\Delta t}) \times F \times V}{8 \times I \times \Delta t} \times 100$$

$$COD\ removal(\%) = \frac{(COD_0 - COD_t)}{COD_0} \times 100$$

where COD_0, COD_t and $COD_{t+\Delta t}$ are the values of COD (in g O_2/L) at times t = 0 s, t = t and t = t + Δt, F is the Faraday constant (96487 C/mol), V is the volume (in L), I is the current intensity (in A), Δt is the time change (in s), and 8 is the O_2 equivalent weight (4 electrons are transferred to reduce 1 mol O_2 into H_2O).

Based on the COD removals and ICE estimated, the lower the current density the higher was ICE ($\approx$40%) for COD removal less than 80% (Fig. 2a inset). After that, ICE dropped for COD removal >80% and no effect of current density was observed due to the mass transport limitations. When the consumption of 58.5 Ah/L was achieved, the COD removal was 97.8, 92.2, and 84.6% for 15, 30, and 60 mA/cm^2,
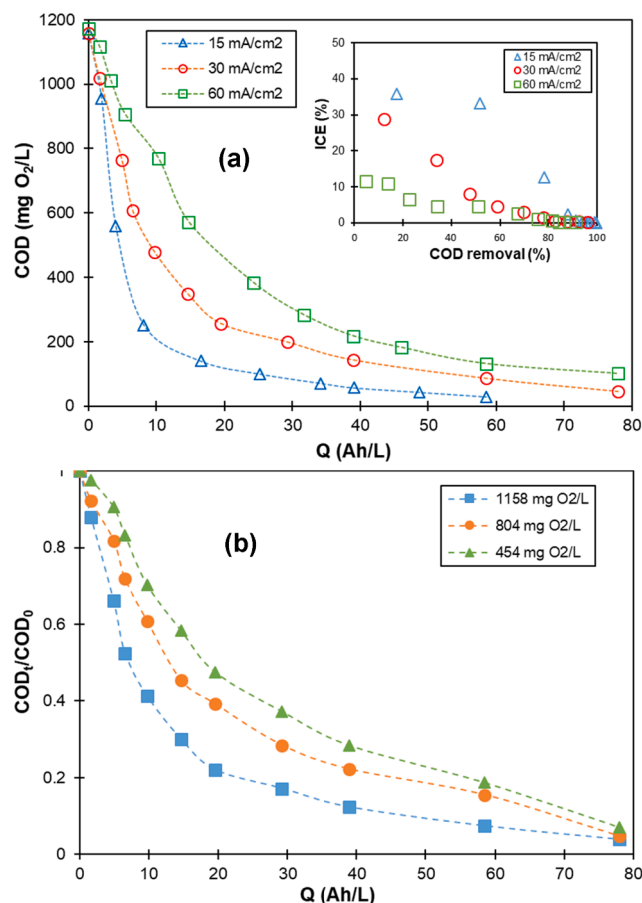

Fig. 2. (a) Effect of the current density on the COD changes with Q (inset changes of IC(%) with COD removal (%)) during galvanostatic electrolysis of 2-CA (5 mM) in single compartment cell: ($\square$) 60 mA/cm^2, ($\circ$) 30 mA/cm^2, ($\triangle$)15 mA/cm^2 ; **(b)** Effect of the COD content on the changes of normalized COD concentration with Q during galvanostatic electrolysis of 2-CA at j = 30 mA/cm^2: ($\blacksquare$) 1158 mg O_2/L, ($\bullet$) 804 mg O_2/L, ($\blacktriangle$) 454 mg O_2/L. Experimental conditions: Anode: BDD (78 cm^2), Cathode: stainless steel (78 cm^2), Electrolyte: 5000 mg/L Na_2SO_4, pH = 7.0, flow rate: 3.5 L/min, T = 25 °C.

