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Chitosan/polyamide nanofibers prepared by Forcespinning® technology: A new adsorbent to remove anionic dyes from aqueous solutions

G.L. Dotto [a, *], J.M.N. Santos [a], E.H. Tanabe [a], D.A. Bertuol [a], E.L. Foletto [a], E.C. Lima [b], F.A. Pavan [c]

[a] Environmental Processes Laboratory (LAPAM), Chemical Engineering Department, Federal University of Santa Maria, UFSM, Roraima Avenue, 1000, 97105–900, Santa Maria, RS, Brazil
[b] Institute of Chemistry, Federal University of Rio Grande do Sul, UFRGS, Porto Alegre, RS, Brazil
[c] Institute of Chemistry, Federal University of Pampa, UNIPAMPA, Bagé, RS, Brazil

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ABSTRACT

Chitosan/polyamide nanofibers (CP nanofibers) were prepared by a new Forcespinning® technology, and used as alternative adsorbent to remove Reactive Black 5 (RB5) and Ponceau 4R (P4R) dyes from aqueous solutions. The results demonstrated that under the best operational conditions (30 G½" needles, spinneret rotation of 12000 rpm for 10 min and chitosan polyamide ratio of 1.00/1.50), chitosan/polyamide nanofibers were produced at a rate of 3 g h^{-1}. CP nanofibers presented a semi–crystalline structure, with several functional groups and diameter from 100 to 500 nm. The adsorption of RB5 and P4R on the CP nanofibers was favored at pH of 1.0. Pseudo–second order (RB5) and Elovich (P4R) models were the more adequate to represent the kinetic data. The equilibrium data followed the Langmuir model, being the maximum adsorption capacities of 456.9 mg g^{-1} for RB5 and 502.4 mg g^{-1} for P4R. The adsorption was spontaneous, favorable and endothermic. Desorption and reuse was possible for four times, maintaining the same adsorption capacity. In brief, it can be concluded that the Forcespinning® technology is an alternative to obtain chitosan/polyamide nanofibers with suitable characteristics. These nanofibers in turn, can be successfully applied to remove dyes from aqueous media.

1. Introduction

Reactive Black 5 (RB5) and Ponceau 4R (P4R) dyes are used in textile and food industries, respectively (Koprivanac and Kusic, 2008). During the industrial processing, a fraction of these dyes is lost, generating colored effluents. It is know that these effluents should be carefully treated to avoid severe environmental impacts and damages to the human health. However, the treatment of colored effluents is complicated since the dye molecules are recalcitrant, non biodegradable and strongly soluble (Khatri et al., 2015). In this sense, several techniques have been used to treat dye containing effluents, each one with advantages and drawbacks (Yagub et al., 2014). One of the most employed ways to remove dyes from aqueous solutions is the adsorption unit operation, since has advantages including low cost, high efficiency, low energetic requirements and ease of implementation and operation (Rouquerol et al., 2014).

In the adsorption/degradation fields, several synthetic, natural or hybrid materials have been used to remove dyes/metals/phenols from aqueous media (Dotto et al., 2015; Ausavasukhi et al., 2016; Rajabi et al., 2013, 2015, 2016). Chitosan based materials including films (Dotto et al., 2013), immobilized films (Nawi et al., 2011a,b; Jawad and Nawi, 2012a) immobilized cross–linked films (Jawad and Nawi, 2012b, 2012c), beads (Mubarak et al., 2016), membranes (Haider and Park, 2009), nanofibers (Aliabadi et al., 2013), hollow fibers (Mirmohseni et al., 2012) and scaffolds (Esquerdo et al., 2014), are used for adsorption purposes, mainly due the presence of amino and hydroxyl groups in the structure. Special attention should be given to chitosan nanofibers, due the extremely large surface area per unit of mass. Aliabadi et al. (2013)

* Corresponding author.
E-mail addresses: guilherme_dotto@yahoo.com.br (G.L. Dotto), juhmnsantos@hotmail.com (J.M.N. Santos), edutanabe@yahoo.com.br (E.H. Tanabe), dbertuol@gmail.com (D.A. Bertuol), efoletto@gmail.com (E.L. Foletto), profederlima@gmail.com (E.C. Lima), flavio.pavan@unipampa.edu.br (F.A. Pavan).

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prepared hydroxyapatite/chitosan nanofibers by electrospinning. The nanofibers were able to remove Pb, Co and Ni from aqueous solutions. Li et al. (2014) prepared chitosan/polyamide nanofibers by electrospinning, to remove Cr(VI) from aqueous solutions. The nanofibers presented diameters of 60–200 nm and were able to remove 90% of Cr(VI). Min et al. (2015) prepared chitosan/PEO nanofibers by electrospinning. The nanofibers presented diameters of 90–220 nm and were efficient to remove As(V) from aqueous solutions.

The abovementioned studies show that chitosan based nanofibers are prepared preferably by electrospinning and, are used mainly to remove metals from aqueous solutions. Based on the best of our knowledge, there are no studies regarding to the preparation of chitosan/polyamide nanofibers by Forcespinning®, and its application for dye removal. The forcespinning® technology was developed to standardize the fiber diameter, avoid the bubbles formation and facilitates the large scale production. While electrospinning is based on electrostatic forces, forcespinning® is based on centrifugal forces. In this technology, rotation, nozzle size, temperature, collector distance and viscosity/concentration of the solution should be controlled to obtain nanofibers with good characteristics (Sarkar et al., 2010; Xu et al., 2015).

