POLYAMIDE – CUO NANOCOMPOSITE MEMBRANES USED FOR MEDICAL WASTEWATER AND E. COLI INHIBITION

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ABSTRACT

The influence of different concentrations of CuO nanoparticles on the Polyamide (PA) membrane properties was studied. By adding CuO nanoparticles like additives to the membrane structure, the permeability increases for concentrations between 0.5 to 1.5 wt% nanoparticles and decreases for higher concentrations because of the aggregation phenomenon that appears. PA membranes were made using four different concentrations of CuO nanoparticles, 0.5, 1, 1.5 and 2 wt%. For membranes with more than 1.5 wt% nanoparticles a better inhibition effect of E coli on the membrane surface was observed after 12 and 24 hours. Porosity evolution is affected in the same way by the nanoparticles' concentration increasing for concentrations less than 1.5wt%. The separation of pollutants is a challenging task in wastewater from the industries in general and the medical sector in particular. PA membranes with CuO nanoparticles have better rejection properties. For methylene blue, rejection is increasing from 87% for membranes with 0.5 wt% nanoparticles to 99% for membranes with 2 wt% nanoparticles.

Keywords: membranes, CuO nanoparticles, rejection

Introduction

Due to climate change, the pure water resources are decreasing, and advanced treatment of industrial water is necessary to ensure water resources for the population. At the same time, because of the population growth, the production of food and materials is increasing, and all these processes need more water. Nanocomposite polymeric membranes have different applications and are used especially for pollutant removal in industrial sectors. In the medical sector, wastewater has an important percent of organic matter and microorganisms, which affect not only the quality of the effluent but also the process due to the fouling effect. Many types of nanoparticles were used as additives to improve the membrane's properties [1-5]. The nanoparticle concentration is still a problem because the optimum concentration is different depending on the polymer type and nanoparticle concentration [6-10]. Membranes with nanoparticles are used in different processes like ultrafiltration [11-13], microfiltration [14-16], nanofiltration [17-19] and reverse osmosis [20,21]. The current study was made to establish the influence of CuO nanoparticles on the permeation and rejection properties of PA membranes and to study the inhibition effect on E coli.

Materials and methods

Polyamide (PA6.6) polymer was used to prepare membranes with different concentrations of CuO nanoparticles (0.5, 1, 1.5 and 2 wt%). Membranes were cast with a thickness of 150 µm on a support layer immersed in deionized water. Solvent, 1-methyl-2-pyrrolidone (NMP, 99%), nanoparticles, and polymer were purchased from Sigma-Aldrich. The casting solution was obtained by adding CuO nanoparticles with dimensions less than 100 nm into NMP and mixed by mechanical stirring at 220 rpm at room temperature. After 12 hours, PA was added and stirred for 36 hours at 40^0C.

To measure the membrane permeability the following equation was used:

$$PWP = \frac{J_w}{\Delta P}$$

Where PWP is the water permeability, Jw is the water flux and ΔP is the pressure.

To measure the rejection capacity of membranes, 550 mL of solution was tested with a given concentration of pollutant, via the following equation:

$$\%R = \frac{Cr - Cp}{Cr} x\ 100$$

Where R is rejection (%), Cr is the pollutant concentration at the feed solution, and Cp is the pollutant concentration at the permeate solution.

Using the” wet and dry” method [23], the membrane porosity was determined using the following equation:

$$\%\varepsilon = \frac{W_1 - W_2}{A.t.q} x100$$

Where ε is the membrane porosity, W_1 is the wet membrane weight, W_2 is the dry membrane weight, A is the membrane area, t is the membrane thickness, and q is the water density. Membranes were immersed in water for 48 hours to ensure wetting of the membrane and after they were weighed. The second step was to dry the membrane at 50^0C for 12 hours and weigh again.

Results

Permeability

To determine the pure water permeability, 400 mL of water was filtered. Figure 1 presents the water permeability evolution depending on the nanoparticle concentration.

