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## Design of a synergistic combined electro dialysis/anodic oxidation system for simultaneous AMX membrane fouling mitigation and enhanced dye degradation

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## Abstract

Electrodialysis (ED) is a common process which is widely applied for water purification and desalination or/and chemical species recovery. Solving the fouling of ion-exchange membranes (IEMs) is the bottleneck of this technology for stable processing along with low maintenance at large scale. This work aims to design combined electrodialysis/anodic oxidation (ED-AO) using as-prepared Pb/PbO<sub>2</sub> anode to boost the oxidation of organic dye (methyl orange, MO) and overcome the issue of AMX membrane fouling. Hybrid ED-AO process works synergistically to accumulate, by ion-exchange reaction, MO species in the anodic Pb/PbO<sub>2</sub> oxidative compartment to be oxidized and mineralized. As compared to single ED, excellent oxidation rates and membrane anti-fouling activities were found in ED-AO process. The characterization of AMX membrane in single ED shows that the fouling was the main issue behind the low oxidation rate, causing as well a significant increase in the cell electrical resistance (CER), unlike in hybrid ED-AO process. Most of operating parameters including applied current density, initial concentration of MO, pH, supporting electrolyte (Na<sub>2</sub>SO<sub>4</sub>) concentration were investigated. The mechanistic pathways of MO oxidation and anti-fouling activity were discussed in depth. Through ten recycling tests, hybrid ED-AO process showed excellent stability and performance.

**Keywords:** Electrodialysis, Anodic oxidation, Pb/PbO<sub>2</sub> anode, AMX membrane anti-fouling, Synergistic oxidation, Hybrid processes.

## 1. Introduction

The textile industry is considered as one of the major sources of dyes water pollution. The amount of dyes discharged in industrial effluents was estimated at around 15% of total annual production [1]. Many types of discharged organic dyes are non-biodegradable which allows their accumulation in the environment, causing several toxic effects [2]. Numerous conventional methods have been adopted for the treatment of dyes water pollution, such as adsorption [3], membrane filtration [4], photocatalysis [5], biological methods [6] and other advanced oxidation processes [7,8].

These processes have different pros and cons based on the type of application, nature and concentration of dye and so on. Physical removal of dyes from water by adsorption, coagulation or filtration leads to transfer simply the pollution from liquid to solid, which in turn needs further purification. These multi-processes usually are expensive and non-sustainable. The industrial community is seeking for single process to reduce the pollution without creating secondary environmental or technology issues. Synergism in processes is the result of cooperative effects that are higher than the sum of additive effects, and also synergism could solve some technological problem, allowing a continuous and effecting processing.

Conventional electrodialysis (ED) is ion-exchange electro-membrane based technology that has been widely used for ionized species removal or recovery under electric effect. At large scale, it is largely used for seawater desalination [9,10], and the recovery of metals or for the separation in several industrial activities [11]. A lot of research groups are investigating the intensification of ED process at a laboratory scale for many applications such as the removal of metals and heavy metals [12,13], fluoride and nitrate from aqueous solutions [14,15], the production of organic acids [16,17], whey proteins separation [18], and for the environmental protection [19,20].

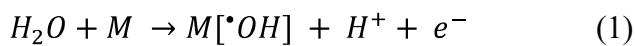
1 ED technique has some considerable drawbacks limiting its effectiveness [10,13]. One  
2 of the main issues of ED is the membrane fouling during the process [21,22]. This  
3 phenomenon is generally due to the deposition of macromolecules or insoluble  
4 compounds on the surface and/or into the membrane. The membrane fouling  
5 consequently leads to a significant increase in its electrical resistance caused by the  
6 passivation of membrane active functional groups [22,23]. This can reduce the  
7 efficiency of the process by preventing the transfer of ionic species through the IEMs  
8 and also increases the energy consumption [24,25]. In general, the membrane fouling  
9 phenomenon can be classified in three types: (i) scaling by mineral precipitation, (ii)  
10 adsorption of organic molecules, proteins or colloidal matter and (iii) poisoning of  
11 membrane active groups by surfactants [25,26]. Under certain conditions, the fouling  
12 of the membranes is mostly irreversible phenomenon, which makes these membranes  
13 unusable and therefore must be cleaned or replaced. In the membrane and  
14 electromembrane processes, the membrane cleaning or replacement operation is  
15 extremely expensive and costs between 40 and 50 % of process cost [27,28]. For this  
16 reason, it is very essential to search reliable and guaranteed solutions to reduce the  
17 fouling phenomenon caused likely by organic matters.

18 Among the offered solutions, the coupling of ED processes with other non-  
19 conventional methods, such as electrochemical oxidation (ECO) [29–31],  
20 photocatalysis [32], electrochlorination [33,34], electro-Fenton [35], bio-electro-Fenton  
21 technology [36] and electro-peroxone process [37]. ECO, which is also known as  
22 anodic oxidation (AO), is one of the most efficient, less expensive and  
23 environmentally-friendly advanced oxidation processes. The AO advantages make this  
24 method is most frequently used for the treatment of wastewaters [38]. Furthermore, it

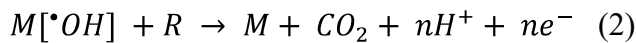
1 has been proven that AO can effectively eliminate the majority of organic pollutants  
2 from wastewaters [39–41].  
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4 Generally, the AO of organic or inorganic pollutants leads to the formation of simpler,  
5 non-toxic and biodegradable compounds [42]. The electrodes used in AO process are  
6 insoluble and active or non-active anodes such as boron-doped diamond (BDD), Pt, Gr,  
7 Ti/IrO<sub>2</sub>, Ti/SnO<sub>2</sub>, Ti/RuO<sub>2</sub>; PbO<sub>2</sub>, SnO<sub>2</sub>, etc [42,43]. These electrodes allow a complete  
8 oxidation of the most organic molecules into CO<sub>2</sub> and H<sub>2</sub>O. Several authors [40,44]  
9 have described the degradation mechanisms of organic compounds by AO which  
10 generally takes place into two stages:  
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21 1<sup>st</sup> stage: Anodic discharge of water and production of hydroxyl radicals (<sup>•</sup>OH) on the  
22 metal oxide electrode surface (M):  
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29 2<sup>nd</sup> stage: Oxidation of organic compounds (R) by <sup>•</sup>OH radicals:  
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34 The different AO advantages make this method a good candidate for combination with  
35 conventional ED, in order to realize a simultaneous effective removal of organic  
36 pollutants and for mitigating the membrane fouling.  
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41 Some recent works have also shown the effectiveness of coupled ED and AO for  
42 different uses such as for the removal of antibiotics [45], degradation of 2,4-  
43 dichlorophenoxyacetic acid [30,46], removal of synthetic dyes [1] and for the oxidation  
44 of mature landfill leachate [47]. For example, Raschitor et al. [46] tested a novel  
45 integrated ED/ECO process to concentrate and oxidize simultaneously the 2,4-  
46 dichlorophenoxyacetic acid. In this process, the pollutant is transferred through an  
47 anionic membrane to an anodic compartment in which it is then concentrated and  
48 oxidized. Interestingly, they demonstrated that this combined process improves the  
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1 degradation rate by more than twice compared to the conventional ECO. Additionally,  
2 in our previous work [48], we studied the removal of sodium dodecyl benzene  
3 sulphonate (SDBS) using ED-AO combined system using Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>/PbO<sub>2</sub> as  
4 oxidative anode. The results showed that the combination enhanced significantly the  
5 SDBS removal rate and also limits the membrane fouling.  
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10 The present study aims to investigate the integration of AO in ED to boost the  
11 oxidation of anionic azo-dye (methyl orange (MO)), and simultaneously overcome the  
12 membrane fouling. The combined AO and ED has two main purposes, (i) realization of  
13 *in-situ* electro-oxidation phenomenon in the same anode of ED, (ii) use of a new ED  
14 configuration permitting the preliminary removal of MO before its adsorption on the  
15 anion-exchange membrane (AEM). Pb/PbO<sub>2</sub> anode was designed to carry out the  
16 oxidation process. It is worthy to mention that Pb/PbO<sub>2</sub> have a particular attention at  
17 large scale of applications due to its high electro-oxidation efficiency, good electrical  
18 conductivity and low cost [49–52].  
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34 The Pb/PbO<sub>2</sub> electrode was prepared by formation of PbO<sub>2</sub> layer on lead plate and  
35 characterized by SEM-EDS method. The AEM fouling was confirmed by SEM-EDS  
36 and FTIR methods. Initially, experiments of ED and ED coupled with AO (ED-AO)  
37 were carried out on MO solution to unravel the feasibility and effectiveness of ED-AO  
38 hybrid process. The influence of some operating parameters on the efficiency of ED-  
39 AO process was studied. Finally, the prepared Pb/PbO<sub>2</sub> electrode reusability was also  
40 tested.  
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## 51 **2. Materials and methods**

### 52 **2.1. Chemicals and Reagents**

53 All chemicals used in this study have an analytical grade and all aqueous solutions  
54 were prepared by using double distilled water. MO (molecular formula:  
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1 C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub>SNa; molar mass: 327.33 g mol<sup>-1</sup>) obtained from Alfa Aesar was chosen as  
2 an organic pollutant. Sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>),  
3 trisodium orthophosphate (Na<sub>3</sub>PO<sub>4</sub>) and sodium chloride (NaCl) were from  
4 BIOCHEM-Chemopharma. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (96%), hydrochloric acid (HCl)  
5 (37%) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. Nitric acid  
6 (HNO<sub>3</sub>) (69%) and oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) (99.9%) were from Fluka. Hydrofluoric acid  
7 (HF) (48%) and Acetone (100%) was respectively obtained from Nice<sup>®</sup> and VWR.  
8 Other chemicals including potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), silver sulfate (Ag<sub>2</sub>SO<sub>4</sub>)  
9 and mercuric sulfate (HgSO<sub>4</sub>) were purchased from Merck.

## 2.2. Ions-exchange membranes

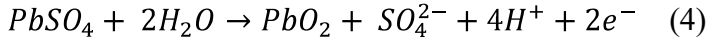
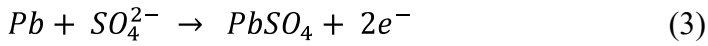
23 The cation and anion exchange membranes (CEM and AEM) used in this study are  
24 Neosepta CMX and AMX (Tokuyama Soda Co., Japan) respectively. The ion-  
25 exchange capacities are 1.4–1.7 meq g<sup>-1</sup> and 1.5–1.8 meq g<sup>-1</sup> for AMX and CMX  
26 membrane respectively. The both membranes have a homogenous hydrocarbonated  
27 structure (polystyrene-co-divinylbenzene), with sulphonated functional groups (–SO<sub>3</sub><sup>-</sup>)  
28 for the CMX and quaternary ammonium groups (–NR<sub>3</sub><sup>+</sup>) for the AMX [53,54]. Before  
29 using, the membranes were pretreated with conventional procedure [55]. Firstly, the  
30 membranes are submerged in NaOH (1 M) under a slight stirring for 24 h, then, in HCl  
31 solution (1 M) for the same period. Finally, these membranes are carefully washed with  
32 double distilled water and saved in NaCl solution (0.5 M).

## 2.3. Pb/PbO<sub>2</sub> electrode preparation

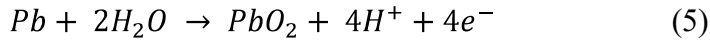
50 As mentioned before, the anodic oxidation process is carried out using Pb/PbO<sub>2</sub>  
51 electrode which is prepared according to the procedure described by several authors  
52 [49,56–58]. The preparation of this electrode type is based on the formation of PbO<sub>2</sub>  
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1 layer on Pb plate surface by electrolysis in H<sub>2</sub>SO<sub>4</sub> solution according to the reactions of  
2 Eqs. (3), (4), and (5) [49]:  
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9 Overall reaction:  
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14 For this, a cylindrical Pb plate was pretreated according the procedure reported by  
15 Awad and Galwa [56] to ensure good formation of PbO<sub>2</sub> layer. Initially, the Pb surface  
16 was roughened by a mechanical abrasion using sand papers to increase the PbO<sub>2</sub> layer  
17 adhesion. It was then cleaned with acetone to remove all solid particles and organic  
18 matters rested in the surface. Next, the metal surface was washed carefully with an  
19 alkali solution containing a mixture of Na<sub>2</sub>CO<sub>3</sub> (20 g L<sup>-1</sup>), NaOH (50 g L<sup>-1</sup>), Na<sub>3</sub>PO<sub>4</sub>  
20 (20 g L<sup>-1</sup>) and H<sub>2</sub>SO<sub>4</sub> (2 g L<sup>-1</sup>). Then, it was cleaned by mixed acid solution (HNO<sub>3</sub>  
21 (400 g L<sup>-1</sup>), HF (5 g L<sup>-1</sup>)) for 2 min and boiled in oxalic acid solution (100 g L<sup>-1</sup>) for 5  
22 min. Finally, in order to oxidize the Pb surface into PbO<sub>2</sub>, the pretreated Pb plate was  
23 placed as anode into electrolysis with H<sub>2</sub>SO<sub>4</sub> solution (10 %) at a stable current density  
24 (*i*) of 50 mA cm<sup>-2</sup> and duration of 1.5 h [49,57,58]. A stainless steel (SS) electrode was  
25 used as the cathode current feeder.  
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#### 44 **2.4. ED and ED-AO experimental set-up** 45

46 A three-compartment cylindrical Plexiglas cell (Fig. 1(a)) was constructed in the  
47 laboratory. These compartments were separated by a pair of AMX and CMX  
48 membranes. Each separating membrane had an effective area of 9.61 cm<sup>2</sup> which equal  
49 to the area of the electrodes placed at the ends of E<sub>1</sub> and E<sub>2</sub> compartments. The  
50 diameter and the thickness of each compartment were 3.5 and 1.4 cm, respectively,  
51 where the volume is 13.45 cm<sup>3</sup>. In the case of ED process, two SS electrodes are used.  
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1 However, in the ED-AO process, the cathode is SS electrode, while the anode is made  
2 of prepared Pb/PbO<sub>2</sub> electrode.  
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4 The new ED configuration applied in this study (Fig. 1(a)) is based in the circulation of  
5 feed solution (0.5 L containing MO and Na<sub>2</sub>SO<sub>4</sub> in all experiments) firstly into the  
6 anodic compartment (E<sub>1</sub>), and it then circulates in the cathodic compartment (E<sub>2</sub>).  
7 Finally, this solution is returned in the same tank by performing a closed circuit. The  
8 flow rate of feed solution is fixed at 40 mL min<sup>-1</sup>. In the central compartment (C)  
9 (concentrate compartment) which delimited by CMX and AMX membranes circulates  
10 0.25 L of H<sub>2</sub>SO<sub>4</sub> (0.05 M). All solutions were agitated in their tanks and injected into  
11 the cell compartments by using peristaltic pumps (Masterflex L/S). A stabilized power  
12 supply (YD18303D DC Power Supplies) was used to apply an electric field between  
13 the electrodes. The current intensity and voltage are controlled by multimeters  
14 (Multimetrix DMM121). The duration of all experiments (ED and ED-AO) was fixed  
15 at 180 min and regular samples of 5 mL were taken from the feed solution.  
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### 33 **2.5. Principles and procedures of ED and ED-AO processes**