respectively. The effect of the initial COD content on the changes of normalized concentration of COD with Q during the EO of 2-CA aqueous solutions containing 5000 mg/L Na_2SO_4 in single compartment cell using BDD anode and stainless steel cathode keeping j = 30 mA/cm^2, pH = 2.0, T = 25 °C, and flow rate = 3.5 L/min in all experiments is illustrated in Fig. 2b. The increase of COD content enhanced the performance of the EO of 2-CA. At the beginning of the electrolysis, the

kinetics of the electrochemical process is controlled by the charge transfer because high concentration of organic pollution exists. In this case, the degradation of organic pollution occurs mainly through a mediated oxidation route via the HO. radicals at the vicinity of BDD anode (Nernst layer) [10,50,61]. A little contribution of direct EO on BDD surface can be also attained. However, as the electrolysis progresses the concentration of organic pollution decreases, and then the kinetics of the electrochemical process is shifted to be mass transfer controlled. The electrogenerated HO. radicals on the surface of BDD having a very short lifetime will combine to form H_2O_2 and/or react with sulfate ions to form sulfate radicals due to the slowness of the diffusion of organic pollution from the bulk solution to BDD anode surface [20]. In this case, the degradation of organic pollution primarily occurs through a mediated route via the stable electrogenerated oxidants including sulfate radicals, persulfate, H_2O_2, and O_3, which are less effective than HO. radicals. At high current density (60 mA/cm^2), the mass transfer is controlling the kinetics of the electrochemical process from the beginning of the electrolysis, and oxygen evolution becomes more competitive with HO. radicals electrogeneration, which reduces the efficiency of COD removal.

Fig. 3 presents the results of 2-CA mineralization during the EO of 2-CA (5 mM) aqueous solution containing 5000 mg/L Na_2SO_4 in single compartment cell using BDD anode and stainless steel cathode under the following experimental condition: j = 30 mA/cm^2, pH = 2.0, T = 25 °C, and flow rate = 3.5 L/min. Fig. 3a shows a continuous decrease of 2-CA and TOC concentrations; however, a more rapid decay of 2-CA than TOC was observed. 2-CA was completely removed after the consumption of 29.25 Ah/L, while for the same consumed Q; TOC removal was only 62%. The continuous TOC decrease with Q indicates that the mineralization of 2-CA was gradually attained during EO using BDD anode. The concentration of the total intermediates (calculated based on mass balance) increased from the beginning of the electrolysis to reach a maximum of 217 mg C/L after the consumption of 14.625 Ah/L, and then it started to decline with the specific electric charge passed. The concentrations of oxalic acid (OAA), maleic acid (MAA), and oxamic acid (OAM), which were identified as intermediates of 2-CA degradation, increased with Q (see Fig. 3a inset) to reach maximum values of 48.2, 24.3, and 28.5 mg C/L at 14.625, 14.6 and 9.75 Ah/L, respectively, and then decreased slowly with Q. At the end of the electrolysis (after consumption of 58.5 Ah/L), small amounts of OAA, MAA, and OAM were detected and more than 85% of TOC was mineralized.

Fig. 3b presents the changes of nitrogen species with Q during the EO of 2-CA using BDD anode single compartment cell. The decrease of 2-CA concentration was accompanied with the increase in both nitrate and ammonium concentrations indicating the transformation of organic nitrogen into inorganic forms. The concentrations of nitrate and ammonium increased from the beginning of the electrolysis, and then they reached their plateaus at 45.2 and 11.5 mg N/L when 2-CA was completely depleted after the consumption of 39 Ah/L. The concentration of TN decreased at the beginning of the electrolysis and then was maintained at 60.6 mg N/L (85% of its initial value). This indicates that 15% of TN was lost from the reactor as volatile organic nitrogen species (ammonia, chloramines, NO_x, and N_2). These results demonstrate that EO of 2-CA using BDD in single compartment cell promotes the complete mineralization of organic nitrogen; however, a mixture of nitrate and ammonium was released in the medium, which is difficult to be valorized and it needs further treatment before discharge into water bodies.

