Asia Pacific Academy of Science Pte. Ltd.

Pollution Study 2024, 5(1), 2073.
https://doi.org/10.54517/ps.v5i1.2073

Article

Cellulosic nanomaterials for adsorption of emerging pollutants

Belkis Coromoto Sulbarán Rangel[1,*], Abigail Eloísa Madrigal Olveira[2], Víctor Hugo Romero Arellano[3], Carlos Alberto Guzmán González[3]

[1] Ingeniera Forestal, maestra en Ciencias de Productos Forestales, Mexico
[2] Ingeniera en Nanotecnología. División de Ingenierías e Innovación Tecnológica
[3] Licenciado en Física, magister en Ciencias, Mexico
*** Corresponding author:** Belkis Coromoto Sulbarán Rangel, belkis.sulbaran@academicos.udg.mx

CITATION

Sulbarán Rangel BC, Madrigal Olveira AE, Romero Arellano VH, Guzmán González CA. Cellulosic nanomaterials for adsorption of emerging pollutants. Pollution Study. 2023; 4(2): 2073. https://doi.org/10.54517/ps.v4i2.2073

ARTICLE INFO

Received: 16 March 2024
Accepted: 08 April 2024
Available online: 20 April 2024

Abstract: Context: At present, nanotechnology can be used in multiple areas of action which, due to its nature, can be implemented with great versatility, given that many advances in nanotechnology base their studies on how to optimize daily and industrial processes and how to favor the environment. In addition, the manipulation of matter at this level allows the creation of solutions with greater scientific, social and economic impact. For the purposes of this research, laboratory results will be shown using cellulosic nanomaterials for the adsorption of emerging antibiotic-type contaminants. **Method:** This research was carried out at laboratory level, where cellulose was modified by chemical methods to obtain nanocellulose by oxidation. A characterization of the material obtained by spectroscopy techniques was carried out, and the adsorption of emerging anti-biotic contaminants such as ciprofloxacin. **Results:** Cellulosic nanomaterials have the potential to be used in tertiary water treatment for the removal of emerging contaminants such as ciprofloxacin. The results show that the cellulosic nanomaterial adsorbs ciprofloxacin by 27 %. **Conclusions:** Nanocellulose membranes have potential for use in a water purification system; those made only with cellulose showed a lower percentage of contaminant adsorption than membranes with nanocellulose.

Keywords: nanomaterials; adsorption; nanotechnology; emerging contaminants

1. Introduction

Water is one of the most abundant and valuable resources for humanity, but its availability for human consumption is minimal. “Extreme weather events cause great challenges for social, economic and environmental sustainability” [1]. In this sense, being the amount so scarce, there are data that confirm that more than 700 million people did not have the provision of drinking water and what may be a little more pre-occupying is where water is available costs have increased due to the increase in the cost of energy, as well as overpopulation, including other environmental problems that may affect it [2].

Despite the problems mentioned above, there is also a search for ways to solve drinking water shortages and reduce the contamination of the precious liquid itself through the use of nanomaterial designs. Different researches have been developed to reduce the impact of contamination on drinking water, but it is not only the remediation of water, but also the cost must be affordable [3]. “In recent years, many countries, including Colombia, have developed environmental legislation limiting discharges that had been deteriorating their water resources over time” [4] (p. 186).

"Mexico suffers from a series of environmental problems that compromise the sustainability of its development" [1] (p. 92). For this reason, treating water serves to try to make it drinkable, which involves conditioning and the use of technologies that modify and eliminate contaminants such as pathogens and unwanted impurities that make the water unfit for consumption, taking into account current standards on maximum permissible levels. The permissible limits vary according to the country where the treatment is applied and is in accordance with the type of contaminants, since, if the latter are present in the water and in limits higher than those indicated, the water must be treated. Treatment or modification of the water to meet the maximum level of contaminants is recommended [5]. Rainwater could also be a source of resource use; however, it has not been taken into account due to the need for further studies on costs and benefits for its collection and use [6].

Some of the most common treatment processes for surface water and groundwater are physical, chemical, or mechanical processes that remove contaminants and modify some of the characteristics of the water prior to additional processes. Sometimes, the addition of chemicals to alter water quality is the only treatment technique used [2].