34 Schematic representation of the principles and procedures of ED and ED-AO processes  
35 is shown in Fig. 1(b) and 1(c). In the two processes, the feed solution containing MO as  
36 an organic pollutant and Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte circulates successively into  
37 the side compartments (E<sub>1</sub> and E<sub>2</sub>). An acidic solution (H<sub>2</sub>SO<sub>4</sub>, 0.05 M) as concentrate  
38 solution circulates in the central compartment (C).  
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48 First of all, ED and ED-AO experiments at the same operating conditions were carried  
49 out to evaluate the feasibilities of simultaneous MO degradation and AMX membrane  
50 fouling mitigation in the ED-AO compared to single ED process. In these experiments,  
51 the initial concentrations of MO and Na<sub>2</sub>SO<sub>4</sub> in feed solution were 25 mg L<sup>-1</sup> and 0.05  
52 M, respectively, with applied current density of 20 mA cm<sup>-2</sup> and natural pH (≈ 6.8). In  
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1 the ED process (Fig. 1(b)), MO anionic molecules do not undergo any degradation and  
2 cannot cross the AMX membrane. However, as shown in Fig. 1(c), in the ED-AO  
3 process, the presence of Pb/PbO<sub>2</sub> anode in E<sub>1</sub> compartment can preliminary degrade the  
4 MO molecules. Then, in order to study the influence of operation factors affecting  
5 performance of the ED-AO process for treating the MO + Na<sub>2</sub>SO<sub>4</sub> mixture solution, the  
6 main factors were studied, including applied current density (1, 7.5, 15, 20, 25 and 30  
7 mA cm<sup>-2</sup>), initial MO concentration (5, 10, 25, 50, 75 and 100 mg L<sup>-1</sup>), initial pH of  
8 feed solution (1.5, 3, 6.8 (natural pH), 8.5 and 11.5) and concentration of supporting  
9 electrolyte (Na<sub>2</sub>SO<sub>4</sub>) (0.025, 0.05, 0.1, 0.2 and 0.4 M). The initial pH of the feed  
10 solution was adjusted by NaOH (1 M) and H<sub>2</sub>SO<sub>4</sub> (1 M) solutions. All the experiments  
11 were conducted in three times. In the other hand, the reusability of prepared Pb/PbO<sub>2</sub>  
12 electrode was investigated. For this, we subjected it to ten cycles of use in the ED-AO  
13 coupling process.

## 31 **2.6. Analytical methods**

32 A morphological characterization of prepared Pb/PbO<sub>2</sub> electrode was carried out to  
33 confirm the formation of PbO<sub>2</sub> layer on the electrode surface. After its preparation, the  
34 Pb/PbO<sub>2</sub> electrode surface was softly rinsed with double distilled water and dried at  
35 room temperature for a night and analyzed by Scanning electron microscopy (SEM)  
36 and by energy dispersive X-ray spectroscopy (EDS) methods. To observe the AMX  
37 membrane fouling phenomenon by MO molecules deposition, the AMX pristine  
38 membrane and those used in the ED and ED-AO processes were analyzed by Fourier  
39 transform infrared (FTIR) and SEM-EDS methods. For this, the membranes samples  
40 were dried under vacuum at 50 °C for 4 h [59] and were then analyzed. MEB-EDS and  
41 FTIR characterization was respectively done using a Phenom Pro X Scanning Electron  
42 Microscope and an Agilent Technologies Cary 630 FTIR Spectrometer.

1 The membrane fouling phenomenon leads to the increase of its electrical resistance as  
2 well as increase in the cell electrical resistance (CER) [22]. It is interesting to follow  
3 the CER variation during the processes. The CER variation was calculated by utilizing  
4 the CER variation during the processes. The CER variation was calculated by utilizing  
5 the voltage measured at regular time intervals during the processes and by Ohm's law  
6 application (Eq. (6)) :  
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$$11 \text{ CER (ohm)} = \frac{U (V)}{I (A)} \quad (6)$$

12 Where U is the voltage measured during the processes and I is the applied current  
13 intensity.  
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16 For determinate the decolorization efficiency, the samples of MO feed solution were  
17 analyzed by using a UV-Vis spectrophotometer, SP-UV 300 SRB (Spectrum  
18 Instruments GMBH) with maximum absorption seen at the wavelength of 464 nm  
19 [1,60]. The concentration of MO in its samples of aqueous solution was calculated  
20 using a calibration curve based on the known concentrations. Finally, the decolorization  
21 rate is calculated using Eq. (7).  
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$$34 \text{ Decolorization rate (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (7)$$

35 Where:  $C_0$  and  $C_t$  are respectively, the MO concentration in the feed solution at initial  
36 and t time of the treatment.  
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43 In order to evaluate the quality of the treated water, the chemical oxygen demand  
44 (COD) removal which also represents global mineralization was determined for the  
45 sample of initial feed solution and that taken at the end of process. COD was  
46 determined by using the dichromate method followed by photometric measurement.  
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53 The COD removal rate was calculated as:

$$54 \text{ COD removal rate (\%)} = \frac{COD_0 - COD_f}{COD_0} \times 100 \quad (8)$$

55 Where:  $COD_0$  and  $COD_f$  are respectively, the initial and final COD of the feed solution.  
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### 3. Results and discussion

#### 3.1. SEM-EDS characterization of prepared Pb/PbO<sub>2</sub> electrode

Several authors have showed the efficiency of PbO<sub>2</sub> layer deposition on lead plate through electrolysis in sulfuric acid solution [49,56,58,61,62]. This method is based on the oxidation of metallic lead and generation of dioxygen on anode surface [61]. Fig. 2 shows SEM images of Pb/PbO<sub>2</sub> electrode surface before and after PbO<sub>2</sub> layer formation. These images show that the original electrode (Fig. 2(a)) has a pseudo homogeneous and relatively uniform surface as well as the pores size was very fine. By contrast, after its electrolysis in sulfuric acid solution as anode for 1.5 h (Fig. 2(b)), the electrode surface is not uniform crystal size and this surface becomes rougher. This can be due to the production of dioxygen on the anode surface which changing the crystal structure during the electrochemical reaction process [58]. From Fig. 2(b) it can be also seen that the formed PbO<sub>2</sub> layer covers the entire electrode surface, along with the formation of tightly packed and pyramid-shaped crystals. In addition, PbO<sub>2</sub> crystal size is approximately uniform.

The results of elementary analysis by EDS of the electrode surface before and after electrolysis are presented in Fig. 2 and Table 1. Firstly, the obtained spectrogram (Fig. 2(c)) indicates the presence of C in electrode surface before electrolysis. This is probably due to the organic trace substances rested from the electrode preparation procedure [63]. Furthermore, this analysis shows that the O and Pb elements are present in electrodes samples before (Fig. 2(c)) and after (Fig. 2(d)) electrolysis. However, the atomic percentage (Table 1) of O is increased in 3 times after electrolysis. On the other hand, the proportion between Pb and O shifts from 1:0.3 (before electrolysis) to 1:1.53 (after electrolysis).

#### 3.2. SEM-EDS and FTIR characterization of AMX membranes

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In order to investigate the efficiency of AMX membrane fouling mitigation in the ED-AO process compared to single ED process, the membranes used in the both processes were analyzed by SEM-EDS and FTIR. These experiments were carried out at the same operating conditions. Fig. 3 shows the SEM images and EDS spectrograms of the AMX pristine membrane, and those used in the studied processes. Table 2 also illustrates the atomic percentage of chemical elements contained in the membrane surfaces. SEM images of pristine membrane (Fig. 3(a)) showed its plane surface. The comparison of this image with those of membranes used in ED (Fig. 3(b)) and in ED-AO (Fig. 3(c)) shows that the morphologies of membrane surface are changed. This difference is undoubtedly due to the formation of organic matters agglomeration. From the Fig. 3(b), it can be seen a large amount of MO agglomerates was deposited and covering an important part of the membrane. It was also observed that the formation of MO agglomerates at the AMX surface is less pronounced in the case of ED-AO process (Fig. 3(c)).

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Indeed, this morphological analysis clearly shows the fouling of the membrane used in ED by MO deposition. However, the surface of membrane used in the ED-AO is less fouled with MO deposits. These results allow demonstrating the significant membrane fouling by MO deposition during the ED compared to ED-AO. Similar results are obtained in our previous work for the AMX membrane fouling by sodium dodecyl benzene sulphonate [48].

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From the EDS spectrograms (Fig. 3(d), 3(e) and 3(f)) and the atomic percentage of chemical elements (Table 2) we firstly note the presence of Cl on the pristine membrane surface. However, this chlorine will be disappeared in the cases of used membranes. The chlorine came from the membrane equilibration by HCl and NaCl solutions during its pretreatment procedure. Additionally, all spectrograms show the

1 presence of C, O and N which constitute the AMX membrane structure [53,54].

2 However, only the membranes used in ED and ED-AO processes showed the presence  
3 of sulfur. This sulfur is due to the adsorption of MO on the membrane surface. The  
4 presence of sulfur and the increase of atomic percentage of oxygen (from 6.73 to 12.65  
5 and 18.38 %) and nitrogen (from 5.16 to 11.64 and 16.14%) (Table 2) in the cases of  
6 used membranes confirm the presence of MO on membrane surface for both processes.

7 One can also see that the atomic percentages of oxygen and sulfur for the membrane of  
8 ED-AO (18.38 and 3.13 % respectively) are more important compared to those of  
9 membrane used in ED (12.65 and 2.37 % respectively), whereas it is the opposite for  
10 nitrogen. This it means that the amount of sulfate ions ( $\text{SO}^{2-}$ ) in the membrane of ED-  
11 AO is more important, while the membrane of ED is richer into MO. Finally, these  
12 results demonstrated that the membrane fouling phenomenon by MO is more  
13 significant in the case of ED compared to ED-AO process.

14 The AMX membranes' fouling by MO deposition during the processes was also  
15 investigated by FTIR. Fig. 4 shows the obtained spectra for the AMX pristine  
16 membrane, and for those used in ED and ED-AO processes. Several peaks observed on  
17 the pristine membrane spectrum are also present on the spectra of used membranes.  
18 Moreover, the comparison of these spectra reveals the presence of new peaks for the  
19 used membranes characterizing the presence of MO on their surfaces. The first peak is  
20 observed at  $1605.9 \text{ cm}^{-1}$ , this peak corresponds to the azo group ( $-\text{N}=\text{N}-$ ) present in  
21 MO structure. Two others peaks at  $1519$  and  $1444 \text{ cm}^{-1}$  are probably due to the C-H  
22 bending in the C=C-H plane. The sulphonic group characterizing MO dye was  
23 confirmed with an intense peak appeared at  $1359 \text{ cm}^{-1}$ .

24 Two peaks are produced at  $1035.9$  and  $946.1 \text{ cm}^{-1}$  which are attributed to the ring  
25 vibration. Stretching of aromatic benzene ring was confirmed with a peak at  $822 \text{ cm}^{-1}$ .

1 The last peaks centered at 698.23, 624.94 and 570.93  $\text{cm}^{-1}$  corresponding to C–S  
2 stretching vibrations.  
3

4 On the other hand, it was noted that there is not a notable difference between both  
5 spectra of used membranes (in ED and in ED-AO), except different intensities in some  
6 peaks. This difference means that the membrane fouling is more significant in the case  
7 of ED compared with that in ED-AO. Finally, the results of SEM-EDS and FTIR  
8 characterization of the AMX membranes mean that the coupling of AO to ED process  
9 reduces the membrane fouling by MO deposition.  
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### 19 **3.3. Efficiency of ED-AO coupling in MO removal and AMX membrane anti-** 20 **fouling** 21

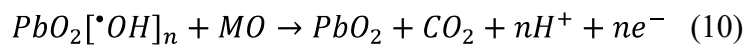
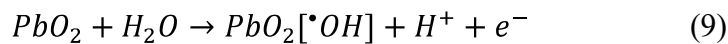
22 To evaluate the performance of combined ED-AO on AMX membrane fouling  
23 mitigation and MO degradation, ED and ED-AO processes were compared. These  
24 experiments were carried out at the same operating conditions and during the same  
25 duration. The results are expressed by using the variation of CER (Fig. 5(a)) and  
26 decolorization rate (Fig. 5(b)) during the processes. COD removal and decolorization  
27 efficiencies (Fig. 5(c)) determined in the end of each experiment will be also discussed.  
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38 In electromembrane process, the CER control is a main factor for detecting the  
39 membrane fouling phenomenon, because the deposition of particles or/and organic  
40 molecules on the membrane surface leads to the increase of its electrical resistance and  
41 consequently causing the increase of CER [64]. Therefore, Fig. 5(a) shows a significant  
42 increase of CER during the ED process where it starts from 58 to reach at 130.46 ohm  
43 after 180 min of process. This notable increase of CER during the ED indicates the  
44 continuous fouling of the AMX membrane by  $\text{MO}^-$  anionic molecules accumulation.  
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1 the CER in the ED-AO process changes slightly between 46.02 and 58.53 ohm. From  
 2 the Fig. 5(a) it can be also seen that the CER has been reduced 2.2 times after 3 hours  
 3 of process by the presence of AO. Accordingly, the coupling of AO to the ED process  
 4 allows keeping a slight change of CER and consequently attenuates considerably the  
 5 AMX membrane fouling. From the same figure (Fig. 5(a)), it was also found that the  
 6 CER at time 0 is slightly different in the two processes (58 and 46.02 ohm for ED and  
 7 ED-AO respectively). This is probably due to the anode nature (into SS for ED and into  
 8 Pb/PbO<sub>2</sub> for ED-AO), because the Pb/PbO<sub>2</sub> electrode has a good electrical conductivity  
 9 compared to the several others types of electrodes [65].  
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11 From Fig. 5(b), it was found that the ED-AO process presents a better decolorization  
 12 effect on the MO molecules where the decolorization rate is reaching around 73.48 %  
 13 after 180 min of treatment. By contrast, in the case of ED process the decolorization  
 14 rate increases slightly during the first 60 min until 26.92 % and it could reach 32.98 %  
 15 at the end of experiment. This 26.92 % of decolorization is possibly due to the MO  
 16 anionic molecules adsorption in the AMX membrane surface in a significant way  
 17 during the cited duration. However, in ED-AO there is an ECO process on Pb/PbO<sub>2</sub>  
 18 electrode which strongly contributes in MO degradation by following the reactions of  
 19 Eqs. 9 and 10.  
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23 As shown in Fig. 5(c), it was also inferred that the COD removal rate reflecting the  
 24 mineralization of feed solution is the better in the case of ED-AO with a value of 68.36  
 25 %. However, it does not exceed 30.21 % in ED process. Indeed, the presence of  
 26 Pb/PbO<sub>2</sub> electrode in ED cell improved the decolorization and COD removal rates  
 27 approximately 2.2 times after 3 hours of process. In addition, the comparison between  
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1 the decolorization rate and COD removal rate values into the end of the both processes  
2 (Fig. 5(c)) reveals that there is not a notable difference between them. Indeed, the  
3 efficiency of Pb/PbO<sub>2</sub> electrode into degradation of several organic pollutants was  
4 demonstrated in numerous previous studies [57,51,66–68], where, in most cases a  
5 pseudo-total degradation of these organic pollutants into CO<sub>2</sub> and H<sub>2</sub>O was obtained.  
6 These results showed clearly the benefit of the introduction of AO on a Pb/PbO<sub>2</sub>  
7 electrode into ED process for attenuate the AMX membrane fouling and for enhance  
8 the MO azo-dye degradation. Generally, the efficiency of electrodes based on lead  
9 dioxide (PbO<sub>2</sub>) surfaces in electro-oxidation organics is could be explained by its good  
10 characteristics such as: the high oxygen overpotential and high electrical conductivity  
11 [51,56].  
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### 27 **3.4. Effect of operating parameters on ED-AO efficiency**

