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Synthesis of adsorbent with fungal chitosan and silica for adsorption of diclofenac sodium

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Abstract

The production of chitosan from the cell wall of fungi presents less environmental pollution compared to commercial chitosan obtained from crustaceans, as it involves the simultaneous extraction of chitin and chitosan under milder operational conditions with the possibility of greater process control. Thus, the aim of this study was to compare the adsorption capacity of sodium diclofenac between fungal chitosan composites and crustacean chitosan composites. Initially, the fungal biomass was obtained from the submerged fermentation of the fungus *Aspergillus niger*. The chitosan, obtained through the deacetylation of chitin, was used in the formulation of adsorbent composites with chitosan, silica, and glutaraldehyde. These materials were evaluated against sodium diclofenac, selected as the model drug. As a result, it was possible to verify an adsorption capacity of 115.5 mg/g and a removal rate of 74.1% by the composite containing fungal chitosan in its formulation. These values are comparable to those obtained with the crustacean chitosan composite, indicating that fungal chitosan is a viable alternative for the formulation of adsorbent composites and the application in the treatment of waters contaminated with pharmaceuticals.

Keywords: biotechnology; emerging contaminants; water treatment.

1. Introduction

Chitosan is a biopolymer derived from chitin and can be considered a promising adsorbent for pharmaceuticals and other emerging contaminants due to its versatility and environmental sustainability. Fungal derived chitosan offers advantages compared to crustacean derived chitosan, such as no seasonal availability issues, lower environmental pollution, shorter extraction time with simultaneous extraction of chitin and chitosan, and retention of its biodegradability, biocompatibility, and non-toxicity properties, as well as preserving amine groups [1, 2, 3, 4].

The sol-gel technique using silica precursors allows for the creation of inorganic-organic composite materials, combining the desirable properties of chitosan and silica [5]. However, composites that combine the properties of chitosan with the sol-gel process still need improvements, especially since there are no studies exploring this aspect with fungal chitosan. Therefore, the aim of this work was to synthesize adsorbent composites with fungal chitosan and evaluate their adsorption capacity for sodium diclofenac in comparison with crustacean chitosan composites.

2. Materials and methods

2.1 Fungal chitosan obtation

The fungal biomass was obtained through submerged fermentation using the fungus *Aspergillus niger* DAOM. The inoculum of the microorganism *A. niger* was prepared in petri dishes containing potato dextrose agar (PDA) medium with two loops of spores and incubated at 30°C for 5 days.

The cultivation medium for submerged fermentation was prepared with 100 mL of potato dextrose broth (PDB), with three mycelial discs of 0.8 cm diameter cut from the previously prepared

petri dishes added [3]. The flasks were then incubated at 30°C for 7 days with shaking at 150 rpm. After the submerged fermentation, the fungal mycelia were separated from the culture medium by centrifugation, washed three times with distilled water, dried in an oven, and milled.

The fungal chitosan was obtained by deacetylating chitin through autoclaving, consisting of adding a 4% NaOH solution (1:40 w/v) to the fungal biomass using an autoclave for 20 minutes at 121°C and 101.3 kPa pressure [6]. The alkali-insoluble material (AIM) was separated by centrifugation, then washed with distilled water and centrifuged again until reaching neutral pH.

To isolate the biocomposite from the AIM, the residues were subsequently extracted using 1% acetic acid (1:100 w/v) at room temperature for 24 hours with mechanical stirring at 500 rpm, with a pH below 5. The acetic acid insoluble residue was then discarded by centrifugation. The filtrate's pH was adjusted to 12 with a 2 mol/L NaOH solution to precipitate the chitosan, and then neutralized to pH 7 with a 1.5 mol/L HCl solution. Subsequently, the solution was centrifuged, and the chitosan was washed with distilled water and lyophilized.

2.2 Synthesis of adsorbents

The adsorbent composites were synthesized according to Machado et al. [7], substituting crustacean chitosan with fungal chitosan. Briefly, 10 mL of the silica precursor was mixed with a solution containing 12 mL of ethyl alcohol and 1 mL of 0.05 mol/L HCl solution, kept at 150 rpm for 2 hours at 35°C. Simultaneously, 100 mL of an aqueous solution containing 1% chitosan (w/v) in 2% acetic acid (w/v) were prepared and stirred until the chitosan was completely dissolved. Subsequently, these two solutions were mixed at room temperature under stirring at 100 rpm for 1 hour. After this step, the silica/chitosan composite was crosslinked with glutaraldehyde using a stoichiometric ratio of 1:0 and 1:8 of D-glucosamine monomeric units of chitosan per glutaraldehyde molecule, under constant mechanical stirring for 1 hour.

For the polycondensation of silica, a volumetric ratio of 1:5 was used, and the mixture obtained in the previous step was slowly added to a solution containing 12.21 mL of ammonium hydroxide and 73.20 mL of ethyl alcohol, which was kept under mechanical stirring at 70 rpm for 5 minutes. Subsequently, the material was aged at 35°C, with complete drying occurring in approximately 5 days.

2.3 Adsorption of sodium diclofenac

To verify the adsorption capacity of the developed composites, they were evaluated for the removal of sodium diclofenac in an aqueous solution. The assays were conducted with 50 mL of the drug solution at a concentration of 200 mg/L, 0.05 g of the adsorbent, at 25°C and 100 rpm, for a period of 210 minutes.