Nanotechnology offers alternatives, since some nanomaterials are poured into bodies of water in order to treat them more efficiently, as they capture chemical or organic waste [7]. Others perform the function of accelerating processes such as adsorption and catalysis; some others even promise to detect the degree of contamination and, based on that, determine the method to follow, when the chemical waste is of great magnitude and the speed at which it is done is such that traditional methods are already inefficient. Therefore, with the new forms of water treatment, it is sought, from the precautionary principle, to establish risk parameters for the use of nanomaterials for this purpose [8]. Today, there is a trend towards remediation methods, especially those that investigate nanomaterials for filtration and adsorption. Despite this, the application of these technologies to combat the water problem continues, while the vital liquid is scarce and only a percentage of less than 30% is adequately treated [5].

This research presents the results of the use of a nanomaterial obtained from biodegradable polymers such as cellulose. The adsorption of emerging anti-biotic contaminants, such as ciprofloxacin, is shown.

2. Methodology

Cellulose from agave bagasse was used, which was modified to scalananan with chemical processes with oxidation with *N*-oxyl-2,2,6,6-tetramethylpiperidine (TEMPO), following the methodology proposed by [9]. The oxidation process occurs by adding 9 mL of NaClO (10%–13% wt) at room temperature with 500 rpm stirring for three hours. The reaction is terminated by adding 5 mL of anhydrous ethanol. The solution is then placed in dialysis for two days.

The degree of oxidation (degree of oxidation-DO) is calculated and expressed as the ratio of the amount of oxidized hydroxymethyl groups to the total hydroxymethyl groups, which was determined by conductimetric titration. A 50 mg sample of TEMPO-oxidized nanocellulose was suspended in 15 mL of 0.01 mol/L hydrochloric acid solutions. After 10 min of stirring, the suspension is titrated with 0.005 mol/L NaOH solution under pressure. The conductivity is monitored using a conductivity meter throughout the titration process. Titration is terminated when the pH reaches 11. The DO is calculated using Equation (1).

$$DO = \frac{162 \times C \times (V_2 - V_1)}{m - 36 \times C \times (V_2 - V_1)} \times 100\% \quad (1)$$

where c is the NaOH concentration, V_1 and V_2 are the volume of NaOH, and m is the weight of the oven-dried sample.

2.1. Preparation of nanostructured membranes

Membranes were made from TEMPO nanocellulose and agave cellulose solutions, which will be used directly in the pollutant adsorption processes. The membranes were produced by casting. This method is characterized by being very simple; in principle, the solution is prepared and poured into a Petri dish. The solvent is chosen so that it evaporates easily. Possible variables to control are concentration, solvent and sometimes ultrasound or magnetism is used to try to control the predominant direction of the fibers [10]. Cellulose and nanocellulose obtained from agave bagasse were characterized by analytical and spectroscopy techniques. The objective was to establish a correlation between the structure, shape and chemical composition of the polymers obtained with their properties. The characterization techniques were: infrared spectroscopy, X-ray diffraction, scanning electron microscopy and atomic force microscopy. Additionally, the porosity of the membrane was evaluated by measuring the pores in the microscopy photographs with the help of ImageJ software.

2.2. Contaminant adsorption test

To determine the potential use of mem-branes in a water purification system in this research, a simplified synthetic water model was prepared using distilled water and a commercial antibiotic called ciprofloxacin at a ratio of 1l of distilled water to 30 g of ciproflaxacin [11]. This is an emerging contaminant reported to be found in drinking water. Using UV-Vis spectroscopy, synthetic water prepared with ciproflaxacin was analyzed, a calibration curve of the ciproflaxacin solution was performed. The calibration curve was constructed by measuring the analytical absorbance signal at each of the ciproflaxacin diso-lutions from 1 % to 50 %. The measured signal value was assigned on the ordinate axis and the concentration of the solution on the abscissa axis. The variables considered in the process were: time, concentration and stirring speed. UV-vis measurements of the water were taken at one hour to determine if the contaminant was adsorbed. In this case, the adsorption percentage or removal efficiency (%) was calculated according to Equation (2).

$$\text{Adsorption efficiency} = [(Ci - Ct)/Ci] \times 100 \quad (2)$$

where Ci and Ct are the initial and any time t (hours) concentrations, respectively, expressed in mg/L in CIP, using UV-Vis spectroscopy. The entire experiment was conducted in triplicate, and the data shown are averages with standard deviation calculations, using Statistics and Machine Learning Toolbox with MatLab version 2015.