28 The effect of some operating parameters such as: applied current density, initial MO  
29 concentration, initial pH of feed solution and concentration of supporting electrolyte  
30 were studied in order to improve the electro-oxidation of MO and to reduce  
31 simultaneously the AMX membrane fouling in ED-AO process. The results of this  
32 study are presented generally in term of variation of CER and decolorization rate  
33 during the process and in term of COD removal rate determined in the end of each  
34 experiment. In addition, the pseudo-first-order model was occasionally applied to  
35 discuss the kinetics of MO degradation.  
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#### 48 **3.4.1. Effect of applied current density**

49 In an ED-AO coupling process, the role of applied electric field is double: transports  
50 the ionic species across the IEMs and generates the hydroxyl radicals ( $\cdot\text{OH}$ ) on the  
51 Pb/PbO<sub>2</sub> electrode surface for degrading the MO molecules. Accordingly, the effect of  
52 various current densities (1 – 30 mA cm<sup>-2</sup>) on the ED-AO process was investigated. It  
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1 was demonstrated that the current density applied in AO processes must be highest  
2 possible for achieving the maximum processing efficiency [65,69,70]. However, in this  
3 study, it is worth noting that, we did not work at very high densities for avoid  
4 approaching to the value of limiting current density. Because in ED process, when this  
5 value is exceeded, the concentration polarization phenomenon in membranes surface is  
6 started which leads to a considerably increase of membranes electrical resistance  
7 [71,72].

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9 From Fig. 6(a), it could be seen that for the two lowest current densities (1 and 7.5 mA  
10 cm<sup>-2</sup>) the CER increases drastically. The similar trend was observed previously in the  
11 case of ED (Section 3.3). The increase of CER at low densities is likely as a result of  
12 the continuous AMX membrane fouling by MO accumulation. However, the increase  
13 of the current density at more than 15 mA cm<sup>-2</sup> makes a slightly variation of CER,  
14 especially for the two highest densities (25 and 30 mA cm<sup>-2</sup>). The increase in current  
15 density reinforces more the degradation of MO by electro-oxidation, and consequently  
16 attenuates its adsorption at AMX membrane surface.

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18 Additionally, as shown in Fig. 6(b) and 6(c), the increase of current density boosts  
19 considerably the degradation of MO in terms of the decolorization and COD removal.  
20 Particularly, the decolorization and COD removal efficiencies improved significantly  
21 (from 42 to 68 % and from 41 to 61 %, respectively) when current density increased  
22 from 7.5 to 15 mA cm<sup>-2</sup>. By contrast, at low current densities, the decolorization and  
23 COD removal rates were the lowest. For example, at density of 1 mA cm<sup>-2</sup>, no obvious  
24 degradation of MO was observed, because these results are extremely similar to those  
25 obtained previously for the ED process (Section 3.3), where there is not any electro-  
26 oxidation. The decolorization and COD removal obtained at low current densities is

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mainly due to the adsorption of MO in the AMX membrane surface, but not to the electro-oxidation phenomenon.

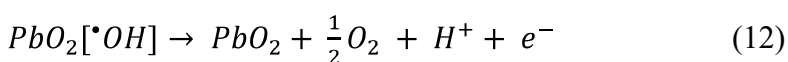
On the other hand, the decolorization of MO solution by electro-oxidation on Pb/PbO<sub>2</sub> electrode has been followed with pseudo-first-order kinetic by applying of Eq. (11). From the obtained results (Fig. 6(d) and Table 3), it was observed that the rate constant (k) for densities 1, 7.5, 15, 20, 25 and 30 mA cm<sup>-2</sup> were increased as follow, 0.24×10<sup>-2</sup>, 0.31×10<sup>-2</sup>, 0.66×10<sup>-2</sup>, 0.73×10<sup>-2</sup>, 0.99×10<sup>-2</sup> and 1.04×10<sup>-2</sup> min<sup>-1</sup>, respectively. From which it was noted that, the increase in the applied current density obviously accelerated the MO degradation reactions.

$$C_t = C_0 e^{-kt} \quad (11)$$

Where, C<sub>0</sub> and C<sub>t</sub> are respectively, the MO concentration in the feed solution at initial and t time of the treatment, and k is the rate constant (min<sup>-1</sup>).

Indeed, it was inferred that the increase of applied current density simultaneously improving the MO degradation and reducing the membrane fouling which is reflected by the decrease of CER. The applied current contributes directly in the generation of hydroxyl radicals (<sup>•</sup>OH) (Eq. (9)) on the Pb/PbO<sub>2</sub> electrode. For that reason, the higher current density led to the production of larger amount of <sup>•</sup>OH and consequently improved the degradation efficiency of organic pollutant (e.g., MO) [73,74,75].

On the other hand, it was also observed that the two densities 25 and 30 mA cm<sup>-2</sup> gave approximately the similar results, although the current density increased by 5 mA cm<sup>-2</sup>. This is probably explained by secondary reactions occurred at higher current density such as oxygen evolution (Eq. (12)), which compete with the MO degradation reaction (Eq. (10)) [76]. Based on these results, the density of 25 mA cm<sup>-2</sup> was chosen for the rest of the work.



### 3.4.2 Effect of initial MO concentration

The effect of initial MO concentration ( $5 - 100 \text{ mg L}^{-1}$ ) on the degradation efficiency and AMX membrane fouling in ED-AO process was investigated. The obtained results were displayed in Fig. 7. From the Fig. 7(a), it can be observed that for all MO concentrations varying in the range  $5 - 25 \text{ mg L}^{-1}$ , there was no obvious effect of these concentrations on the CER. However, for concentrations equal to or higher than  $50 \text{ mg L}^{-1}$ , the increasing of MO concentration increases significantly the CER during the process. This evolution of CER in the cases of three highest MO concentration signifies that, the abundance of large amount of  $\text{MO}^-$  anion in close proximity to the membrane surface reinforces its fixation over the membrane active functional sites. The molecular size of  $\text{MO}^-$  ion and its high concentration in the solution makes it more difficult for this organic anion to pass through the AMX membrane or to desorb toward the solution. The adsorption of large amount of organic compound ions (e.g.,  $\text{MO}^-$ ) in the membrane surface leads to its continuous fouling which consequently leads to the deterioration of its electrical proprieties [23,77]. For that reason, the CER increases considerably during the process when the organic compound concentration in the solution is very higher.

On the other hand, the increase of initial MO concentration from  $5$  to  $100 \text{ mg L}^{-1}$  decreased gradually the decolorization efficiencies (from  $88.21$  to  $68.23\%$ ) and the COD removal rates (from  $85.44$  to  $57.35\%$ ) (Fig. 7(b)). Several authors [1,51,78] attributed the decreasing of decolorization efficiency for the higher initial dye concentration to the competition of generated intermediate by-products, with the original dye molecules to react with oxidizing species through the ECO process. Moreover, at constant current density, the increasing of organic compound concentration (e.g., MO) leads to a decrease in the  $\cdot\text{OH}/\text{MO}$  molar ratio, which

1 consequently decreases the probability of encounter between  $\cdot\text{OH}$  radicals and MO  
2 molecules [48].  
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4 In addition, from the Fig. 7(b), it can be seen that the increase of the initial  
5 concentration from 5 to 100 mg L<sup>-1</sup> leads to the increase of the difference between  
6 decolorization and COD removal rates. Meanly, there is not any consistency between  
7 them during the increase of initial concentration. The possible reason is that, with the  
8 increase of initial MO concentration, the most of generated  $\cdot\text{OH}$  radicals can be  
9 consumed during the oxidation of MO into by-products, but not by the mineralization  
10 into CO<sub>2</sub> and H<sub>2</sub>O [76,79]. Finally, the concentration 25 mg L<sup>-1</sup> was adopted in the rest  
11 of the work to avoid any obvious increase in CER and any strong decrease in process  
12 efficiency.  
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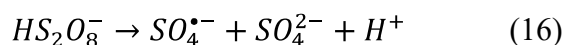
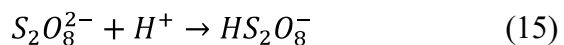
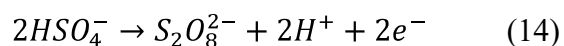
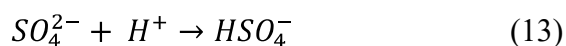
### 26 **3.4.3 Effect of pH of feed solution**

27 In ECO processes, the pH of pollutant solution affects the  $\cdot\text{OH}$  generated amounts,  
28 oxygen overpotential and stability of electrodes, which consequently affects the  
29 efficiency of the process [41,65]. For this, some experiments of ED-AO on MO  
30 solution (25 mg L<sup>-1</sup>) were performed at different initial pH values varying in the range  
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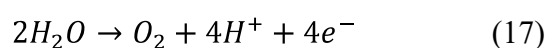
41 As shown in Fig. 8(a) and 8(b), the variation of pH value from 6.8 (natural pH) to 11.5  
42 has no obvious effect on the decolorization and COD removal. However, the  
43 decolorization and COD removal rates were increased from 82.16 to 97.62 % and from  
44 76.33 to 95.75%, respectively when pH was adjusted from 6.8 to 3. In addition, at  
45 strong acid pH (pH 1.5) the decolorization of MO solution was total (> 99 %) and the  
46 COD removal was quasi-total (> 98 %). Above results indicated that lower pH values  
47 were the benefit of the MO degradation and mineralization in ED-AO process. In  
48 addition, from the Fig. 8(a) it can be also seen that the decolorization rate reaches about  
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1 93 and 70 % after the first 60 min for the two acidic pHs 1.5 and 3, respectively, while  
2 within the same time it does not exceed 49 % for pHs equal to or higher than 6.8.  
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4 Accordingly, the results of kinetic analysis (Fig. 8(c) and Table 3) also showed that the  
5 rate constant (k) values in the cases of acid pH were the highest. Subsequently, k  
6 decreased with the increase of pH value indicating that, the lower the pH, the more  
7 rapidly the MO degradation reaction.  
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14 Many previous works [63,74,80–82] have reported that the AO of organic compounds  
15 is favored in acid pHs. A study by Ghalwa et al. [66] also found that the maximum  
16 removal of linuron and COD are obtained at pH 1.5 by using Pb/PbO<sub>2</sub> electrode, which  
17 is in agreement with that obtained in this study for MO degradation. Maharana et al.  
18 [74] and Zhao et al. [80] have mentioned that the generation of <sup>•</sup>OH radical is more  
19 favored at the low pH level. In contrast, the increase of pH value decreases the <sup>•</sup>OH  
20 generated amount. Li et al. [83] have also ascribed the improvement of degradation of  
21 Reactive Blue 19 in acidic conditions and in presence of SO<sub>4</sub><sup>2-</sup> to the production of  
22 sulfate radicals (SO<sub>4</sub><sup>•-</sup>) and peroxodisulfate ions (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) by acid-catalyzed reactions  
23 according to Eqs. (13), (14), (15), and (16). These species present a high oxidation  
24 power and it could quickly attack any organic pollutant [84–86], increasing  
25 consequently the degradation rate. In addition, since its electrophilic characteristic, the  
26 SO<sub>4</sub><sup>•-</sup> radical is considered as stronger oxidant of organic matter (e.g., MO) when  
27 compared with <sup>•</sup>OH. Therefore, a smaller amount of this oxidant is sufficient to ensure  
28 complete mineralization [86,87].  
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1 On the other hand, the decrease of decolorization and COD removal rates at pHs  $\geq 6.8$ ,  
2 especially for alkaline pHs (8.5 and 11.5) (Fig. 8(a) and 8(b)) compared to acidic pHs is  
3 probably due to the evolution of oxygen generation which is favored into alkaline  
4 medium [62,88]. Consequently, the evolution of oxygen (Eqs. (12) and (17)) reduces  
5 the current efficiency and it can also prevent the diffusion of organic anions towards  
6 the anode surface [89].  
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16 In this manner, the decolorization and mineralization of MO solution is favored in  
17 acidic pH. Therefore, in the ED-AO process, working in acidic conditions can  
18 accelerate significantly the degradation of organics contained in the solution, thus  
19 reduce the possibility of membrane fouling by these organics.  
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#### 27 **3.4.4. Effect of supporting electrolyte concentration**

