Coupling a Boron Doped Diamond Anode with a Solid Polymer Electrolyte to Avoid the Addition of Supporting Electrolyte in Electrochemical Advanced Oxidation Processes

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The application of electrochemical technologies to wastewater treatment is limited by solution conductivity. In this paper, a solid polymer electrolyte Nafion® membrane has been used sandwiched between a boron doped diamond (BDD) anode and Ti/RuO$_2$ cathode meshes to treat Bismarck Brown Y (BBY) solutions with very low conductivity. BBY has been chosen as model compound to the system, and the influence of several process parameters has been investigated. During the experiments the evolution of chemical oxygen demand (COD), color removal and nitrogen compounds have been monitored. The performances were strongly related with applied current and stirring rate, changed in a range of 0.5–2 A and 200 and 850 rpm, respectively. Their increment leads to a decrease of oxidation time required to remove BBY completely. The effect of the presence of Na$_2$SO$_4$ (2 and 7 mM) as supporting electrolyte has been also evaluated. Results were compared with a removal treatment carried out with a conventional batch system, using a flow cell containing liquid supporting electrolyte (Na$_2$SO$_4$). This comparison highlighted that the new cell setup is performing better in removing organic compounds, and thus, can be considered as effective process for the treatment of solutions with a low conductivity.

1. Introduction

Nowadays wastewater treatment plays a primary role both environmental protection and water recovery. Traditional approaches such as biological or physicochemical are the most used treatment but some problems, as the formation of sludge and the pollutants toxicity for some microorganisms employed, are not still overcome.

Electrochemical treatments, a particular Advanced Oxidation Processes (AOPs),[1–3] are a possible solution which offer different advantages. Among them, a fundamental factor is represented by their ability to oxidize a wide range of organic pollutants (e.g. herbicides,[4] drugs,[5] food industry,[6] surfactants[7] and dyes[8]) with high efficiency and low formation of exhausted materials. In the last decades, many AOPs have been investigated including photocatalysis,[9,10] ozone oxidation,[11] Fenton's reagent[12] and electrochemical oxidation.[13–15] In general, the electrochemical processes are complex systems and a large number of parameters affects the performance. The optimization of these systems requires a careful choice of the main parameters to investigate and to reduce operating costs, and a key role is covered by the solution conductivity. In fact, running costs are strongly dependent by this parameter because an increasing of conductivity reduces the voltage drop and the energy consumption. Nevertheless, some wastewaters (e.g. pharmaceutical industries, food industries and hospital wastewater) present a too low conductivity to be directly treated with electrochemical processes.[16] To apply electrochemical oxidation to solution of this kind is necessary to add a supporting electrolyte. The introduction of a compound, such as a salt (Na$_2$SO$_4$, NaHCO$_3$), brings positive effects, among them drop in cell voltage and then a possible reduction in energy consumption, but introduce also some drawbacks. The first is the material cost, but also technical problems can show up. Recently Ma et al.[17] reported that the addition of Na$_2$SO$_4$ for the treatment of wastewater with low conductivity leaded to a lower removal of total organic carbon (TOC), and then new cell setup are needed for the treatment of these wastewater matrices. A first proposal, to reduce the cell voltage and substitute the conventional tank, was the employment of microfluidic flow reactor as proposed in the last years.[18–19] Another possible and interesting technological solution is the use of a solid polymer electrolyte, made by a solid thin film electrolyte between the cathode and the anode side.[20] The presence of this membrane allows a current flux between electrodes with a low cell voltage even if the solution provides a low conductivity. This kind of system based on SPE is already used for electrochemical production of ozone,[21–22] and can be a promising system for wastewater treatment.

Therefore, the idea behind the cell introduced above is to pair a solid membrane, which provides ionic conductivity, and electroactive electrode for oxidizing organic compounds. Among them boron doped diamond (BDD) is widely study for its excellent properties.[23–30] In fact, it has wide potential window, high-oxygen-overvoltage anodes, inert surface with