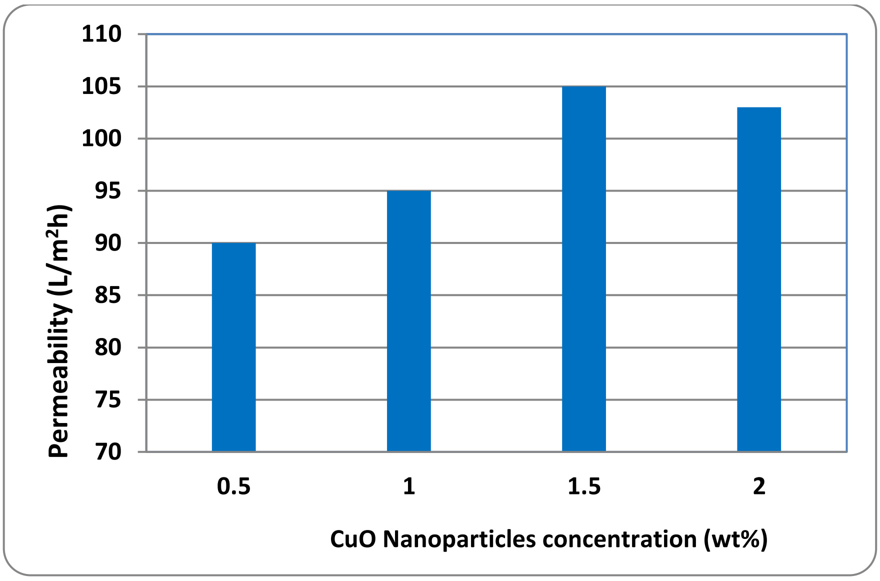

Figure 1. *Membrane permeability*

By increasing the nanoparticles concentration from 0.5 to 1.5 wt%, the permeability increases due to the increased membrane porosity. At a higher concentration of nanoparticles, the permeability decreases. This phenomenon appears because of the negative influence of a higher concentration, which can cause the aggregation of nanoparticles and, at the same time, block the pores.

Rejection

The main purpose of membranes is to treat water. In order to establish the rejection capacity of membranes at different concentrations of nanoparticles, a solution of 500 mL with a known concentration of Methylene Blue was tested. The rejection capacity is presented in figure 2.

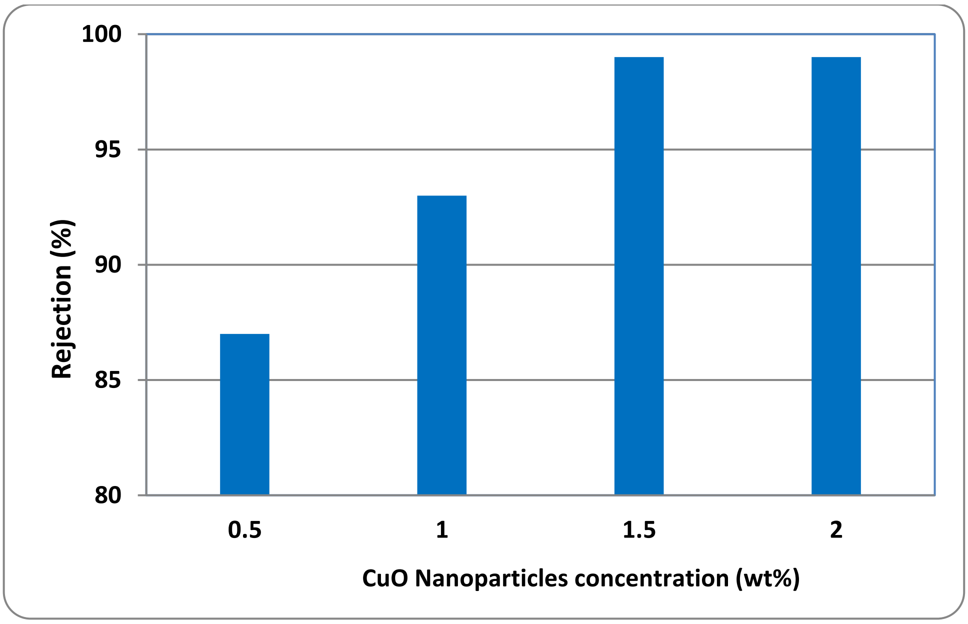

Figure 2. *Membrane's rejection capacity*

Increasing the nanoparticle concentration, the rejection increases from 87% for membranes with 0.5 wt% nanoparticle concentration to 99% for membranes with 1.5 wt% nanoparticles. Membranes with 2 wt% nanoparticles have the same rejection capacity as membranes with 1.5wt%.