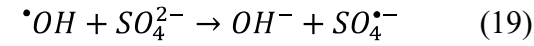
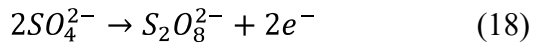
28 In ECO processes, the role of supporting electrolyte is normally to provide a  
29 conductive medium and to decrease the voltage drop. Sodium sulfate ( $Na_2SO_4$ ) is  
30 usually used for its high solubility, its good conductivity and no parasitic reactions  
31 occurred with the use of this electrolyte [82,90]. Consequently, in order to investigate  
32 their effect on MO degradation by ED-AO, different concentrations (0.025 – 0.4 M) of  
33  $Na_2SO_4$  supporting electrolyte were applied.  
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44 The obtained results (Fig. 9(a) and 9(b)) show that the increase in  $Na_2SO_4$  concentration  
45 into the range 0.025 – 0.1 M resulted a significant increase in both decolorization and  
46 COD removal rates where reached 98.67 and 96.17%, respectively. However, for the  
47 two highest concentrations (0.2 and 0.4 M), a total decolorization (>99%) with a slight  
48 regression in COD removal (from 96.17 to 92.27% and to 89.35%) were registered. It  
49 is also noticeable that the degradation of MO in the cases of three highest  
50 concentrations of  $Na_2SO_4$  (0.1, 0.2 and 0.4 M) (Fig. 9(c) and Table 3) is very faster  
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1 during the first 60 min ( $k= 3.39\times 10^{-2}$ ,  $4.34\times 10^{-2}$  and  $5.21\times 10^{-2}$   $\text{min}^{-1}$ , respectively),  
2 then it became relatively slower ( $k= 1.91\times 10^{-2}$ ,  $2.13\times 10^{-2}$  and  $2.02\times 10^{-2}$   $\text{min}^{-1}$   
3 respectively) until the end of experiment. This tendency was not observed for the two  
4 others concentrations (0.025 and 0.05 M), where the degradation rate is slow from the  
5 starting of the experiment.  
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8 The greatly improvement in decolorization can possibly be attributed to the  
9 contribution of the mediated oxidation of MO by  $\text{S}_2\text{O}_8^{2-}$  and direct oxidation by  $\text{SO}_4^{\bullet-}$ ,  
10 which are formed from the oxidation and  $\cdot\text{OH}$  attack of  $\text{SO}_4^{2-}$  according to Eqs. (18),  
11 (19), and (20) [63,85,91]. Probably, the same reason made the COD removal increased  
12 for the range 0.025 – 0.1 M of  $\text{Na}_2\text{SO}_4$ , although it has slightly regressed in the cases of  
13 the two others concentrations (0.2 and 0.4 M). Moreover, the increasing in supporting  
14 electrolyte concentration improves the medium conductivity, and consequently  
15 accelerates charge and mass transfer, thus benefiting the ECO reactions [90].  
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34 Ma et al. [91] and Zhang et al. [92] have inferred that the oxidation of  $\text{SO}_4^{2-}$  into  
35  $\text{S}_2\text{O}_8^{2-}$  is increasingly favored with the increase in its concentration. However, these  
36 authors have also found that at moderately high current density and with the increase of  
37  $\text{Na}_2\text{SO}_4$  concentration, a slight abatement in the degradation of targeted organics is  
38 registered. The same trend was observed in this study concerning the regression of  
39 COD removal for concentrations of  $\text{Na}_2\text{SO}_4$  at more than 0.1 M (Fig. 9(b)). The  
40 negative effect of  $\text{Na}_2\text{SO}_4$  at higher concentrations on the completely mineralization of  
41 organics, is possibly ascribed to the following reasons:  
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i) The consumption of generated  $\cdot\text{OH}$  by  $\text{SO}_4^{2-}$  at anode surface for giving  $\text{SO}_4^{\cdot-}$  (Eq. (19)) which is retransformed into  $\text{S}_2\text{O}_8^{2-}$  (Eq. (20)). The  $\text{S}_2\text{O}_8^{2-}$  ion is relatively stable at room temperature [83], so it is majority in the system, this it makes the degradation of small molecules of by-products generated in the middle of degradation process is more difficult.

ii) The competition between  $\text{SO}_4^{2-}$  oxidation (Eq. (18)) and  $\cdot\text{OH}$  generation (Eq. (9)) at the surface of anode. This can reduce the extent of the direct oxidation of organic compounds (e.g., generated by-products) by  $\cdot\text{OH}$  and consequently affects their completely mineralization [83,91].

On the other hand, a slightly decrease of CER after about 90 min of process was obtained when the  $\text{Na}_2\text{SO}_4$  concentration equal to or higher than 0.1 M (Fig. 9(d)), where it reaches in the end of experiments at 38.85, 32.53 and 29.25 ohm for concentrations 0.1, 0.2 and 0.4 M respectively. In contrast, a slightly increase of CER is observed in the cases of the two lowest concentrations (0.025 and 0.05 M) and values of 61.75 and 50.38 ohm were respectively registered at the end of experiments. In fact, the increase of supporting electrolyte concentration not only improves the MO degradation for attenuate the membrane fouling, but also increases significantly the feed solution conductivity. In view of this, the better concentration of  $\text{Na}_2\text{SO}_4$  is 0.1 M because it gives a quasi-total decolorization (> 98%), the best COD removal (96.27%) and a CER approximately constant.

### 3.5. Reusability of Pb/PbO<sub>2</sub> electrode

The reusability and continued effectiveness of electrodes is an important factor for a practical application, especially at industrial scale. Herein, ten experiments of ED-AO were performed at optimal conditions ( $i = 25 \text{ mA cm}^{-2}$ ,  $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$ , natural pH ( $\approx 6.8$ ) and  $[\text{Na}_2\text{SO}_4] = 0.1 \text{ M}$ ). The results of Pb/PbO<sub>2</sub> electrode reusability are mainly

1 discussed in term of decolorization and COD removal efficiencies after 3 hours of  
2 treatment. Besides, to confirm whether its reuse affects the membrane fouling  
3 mitigation, the CER values determined at the end of experiments are also discussed. As  
4 shown in Fig. 10, the decolorization rate remained virtually constant (balancing  
5 between 97.45 and 99.37 %) during 10 cycles. However, COD removal rate slightly  
6 decreases from the seventh cycle, where it has reached at 86 % in the tenth cycle. The  
7 regression in COD removal is probably due to the fact that the reuse of Pb/PbO<sub>2</sub>  
8 electrode for seven cycles makes the degradation of generated by-products is more  
9 difficult. This is can be explained by the change of electrode surface properties, which  
10 can reduce slightly the extent of the hydroxyl radicals generation. On the other hand,  
11 Fig. 10 shows that there is not obviously evolution in CER value, where it does not  
12 deviate from the range 37.75 – 41.91 ohm in the all cycles. Mainly, there is not any  
13 significant fouling of the AMX membrane during these experiments.

#### 31 **4. Conclusions**

32 A novel configuration of ED with AO integration was investigated in order to eliminate  
33 the MO anionic azo-dye, and to reduce simultaneously the AMX membrane fouling.

34 From this work, the following conclusions can be taken:

- 35 • The characterization results showed that the PbO<sub>2</sub> layer has been successfully and  
36 effectively deposited at Pb plate surface by using electrolysis in acidic solution. In  
37 addition, the membrane fouling by deposited MO was less significant in the case of  
38 ED-AO compared to ED process. Besides, the presence of sulfate ions in the  
39 membrane of ED-AO was the strongest.
- 40 • The results of ED and ED-AO experiments demonstrated that the coupling of AO to  
41 ED process attenuated significantly the membrane fouling caused by MO deposition.  
42 The presence of Pb/PbO<sub>2</sub> electrode in ED cell also reduced the CER and improved

1 the decolorization and COD removal rates approximately 2.2 times after 3 hours of  
2 process.  
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- 4 • The study of operating parameters effect on ED-AO process showed that the  
5 increase of applied current density improving the MO degradation and reducing  
6 simultaneously the CER evolution. In the other hand, the increase of initial MO  
7 concentration decreased gradually the decolorization and COD removal efficiencies.  
8 The decolorization and mineralization of MO solution is favored in acidic pH. It was  
9 also found that the increase in Na<sub>2</sub>SO<sub>4</sub> concentration as supporting electrolyte led to  
10 a significant increase in MO degradation, where a pseudo-total and total  
11 decolorization was obtained when the concentration is high. However, a slight  
12 regression in the mineralization for the highest concentrations was observed. In all  
13 cases, the improvement of decolorization and mineralization of MO led to reducing  
14 the CER evolution and the AMX membrane fouling successively.  
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- 16 • The study of Pb/PbO<sub>2</sub> electrode reusability showed that the decolorization of MO  
17 solution remained effective ( $\geq 97\%$ ) during ten cycles of use. However, there is a  
18 slight regression in COD removal begins from the seventh cycle.  
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20 Finally, this work showed clearly the benefit of AO combined with ED process to  
21 control the AMX membrane fouling and for enhanced MO azo-dye degradation. ED-  
22 AO could be a useful synergistic process for enhanced oxidation of organic pollutants  
23 along with continuous processing which are very recommended factors at large scale.  
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#### 25 **CRedit authorship contribution statement**

26 A. Mehellou: Writing, Experimental and characterization, R. Delimi: Visualization,  
27 Supervision and Methodology, L. Allat: Visualization and Methodology, R. Djellabi:  
28 Writing, Visualization, Validation and Revision, A. Rebiai: Writing and English  
29 revision, C. Innocent: Supervision and Methodology.  
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## 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.

## Data availability

No data was used for the research described in the article.

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## References

- [1] Shi, J., Zhang, B., Liang, S., Li, J., Wang, Z. (2018). Simultaneous decolorization and desalination of dye wastewater through electrochemical process. *Environmental Science and Pollution Research*, 25, 8455-8464. <https://doi.org/10.1007/s11356-017-1159-8>.
- [2] Mani, S., Chowdhary, P., Bharagava, R. N. (2019). Textile wastewater dyes: toxicity profile and treatment approaches. *Emerging and eco-friendly approaches for waste management*, 219-244. [https://doi.org/10.1007/978-981-10-8669-4\\_11](https://doi.org/10.1007/978-981-10-8669-4_11).
- [3] Yagub, M. T., Sen, T. K., Afroze, S., Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: a review. *Advances in colloid and interface science*, 209, 172-184. <https://doi.org/10.1016/j.cis.2014.04.002>.
- [4] Muthu, S. S., Khadir, A. (2022). *Membrane Based Methods for Dye Containing Wastewater*. Springer Singapore.
- [5] Saeed, M., Muneer, M., Haq, A. U., Akram, N. (2022). Photocatalysis: An effective tool for photodegradation of dyes—A review. *Environmental Science and Pollution Research*, 29, 293–311. <https://doi.org/10.1007/s11356-021-16389-7>.
- [6] Zafar, S., Bukhari, D. A., Rehman, A. (2022). Azo dyes degradation by microorganisms-An efficient and sustainable approach. *Saudi Journal of Biological Sciences*, 103437. <https://doi.org/10.1016/j.sjbs.2022.103437>.
- [7] Brillas, E., Martínez-Huitle, C. A. (2015). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Applied Catalysis B: Environmental*, 166, 603-643. <https://doi.org/10.1016/j.apcatb.2014.11.016>.
- [8] Martínez-Sánchez, C., Robles, I., Godínez, L. A. (2022). Review of recent developments in electrochemical advanced oxidation processes: application to remove dyes, pharmaceuticals, and pesticides. *International Journal of*

Environmental Science and Technology, 19(12), 12611-12678.  
<https://doi.org/10.1007/s13762-021-03762-9>.

- [9] Baker, R. W. (2012). Membrane technology and applications. John Wiley & Sons.
- [10] Al-Amshawee, S., Yunus, M. Y. B. M., Azoddein, A. A. M., Hassell, D. G., Dakhil, I. H., Hasan, H. A. (2020). Electrodialysis desalination for water and wastewater: A review. *Chemical Engineering Journal*, 380, 122231. <https://doi.org/10.1016/j.cej.2019.122231>.
- [11] Schorr, M. (Ed.). (2011). Desalination: Trends and technologies. BoD–Books on Demand.
- [12] Gering, K. L., & Scamehorn, J. F. (1988). Use of electrodialysis to remove heavy metals from water. *Separation Science and Technology*, 23(14-15), 2231-2267. <https://doi.org/10.1080/01496398808058452>.
- [13] Juve, J. M. A., Christensen, F. M. S., Wang, Y., Wei, Z. (2022). Electrodialysis for metal removal and recovery: A review. *Chemical Engineering Journal*, 435, 134857. <https://doi.org/10.1016/j.cej.2022.134857>.
- [14] Xu, D., Li, Y., Yin, L., Ji, Y., Niu, J., Yu, Y. (2018). Electrochemical removal of nitrate in industrial wastewater. *Frontiers of environmental science & engineering*, 12, 1-14. <https://doi.org/10.1007/s11783-018-1033-z>.
- [15] Aliaskari, M., Schäfer, A. I. (2021). Nitrate, arsenic and fluoride removal by electrodialysis from brackish groundwater. *Water Research*, 190, 116683. <https://doi.org/10.1016/j.watres.2020.116683>.
- [16] Huang, C., Xu, T., Zhang, Y., Xue, Y., Chen, G. (2007). Application of electrodialysis to the production of organic acids: State-of-the-art and recent developments. *Journal of membrane science*, 288(1-2), 1-12. <https://doi.org/10.1016/j.memsci.2006.11.026>.
- [17] Wang, Y., Zhang, X., Xu, T. (2010). Integration of conventional electrodialysis and electrodialysis with bipolar membranes for production of organic acids. *Journal of Membrane Science*, 365(1-2), 294-301. <https://doi.org/10.1016/j.memsci.2010.09.018>.
- [18] Casademont, C., Sístat, P., Ruiz, B., Pourcelly, G., & Bazinet, L. (2009). Electrodialysis of model salt solution containing whey proteins: Enhancement by pulsed electric field and modified cell configuration. *Journal of membrane science*, 328(1-2), 238-245. <https://doi.org/10.1016/j.memsci.2008.12.013>.
- [19] Dumée, L., Scholes, C., Stevens, G., & Kentish, S. (2012). Purification of aqueous amine solvents used in post combustion CO<sub>2</sub> capture: A review. *International Journal of Greenhouse Gas Control*, 10, 443-455. <https://doi.org/10.1016/j.ijggc.2012.07.005>.
- [20] Gurreri, L., Tamburini, A., Cipollina, A., Micale, G. (2020). Electrodialysis applications in wastewater treatment for environmental protection and resources recovery: A systematic review on progress and perspectives. *Membranes*, 10(7), 146. <https://doi.org/10.3390/membranes10070146>.
- [21] Oztekin, E., & Altin, S. (2016). Wastewater treatment by electrodialysis system and fouling problems. *Tojsat*, 6(1), 91-99.

