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A comparative study between a system of commercial mixed oxide ceramic membranes and a system of mixed oxide ceramic membranes impregnated with porcine gelatin for the removal of emergent pollutants

Estudio comparativo entre un sistema de membranas cerámicas de óxidos mixtos comerciales y un sistema de membranas cerámicas de óxidos mixtos impregnadas con gelatina porcina para la remoción de contaminantes emergentes

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Abstract

A comparison was made between a tangential flow system with mixed oxide ceramic membranes and a tangential flow system with mixed oxide ceramic membranes impregnated with porcine gelatin for emerging contaminants such as tetracycline. For the impregnation of the ceramic membranes, a tangential flow system and a 1% porcine gelatin solution were improved. The surface of the membranes before and after impregnation was characterized by Scanning Electron Microscopy (SEM) to observe the deposition of porcine gelatin in the pores. For the removal tests, ceramic membranes of mixed oxides of 1 KD and 5 KD and a Tetracycline solution of 80 mg/L were used, taking samples at 10, 30 and 60 min, which were analyzed by means of UV-Vis spectroscopy. The objective of this work was to compare the removal capacity of emerging contaminants by means of a membrane system impregnated with porcine gelatin. A removal above 70% of Tetracycline was obtained in the 5KD membranes with impregnation.

Membranes, porcine, emerging, impregnation, removal

Resumen

Se realizó una comparación entre un sistema de flujo tangencial con membranas cerámicas de óxidos mixtos y un sistema de flujo tangencial con membranas cerámicas de óxidos mixtos impregnadas con gelatina porcina para contaminantes emergentes como la Tetraciclina. Para la impregnación de las membranas cerámicas se utilizó un sistema de flujo tangencial y una solución de gelatina porcina al 1%. Se caracterizó la superficie de las membranas antes y después de la impregnación por medio de Microscopia Electrónica de Barrido (MEB) para observar el depósito de la gelatina porcina en los poros. Para las pruebas de remoción se utilizaron membranas cerámicas de óxidos mixtos de 1 KD y 5 KD y una solución de Tetraciclina de 80 mg/L tomando muestras a los 10, 30 y 60 min que fueron analizadas por medio de espectroscopia de UV-Vis. Se obtuvo una remoción arriba del 70% de Tetraciclina en las membranas de 5KD con impregnación. El objetivo del presente trabajo fue comparar la capacidad de remoción de contaminantes emergentes mediante un sistema de membranas impregnadas con gelatina porcina.

Membranas cerámicas, porcino, impregnación, remoción

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Introduction

Emerging pollutants are poorly regulated compounds that have different negative effects when they enter to different water bodies (Devi *et al*., 2020). Among them are pharmaceutical products, pesticides, personal care products and drugs (Zacarías *et al*., 2017). Different compounds such as antibiotics reach the water through the feces of humans and animals feces and urine (Saremi *et al*., 2020).

Antibiotics are medicines that are used both in humans and in animal production and their consumption has increased in recent years, causing its accumulation on the environment and resulting on negative effects for the different ecosystems (Xuequing Zhong., 2021).

Tetracycline

Among the most used antibiotics is Tetracycline (TC), a broad-spectrum antibiotic used primarily on animal husbandry as a growth promotor and in disease control. TC represents 29 % of the total consumption of antibiotics (Rizzi, *et al*., 2020). TC is not completely metabolized by humans or animals, thus 50-80% its directly discharged to water through urine and feces of animals and humans (Chen, Wang, Duan, Yang, & Gao., 2016).

TC accumulation on water has caused many negative effects on the environment. First, it is related with the disappearance of different kind of aquatic microorganisms as cyanobacteria, protozoa, fungi among others (Grenni *et al*., 2018).

Second, its presence on the environment is related with the generation of bacterial resistance (Roy *et al*., 2021). Then, removing TC of water bodies is an environmental concern, and it has been proposed many technologies for its removal.

Ceramic membranes

Ceramic membranes have turned out to be a low-cost and highly efficient technology in water treatment. Unlike polymeric membranes, ceramic membranes show greater chemical and thermal stability, which increases the useful life of the membrane, allowing it to be washed and sterilized for reuse (Dong & Yiqun, 2021).

Ceramic membranes work through a pressure difference; however, different compounds have been studied to coat them with the intention of improving their hydrophobic properties and increasing their efficiency (Merlet *et al*., 2020).