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    An invited contribution to a Special Collection dedicated to Trends in Synthetic Diamond for Electrochemical Applications
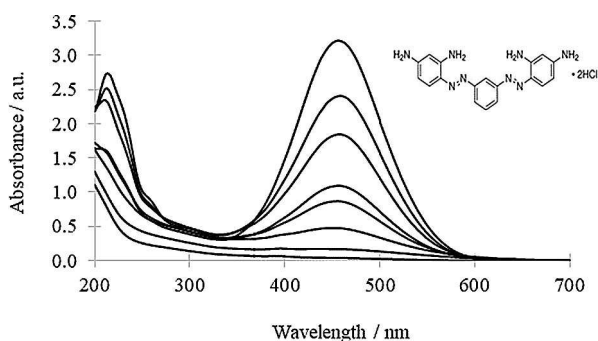
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low surface adsorption properties and good corrosion stability also in aggressive environment.[31] Furthermore, its effectiveness has been demonstrated to treat solutions containing many type of compound, as surfactants,[32] herbicides,[33] antibiotic[34] and dyes.[35–38] In most of the applications, strong oxidant power is provided by the electro-generation of hydroxyl radicals ($^\bullet$OH) at BDD surface from water discharge as shown in Equation (1):

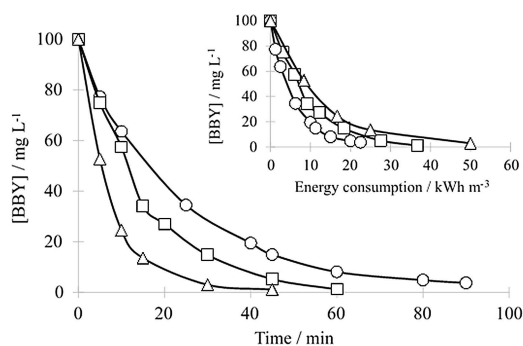$$H_2O \rightarrow {}^\bullet OH + H^+ + e^- \qquad (1)$$

To test the performance of this cell a Nafion® membrane was used as solid polymer electrolyte to investigate the removal of Bismarck Brown Y (BBY), a dye widely used for biological and microbiological analysis, for which the electrochemical removal was not well investigated in literature to the best of author knowledge. The solid electrolyte was sandwiched with a BDD anode and Ti/RuO$_2$ cathode, and the effects of different parameters (i.e. applied current, stirring rate and conductivity) on color and chemical oxygen demand (COD) removal were discussed.

2. Results and Discussion

The UV-vis spectra, shown in Figure 1, describes the electrolysis of 100 mg L^{-1} of Bismarck Brown Y in distilled water with an applied current of 1 A at 20 °C. In the UV-spectra two bands are detected at 458 nm and 212 nm, respectively. The first, in the visible region, is attributed to BBY concentration, while the latter regards the π→π* transitions of the aromatic rings. Progressively the absorbance band decrease, becoming negligible after 1 h of electrochemical treatment. As described below differences among the removal rate of BBY (458 nm), aromatic compounds (212 nm) and COD indicate that during the process some intermediate are formed. Nevertheless, all the organic specie present were well oxidized to CO$_2$ and water thanks to the hydroxyl radicals produced on the BDD surface as reported by Eq. 2. Figure 2 reports the evolution of BBY concentration as a function of time for experiments performed at at 0.5, 1.0 and 2.0 A. For all the three current values a high removal has been achieved, but the higher is the applied current the faster is the
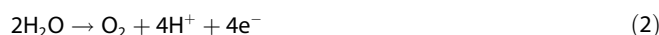

Figure 2. Influence of current density on the evolution of BBY concentration. Conditions: BBY initial concentration: 100 mg L^{-1} in distilled water; stirring rate = 850 rpm; T = 20 °C. The inset shows the BBY concentration as a function of energy consumption at different applied current: 0.5 A (○), 1 A (□), and 2 A (△).
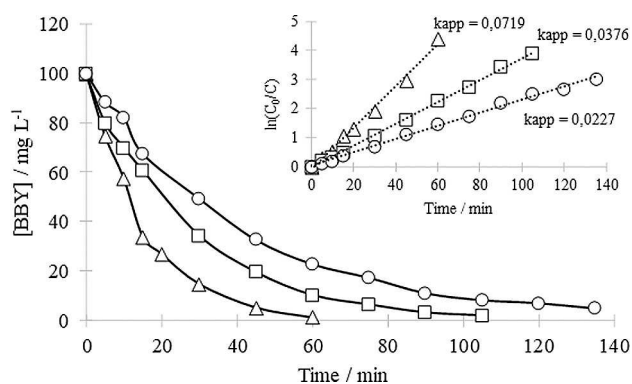
BBY removal, due to the higher generation of hydroxyl radicals from Eq. 2. To obtain the 97 % of removal a time of 90, 45 and 30 minutes is required for experiments performed at 0.5 A, 1 A and 2 A, respectively. Nevertheless, from the inset of Figure 2, it is evident that increasing the current the specific energy consumption grows from 22.5 kWh m^{-3} operating with 0.5 A to 50 kWh m^{-3} at a current of 2 A.

