Chemical Engineering Journal 229 (2013) 42–49

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Obtaining of eucalyptus microfibrils for adsorption of aromatic compounds in aqueous solution

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HIGHLIGHTS

- Two extraction methods of cellulose microfibrils: chemical and mechanical.
- Examination size and properties changes in the different microfibrils.
- Study of the adsorption capacity and adsorption kinetic of different microfibrils.
- Mechanical nanofibers considerably improve the adsorption capacity.

ARTICLE INFO

Article history:
Received 12 March 2013
Received in revised form 23 May 2013
Accepted 26 May 2013
Available online 5 June 2013

Keywords:
Eucalyptus
Microfibrils
Adsorption
Organic solute
Kinetic model

ABSTRACT

Chemical and mechanical treatments have been used to obtain cellulose microfibrils using bleached eucalyptus pulp as raw material. Chemical microfibrils have been obtained with the combination of three chemical treatments: mercerization with NaOH, acetylating with nitric acid and acetic acid, and finally hydrolysis with sulphuric acid. Moreover, mechanical microfibrils have been obtained by high pressure homogenizer. All the microfibrils have been characterized by FTIR, TGA, contact angle measurements, AFM and XRD. Finally, the microfibrils were modified to enhance their adsorption capacities obtaining values up to 610 μmol/g for trichlorobenzene when using mechanical microfibrils. The adsorption capacity of mechanical microfibrils was determined for various organic solutes and a pseudo-second order kinetic model and Langmuir isotherms were established.

1. Introduction

Nowadays, the chemical contamination of water by aromatic molecules from industrial waste represents a topic of concern. Among all the treatments proposed, adsorption using sorbents is one of the most commonly applied methods since it is an effective, efficient and economic method for water decontamination. Numerous studies have been performed to develop a cheaper and biodegradable adsorbent containing natural polymers [1–4].

Cellulose is one of the most important biopolymers that can be found in nature. It is a polysaccharide composed exclusively of glucose molecules, rigid, insoluble in water and contains from several hundred to several thousand units of β-glucose. It is the most abundant organic biomolecule as it forms the bulk of terrestrial biomass [5–7].

In recent years, the study of cellulose has been increased due to its high availability; annually produce about 100 million tons of cellulose in plants around the world [8,9].

The obtaining of cellulose nanofibers has attracted significant interest in the last few decades due to the unique characteristics they endow, such as high surface area-to-volume ratio, high surface area, high Young's modulus, high tensile strength, and low coefficient of thermal expansion [10] and due to the potential of cellulose in several applications.

Chemical and mechanical treatments or combinations are used for the production of cellulose nanofibers [11]. Different sequences of chemical treatments with acids or bases promote and improve the removal of hemicelluloses and lignin [12]. Mechanical treatments such as high pressure homogenization and ultrasound techniques are used to reduce the size of the cellulose fibers to the nanosize scale where the properties of the cells vary considerably [13,14].

The adsorption capacity of cellulose is an aspect that has attracted considerable interest in recent years [15–17] due to the possibility of organic matter removing by adsorption onto waste materials at low cost [18–22]. Also, it has been demonstrated the ability of cellulose to fix metal ions by adsorption [23–26]. However, the characteristic of adsorption of native cellulose are not constant and vary depending on the origin of the cellulose and

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http://dx.doi.org/10.1016/j.cej.2013.05.098

the preliminary treatments. Native cellulose has a relatively low adsorption capacity that can be increased by chemical functionalization of the fibers. The adsorption capacity of modified cellulose fibers increases even 10 times than the same fibers without any treatments. This can be achieved by introducing chemical groups that exhibit a high affinity for chemical species in aqueous solution such as acrylamide and acrylic acid to adsorb water, heavy metals or Cu^{2+} ions by cellulose graft copolymer [27–29].

Numerous studies on this subject [30,31,3] have shown that the retention capacity can reach 300–600 μmol/g substrate. However achieving this relatively high level, require the increase of the surface area beyond 300–500 m^2/g. To achieve this surface, the use of nanoparticles o microporous (50–100 nm) is relatively expensive.

Two important factors have great influence on the adsorption capacity of cellulose: the hydrophobicity and the water solubility of organic solute. But these are not the unique factors to take into account, others as the hydrodynamic volume, the shape of the molecule, and the interaction potential between the adsorbent and adsorbate are likely to play an important role [32].

In this work, chemical and mechanical treatments have been used to obtain cellulose microfibils using bleached eucalyptus pulp as raw material. These microfibrils were chemically modified and their use as potential adsorbent has been assessed.

2. Materials and methods

2.1. Materials

Bleached eucalyptus pulp used in this work was kindly supplied by Papelera Guipuzcoana de Zicuñaga, S.A. from Hernani (Spain). The raw material was characterized according to the standard methods [33] and bibliographic procedures [34]. Moisture 7.30% ± 0.03, extracts 0.33% ± 0.04, lignin 0.20% ± 0.18 hemicelluloses 13.52% ± 0.09 (65% xylose, 24% arabinose and 11% glucose) and α-cellulose 80.35% ± 0.45.