Inhibition of E. coli

The PA-CuO membranes show better permeability and dye rejection, but due to the effect of CuO nanoparticles on the membrane surface, there appears an inhibition phenomenon of the bacterial growth. The bacteriostatic studies show that the membranes with a higher concentration of CuO nanoparticles inhibited the bacterial growth up to 85% after 12 hours, figure 3 and up to 98% after 24 hours, figure 4.

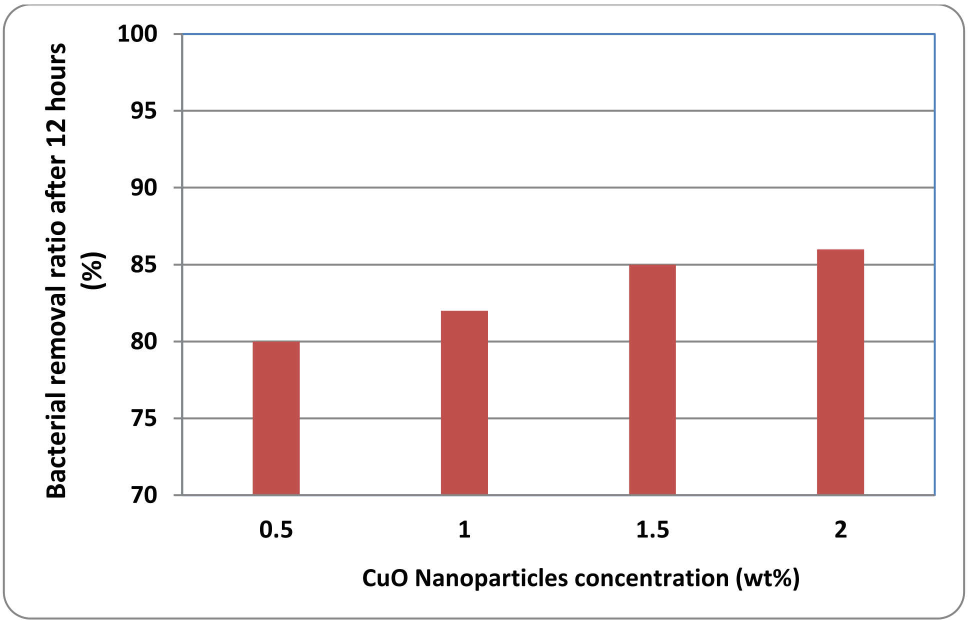

Figure 3. *Bacterial removal ratio of PA-CuO membranes against E.coli after 12 hours*

After 12 hours, bacteriostatic studies shows that membranes with 2 wt% nanoparticles have an inhibition effect on the E coli of 86%, with 6% more than membranes with 0.5wt% nanoparticles.

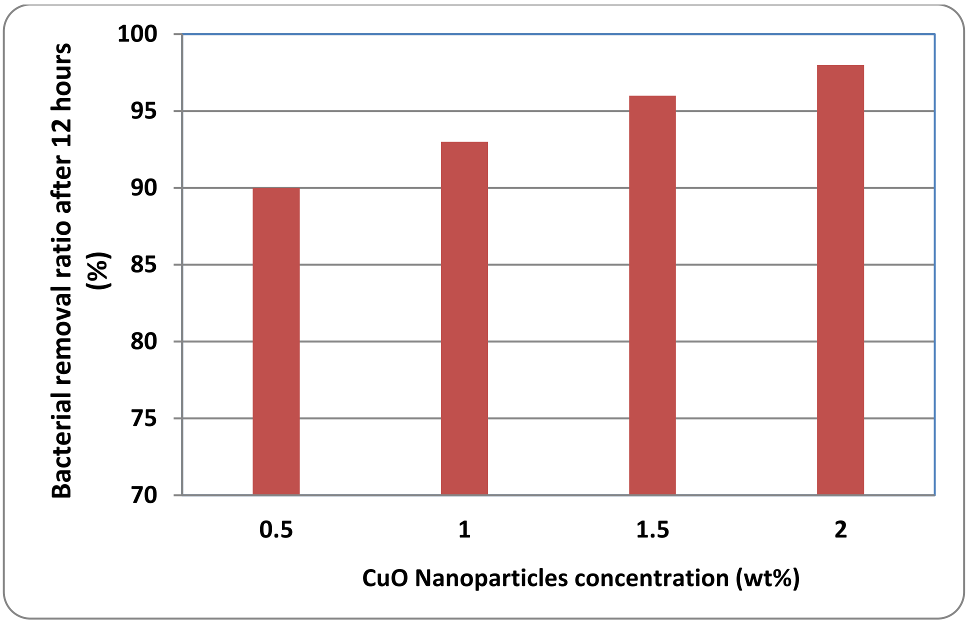

Figure 4. *Bacterial removal ratio of PA-CuO membranes against E.coli after 24 hours*

