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Ahmed Mehellou, Rachid Delimi, Lamia Allat, Ridha Djellabi, Abdelkrim Rebiai, et al.. Design of a synergistic combined electro dialysis/anodic oxidation system for simultaneous AMX membrane fouling mitigation and enhanced dye degradation. *Chemical Engineering and Processing: Process Intensification*, 2024, 196, pp.109663. <10.1016/j.cep.2024.109663>. <hal-04396276>

HAL Id: hal-04396276

<https://hal.science/hal-04396276v1>

Submitted on 15 Jan 2024

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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/PbO₂ 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/PbO₂ 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 (Na₂SO₄) 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/PbO₂ 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].

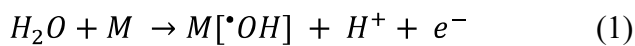
1 ED technique has some considerable drawbacks limiting its effectiveness [10,13]. One
2 of the main issues of ED is the membrane fouling during the process [21,22]. This
3 phenomenon is generally due to the deposition of macromolecules or insoluble
4 compounds on the surface and/or into the membrane. 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

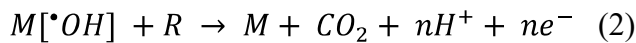
1 has been proven that AO can effectively eliminate the majority of organic pollutants
2 from wastewaters [39–41].
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4 Generally, the AO of organic or inorganic pollutants leads to the formation of simpler,
5 non-toxic and biodegradable compounds [42]. 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/IrO₂, Ti/SnO₂, Ti/RuO₂; PbO₂, SnO₂, etc [42,43]. These electrodes allow a complete
8 oxidation of the most organic molecules into CO₂ and H₂O. 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 1st stage: Anodic discharge of water and production of hydroxyl radicals ([•]OH) on the
22 metal oxide electrode surface (M):
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29 2nd stage: Oxidation of organic compounds (R) by [•]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/SnO₂-Sb₂O₃/PbO₂ 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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11 The present study aims to investigate the integration of AO in ED to boost the
12 oxidation of anionic azo-dye (methyl orange (MO)), and simultaneously overcome the
13 membrane fouling. The combined AO and ED has two main purposes, (i) realization of
14 *in-situ* electro-oxidation phenomenon in the same anode of ED, (ii) use of a new ED
15 configuration permitting the preliminary removal of MO before its adsorption on the
16 anion-exchange membrane (AEM). Pb/PbO₂ anode was designed to carry out the
17 oxidation process. It is worthy to mention that Pb/PbO₂ have a particular attention at
18 large scale of applications due to its high electro-oxidation efficiency, good electrical
19 conductivity and low cost [49–52].
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The Pb/PbO₂ electrode was prepared by formation of PbO₂ layer on lead plate and characterized by SEM-EDS method. The AEM fouling was confirmed by SEM-EDS and FTIR methods. Initially, experiments of ED and ED coupled with AO (ED-AO) were carried out on MO solution to unravel the feasibility and effectiveness of ED-AO hybrid process. The influence of some operating parameters on the efficiency of ED-AO process was studied. Finally, the prepared Pb/PbO₂ electrode reusability was also tested.

2. Materials and methods

2.1. Chemicals and Reagents

All chemicals used in this study have an analytical grade and all aqueous solutions were prepared by using double distilled water. MO (molecular formula:

1 C₁₄H₁₄N₃O₃SNa; molar mass: 327.33 g mol⁻¹) obtained from Alfa Aesar was chosen as
2 an organic pollutant. Sodium sulphate (Na₂SO₄), sodium carbonate (Na₂CO₃),
3 trisodium orthophosphate (Na₃PO₄) and sodium chloride (NaCl) were from
4 BIOCHEM-Chemopharma. Sulfuric acid (H₂SO₄) (96%), hydrochloric acid (HCl)
5 (37%) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. Nitric acid
6 (HNO₃) (69%) and oxalic acid (C₂H₂O₄) (99.9%) were from Fluka. Hydrofluoric acid
7 (HF) (48%) and Acetone (100%) was respectively obtained from Nice[®] and VWR.
8 Other chemicals including potassium dichromate (K₂Cr₂O₇), silver sulfate (Ag₂SO₄)
9 and mercuric sulfate (HgSO₄) were purchased from Merck.

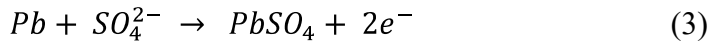
22 **2.2. Ions-exchange membranes**

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⁻¹ and 1.5–1.8 meq g⁻¹ for AMX and CMX
26 membrane respectively. The both membranes have a homogenous hydrocarbonated
27 structure (polystyrene-co-divinylbenzene), with sulphonated functional groups (–SO₃⁻)
28 for the CMX and quaternary ammonium groups (–NR₃⁺) 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).

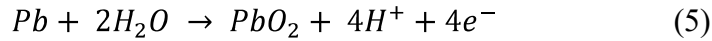
48 **2.3. Pb/PbO₂ electrode preparation**

49 As mentioned before, the anodic oxidation process is carried out using Pb/PbO₂
50 electrode which is prepared according to the procedure described by several authors
51 [49,56–58]. The preparation of this electrode type is based on the formation of PbO₂
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1 layer on Pb plate surface by electrolysis in H₂SO₄ 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 PbO₂ layer. Initially, the Pb surface
16 was roughened by a mechanical abrasion using sand papers to increase the PbO₂ 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 Na₂CO₃ (20 g L⁻¹), NaOH (50 g L⁻¹), Na₃PO₄
20 (20 g L⁻¹) and H₂SO₄ (2 g L⁻¹). Then, it was cleaned by mixed acid solution (HNO₃
21 (400 g L⁻¹), HF (5 g L⁻¹)) for 2 min and boiled in oxalic acid solution (100 g L⁻¹) for 5
22 min. Finally, in order to oxidize the Pb surface into PbO₂, the pretreated Pb plate was
23 placed as anode into electrolysis with H₂SO₄ solution (10 %) at a stable current density
24 (*i*) of 50 mA cm⁻² 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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43 **2.4. ED and ED-AO experimental set-up**

