Manufacture of cellulose acetate membranes and chitosan nanoparticles for the retention of mercury in water

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Abstract. In Colombia, an average of 75 tons of mercury is released annually due to the illegal mining activity of gold, causing natural water sources to be contaminated in regions that collect water through rivers and streams, generating mercury poisoning. Nanochitosan, a biopolymer synthesized at the nanoscale, has shown its ability to retain different heavy metals in wastewater due to its greater availability of amino groups at its surface. In this work, a set of preliminary parameters were identified and established for the development of cellulose acetate membranes with chitosan nanoparticles for mercury retention. Nanoparticles were synthesized by ionic gelation, varying the addition rate of sodium tripolyphosphate. The membranes were prepared by solvent exchange, varying the concentration of polyethylene glycol, the pore-forming agent. Finally, the samples were characterized by scanning electron microscopy and dynamic light scattering. The results showed that there is a proportional relationship between the rate of addition and the size of the particles obtained, while, for the membranes, 11% polyethylene glycol produced a porous network with cellulose acetate fibers inside the pores.

1. Introduction
In Colombia, an average of 75 tons of mercury is released per year from artisanal and small-scale gold mining, positioning the country as the third with the freest mercury in the world, behind China and Indonesia [1,2]. Due to this, 232 of the 1,150 water sources that cross the country pass through mining areas. According to the “Sistema Nacional de Vigilancia en Salud Pública (Sivigila)” of the “Instituto Nacional de Salud (INS)”, 1,126 cases of mercury poisoning in Colombia have been reported, between 2013 and 2015, in 59 municipalities and 18 departments throughout the country, with the most affected departments being Antioquia (312 cases), Chocó (218), Córdoba (206), Bolívar (167) and Sucre (143), [3].

The main issue with the release of mercury is that when it comes in contact with water, it interacts with its components and thanks to the microbial metabolism is able to transform to methylmercury, a powerful neurotoxin [4]. This process is responsible for the epidemics of mercury poisoning, which are characterized by paresthesia, intense ataxia that end in paralysis, deafness, blindness, coma and finally, death [4]. Intrauterine children may have cerebral palsy, developmental delay, blindness, deafness, and spasticity [4].

Bearing in mind that there is no public aqueduct in all regions of Colombia, there are other ways in which water is collected. In most cases, water isn’t properly treated to ensure low concentrations of toxic agents. A study carried out by “Profamilia” what is an organization in charge of promoting the respect and exercise of the sexual and reproductive rights of the Colombian population throughout its territory,
shows that Colombians collect water in different ways, including the use of public and communal aqueducts, the collection of rivers and streams, as well as rainwater and wells [5].

It has been shown that decreasing the size of the chitosan increases the surface area thus improving the potential for adsorption and desorption of substances, mainly due to the high content of functional groups such as amines and hydroxyl groups, which act as agents for the removal of contaminants. Also, as they are negatively charged, it favors the interaction with cations, attracting or releasing the adsorbate according to the pH in which they are mainly immersed [6].

Therefore, these two properties show the potential of nanochitosan to be used in water treatment, especially for industrial wastewater where there is a high content of heavy metal ions such as copper, cobalt, manganese, and mercury, which are toxic to humans and to other living organisms [7]. The objective of this work the manufacture and study of cellulose acetate membranes and chitosan nanoparticles for his potential use in the retention of mercury in water.

2. Experimental procedure

Low molecular weight chitosan and cellulose acetate (Sigma Aldrich), glacial acetic acid and N-N dimethylformamide (DMF) (Merck), sodium tripolyphosphate (Protokimica) and Polyethylene glycol 400 (PEG 400) (Bellchem) were used as precursor reagents.

As described in detail in the literature [8], the membranes were prepared by diluting cellulose acetate in PEG 400 and DMF (which act as a pore former and solvent), respectively. Concentrations were varied, as described in Table 1. The resultant mixture was kept in constant agitation until air bubbles were eliminated and were sonicated for 20 min. Then, three types of cellulose acetate membranes were frozen with N2 at -78 ° C for 48 hours and then lyophilized for 24 hours. Longitudinal and transverse cuts were made to the membranes and the resulting samples were placed in the sample holder. They were analyzed by scanning electron microscope (SEM) (JEOL JSM-6000 Plus) after gold deposition by sputtering (Denton Vacuum Desk V TSC).

| Table 1. Membrane formulations. |
|-------------------------------|
| Cellulose acetate | Type 1 (weight %) | Type 2 (weight %) | Type 3 (weight %) |
| Cellulose acetate | 18 | 18 | 18 |
| PEG 400 | 9 | 11 | 13 |
| DMF | 73 | 71 | 69 |

The particles were synthesized by ionic gelation, a method widely discussed in the literature [8,9] [10-12], which consists of a 1% acetic acid solution, which dilutes 0.3 g of chitosan under constant magnetic stirring for approximately 45 minutes. Subsequently, this solution was filtered under vacuum with filter paper to remove particles of large sizes. Further, a solution of sodium tripolyphosphate was added at controlled rates of 1 mL/min, 2 mL/min and 3 mL/min.

