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Research paper

Development and characterization of porous membranes based on kaolin/chitosan composite

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ABSTRACT

Chitosan/kaolin composite porous membranes were successfully prepared by solvent casting and evaporation process. The suspensions with different concentration of kaolin and chitosan showed a Newtonian behaviour. Strong interaction between chitosan and kaolin was revealed by FTIR and thermogravimetric analysis. The effect of kaolin content on the morphology and properties of the obtained membranes was studied. It was found by SEM observation that the kaolin particles were well dispersed in the chitosan matrix generating a porous microstructure. Incorporation of kaolin particles also improved the mechanical and thermal properties of the membranes and reduced drastically the water washout of chitosan in moderate acidic medium. Owing to their porous structure, the water permeability of the composite chitosan/kaolin membrane was significantly enhanced. The better formulation of the dope suspension in the range studied was 4% chitosan and 5% kaolin in acetic acid. These membranes made from naturally occurring materials might play an important role in advanced research in water treatment and environmental science.

1. Introduction

Water of good quality a fundamental and vital resource for humans is becoming scarce due to population, industrial development and environmental pollution. Hence, efficient and low-cost strategies for sewage treatment and desalination are needed. Incessant efforts are in progress in the membrane technology field to make water treatment an environmentally benign process. The cost effective and eco–friendly polymer membranes derived from renewable sources can be a promising substitute for common synthetic polymers used in membrane filtration such as polysulfone, polyethersulfone, polyethylene, polyimide, poyetherketone, polyphenylene oxide and polyphenylene sulphate that mainly rely on oil (Ravanchi et al., 2009; Pendergast and Hoek, 2011). In this direction, use of biodegradable and biocompatible materials as membrane material serves as an important criterion to be fulfilled. The most widespread biopolymers are polysaccharides. Many polysaccharides possess film-forming properties that render them suitable for the preparation of membranes with different characteristics. Polysaccharide-based membranes found practical applications in pharmaceutics, medicine, agriculture, food industry and different industrial processes. To date, in all applications mentioned above, membranes prepared from polysaccharides extracted from algae (alginates), plants (starch) or animal sources (chitosan) are mainly used.

Chitosan is a cationic polysaccharide formed by a linear chain of D-glucosamine and *N*-acetyl-D-glucosamine residues linked by β-(1–4) bonds (Rinaudo, 2006; Ling et al., 2015). It is obtained by deacetylation of chitin that is the second most common natural polymer after cellulose (Muzzarelli, 2012). Chitosan is one such candidate which has been a matter of growing interest in past years. The main reason for this attention is its excellent properties, such as biodegradability, biocompatibility, non-toxicity, hydrophilicity, cationicity and ease of modification (Rinaudo, 2006; Kumar et al., 2013; Lavorgna et al., 2014). Therefore, chitosan is considered as a potential green polymer candidate for applications in many industrial areas (No et al., 2000; Vandenbossche et al., 2013; Cheung et al., 2015; Hamed et al., 2016). The presence of chemical reactive groups (hydroxyl groups and highly reactive amino groups) makes it an attractive adsorbent for removing many kinds of pollutants from effluents (Unagolla and Adikary, 2015). Moreover, the desirable combination of properties of chitosan and its widespread availability makes this polymer especially interesting for preparation of membranes applicable in various technologies including pervaporation, reverse osmosis, gas separation, purification processes, drug delivery and microbial fuel cell (Cooper et al., 2013; Uragami et al., 2015; Prasad et al., 2016; Liu et al., 2016). Nonetheless, pristine chitosan based membranes are generally mechanically unstable, pH sensitive, and susceptible to swelling (Cooper

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et al., 2013). As an example, chitosan can easily dissolve in acidic medium, which can have a bad impact on the properties of membranes applicable in the treatment of aggressive solution. These drawbacks present decisive problems and limit their use for filtration applications. Hence, it is essential to improve their physical, mechanical, thermal and structural properties. Many strategies have been explored to improve the thermal and mechanical properties of chitosan based films including the addition of other biodegradable polymers or by incorporating nano-scale filler (Casariego et al., 2009). In this sense, chitosan with reactive functional groups in its backbone can be used for the preparation of composite membranes.

In recent years, natural polymer/clay composites have attracted considerable interest because they combine the structure, physical and chemical properties of inorganic and organic materials (Lewandowska et al., 2014; Wang et al., 2016). Natural inorganic clays have become the flagship of the composite manufacturing due to several factors including their renewable nature, wide availability, relatively low cost and easy surface functionalization. A number of reports in the literatures describe the use of clay in the chitosan film as a reinforcing agent for improving physical, mechanical and structural properties of obtained film such as montmorillonite, bentonite, saponite, etc. (Deng et al., 2012; Lewandowska et al., 2014; Huang et al., 2015; Costa et al., 2016; Pankaj et al., 2016; Salehi et al., 2016; Wang et al., 2016). These composites have been used as antimicrobial agents and drug carriers or as adsorbents for the removal of dyes and heavy metals. However, there are only few reports on preparation of chitosan/kaolin composites (Zhu et al., 2010; Dey et al., 2016). Moreover, to our knowledge, the use of these kinds of composites for the fabrication of membrane filtration has not gained enough attention.