44 A three-compartment cylindrical Plexiglas cell (Fig. 1(a)) was constructed in the
45 laboratory. These compartments were separated by a pair of AMX and CMX
46 membranes. Each separating membrane had an effective area of 9.61 cm² which equal
47 to the area of the electrodes placed at the ends of E₁ and E₂ compartments. The
48 diameter and the thickness of each compartment were 3.5 and 1.4 cm, respectively,
49 where the volume is 13.45 cm³. 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/PbO₂ 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 Na₂SO₄ in all experiments) firstly into the
6 anodic compartment (E₁), and it then circulates in the cathodic compartment (E₂).
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⁻¹. In the central compartment (C)
9 (concentrate compartment) which delimited by CMX and AMX membranes circulates
10 0.25 L of H₂SO₄ (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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34 **2.5. Principles and procedures of ED and ED-AO processes**

35 Schematic representation of the principles and procedures of ED and ED-AO processes
36 is shown in Fig. 1(b) and 1(c). In the two processes, the feed solution containing MO as
37 an organic pollutant and Na₂SO₄ as supporting electrolyte circulates successively into
38 the side compartments (E₁ and E₂). An acidic solution (H₂SO₄, 0.05 M) as concentrate
39 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 Na₂SO₄ in feed solution were 25 mg L⁻¹ and 0.05
52 M, respectively, with applied current density of 20 mA cm⁻² 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/PbO₂ anode in E₁ 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 + Na₂SO₄ mixture solution, the
6 main factors were studied, including applied current density (1, 7.5, 15, 20, 25 and 30
7 mA cm⁻²), initial MO concentration (5, 10, 25, 50, 75 and 100 mg L⁻¹), initial pH of
8 feed solution (1.5, 3, 6.8 (natural pH), 8.5 and 11.5) and concentration of supporting
9 electrolyte (Na₂SO₄) (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 H₂SO₄ (1 M) solutions. All the experiments
11 were conducted in three times. In the other hand, the reusability of prepared Pb/PbO₂
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/PbO₂ electrode was carried out to
33 confirm the formation of PbO₂ layer on the electrode surface. After its preparation, the
34 Pb/PbO₂ 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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$$10 \text{ CER (ohm)} = \frac{U (V)}{I (A)} \quad (6)$$

11 Where U is the voltage measured during the processes and I is the applied current
12 intensity.
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15 For determinate the decolorization efficiency, the samples of MO feed solution were
16 analyzed by using a UV-Vis spectrophotometer, SP-UV 300 SRB (Spectrum
17 Instruments GMBH) with maximum absorption seen at the wavelength of 464 nm
18 [1,60]. The concentration of MO in its samples of aqueous solution was calculated
19 using a calibration curve based on the known concentrations. Finally, the decolorization
20 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/PbO₂ electrode

Several authors have showed the efficiency of PbO₂ 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/PbO₂ electrode surface before and after PbO₂ 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 PbO₂ layer covers the entire electrode surface, along with the formation of tightly packed and pyramid-shaped crystals. In addition, PbO₂ 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)).

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].

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 (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 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 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 cm^{-1} .

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

1 The last peaks centered at 698.23, 624.94 and 570.93 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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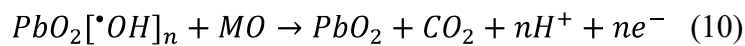
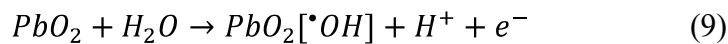
19 **3.3. Efficiency of ED-AO coupling in MO removal and AMX membrane anti-** 20 **fouling** 21

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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39 In electromembrane process, the CER control is a main factor for detecting the
40 membrane fouling phenomenon, because the deposition of particles or/and organic
41 molecules on the membrane surface leads to the increase of its electrical resistance and
42 consequently causing the increase of CER [64]. Therefore, Fig. 5(a) shows a significant
43 increase of CER during the ED process where it starts from 58 to reach at 130.46 ohm
44 after 180 min of process. This notable increase of CER during the ED indicates the
45 continuous fouling of the AMX membrane by 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/PbO₂ for ED-AO), because the Pb/PbO₂ electrode has a good electrical conductivity
 9 compared to the several others types of electrodes [65].
 10

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/PbO₂
 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/PbO₂ 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/PbO₂ 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 CO₂ and H₂O was obtained.
6 These results showed clearly the benefit of the introduction of AO on a Pb/PbO₂
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 (PbO₂) 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/PbO₂ electrode surface for degrading the MO molecules. Accordingly, the effect of
52 various current densities (1 – 30 mA cm⁻²) 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].

8
9 From Fig. 6(a), it could be seen that for the two lowest current densities (1 and 7.5 mA
10 cm⁻²) 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⁻² makes a slightly variation of CER,
14 especially for the two highest densities (25 and 30 mA cm⁻²). 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.

17
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⁻². By contrast, at low current densities, the decolorization and
23 COD removal rates were the lowest. For example, at density of 1 mA cm⁻², 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.

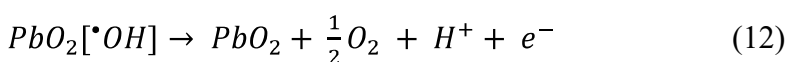
On the other hand, the decolorization of MO solution by electro-oxidation on Pb/PbO₂ electrode has been followed with pseudo-first-order kinetic by applying of Eq. (11). From the obtained results (Fig. 6(d) and Table 3), it was observed that the rate constant (k) for densities 1, 7.5, 15, 20, 25 and 30 mA cm⁻² were increased as follow, 0.24×10⁻², 0.31×10⁻², 0.66×10⁻², 0.73×10⁻², 0.99×10⁻² and 1.04×10⁻² min⁻¹, 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, C₀ and C_t are respectively, the MO concentration in the feed solution at initial and t time of the treatment, and k is the rate constant (min⁻¹).