Fig. 3c presents the changes of chlorine species concentrations with Q during the EO of 2-CA using BDD anode in single compartment cell. Chloride ions concentration increased sharply with Q since the start of the experiment indicating the rapid release of organic chlorine as Cl$^-$ ions by EO of 2-CA. Chloride ions concentration reached a maximum value of 101.8 mg Cl/L (around 60% of the theoretical chlorine concentration = 177.25 mg/L) at 14.625 Ah/L, and then it slowly declined with Q till the end of the electrolysis. As will be demonstrated below, free chlorine (HClO/ClO$^-$), chlorate (ClO$_3$) and perchlorate (ClO$_4$) ions
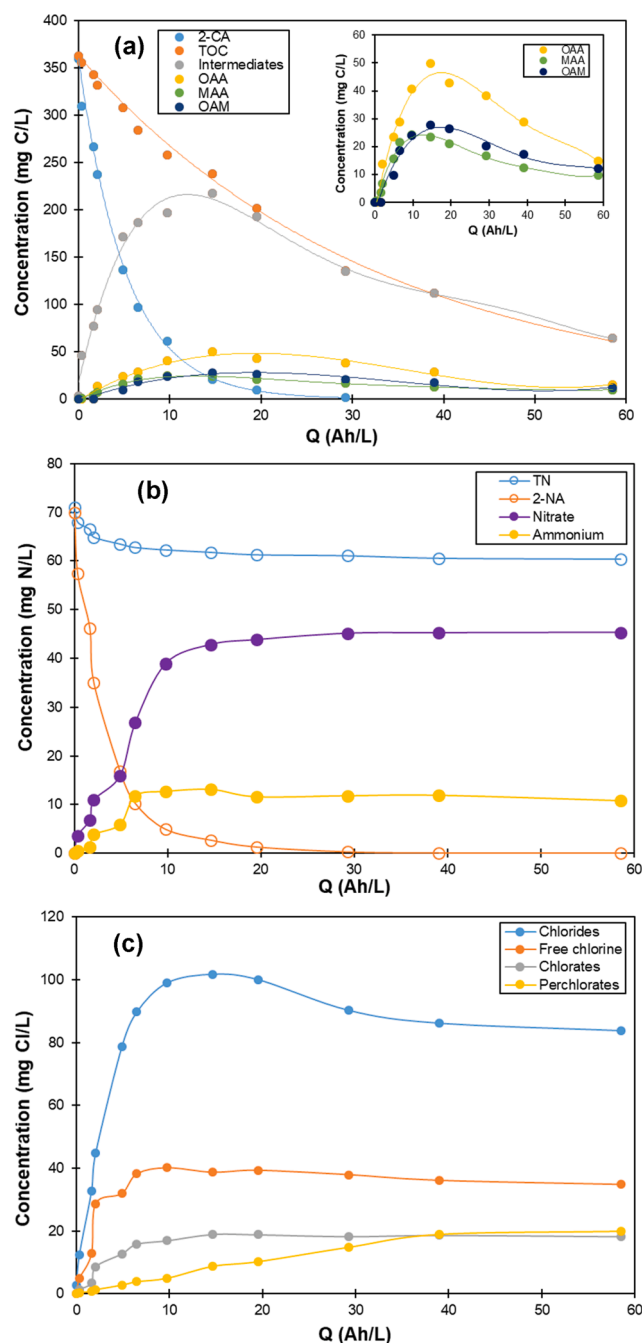

Fig. 3. Mineralization of 2-CA (5 mM) in single compartment cell: Changes with Q of **(a)** Carbon intermediates (inset: changes of OAA and MAA concentrations with Q), **(b)** Nitrogen species, **(c)** Chlorine species. Experimental conditions: Anode: BDD (78 cm^2), Cathode: stainless steel (78 cm^2), Electrolyte: 5000 mg/L Na_2SO_4, j = 30 mA/cm^2, pH = 7.0, flow rate: 3.5 L/min, T = 25 °C.

are gradually formed and their concentrations increased with Q to reach plateaus at 18.6 and 18.9 mg Cl/L after 39 Ah/L, respectively. The formation of these hazardous chlorine species by direct oxidation of Cl$^-$ ions on BDD and/or by mediated oxidation with HO. radicals was well-documented in literature [7,19,44]. The formation of chlorate and perchlorate by EO of chlorinated compounds using BDD anode is unavoidable in single compartment cells owing to the easy oxidation of the released chloride ions on BDD surface and via HO. radicals. Due to the hazard, these species can cause serious problems to the human health and environment, a post-treatment following the electrochemical treatment seems to be a must to remove ClO$_3$ and ClO$_4$ before

discharging the treated water. An alternative solution to this drawback consists on the separation of the anodic and cathodic compartments during the EO of 2-CA and investigating its effect on the formation of ClO_3^- and ClO_4^-. The idea was inspired from the recent reports published in literature [3,37,74,79] showing the importance of membrane separation of the electrochemical cell compartments in reducing the amounts of disinfection by-products and recovering of ammonium ions during the treatment of industrial wastewaters.