Within these compounds is the activation of certain functionals such as carboxyls through a layer of porcine gelatin that favors the adsorption of certain compounds (Cazes, Belleville, Mougel, Kellner, & Marcano, 2015).

Methodology

Assembly of tangential flow system

For the assembly of the system, it was necessary to make the selection and coupling of the hoses that connected the tangential flow system to the recirculation vessel. This container is where the synthetic water was deposited. A pump was placed that allowed the flow to pass through the membrane, working at room temperature. In turn, the system of pressure gauges and valves was installed that allowed us to regulate the system pressure. Finally, the membrane was placed in the tangential flow cartridge and the outlet hoses for the permeate were also connected.

For the operation of the system, the following operating conditions were established: temperature: 20°C, pH: 7, pressure: 2 bars, pump power: 90 rpm.

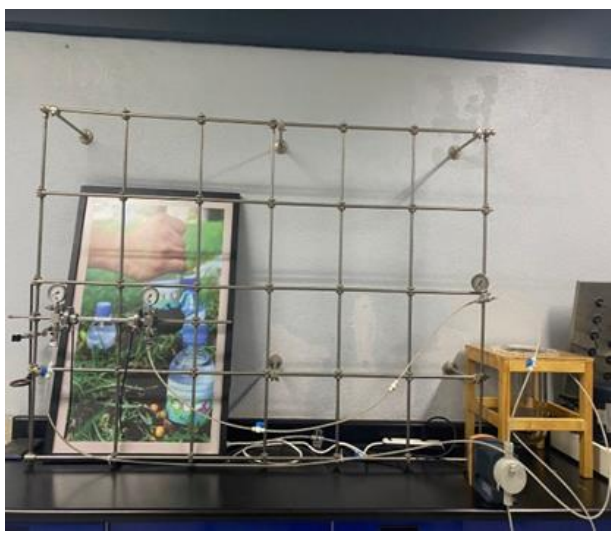

Figure 1 Tangential flow system

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Flow measurement

Once the absence of leaks was confirmed and the system pressure had stabilized, the flow measurements were made. Flow measurement consisted of measuring the time in which a litre of water recirculated through the system. This measurement was made prior to impregnation and again with the impregnated membrane in order to compare the flux through the membrane impregnated with porcine gelatine. Flow measurements were expressed in l/min.

Preparation of solutions for membrane impregnation

For the preparation of the solutions, type A pork skin gelatin (Sigma-Aldrich Co., St. Louis, MO), grade II glutaraldehyde at 25% in H_2 O (Sigma-Aldrich Co., St. Louis, MO) and Tetracycline 98.0-102% (HPLC) (Sigma-Aldrich Co., St. Louis, MO).

- Preparation of the phosphate solution: A phosphate solution was prepared with deionized water and 5.43 g of dibasic sodium phosphate dihydrate and 4.56 g of monobasic sodium phosphate dihydrate. This solution served us to maintain the pH in the preparation of the other solutions.

- Preparation of porcine gelatin solution for impregnation: for this case, 10 g (1%) of pork skin gelatin was added to a liter of phosphate solution at a temperature of 40 °C and left under stirring for 10 hours.

- Preparation of tetracycline solution: 100 mg were added to 1 liter of deionized water and left under stirring for 20 minutes at room temperature.

- Glutaraldehyde solution: 2 ml of glutaraldehyde solution in 25 ml of deionized water were added.

Membrane preparation and tetracycline removal capacity evaluation

The ceramic membranes used (TAMI industries, ZrO_2/TiO_2, 250 mm long, 6 mm internal ∅, 10 mm external ∅, surface area of 0.0047 m^2 and 0.4 µm pore diameter) were prepared according to the procedure proposed by the European Membrane Institute (Cazes *et al*., 2015).

Figure 2 Ceramic membrane TAMI Industries

One of the membranes was subjected to morphological characterization by Scanning Electron Microscopy to see the surface structure and be able to compare it with the already impregnated membrane. For this technique, the membrane was crushed to be able to analyze it in the equipment.

Four membranes were used for the experiments, two 1KD membranes, one unimpregnated and the other impregnated, and two 5KD membranes, one unimpregnated and the other impregnated with porcine gelatin. The impregnation was carried out with the phosphate gelatin solution prepared at 1% (10 g/L).

