



## Feasibility of electrodialysis in heavy metals removal from brassware wastewaters

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### ABSTRACT

The surface treatment workshops (brassware) are among the artisanal specialties of the city of Fez, which generate toxic and harmful effluents. In fact, the large amount of produced effluents is rich in heavy metals. Hence it is necessary to treat these effluents before returning them to the natural environment or for reuse. In the brassware workshops, the production of craft items passes through a chain of surface treatment and rinsing baths. Various rinsing baths are used: degreasing baths, alkaline copper-plating baths, acid copper-plating baths, nickel-plating baths and silver-plating baths. These rinsing baths are loaded with heavy metals (copper, silver and nickel). In order to treat these effluents to comply with the discharge limit values, the Ministry of Tourism, Crafts of Air Transport and Social Economy and Ibn Tofail University have agreed to launch a research collaboration to study the feasibility of membrane-based processes — electrodialysis (ED), nanofiltration and reverse osmosis — in the treatment of these effluents. This first study aims to investigate the removal of heavy metals from rinsing baths by ED. Two couples of ion-exchange membranes have been tested ACS/CMX and AXE/CMX. Using the selected couple of ion-exchange membranes (CMX/AXE), the treatment by ED of mixing of all rinsing baths, brassware wastewater loaded with copper, silver, nickel is performed. Removal of 98%, 95%, 97% of copper, nickel and silver are respectively achieved.

*Keywords:* Ion-exchange membrane; Electrodialysis; Brassware wastewater; Heavy metals removal; Copper ions, Silver ions, Nickel ions

### 1. Introduction

The art of brassware dates back to the twelfth century and blossoms in the fourteenth century in Morocco and it is well known as a traditional handicraft industry in the city of Fez. The brassware workshops of Fez include baths and a treatment area well-equipped with materials and products necessary for this process. The surface treatment carried out by electrolytic pathway (wet-laid) represents

today and probably for a long time, the main part for metal surface treatment and coating. It consists in applying a deposit on the parts to be processed and is based on the electrolysis process. It aims to modify and transform the surface of the metal part to give it new properties, either the mechanical characteristics of a product (electric conductivity, anti-corrosion, stainless protection, etc.) or its aesthetic properties (silver deposit, gilding, chrome plating, nickel plating, copper plating, etc.). The brassware activity

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(the surface treatment workshops) produces handicrafts items, which pass through a chain of surface treatment and rinsing baths. These baths are numerous; degreasing bath, alkaline rinsing bath, acid rinsing bath, nickel rinsing bath and silver rinsing bath. Both nickel plating and silver baths are followed by a rinsing bath, which is more dangerous because of their composition in toxic elements. Thus, the effluents generated by this industry are very harmful and rich in heavy metals like nickel, copper and silver. These elements are the main pollutants in brassware (mixture of all rinsing baths) and result from the use of copper salts, nickel chlorides, nickel sulfate and silver cyanide during copper plating, nickel plating and silver-plating operations. All heavy metals are deleterious to human health even at low content [1,2]. Their toxicity may be the origin of several illnesses such as nervous activities, damage to the lungs, liver, kidneys, blood compositions and other fundamental organs. Moreover, these metals may cause muscular dystrophy, Alzheimer's disease, different types of cancers and multiple sclerosis [3,4]. In addition, they are not degradable in the receptor environment and are harmful to creatures and plants when their concentrations exceed the permissible limits. Accordingly, the brassware effluent's direct discharge into the river of Sebou causes aquatic and environmental disturbance. It is, therefore, necessary to treat this wastewater before returning them to the natural environment. Many methods to treat such effluent charged with heavy metals are reported in the literature such as: adsorption [5], surfactants [6], precipitation [7,8], chemical coagulation/flocculation [9], ion-exchange resins [10,11], reverse osmosis (RO), nanofiltration (NF) [12,13], ultrafiltration [14,15] and electrodialysis (ED) [16,17]. ED is an electro membrane separation process, based on the selective migration of ions through ion-exchange membranes as a result of an electrical driving force [18]. The most ED applications are demineralization of whey [19], nitrate removal from groundwater [20], desalination of brackish water [21–23], sugar industry [24], removal of fluoride [25] wastewater treatment [26], recovery and removal of heavy metals [27–29]. In this way, Guvenc and Karabacakoglu [17] used ED cell made of Plexiglas with two couple of ion-exchange membrane I (Nafian-424/Ionac MA-3475) and II (K-501/A-501) to remove silver ions from wastewater with a concentration of 101 mg/L. Under an electrical voltage of 15 V, they removed silver ions with faradic efficiency of 100%. In addition, Benvenuti et al. [16] used ED to treat nickel electroplating rinse water. They removed 97.43% of nickel at a demineralization rate (DR) of 94.61% by using a cation-exchange membrane (Ionac MC-3470) and anion-exchange membrane (Ionac MA-3475). The diluate was reused in the nickel-plating rinsing bath and the concentrate was returned to the nickel bath as a reinforcement. In another study, Scarazzato et al. [28] conducted ED tests on a cyanide-free copper plating bath. With a DR of 90%, they extracted more than 80% of ions. Laidi et al. [30] study the treatment of the brassware effluents in the city of Fez using a sequential batch reactor at low and medium organic load. The results showed a significant reduction in carbon organic demand and biochemical oxygen demand (BOD<sub>5</sub>) for both applied organic loads. In contrast, the obtained abatements of heavy metals such as silver, copper and nickel with low and medium load were 32.87%, 41.42%, 30.98%