After another 12 hours, the bacteriostatic study shows that the membranes with 2 wt% nanoparticles have an inhibition effect on E coli of 98%, increasing from 86% (after 12 hours), and more with 8% than membranes with 0.5% nanoparticles.

Pore size and porosity

To explain the permeability evolution, the membrane porosity was studied, figure 5.

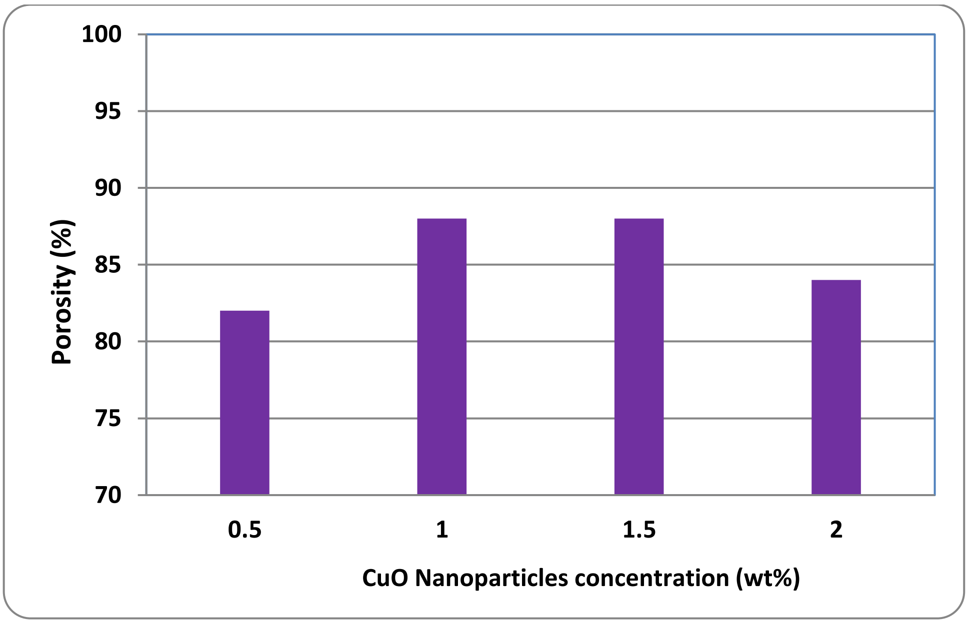

Figure 5. *Membrane porosity at different concentration of nanoparticles*

Increasing the nanoparticles concentration from 0.5 to 1%, the porosity increases from 82% to 88% giving a better permeability property for membranes. After 1.5%

nanoparticle concentration, the porosity decreases because of the nanoparticle aggregation and blocking pores.

SEM analysis

To explain the membrane permeability and rejection, a SEM analysis was made and the results are presented in figure 6.