Membrane impregnation with porcine gelatin solution

For the preparation of the membrane, the gelatin solution was first heated at 40 °C for 30 minutes. Deionized water was passed through the membrane for 20 min to fill the pores and saturate them.

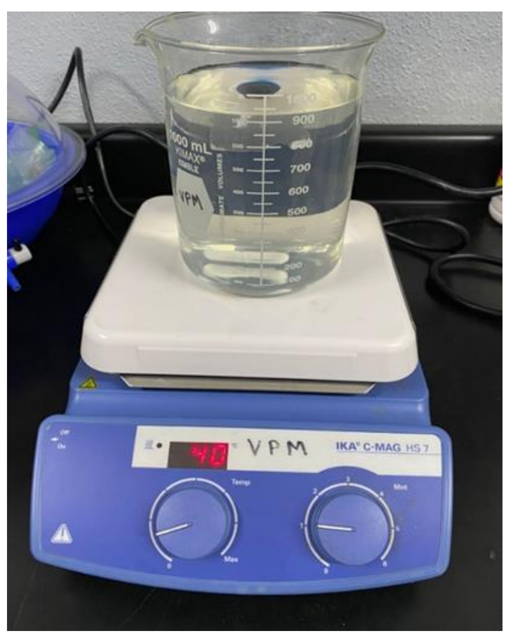

Figure 3 Porcine gelatin solution

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Subsequently, the gelatin solution was passed through the membrane for 25 minutes at 20 °C and with a transmembrane pressure of 2 MPa (2 bars) with a tangential speed of 1 m/s to give rise to the formation of the gelatin layer.

Then, the membrane was washed with pH 7 phosphate buffer solution. A 2% (w/v) glutaraldehyde solution was prepared with pH 7 phosphate solution. The membrane was placed vertically, and one end was covered with a stopper. then the interior of the membrane was filled with the prepared glutaraldehyde solution for 30 min at 20°C. This process was what allowed the carboxyl group in the ceramic membrane to be activated.

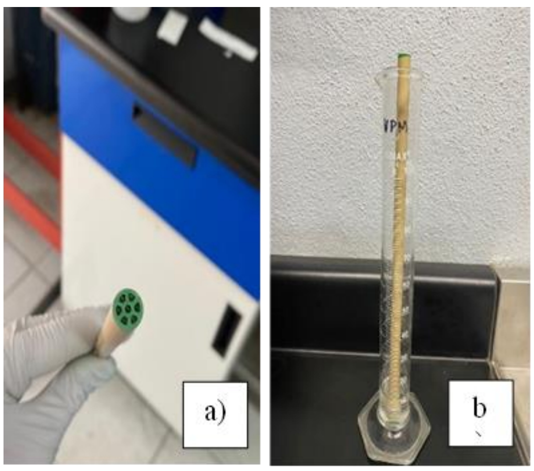

Figure 4 Incorporation of glutaraldehyde a) covered membrane pores, b) vertical location of the membrane

Flow measurement

Recirculation times of 1 liter of water were taken to determine the change over time as the water passed through the system with the membranes without impregnation and with the membranes impregnated.

Tetracycline removal assays

Once the membranes were prepared, tetracycline removal tests were carried out in synthetic water. For this, the membrane was placed in the circulation system, taking samples every 10 minutes for 1 hour to quantify the decrease in tetracycline.

Figure 5 Membrane permeates for sampling

The samples taken were analyzed by UV Vis spectroscopy at a wavelength of 234 to determine the decrease in the concentration of tetracycline over time. Removal tests were carried out with impregnated membranes of 1 KD and 5 KD and unimpregnated membranes of 1 KD and 5 KD to check the adsorption mechanism in the impregnated membranes and verify if the efficiency is higher than in the membranes without the treatment. Both assays were performed in triplicate.

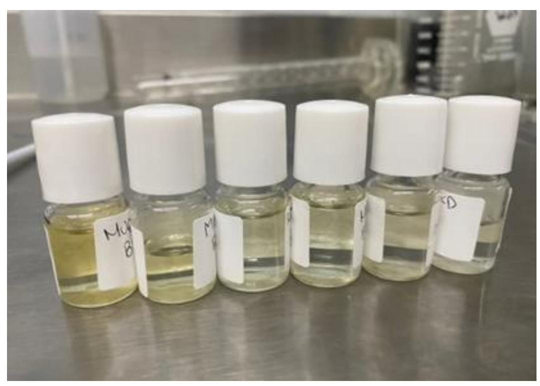

Figure 6 Samples after removal essays

Results

Change in the surface morphology of ceramic membranes after impregnation with porcine gelatin.