and 27.77%, 34.63%, 26.06% respectively. These values are still very low since the biological treatment is efficient for organic matter pollution and not for metallic ions. It seems that membrane-based processes, such as ED, NF and RO are promising for the treatment of this kind of effluent. The overall objective of this research is to study the feasibility of ED, NF and RO in the treatment of brassware effluents loaded with heavy metals, in order to comply with the Moroccan discharge limit values and protect the environment. The purpose of this study, which is the first step of this research, is dedicated to evaluating the feasibility of ED, in the removal of heavy metals from the rinsing baths of brass workers of Fez.

## 2. Material and methods

The ED operation is carried out on a lab-scale pilot provided by Eurodia French Company, which was already described in previous works [31,32]. The membranes used are two couples of ion-exchange membranes: AXE/CMX and ACS/CMX manufactured by Tokuyama Corp., (Japan).

Table 1 compiles the main characteristics of the three ion-exchange membranes.

In all tests, a conductivity meter (Inolab WTW, WTW Company located in France) is used to measure the electrical conductivity (E) and temperature of the samples. A pH-meter (Jenway 3510 pH-Meter, Cole-Parmer Company located in France) is used for measuring the pH of the solutions, heavy metals concentrations are determined by the technique of inductively coupled plasma spectrometry ICP-OES (PerkinElmer Optima 8000, PerkinElmer Company located in United States), bicarbonate ions are analyzed by titration (HCl 0.1 M), Ca<sup>2+</sup> and Mg<sup>2+</sup> are analyzed by atomic absorption spectroscopy, chloride and cyanide ion concentrations are determined by ionometer (Mettler Toledo, Greifensee, Switzerland).

The ED operations are conducted on a copper acid rinse bath and a brassware effluent (mixture of all the baths) and the analytical results are calculated by using three different measurements for untreated water, the average indicated in Table 2.

Fig. 1 represents a picture of the ED pilot and the ED stack design characteristics are given in Table 3. After experiments, the membranes are cleaned using alkaline and acidic solutions according to the manufacturer's recommendations. The DR reflects the total amount of salts removed, it can be calculated from the electric conductivity values using the following equation [34,35]:

Table 1  
Characteristics of AXE, ACS and CMX membranes [25]

Commercial name	ACS	AXE	CMX
Membrane type	AEM	AEM	CEM
Thickness, mm	0.17	0.17	0.18
Electrical resistance, ohm cm <sup>2</sup>	2.0	1.4	3.0
Exchange capacity, meq g <sup>-1</sup>	1.8	2.0	1.65
Burst strength, mPa cm <sup>-2</sup>	0.40	0.14	5.5

CEM: cation-exchange membrane; AEM: anion-exchange membrane.

$$D_R = \left(1 - \frac{E_t}{E_0}\right) \times 100 \quad (1)$$

where  $E_0$  and  $E_t$  are the electric conductivities of the diluate before and after treatment (expressed in  $\text{mS cm}^{-1}$ ) respectively.

The ion removal ( $R\%$ ) is calculated using the following expression:

$$R\% = \left(1 - \frac{C_p}{C_0}\right) \times 100 \quad (2)$$

where  $C_p$  and  $C_0$  are respectively the permeate and the initial concentration.

### 3. Results and discussion

#### 3.1. Physicochemical and metal characterization of effluent brassware

The physicochemical and metallic analyses of acid copper rinsing bath (ACRB) and the mixture of all rinsing baths (MARB) give a clear idea of the nature and degree of pollution of these effluents. Table 2 shows the analytical results for ACRB and MARB. The characterization of ACRB shows that it is highly charged in copper, nickel and silver. All these metal ions exceed the Moroccan discharge limit values especially copper which is the main component in this bath and which comes essentially from the use of the copper sulfate ( $\text{CuSO}_4$ ). The sulfate content ( $384.27 \text{ mg/L}$ ) is high but remains in the limit values of discharge standards. Finally, the ACRB is characterized by a low electric conductivity ( $1,161 \text{ }\mu\text{S/cm}$ ), a pH of 5.56 and a temperature of  $17.4^\circ\text{C}$ . The MARB (degreasing bath, alkaline rinsing bath, acid rinsing bath, nickel rinsing



Fig. 1. ED pilot plant.