- 1 [22] Wang, W., Fu, R., Liu, Z., Wang, H. (2017). Low-resistance anti-fouling ion  
2 exchange membranes fouled by organic foulants in  
3 electro dialysis. *Desalination*, 417, 1-8. <https://doi.org/10.1016/j.desal.2017.05.013>.
- 4 [23] Mikhaylin, S., Bazinet, L. (2016). Fouling on ion-exchange membranes:  
5 Classification, characterization and strategies of prevention and control. *Advances*  
6 *in colloid and interface science*, 229, 34-56.  
7 <https://doi.org/10.1016/j.cis.2015.12.006>.
- 8 [24] Banasiak, L. J., Schäfer, A. I. (2009). Removal of boron, fluoride and nitrate by  
9 electro dialysis in the presence of organic matter. *Journal of Membrane*  
10 *Science*, 334(1-2), 101-109. <https://doi.org/10.1016/j.memsci.2009.02.020>.
- 11 [25] Hansima, M. A. C. K., Makehelwala, M., Jinadasa, K. B. S. N., Wei, Y.,  
12 Nanayakkara, K. G. N., Herath, A. C., Weerasooriya, R. (2021). Fouling of ion  
13 exchange membranes used in the electro dialysis reversal advanced water  
14 treatment: A review. *Chemosphere*, 263, 127951.  
15 <https://doi.org/10.1016/j.chemosphere.2020.127951>.
- 16 [26] Guo, W., Ngo, H. H., Li, J. (2012). A mini-review on membrane  
17 fouling. *Bioresource technology*, 122, 27-34.  
18 <https://doi.org/10.1016/j.biortech.2012.04.089>.
- 19 [27] Grebenyuk, V.D., Chebotareva, R. D., Peters, S., Linkov, V. (1998). Surface  
20 modification of anion-exchange electro dialysis membranes to enhance anti-fouling  
21 characteristics. *Desalination*, 115(3), 313-329. [https://doi.org/10.1016/S0011-](https://doi.org/10.1016/S0011-9164(98)00051-4)  
22 [9164\(98\)00051-4](https://doi.org/10.1016/S0011-9164(98)00051-4).
- 23 [28] Mallya, D. S., Abdikheibari, S., Dumée, L. F., Muthukumaran, S., Lei, W.,  
24 Baskaran, K. (2023). Removal of natural organic matter from surface water  
25 sources by nanofiltration and surface engineering membranes for fouling  
26 mitigation—A review. *Chemosphere*, 138070.  
27 <https://doi.org/10.1016/j.chemosphere.2023.138070>.
- 28 [29] Yeon, K. H., Song, J. H., Shim, J., Moon, S. H., Jeong, Y. U., Joo, H. Y. (2007).  
29 Integrating electrochemical processes with electro dialysis reversal and electro-  
30 oxidation to minimize COD and TN at wastewater treatment facilities of power  
31 plants. *Desalination*, 202(1-3), 400-410.  
32 <https://doi.org/10.1016/j.desal.2005.12.080>.
- 33 [30] Llanos, J., Raschitor, A., Cañizares, P., Rodrigo, M. A. (2018). Exploring the  
34 applicability of a combined electro dialysis/electro-oxidation cell for the  
35 degradation of 2, 4-dichlorophenoxyacetic acid. *Electrochim. Acta* 269, 415–421.  
36 <http://dx.doi.org/10.1016/j.electacta.2018.02.153>.
- 37 [31] Pan, Z., Song, C., Li, L., Wang, H., Pan, Y., Wang, C., Li, J., Wang, T., Feng, X.  
38 (2019). Membrane technology coupled with electrochemical advanced oxidation  
39 processes for organic wastewater treatment: Recent advances and future  
40 prospects. *Chemical Engineering Journal*, 376, 120909.  
41 <https://doi.org/10.1016/j.cej.2019.01.188>.
- 42 [32] Aydin, M. I., Selcuk, H. (2023). Development of a UV-based photocatalytic  
43 electro dialysis reactor for ion separation and humic acid removal. *International*  
44 *Journal of Environmental Science and Technology*, 20(6), 5913-5924.  
45 <https://doi.org/10.1007/s13762-022-04358-7>

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65
- [33] Badruzzaman, M., Oppenheimer, J., Adham, S., Kumar, M. (2009). Innovative beneficial reuse of reverse osmosis concentrate using bipolar membrane electro dialysis and electrochlorination processes. *Journal of Membrane Science*, 326(2), 392-399. <https://doi.org/10.1016/j.memsci.2008.10.018>.
- [34] Llanos, J., Cotillas, S., Cañizares, P., Rodrigo, M. A. (2014). Novel electro dialysis–electrochlorination integrated process for the reclamation of treated wastewaters. *Separation and Purification Technology*, 132, 362-369. <https://doi.org/10.1016/j.seppur.2014.05.017>.
- [35] Leng, Q., Xu, S., Wu, X., Wang, S., Jin, D., Wang, P., Wu, D., Dong, F. (2022). Degrade methyl orange by a reverse electro dialysis reactor coupled with electrochemical direct oxidation and electro-Fenton processes. *Electrocatalysis*, 13(3), 242-254. <https://doi.org/10.1007/s12678-022-00712-y>.
- [36] Li, X., Jin, X., Zhao, N., Angelidaki, I., & Zhang, Y. (2017). Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electro dialysis electrolysis cell. *Bioresource technology*, 228, 322-329. <https://doi.org/10.1016/j.biortech.2016.12.114>.
- [37] Wu, D., Zhou, C., Lu, G., Zhou, Y., Shen, Y. (2019). Simultaneous membrane fouling mitigation and emerging pollutant benzophenone-3 removal by electro-peroxone process. *Separation and Purification Technology*, 227, 115715. <https://doi.org/10.1016/j.seppur.2019.115715>.
- [38] Moreira, F. C., Boaventura, R. A., Brillas, E., Vilar, V. J. (2017). Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. *Applied Catalysis B: Environmental*, 202, 217-261. <https://doi.org/10.1016/j.apcatb.2016.08.037>.
- [39] Martínez-Huitle, C. A., Panizza, M. (2018). Electrochemical oxidation of organic pollutants for wastewater treatment. *Current Opinion in Electrochemistry*, 11, 62-71. <https://doi.org/10.1016/j.coelec.2018.07.010>.
- [40] Hu, Z., Cai, J., Song, G., Tian, Y., Zhou, M. (2021). Anodic oxidation of organic pollutants: anode fabrication, process hybrid and environmental applications. *Current Opinion in Electrochemistry*, 26, 100659. <https://doi.org/10.1016/j.coelec.2020.100659>.
- [41] Jiang, Y., Zhao, H., Liang, J., Yue, L., Li, T., Luo, Y., Liu, Q., Lu, S., Asiri, A.M., Gong, Z., Sun, X. (2021). Anodic oxidation for the degradation of organic pollutants: anode materials, operating conditions and mechanisms. A mini review. *Electrochemistry Communications*, 123, 106912. <https://doi.org/10.1016/j.elecom.2020.106912>.
- [42] Zavisca, F., Drogui, P., Mercier, G., Blais, J. F. (2009). Advanced oxidation processes for waters and wastewaters treatment : Application to degradation of refractory pollutants, *Journal of Water Science*, 22(4), 535–564, <https://doi.org/10.7202/038330ar>.
- [43] Panizza, M., Cerisola, G. (2010). Applicability of electrochemical methods to carwash wastewaters for reuse. Part 1: Anodic oxidation with diamond and lead dioxide anodes. *Journal of Electroanalytical Chemistry*, 638(1), 28-32. <https://doi.org/10.1016/j.jelechem.2009.11.003>.



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- [44] McBeath, S. T., Wilkinson, D. P., & Graham, N. J. (2019). Application of boron-doped diamond electrodes for the anodic oxidation of pesticide micropollutants in a water treatment process: a critical review. *Environmental Science: Water Research & Technology*, 5(12), 2090-2107. <https://doi.org/10.1039/C9EW00589G>.
- [45] Shi, L., Hu, Z., Wang, Y., Bei, E., Lens, P. N., Thomas, O., Hu, Y., Chen, C., Zhan, X. (2021). In situ electrochemical oxidation in electrodialysis for antibiotics removal during nutrient recovery from pig manure digestate. *Chemical Engineering Journal*, 413, 127485. <https://doi.org/10.1016/j.cej.2020.127485>.
- [46] Raschitor, A., Llanos, J., Cañizares, P., Rodrigo, M. A. (2017). Novel integrated electrodialysis/electro-oxidation process for the efficient degradation of 2, 4-dichlorophenoxyacetic acid. *Chemosphere*, 182, 85-89. <https://doi.org/10.1016/j.chemosphere.2017.04.153>.
- [47] Bagastyo, A. Y., Sari, P. P. I., Direstiyani, L. C. (2021). Effect of chloride ions on the simultaneous electrodialysis and electrochemical oxidation of mature landfill leachate. *Environmental Science and Pollution Research*, 28, 63646-63660. <https://doi.org/10.1007/s11356-020-11519-z>.
- [48] Allat, L., Delimi, R., Mehellou, A. (2022). Mitigation of an anion exchange membrane fouling by coupling electrodialysis to anodic oxidation. *Chemical Engineering Research and Design*, 186, 136-148. <https://doi.org/10.1016/j.cherd.2022.07.042>.
- [49] Quiroz, M. A., Reyna, S., Martinez-Huitle, C. A., Ferro, S., De Battisti, A. (2005). Electrocatalytic oxidation of p-nitrophenol from aqueous solutions at Pb/PbO<sub>2</sub> anodes. *Applied Catalysis B: Environmental*, 59(3-4), 259-266. <https://doi.org/10.1016/j.apcatb.2005.02.009>.
- [50] Panizza, M., Sirés, I., Cerisola, G. (2008). Anodic oxidation of mecoprop herbicide at lead dioxide. *Journal of Applied Electrochemistry*, 38, 923-929. <https://doi.org/10.1007/s10800-008-9497-3>.
- [51] Yahiaoui, I., Aissani-Benissad, F., Madi, K., Benmehdi, N., Fourcade, F., Amrane, A. (2013). Electrochemical pre-treatment combined with biological treatment for the degradation of methylene blue dye: Pb/PbO<sub>2</sub> electrode and modeling-optimization through central composite design. *Industrial & Engineering Chemistry Research*, 52(42), 14743-14751. <https://doi.org/10.1021/ie401367q>.
- [52] Zhou, Q., Zhou, X., Zheng, R., Liu, Z., Wang, J. (2022). Application of lead oxide electrodes in wastewater treatment: A review. *Science of The Total Environment*, 806, 150088. <https://doi.org/10.1016/j.scitotenv.2021.150088>.
- [53] Xu, T. (2005). Ion exchange membranes: State of their development and perspective. *Journal of membrane science*, 263(1-2), 1-29. <https://doi.org/10.1016/j.memsci.2005.05.002>.
- [54] Kariduraganavar, M. Y., Nagarale, R. K., Kittur, A. A., Kulkarni, S. S. (2006). Ion-exchange membranes: preparative methods for electrodialysis and fuel cell applications. *Desalination*, 197(1-3), 225-246. <https://doi.org/10.1016/j.desal.2006.01.019>.
- [55] Mehellou, A., Delimi, R., Benredjem, Z., Innocent, C. (2015). Affinity of cation-exchange membranes towards metallic cations: application in continuous

electropermutation. *Separation Science and Technology*, 50(4), 495-504. <https://doi.org/10.1080/01496395.2014.968260>.

- [56] Awad, H. S., Galwa, N. A. (2005). Electrochemical degradation of Acid Blue and Basic Brown dyes on Pb/PbO<sub>2</sub> electrode in the presence of different conductive electrolyte and effect of various operating factors. *Chemosphere*, 61(9), 1327-1335. <https://doi.org/10.1016/j.chemosphere.2005.03.054>.
- [57] Vazquez-Gomez, L., de Battisti, A., Ferro, S., Cerro, M., Reyna, S., Martínez-Huitle, C. A., Quiroz, M. A. (2012). Anodic oxidation as green alternative for removing diethyl phthalate from wastewater using Pb/PbO<sub>2</sub> and Ti/SnO<sub>2</sub> anodes. *Clean–Soil, Air, Water*, 40(4), 408-415. <https://doi.org/10.1002/clen.201000357>.
- [58] Wang, Y. S., Yang, F., Liu, Z. H., Yuan, L., & Li, G. (2015). Electrocatalytic degradation of aspen lignin over Pb/PbO<sub>2</sub> electrode in alkali solution. *Catalysis Communications*, 67, 49-53. <https://doi.org/10.1016/j.catcom.2015.03.033>.
- [59] Choi, J. H., Moon, S. H. (2003). Structural change of ion-exchange membrane surfaces under high electric fields and its effects on membrane properties. *Journal of Colloid and Interface Science*, 265(1), 93-100. [https://doi.org/10.1016/S0021-9797\(03\)00136-X](https://doi.org/10.1016/S0021-9797(03)00136-X).
- [60] Adachi, A., Ouadrhiri, F. E., Kara, M., El Manssouri, I., Assouguem, A., Almutairi, M. H., ... & Lahkimi, A. (2022). Decolorization and degradation of methyl orange azo dye in aqueous solution by the electro fenton process: Application of optimization. *Catalysts*, 12(6), 665. <https://doi.org/10.3390/catal12060665>.
- [61] Li, X., Pletcher, D., Walsh, F. C. (2011). Electrodeposited lead dioxide coatings. *Chemical Society Reviews*, 40(7), 3879-3894. <https://doi.org/10.1039/C0CS00213E>.
- [62] Barbari, K., Delimi, R., Benredjem, Z., Saaidia, S., Djemel, A., Chouchane, T., ... & Oturan, M. A. (2018). Photocatalytically-assisted electrooxidation of herbicide fenuron using a new bifunctional electrode PbO<sub>2</sub>/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>/Ti//Ti/TiO<sub>2</sub>. *Chemosphere*, 203, 1-10. <https://doi.org/10.1016/j.chemosphere.2018.03.126>.
- [63] Saaidia, S., Delimi, R., Benredjem, Z., Mehellou, A., Djemel, A., Barbari, K. (2017). Use of a PbO<sub>2</sub> electrode of a lead-acid battery for the electrochemical degradation of methylene blue. *Separation Science and Technology*, 52(9), 1602-1614. <http://dx.doi.org/10.1080/01496395.2017.1291681>.
- [64] Zhao, Z., Shi, S., Cao, H., Li, Y. (2017). Electrochemical impedance spectroscopy and surface properties characterization of anion exchange membrane fouled by sodium dodecyl sulfate. *Journal of Membrane Science*, 530, 220-231. <https://doi.org/10.1016/j.memsci.2017.02.037>.
- [65] Niu, J., Li, Y., Shang, E., Xu, Z., Liu, J. (2016). Electrochemical oxidation of perfluorinated compounds in water. *Chemosphere*, 146, 526-538. <https://doi.org/10.1016/j.chemosphere.2015.11.115>.
- [66] Ghalwa, N. A., Hamada, M., Shawish, H. M. A., Shubair, O. (2016). Electrochemical degradation of linuron in aqueous solution using Pb/PbO<sub>2</sub> and

C/PbO<sub>2</sub> electrodes. *Arabian Journal of Chemistry*, 9, S821-S828.  
<https://doi.org/10.1016/j.arabjc.2011.08.006>.

