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ORIGINAL PAPER

Electrocombustion of humic acid and removal of algae from aqueous solutions

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Abstract This paper reports experiments involving the electrochemical combustion of humic acid (HA) and removal of algae from pond water. An electrochemical flow reactor with a boron-doped diamond film anode was used and constant current experiments were conducted in batch recirculation mode. The mass transfer characteristics of the electrochemical device were determined by voltammetric experiments in the potential region of water stability, followed by a controlled current experiment in the potential region of oxygen evolution. The average mass transfer coefficient was 5.2×10^{-5} m s^{-1}. The pond water was then processed to remove HA and algae in the conditions in which the reaction combustion occurred under mass transfer control. To this end, the mass transfer coefficient was used to estimate the initial limiting current density applied in the electrolytic experiments. As expected, all the parameters analyzed here—solution absorbance at 270 nm, total phenol concentration and total organic carbon concentration—decayed according to first-order kinetics. Since the diamond film anode successfully incinerated organic matter, the electrochemical system proved to be predictable and programmable.

Keywords Humic acid · Algae · Boron-doped diamond · Electrochemical reactor · Water supply treatment

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1 Introduction

Humic compounds are light brown organic polymers, which include high molecular mass fractions ranging from 1,500 to 100,000 Da [1]. Among them, humic acid (HA), with its complex chemical structure, is capable of complexing metallic ions [2] and often undergoes polymerization in aqueous media, acting as a substrate for biofilm formation and microorganism growth [3]. Hence, HA present in aqueous solutions may catalyze microbiological corrosion in flow pipes and reservoirs [4]. Humic substances are usually targeted for removal from water supplies because they can affect appearance and taste adversely. Furthermore, the oxidative treatment with chlorine and derivatives may form chloramines, trihalomethanes and other carcinogenic chlorinated organic compounds.

The control of algae growth in water supply systems is also a matter of concern, particularly in tropical and subtropical countries [5]. Algae may cause allergic reactions, gastric disorders, and poisoning by neuro and hepato-toxins formed by their metabolic activity [6, 7]. Traditionally, HA and algal biomass is removed from water supplies by different forms of chlorination, the most common one being the addition of chlorine dioxide [7].

There is a paucity of studies in the literature concerning the use of alternative technologies for algal biomass control in aqueous media. Electrolysis with soluble copper and zinc anodes effectively removes algal biomass using Cu and Zn ions as algicides. Though efficient, the process has the disadvantage of accumulating heavy metals in solution [5]. Ozonation [6, 8] and oxidation with permanganate or hydrogen peroxide [9] have also been used as pretreatments for coagulation and filtration. These processes, albeit expensive and slow, are effective in the removal of microalgae and cyanobacteria from drinking water.

Humic substances have been targeted for the application of innovative removal processes. Studies of the degradation of HA have been carried out using different techniques such as membrane separation [10], coagulation/flocculation [11], oxidation with ozone [12], heterogeneous photocatalysis [13–18], and photochemical [19–22], electrochemical [23–26] and photo-assisted electrochemical treatments [27–29]. Most of the studies reported in the literature involving electrochemical and photo-assisted electrochemical treatments used oxide-coated titanium electrodes (MO_x) to remove HA [24–29]. In this material, the anodic oxidation of organic pollutants in aqueous solutions is mediated by active species (MO_{x+1}) formed through the discharge of water under conditions of simultaneous oxygen evolution [30, 31]. This process is efficient in breaking chemical bonds, rearranging molecular structures, and converting organic species into lighter and more biodegradable compounds, and forms a set of intermediates. However, the conversion of organics into carbon dioxide is rarely observed [32]. Furthermore, since oxygen evolution is a competitive process, the efficiency and energy consumption of each system must be evaluated.

