Applied Surface Science 285P (2013) 56–64

Contents lists available at ScienceDirect

Applied Surface Science

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

A study of dyes sorption on biobased cryogels

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ARTICLE INFO

Article history:
Received 10 April 2013
Received in revised form 10 July 2013
Accepted 24 July 2013
Available online 8 August 2013

Keywords:
Poly (vinyl alcohol)
Scleroglucan
Cellulose microfibers
Zein
Methylene blue
Sorption kinetic
Sorption isotherm

ABSTRACT

Three types of biopolymers based materials were synthesized and tested as adsorbents for the dyes from aqueous solutions. Blends based on poly (vinyl alcohol) [PVA] and scleroglucan [Scl], cellulose microfibres [cel] and zein, respectively, have been prepared by repeated freezing–thawing cycles. Methylene blue [MB] was selected as a model dye in order to evaluate the capacity of the prepared materials to remove the dyes from aqueous solutions. The effects of the initial dye concentration, contact time and the composition of materials on the kinetic and thermodynamic parameters of sorption were discussed. The pseudo-second-order kinetics was found to better fit the experimental data thus being able to consistently predict the amount of dye adsorbed over the entire sorption period. The sorption equilibrium data obey Freundlich isotherm. Sorption capacity was evaluated both by dye solution and cryogel analysis by using VIS spectrometry and image analysis with CIELAB system. The sorption of monomer or aggregated dye molecules was identified and correlated with the type and morphology of the gel. The highest efficiency in MB removal was obtained for Scl/PVA cryogels in 1:9 weight ratio (9.5279 mg/g MB for an initial concentration by 8×10^{-5} mol/L in MB). These materials are suitable as sorbents for the advanced removal of dyes from waste water.

1. Introduction

Dyes sorption from aqueous solutions is an important goal for many applications such as: water purification [1,2], dyes separation, antimicrobial dyes loading in polymeric matrices by sorption, aiming their controlled release. Also, some dyes have been used as models for characterization of sorptive and morphological properties of different substrates, due to the easy ways to determine their concentration in aqueous solution. Nowadays, due to the environmental policy constraints, researchers are looking for ecological substrates for sorption [3,4]. Natural substrates such as agricultural wastes or ash, even cheap, have a lot of drawbacks due to the release of toxic or pollutant compounds [5–14]. Poly(vinyl alcohol) [PVA] is a versatile candidate for this aim, due to its properties: water solubility, non-toxicity, non-carcinogenity, biodegradability, biocompatibility, capacity to form gels with tailored morphology by cryogenic techniques, avoiding toxic crosslinkers use [15–18]. Also, its capacity to be blend with other polymers or to be matrix for different fillers allows obtaining of new materials with controlled properties.

The aim of this research is to prepare and test biopolymers-based materials as adsorbents for the dyes from aqueous solutions. Natural polymers, having different functional groups, such as scleroglucan, microfibers of cellulose and zein, respectively, have been selected to be embedded in PVA matrix.

Scleroglucan is a natural polysaccharide, produced by fungi of the genus *Sclerotium* (Fig. 1). It adopts a stable triple-stranded helical conformation held together by hydrogen bonds. This structure plays a fundamental role in determining the mechanism of sorption outside and inside of the helix [19–21].

Cellulose microfibers (cel) exhibit high specific surface area compared to other conventional cellulose fibres. It could be also a very promising reinforcement for polymers due to the removal of amorphous regions by acid hydrolysis [22,23].

Zein is a prolamine, the major storage protein of corn, which comprises about 45–50% of its protein content [24]. Zein from corn has good potential to interact with other compounds due to amino or carboxyl groups present in its structure.

Methylene blue [MB] is a cationic dye, selected as a model compound in order to evaluate the capacity of cryogels to remove the dye (methylene blue) from its aqueous solutions. MB has been selected both due to its high absorbance and to its capacity to aggregate differently in function of the interaction with the substrate. These will determine the shift of the VIS absorption bands maxima [25]. So, by analysing the colour of the MB loaded cryogels, information concerning the gels morphology could be obtained.

To the best of our knowledge there is no reported data in the literature related to the obtaining and characterization as sorbent substrates of the proposed cryogels.

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http://dx.doi.org/10.1016/j.apsusc.2013.07.164

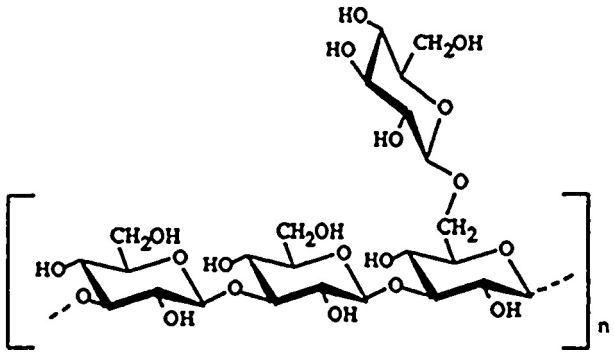

Fig. 1. Scleroglucan structure.

