How the polarity of plasma influences the interaction with bittern

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Abstract: Cold atmospheric plasma – bittern interaction was investigated. Electric discharge between an electrode and the bittern surface was produced by 7 kV pulses at a frequency of 1 kHz and distance of 5 mm. Physical-chemical analysis of the bittern were performed before and after interaction with plasma. This work reports on how voltage polarity affects the plasma-liquid interactions. While in the cathodic plasma the concentration of Cl, Na and Mg was reduced, in the anodic only Cl was reduced.

Keywords: Cold atmospheric plasma, bittern, plasma over liquid, polarity, desalination.

1. Introduction

The term “bittern” refers to the very bitter-tasting solution that remains after evaporation and crystallization of sodium chloride from brines and seawater, either as by-products, or as waste products. It is a concentrated form of a collection of magnesium, potassium, sulfate and chloride salts, such as KCl, $MgCl_2$, $MgSO_4$ and double salts [1]. Previous works related to the recovery of chemicals from bittern have been predominantly in the development of conventional processes of evaporation-crystallization, ion exchange and solvent extraction [2-4]. Recent developments in cold atmospheric plasma (CAP) in liquid have heightened the need for investigate CAP-Bittern interaction aiming recovery of chemicals [5-7]. This paper reports on a study where pulsed plasma was applied on bittern using cathodic or anodic polarity.

2. Materials and methods

A 4.2 ml cuvette was filled with bittern and placed inside a hermetically sealed system Fig. 1. Gas helium with flow **of 100 ml / min was used as the atmosphere. To maintain** atmospheric pressure an outlet was placed for a bubbler. Between the cathode and the bittern a pulsed voltage of 7 kV, repeated at the frequency of 1 kHz, was applied to produce the discharge. The distance between the cathode tip and the bittern surface was 5 mm.

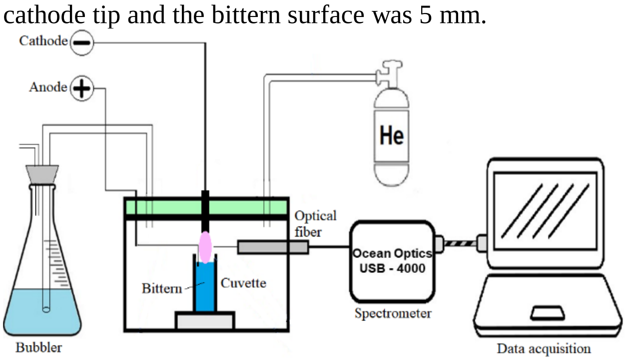

Fig. 1. Experimental setup used in this work

An optical fiber coupled to an optical emission spectrometer (OES) was placed close to the discharge. After 30 minutes of plasma application, chemical and pH analysis were performed on the solution and bubbler water. These results were compared with those prior to plasma application. In addition, the salts precipitated in the solution were analysed by X-ray diffraction. The same experiment was also repeated for the reverse polarity, ie, anodic plasma.

3. Results and discussion

Using the experimental setup pictured in Fig. 1, plasma species identification was taken as a function of three different plasma exposure time as showed in Fig. 2.

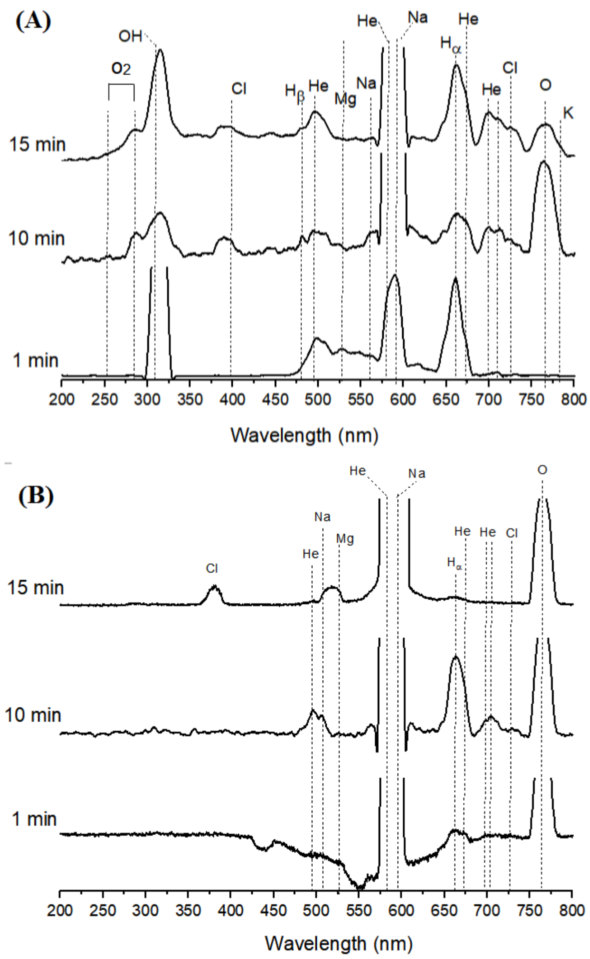

Fig. 2. Principal emission lines of He plasma applied on bittern surface (A) cathodic plasma and (B) anodic plasma