3. Results

Figure 1 shows the characterization of the nanomaterial by infrared spectroscopy where TEMPO nanocellulose, unlike agave cellulose, presents a new band at 1600 cm $^{-1}$, which corresponds to the C=O stretching vibration of the carboxyl groups in their acid form. This suggests that the hydroxymethyl groups of the D-glucose unit were successfully converted to carboxyl groups.

For the analysis of cellulose and nanocellulose morphology, the samples were analyzed in the scanning electron microscope at different magnifications in order to observe the change between cellulose and TEM-PO nanocellulose. **Figure 2** shows the SEM image of agave cellulose without TEMPO modification, observing fibers with a thickness ranging from 10–40 µm.

With the nanocellulose samples oxidized with TEMPO under the aforementioned conditions, membranes were prepared (**Figure 3**). As for the morphology of the samples at macroscopic scale, they are observed as a sheet of cellulosic pulp generally of irregular conformation. To better analyze the morphology of the cellulose nanofibers, the samples were observed under the scanning electron microscope at different magnifications, in order to see the conformation of the membranes and porosity.

The membranes were placed in a solution of synthetic water with 30 ml/L concentration of ciproflaxacin for one hour. UV spectroscopy measurements were made and the percent removal of the contaminant by the membranes was determined from the calibration curve (**Table 1**).

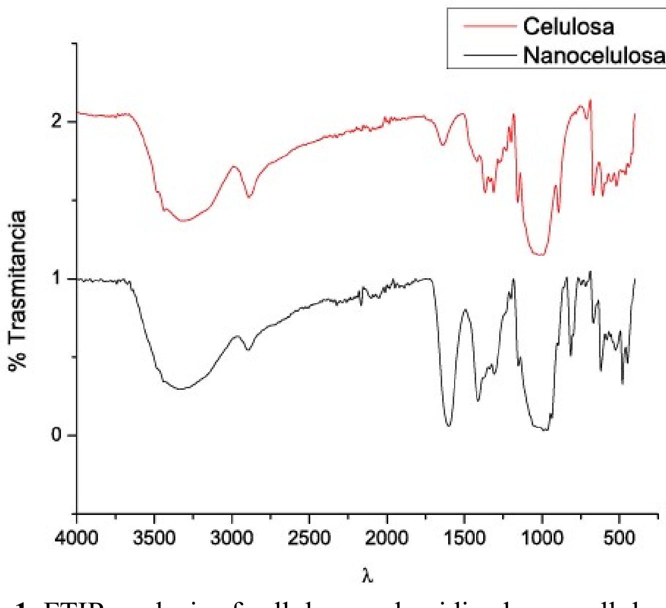

Figure 1. FTIR analysis of cellulose and oxidized nanocellulose with TEMPO.
Source: Own elaboration.