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 ([•]OH) (Eq. (9)) on the Pb/PbO₂ electrode. For that reason, the higher current density led to the production of larger amount of [•]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⁻² gave approximately the similar results, although the current density increased by 5 mA cm⁻². 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⁻² 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 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 MO^- anion in close proximity to the membrane surface reinforces its fixation over the membrane active functional sites. The molecular size of 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., 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 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⁻¹ 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 CO₂ and H₂O [76,79]. Finally, the concentration 25 mg L⁻¹ 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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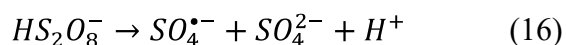
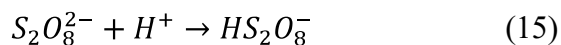
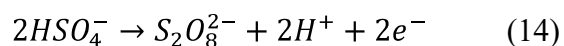
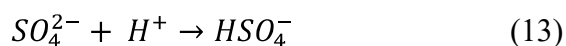
26 **3.4.3 Effect of pH of feed solution**

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⁻¹) were performed at different initial pH values varying in the range
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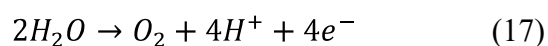
41 As shown in Fig. 8(a) and 8(b), the variation of pH value from 6.8 (natural pH) to 11.5
42 has no obvious effect on the decolorization and COD removal. However, the
43 decolorization and COD removal rates were increased from 82.16 to 97.62 % and from
44 76.33 to 95.75%, respectively when pH was adjusted 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/PbO₂ 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 [•]OH radical is more
19 favored at the low pH level. In contrast, the increase of pH value decreases the [•]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 SO₄²⁻ to the production of
22 sulfate radicals (SO₄^{•-}) and peroxodisulfate ions (S₂O₈²⁻) 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 SO₄^{•-} radical is considered as stronger oxidant of organic matter (e.g., MO) when
27 compared with [•]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 ≥ 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].
7



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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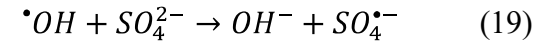
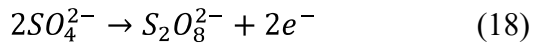
22 **3.4.4. Effect of supporting electrolyte concentration**

23 In ECO processes, the role of supporting electrolyte is normally to provide a
24 conductive medium and to decrease the voltage drop. Sodium sulfate (Na_2SO_4) is
25 usually used for its high solubility, its good conductivity and no parasitic reactions
26 occurred with the use of this electrolyte [82,90]. Consequently, in order to investigate
27 their effect on MO degradation by ED-AO, different concentrations (0.025 – 0.4 M) of
28 Na_2SO_4 supporting electrolyte were applied.
29

30 The obtained results (Fig. 9(a) and 9(b)) show that the increase in Na_2SO_4 concentration
31 into the range 0.025 – 0.1 M resulted a significant increase in both decolorization and
32 COD removal rates where reached 98.67 and 96.17%, respectively. However, for the
33 two highest concentrations (0.2 and 0.4 M), a total decolorization (>99%) with a slight
34 regression in COD removal (from 96.17 to 92.27% and to 89.35%) were registered. It
35 is also noticeable that the degradation of MO in the cases of three highest
36 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 ($k= 3.39 \times 10^{-2}$, 4.34×10^{-2} and $5.21 \times 10^{-2} \text{ min}^{-1}$, respectively),
 2 then it became relatively slower ($k= 1.91 \times 10^{-2}$, 2.13×10^{-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.
 6

7 The greatly improvement in decolorization can possibly be attributed to the
 8 contribution of the mediated oxidation of MO by $S_2O_8^{2-}$ and direct oxidation by $SO_4^{\bullet-}$,
 9 which are formed from the oxidation and $\cdot OH$ attack of SO_4^{2-} according to Eqs. (18),
 10 (19), and (20) [63,85,91]. Probably, the same reason made the COD removal increased
 11 for the range 0.025 – 0.1 M of Na_2SO_4 , although it has slightly regressed in the cases of
 12 the two others concentrations (0.2 and 0.4 M). Moreover, the increasing in supporting
 13 electrolyte concentration improves the medium conductivity, and consequently
 14 accelerates charge and mass transfer, thus benefiting the ECO reactions [90].
 15



19 Ma et al. [91] and Zhang et al. [92] have inferred that the oxidation of SO_4^{2-} into
 20 $S_2O_8^{2-}$ is increasingly favored with the increase in its concentration. However, these
 21 authors have also found that at moderately high current density and with the increase of
 22 Na_2SO_4 concentration, a slight abatement in the degradation of targeted organics is
 23 registered. The same trend was observed in this study concerning the regression of
 24 COD removal for concentrations of Na_2SO_4 at more than 0.1 M (Fig. 9(b)). The
 25 negative effect of Na_2SO_4 at higher concentrations on the completely mineralization of
 26 organics, is possibly ascribed to the following reasons:
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i) The consumption of generated $\cdot\text{OH}$ by 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 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 Na_2SO_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 Na_2SO_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/PbO₂ 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 (≈ 6.8) and $[\text{Na}_2\text{SO}_4] = 0.1 \text{ M}$). The results of Pb/PbO₂ 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/PbO₂
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 PbO₂ 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/PbO₂ 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.
3

- 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 Na₂SO₄ 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/PbO₂ 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.
24

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.
30

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.

Acknowledgments

The authors sincerely thank the Ministry of Higher Education and Scientific Research of Algeria for the financial support for this work. The authors also would like to acknowledge the European Institute of Membranes (Montpellier, France) for their collaboration.

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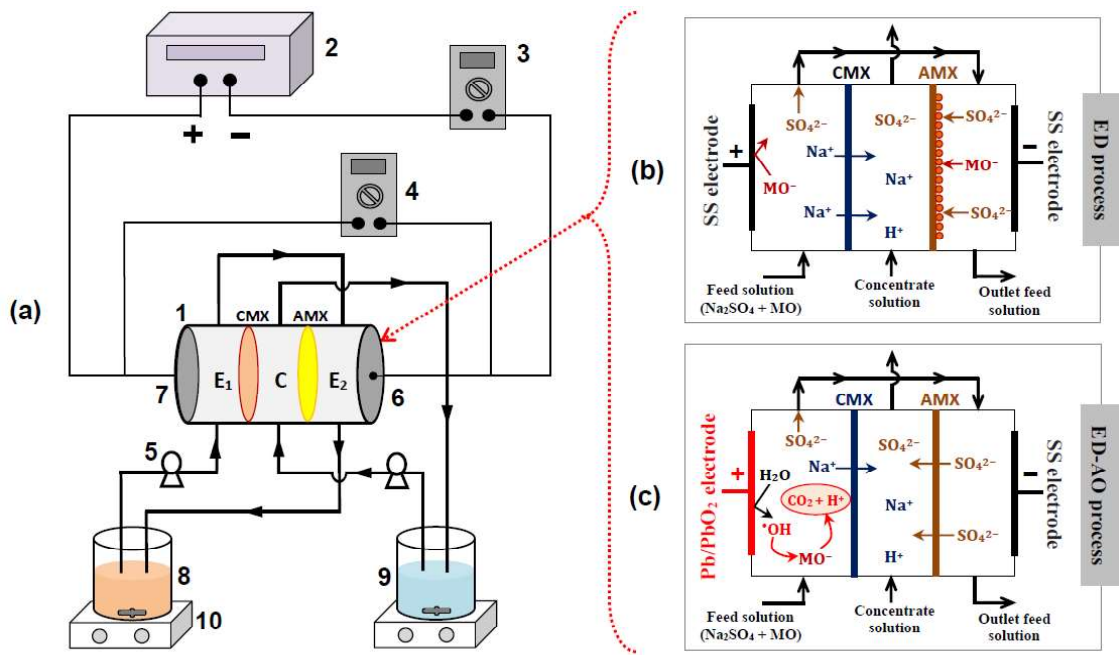