This increase in the energy consumption with current, can be ascribed to two main factors: (i) an enhancement of the cell potential and (ii) an activation of parasitic reaction of oxygen evolution [Eq. (2)].

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

From these results a current value of 1 A is a possible compromise between time of removal and energy consumption.

Further information about the process were obtained by the experiments conducted applying a current of 1 A at different stirring rate, 200 550 and 850 rpm, corresponding to a mass transfer coefficient km equal to 1.05×10^{-5}, 1.43×10^{-5} and 1.61×10^{-5} m s^{-1}, respectively. As shown in Figure 3, the

Figure 1. Evolution of the UV spectra as a function of time during treatment of 100 mg L^{-1} of BBY dissolved in double distilled water. Conditions: applied current: 2 A; stirring rate = 850 rpm; T = 20 °C.

Figure 3. Influence of stirring rate on the evolution of BBY concentration. Conditions: BBY initial concentration: 100 mg L^{-1} in distilled water; applied current = 1 A; T = 20 °C. The inset shows the kinetic analysis at different stirring rate: 200 rpm (○), 550 rpm (□△), and 850 rpm (□).

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enhancement of this parameter leads to a faster removal of BBY and allow concluding that the process is under mass-transfer control. This means that the electron transfer is faster than the BBY transport and hence the oxidation of BBY is in competition with the secondary oxygen evolution reaction [Eq. (2)].

Within this stirring range all the removal process followed with a good agreement a pseudo-first order kinetic, described by an exponential decay of BBY concentration [Eq. (3)]:
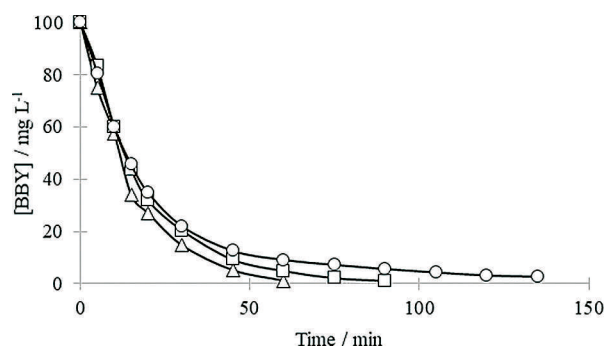
$$-\frac{d[BBY]}{dt} = k_{app} \cdot [BBY] \tag{3}$$

The results obtained by the integration of Equation (3) were reported in the inset of Figure 3, and values for the kinetic constant k_{app} were extrapolated in a range of 0.023 min^{-1} to 0.072 min^{-1}.

In order to investigate the influence of the conductivity of solution on the removal of BBY, several experiments were performed adding different amount of Na$_2$SO$_4$ in the range 2–7 mM. The presence of a supporting electrolyte decreases cell voltage (Table 1) but requires a higher time to remove the same amount of BBY (Figure 4). This behavior, summarized in Table 1, shows that to reach a pollutants removal of 97% the electrolysis time is 45 min and 120 min for the experiment conducted with distilled water and 6.62 mS cm^{-1} solution, respectively, causing a not acceptable rise of the energy consumption from 27.5 to 64.7 kWh m^{-3}. A possible explanation about the worsening of process performance with the introduction of supporting electrolyte is the presence of sulphates,

which can react in the secondary reaction with the production of persulfate [Eq. (4)]:

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2H^+ + 2e^- \tag{4}$$

The role of persulfate as oxidants is not clear and conflicting results were reported in literature. In fact, several authors highlighted beneficial effects about the presence of persulfate ions into the bulk solution, overcoming the mass-transfer limitation and then enhanced process efficiency.[39–41] On the other hand, it was reported that under particular conditions, such for electrolysis performed at a current density higher than 8 mA cm^{-2} and with a sulphate concentration lower than 50 mM, the formation of persulfate leaded to a loss of performance.[42] In the specific case considered here, selected operating conditions ([Na$_2$SO$_4$] = 2 mM or 7 mM and i = 33 mA cm^{-2}) are not favorable to obtain a positive effect on BBY removal. Another possible reason about the decreasing in performance is related with the operating temperature (20 °C) that penalizes S$_2$O$_8^{2-}$ oxidation power if compare with those of hydroxyl radicals, leading to a decreasing of $^{\bullet}$OH concentration and then a worsening of removal rate. Nevertheless, a further addition of sulfate to obtain a positive effect is contrary to the purpose of this study, and more important is limited by Italian law (D. Lgs 152/06) that fixed an upper limit of 1000 mg L^{-1} (10.4 mM) for sulfate.