- [67] Othmani, A., Kesraoui, A., Akrou, H., López-Mesas, M., Seffen, M., Valiente, M. (2019). Use of alternating current for colored water purification by anodic oxidation with SS/PbO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes. *Environmental Science and Pollution Research*, 26, 25969-25984. <https://doi.org/10.1007/s11356-019-05722-w>.
- [68] Chen, Z., Xie, G., Pan, Z., Zhou, X., Lai, W., Zheng, L., Xu, Y. (2021). A novel Pb/PbO<sub>2</sub> electrodes prepared by the method of thermal oxidation-electrochemical oxidation: Characteristic and electrocatalytic oxidation performance. *Journal of Alloys and Compounds*, 851, 156834. <https://doi.org/10.1016/j.jallcom.2020.156834>.
- [69] Lin, H., Niu, J., Ding, S., Zhang, L. (2012). Electrochemical degradation of perfluorooctanoic acid (PFOA) by Ti/SnO<sub>2</sub>-Sb, Ti/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> and Ti/SnO<sub>2</sub>-Sb/MnO<sub>2</sub> anodes. *Water research*, 46(7), 2281-2289. <https://doi.org/10.1016/j.watres.2012.01.053>.
- [70] Yu, H., Song, Y., Zhao, B., Lu, Y., Zhu, S., Qu, J., ... & Qin, W. (2018). Efficient Electrocatalytic Degradation of 4-Chlorophenol Using a Ti/RuO<sub>2</sub>-SnO<sub>2</sub>-TiO<sub>2</sub>/PbO<sub>2</sub>-CeO<sub>2</sub> Composite Electrode. *Electrocatalysis*, 9, 725-734. <https://doi.org/10.1007/s12678-018-0484-0>.
- [71] Choi, J. H., Lee, H. J., Moon, S. H. (2001). Effects of electrolytes on the transport phenomena in a cation-exchange membrane. *Journal of colloid and interface science*, 238(1), 188-195. <https://doi.org/10.1006/jcis.2001.7510>.
- [72] Lee, H. J., Strathmann, H., Moon, S. H. (2006). Determination of the limiting current density in electro dialysis desalination as an empirical function of linear velocity. *Desalination*, 190(1-3), 43-50. <https://doi.org/10.1016/j.desal.2005.08.004>.
- [73] Niu, J., Bao, Y., Li, Y., Chai, Z. (2013). Electrochemical mineralization of pentachlorophenol (PCP) by Ti/SnO<sub>2</sub>-Sb electrodes. *Chemosphere*, 92(11), 1571-1577. <https://doi.org/10.1016/j.chemosphere.2013.04.035>.
- [74] Maharana, D., Xu, Z., Niu, J., Rao, N. N. (2015). Electrochemical oxidation of 2, 4, 5-trichlorophenoxyacetic acid by metal-oxide-coated Ti electrodes. *Chemosphere*, 136, 145-152. <https://doi.org/10.1016/j.chemosphere.2015.04.100>.
- [75] Xu, Z., Liu, H., Niu, J., Zhou, Y., Wang, C., Wang, Y. (2017). Hydroxyl multi-walled carbon nanotube-modified nanocrystalline PbO<sub>2</sub> anode for removal of pyridine from wastewater. *Journal of hazardous materials*, 327, 144-152. <https://doi.org/10.1016/j.jhazmat.2016.12.056>.
- [76] Duan, X., Xu, F., Wang, Y., Chen, Y., Chang, L. (2018). Fabrication of a hydrophobic SDBS-PbO<sub>2</sub> anode for electrochemical degradation of nitrobenzene in aqueous solution. *Electrochimica Acta*, 282, 662-671. <https://doi.org/10.1016/j.electacta.2018.06.098>.
- [77] Suwal, S., Doyen, A., Bazinet, L. (2015). Characterization of protein, peptide and amino acid fouling on ion-exchange and filtration membranes: Review of current

and recently developed methods. *Journal of Membrane Science*, 496, 267-283.  
<https://doi.org/10.1016/j.memsci.2015.08.056>.

- [78] Panizza, M., Oturan, M. A. (2011). Degradation of Alizarin Red by electro-Fenton process using a graphite-felt cathode. *Electrochimica Acta*, 56(20), 7084-7087.  
<https://doi.org/10.1016/j.electacta.2011.05.105>.
- [79] Comninellis, C., Pulgarin, C. (1991). Anodic oxidation of phenol for waste water treatment. *Journal of applied electrochemistry*, 21, 703-708.  
<https://doi.org/10.1007/BF01034049>.
- [80] Zhao, B. X., Li, X. Z., Peng, W. (2007). Degradation of 2, 4-dichlorophenol with a novel TiO<sub>2</sub>/Ti-Fe-graphite felt photoelectrocatalytic oxidation process. *Journal of Environmental Sciences*, 19(8), 1020-1024. [https://doi.org/10.1016/S1001-0742\(07\)60165-X](https://doi.org/10.1016/S1001-0742(07)60165-X).
- [81] Giraldo, A. L., Erazo-Erazo, E. D., Flórez-Acosta, O. A., Serna-Galvis, E. A., & Torres-Palma, R. A. (2015). Degradation of the antibiotic oxacillin in water by anodic oxidation with Ti/IrO<sub>2</sub> anodes: evaluation of degradation routes, organic by-products and effects of water matrix components. *Chemical Engineering Journal*, 279, 103-114. <https://doi.org/10.1016/j.cej.2015.04.140>.
- [82] Asim, S., Zhu, Y., Batool, A., Hailili, R., Luo, J., Wang, Y., Wang, C. (2017). Electrochemical treatment of 2, 4-dichlorophenol using a nanostructured 3D-porous Ti/Sb-SnO<sub>2</sub>-Gr anode: Reaction kinetics, mechanism, and continuous operation. *Chemosphere*, 185, 11-19.  
<https://doi.org/10.1016/j.chemosphere.2017.06.125>.
- [83] Li, W., Liu, G., Miao, D., Li, Z., Chen, Y., Gao, X., ... & Yu, Z. (2020). Electrochemical oxidation of Reactive Blue 19 on boron-doped diamond anode with different supporting electrolyte. *Journal of Environmental Chemical Engineering*, 8(4), 103997. <https://doi.org/10.1016/j.jece.2020.103997>.
- [84] Liang, C., Wang, Z. S., Bruell, C. J. (2007). Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere*, 66(1), 106-113.  
<https://doi.org/10.1016/j.chemosphere.2006.05.026>.
- [85] Mora-Gómez, J., García-Gabaldón, M., Carrillo-Abad, J., Montañés, M. T., Mestre, S., Pérez-Herranz, V. (2020). Influence of the reactor configuration and the supporting electrolyte concentration on the electrochemical oxidation of Atenolol using BDD and SnO<sub>2</sub> ceramic electrodes. *Separation and Purification Technology*, 241, 116684. <https://doi.org/10.1016/j.seppur.2020.116684>.
- [86] Ushani, U., Lu, X., Wang, J., Zhang, Z., Dai, J., Tan, Y., ... & Zhen, G. (2020). Sulfate radicals-based advanced oxidation technology in various environmental remediation: A state-of-the-art review. *Chemical Engineering Journal*, 402, 126232. <https://doi.org/10.1016/j.cej.2020.126232>.
- [87] Tully, F. P., Ravishankara, A. R., Thompson, R. L., Nicovich, J. M., Shah, R. C., Kreutter, N. M., & Wine, P. H. (1981). Kinetics of the reactions of hydroxyl radical with benzene and toluene. *The Journal of Physical Chemistry*, 85(15), 2262-2269. <https://doi.org/10.1021/j150615a025>.
- [88] Li, Q., Zhang, Q., Cui, H., Ding, L., Wei, Z., Zhai, J. (2013). Fabrication of cerium-doped lead dioxide anode with improved electrocatalytic activity and its

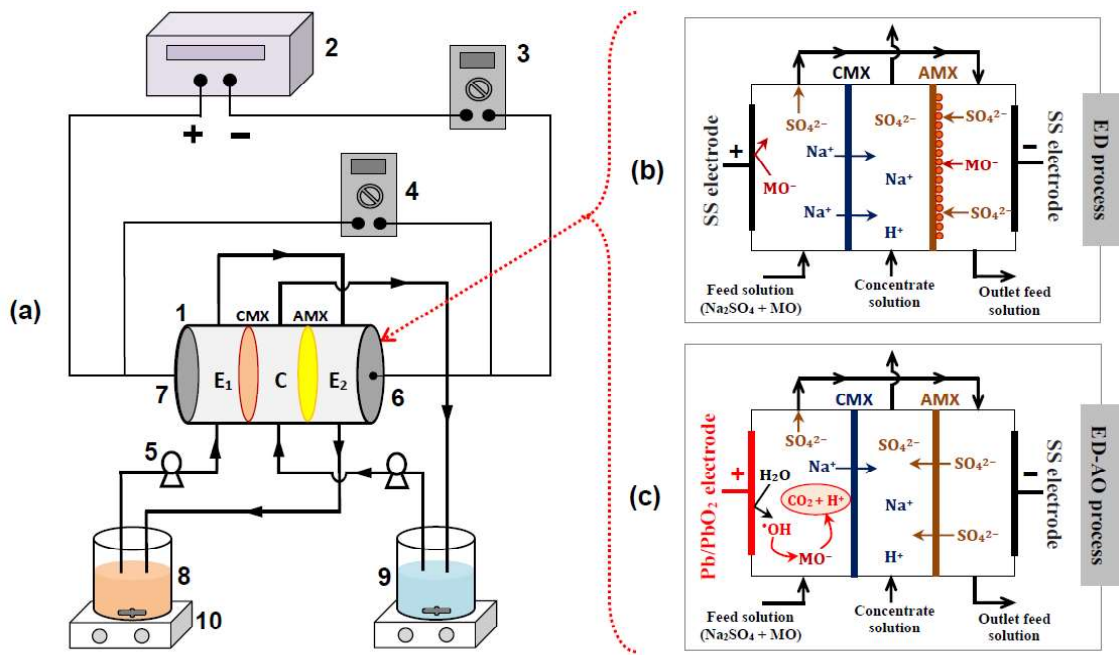
1 application for removal of Rhodamine B. *Chemical Engineering Journal*, 228, 806-  
2 814. <https://doi.org/10.1016/j.cej.2013.05.064>.

3 [89] Song, S., Fan, J., He, Z., Zhan, L., Liu, Z., Chen, J., Xu, X. (2010).  
4 Electrochemical degradation of azo dye CI Reactive Red 195 by anodic oxidation  
5 on Ti/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> electrodes. *Electrochimica Acta*, 55(11), 3606-3613.  
6 <https://doi.org/10.1016/j.electacta.2010.01.101>.

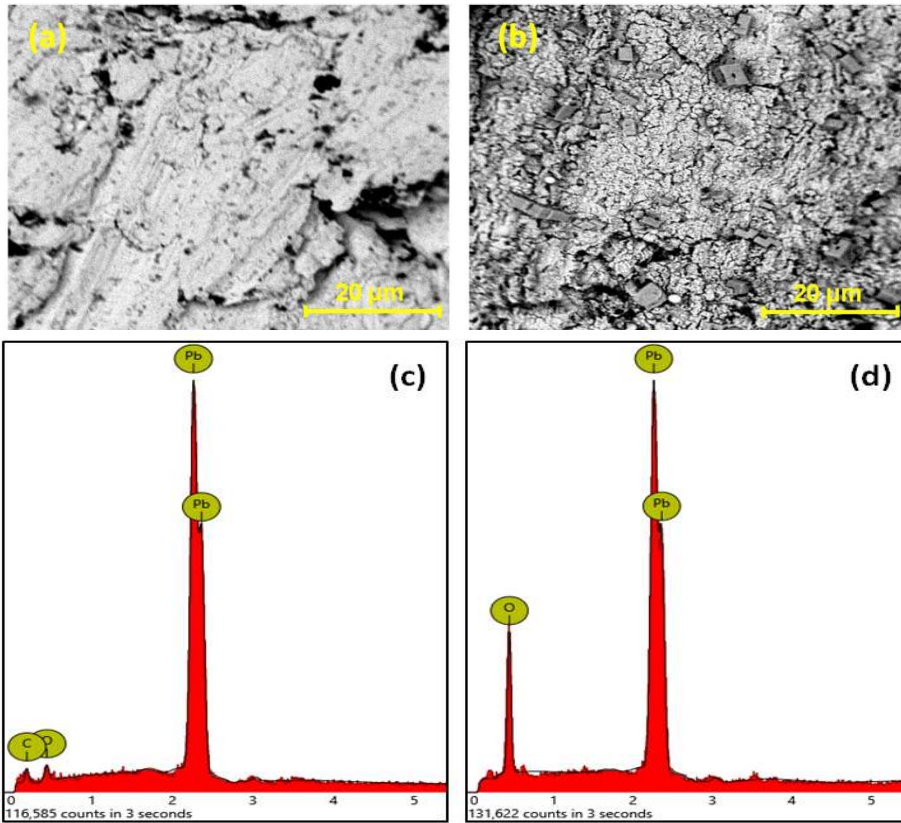
7  
8 [90] Nidheesh, P. V., Gandhimathi, R. (2012). Trends in electro-Fenton process for  
9 water and wastewater treatment: an overview. *Desalination*, 299, 1-15.  
10 <https://doi.org/10.1016/j.desal.2012.05.011>.

11  
12 [91] Ma, P., Ma, H., Sabatino, S., Galia, A., Scialdone, O. (2018). Electrochemical  
13 treatment of real wastewater. Part 1: Effluents with low conductivity. *Chemical*  
14 *Engineering Journal*, 336, 133-140. <https://doi.org/10.1016/J.CEJ.2017.11.046>.