Fig. 1. (a) Experimental set-up; Procedures and principle of (b) ED and (c) ED-AO. (1): ED cell; (2): Power supply; (3) and (4): Multimeters; (5): Peristaltic pump; (6): SS electrode; (7): SS electrode in ED process or Pb/PbO₂ electrode in ED-AO process; (8): Feed solution tank; (9): Concentrate solution tank; (10): Magnetic stirrer.

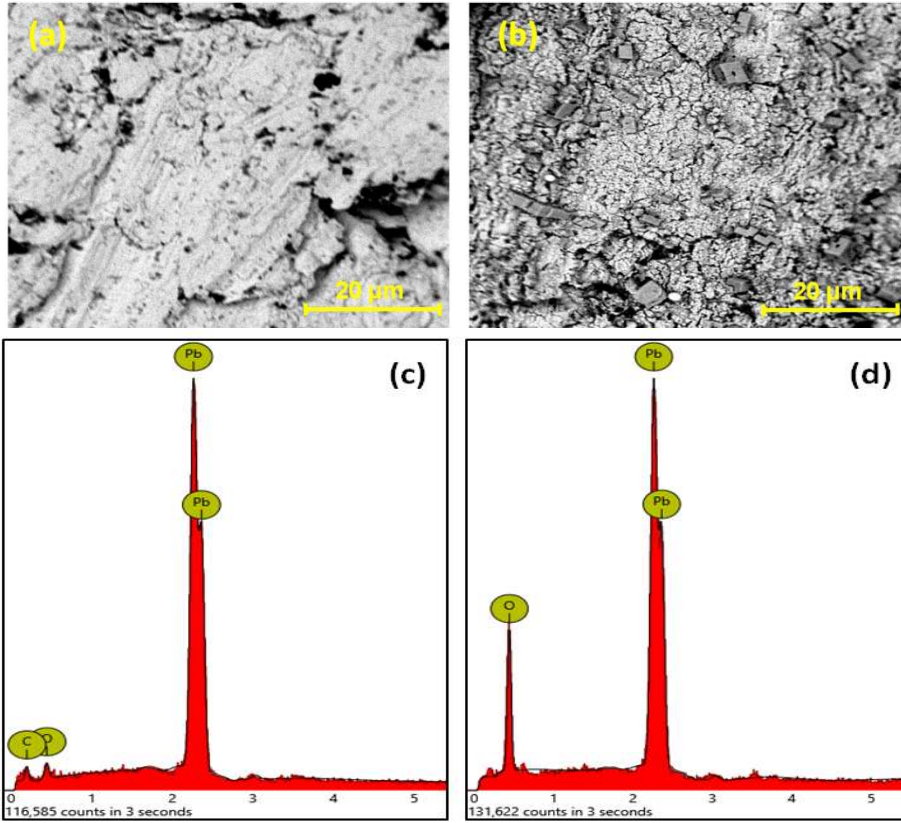


Fig. 2. SEM images of Pb/PbO₂ electrode (a) before electrolysis (c) its EDS spectrogram, (b) after electrolysis (d) its EDS spectrogram.

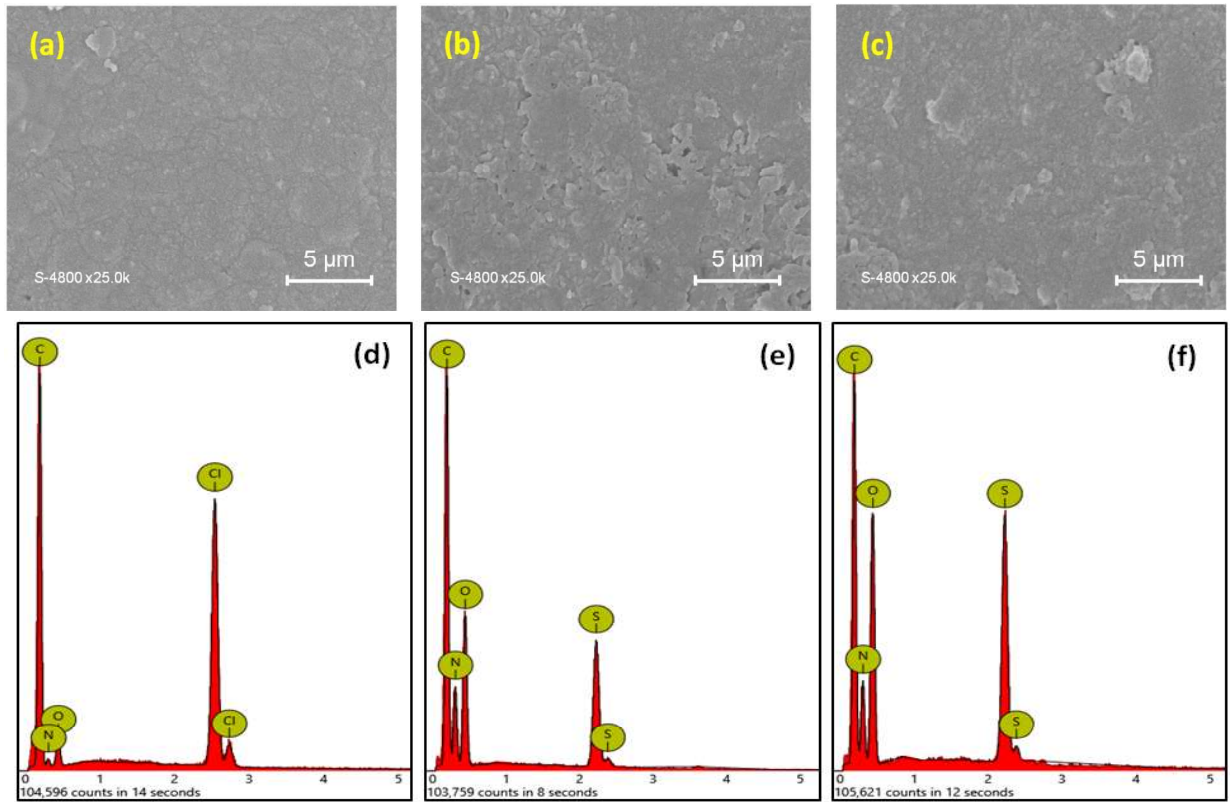


Fig. 3. SEM images of AMX (a) pristine membrane (d) its EDS spectrogram, (b) membrane used in ED (e) its EDS spectrogram, (c) membrane used in ED-AO (f) its EDS spectrogram. (ED and ED-AO operating conditions: $i = 20 \text{ mA cm}^{-2}$, $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$, natural pH (≈ 6.8) and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