To evaluate the SPE-based system effectiveness to operate with different pollutant loading, experiment with a lower or higher BBY concentration than 100 mg L^{-1} were performed as reported in Figure 5.

For all the BBY loading, electrochemical cell provided a complete removal but the higher is the concentration, the longer is the oxidation process, because of the presence of a greater quantity of BBY in solution. As expected from previous discussion, and reported in the inset of Figure 5, the process followed a first kinetic order reaction, and the kinetic rate constant trends pointed out that increasing the initial BBY concentration the reaction between hydroxyl radicals and sub-products took on a weight role if compare with the dye oxidation reactions.
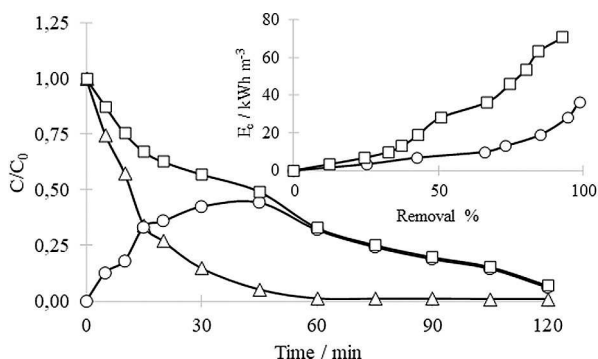
Table 1. Influence of solution conductivity on cell voltage, time required to remove 97% of BBY and energy consumption.

Test	ΔVcell [V]	Time[a] [min]	Energy Consumption [kWh m^{-3}]
Distilled Water	11,35	45	27,5
Na$_2$SO$_4$ (2 mM)	10,85	75	45,4
Na$_2$SO$_4$ (7 mM)	9,65	120	64,7
[a] 97% removal.			

Figure 4. Influence of conductivity on the evolution of BBY concentration. Conditions: BBY initial concentration: 100 mg L^{-1}; applied current = 1 A; T = 20 °C. Distilled water (□△), Na$_2$SO$_4$ 2.06 mS cm^{-1} (□), Na$_2$SO$_4$ 6.62 mS cm^{-1} (○).

Figure 5. Influence of BBY concentration. Conditions: I = 1 A; stirring rate = 850 rpm; T = 20 °C; Concentration: 50 mg L^{-1} (□△), 100 mg L^{-1} (□), 150 mg L^{-1} (○).
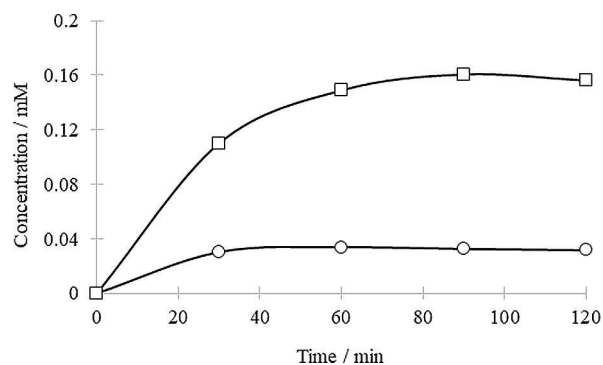
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After discussing about the effects of these parameters, the best compromise between performance and costs is represented by intermediate current (1 A), high stirring rate (850 rpm), low solution conductivity and avoiding the heating of solution. Taking into account these conditions as optimum, a COD analysis was made to evaluate also the byproducts removal (Figure 6). In fact, a complete removal of pollutant after 60 minutes does not indicate a completely removal of all organic compounds present in the solution. Doubling the time, a COD removal close to 93% was achieved pointing out that also BBY mineralization products were oxidized. The faster decrease of BBY concentration compared to the removal of COD indicated that some intermediates are produced during the oxidation. The evolution of these intermediated were obtained by the difference between COD and BBY concentration, and it increased in the first 50 min and then it progressively decreased up to zero. This time gap between BBY and COD removal is reflected also by energy consumption (Figure 6, inset), that increases from 36.3 kWh m^{-3} to completely degrade dye to 70 kWh m^{-3} to obtain the removal of 93% of initial COD.

