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Study of Methylene Blue adsorption on keratin nanofibrous membranes

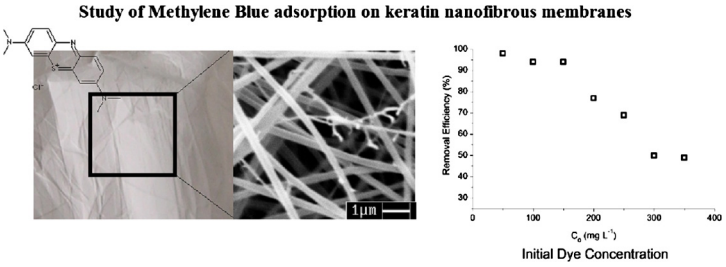
A. Aluigi [a,*], F. Rombaldoni [b], C. Tonetti [b], L. Jannoke [c]

[a] CNR-ISOF, National Research Council-Institute of Organic Synthesis and Photoreactivity, Via P. Gobetti, 101, 40129 Bologna, Italy
[b] CNR-ISMAC, National Research Council-Institute for Macromolecular Studies, C. so G. Pella, 16, 13900 Biella, Italy
[c] Politecnico di Torino, Department of Materials Science and Chemical Engineering, C.so Duca degli Abruzzi 24, 10129 Torino, Italy

HIGHLIGHTS

- Membranes of keratin nanofibers (220 nm diameter) were prepared by electrospinning.
- The membranes were tested as adsorbents for Methylene Blue dye from water.
- The adsorption capacity increases with increasing the initial dye concentration and pH.
- The adsorption capacity decreases with increasing the adsorbent dosage and temperature.
- Results suggest that keratin nanofibrous membranes could be promising dye adsorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, keratin nanofibrous membranes (mean diameter of about 220 nm) were prepared by electrospinning and tested as adsorbents for Methylene Blue through batch adsorption tests. The adsorption capacity of the membranes was evaluated as a function of initial dye concentration, pH, adsorbent dosage, time and temperature. The adsorption capacity increased with increasing the initial dye concentration and pH, while it decreased with increasing the adsorbent dosage and temperature, indicating an exothermic process. The adsorption results indicated that the Langmuir isotherm fitted the experimental data better than the Freundlich and Temkin isotherm models.

A mean free energy evaluated through the Dubinin–Radushkevich model of about 16 kJ mol^{-1}, indicated a chemisorption process which occurred by ion exchange. The kinetic data were found to fit the pseudo-second-order model better than the pseudo-first-order model. The obtained results suggest that keratin nanofibrous membranes could be promising candidates as dye adsorption filters.

1. Introduction

The effluents from industries using dyes as food, textiles, papers, cosmetics and other industries, are the main sources of dye pollution [1]. Since many dyes and their break down products are toxic for human and living organisms, removal of dyestuffs from wastewater has received considerable attention over the past decades. Synthetic dyes are stable to biodegradation, therefore biological aerobic wastewater treatment systems are not successful in removing color from wastewater. Moreover, degradation products of some dyes are toxic. For these reasons several physic-chemical methods as filtration, flocculation, chemical and electrochemical oxidation, ozone treatment and adsorption were developed [2]. Among the aforementioned methods, the adsorption process is

* Corresponding author. Tel.: +39 0516399785; fax: +39 0516399844.
E-mail address: annalisa.aluigi@isof.cnr.it (A. Aluigi).

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one of the most effective and low cost technique widely studied in recent years to remove dyes from wastewater. The adsorption process uses an adsorbent, a material able to bind the toxic substance or molecule to its surface. Adsorption methods are superior to other techniques not only in terms of cost, but also in terms of flexibility, simplicity of design, ease of operation, etc. Moreover, adsorption methods do not produce secondary harmful substances and the surface of an adsorbent can be functionalized and designed in order to increase the adsorption performances toward the toxic substances to be removed [3].

Powders of activated carbons and of various low cost biomaterials have been demonstrated to be good adsorbents for many organic compounds included dyes [4,5]. However, the major drawbacks of using adsorbents in form of fine powder for wastewater treatment are the production of large amount of sludge which may cause a secondary pollution and problems in regeneration [6,7].

Membrane technologies offer a potential solution for wastewater treatment and, for this reason, their industrial applications have considerably expanded in the last 50 years. Although membrane processes are well established technologies for water remediation, many efforts are being made to design new membranes with enhanced adsorption performances toward toxic substances [8,9].

In this context, electrospun nanofibrous membranes, due to their interesting characteristics such as high porosity, high specific surface area, high water permeability, small interfibrous porous size, and interconnected open pore structures, are potentially advanced systems that can offer removal of pollutants from water at lower energy and cost [10]. Electrospinning is the most simple and low cost process which produces ultrafine polymer fibres through the action of an external electric field imposed on a polymer fluid (polymer solution or melt) [11]. At the same pressure drop, filters made of fibres having a mean diameter finer than half a micron (as nanofibres) show a higher capability to collect finer particles compared to conventional filter fibres because the slip flow around the nanofibres increases the diffusion, interception and inertial impactions efficiencies [12]. More specifically, nanofibrous membranes were studied for microfiltration and ultrafiltration.