3.2. Degradation of 2-CA using divided compartment flow electrochemical cell

In this section, a divided electrochemical cell was used to degrade 2-CA, in which the anodic (anolyte) and cathodic (catholyte) compartments were separated by an anion exchange membrane (AEM). It should be noted that in divided cell configuration 2-CA (5 mM) was added to the anolyte containing 5000 mg/L Na_2SO_4 at pH = 2.0, while the catholyte was 5000 mg/L Na_2SO_4 at aqueous solution at pH = 2.0. Fig. 4 shows the changes of COD with the specific electrical charge during the EO of 2-CA using BDD anode and stainless steel cathode in single and divided compartment cell keeping the same operating conditions (2-CA concentration: 5 mM, Electrolyte: 5000 mg/L Na_2SO_4, j = 30 mA/cm^2, pH = 2.0, flow rate = 3.5 L/min, T = 25 °C). As it can be seen in Fig. 4, a more rapid decrease of COD was observed with divided compartment cell. Divided electrochemical cell configuration reached 99% of COD removal after 29.25 Ah/L, whereas higher specific electrical charge (≈78 Ah/L) was needed to reach the same COD removal using single electrochemical cell configuration. At this point, the energy consumption (EC) for each configuration can be estimated according to the equation:

$$EC\left(\frac{kWh}{kgCOD}\right) = \frac{U(V) \times I(A) \times t(h)}{V(m^3) \times (COD_0 - COD_t)\left(\frac{kgO_2}{m^3}\right)}$$

where U is the cell voltage in V (9.2 V for divided compartment cell and 5.2 V for single compartment cell), I is the current intensity in A, t is the time needed to reach 99% COD removal in hours, V the volume of the solution in m^3, COD_0 and COD_t are the COD values measured at t = 0 s, and t = t. The estimated EC values for single and divided compartment cells were 395 and 234 kWh/kg COD, respectively. Divided electrochemical cell configuration decreased EC by 40% compared to single electrochemical cell configuration. The higher cell voltage of divided electrochemical cell configuration (9.2 V for divided compartment cell and 5.2 V for single compartment cell) was offset by the lower charge
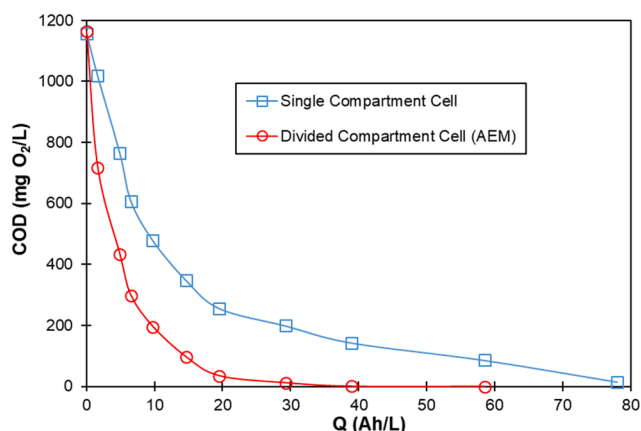
consumption (29.25 Ah/L for divided compartment cell and 78 Ah/L for single compartment cell). In addition to energy consumption reduction, divided electrochemical cell configuration affected the speciation of nitrogen and chlorine species in anolyte and catholyte, as shown in Figs. 5 and 6.