During BBY electrolysis, the release of nitrogen was expected, and it can occur through different species. The possible formation of NH_4^+, NO_2^- and NO_3^- was also monitored and the results are reported in Figure 7. During the process only, the formation of NO_3^- and NH_4^+ was detected with a concentration of 0.03 mM and 0.15 mM after 2 hours of treatment, even if nitrates reached a stable value after 30 minutes and NH_4^+ after 1 hour, that correspond to the time of dye removal. No nitrites and chloroamine were detected.

The results discussed above, obtained without the addition of supporting electrolyte in solution were compared with those obtained for BBY electrolysis carried out in a more conventional batch system, using a flow cell with parallel plate electrodes and containing liquid supporting electrolyte (Na_2SO_4). Based on cell geometry and on the chosen flow rate (200 L h^{-1}) a comparable mass transfer coefficient with those calculated for SPE system was obtained. From these assumptions, three experiments were carried out with two Na_2SO_4 concentration. The supporting electrolyte concentration used were 10 mM (a
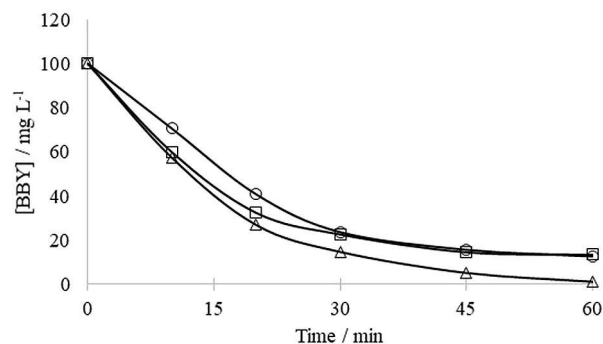

Figure 7. Evolution of concentration of NH_4^+ (□) and NO_3^- (○) during the treatment of BBY solution in distilled water. Conditions: I = 1 A; [BBY] = 100 mg L^{-1}, stirring rate = 850 rpm; T = 20 °C.

lower value caused a too high cell voltage) and 20 mM to have a cell voltage equal to the value obtained for the optimized experiment with solid electrolyte (~ 11.4 V).

As reported in Figure 8 the BBY degradation in the flow cell with parallel plate electrodes was lower than in the SPE cell and for both concentration of Na_2SO_4, dye removal reached a plateau value of 89% after 60 minutes. Using the solid polymer electrolyte, the same electrolysis time allowed to obtain a complete removal of pollutant, confirming the suitability of this kind of systems. As regards energy consumption, after 1 hour of treatment energy consumption for two BDD setup cell are very close: 39.6 and 40.3 kWh m^{-3} for conventional BBD and SPE cell, respectively. Nevertheless, after 60 minutes the first one reaches a removal plateau at 87%, while the new electrochemical cell allows obtaining a complete removal of pollutant.

3. Conclusions

The cell made by a solid polymer electrolyte membrane sandwiched between a Ti/RuO$_2$ cathode and BDD anode has been investigated to treat BBY solutions with low conductivity. The results showed that this system is able to completely

Figure 6. Trends of BBY (△), intermediates (□○) and COD (□) concentration as a function of time. Inset: Inset: Evolution of energy consumptions for BBY (○) and COD (□) removal. Conditions: I = 1 A; stirring rate = 850 rpm; T = 20 °C; [BBY] concentration: 100 mg L^{-1}.

Figure 8. Comparison between BBY removal using SPE cell (△) and BDD anode in a batch system with flow cell in presence of supporting electrolyte Na_2SO_4 10 mM (○) and 20 mM (□). Conditions: I = 1 A; [BBY] = 100 mg L^{-1}; stirring rate = 850 rpm (SPE system); Flow rate = 200 L h^{-1}.

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oxidize the BBY content in 60 minutes and remove a high fraction of COD, with the electrolysis of organic sub-products.

The influence of different parameters highlighted that the increase of applied current and stirring rate decrease the time required to obtain a complete removal of pollutant. An improvement of conductivity with the introduction of supporting electrolyte such as Na_2SO_4 decreased the cell voltage, but led to a longer oxidation time and more energy consumption. This worsening in performance are mainly due to the presence of persulfate and its weaker oxidant potential in used operating condition. Moreover, SPE system was able to operate properly in a pollutant concentration range between 50–150 mg L^{-1}. A COD removal of 93% after 2 hours was obtained selecting the best electrolysis condition, nitrates and ammonia were detected, while was avoided the production of nitrites and chloroamine.

