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Polymeric membranes containing S-doped mesoporous carbon for the removal of copper in real effluent

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Abstract

In this study, novel polymeric membranes based on polyacrylonitrile containing sulfur-doped mesoporous carbons (hPAN@C-URK_s) were synthesized, characterized, and applied to the removal of Cu (II) ions from a real effluent. The new membranes and the S-doped mesoporous carbon, after being synthesized, were subjected to specific characterization techniques, including infrared spectroscopy, transmission and scanning electron microscopy, and X-ray photoelectron spectroscopy. The Cu (II) uptake was studied by varying several aspects, including, pH, contact time, and temperature. The membranes had an adsorption capacity of 36.09 mg/g (70.3%) at pH 5.5 using a real electroplating effluent, indicating the new membranes as potential adsorbents for the treatment of electroplating effluents.

Keywords: Adsorption; electroplating effluente; copper; wastewater treatment.

1. Introduction

With the growth in the application of metals and chemicals in industrial processes, the production of effluents with notable levels of heavy metals ends up causing environmental problems because of their non-degenerative and resistant nature [1].

Copper is seen as one of the most valuable metals in existence and it is used in various industrial areas, being found in accumulation in wastewater as well as being one of the main metals causing environmental risk, making it potentially toxic [2].

Adsorption has proved to be efficient and economically attractive, since it has a low implementation cost, does not generate large quantities of sludge and there is the possibility of reusing the adsorbent. The use of porous carbons has stood out due to their characteristics such as high porosity, large surface area, low production cost and ease of preparation [3]. Heteroatoms and halogens combined with layers of carbon atoms can adjust the chemical properties of the surfaces of these materials [4].

The goal of this project is to produce mesoporous carbon doped with sulfur to improve the interactions between the adsorbent and Cu (II) ions of the effluent.

2. Methods

2.1. Polymeric membranes based on sucrose mesoporous carbon doped with sulfur production (hPAN@C-URK_s)

Mesoporous carbon nanomaterials were produced using a mixture of sucrose and thiourea. In a furnace tube under air flow, this mixture was pyrolyzed at 800 °C for 1 h with a heating rate of 3.2 °C/min. The polymeric membranes were prepared using a mixture of polyacrylonitrile and sulfur-doped mesoporous carbon nanomaterials (at 30% of content). The membranes were hydrolyzed in a NaOH solution at 45 °C for 1.5 hours.

2.2. Adsorption experiments

The materials' adsorption performance was evaluated under several conditions, including contact time, materials concentration, temperature, and pH.

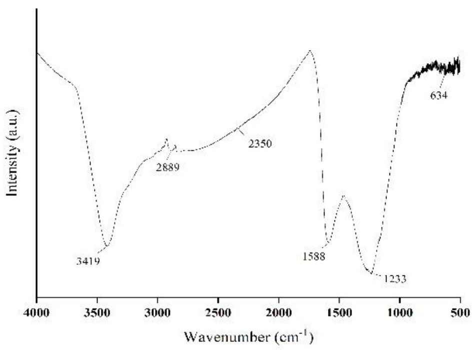
3. Results and discussion

3.1. Materials characterization

Sulfur-doped mesoporous carbon (C-URK_s)

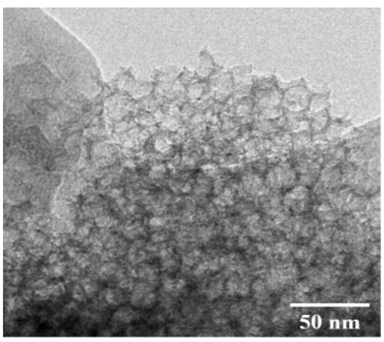
The Fourier Transform Infrared (FTIR) analysis (Figure 1) of the mesoporous carbon (C-URK_s) revealed the presence of water molecules and C-H stretching, as indicated by the band observed at 3419 cm^{-1} and 2889 cm^{-1}, respectively. The band at 1588 cm^{-1} refers to the deformation of the N-H bond, indicating the presence of thiourea in the material. The band at 1233 cm^{-1} refers to an N-H bending and a C-N stretching vibration (amide III), referring to thiourea. The band at 634 cm^{-1} is related to the presence of sulfur in the mesoporous carbon nanomaterial

Figure 1: FTIR of the S-doped mesoporous carbon



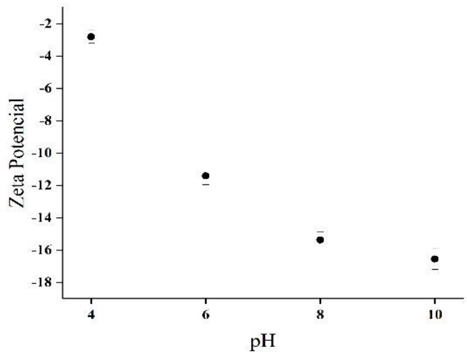
The morphology of C-URK_s was studied via Transmission Electron Microscopy (TEM) in Figure *2*. The image TEM of C-URK_s reveals that the material has undergone a transformation, acquiring a three-dimensional porous structure.

Figure 2: TEM image of C-URK_s



The zeta potential of C-URK_s surface was analyzed in the pH range of 4-10, and the results are presented in Figure 3. The material exhibited an electronegative nature at all the pH values evaluated, with the electronegative charge of the nanomaterial increasing from −2.81 to −16.56 mV. This phenomenon may be attributed to the chemical composition of C-URK_s, which contains carboxyl and hydroxyl groups, thereby contributing to the electronegative process of the nanomaterial [5].