Fig. 5 presents the changes of the concentrations of nitrogen and chlorine species in the anolyte as a function of Q during the EO of 2-CA in divided compartment cell using BDD anode and stainless steel cathode. The concentration of TN in the anolyte remained almost unchanged during the electrolysis (Fig. 5a), which is different from in single compartment cell where 15% TN was lost from the reactor at the end of the electrolysis. This indicates that no volatile nitrogen species were formed during the EO of 2-CA in the anolyte when divided compartment cell was used with BDD anode. Furthermore, 2-CA concentration was rapidly decreased and was completely depleted after the consumption of 14.625 Ah/L. The concentration of nitrate ions increased from the beginning of the electrolysis to reach a plateau at 67.9 mg N/L (≈ TN in mg N/L) after the consumption of 39 Ah/L. Small amounts of ammonium was detected during the electrolysis that end to be oxidized into nitrate ions at the end of the electrolysis. The simultaneous decrease of 2-CA concentration and increase of nitrate ions concentration demonstrate that the EO of 2-CA in the anolyte of divided compartment cell using BDD anode achieved the release of organic nitrogen into the form of nitrate ions; in contrast to single compartment cell in which a mixture of nitrate and ammonium was measured at the end of the electrolysis. Therefore, the separation of anolyte and catholyte by AEM membrane
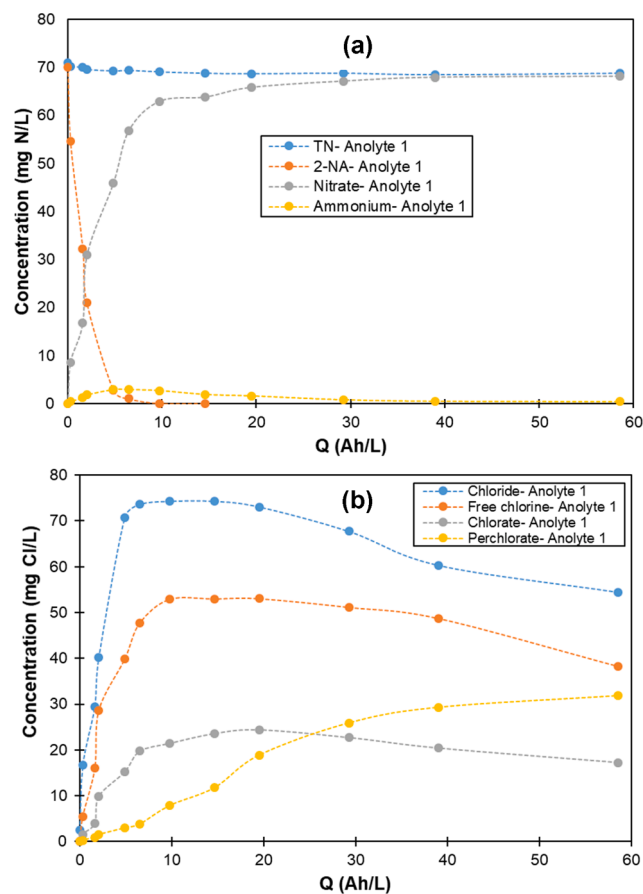

Fig. 5. Changes of the concentrations of: **(a)** nitrogen, and **(b)** chlorine species with Q in anolyte 1 during galvanostatic electrolysis of 2-CA (5 mM) in divided compartment cell. Experimental conditions: Anode: BDD (78 cm^2), Cathode: stainless steel (78 cm^2), Electrolyte: 5000 mg/L Na_2SO_4, Anion exchange membrane: AMI 7001, j = 30 mA/cm^2, pH = 7.0, flow rate: 3.5 L/min, T = 25 °C.

Fig. 4. COD changes with Q during galvanostatic electrolysis of 2-CA (5 mM) in single (□) and divided (○) compartment cells. Experimental conditions: Anode: BDD (78 cm^2), Cathode: stainless steel (78 cm^2), Electrolyte: 5000 mg/L Na_2SO_4, Anion exchange membrane: AMI 7001, j = 30 mA/cm^2, pH = 7.0, flow rate: 3.5 L/min, T = 25 °C.
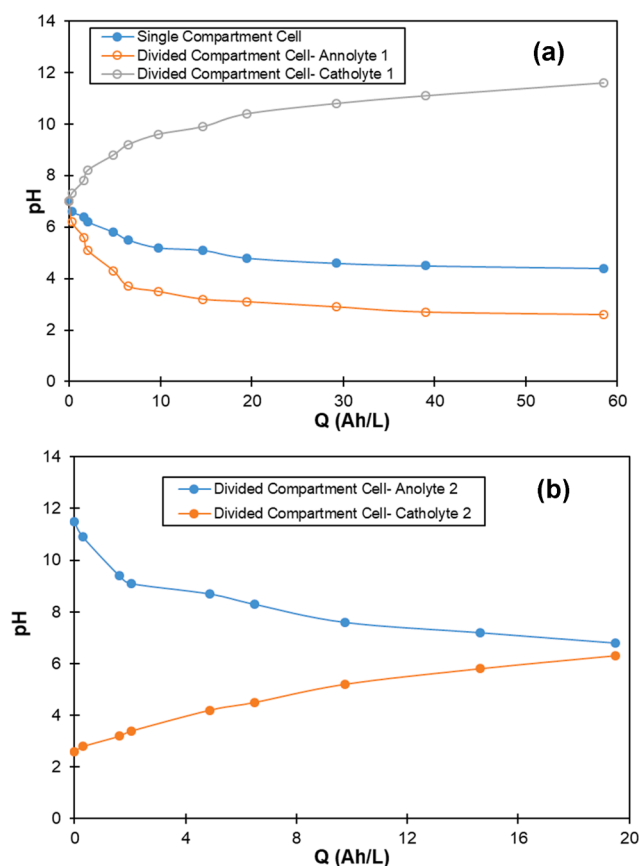
Fig. 6. Changes of pH with Q in **(a)** single compartment cell, anolyte 1 and catholyte 1 of divided compartment cell during galvanostatic electrolysis of 2-CA (5 mM) aqueous solution at j = 30 mA/cm^2, and (b) anolyte 2 and catholyte 2 1 of divided compartment cell during galvanostatic electrolysis of the treated water at j = 5 mA/cm^2. Experimental conditions: Anode: BDD (78 cm^2), Cathode: stainless steel (78 cm^2), Electrolyte: 5000 mg/L Na$_2$SO$_4$, Anion exchange membrane: AMI 7001, flow rate: 3.5 L/min, T = 25 °C.