For the first moment a violet glow discharge takes place between tip electrode and bittern surface. At this moment, small crystals begin to appear on the surface of the bittern until the discharge becomes very intense and predominantly yellow (after ~ 2min). It’s possible that the formation of salt crystals on the surface occurs due to evaporation on the surface of the bittern. The rate of evaporation being higher than the diffusion of supersaturated ions results in the precipitation of the salts on the surface. The most interesting visual aspect of this two moments is the presence of micro-arcs directed to crystals. Our hypothesis is that the micro-arcs cause dissociation of the salt crystals which begin to populate the plasma. The presence of chlorine and sodium peaks in OES reinforces our hypothesis. It was observed that in the cathodic plasma after 1 min there is abrupt increase of the peak relative to sodium, whereas in the anodic plasma this happens before emergence of micro-arcs. Another difference between cathodic and anodic plasma was the presence of OH e O peaks in the OES in the cathodic plasma. In saline aqueous solutions, hydrogen (H_2), oxygen (O_2) and chlorine (Cl_2) gas can be electrochemically produced at sufficiently high potentials by the electrolysis via the following reactions [7]:

$$2e^- + 2H_2 \rightarrow 2OH^-(aq) + H_2(g) \quad (1)$$

$$4OH^- \rightarrow O_2(g) + 2H_2O + 4e^- \quad (2)$$

$$2Cl^-(aq) \rightarrow 2e^- + Cl_2(g) \quad (3)$$

$$2NaCl(aq) + 2H_2O \rightarrow 2NaOH(aq) + H_2\,(g) + Cl_2(g) \quad (4)$$

For a better understanding of the reactions occurred in the plasma-bittern interaction, chemical and pH analysis were performed on the bittern before and after plasma treatment Fig. 3.

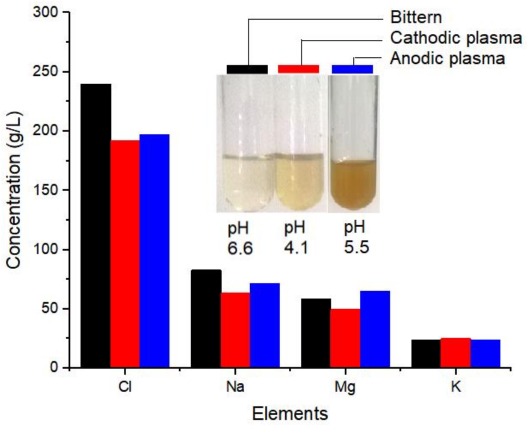

Fig. 3. Chemical composition and pH value of bittern before and after plasma treatment.

It is interesting to note that the all elements concentration in the bittern are reduced after plasma treatment, except potassium that had a slight increase. This decrease occurs due salt precipitation and evaporation. The results of x-ray diffraction of salt crystals precipitated Fig. 4 shows that NaCl is predominantly the phase for cathodic plasma while $MgCl_2$ is the phase for anodic plasma. This finding is consistent with results during plasma treatment Fig. 4. It was also observed an increase of Cl and Na in the bubble water, resulting from the vapor formed in the plasma.

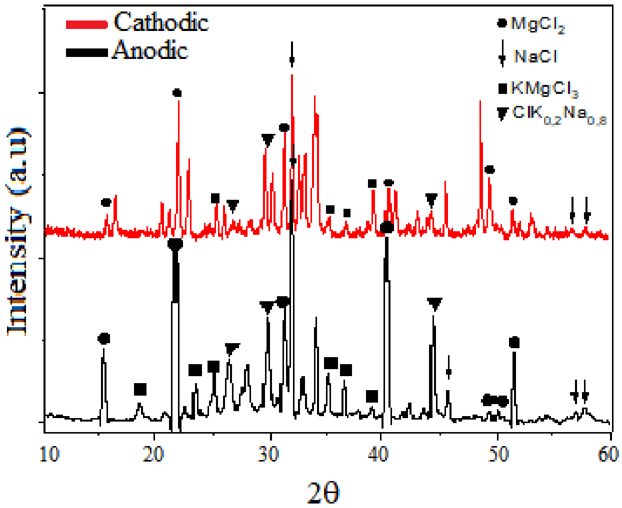

Fig. 4. Powder x-ray diffraction (XRD) patterns of salt crystals precipitated during plasma treatment.

4. Conclusions

The main goal of the current study was to determine the effect of plasma atmospheric on extraction/separation of chemical elements from bittern. Despite the complexity of the studied system and the several plasma variables that influence in the plasma-bittern interaction, we can conclude that atmospheric plasma is an important energetical source para water treatment technology. From ours results we can to conclude that:

i) Dependent of plasma polarization, it is possible to extract different minerals from bittern.
ii) The cathodic polarization showed higher extraction efficiency
iii) The concentration of potassium ions remained constant, meaning that it is possible to selectively extract metals.
iv) Chlorine evaporation was obtained during plasma treatment

5. References

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