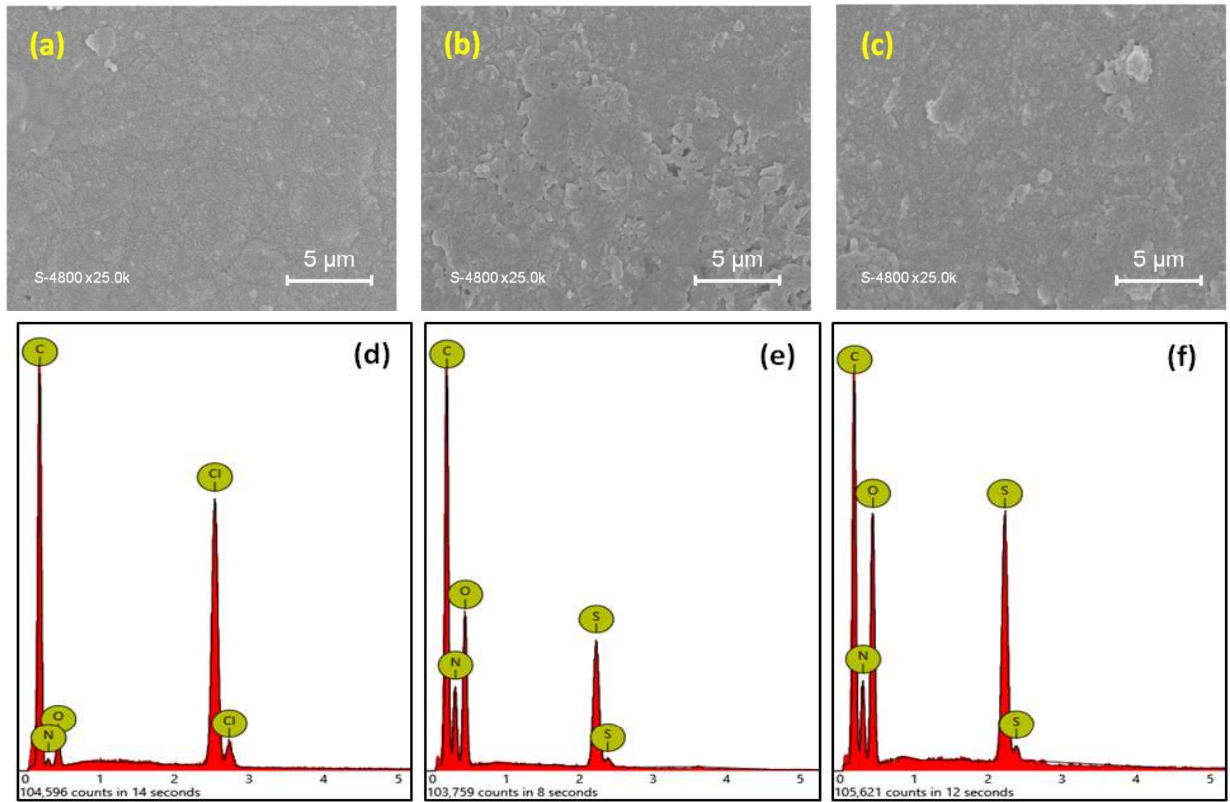
15  
16 [92] Zhang, C., He, Z., Wu, J., Fu, D. (2015). The peculiar roles of sulfate electrolytes  
17 in BDD anode cells. *Journal of The Electrochemical Society*, 162(8), E85. DOI:  
18 10.1149/2.0361508jes  
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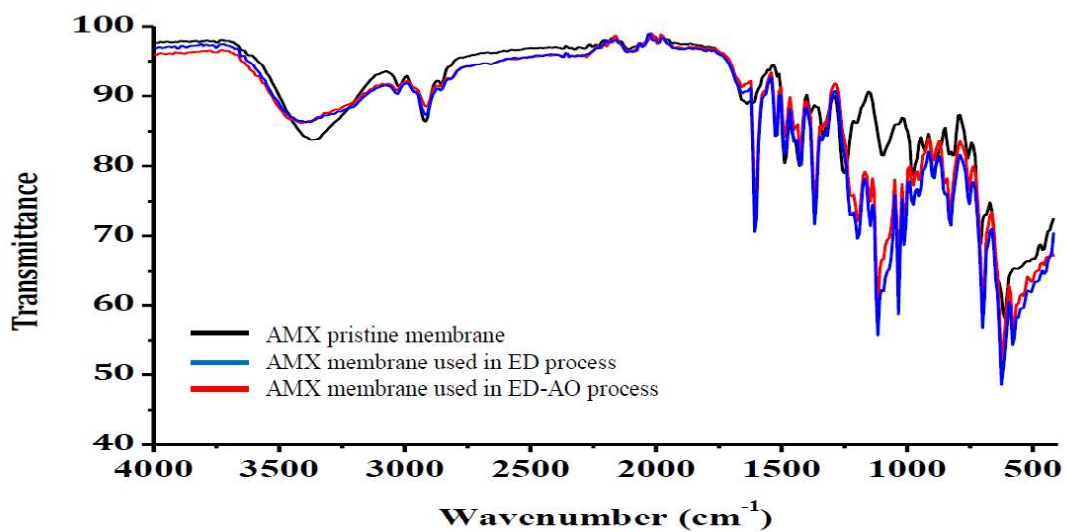
**Fig. 1.** (a) Experimental set-up; Procedures and principle of (b) ED and (c) ED-AO. (1): ED cell; (2): Power supply; (3) and (4): Multimeters; (5): Peristaltic pump; (6): SS electrode; (7): SS electrode in ED process or Pb/PbO<sub>2</sub> electrode in ED-AO process; (8): Feed solution tank; (9): Concentrate solution tank; (10): Magnetic stirrer.



**Fig. 2.** SEM images of Pb/PbO<sub>2</sub> electrode **(a)** before electrolysis **(c)** its EDS spectrogram, **(b)** after electrolysis **(d)** its EDS spectrogram.

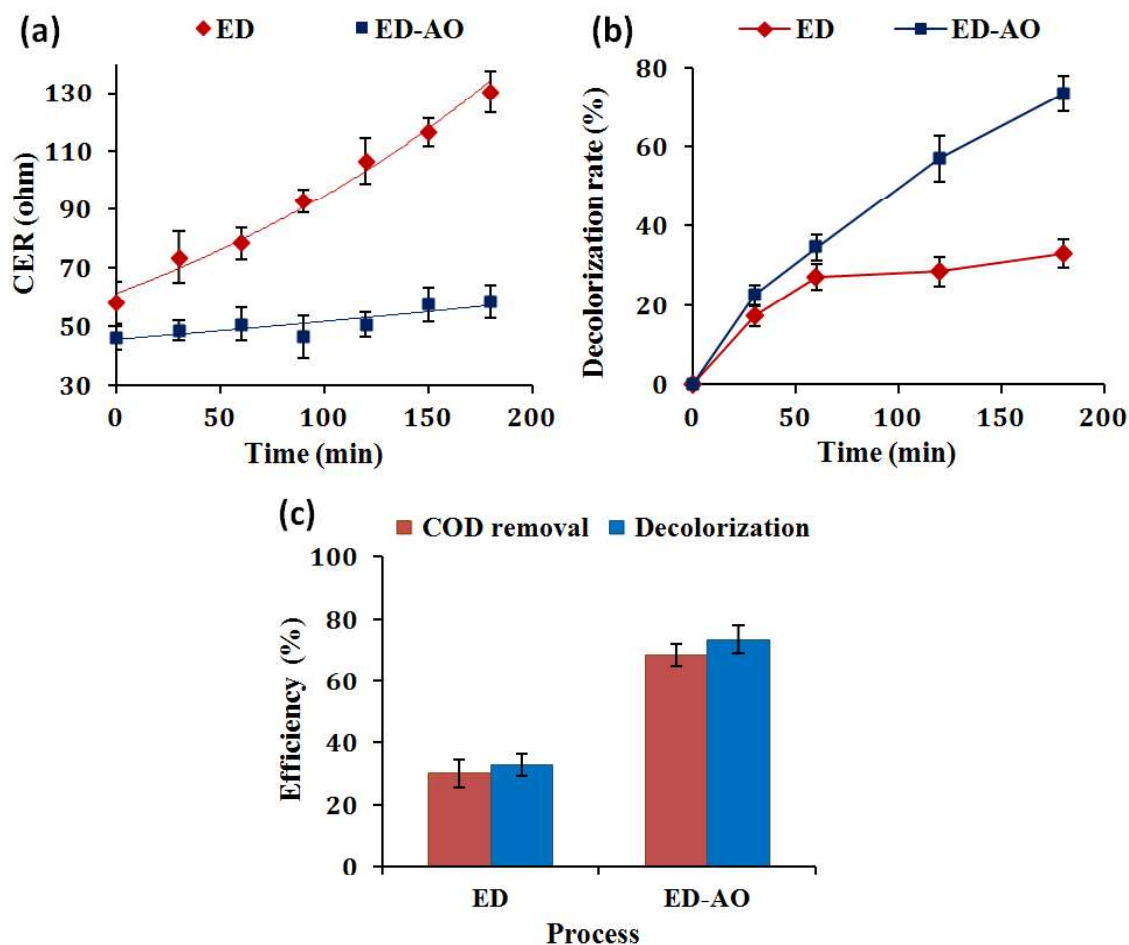


**Fig. 3.** SEM images of AMX (a) pristine membrane (d) its EDS spectrogram, (b) membrane used in ED (e) its EDS spectrogram, (c) membrane used in ED-AO (f) its EDS spectrogram. (ED and ED-AO operating conditions:  $i = 20 \text{ mA cm}^{-2}$ ,  $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$ , natural pH ( $\approx 6.8$ ) and  $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ).