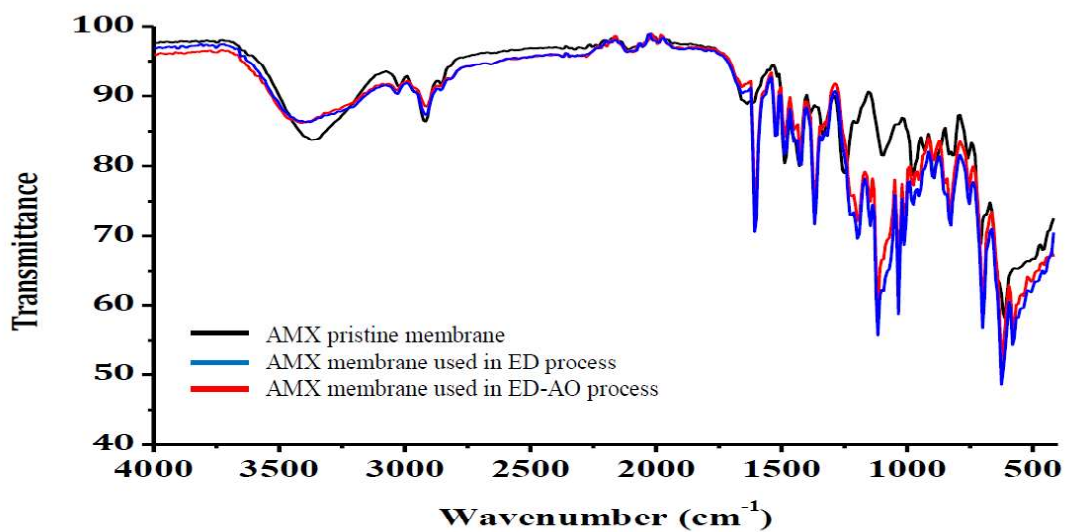


Fig. 4. FTIR Spectra of AMX pristine membrane, and those used in ED and ED-AD processes.

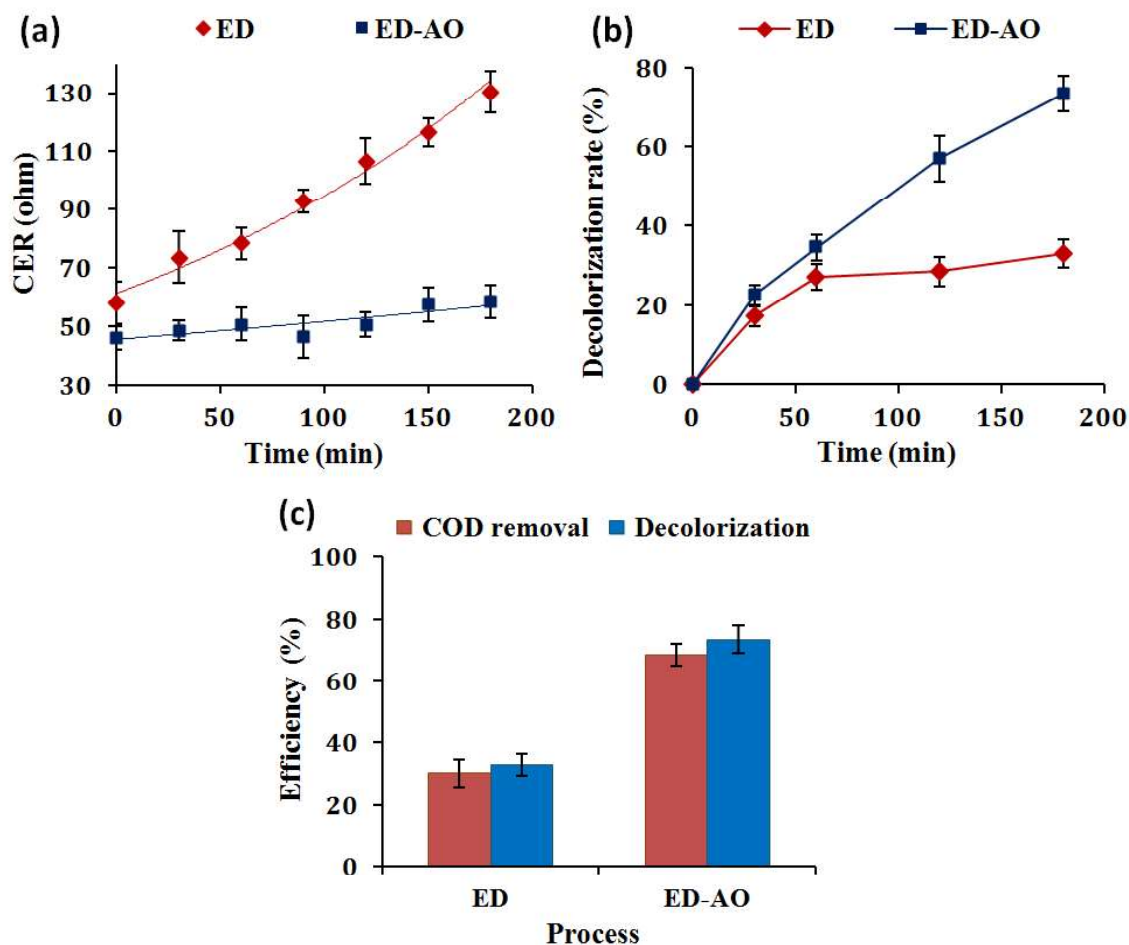


Fig. 5. Representation of (a) CER variation, (b) decolorization rate variation and (c) COD removal and decolorization efficiencies in the ED and ED-AO processes. (ED and ED-AO operating conditions: $i = 20 \text{ mA cm}^{-2}$, $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$, natural pH (≈ 6.8) and $[\text{Na}_2\text{SO}_4]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