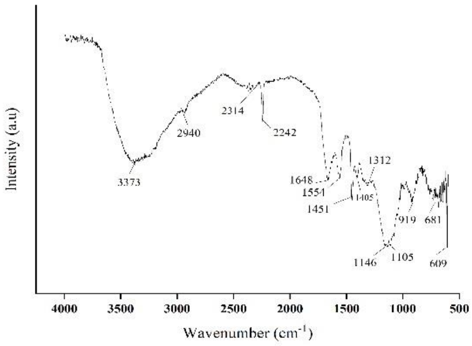
Figure 3: Zeta potencial of the mesoporous carbon



Sulfur-doped mesoporous carbon membranes (hPAN@C-URK_s)

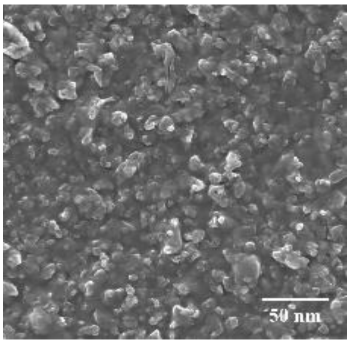
The FTIR analysis of the membrane revealed the presence of clear bands at 3373 cm^{-1}, 2242 cm^{-1}, 2940 cm^{-1} and 1405 cm^{-1}, which can be attributed to the OH, nitrile groups, C-C and C-H of the aromatic rings, respectively. Furthermore, the band at 681cm^{-1} and 1146 cm^{-1} bands confirmed the presence of sulfur in the membranes as shown in Figure 4.

Figure 4: FTIR of the membrane



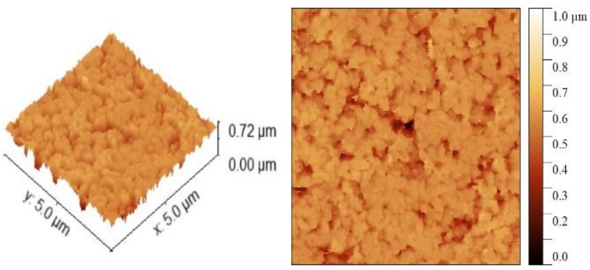
The surface morphology of the membrane, hPAN@C-URK_s, was studied using Scanning Electron Microscopy (SEM), as illustrated in Figure 5. The SEM image demonstrates the presence of inhomogeneous particles attached to the surface membrane, probably due to the presence of C-URK_s.

Figure 5: SEM image of hPAN@C-URK_s



The surface morphology of the hPAN@C-URK_s was evaluated by atomic force microscopy (AFM) in a liquid medium, as shown in Figure *6*. The membrane showed a porous irregular surface, with a thickness of 0.72 um and a roughness of (63.70 nm).

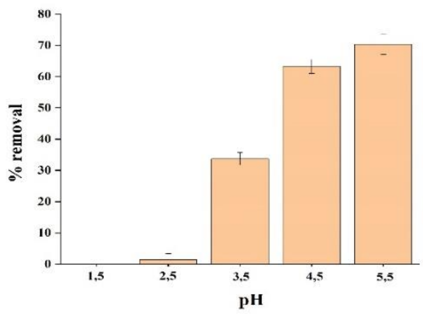
Figure 6: AFM image of the hPAN@C-URK_s



3.2. Adsorption of Cu (II) by hPAN@C-URK_s

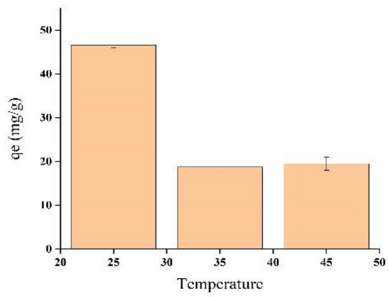
The membranes were evaluated through the adsorption of Cu (II) from a real electroplating effluent. The influence of pH on the adsorption process was studied in the range 1.5 to 5.5. At acidic pH, low removal capacity was observed due to competition between H^+ and Cu (II) ions present in the solution. The best removal capacity was achieved at pH 5.5 as shown in the Figure 7, probably due to electrostatic interactions between the adsorbent and the metal [6].

Figure 7: pH effect



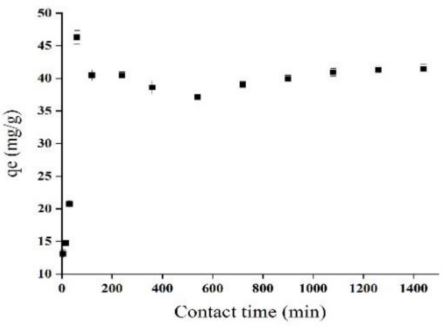
The effect of the temperature on Cu (II) adsorption by the hPAN@C-URK_s membrane was evaluated in the range 25 °C to 45 °C. The highest adsorption potential was reached at 25 °C (46.65 mg/g – 70%). The adsorption capacity decreased with increasing temperature to 19.69 and 18.75 mg/g at 35 °C and 45 °C, respectively. These results are to be expected since high temperatures increase the molecular agitation of the system, indicating an exothermic adsorption profile as shown in the Figure 8 [7].

Figure 8: Temperature effect



The influence of the contact time in the adsorption process was evaluated from 5 to 1440 min according to Figure 9. The highest adsorption capacity was achieved after 1 h, reaching a qe of 46.65 mg/g – 70%. Following this, a decrease in capacity was observed and equilibrium was reached in 18 h.

Figure 9: Contact time of the hPAN@C-URK_s



4. Conclusions

A S-doped mesoporous carbon material based on sucrose and thiourea was prepared and immobilized into polymeric membranes. The material showed excellent results in the adsorption of Cu (II) ions in real effluent, demonstrating its efficiency in industrial water treatment.

Acknowledgements

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