By electrospinning polymers having chemical functional groups able to bind specific toxic adsorbents, it is possible to prepare membranes for water depuration that can offer both adsorption and filtration. Therefore, electrospun nanofibrous membranes of various synthetic and natural polymers as polyvinyl alcohol [13], amidoxime-modified polyacrylonitrile [10], silk fibroin [14], or nanofibrous membranes functionalized through the introduction of inorganic nanoparticles like montmorillonite (MMT) into the polymer matrix [15], were prepared and tested for adsorption of specific materials from aqueous solutions. The great advantage of using nanostructured membranes with high surface area is in their good adsorption performances even at low adsorbent dosages.

Research interest in the metal adsorption capacity of new membranes made of protein nanofibres has been intensified in recent years. Among the natural proteins, keratin, being the major component of wools, hairs, horns, nails, and feathers, is an abundant non-food protein characterized by a large number of hydrophilic amino acids with high affinity to ionic species (e.g. heavy-metals or dyes). Moreover, keratin wastes as feathers, horns-nails from butchery, poor quality raw wools from sheep breeding and by-products from the textile industry account worldwide for more than five millions tons per year. For the aforementioned reasons, keratin is an interesting low cost biomass to be exploited. Electrospun nanofibrous membranes based on keratin have been widely investigated for the heavy-metal ions removal from water both in batch and in dynamic conditions [16–18]. However, to the best of our knowledge, there is no literature focusing on the adsorption capacity of cationic dyes onto the keratin-based nanofibrous membranes.

In this work, nanofibrous membranes made of keratin extracted from wool were prepared by electrospinning process and characterized in their morphology, diameter distribution, thickness, porosity and specific surface area.

Afterwards, the prepared membranes were tested as adsorbents for Methylene Blue from aqueous solution through preliminary adsorption tests carried out in batch.

In particular, the adsorption capacity and the removal efficiency of keratin nanofibrous membranes were evaluated in function of initial dye concentration, pH, adsorbent dosage, time and temperature.

Moreover, equilibrium (Langmuir, Freundlich, Dubinin–Radushkevich and Temkin) and kinetic (pseudo-first order, pseudo-second order) models were used to fit experimental data and the isosteric heat of adsorption was calculated.

2. Experimental

2.1. Materials

Keratin protein was extracted from Australian Merino wool (21 μm fineness).

Methylene Blue (MB) is a basic and cationic dye with CI Classification Number 52015. All chemicals were of analytical grade and were purchased from Sigma–Aldrich.

2.2. Keratin nanofibrous membrane preparation and characterization

Keratin was extracted from wool by sulphitolysis and purified as described in a previous work [16]. Afterwards, keratin powder was transformed into nanofibrous membranes through electrospinning process by slightly modifying the electrospinning parameters used in a previous work [17]. Practically, keratin solutions with a final concentration of 15 wt%, were prepared by dissolving the protein in pure formic acid (98%), under shaking, at room temperature, overnight. The prepared keratin solution was placed in a 5 mL syringe with a stainless needle tip having an internal diameter of 0.2 mm. The needle tip (cathode) was connected to a high voltage generator (SL50 Spellman High Voltage Electronics Corporation, USA) and the polymer solution was electrospun toward a grounded stainless steel collector (20 cm × 20 cm) using a “bottom up” configuration, in which the jet-emitting source was positioned below the grounded collector [17]. The electrospinning process was carried out using a voltage of 25 kV, a needle tip-collector distance of 20 cm, a solution feeding rate of 1 $\mu l\,min^{-1}$, controlled with a syringe pump (KDS, KD Scientific *nc.*, USA) and a deposition time of 60 min. During the electrospinning process, the environmental conditions were controlled to be the following: a temperature in the range 20–25 °C and a relative humidity in the range 45–50%. In order to increase the stability in water, the prepared keratin nanofibrous membranes were treated at 180 °C for 2 h.

The electrospun nanofibre morphology was observed under a scanning electron microscope (SEM) using a LEO 435 VP (LEO Electron Microscopy Ltd, UK), with and acceleration voltage of 15 kV, a current probe of 100 pA and a working distance of about 20 mm. Before SEM analysis, the membranes were sputter coated with a gold layer using an Emitech (UK) K550 sputter coater setting a current of 20 mA for 240 s. The fibre diameters of the keratin nanofibrous membranes were analyzed by means of a freely distributed software GIMP 2.8 (GNU Image Manipulation Program). In particular the nanofibre mean diameter and the diameter distribution were evaluated from 100 measurements randomly gathered from several SEM photos of several nanofibrous membranes. The thickness of keratin nanofibrous membranes was measured by using