In the current work, chitosan has been blended with kaolin for making composite membranes. The interaction between chitosan and kaolin has been examined based on the specific and characteristic features of both components. Rheological properties of the dope mixtures used to prepare the composite membranes were investigated focusing on the effects of shear rate, concentration and temperature on the dynamic viscosities and shear stress of different aqueous solutions of chitosan/kaolin solubilized in acetic acid. Then, the membranes obtained by solvent casting and evaporation methods and containing various amount of kaolin were characterized in terms of surface chemistry, chemical stability and performance by using techniques as water contact angle, water resistance and pure water permeability.

2. Materials and methods

2.1. Materials

Chitosan (CS) was supplied as flakes by France Chitine (Batch type 342 from shrimp shells). The sample had a viscosity of 100 cP at 25 °C (producer data) with a mass average molecular weight of 180.000 $g \cdot mol^{-1}$ and a degree of acetylation of about 20%. The clay used in the present study was a kaolin Codex (noted as KO) provided by the L.P.M Cerina (Laboratoire des Plantes Médicinales, Tunisia) with a mean particle size distribution of 4 μm. The KO chemical composition is given in Table 1, where the main impurities are CaO, K_2O and Fe_2O_3. It reveals that the major components were silica (SiO_2: 47.85%) and aluminium oxide (Al_2O_3: 37.60%).

Acetic acid and sodium hydroxide were laboratory grade chemicals. Deionized water was used throughout the entire study.

Table 1
Chemical composition of the used kaolin (wt%).

SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	CaO	TiO_2	LOI[a]
47.85	37.60	0.83	0.17	0.97	0.57	0.74	11.27

[a] LOI: loss on ignition at 1000 °C.

2.2. Composite membrane preparation

2.2.1. Solution preparation

CS solutions were obtained by dissolving CS powder in diluted acetic acid solution (0.1 M) to achieve stoichiometric protonation of the amine moieties according to the following chemical reaction:

$$CS{-}NH_2 + AcOH \leftrightarrow CS{-}NH_3^+ + AcO^-$$

where $CS{-}NH_2$ and AcOH are the free amine form of chitosan and the undissociated acetic acid form, respectively. $CS{-}NH_3^+$ is representing the protonated form of chitosan, soluble in water and AcO^- the acetate counter ion.

The final CS concentration ranged from 3% to 4% (w/v). Below 3% (w/v), the mechanical properties of prepared membranes were not sufficient for handling the samples and higher concentrations gave final solutions too viscous to obtain a homogeneous casting. The CS mixtures were stirred until the solution looked transparent and homogeneous. The kaolin powder was then slowly added upon stirring to yield the dope suspensions named as CKn, n denoting the KO powder ratio (%). The mixtures were further stirred for 24 h at room temperature to ensure a complete homogenization. Table 2 shows the different compositions of the prepared dope mixtures. In all the samples the CS amount was fixed at about 4% (w/v) and the KO amount was varied from 0 to about 5% (w/v).

2.2.2. Membrane preparation

CKn mixtures were casted on a glass plate with a 700-μm gap casting knife using an automatic coater (K Control coater, Erichsen). The cast film was dried at room temperature to partially evaporate the solvents. Subsequently, the composite membranes were neutralized by immersing them into a 1 mol l^{-1} NaOH solution. Treating the composite with NaOH was found to significantly improve the composite resistance to water washout. After 24 h immersion duration, the obtained membranes were thoroughly rinsed with deionized water to remove the excess of NaOH and reach a neutral pH value. The membranes were then stored in deionized water. The preparation procedure of pure CS membrane was similar to that described above.

2.3. Membrane characterization

2.3.1. Rheological measurements

The rheological behaviour of mixtures (CKn) was monitored with an Anton Paar MCR301 Rheometer, using 50 mm plate-plate geometry as a measurement system. The influence of temperature on the dynamic viscosity of the mixtures with different compositions was also observed. The temperature sweep tests were performed in a range from 25 °C to 80 °C.

2.3.2. Infrared spectra measurements

Infrared spectra of composite membranes were recorded using Nicolet 710 Fourier-transform infrared (FTIR) spectrometer with attenuated total reflection (ATR). The spectra were acquired in the wavenumber range from 4000 to 650 cm^{-1} with 64 scans at a 4 cm^{-1} resolution.

Table 2
Composition of the prepared dope mixtures.

Sample name	Chitosan powder (w/v)	Kaolin powder (w/v)
CK0	4	0
CK1	4	1
CK3	4	3
CK5	4	5