Membranes decorated with copper(II) complex for produced water treatment

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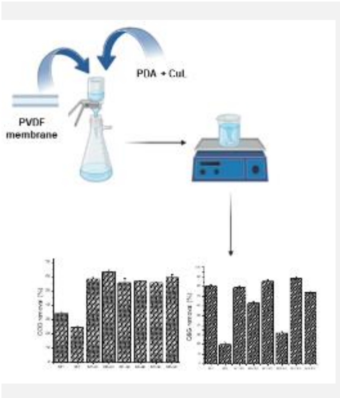

Produced water (PW) represents the largest volume of waste in the oil and gas industry. Due to its complex composition, with significant levels of oils and greases (O&G) and Chemical Oxygen Demand (COD), its management is challenging. The techniques conventionally used for framing do not always generate sufficient current quality for an intended destination. Membranes with copper (II) complex (CuL) associated with hydrogen peroxide (H_2O_2) have the potential to separate oil and mineralize organic compounds in a pH range around the neutrality. Therefore, this study aims to obtain membranes with CuL for PW treatment. Removals of up to 55.62±3.01%, 85.42±2.12% and 96.91±0.14% were obtained for COD, O&G and turbidity, respectively, using membranes with lower mass of CuL and 5. 85 x 10^{-3} mol/L of H_2O_2 after 60 min of testing. These results suggest that these materials are promising for this application.

Introduction

Production water (PW) is a combination of water present in the production well, injection water, and chemicals used during production and treatment, and is extracted together with material from the reservoir. [1] Owing to its complex composition, its management represents a challenge for the oil and gas industry.

Conventional treatment does not always meet these requirements, driving the search for more effective and advantageous processes.[2] Membrane separation processes (PSM) have emerged as viable alternatives, although fouling is a common problem.

Modifying the surface of membranes with metals such as iron, copper or cobalt, for example, can reduce this problem. The association of these metals with hydrogen peroxide (H_2O_2) can generate hydroxyl radicals, allowing not only the removal of oil but also the mineralization of the organic components of PW.[3]

In this context, this study sought to develop membranes decorated with copper (II) complex (CuL) for the treatment of AP. The CuL was chosen for its ability to operate pH range close to neutrality.[4]

Material and Methods

CuL was synthesized under magnetic stirring for 2h, adding a methanolic solution of copper (II) acetate monohydrate (1:2) to the ligand obtained by the condensation of salicylaldehyde with ethanolamine (1:1).[4] The solution was filtered through a qualitative filter paper and kept at rest, and the precipitate was dried at room temperature and then conditioned.

Membranes were obtained using the methodology described by Sun et al. (2022),[5] with some modifications. Commercial PVDF membranes were immersed in ethanol for 1 h to remove surface impurities, and then washed with distilled water for further use. A Tris-HCl buffer solution (40 mmol/L, pH 8.5) was prepared and then 0.2 g of dopamine was added and dissolved in 40 mL of this solution in Falcon tubes. Polydopamine (PDA) was crosslinked at 160 rpm for 1 h. The membrane was then immersed in cross-linked PDA for 3 h. Finally, the catalyst mass was added to the cross-linked PDA and filtered under vacuum by membrane suction. The decorated membranes were dried at room temperature and characterized using hydraulic permeance (HP), contact angle (CA), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and infrared (IR) spectroscopy. The process was evaluated with the membranes obtained using recirculating filtration equipment, keeping the pressure difference across the membrane constant at 1.0 bar. The volume of synthetic PW, obtained with the aid of ultraturrax equipment, was 1.0 L, and the concentration of H_2O_2 was 5.85 x 10^{-3} mol/L, based on experiments carried out with CuL in solution. The effluent presented concentrations of 100,000 mg/L, 100±5 mg/L, 267.72±0.53 mg/L and 124.48±0.58 mg/L of concentration of sodium chloride (NaCl), O&G, COD and soluble COD, respectively. Based on the amount of CuL used to obtain the membrane, they were named M1 (2.89 g/m²) and M5 (14.46 g/m²).