Electrochemical techniques for treating wastewater containing organic pollutants may benefit from the use of anodes with higher overvoltages for oxygen evolution. Electrodes coated with boron-doped diamond film (BDD) present such a characteristic. They promote the electro-oxidation of organics via adsorbed hydroxyl radicals and reduce the side reaction of oxygen evolution [32, 33]. In this electrode material, hydroxyl radicals are generated from the discharge of water, according to:

$$H_2O \rightarrow (^{\bullet}OH)_{ad} + H^+ + e^- \tag{1}$$

where the electrode surface is "non-active" and does not participate in the anodic discharge of water. Thus, the adsorbed hydroxyl radicals are responsible for the combustion of an organic substrate (R) into carbon dioxide, as follows:

$$R + n\,^{\bullet}OH \rightarrow n/2\ CO_2 + n\ H^+ + ne^- \tag{2}$$

For this reason, BDD anodes have been used in the electrochemical oxidation of organics and the treatment of wastewater. Furthermore, if the anode material promotes electro-oxidation according to a defined and known reaction (Eq. 2), the electro-oxidation process can be carried out under conditions of mass transport limitation relative to the concentration of R, and limiting currents can be estimated. Because BDD anodes also reduce the oxygen evolution reaction, an improvement in the current efficiency is also expected.

This paper reports on experiments of electrochemical combustion of HA and algae in pond water. An electrochemical flow reactor with a BDD anode was used and constant current experiments were conducted in batch recirculation mode. HA and algae removal rates were monitored and the apparent rate constants of the electrochemical reaction were found through a kinetic analysis. The study was carried out in two parts. The mass transfer characteristics of the electrochemical flow reactor were determined first by voltammetric experiments in the potential region of water stability, followed by a controlled current experiment in the potential region of oxygen evolution. The pond water was then processed to remove HA and algae.

2 Experimental procedure

2.1 Solutions and operational parameters of the reactor

The reactor mass transfer performance in the region of water stability was determined using the benzoquinone/hydroquinone redox couple. Voltammetric experiments were run in the range of 0.0 to 2.5 V using a saturated calomel electrode (SCE) at 50 mV s^{-1}. Limiting currents were obtained as a function of hydroquinone concentration. Concentrations of hydroquinone of 0.25, 0.51, 0.79 and 1.06 g L^{-1} were used in a supporting electrolyte of 1 mol L^{-1} of H_2SO_4. A volume of 3 L of solution was pumped at 850 L h^{-1} (0.5 m s^{-1}). The mass transfer coefficient value was then confirmed by a series of controlled current experiments within the potential region of oxygen evolution. A 0.1 mol L^{-1} potassium sulfate supporting electrolyte with 200 mg L^{-1} of phenol was used in the experiments. To determine the electrochemical reactor mass transfer coefficient during phenol oxidation in the potential region of oxygen evolution, an applied current density of 30 mA cm^{-2} was used. The same volume of solution was kept under recirculation at the same flow rate.

For the experiments of HA and algae removal, the limiting current density was calculated as a function of the total organic carbon concentration (TOC) and the reactor mass transfer coefficient, according to Eq. 5. In these experiments, a sample of water was collected at the bank of a pond located near the State University of Campinas Department of Biology. To this aqueous sample, 50 mg L^{-1} of HA (Aldrich) were added to increase the organic load and simulate extreme conditions. The final solution had a pH of 7.2, conductivity of 3.5 mS, $[TOC(0)] = 90.7$ mg L^{-1} and an initial absorbance of 0.9 a.u. at $\lambda = 270$ nm. The initial concentration of chlorophyll *a*, as an indication of algae activity, was 66.2 mg L^{-1}. This solution was also processed in the flow reactor under same conditions as the phenol solution.