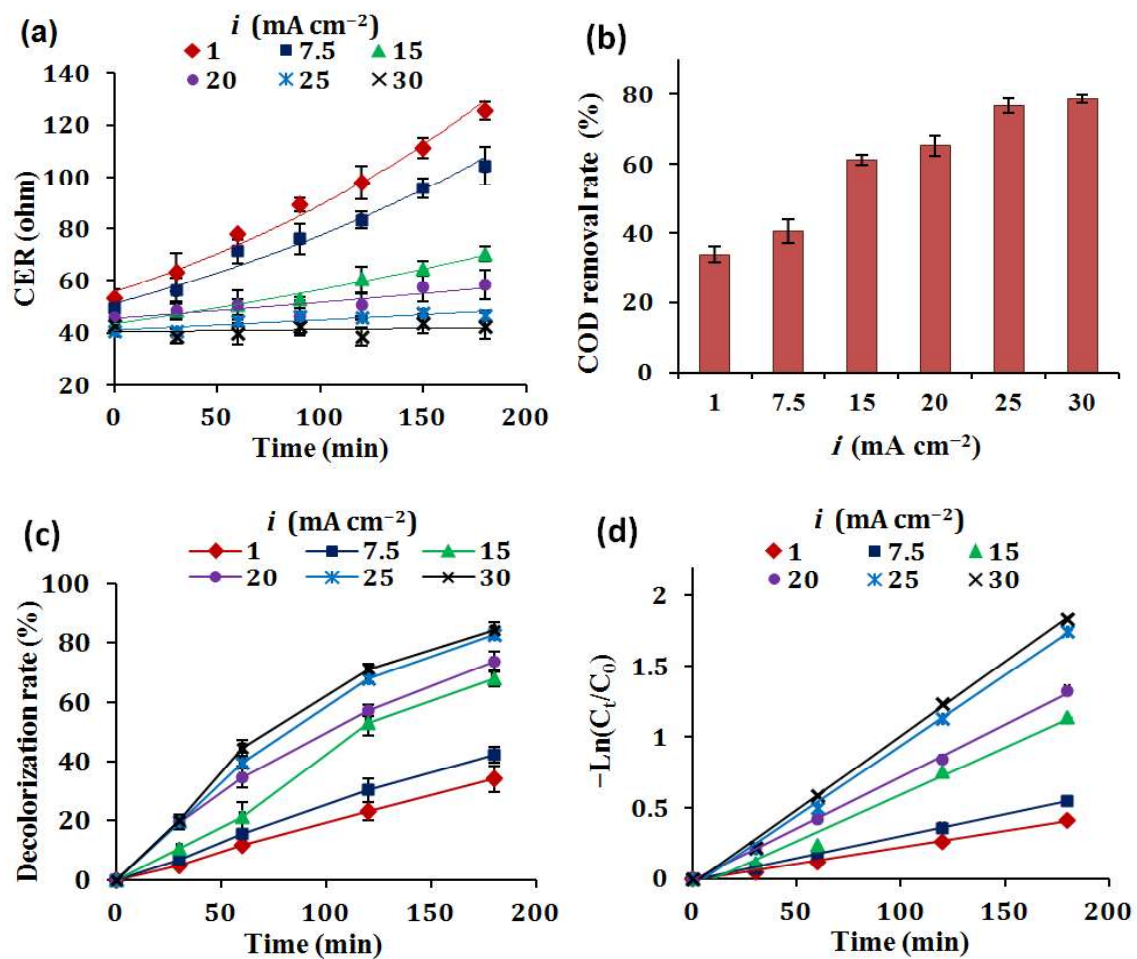


**Fig. 4.** FTIR Spectra of AMX pristine membrane, and those used in ED and ED-AD processes.

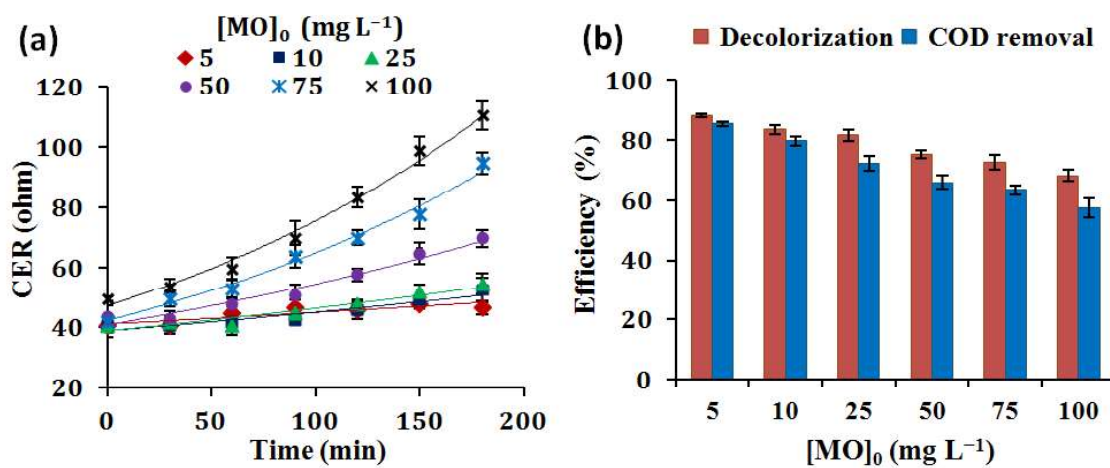




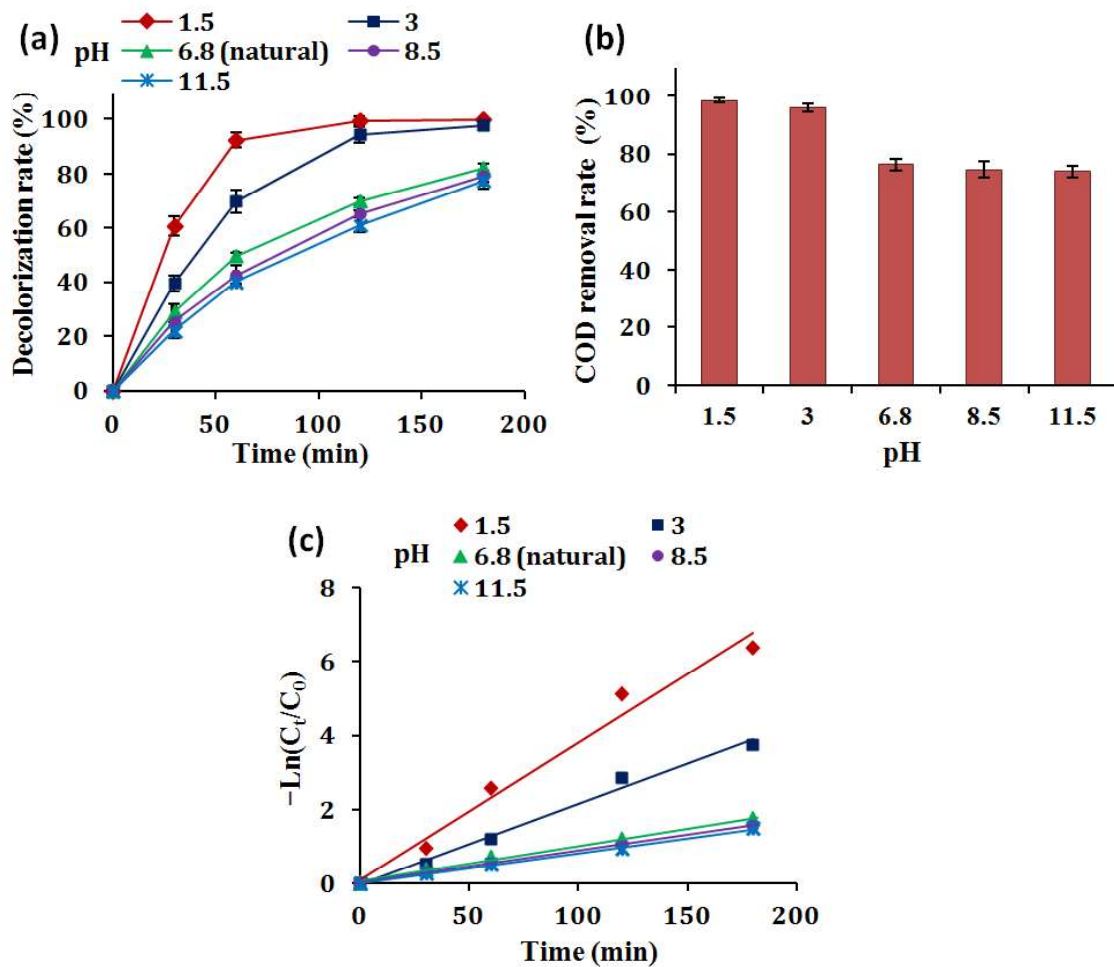
**Fig. 5.** Representation of (a) CER variation, (b) decolorization rate variation and (c) COD removal and decolorization efficiencies in the ED and ED-AO processes. (ED and ED-AO operating conditions:  $i = 20 \text{ mA cm}^{-2}$ ,  $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$ , natural pH ( $\approx 6.8$ ) and  $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ).



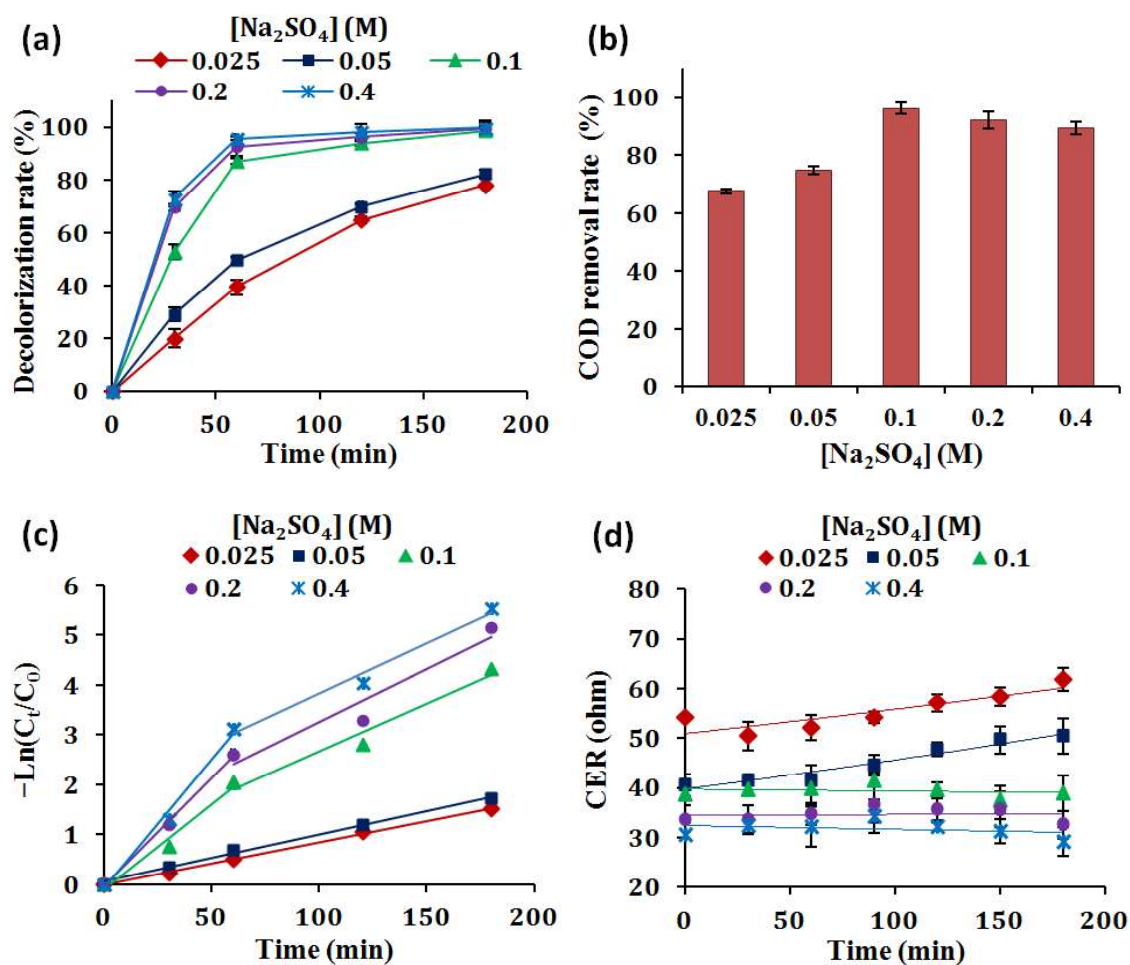
**Fig. 6.** Representation of (a) CER variation, (b) COD removal rate, (c) decolorization rate variation and (d) pseudo-first-order kinetics for different applied current densities. (ED-AO operating conditions:  $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$ , natural pH ( $\approx 6.8$ ) and  $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ).



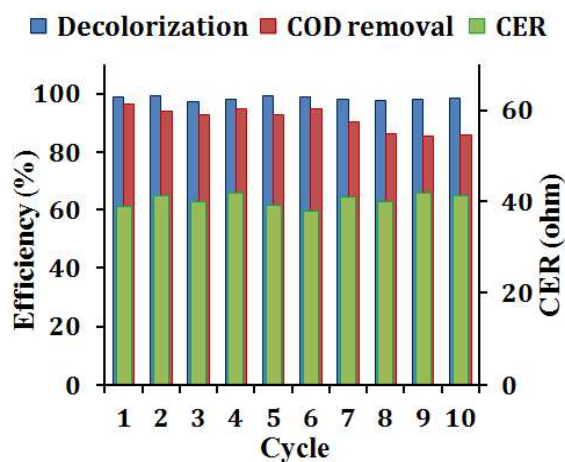
**Fig. 7.** Representation of (a) CER variation, (b) COD removal and decolorization efficiencies for different initial MO concentrations. (ED-AO operating conditions:  $i = 25 \text{ mA cm}^{-2}$ , natural pH ( $\approx 6.8$ ) and  $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ).



**Fig. 8.** Representation of (a) decolorization rate variation, (b) COD removal rate values and (c) pseudo-first-order kinetics for different pHs. (ED-AO operating conditions:  $i = 25 \text{ mA cm}^{-2}$ ,  $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$  and  $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ).



**Fig. 9.** Representation of (a) decolorization rate variation, (b) COD removal rate, (c) pseudo-first-order kinetics and (d) CER variation for different supporting electrolyte ( $\text{Na}_2\text{SO}_4$ ) concentrations. (ED-AO operating conditions:  $i = 25 \text{ mA cm}^{-2}$ ,  $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$ , and natural pH ( $\approx 6.8$ )).



**Fig. 10.** MO degradation efficiency (decolorization and COD removal) and CER value at the end of ED-AO experiment using Pb/PbO<sub>2</sub> electrode for 10 cycles. (ED-AO operating conditions:  $i = 25 \text{ mA.cm}^{-2}$ ,  $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$ , natural pH ( $\approx 6.8$ ) and  $[\text{Na}_2\text{SO}_4] = 0.1 \text{ M}$ ).

**Table 1**

Chemical elements analysis results of Pb/PbO<sub>2</sub> electrode surface by EDS before and after electrolysis.

Pb/PbO <sub>2</sub> electrode	Atomic percentage (%)		
	Pb	O	C
Before electrolysis	67.30	20.67	12.03
After electrolysis	39.45	60.55	0

**Table 2**

Chemical elements analysis results of the membrane surface by EDS.

AMX	Atomic percentage (%)				
	C	O	Cl	N	S
Pristine membrane	82.88	6.73	5.22	5.16	0
Membrane used in ED	68.84	12.65	0	16.14	2.37
Membrane used in ED-AO	66.85	18.38	0	11.64	3.13

**Table 3**

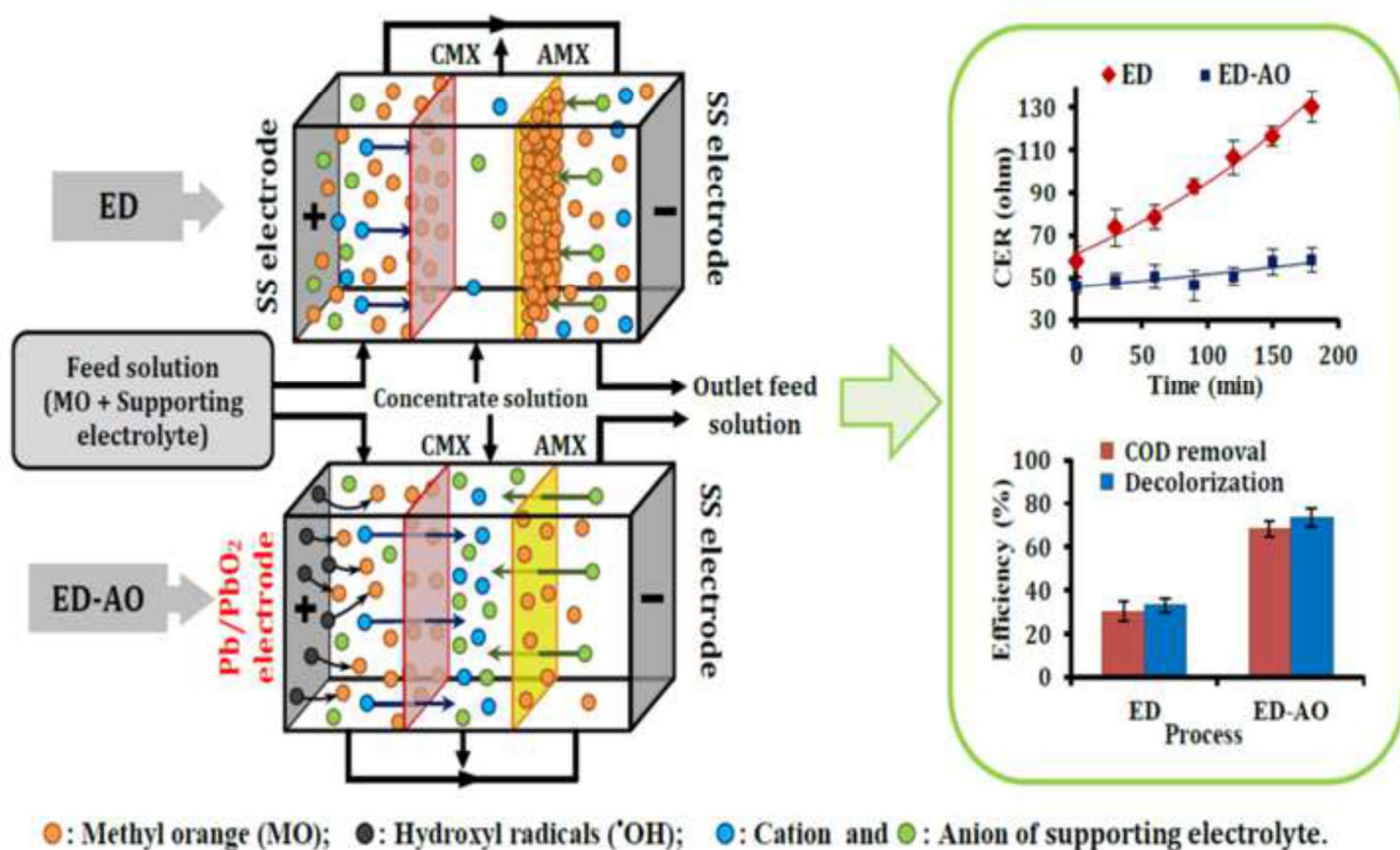
Pseudo-first-order kinetic parameters.

Parameter	Value	$k$ ( $10^{-2} \text{ min}^{-1}$ )	$R^2$	
$i$ ( $\text{mA cm}^{-2}$ )	1	0.24	0.9972	
	7.5	0.31	0.9985	
	15	0.66	0.9848	
	20	0.73	0.999	
	25	0.99	0.9973	
	30	1.04	0.998	
pH	1.5	3.70	0.9786	
	3	2.18	0.9887	
	6.8	0.94	0.9956	
	8.5	0.86	0.9994	
	11.5	0.81	0.9984	
[Na <sub>2</sub> SO <sub>4</sub> ] (M)	0.025	0.85	0.9989	
	0.05	0.94	0.9956	
	0.1	Part 1	3.39	0.9779
		Part 2	1.91	0.9655
	0.2	Part 1	4.34	0.9974
		Part 2	2.13	0.9309
	0.4	Part 1	5.21	0.991
		Part 2	2.02	0.9797

## **Highlights**

- Electrodialysis membranes fouling leads to the increase of cell electrical resistance.
- ED-AO coupling reduces successfully the AMX membrane fouling by organics.
- ED-AO coupling intensifies the decolorization and COD removal.
- Hybrid ED-AO efficiency strongly depends on the current density, organic pollutant concentration, pH of feed solution and concentration of supporting electrolyte.





**Declaration of interests**

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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## Statement of novelty and significance

Water pollution by organic dyes is considered one of the most dangerous pollution forms. Numerous methods have been investigated for the treatment of such pollution. However, very few works have been reported on the study treating this type of pollution by electro dialysis process. This is probably due to the problem of membranes fouling by dye molecules.

In this work, a new combination of electro dialysis/anodic oxidation (ED-AO) was achieved, in order to intensify the degradation of an organic dye and to solve the problem of membranes fouling by this pollutant. The results show an excellent performance of the hybrid ED-AO system.