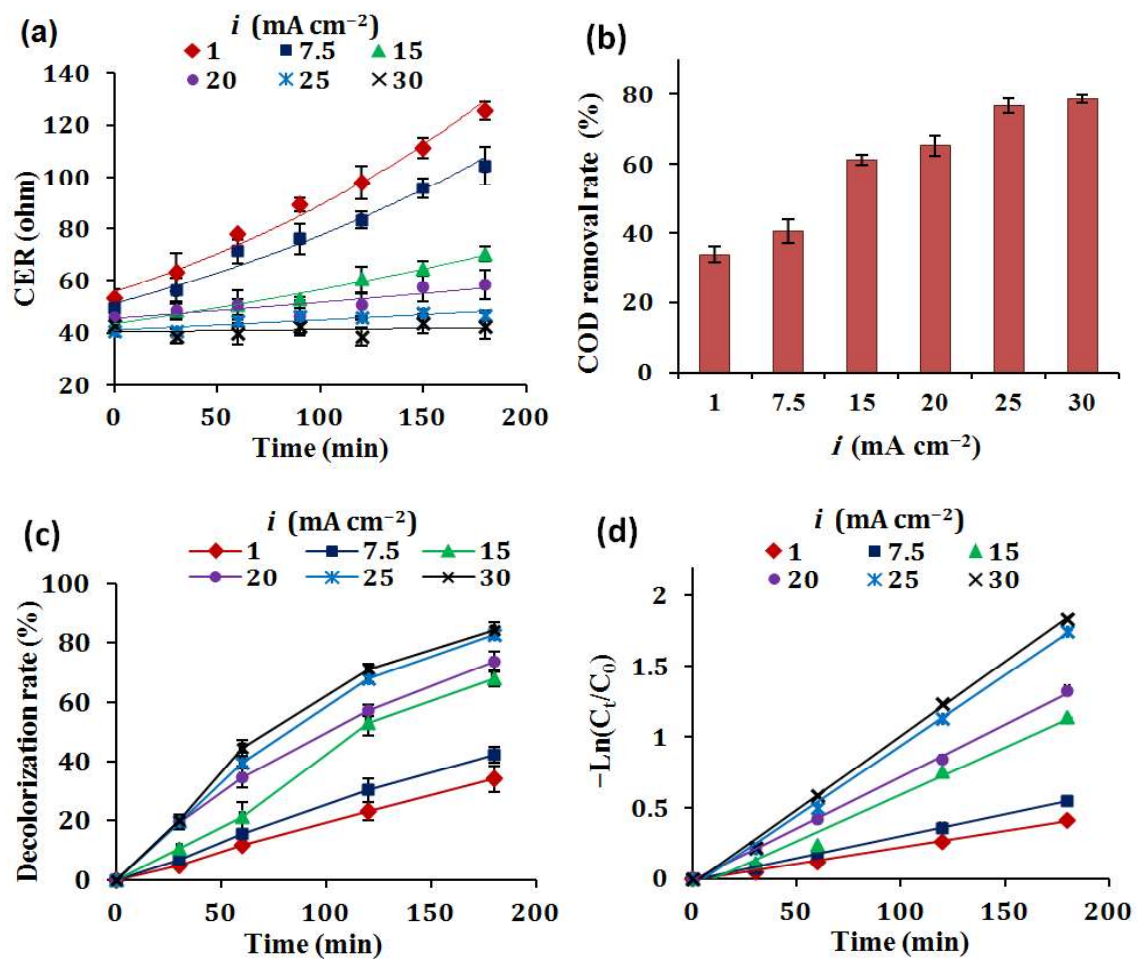


Fig. 6. Representation of (a) CER variation, (b) COD removal rate, (c) decolorization rate variation and (d) pseudo-first-order kinetics for different applied current densities. (ED-AO operating conditions: $[MO]_0 = 25 \text{ mg L}^{-1}$, natural pH (≈ 6.8) and $[Na_2SO_4] = 0.05 \text{ M}$).

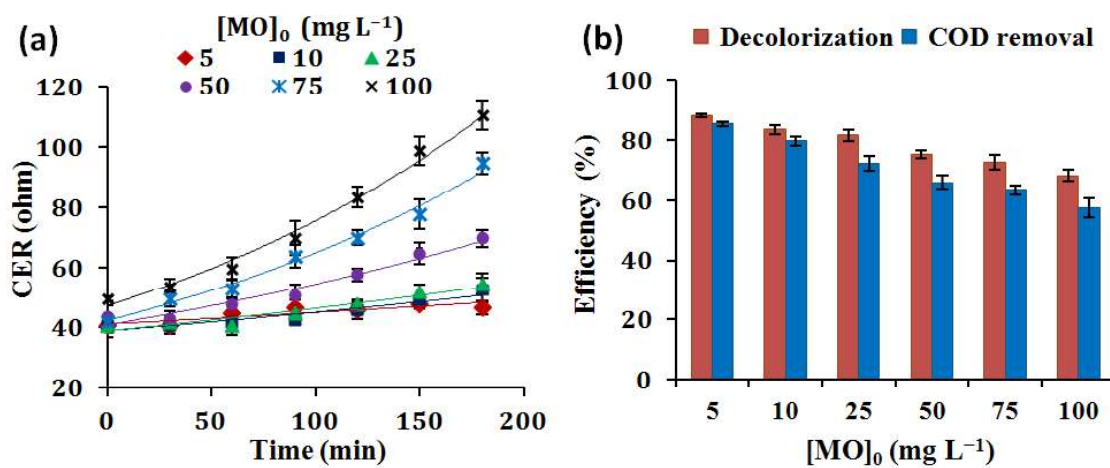


Fig. 7. Representation of (a) CER variation, (b) COD removal and decolorization efficiencies for different initial MO concentrations. (ED-AO operating conditions: $i = 25 \text{ mA cm}^{-2}$, natural pH (≈ 6.8) and $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$).