Sodium hydroxide, acetic acid, nitric acid, sulphuric acid, palmitic acid, N-N′Dicyclohexylcarbodiimide (DCC), Dimetilaminopiridine (DMAP) and Dimetilformamide (DMF) were all obtained from Sigma–Aldrich.

Toluene, trichlorobenzene, benzene, nitrobenzene and phenol obtained from Sigma –Aldrich with high purity (99%) were used in adsorption studies as model contaminants. Their chemical structure, water solubility, and molar volume, are shown in Table 1.

2.2. Chemical extraction of cellulose microfibrils

For this purpose, different chemical treatments combinations were used. Before carrying out the treatments, two pretreatments have been used for the elimination of residual extracts. Bleached eucalyptus pulp was washed for 3 h in a hot water. Then, the fibers were treated in alkaline sodium hydroxide (1%) for 24 h. After that, the fibers were mercerized: 5 g of fibers were added to a solution containing 100 ml of NaOH (7.5%) and heated to boiling point for 90 min with continuous agitation. Then, the fibers were washed and dried. This process eliminates the non cellulosic materials such as lignin. In a second step, acetylating was carried out destroying microstructure, 0.6 g of mercerized fibers were added to a solution containing 2 ml of nitric acid and 12 ml of acetic acid and heated to boiling point for 30 min with continuous agitation [11,12,14]. Then, the fibers were washed and dried. Finally, a hydrolysis process was carried out, 1 g of mercerized and acetylated fibers were added to a solution containing 8.75 ml of H_2SO_4 and heated to 45 °C for 1 h. Then, the fibers were washed, dried and kept in a plastic bag to protect them against moisture.

2.3. Mechanical extraction of cellulose microfibrils

Three grams of dried bleached eucalyptus pulp was dispersed in three liters of water. The suspension was treated in an ultrasonic bath for 30 min to separate the fibril bundles. The homogenization of the cellulose fibrils were performed with Niro Soavi homogenizer using 40 passes at a pressure of 1000 bar. The fundamental mechanism of the high-pressure homogenizer is to pump a fluid stream against itself within interaction chambers of fixed geometry at very high energy, resulting directly in the breakup and dispersion of the slurry. High pressure, high velocity and a variety of forces on the fluid stream are capable of generating shear rates within the product stream, reducing particles to nanoscale.

2.4. Functionalization of microfibrils

The functionalization was carried out by esterification of the fibers through the elimination of water by azeotropic distillation, followed immediately by addition of palmitic acid, a dehydration agent N-N′Dicyclohexylcarbodiimide (DCC), and the catalyst (DMAP) [31,3,32,35–38], and putting all in a toluene/DMF (60/40) mixing at 80 °C for 3 h with reflux. Bleached eucalyptus pulp fibers (3 g) were swelling in hot water, filtered and then introduced in the flask containing 100 ml of a mixture of toluene/DMF (60/40 v/v). The solution was heated under reflux for the elimination of water remained on the fibers, then it was removed by azeotropic distillation for 3 h. Immediately 5 g of a dehydration agent DCC + 6 g of palmitic acid + 0.5 g of catalyst DMAP were added at 80 °C for 3 h. Finally, the obtained product was cooled and then purified by soxhlet extraction with THF/Ethanol (50/50 v/v) for 24 h. The obtained modified fibers were dried and kept in plastic bags. After esterification process, chemically obtained cellulose microfibrils are called modified chemical microfibrils, and the mechanically obtained cellulose microfibrils are called modified mechanical microfibrils.

2.5. Atomic Force Microscopy (AFM)

AFM images were obtained operating in tapping mode with a scanning probe microscope (Nanoscope IIIa, Multimode™ from Digital Instruments, Veeco) equipped with an integrated silicon tip cantilever having a resonance frequency of 300 kHz, from the same manufacturer. To obtain representative results, different regions of the specimens were scanned. Similar images were obtained, thus demonstrating the reproducibility of the results.

2.6. X-ray diffraction (XRD)

The X-ray powder diffraction patterns were collected by using a PHILIPS X'PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta–theta configuration, secondary monochromator with Cu Kα radiation (λ = 1.5418 Å) and a PIXcel solid state detector (active length in 2θ 3.347°). The samples were mounted on a zero background silicon wafer fixed in a generic sample holder. Data were collected from 5 to 70° 2θ (step size = 0.026 and time per step = 80 s) at RT. A fixed divergence and antiscattering slit giving a constant volume of sample illumination were used.

2.7. Fourier transforms infrared spectroscopy (FT-IR)

The FTIR spectra were recorded on a Perkin–Elmer 16PC instrument, by direct transmittance with an MKII Golden Gate SPEACAC accessory in the range of 400–4000 cm^{-1} with a resolution of 8 cm^{-1} and 20 scans.