For the characterization of the chitosan particles, a dilution process was made. First, the solutions were centrifuged 15 minutes at 1600 rpm and the supernatant was taken and diluted in factors of 1/10 and 1/20 (v/v). Afterward, the dilutions were placed in a probe sonicator for 5 minutes at an amplitude of 40% and steps of 1 minute. Drops of the dilutions were placed in the sample holder and taken to the sputtering equipment. Subsequently, samples were analyzed by SEM (JEOL JSM-6000 Plus). Finally, dynamic light scattering (DLS) (Microtrac Zetatrac) was used in order to analyze the average size of the particles. Intensity distribution mode of work was performed, the particles were assumed as transparent and irregular, besides the sample density is the water density.

3. Results and discussion

Figure 1 shows the SEM images obtained for membrane type 1. A non-porous membrane can be observed in longitudinal section (Figure 1(a) and Figure 1(b)), but in transversal section are not any porous network, therefore pores founded are closed (Figure 1(c), Figure 1(f), Figure 1(g) and Figure 1(h)). Strange substance is founded in the membrane which could be accumulations of cellulose acetate.
Some pores are observable in the lower part of the membrane (Figure 1(c)). Interior of this pores shows an interesting configuration in the form of cellulose acetate spheres around the walls (Figure 1(d)).

Figure 1. SEM images of longitudinal and transversal cuts of type 1 membrane. Longitudinal: (a) general image, (b) an approach to the general image, (c) pores, (d) inside the pores. Transversal: (e) strange substance, (f) general image, (g) an approach to the substance, (h) an approach to the general image.

Figure 2 shows the SEM images of the longitudinal and transversal cuts of membrane type 2. Mesopores and micropores in the membrane surface can be observed (Figure 2(a) and Figure 2(d)), which form networks inside the membrane (Figure 2(e)). An approach to the mesopores shows an organization of cellulose acetate within forming isolated sets of fibers (Figure 2(b) and Figure 2(f)). In the wall of the pores, this conformation is similar to the one described in the previous membrane (Figure 1(d)) but these are smaller spheres made of tiny fibers (Figure 2(c), Figure 2(g) and Figure 2(h)).

Figure 2. SEM images of longitudinal and transversal cuts of type 2 membrane. Longitudinal: (a) general image, (b) pore, (c) inside the pore, (d) wall of membrane. Transversal: (e) general image, (f) pore, (g) inside the pore, (h) an approach inside the pore.

Finally, longitudinal and transversal cuts of the type 3 membrane are shown in Figure 3. Mesopores are observed in the membrane surface (Figure 3(a)), but, they did not form a porous network (Figure 3(e)) as the pores of the type 2 membrane does, therefore, they are closed pores. Inside these pores, the conformation takes the form of a fiber network (Figure 3(b) and Figure 3(f)), in contrast to the spheres made of fibers showed in the previous membranes. The fibers have fewer diameters than fibers of type
1 and 2 membranes (Figure 3(c)). Also, micropores can be observed in the membrane surface (Figure 3(d)) like the ones shown before in type 2 membrane. A new morphology in the surface is showed and take a form like valleys around the mesopores (Figure 3(g) and Figure 3(h)).

Figure 3. SEM images of longitudinal and transversal cuts of type 3 membrane. Longitudinal: (a) general image, (b) pore, (c) inside the pore, (d) wall of the membrane. Transversal: (e) general image, (f) inside the pore, (g) valley around the pore, (h) general image of the wall of the membrane.

Nanoparticles characterization with SEM can be observed in Figure 4. The image showed chitosan nanoparticles aggregation with an irregular shape and a smooth surface. Size distribution obtained with DLS for the three samples is shown in Figure 5. Nanoparticles synthesized with an addition rate of 1 mL/min shows polydispersity with a mean particle size of 270 nm. Likewise, polydisperse nanoparticles were also found at an addition rate of 3 mL/min, with a mean particle size of 450 nm. Finally, the samples with an addition rate of 2 mL/min were the most monodisperse and their mean particle size was 330 nm. Results obtained with DLS were as expected, as there is a proportional relation between particle size and addition rate, with the sample at 1mL/min having the smallest particle size.

Figure 4. SEM images of chitosan nanoparticles.

Figure 5. Size distribution of chitosan nanoparticles.
In the same way as the previously executed comparison of algorithms, the performance of the proposed codes was evaluated with the calculation of the detection percentage for several test images. Figure 5 shows the results obtained for the algorithm based on the detection of geometric figures and RGB color masks. The effectiveness of this method is almost negligible, only presenting a satisfactory result test image 1 for a range between 40 and 80 centimeters.

4. Conclusions
Based on the results of cellulose acetate membrane morphology, it can be concluded that the concentration of polyethylene glycol has a significant effect on the porosity of the membranes, with the concentration of 11% being the most adequate as it shows greater porosity and, in addition, presents a porous network inside. On the other hand, the results of the morphology and the size of the chitosan particles indicated that the size of the particles is affected by the tripolyphosphate (TPP) addition rate, with an addition rate of 1 mL/min, which has diameters of the average particle with lower polydispersity behavior. Finally, being able to establish the values of the parameters opens the door to the next phase: the incorporation of the particles in the membranes and test their mercury adsorption capacity, for a possible application in the treatment of water contaminated with this heavy metal.

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