2.2 Electrochemical flow reactor

The electrochemical reactor was an undivided filter press-type reactor like the one illustrated in Fig. 1, having two 18 mm thick (300 mm length × 150 mm wide) acrylic end plates on which the electrodes were mounted. A rubber gasket was used to maintain an inter-electrode gap of 6.8 mm. The anode was a 1 mm thick p-silicon coated with diamond film (CSEM-Switzerland) doped with 5000 ppm of boron, and the cathode was a 304 stainless steel plate. The area of the electrode was 59.6 cm^2. A Luggin capillary was inserted through the cathode facing the anode surface. The recirculation system consisted of a polypropylene centrifugal hydraulic pump (0.5 HP), a flow meter, a 3.5 L reservoir and 25 mm PVC connecting pipes.

2.3 Analytical control

In the experiments to calculate the reactor mass transfer coefficient, the phenol concentration was monitored in a Shimadzu HPLC chromatograph with a Shin-Pack CLC-ODS column and a UV–VIS detector, using a wavelength of 265 nm. TOC values were obtained in a Shimadzu TOC 5000 analyzer.

The disappearance of the phenolic substances was monitored with a Shimatzu UV–Vis, UV-1601PC spectrophotometer at a scanning wavelength of 200 to 800 nm. A shoulder in the UV–Vis spectra should be observed in the wavelength range of 260–290, corresponding to the degradation products of phenolic compounds [21, 24, 26]. Because the degradation of humic acid leads to diverse phenolic fragments, including benzenediols, pyrogallols, benzoic acids, cinnamic acids, diphenyl ethers and alkyl groups, total phenols concentration (TPh) decay is also an acceptable parameter to estimate the decrease of unsaturated compounds in solution [24, 26, 29]. The TPh concentration was determined by UV–Vis colorimetric analysis, according to the standard Folin–Ciocalteau procedure. In this analysis, an analyte sample of 1 mL was added to 250 µL of carbonate-tartrate buffer and 25 µL of Folin–Ciocalteau reactant (Aldrich). After 30 min at 20 °C, the absorbance of the solution was recorded at 700 nm.

The algal biomass concentration was determined by monitoring chlorophyll *a* absorbance. The measure of the concentration of photosynthetic pigments can be used to estimate the composite biomass of phytoplanktonic populations. It has been found that all photosynthetic plankton groups and green algae possess chloroplasts with chlorophyll *a*; thus, pigment analyses can yield a sensitive approximation of the algal biomass. Following a complete procedure described elsewhere [34], samples of 100 mL were filtered through a cellulose membrane (0.45 µm Millipore), which was dissolved in a 90% alkaline acetone solution. Chlorophyllous pigments in which chlorophyll *a* is the most dominant pigment are readily extracted by centrifugation. Turbidity was then measured at 665 and 750 nm.

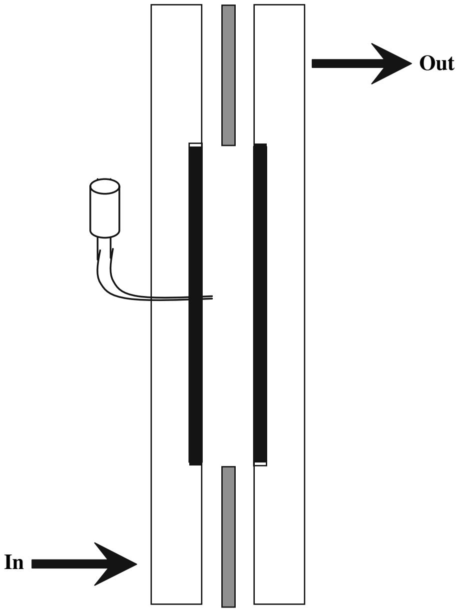


Fig. 1 Schematic view of the electrochemical flow reactor with BDD anode, a 304 SS cathode and a Luggin capillary for reference electrode

3 Results and discussion

3.1 Determination of the electrochemical flow reactor mass transfer coefficient in the potential region of water stability