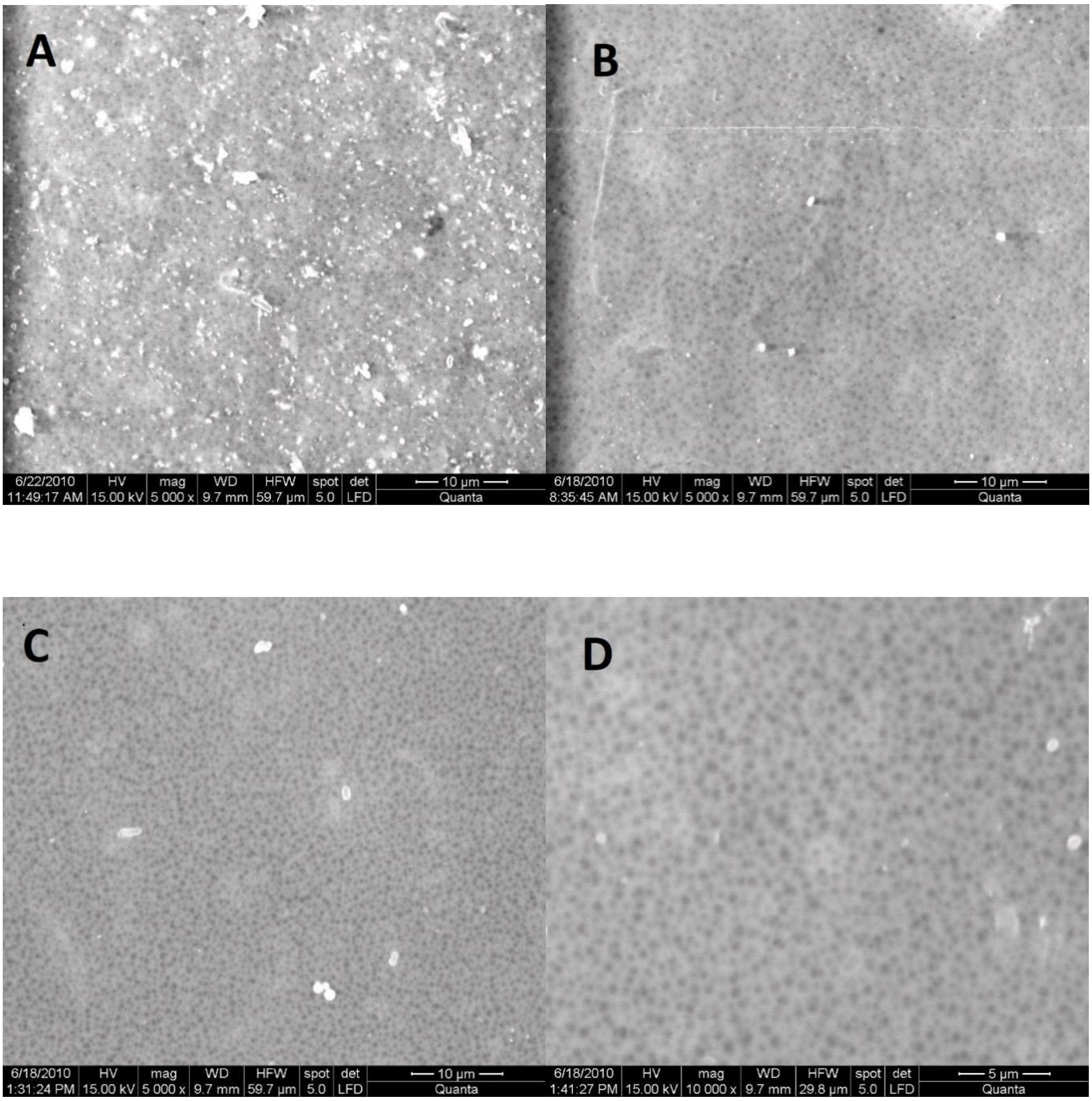

Figure 6. *SEM Analysis, a) 2wt% CuO, b) 1.5 wt% CuO, c) 1 wt% CuO, d) 0.5 wt% CuO*

At 2wt% CuO nanoparticles, figure 6 a, aggregation of nanoparticles can be observed on the membrane surface, affecting the permeability properties and the membrane porosity. This aggregation has a positive impact on the inhibition rate of E. coli. By decreasing the nanoparticle concentration, figure 6 b – 1.5 wt%, figure

6 c – 1 wt% and figure 6 d – 0.5 wt%, the nanoparticle aggregation disappears and the pores are uniformly distributed on the membrane surface.

Conclusions

Nanocomposite membranes are used for many applications, and the optimal concentration of nanoparticles is still a problem. This study investigates the influence of CuO nanoparticles at 4 different concentrations from 0.5 to 2 wt%. Using CuO nanoparticles, membranes have better permeability and rejection properties. Considering the results, the optimal concentration of nanoparticles is 1.5 wt%. At higher concentrations, membrane properties decrease because of the nanoparticle aggregation. Porosity increases at a maximum of 88% for 1 wt% nanoparticles and decreases for 2wt% CuO nanoparticles.

The permeability increases from 20 L/m^2h for membranes at 0.5 wt% nanoparticles to 105L/m^2h for membranes at 1.5 wt% nanoparticles; after this, concentration permeability decreases if the nanoparticles concentration increases.

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