Table 2  
Characteristics of untreated wastewater

	Acid copper rinsing bath (ACRB)	Mixture of all rinsing baths (MARB)	Discharge limits values [33]
Temperature, $^\circ\text{C}$	17.4	20.3	30
pH	5.56	9.62	6–9
E, $\mu\text{S/cm}$	1,161	3,420	2,700
$\text{Cu}^{2+}$ , ppm	<b>78.85</b>	<b>51.99</b>	4
$\text{Ag}^+$ , ppm	<b>0.672</b>	<b>87.26</b>	0.1
$\text{Ni}^{2+}$ , ppm	<b>13.45</b>	<b>50.86</b>	5
$\text{Cd}^{2+}$ , ppm	<DL	<DL	1
$\text{Cr}^{3+}$ , ppm	0.132	0.09	5
$\text{Pb}^{2+}$ , ppm	0.105	<DL	1
$\text{Zn}^{2+}$ , ppm	1.612	<DL	10
$\text{Ca}^{2+}$ , ppm	55.94	42	–
$\text{Mg}^{2+}$ , ppm	46	16.82	–
$\text{HCO}_3^-$ , ppm	55	451	–
$\text{SO}_4^{2-}$ , ppm	384.27	430	600
$\text{Cl}^-$ , ppm	68.5	390	–
$\text{CN}^-$ , ppm	–	0.32	0.5

DL: detention limit

Table 3  
ED stack design

Membrane area, cm <sup>2</sup>	200
CEM	CMX Tokuyama Corp., (Japan)
AEM	ACS, AXE Tokuyama Corp., (Japan)
Number of cell pair	10
Separator	PE + PP
Electrode	DES
Flow of dilute and concentrate compartments, L/h	180–200
Flow of electrode compartment, L/h	150
Current max, A	9
Maximum voltage, V/cell	1.5
Polarity reversal	Manual

bath and silver rinsing bath, nickel plating and silver baths = brassware effluents) is characterized by an alkaline pH (9.62), a temperature of 20.3°C, a high electric conductivity (3,420  $\mu\text{S}/\text{cm}$ ) and a high content of copper, silver and nickel (51.99, 87.26, and 50.86 mg/L respectively), which exceed the Moroccan discharge limit values. These high concentrations are due to the use of chemicals in the electrolytic baths (copper cyanide, copper sulfate, nickel sulfate, nickel chloride, silver cyanide).

The ED operations are conducted for the ACRB in order to compare the performance of two anion-exchange membranes ACS and AXE using in couple with the cation-exchange membrane CMX.

### 3.1.1. Treatment of ACRB by ACS/CMX membrane couple

The ED experiments are conducted under the following operating conditions: initial current intensity is 0.4 A, electrical voltage is 10 V, the flow of dilute and concentrate are 120 L/h and flow of the electrode compartment is 150 L/h.

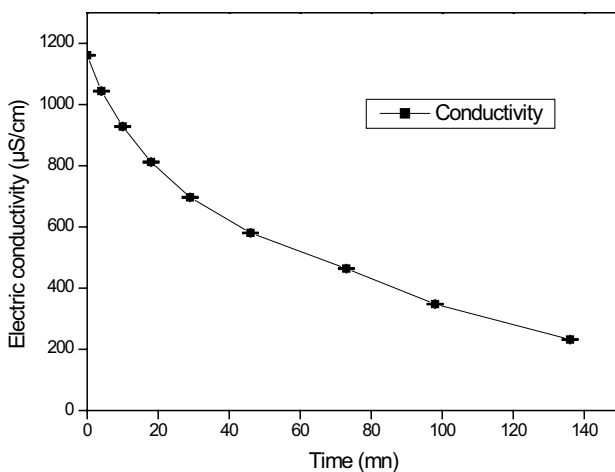


Fig. 2 shows the variation of electric conductivity and pH of diluate during ED. Fig. 3a and b show the variation of % removal of the most anions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ag}^+$ ) as a function of DR.

According to the results in Fig. 2, the electric conductivity decreases during ED operation and reaches 232  $\mu\text{S}/\text{cm}$  after 136 min, which corresponds to a DR of 80%. After this time, precipitation appears in the concentrate. At the same time, a slight increase in pH is observed in the diluate, due to the removal of  $\text{HCO}_3^-$  ions.

Fig. 3a shows the DR of cations and anions from ACRB during ED. The % removal of anions increases with DR for the three anions, it follows the following order:

$$\text{Cl}^- (94\%) > \text{HCO}_3^- (74\%) > \text{SO}_4^{2-} (72\%)$$

The transport of chloride and bicarbonate ions across the membrane ACS is greater than that of sulfate. This result is due to the nature of the ACS membrane which is preferentially selective to monovalent ions. The size of the chloride and bicarbonate ions may have an additional effect; the larger the ion, the more it is sterically hindered in its transport across the membrane [36]. The hydrated chloride has a radius of 0.347 nm, and its mobility is large compared to that of bicarbonate.