Results and Discussion

The HP tests demonstrated a 25% increase compared to the virgin membrane. This was supported by CA analysis, as the angle decreased from 43.7° for the commercial PVDF membrane to 40.1° for the M1 membrane, demonstrating a slight increase in membrane hydrophilicity. Figure 1 shows the SEM and EDS images of the membranes.

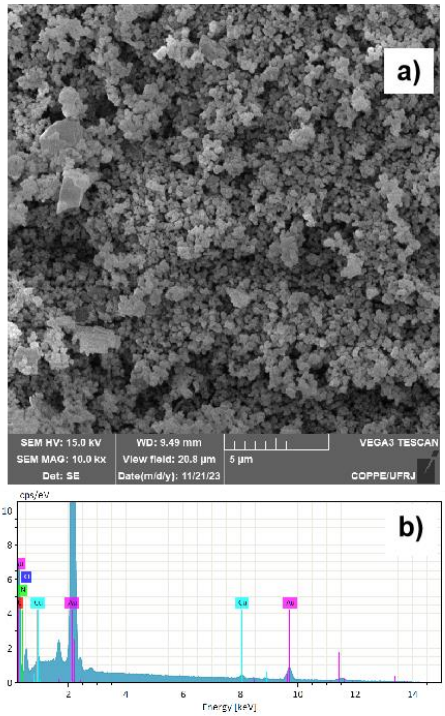

Figure 1. a) SEM and b) EDS of the M1 membrane.

SEM (Fig. 1a) and EDS (Fig. 1b) revealed agglomerated CuL on the surface and the presence of Cu, respectively. The IR spectra (data not shown) showed typical PVDF peaks, with the appearance of υ–C=N stretch characteristic of this complex in the modified membrane. Figure 2 shows the performances of the obtained membranes. The tests were carried out with both M1 and M5 at 30 (M1-30 and M5-30), 60 (M1-60 and M5-60), and 90 (M1-90 and M5-90) min.

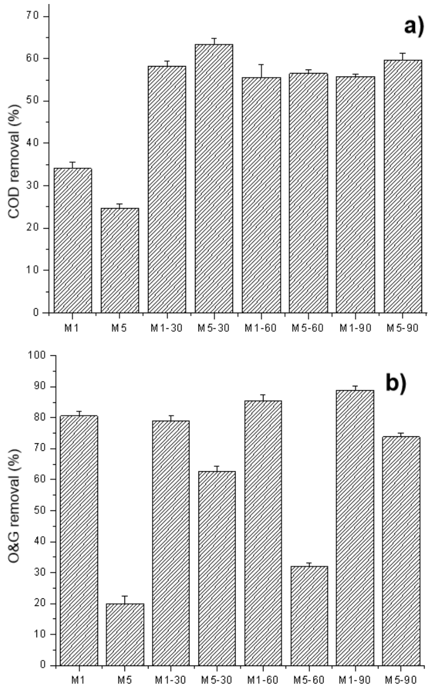

Figure 2. Membrane performance in terms of a) COD, and b) O&G removal. Conditions: pH~6.0, initial concentration of H_2O_2= 5.85 x 10^{-3} mol/L.

In the COD removal study (Fig. 2a), loading with CuL increased the efficiency of the membranes; however, there were no significant changes over time. Comparing M1 and M5, depositing more catalyst did not improve the results. The addition of more CuL impaired the O&G removal (Fig. 2b). However, there has been an increase in removal over time. The best condition was achieved in 60 min of testing, with removals of 55.62±3.01% for COD, 85.42±2.12% for O&G and 96.91±0.14% for turbidity, using membranes with lower mass of CuL.

Conclusions

Polyvinylidene fluoride (PVDF) membranes decorated with CuL were obtained and characterized. The results demonstrated that the treatment of PW with modified membranes is promising. The best condition was achieved in 60 min of testing, with removals of 55.62±3.01% for COD, 85.42±2.12% for O&G and 96.91±0.14% for turbidity, using membranes with lower mass of CuL. New tests will indicate the possibility of reuse and stability of the material obtained, as well as information on the leaching of CuL into the permeate.

Acknowledgments

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