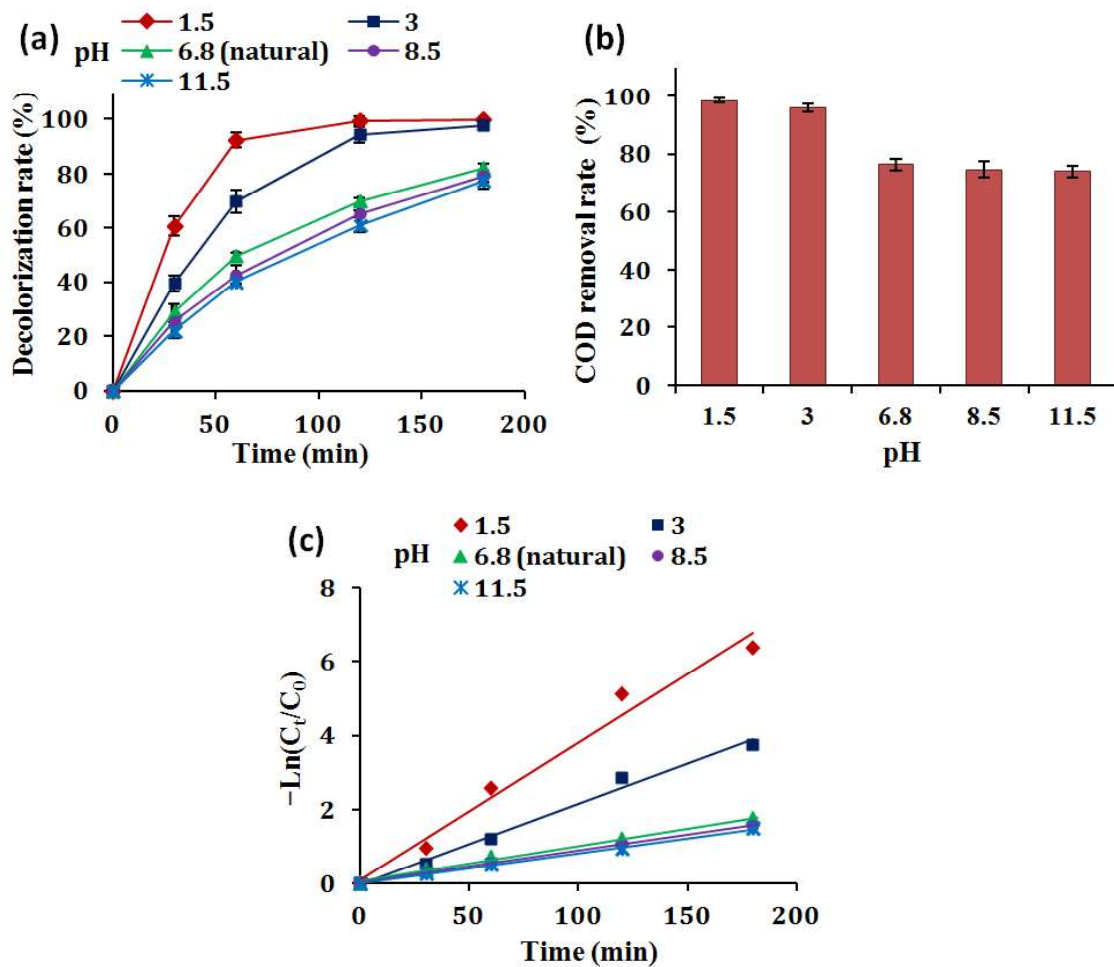


Fig. 8. Representation of (a) decolorization rate variation, (b) COD removal rate values and (c) pseudo-first-order kinetics for different pHs. (ED-AO operating conditions: $i = 25 \text{ mA cm}^{-2}$, $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$ and $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$).

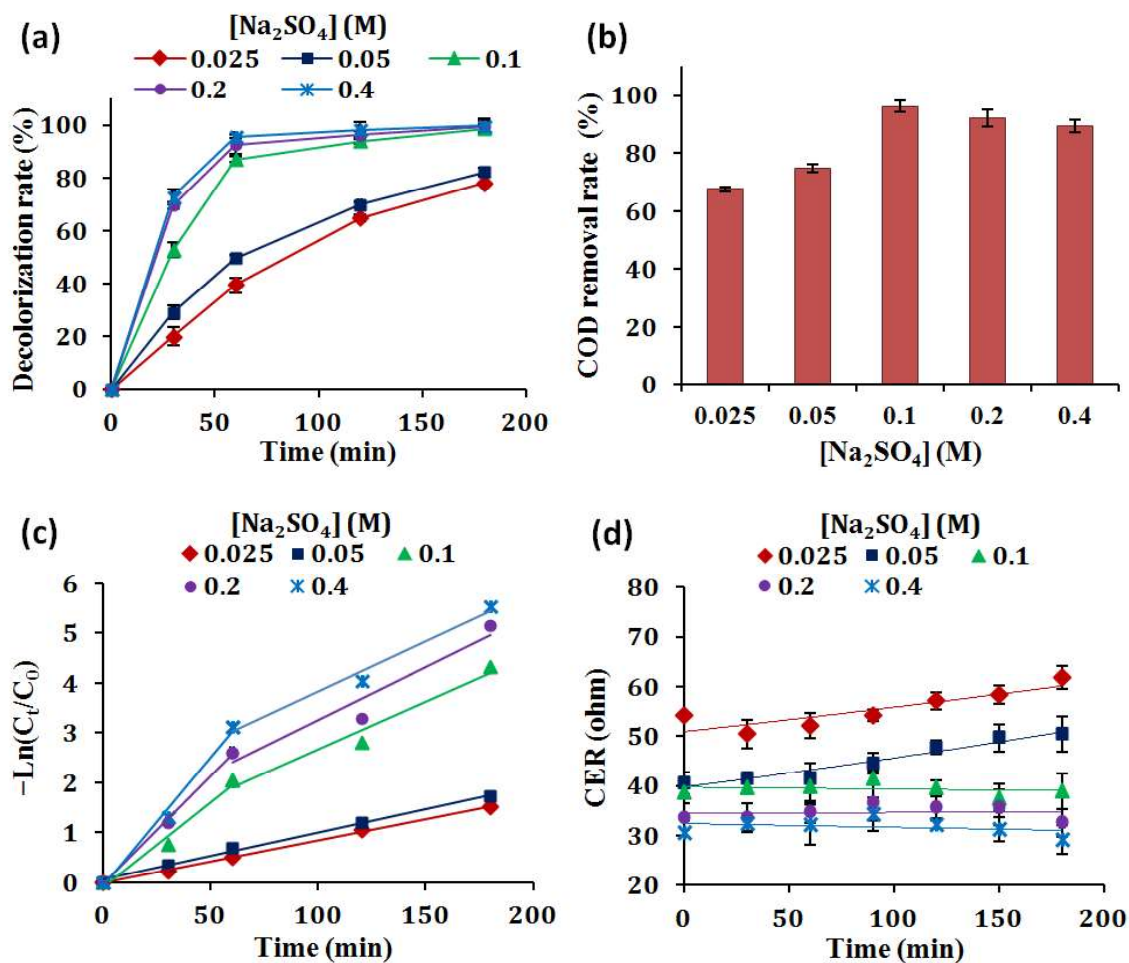


Fig. 9. Representation of (a) decolorization rate variation, (b) COD removal rate, (c) pseudo-first-order kinetics and (d) CER variation for different supporting electrolyte (Na_2SO_4) concentrations. (ED-AO operating conditions: $i = 25 \text{ mA cm}^{-2}$, $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$, and natural pH (≈ 6.8)).