For cations, Fig. 3b shows that a linear increase in copper removal is achieved; a % removal of 97% is obtained at DR of 80%. During the same time and for the same DR, the % removal of chloride, bicarbonate and sulfate ions reach 94%, 74% and 72% respectively. The % removal of silver obtained for a DR of 30% is 95% and the % removal obtained for nickel is 93% for a DR of 10%.

For metallic cations, the % removal of follows the following order:

$$\text{Ag}^+ > \text{Ni}^{2+} > \text{Cu}^{2+}$$

The % removal of  $\text{Ag}^+$  ions is higher than the % removal of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions even though the charge is lower than that of these two ions. This behavior is due to both selectivities of the ACS membrane and the initial  $\text{Ag}^+$  concentration

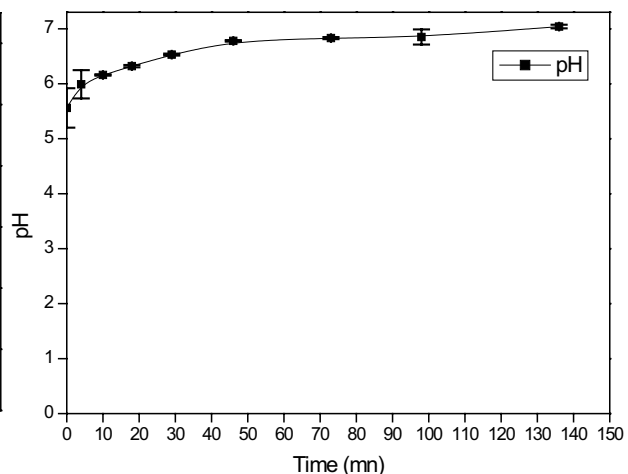


Fig. 2. Electric conductivity and pH of diluate vs. time.

which does not exceed 0.6 mg/L. On the other hand, for Ni<sup>2+</sup> and Cu<sup>2+</sup> ions, the % removal of Cu<sup>2+</sup> is lower than the % removal of Ni<sup>2+</sup> even though they have the same charge. The concentration of Ni<sup>2+</sup> ions is much lower than that of Cu<sup>2+</sup> ions. For Cu<sup>2+</sup> the removal rate of 97% is achieved for a DR of 80%. For Ni<sup>2+</sup> the rejection reaches 95% after only 20% of DR. For Ag<sup>+</sup>, the elimination is instantaneous and the % removal obtained is 93%. This behavior is due essentially to the difference in the initial concentration of the three metallic ions.

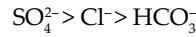
3.1.2. Treatment of ACRB by AXE/CMX membrane couple

The ED is conducted under the same operating conditions as with the first couple ACS/CMX with the only difference of the initial current intensity which has been fixed at 0.8A. Fig. 4 shows the variation of electric conductivity and pH as a function of the time of ED using the AXE/CMX membrane couple. Fig. 5 represents the variations of %

removal of all anions (Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and cations (Cu<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>) as a function of DR.

As shown in Fig. 4 with the first couple, ED using the AXE/CMX membrane couple, the electric conductivity decreases and reaches a value of 232 μS/cm after only 21 min (136 min for the couple ACS/CMX). At the same time, a slight increase in pH is attributed to the removal of bicarbonate ions.

Fig. 5a depicts that the % removal of anions increases with DR. For the three studied anions, this removal follows the following order:



The transport of sulfates is higher than that of chloride and bicarbonate due to the nature of the AXE membrane, which is a non-selective membrane [37] unlike the ACS membrane of the first couple which is preferentially selective to monovalent ions. Then, the AXE membrane will favor the removal of the most charged ions first. For ions having the