avoids the electrochemical reduction of nitrate ions resulting in their predominance as the main inorganic nitrogen species. Fig. 5b shows that lower chloride ions concentration were measured in the anolyte during the electrolysis and at the end of the electrolysis in the anolyte of the divided compartment cell compared with the single compartment cell (see Fig. 3c). However, higher concentrations of free chlorine, chlorate and perchlorate ions were also monitored at the end of the electrolysis using divided compartment cell. These results clearly demonstrated that the EO of 2-CA in the anolyte of divided compartment cell using BDD anode released the organic chlorine into the form of chloride ions. After that, the formation of free chlorine and active chlorine is achieved. Meanwhile, free chlorine in solution is partially oxidized into chlorate and perchlorate ions. The higher concentrations of free chlorine, chlorate and perchlorate ions can be explained by the larger quantities of oxidants available in the anolyte of the divided compartment cell compared to that in single compartment cell. Fewer quantities of oxidants are available in single compartment cell because these can partially undergo chemical reduction by hydrogen gas and/or electrochemical reduction at the surface of the cathode. It should be noted that chlorine and nitrogen species were not detected in the catholyte of the divided compartment cell. The treated solution in the anolyte cannot be reused or discharged directly into the environment due to high amounts of chlorate and perchlorate ions. In order to improve the quality of the treated water, an additional treatment was used to reduce the hazardous chlorine species and separate chloride and nitrate ions in one compartment. In this treatment, the anolyte and catholyte were

exchanged: Anolyte 1 was transferred to the cathodic compartment (catholyte 2) and catholyte 1 was transferred to the anodic compartment (anolyte 2). Galvanostatic electrolysis was operated under low current density of 5 mA/cm^2 to minimize the amounts of chlorate and perchlorate ions electrogenerated by chemical and EO of chloride ions. In the cathodic compartment, protons are reduced into hydrogen gas, which neutralizes the acidic treated water; while anions pass across the AEM membrane to the anodic compartment (electro-dialysis).

Fig. 6 presents the changes of pH with Q during the EO of 2-CA using single compartment cell and divided compartment cell during the two consecutive stages (electrolysis 1 and electrolysis 2). In single compartment cell, the pH decreased from 7.0 to a final value of 4.4 at the end of electrolysis. In divided compartment cell, anolyte 1 was acidified and its final pH was 2.6; while catholyte 1 was alkalinized and its final pH was 11.6. Switching anolyte 1 to be catholyte 2 and catholyte 1 to be anolyte 2, a neutralization of both compartments was accomplished and the final pH values were 6.8 and 6.2 for catholyte 2 and anolyte 2, respectively. The results showed that the second stage of the electrochemical treatment in divided compartment cell resulted in the neutralization of the treated 2-CA aqueous solution.

Fig. 7 shows an increase in the nitrate ions concentration in anolyte 2 to reach a maximum of 47.3 mg N/L at the end of the electrolysis. This increase was accompanied with a decrease of the concentration nitrate ions in catholyte 2 from 68.1 mg N/L to 0.05 mg N/L at the end of the electrolysis. The concentration of ammonium ions in catholyte 2 increased with Q during the electrolysis to reach a maximum of 14.3 mg N/L after the consumption of 6.5 Ah/L, and then it slowly declined to 11.7 mg N/L at the end of the electrolysis. The formation of ammonium ions in catholyte 2 resulted from the chemical reduction via hydrogen gas and/or electrochemical reduction of nitrate ions. The decrease of ammonium concentration at the end of the electrolysis is probably due to the neutralization of catholyte 2 enabling the partial transformation of ammonium ions (NH_4^+) into ammonia (NH_3) that can be released to air due to its high volatility. The changes of TN concentration in anolyte 2 (increase) and in catholyte 2 (decrease) confirmed the migration of nitrate ions to anolyte 2 and the formation of ammonium ions in catholyte 2. These results demonstrate that the major part of nitrate ions (70%) migrated through AEM from catholyte 2 to anolyte 2 by electro-dialysis; while the remaining part was reduced into ammonium/ammonia and remains in anolyte 2.

