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# Electrospun chitosan/poly(ethylene oxide) nanofibers applied for the removal of glycerol impurities from biodiesel production by biosorption



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#### ABSTRACT

Electrospun chitosan/poly(ethylene oxide) nanofibers were synthetized, characterized and applied as alternative biosorbents to remove pigments from pretreated crude glycerol. The pigments removal efficiency of electrospun nanofibers was examined by comparing the adsorption capacity of nanofibers with other chitosan-based biosorbents. Pseudo–first order, pseudo–second order and Elovich models were used to estimate kinetic parameters. The nanofibers exhibited continuous fibers, with the average fibers diameter of  $526 \pm 101$  nm. The results also indicated interactions between chitosan and poly(ethylene oxide) molecules, without changing the main adsorptive sites of chitosan. Furthermore, chitosan/poly(ethylene oxide) nanofibers exhibited higher relative adsorption capacity ( $120 g^{-1}$ ) than chitosan powder ( $35 g^{-1}$ ) and chitosan biopolymeric film ( $58 g^{-1}$ ). The pseudo–first order and Elovich models were the most suitable models to represent the kinetic behavior of the composite nanofiber.

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#### 1. Introduction

Biodiesel has been gaining attention because it can be manufactured by renewable and low-cost raw materials. Transesterification is the most common method for biodiesel production. The process comprises a chemical reaction between a fatty acid (fat or oil) and a short chain alcohol (methanol or ethanol), in the presence of an acid or basic catalyst. Glycerol is a by-product of the reaction, and each kilogram of biodiesel produces 0.10 kg of glycerol. This crude glycerol contains several compounds, such as esters, alcohol, salts, glycerides and pigments [1–3]. While crude glycerol has limited applications because of its impurities, pure glycerol has a huge market in pharmaceutical, food and chemical products [4].

Traditionally, crude glycerol purification involves three steps. The first step is performed by neutralization reaction, which removes some salts and free fatty acids. The second step occurs by evaporation, whereby alcohol is removed. The third step is the refining, which allows achieving the desired degree of purity, reducing even more the color, fatty acids and traces of other components. Among the techniques that can be applied in the last step, adsorption is recognized as an economical and efficient operation to remove organic molecules from aqueous solution [5, 6]. However, only activated carbon has already been applied to drastically reduce the pigments compounds from crude glycerol [7–9].

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Chitosan is a biopolymer composed by 2-acetamido-2-deoxy- $\beta$ -Dglucopyranose and 2-amino-2-deoxy- $\beta$ -D-glucopyranose residues, which is produced by partial deacetylation of chitin. Among the properties of chitosan, its polycationic character stands out for biosorption applications [10, 11]. In fact, a variety of chitosan-based biosorbents has been efficiently applied to remove pigments from food and textile dyes [12–16]. Moreover, it is well established that enhancing specific surface area of an adsorbent results in higher adsorption capacity, so the development of chitosan-based nanomaterials can improve its characteristics [17. 18]. This objective can be obtained via electrospinning, which is one of the most versatile and promising techniques for generating continuous and ultrathin nanofibers [19-21]. The electrospun nanofiber has also the advantages of a bulk material, which allows the separation of the adsorbent from solution [22, 23]. However, chitosan is considered a challenging biopolymer to electrospun due to its complex chemical structure [24]. In fact, the addition of other polymers such as poly(ethylene oxide) (PEO) can enhance the spinnability of chitosan by wrapping and unwinding the polysaccharide chains, which facilitates flow and orientation of chitosan molecules [25-27].

However, there were not cited works in the literature reporting the use of biomaterial in nanoscale to adsorb impurities from the glycerol. Thus, the aim of this study was to synthesize and characterize electrospun chitosan/poly(ethylene oxide) nanofibers (CP–EN) for biosorption of pigments from pretreated industrial glycerol. The CP–EN were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT–IR), thermogravimetric analysis

(TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Furthermore, the pigments removal efficiency of CP–EN was examined by comparing the adsorption capacity of CP–EN with other conventional chitosan physical forms (powder and biopolymeric film). The kinetic study was obtained by using the pseudo–first order (PEO), pseudo–second order (PSO) and Elovich models.

#### 2. Material and methods

#### 2.1. Materials

Chitosan in powder (CH–P) (molecular weight (MW) =  $150.3 \pm 1.4$  kDa; deacetylation degree (DD) =  $85.2 \pm 1.1\%$ ; particles size (PS) =  $100 \pm 10 \,\mu\text{m}$ ) was obtained from shrimp wastes (*Penaeus brasiliensis*). The shrimp wastes went through the steps of demineralization, deproteinization and deodorization. Then, deacetylation reaction was performed followed by the purification and drying steps, according to our previous works [28, 29]. Poly(ethylene oxide) powder (PEO–P) (MW =  $900 \pm 5.5$  kDa) was purchased from the Sigma–Aldrich (Sigma-Aldrich®, USA). The industrial pretreated glycerol (pH of  $4.6 \pm 0.1$ , yellowness index of 15.0 and redness index of 7.5) was obtained from a local biodiesel production plant in Brazil. The industrial pretreatment of the crude glycerol aimed to remove salts, free fatty acids, catalyst and methanol by neutralization and vacuum distillation.

#### 2.2. Development of chitosan biopolymeric films

The filmogenic solution was obtained by dissolving CH–P (1.5 g) into 50 mL of acetic acid solution (0.1 mol L<sup>-1</sup>) at 25  $\pm$  1 °C, under magnetic stirring (300 rpm) (Fisatom, 752, São Paulo, SP, Brazil) for 12 h. The solution was poured onto a level Plexiglas plate, and then, the chitosan biopolymeric films (CH–F) were obtained by solvent evaporation in an oven, with air circulation at 40  $\pm$  2 °C for 24 h [29, 30].