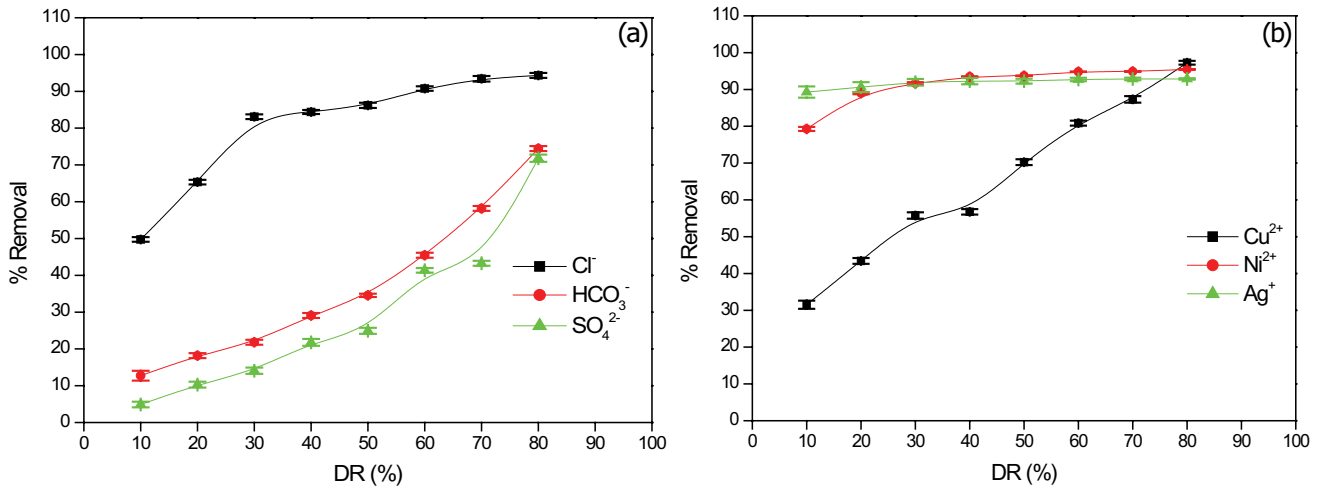


Fig. 3. % removal of anions and cations vs. DR.

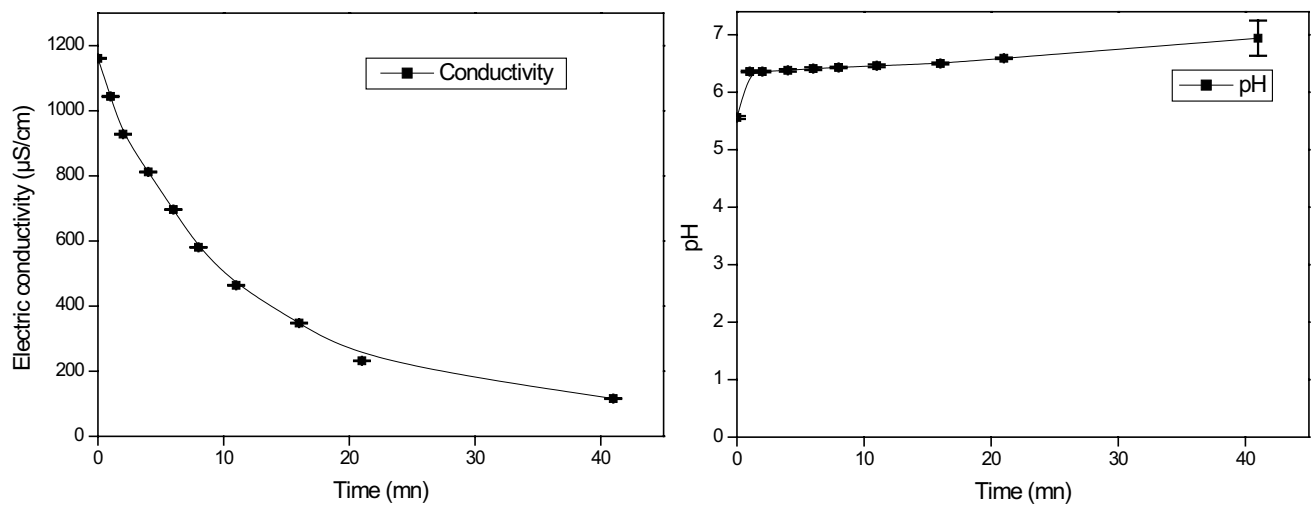


Fig. 4. Electric conductivity and pH of diluate vs. time.

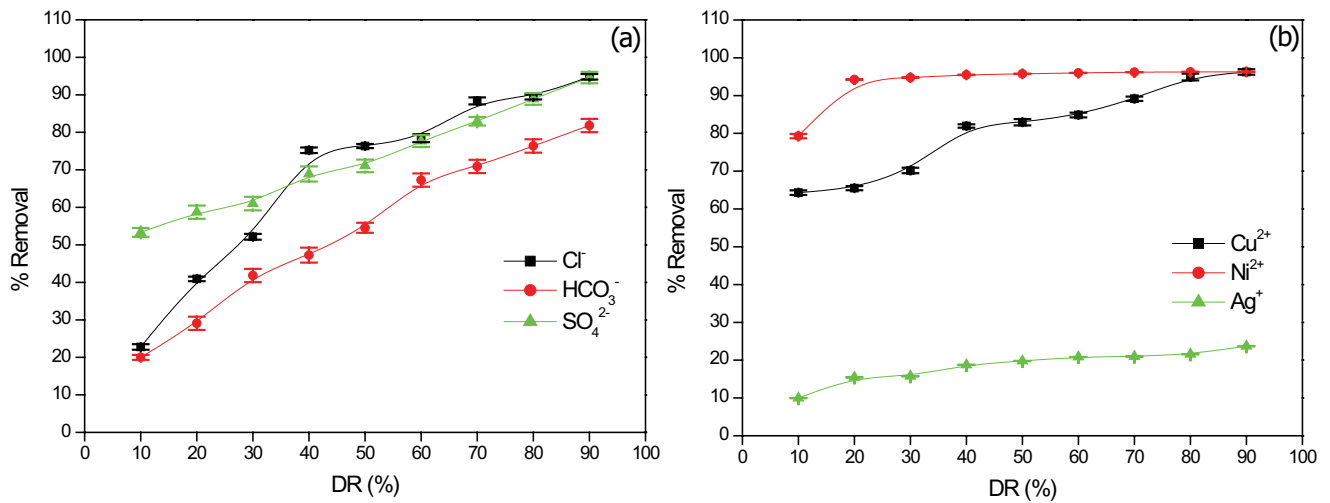
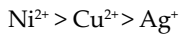