Fig. 8 presents the changes of chlorine species concentrations with Q in anolyte 2 and catholyte 2 during the electrolysis of the treated water. Chloride ions concentration in anolyte 2 increased rapidly at the beginning of the electrolysis, and then its ascending slope was decreased after 6.5 Ah/L to reach a final concentration of 93.5 mg Cl/L (Fig. 8a). Chloride ions concentration in catholyte 2 decreased from 54.8 mg Cl/L to reach 2.8 mg Cl/L at the end of the electrolysis (Fig. 8b) confirming the migration of chloride ions through the AEM from catholyte 2 to anolyte 2 by electro-dialysis. The final concentration of chloride ions in anolyte 2 was higher than its initial concentration in catholyte 2 indicating the formation of additional chloride ions in catholyte 2 from chemical and electrochemical reduction of free chlorine, and chlorate and perchlorate ions. The concentrations of chlorate and perchlorate ions in anolyte 2 increased with Q to reach maximum values of 2.8 and 12.1 mg Cl/L, respectively. The concentration of chlorate and perchlorate ions in catholyte 2 decreased with Q to reach values of 0.9 and 18.3 mg Cl/L, respectively. It should be noted that the total concentration of perchlorate ions did not change during the second stage of treatment using divided compartment cell by AEM membrane indicating that they did not undergo a chemical or electrochemical reduction during this post-treatment. About 60% of perchlorate ions remained in catholyte 2. However, the total concentration of chlorate ions dropped from 17.1 to 3.7 mg Cl/L during the second stage of the electrochemical treatment indicating that chlorate ions were reduced in catholyte 2 (Fig. 8b). The concentration of free chlorine in anolyte 2 increased with Q to attain 8.6 mg Cl/L, while its concentration in catholyte 2 decreased from 37.3 to
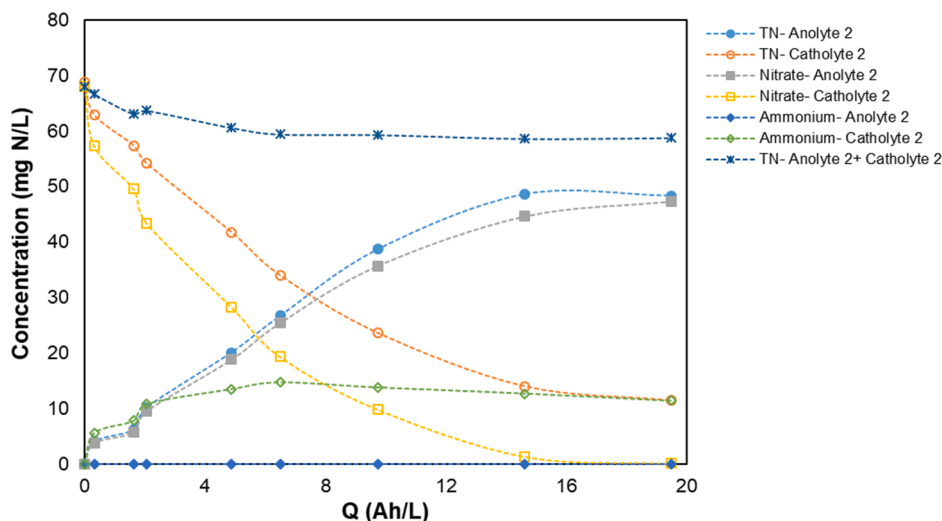
Fig. 7. Changes of nitrogen species concentrations with Q in the anolyte 2 (filled markers) and catholyte 2 (open markers) during galvanostatic electrolysis of the treated solution in divided compartment cell. Experimental conditions: Anode: BDD (78 cm^2), Cathode: stainless steel (78 cm^2), Electrolyte: 5000 mg/L Na$_2$SO$_4$, Anion exchange membrane: AMI 7001, j = 5 mA/cm^2, flow rate: 3.5 L/min, T = 25 °C.