This work aimed to develop chitosan/polyamide nanofibers (CP nanofibers) by a new forcespinning® technology, to be used as adsorbents of Reactive Black 5 (RB5) and Ponceau 4R (P4R) dyes. Firstly, the appropriate operational conditions and the chitosan/polyamide ratio were defined. After, CP nanofibers obtained under the more adequate conditions were characterized by scanning electron microscopy (SEM), X–ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Finally, the adsorption of RB5 and P4R dyes on the CP nanofibers was studied. In the adsorption studies, kinetic, equilibrium, thermodynamics, desorption and reuse were addressed. This work employs a new alternative technique (forcespinning®) to obtain an eco–friendly nano adsorbent, contributing for solid wastes management (chitosan from shrimp wastes) and also, for the treatment of colored effluents.

2. Materials and methods

2.1. Raw materials, dyes and reagents

Powdered chitosan (deacetylation degree of 85± 1%, molecular weight of 150 ± 3 kDa and particle size of 72 ± 3 μm) was obtained from shrimp wastes (*Penaeus brasiliensis*) (Moura et al., 2015). Polyamide–6 (5 mm pellets) was purchased from Sigma–Aldrich (USA). The analytical grade reagents, formic acid (98%), NaOH (99%) and HCl (37%) were purchased from Aproquímica (Brazil). Deionized water was used to perform all procedures.

Reactive Black 5 (RB5) (purity of 95.0%, color index 20505, molecular weight of 991.8 g mol^{-1}, $\lambda_{max} = 596$ nm) and Ponceau 4R (P4R) (purity of 95.0%, color index 16255, molecular weight of 604.4 g mol^{-1}, $\lambda_{max} = 505$ nm) dyes were obtained from Duas Rodas Ltda. (Brazil). The dyes purity was considered in the calculations. These dyes were selected since are common in effluents from textile and food industries, respectively. The structural formulae of the dyes is presented in Fig. 1(S) (supplementary material).

2.2. Preparation of chitosan/polyamide nanofibers by Forcespinning®

Chitosan/polyamide nanofibers were prepared in a Forcespinning® equipment (Fiberio, L1000-MS, USA) as presented in Fig. 1, by the following steps: (I) 2.50 g of polymers (chitosan + polyamide) were mixed with 7.50 g of formic acid (98%)

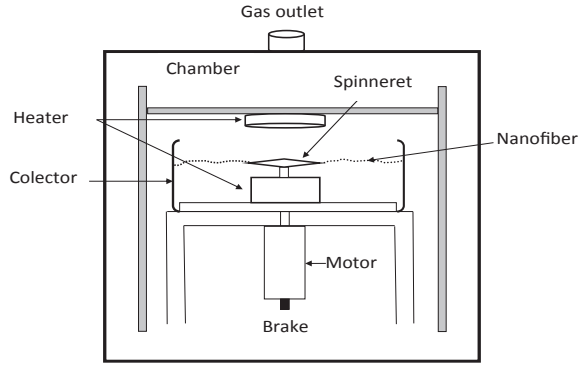

Fig. 1. Schematic representation of the forcespinning equipment used to produce the nanofibers.

under constant magnetic agitation at 313 K for 6 h, to form a homogeneous solution. In this step, the influence of chitosan/polyamide ratio ($g_{chitosan}$ $g^{-1}_{polyamide}$) (0/2.50, 0.25/2.25, 0.50/2.00, 0.75/1.75 and 1.00/1.50) was evaluated; (II) the spinneret was filled with the polymeric solution; (III) a 30 G½" needles were connected at the spinneret solution; (IV) the chamber was sealed and maintained at ambient temperature; (V) the spinneret was turned on at 12000 rpm for 10 min, being the fibers collected in a 4" collector plate with 16 metal panels (components of the ARC Collection system). The fibers were stored in plastic bags for further characterization and use. The experimental conditions were determined by preliminary tests and according to information provided by Fiberio.

The nanofibers prepared with different chitosan/polyamide ratios were evaluated in terms of production rate (g fiber produced per hour), mean diameter (see section 2.3) and adsorbent potential (see section 2.4), in order to select the more adequate chitosan/polyamide ratio to produce the fibers.

2.3. Characterization of chitosan/polyamide nanofibers

The textural characteristics of CP nanofibers were verified by scanning electron microscopy (SEM) using accelerating voltage of 5 kV (Tescan, VEGA–3G, Czech Republic) (Goldstein et al., 1992). The mean diameter of the CP nanofibers was determined through the SEM micrographs by Image J software (NIH Image, USA) (analyze particle method) (Li et al., 2010). X–ray diffraction (XRD) (Rigaku, Miniflex 300, Japan) was used to verify the structure of CP nanofibers (Saygili and Güzel, 2016). The functional groups were identified by Fourier transform infrared spectroscopy (FT–IR) (Prestige, 21210045, Japan) (Silverstein et al., 2007).

2.4. Batch adsorption experiments

All the adsorption experiments were performed in batch mode at 150 rpm using a thermostated agitator (Marconi, MA 093, Brazil). Firstly, the adsorbent potential of the nanofibers prepared with different chitosan/polyamide ratios was investigated. For this purpose, 15 mg of CP nanofibers were added to 50 mL of dye solutions (RB5 or P4R) with initial concentration of 50 mg L^{-1}. The solutions were stirred for 4 h at 298 K. Secondly, (using the nanofiber prepared in the more appropriate condition) the pH effect was investigated from 1.0 to 10.0 (adjusted with 0.1 mol L^{-1} NaOH or HCl), at 298 K, with initial dye concentration of 50 mg L^{-1}, contact time of 4 h, volume of solution of 50 mL and adsorbent dosage of 200 mg L^{-1}. After, in the best pH, kinetic curves were constructed (contact time from 0 to 180 min) at 298 K, initial dye concentration of 50 mg L^{-1} and adsorbent dosage of 200 mg L^{-1}. Finally,