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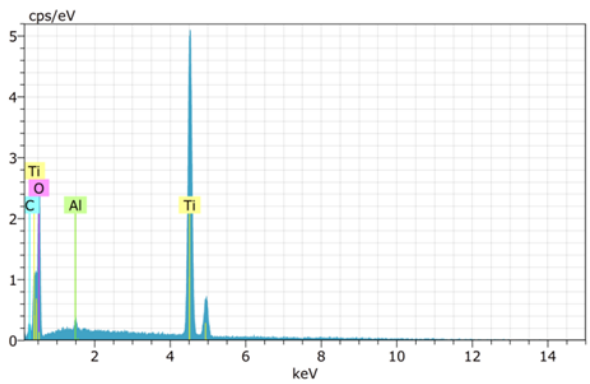
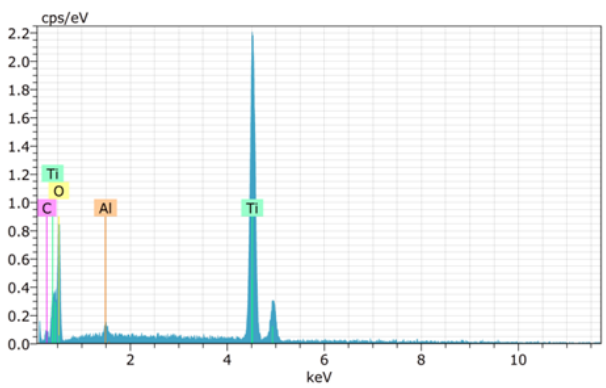
Figure 7 shows the initial structure of the membrane and its chemical composition. In figure 5 Titanium, Aluminum, Carbon, and Oxygen are present. This confirms the characteristics of the membrane composed of mixed oxides (Aluminum Oxide and Titanium Oxide).



Spectrum: SG

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	1.66	1.51	2.97	0.48
O	8	K-series	53.70	48.87	72.30	7.52
Al	13	K-series	0.55	0.50	0.44	0.06
Ti	22	K-series	53.97	49.12	24.28	1.61
		Total:	109.88	100.00	100.00	

Figure 7 Elemental analysis of the ceramic membrane without the impregnation performed by EDS



Spectrum: CG

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	1.64	1.54	3.25	0.65
O	8	K-series	44.91	42.38	66.87	7.82
Al	13	K-series	0.84	0.80	0.74	0.09
Ti	22	K-series	58.57	55.28	29.14	1.79
		Total:	105.96	100.00	100.00	

Figure 8 Elemental analysis of the ceramic membrane with the impregnation performed by EDS

The SEM images (fig 8) of the membranes before (a) and after impregnation (b) with gelatin show that there is no homogeneous layer of the polymer on the surface of the support. However, once the membrane is impregnated, the porcine gelatine agglomerates seem to have penetrated the porosity of the ceramic support.