Figure 2a presents the voltammograms obtained from four different concentrations of hydroquinone. Rising current values are visible starting from 0.6 V using a SCE, indicating that hydroquinone oxidation and limiting current plateaus were formed starting from 1.2 V. Currents corresponding to oxygen evolution are visible from 2.3 V. Current values, taken at 1.7 V, were plotted as a function of hydroquinone concentration, as shown in Fig. 2b. For a controlled mass transfer reaction, the slope from the straight line is proportional to the mass transfer coefficient (k_m), according to:

$$\frac{J_L}{C} = nFk_m \quad (3)$$

where J_L is the limiting current density, C is the hydroquinone concentration, n is the number of exchanged

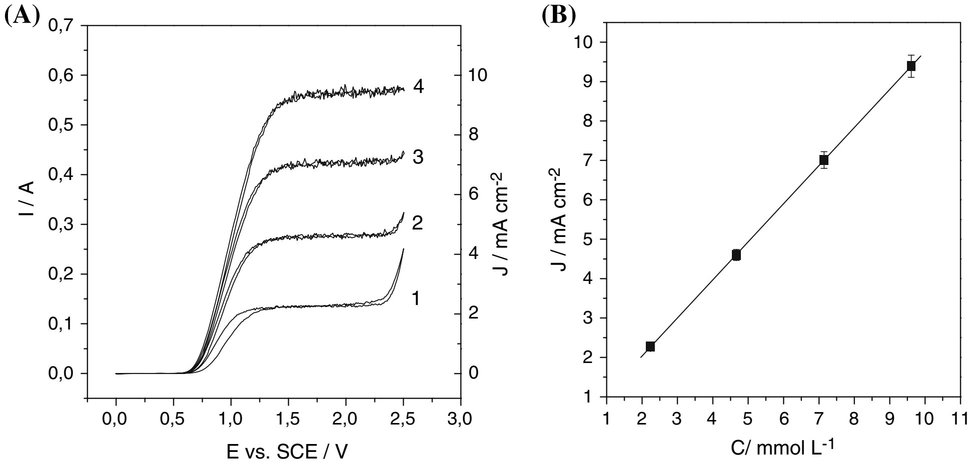


Fig. 2 (**a**) *J*/*E* couples for four different hydroquinone concentrations. (**b**) Limiting current density values taken at 1.7 V with a SCE for the oxidation of hydroquinone to benzoquinone as a function of hydroquinone concentration. Hydroquinone concentrations: 2.23 mmol L^{-1} (1); 4.66 mmol L^{-1} (2); 7.14 mmol L^{-1} (3); 9.60 mmol L^{-1} (4). Scan rate = 50 mV s^{-1}; flow rate of 850 L h^{-1} (0.5 m s^{-1}); $T = 30$ °C

electrons for the hydroquinone/benzoquinone couple ($n = 2$), and F is the Faraday constant. The slope in Fig. 2b is 9.66 A m mol^{-1} and the calculated mass transfer coefficient is 5.2×10^{-5} m $s^{-1\cdot}$ Although the mass transfer coefficient is a characteristic of the electrochemical device, this value is of the same order of magnitude as that of similar experiments reported in the literature [33].

3.2 Determination of the electrochemical flow reactor mass transfer coefficient in the potential region of oxygen evolution

Controlled current experiments were carried out using a current density of 30 mA cm^{-2}. At this current density, the BDD anode operates at a potential of 5 V vs. SCE. As stated before, 200 mg L^{-1} of phenol in a K_2SO_4 (0.1 mol L^{-1}, pH 7.2) solution was used in these experiments.