Fig. 5. % removal of anions and cations as a function of DR.

same charge, the mobility of chloride is greater than that of bicarbonate.

For cation removal, the same evolution obtained previously with ACS/CMX couple is exhibited with the AXE/CMX couple. A quasi-linear removal of copper is achieved as a function of DR. For a DR of 80%, 97% of copper is removed (Fig. 5b).

The removal of metallic cations follows the following order:



The % removal of nickel and copper increases in parallel with DR. Also, almost removal of 96% is obtained for nickel and copper for a DR of 30% and 90% respectively. Silver is eliminated with a much slower speed than copper and nickel according to DR. An increase of DR from 10% to 90%, leads to a variation in silver removal of 10% to 20% only. The elimination of silver ions is poor compared to the divalent ions

( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ). Because of the low concentration of nickel ions compared to copper, the elimination of nickel by ED is higher than that of copper.

Finally, the treatment by ED of ACRB with two couple of cation-exchange membrane (CEM) and anion-exchange membrane (AEM) was used with the aim of selecting the best ion-exchange membranes couple. The results show that the couple AXE/CMX exhibits the greater % removal of copper ions which is 94% after 21 min at a DR of 80%. On the other hand, the couple ACS/CMX performance in % removal of copper ions is 97% at a DR of 78% and during 128 min.

For both pairs of membranes, and without the use of any sequestering agent or addition of acid, precipitation in the concentrate compartment is only observed with the naked eye after the DR of 80%.

This result can be explained by the characteristics of the AXE membrane which is a sieve and a non-selective membrane which lowers the resistance of the cell and facilitates

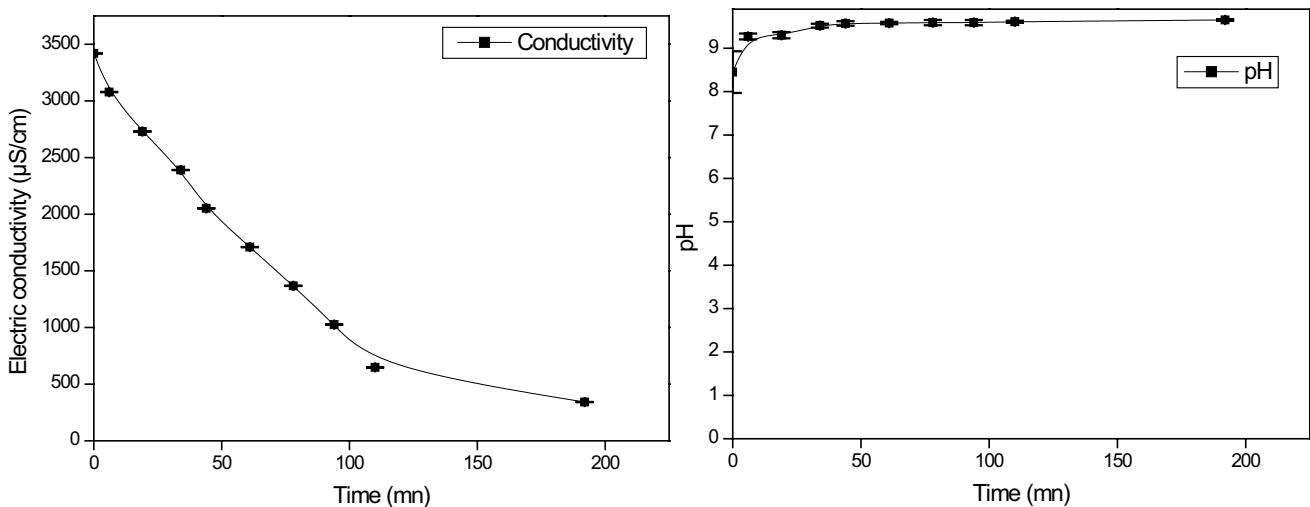


Fig. 6. Electric conductivity and pH of diluate vs. time.

the passage of ions compared to the ACS membrane which is selective monovalent ions [24].

Hence, the best couple of membranes is AXE/CMX and the next tests of ED will be performed with these couple of membranes.