3. Results

Figures 1 and 2 present the data obtained from the adsorption tests with the XE 1:8 composite derived from fungal chitosan, compared to the XE 1:8 composite from crustacean chitosan.

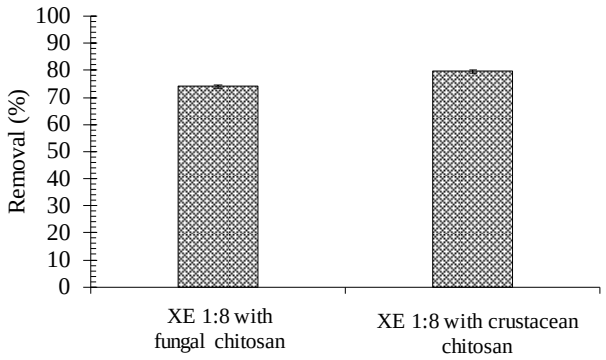

Fig. 1. Removal of sodium diclofenac comparing fungal and crustacean chitosan adsorbents

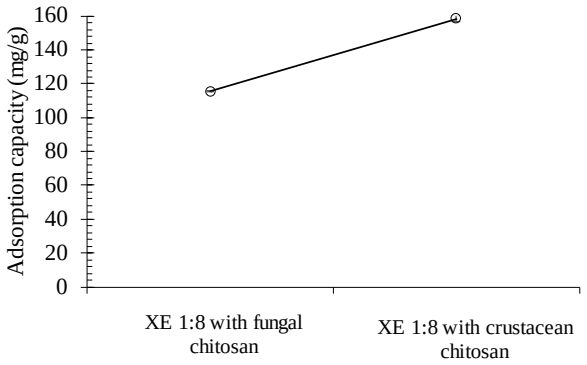

Fig. 2. Adsorption capacity of sodium diclofenac comparing fungal and crustacean chitosan adsorbents

The composite with fungal chitosan achieved an adsorption capacity of 115.5 mg/g and a removal efficiency of 74.1%. Meanwhile, the composite with crustacean chitosan had an adsorption capacity of 158.6 mg/g and a removal efficiency of 79.6%. Thus, it can be observed from the data that fungal

chitosan produced comparable results in sodium diclofenac removal capacity compared to crustacean chitosan. Therefore, fungal chitosan was capable of interacting with glutaraldehyde, resulting in active sites capable of removing sodium diclofenac.

The assays with the XE 1:0 composite and fungal chitosan showed no adsorption capacity, similar to findings by Machado et al. [7], where the XE 1:0 composite with crustacean chitosan in its formulation also showed no capacity to remove the drug.

4. Conclusion

This study provided promising preliminary results for the use of fungal chitosan in adsorbent composites aimed for the treatment of water contaminated with pharmaceuticals. The data indicate that fungal chitosan has a sodium diclofenac removal capacity comparable to traditional crustacean chitosan composites. Furthermore, crosslinking with glutaraldehyde proved to be a significant factor in enhancing the properties of this composite, highlighting its potential for future applications in water treatment systems.

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References

[1] Yuan Y, Li H, Leite W, Zhang Q, Bonnesen PV, Labbé JL, Weiss KL, Pingali, SV, Hong K, Urban VS, Salmon S, O'neill, H. Biosynthesis and characterization of deuterated chitosan in filamentous fungus and yeast. Carbohydr Poly 2021; 257:117637.

[2] Cabrera-Barjas G, Gallardo F, Nesic A, Taboada E, Marican A, Mirabal-Gallardo Y, Avila-Salas F, Delgado N, Armas-Ricard M, Valdes O. Utilization of industrial by-product fungal biomass from *Aspergillus niger* and *Fusarium culmorum* to obtain biosorbents for removal of pesticide and metal ions from aqueous solutions. J Environ Chem Eng, 2020; 8:104355.

[3] Abel-Gawad KM, Hifney AF, Fawzy, MA, Gomma M. Technology optimization of chitosan production from *Aspergillus niger* biomass and its functional activities. Food Hydrocolloids 2017; 63:593-601.

[4] Vakili M, Rafatullah M, Salamatinia B, Abdullah AZ, Ibrahim MH, Tan KB, Gholami Z, Amouzgar, P. Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review. Carbohydr Polym 2014; 113: 115-130.

[5] Kołodyńska D, Bundyak TM, Hubicki Z, Tertykh VA. Sol-gel derived organic-inorganic hybrid ceramic materials for heavy metal removal. In: Mishra AK. Sol-Gel Based Nanoceramic Materials: Preparation, Properties and Applications; 2017. p. 253-274.

[6] Machado TS, Melara F, De Mello JR, Crestani L, Alessandreti I, Damini G, Da Silva LK, Colla L, Piccin JS. Avaliação de processo alcalino para obtenção de quitosana fúngica. Acta Brasiliensis 2020; 4:168-17

[7] Machado TS, Crestani L, Marchezi G, Melara F, Mello JR, Dotto GL, Piccin JS. Synthesis of glutaraldehyde-modified silica/chitosan composites for the removal of water-soluble diclofenac sodium. Carbohydr Polym 2022; 118868.