The phenol combustion reaction can be represented by the combination of Eqs 1 and 2:

$$C_6H_5OH + 11H_2O \rightarrow 6CO_2 + 28H^+ + 28e^- \quad (4)$$

For a reaction limited by the rate of mass transport to the anode, the applied current density must follow Eq. 3. For phenol (Ph), $n = 28$ in Eq. 3 and, for total organic carbon (TOC), the average number of exchanged electrons is 4.67 [32]. If this condition is fulfilled, phenol and TOC decay follow a first-order kinetics, and the removal rate (r) can be written as:

$$r = \frac{J_L}{28F} = k_m[\mathrm{Ph}] = k_\mathrm{m}\frac{[\mathrm{TOC}]}{6} \quad (5)$$

Integration of the mass balance of the whole system within the appropriate limits results in:

$$\ln\frac{[\mathrm{Ph}(t)]}{[\mathrm{Ph}(0)]} = \ln\frac{[\mathrm{TOC}(t)]}{[\mathrm{TOC}(0)]} = -\frac{Ak_m}{V}t \quad (6)$$

where A is the electrode area and V is the total volume of the solution being processed.

Figure 3 shows the normalized concentrations of phenol (a) and total organic carbon (b), both plotted as a function of electrolysis time, according to Eq. 6. The linear relationship allows for calculation of the mass transfer coefficient at the ratio of $A/V = 1.99$ m^{-1}. The calculated values of the mass transfer coefficients were 5.4×10^{-5} m s^{-1} and 5.0×10^{-5} m s^{-1} for phenol and TOC, respectively. By considering all k_m values obtained so far in the potential region of water stability and of oxygen evolution, an average value of $5.2 \pm 0.2 \times 10^{-5}$ m s^{-1} was considered as the characteristic mass transfer coefficient of the electrochemical flow reactor.

3.3 Electrochemical removal of HA

The solution used in these controlled current experiments was pond water with the addition of 50 mg L^{-1} of HA. The resulting concentrations were [TOC(0)] = 90.7 mg L^{-1} (7.5×10^{-3} mol L^{-1}), [COD(0)] = 42.8 mg L^{-1} of O_2 (1.34×10^{-3} mol L^{-1} of O_2), [TPh(0)] = 33.0 mg L^{-1}, pH = 7.2, conductivity of 3.5 mS, and initial absorbance of 0.9 au at $\lambda = 270$ nm. The initial concentration of chlorophyll *a*, as an indicative of algae activity, was 66.2 mg L^{-1}. The resulting TOC concentration and the average mass transfer coefficient (5.2×10^{-5} m s^{-1}) applied in Eq. 5 resulted in a limiting current density of 17.5 mA cm^{-2}, which was taken as the applied current density for the HA and algae removal experiments.

The UV–Vis spectra of samples collected during the electrolysis at 17.5 mA cm^{-2} are shown in Fig. 4a. A continuous decline in absorbance values was observed as electrolysis proceeded, evidencing the disappearance of unsaturated compounds. The behavior of absorbance profiles differed from those reported in the literature [26]. In the oxide electrodes, a well-defined absorbance shoulder appeared at 290 nm, rising at the beginning of the electrolysis and then decreasing. This increase in absorbance