A further confirmation about the suitability of Nafion® membrane as solid electrolyte was confirmed by the comparison with a conventional electrolysis cell that required liquid supporting electrolyte. Therefore, the results confirm that this technology is promising for the treatment of wastewater with a low conductivity.

Experimental Section

The investigation of electrochemical oxidation of BBY was conducted in an open, cylindrical and undivided glass cell with a solution volume of 300 mL. The solution was stirred using a magnetic stirrer and the rotation speed was changed between 200 and 850 rpm, and mass transfer coefficients were determined by limiting-current technique with the ferri/ferrocyanide couple. The cell had an anode/membrane/cathode structure with a Nafion® N324 membrane sandwiched between a Ni/BDD mesh anode and a Ti/RuO_2 mesh cathode as sketched in Figure 9.

The electrodes had dimensions of 3.5 cm × 7.5 cm and spaced 0.15 mm. The diamond electrodes are purchased from Condias, and has a diamond layer about 5 μm and contains 3500 ppm of boron deposited on a niobium substrate (thick 1.5 mm) with six boreholes (diameter 4.5 mm). Conventional batch system used as comparison was a flow cell with parallel plate electrodes and containing liquid supporting electrolyte (Na_2SO_4). The electrodes were a BDD anode and stainless steel (AISI304) as cathode. Each electrode was square and had a geometric area of 30 cm^2, with a electrode gap of 0.5 cm.
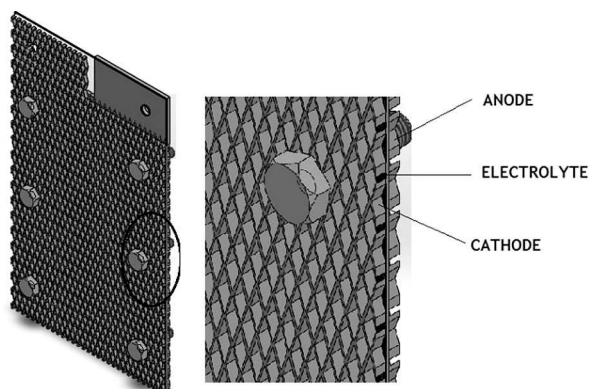

Figure 9. Solid polymer electrolyte cell.

The solution was recirculated with a flow-rate of 200 L h^{-1}, corresponding to a mass-transfer coefficient of about 1.6 × 10^{-5} m s^{-1}. Further details about this cell setup are reported elsewhere.[43] The solutions were prepared by dissolving BBY ($C_{18}H_{18}N_8 \cdot 2HCl$ Sigma Aldrich) in double distilled water (conductivity 0.002 mS cm^{-1}). In some experiences different amount of Na_2SO_4 (Sigma Aldrich, reagent grade > 99%) were added to solution to study the effect of solution conductivity. The electrochemical oxidation was evaluated by UV-vis spectroscopy using a Jasco V-630 spectrophotometer with cells with a 1 cm path length. The chemical oxygen demand (COD) of the solution, NO_3^- and NH_4^+ ions, were measured with Hach-Lange reagents set and a Dr. Lange LASA 3900 spectrophotometer. The energy consumption (E_c, kWh m^{-3}) was calculated according to Equation (5):

$$E_C = \frac{U_{cell} \cdot I \cdot t}{3600 \cdot V_S} \tag{5}$$

where U_{cell} (V) is the average cell voltage, I the applied current (A), t (s) is the mineralization time and V_s (L) the volume of treated solution.

Conflict of Interest

The authors declare no conflict of interest.
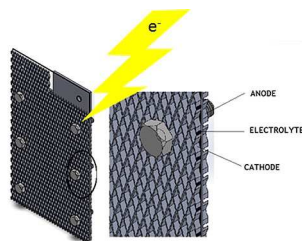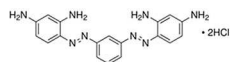
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ARTICLES

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1 – 7

Coupling a Boron Doped Diamond Anode with a Solid Polymer Electrolyte to Avoid the Addition of Supporting Electrolyte in Electrochemical Advanced Oxidation Processes

Garbage in, clean water out: A solid polymer electrolyte Nafion® membrane is used sandwiched between a boron doped diamond (BDD) anode and Ti/RuO$_2$ cathode meshes to treat solutions with very low conductivity containing Bismarck Brown Y (BBY) as model compound for waste water treatment. The new cell setup is performing good in removing organic compounds, and thus, can be considered as effective process for the treatment of solutions with a low conductivity.