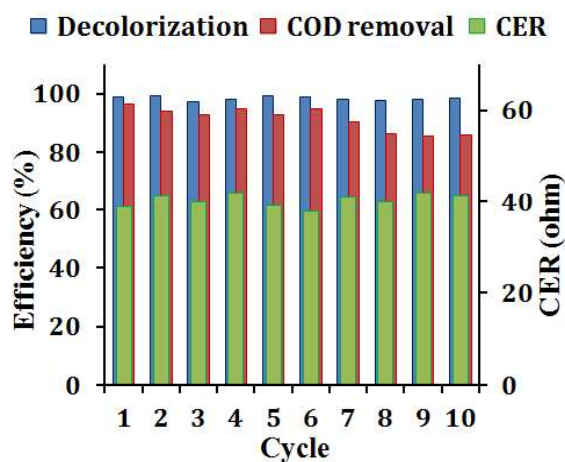


Fig. 10. MO degradation efficiency (decolorization and COD removal) and CER value at the end of ED-AO experiment using Pb/PbO₂ electrode for 10 cycles. (ED-AO operating conditions: $i = 25 \text{ mA.cm}^{-2}$, $[\text{MO}]_0 = 25 \text{ mg L}^{-1}$, natural pH (≈ 6.8) and $[\text{Na}_2\text{SO}_4] = 0.1 \text{ M}$).

Table 1

Chemical elements analysis results of Pb/PbO₂ electrode surface by EDS before and after electrolysis.

Pb/PbO ₂ 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

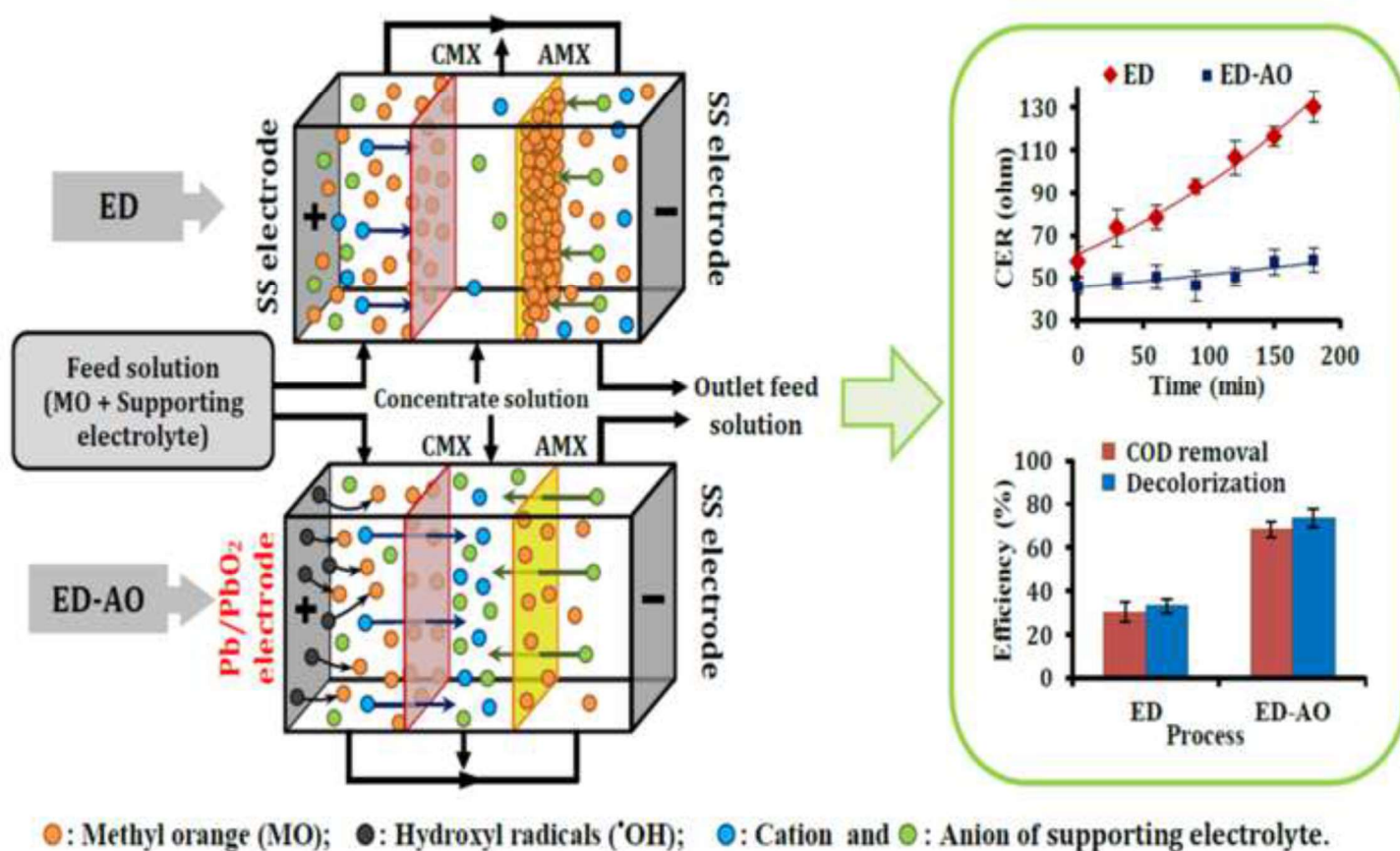
Table 3

Pseudo-first-order kinetic parameters.

Parameter	Value	k (10^{-2} min^{-1})	R^2	
i (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 ₂ SO ₄] (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.