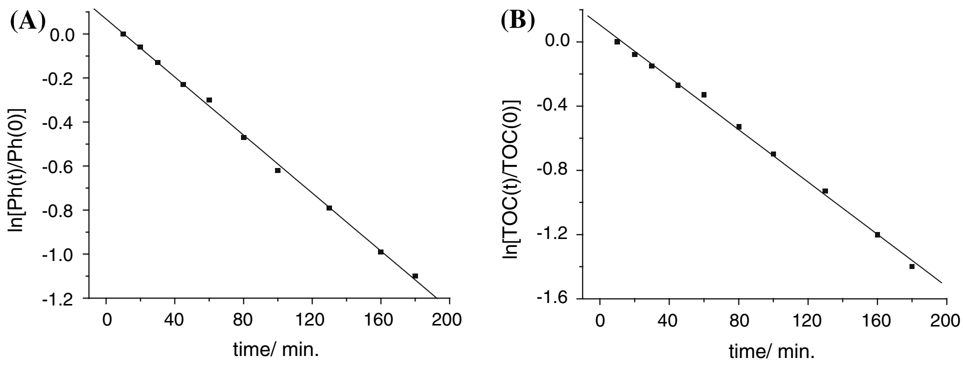


Fig. 3 (**a**) Logarithm of phenol normalized concentration as a function of electrolysis time. (**b**) Logarithm of TOC normalized concentration as a function of electrolysis time. Flow rate of 850 L h^{-1} (0.5 m s^{-1}); volume in recirculation = 3 L, J_{app} = 30 mA cm^{-2}, [Ph(0)] = 200 mg L^{-1}, [TOC(0)] = 141.9 mg L^{-1}, pH = 7.2, T = 30 °C and Λ = 20 mS

values was associated with the n-π^* electronic transition during the breakdown of carboxylic bonds of the HA. The absorbance values began to decrease through π–π^* electron transitions corresponding to the transformation of saturated into unsaturated groups [21, 26]. Normalized absorbance values, measured at 270 nm, were plotted against electrolysis time, as indicated in Fig. 4b. A linear relationship similar to that of Eq. 6 allows for the estimation of the apparent rate constant (k_{app}). Because the mass balance of a mass transport-controlled electrochemical reaction results in a pseudo-first-order kinetic expression, the mass transfer coefficient in Eq. 6 can be considered the apparent rate constant for the removal of a species. The calculated k_{app} for the decrease in absorbance values and, hence, for the disappearance of the phenolic substances, was 3.2 × 10^{-5} m s^{-1}. Table 1 summarizes the k_{app} values of all the parameters of the organic load analytically monitored in this study.

The electrocombustion process on BDD film, though very effective in the conversion of organics into carbon dioxide, is not an instantaneous process and HA mineralization is apparently preceded by the formation of ring-opened intermediates. This is indicated by the behavior of the total phenol concentration, which gradually decayed during the course of the electrolysis. Figure 5 shows (a) the decay of the total phenol concentration, and (b) the plot of the logarithm of the normalized [TPh] decay following a pseudo-first-order kinetics. The slope in Fig. 5b resulted in an apparent rate constant value of 3.4 × 10^{-5} m s^{-1} for total phenols removal.

Consistently with the time-dependent disappearance of saturated compounds and TPh, TOC removal also followed a pseudo-first-order kinetics. Figure 6 shows this behavior. Within the time interval of electrolysis, 70% of organic matter was converted into CO_2. The k_{app} value was calculated as 1.8 × 10^{-5} m s^{-1} from the slope of Fig. 6. The apparent rate constants for the decrease in absorbance values, removal of TPh and TOC are shown in Table 1 for purposes of comparison.

In an electrocombustion process on a BDD anode, the organic load is expected to be converted directly into