#### 2.3. Development of electrospun nanofibers

Firstly, CH–P (5% w/v) was dissolved in acetic acid (90% v/v) and, then, PEO–P (3% w/v) was added into the solution. The polymeric solution was prepared at 25  $\pm$  1 °C under magnetic stirring (300 rpm) (Fisatom, 752, São Paulo, SP, Brazil). The complete mixing was achieved in 12 h. The chitosan/poly(ethylene oxide) nanofiber (CP–EN) were produced using electrospinning technique. Briefly, the solution was transferred into a capillarity, and electrospun under the capillary diameter, capillarity–collector distance, electric potential and feed rate of 0.55 mm, 150 mm, 25 kV and 600 µL h<sup>-1</sup>, respectively (based on preliminaries tests). The nanofiber synthesis was carried out at 25  $\pm$  1 °C and relative humidity of 65  $\pm$  1%.

#### 2.4. Characterization of the nanofibers

The diameter of the nanofibers and the surface morphology of CP– EN, prior and after biosorption process, were obtained by scanning electron microscope (SEM) (JEOL, JSM–6610, Akishima–shi, Tokyo, Japan). The analysis was operated at 10 kV, with different magnifications. Prior to SEM imaging, the samples were placed on stainless steel supports and coated with 1 nm of gold layer [31]. The average fibers diameter was calculated by the randomly selected diameter of 50 nanofibers from each sample.

Differential scanning calorimetry (DSC) analysis (Shimadzu, DSC– 60, Nakagyo–ku, Kyoto, Japan) was carried out to analyze endothermic and exothermic structural transitions of the materials. Approximately, 3 mg of each sample (CH–P, PEO–P and CP–EN) were weighted in an aluminum pan hermetically sealed. The tests were performed under a nitrogen atmosphere (50 mL min<sup>-1</sup>) from 25 °C to 275 °C, with a heating rate of 10 °C min<sup>-1</sup> [32].

The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), simultaneously (Shimadzu, DTG-60, Nakagyo–ku, Kyoto, Japan) [33]. The thermal study was performed by weighing 3 mg of each sample (CH–P, PEO–P and CP–EN) in an aluminum pan. The analysis was carried out from 25 °C to 500 °C under a nitrogen atmosphere (30 mL min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup>.

The functional groups, as well as possible structural changes on the nanofibers surface, were characterized by Infrared analysis (FTIR) with attenuated total reflectance (Shimadzu, Prestige 21, Nakagyo–ku, Kyoto, Japan). In order to identify the functional groups involved in the biosorption process, the CP–EN were also evaluated after the biosorption of glycerol pigments. The samples (CH–P, PEO–P and CP–EN) were submitted to the spectroscopic determination at 20 °C, with wavenumber in the range from 500 to 4000 cm<sup>-1</sup> [34].

#### 2.5. Equilibrium study

The equilibrium biosorption study was performed with different physical shape of chitosan–based biosorbents (CH–P, CH–F and CP–EN). The assays were carried out in a thermostatic shaker (Fanem, 315 SE, São Paulo, SP, Brazil) with the following conditions: biosorbent dosage of 250 mg kg<sup>-1</sup> and temperature of  $60 \pm 1$  °C. Aliquots were measured when the equilibrium was reached. The pigments removal was detected by UV–visible spectrophotometry (Shimadzu, UV–2550, Nakagyo–ku, Kyoto, Japan), with a wavelength of 265 nm. All assays were performed in triplicate (n = 3). The amount of pigments adsorbed,  $q_e$  ( $g^{-1}$ ), is presented by Eq. (1):

$$q_e = \frac{m_o - m_f}{m_{ad}} \tag{1}$$

where  $m_o$  and  $m_f(g)$  are, respectively, the amounts of glycerol pigments in the initial and after the equilibrium, and  $m_{ad}(g)$  is the amount of adsorbent.

Even though the types of pigments present in glycerol are not known, the pigments can still be quantified using a relative adsorption capacity ( $q_r$ ) (Eq. (2)), associated to Lambert–Beer law (Eq. (3)) [35].

$$q_r = \frac{m_o - m_f}{m_{ad} m_o} \tag{2}$$

$$m = CV = \frac{A}{\epsilon c} V f$$
(3)

where A is the glycerol pigments absorbance,  $\epsilon c$  is a constant, which depends on analyte nature, as well as of cuvette size, V is the volume and f is the dilution factor.

The insertion of Eq. (3) into Eq. (2) leads to Eq. (4).

$$q_{re} = \frac{1}{m_{ad}} \left( 1 - \frac{A_e}{A_0} \right) \tag{4}$$

where  $q_{re}$  (g<sup>-1</sup>) is the equilibrium relative adsorption capacity,  $A_o$  and  $A_e$  are, respectively, the initial and equilibrium pigments absorbances.

#### 2.6. Kinetic study

The biosorption kinetic assays were also executed with different physical shape of chitosan–based biosorbents (CH–P, CH–F and CP–EN). The assays were conducted in a jar–test (Nova Ética, 218 MBD, SP, Vargem Grande Paulista) with the following conditions: biosorbent dosage of 250 mg kg<sup>-1</sup> and temperature of  $60 \pm 1$  °C. Aliquots were measured at predetermined time intervals (from 0 to 3600 s). The pigments removal was detected by UV–visible spectrophotometry (Shimadzu, UV–2550, Nakagyo–ku, Kyoto, Japan), with a wavelength of 265 nm. All assays were performed in triplicate (n = 3). The amount

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