3.2. Treatment of MARB effluents by ED

This part is dedicated to study the performance of the AXE/CMX membranes couple in the treatment of MARB effluents by ED. As indicated in Table 2, these effluents are mainly loaded by nickel, silver and copper ions, 50.86, 87.26 and 51.99 mg/L respectively. The ED experiments on these effluents are performed under the following operating conditions: Initial current intensity is 0.55 A, electrical voltage is 15 V, the flow of diluate and concentrate are 120 L/h and flow of the electrode compartment is 150 L/h. The voltage is increased because the effluent is too loaded with metals ions (Fig. 6).

As shown in the previous section concerning the selection of the best couple of ion-exchange membrane of ACRB

and MARB effluents during ED, the abatement of electric conductivity is high and reaches 96.7% during only 41 min of ED using AXE/CMX membranes couple. At the same time, a slight increase in pH is observed which should be attributed to the removal of bicarbonate ions.

Fig. 7a shows that the % removal by ED of all followed anions (chloride, bicarbonate and sulfate) of MARB effluent increases with DR, and respectively reaches 76%, 86% and 94% at DR 90%. In all the range studied of DR, the % removal of bicarbonate appears to be greater than that of chloride.

Fig. 7b shows that the % removal by ED of copper, nickel and silver from MARB effluent increase significantly with a DR and tend towards a plateau for the high DR values. A DR of 30% is sufficient to eliminate more than 95% of these three cations. The apparition of a plateau for a DR upper than 90% means that even DR increases, there will be no influence on the % removal of these cations. This behaviour is attributed to the concentration polarization which limits the ions transfer at the membrane-solution interface, the

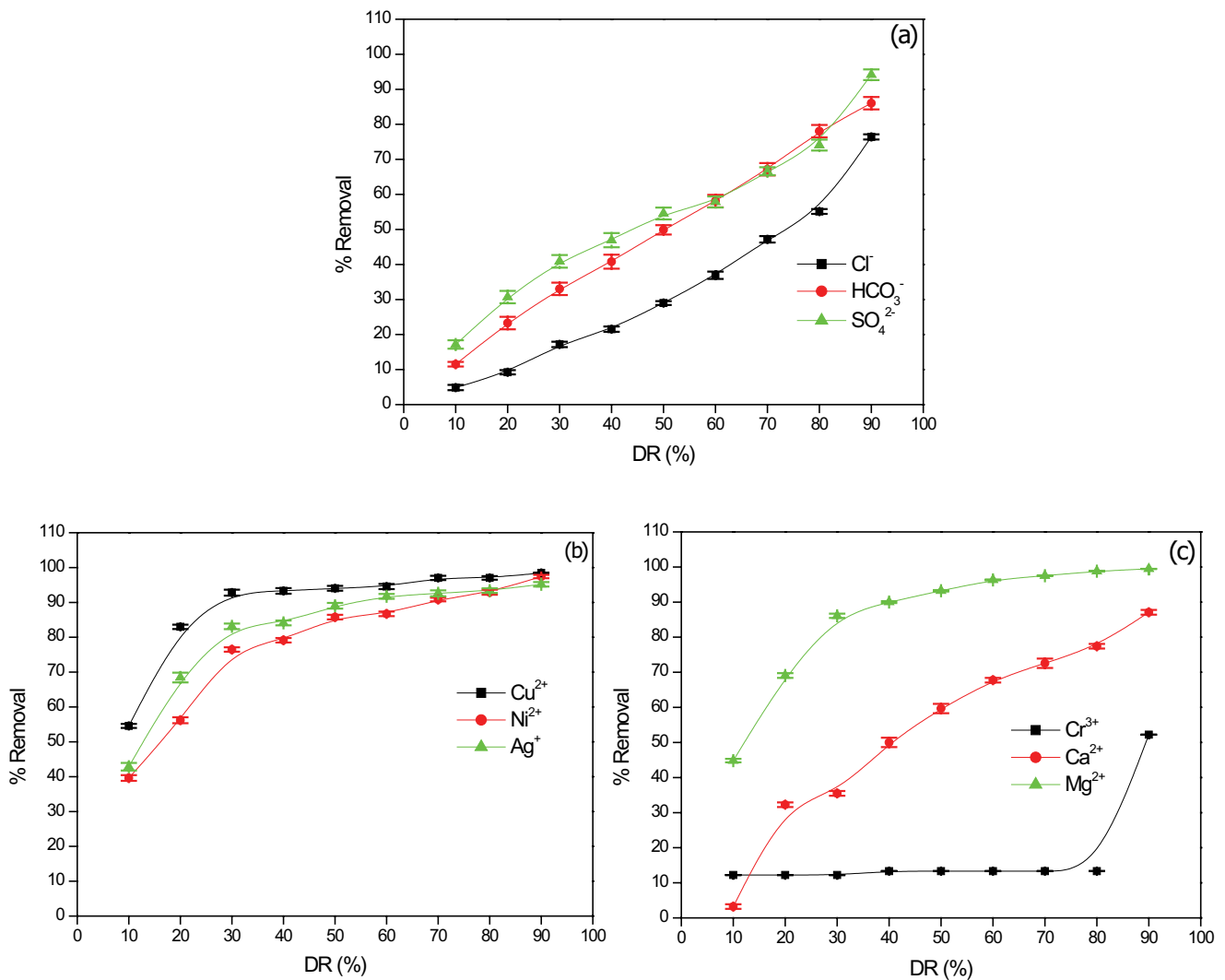


Fig. 7. % removal of anions and cations as a function of DR.