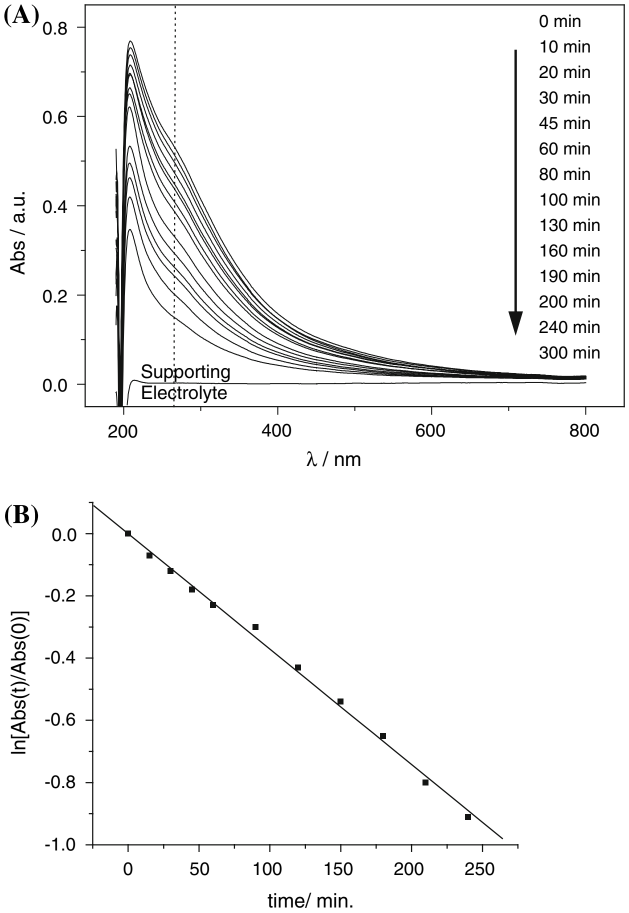
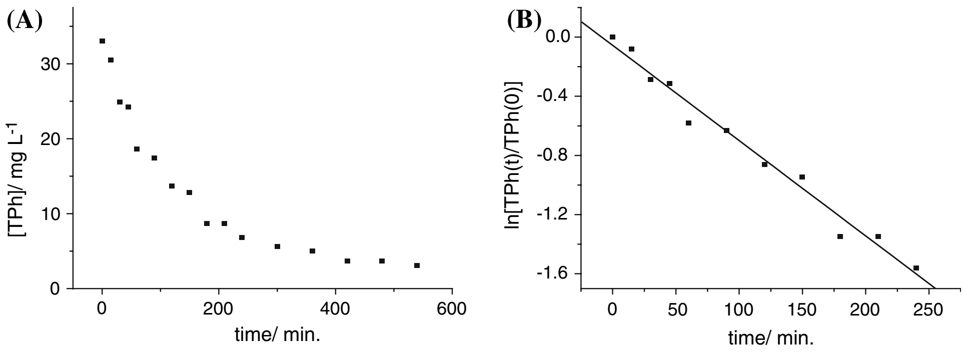


Fig. 4 (**a**) Absorbance decay as a function of electrolysis time within the range of wavelengths shown. (**b**) Linearized plot of the normalized absorbance values, taken at 270 nm, as a function of electrolysis time. Flow rate of 850 L h^{-1} (0.5 m s^{-1}); volume in recirculation = 3 L, J_{app} = 17.5 mA cm^{-2}, [HA(0)] = 50 mg L^{-1}, pH = 7,2, T = 30 °C and Λ = 3.5 mS

Table 1 Reactor mass transfer coefficient and apparent rate constants for organic load removal

Reactor mass transfer coefficient k_m/m s^{-1}	First order apparent rate constants k_{app}/m s^{-1}		
5.2 × 10^{-5}	Chlorophyll *a*	TPh	TOC
	3.2 × 10^{-5}	3.4 × 10^{-5}	1.8 × 10^{-5}

Fig. 5 (**a**) Total phenols concentration as a function of electrolysis time. (**b**) Linearized plot of the normalized total phenols concentration as a function of electrolysis time. [TPh(0)] = 33.0 mg L^{-1}. See Fig. 4 for other operational conditions



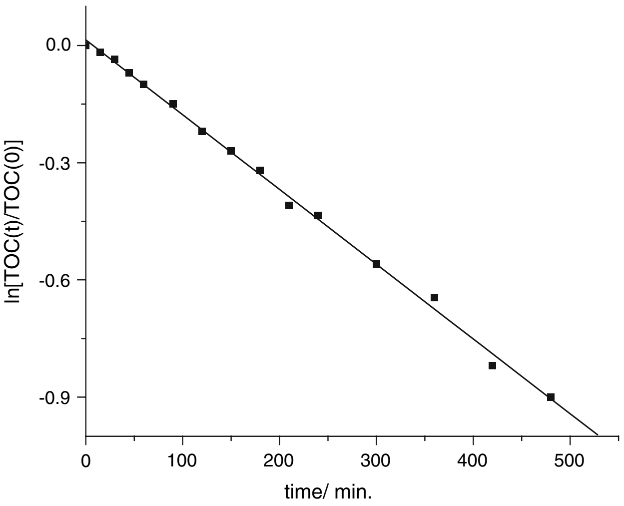


Fig. 6 Linearized plot of the normalized TOC as a function of electrolysis time. [HA(0)] = 50 mg L^{-1}, [TPh(0)] = 33.0 mg L^{-1}, [TOC(0)] = 90.7 mg L^{-1}. See Fig. 4 for other operational conditions