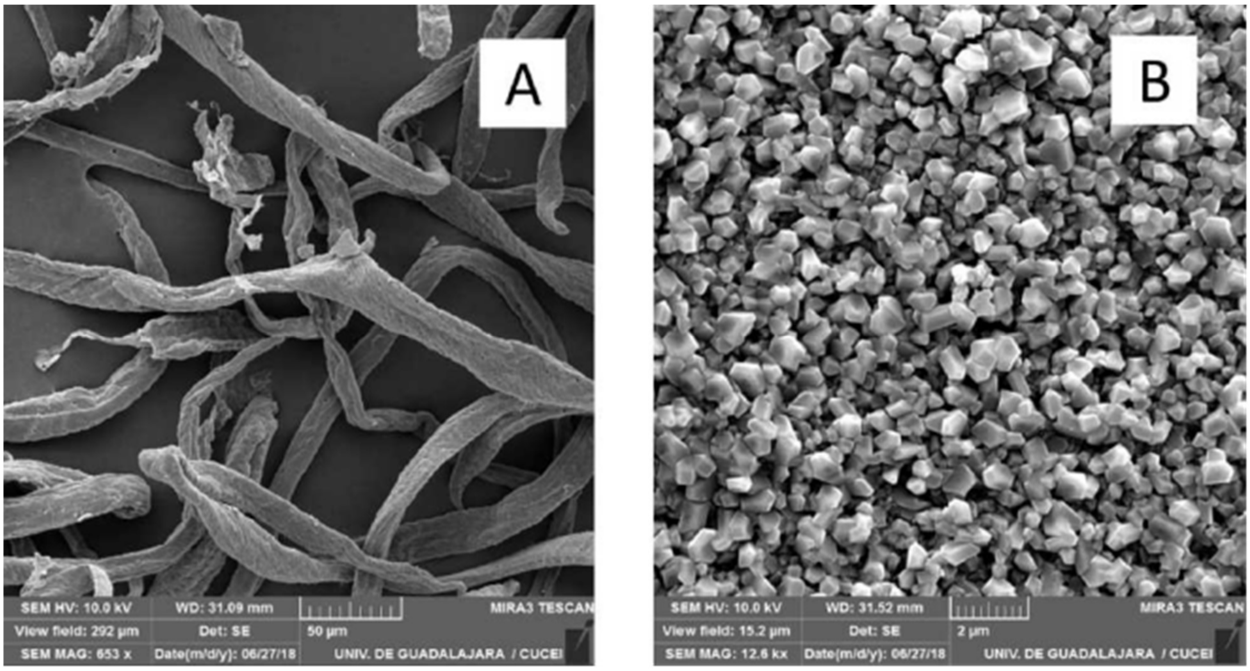

Figure 2. SEM image. **(A)** Bagasse cellulose; **(B)** Nanocellulose oxidized with TEMPO. Source: Own elaboration.

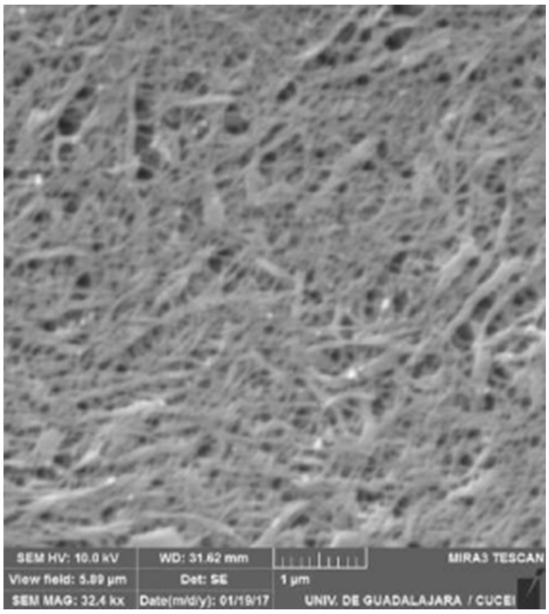

Figure 3. SEM images of the membrane surface at microscopic scale 5 µm. Source: Own elaboration.

Table 1. Performance of TEMPO nanocellulose membranes in the adsorption of ciploflaxacin.

Membrane	% removal
100 % cellulose	15.03 ± 1.00
50 % cellulose 50 % nanocellulose TEMPO	27.76 ± 6.01
70 % cellulose 30 % nanocellulose TEMPO	18.57 ± 6.61

Source: Own elaboration.

The adsorption of ciprofloxacin (CIP) by nanocellulose membranes could be attributed to the attraction between the negatively charged surfaces of the membrane and the positive charges of the CIP molecules, similar to those reported by other authors and comparable to the effect of pH on the adsorption of CIP with minerals such as goethite, smectite and kaolin. Various adsorption methods tend to be more effective across the board in removing most contaminants, organic and inorganic. In general, carbon-based nanomaterials are used to trap contaminant molecules within porous structures; however, because adsorption removes the contaminant (not eliminates or trans-forms it) it must be handled in a proper manner as you have a hazardous waste [12].