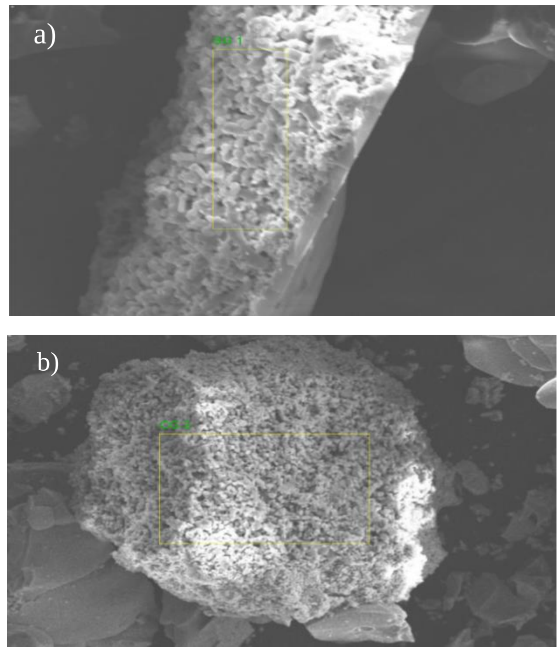


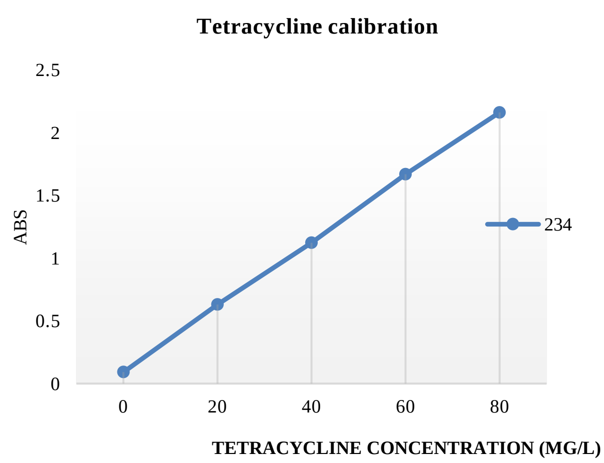
Figure 9 Superficial structure of ceramic membrane after impregnation with porcine gelatin

Before impregnation		After impregnation	
Time (min)	Volume (L)	Time (min)	Volume (L)
5	1.01	5	0.78

Table 1 Flow measurement on crossflow system before and after the impregnation.

Tetracycline quantification curve by UV Vis

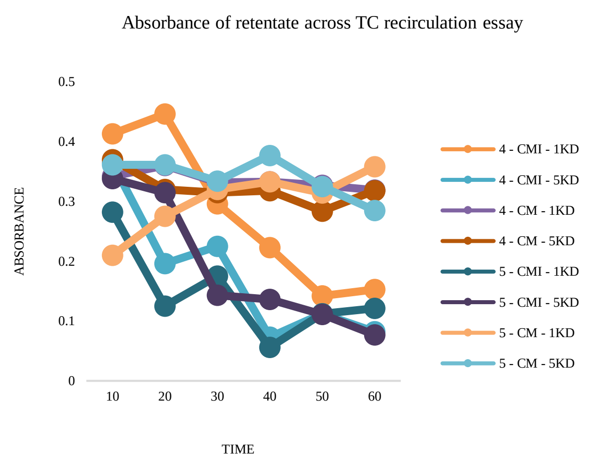
Figure 11 shows the absorbances obtained from the standard curve made in UV vis, we can see that linearity is maintained at X concentrations and the most significant are between 0 and 80 mg/L, which gave us guidelines to select the concentration of 80 mg/L as the initial concentration to carry out the removal.



Graphic 1 Tetracycline calibration curve

Tetracycline removal essays

As shown in figure 12 at the end of the assays there are two clear groups of results, ceramic membranes impregnated (CMI) and ceramic membranes (CM). To test the statistical difference amongst the groups a two-way ANOVA with repetition was performed using EXCEL 365® statistics package using treatment as columns and pore size as row and .05 alfa. There was a mild significant difference between pore size and absorbance at 60 minutes of the essay (p= .035), also there was a highly significant difference (p=.0001) for the membrane treatment Which shows that the decrease in TC concentration is highly linked to the treatment, which points to porcine gelatine being a great option to increase the removal of TC in treatment.



Graphic 2 Tetracycline concentration across the essays

Conclusions

Ceramic membranes were successfully impregnated with the porcine gelatine via crossflow. Optimal conditions for the system were pH 7 and room temperature. The action mechanism of the impregnation of porcine gelatine was adsorption and this was proved by the absorbance obtained on the impregnated membranes. The results on the TC absorbance shows that the treatment with porcine gelatine had a significant relationship on the removal on the compound. The minimum absorbance obtained was 0.73 AU on the ceramic membrane impregnated of 5 KD. The impregnation of porcine gelatine tests has proved to be an efficient treatment for ceramic membranes and demonstrates that it improves the removal of TC in water.

These impregnated membranes have promising potential for the removal of lower or higher molecular weight like Sulfadiazine, Ciprofloxacin, Erythromycin and others or separation of mixtures of low and high molecular weight antibiotics.

Discussion

A FTIR analysis is recommended to confirm the mechanism of interaction between the porcine gelatine and the tetracycline.

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