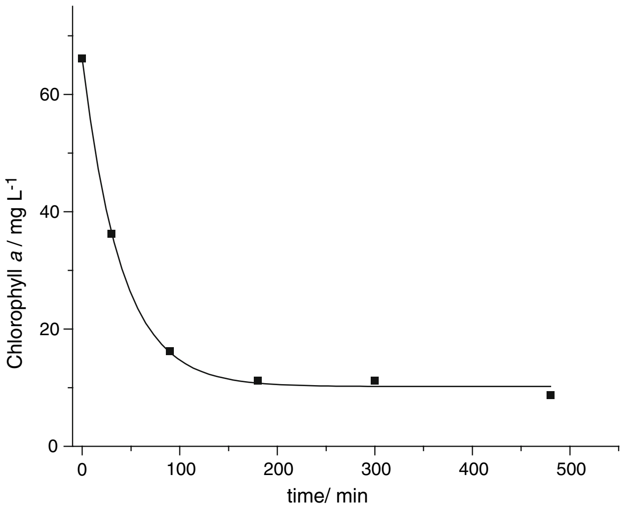


Fig. 7 Chlorophyll *a* (algae) concentration decay during electrolysis. [Chlorophyll *a*(0)] = 66.2 mg L^{-1}, [HA(0)] = 50 mg L^{-1}, [TOC(0)] = 90.7 mg L^{-1}. See Fig. 4 for other operational conditions

carbon dioxide. However, due to the complexity of humic substances, their mineralization does not occur instantaneously but is preceded by the formation of intermediates. The apparent rate constants for the organic load removal, which are smaller than the reactor mass transfer coefficient summarized in Table 1, indicate a number of successive intermediate oxidations prior to the formation of CO_2. It is worth noting that the use of BDD anodes allows for the conversion of higher fractions of organic load into carbon dioxide than with other anodes. In fact, the TOC removal was about 70% on BDD anode, whereas similar experiments carried out in the past using oxide anodes [26] resulted in 30% of TOC removal. However, if only combustion reaction had taken place, k_m value(see Eqs. 5 and 6) would have been equal to k_{app} values.

3.4 Electrochemical removal of algae

Considering the removal rates observed so far, the time required to remove an appreciable amount of algae is far shorter, as shown in Fig. 7. In less than one hour, 50% of algae were removed and after two hours of experiment, only 20% of the initial concentration of chlorophyll *a* remained in solution. Although the algal removal was not a first order process, the electrochemical treatment was highly effective. Note that the turbidity also followed the decay of the chlorophyll *a* concentration, with increasing transparency of the solution.

4 Conclusions

Electrochemical oxidation on boron-doped diamond films has proved to be an effective technology for the removal of humic acid and algae from aqueous solutions. Once the mass transfer coefficient of the electrochemical reactor is known, combustion reactions of organics can be carried out under controlled mass transfer conditions and limiting currents can be estimated. In the case of a solution containing a set of undetermined compounds, as in solutions of humic substances, the total organic carbon concentration can be used to predict the limiting current density for the operation of the electrochemical device and the time scale of the experiments to reach a specified final organic load concentration. However, due to the complexity of humic substances, mineralization to carbon dioxide is preceded by the formation of intermediates, and although the electrochemical removal of the organic load follows a first-order kinetics, it is not controlled solely by mass transport.

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