Ion exchange is another form of adsorption that is commonly used to remove heavy metal ions as well as other non-metallic ions; what happens by this method is to replace the solution with less toxic ions, this process being very characteristic in va-por waste where there is a high concentration of meta-les and other ions [13].

4. Conclusion

Nanotechnology applications in water purification and environmental remediation have been considered to have potential. Based on the results of the adsorption of the emerging ciprofloxacin-type contaminant, it is concluded that cellulosic nanomaterials could be used in a tertiary water treatment system. Membranes made only with cellulose showed a lower percentage of adsorption of the contaminant than membranes prepared with nanocellulose, being membranes with 50 % of nanocellulose-TEMPO the ones that presented the highest adsorption percentage.

Author contributions: Conceptualization, VHRA and CAGG; methodology, AEMO; writing—original draft preparation, BCSR; writing—review and editing, BCSR and VHRA. All authors have read and agreed to the published version of the manuscript.

Conflict of interest: The authors declare no conflict of interest.

References

1 González G, Retamoza JG, Álborez Arazate H, Guerrero de León A. Integrated watershed management: an alternative to the sustainability of water resources in Mexico. Lacan- donia, 2016; 10(1): 91-98.

2 Scholz M. Water Treatment. Wetlands for Water Pollution Control. 2016: 9-11. doi: 10.1016/b978-0-444-63607-2.00002-2

3 Gautam RK, Chattopadhyaya MC. Chap-ter 1. Nanotechnology for Water Cleanup. In: Gautam RK, Chattopadhyaya MC (editors). Nanoma-terials for Wastewater Remediation. Boston: Butterworth-Heinemann; 2016.

4 Suárez F, García A, Vaca L. Identification and evaluation of water pollution by tanneries in the municipality of Villapinzón. Tecnu- ra. 2012; 16(1): 185-194.

5 Olvera RC, Silva SL, Robles-Belmont E, et al. Review of nanotechnology value chain for water treatment applications in Mexico. Resource-Efficient Technologies. 2017; 3(1): 1-11. doi: 10.1016/j.reffit.2017.01.008

6 León A, Córdoba JC, Carreño UF. Review of the state of the art in rainwater harvesting and harvesting in urban areas and airports. Tecnura. 2016; 20(50): 141-153.

7 Qu X, Alvarez PJJ, Li Q. Applications of nanotechnology in water and wastewater treatment. Water Research. 2013; 47(12): 3931-3946. doi: 10.1016/j.watres.2012.09.058

8 Adeleye AS, Conway J, Garner K, et al. Engineered nanomaterials for water treatment and remediation: Costs, benefits, and applicability. Chemical Engineering Journal 2016; 286(4): 640-662. doi:10.1016/j.cej.2015.10.105

9 Lin N, Bruzzese C, Dufresne A. TEMPO-Oxidized Nanocellulose Participating as Crosslinking Aid for Alginate-Based Sponges. ACS Applied Materials & Interfaces. 2012; 4(9): 4948-4959. doi: 10.1021/am301325r

10 Abdul Khalil HPS, Davoudpour Y, Islam MN, et al. Production and modification of na- nofibrillated cellulose using various mechanical processes: A review. Carbohydrate polymers. 2014; 649-665. doi: 10.1016Zj. carbpol.2013.08.069.

11 Garcia-Alonso JA, Zurita-Martinez F, Guzmán-González CA, et al. Nanostructured diatomite and its potential for the removal of an antibiotic from water. Bioinspired, Biomimetic and Nanobiomaterials. 2018; 7(3): 167-173. doi: 10.1680/jbibn.18.00020

12 Rostamian R, Behnejad H. A compre-hensive adsorption study and modeling of anti-biotics as a pharmaceutical waste by graphene oxide nanosheets. Ecotoxicology and Environmen-tal Safety. 2018; 147, 1 17-123.

13 Thakkar M, Wu Z, Wei L, et al. Water defluoridation using a nanostructured diatom–ZrO 2 composite synthesized from algal Biomass. Journal of Colloid and Interface Science. 2015; 450: 239-245. doi: 10.1016/j.jcis.2015.03.017