Fig. 8. Changes of chlorine species concentrations with Q in **(a)** anolyte 2 and **(b)** catholyte 2 during galvanostatic electrolysis of the treated solution in divided compartment cell (Inset: Electrolysis of hypochlorite, chlorate, perchlorate aqueous solutions in the catholyte of the divided electrochemical cell). Experimental conditions: Anode: BDD (78 cm^2), Cathode: stainless steel (78 cm^2), Electrolyte: 5000 mg/L Na$_2$SO$_4$, Anion exchange membrane: AMI 7001, j = 5 mA/cm^2, flow rate: 3.5 L/min, T = 25 °C.

1.8 mg N/L at the end of the electrolysis. The total concentration of free chlorine declined from 37.3 to 10.4 mg/L indicating the reduction of free chlorine in catholyte 2. Free chlorine and chlorate ions were reduced in catholyte 2 into chloride ions, which migrate rapidly to anolyte 2 by electro-dialysis (see Fig. 8b inset). The second stage of

electrochemical treatment of the treated 2-CA aqueous solution in the catholyte of the divided compartment cell using AEM membrane resulted in the neutralization of both anolyte and catholyte, the migration of chloride and nitrate ions in the anolyte, the reduction of free chlorine and chlorate ions into chloride ions, and the retaining of perchlorate ions in the catholyte.

4. Conclusion

This work confirmed that 2-CA can completely degraded with high mineralization yield by EO using BDD anode in single and divided compartment electrochemical cells. The degradation of 2-CA by EO using BDD anode in single compartment cell achieved the complete removal of 2-CA and COD removal. The separation of anolyte and catholyte by AEM membrane enhanced the efficiency of the EO of 2-CA and reduced the energy consumption by 40%. Divided electrochemical cell configuration affected the speciation of nitrogen and chlorine species in the anolyte compared to single compartment cell. Higher quantities of nitrate ions, free chlorine, and chlorate and perchlorate ions were measured in the anolyte of the divided compartment cell. A second electrochemical treatment of the treated 2-CA aqueous solution by its transfer to the catholyte using the same AEM membrane was effective in reducing free chlorine and chlorate ions in the catholyte and transferring nitrate and chloride ions across AEM by electro-dialysis to the anolyte enabling its safe reuse. Finally, in this context, in this work was also proved that the traditional way to treat effluents by anodic oxidation is also a feasible pathway to promote the electrochemical conversion of a waste into high-added value products, such as carboxylic acids, mainly, OAA, MAA, and OAM.

CRediT authorship contribution statement

Nasr Bensalah: Conceptualization, Methodology, Validation, Data curation, Resources, Writing - review & editing, Supervision. **Mohamed Faouzi Ahmadi:** Investigation, Formal analysis, Writing - original draft. **Carlos A. Martinez-Huitle:** Methodology, Validation, Data curation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence
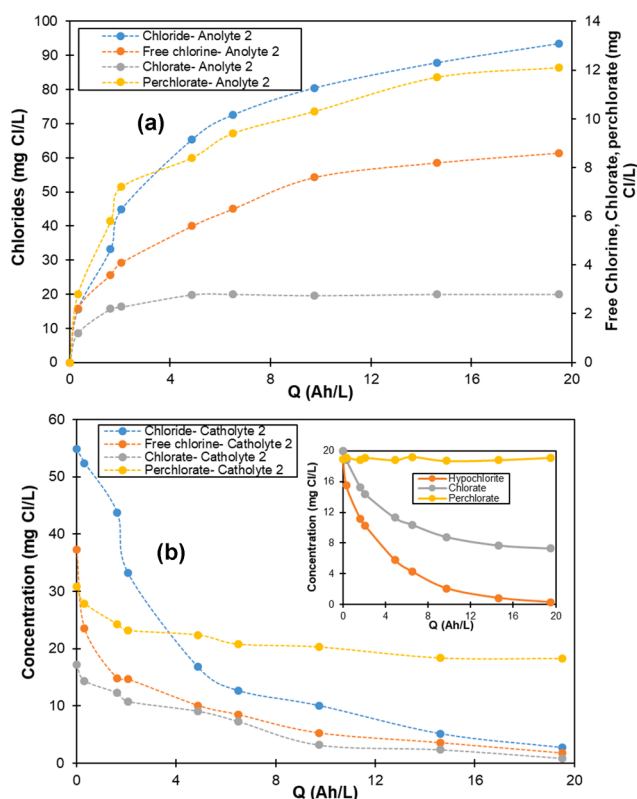
the work reported in this paper.

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