Table 4  
Characteristics of the treated water by ED, DR = 90%

Parameter	Values	Discharge limits values [33]
Temperature, °C	29.4	30
pH	8.45	6–9
E, $\mu\text{S}/\text{cm}$	342	2,700
$\text{Cu}^{2+}$ , mg/L	0.807	4
$\text{Ag}^+$ , mg/L	4.192	0.1
$\text{Ni}^{2+}$ , mg/L	1.34	5
$\text{Cd}^{2+}$ , mg/L	<DL	1
$\text{Cr}^{3+}$ , mg/L	0.043	5
$\text{Pb}^{2+}$ , mg/L	<DL	1
$\text{Zn}^{2+}$ , mg/L	<DL	10
$\text{Ca}^{2+}$ , mg/L	8	–
$\text{Mg}^{2+}$ , mg/L	0.2	–
$\text{HCO}_3^-$ , mg/L	63	–
$\text{SO}_4^{2-}$ , mg/L	25.21	600
$\text{Cl}^-$ , mg/L	92	–

DL: detention limit

precipitation appears in the concentrate and the operation should be stopped immediately.

Fig. 7c shows that the % removal by ED of calcium and magnesium from MARB effluent increases almost linearly with DR. In all the studied range of DR, % removal of magnesium is greater than that of calcium. During the same time, the % removal of chromium III stills low (<10%) and constant until DR of 80%. Afterwards it seems to increase due to its low concentration. This behaviour shows that removal of chromium III starts when the quasitotality of calcium and magnesium is removed.

Table 4 summarizes the concentration of different ions in the diluate compartment of MARB effluent treated by ED using the AXE/CMX membranes couple. The obtained values are compared to the Moroccan discharge limit values.

The concentrate is too loaded with metallic elements that can be recovered and reused either by precipitation or by using other membrane-based filtration methods such as NF and RO.

According to the obtained results, the physicochemical quality of the treated water shows that the ED is able to bring all ion concentrations of the brassware effluents under the Moroccan discharge limit values. No precipitation is observed in the concentrate during the experiments, which is the main limitation of the ED.

In terms of electric conductivity, the abatement of this magnitude is significant, due to the fact that MARB effluent treated by ED is not characterized by high values of total dissolved solids.

The only ion whose content has not been brought below the standards is silver. The explanation of this behaviour is mainly due to the high concentration of silver ion in the feed solution and also to the fact that, compared to copper and nickel ions, silver is a monovalent cation. Therefore, others options should be proposed to bring the silver content to standards of discharge limit. Among these possibilities, an

additional treatment may be conducted on the diluate at the outlet of ED such as second stage of ED or by combining ED and ion-exchange resin. The other option would be to lower the silver concentration at the entrance of ED by setting up a pretreatment step upstream of ED. Precipitation of the silver could lead to the desired result and make sure that, ED downstream leads to bring concentration of silver ions to agree with the discharge limit. These two options are currently under consideration and results will be published soon.

#### 4. Conclusion

This work is devoted to study the effectiveness of ED in the treatment of brassware effluents in the city of Fez. These wastewaters are known to be highly loaded with heavy metals, toxic and harmful for humans and environment. ED is used to remove heavy metals pollutants heavy metals and to bring the main characteristics of these effluents to comply with the discharge limit values. Further studies will be carried out to develop a method for recovering these metals and reusing them in the brassware industry.

This study shows the effectiveness of ED in the treatment of ACRB. Two couples of AEM (ACS and AXE) coupled with the CMX CEM are compared in the elimination of heavy metals ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ag}^+$ ). The obtained results confirm the feasibility of the ED in the treatment of ACRB and the AXE/CMX membrane couple exhibits the best performance in terms of metallic ion removal (at DR 80%, % copper removal is 94% and for the other ions the % removal reaches 96%).

For the treatment of MARB by ED and with the AXE/CMX couple, the % removal of 98%, 95% and 97% is achieved for copper, silver and nickel, respectively.

The concentrations of these ions in the treated effluent are below the discharge limits except for  $\text{Ag}^+$ . Due to the high initial concentration and charge of silver ion introduced, further treatment is required. Otherwise, a pre-treatment step should be performed upstream of ED to decrease the silver ion content and allow the treated water to comply the limit discharges standards.

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