2. Experimental

2.1. Materials

PVA 98–99% hydrolysed (M = 146,000–186,000) was purchased from Sigma–Aldrich. Scleroglucan (Actigum CS 11, M_w = 1,000,000 Da) was purchased from Cargill, St-Germain-en-Laye, France.

Zein from maize was purchased from Sigma–Aldrich. The polymers have been used without further purification.

Microfibers of cellulose were prepared by HCl assisted hydrolysis of cotton, method adapted by that described by Kim et al. [27]. After hydrolysis, the obtained suspension was diluted using distilled water, left to decant and washed until neutral pH. Suspension was further used to obtain the cryogel.

Methylene blue was purchased from USP, Powder, American Cyanamid Company, New Jersey and it was used as received without further purification. The structure of the dye is presented in Fig. 2.

Solutions of MB at desired concentrations (8.00×10^{-6}, 2.40×10^{-5}, 4.00×10^{-5}, 5.60×10^{-5}, 8.00×10^{-5} mol/L) were prepared by using distilled water. The concentration range considered was selected taking into account the solubility of dye in water (40 g/L) [28].

2.2. Preparation of PVA and PVA/natural polymers cryogels

The solutions of PVA and Scl respectively, have been prepared according to the method described by Patachia et al. [29].

PVA cryogels have been obtained by following the same procedure [29].

PVA/Scl hydrogels (cryogels) have been prepared by mixing solutions of PVA (10%) and Scl (1%) for a few minutes in a beaker and then pouring them in a PVC cylindrical recipient and submitting it to freezing at −40 °C for 12 h, followed by thawing at room temperature (22 °C) for 12 h [29]. The abovementioned freezing–thawing procedure was repeated three times.

To obtain PVA/cel cryogel, the dispersion of cellulose microfibres (solid content by 36.2%) has been mixed with PVA solution (10%) (in 9:1 weight ratio of polymers) under continuous stirring for 1 h.

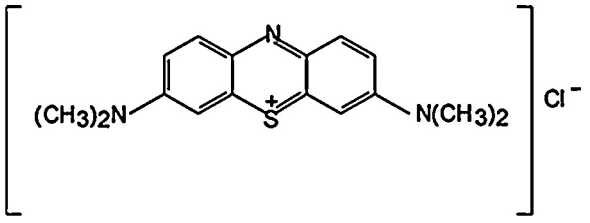

Fig. 2. The structure of methylene blue.

To prepare PVA/zein cryogel, zein powder was dispersed into PVA aqueous solution (10%) (in 9:1 weight ratio of polymers), under continuous stirring for 1 h. Three cycles of freezing and thawing followed.

To improve flexibility and mechanical strength of cryogels each one was immersed in KOH 4 M solution for 30 min, a procedure adapted from Fu et al. [30]. The adsorbed KOH on the surface of the cryogel was removed by rinsing it in distilled water numerous times, until neutral pH. Then the cryogels were stored in distilled water for later use.

2.3. Methods for cryogels characterization

2.3.1. Determination of the solid content of the cryogels

The obtained cryogels have been kept immersed in distilled water aiming to reach the swelling equilibrium. The solid content of the obtained materials in swollen state has been determined by cutting out of cylindrical samples, (diameter: 0.5–1 cm) weighing (m_e), submitting them in a thermosetting oven at 105 °C for 5 h and weighing the dried samples ($m_{xerogel}$). The solid content (SC) of the material has been calculated with Eq. (1):

$$SC(\%) = \frac{m_{xerogel}}{m_e} \times 100 \quad (1)$$

2.3.2. Monitoring of dye sorption

Circular samples of 1 cm diameter with mass between 0.10 and 0.30 g were immersed in MB solutions of different concentrations. The sorption of MB was monitored through colour analysis of the gel and through the analysis of the immersion solutions.

(a) Solution analysis

The change in solution absorbance was monitored through VIS spectroscopy, at different time periods after the sample immersion (λ_{MB} = 640 nm) using an UV/VIS Perkin Elmer spectrophotometer, Lambda 25-model. The sorption was monitored daily and the equilibrium of sorption was reached after 20 days. The experiments occurred at room temperature.

The amount of the dye sorbed by cryogels was determined by monitoring the concentration of the MB dye solutions as a function of the cryogel nature and as a function of time. The amount of MB adsorbed by the weight unit of cryogels, q_t (mg/g), was calculated by using Eq. (2):

$$q_t = \frac{(c_0 - c_t) \cdot \mu \cdot V}{m_{xerogel} \cdot 1000} \quad (2)$$

where: c_0 (mol/L) and c_t (mol/L) are the solutions concentration at time t = 0 and at equilibrium time t respectively; μ is the molar mass of MB; V (L) is the volume of MB solution and $m_{xerogel}$ (g) is the mass of dried polymer.

(b) Cryogel analysis

During the dye sorption, the cryogels change their colour from white to blue. The change in colour and in aspect was analysed through CIEL*a*b* system (CIELAB). CIELAB gives the possibility to make difference between two very close colours by taking into account parameters such as: hue, saturation and luminosity. To describe the colour, CIELAB uses the following parameters of the colour space: L^*, a^*, b^* and represent the logarithmic answer of the eye to the light stimuli. L^* represents the colour luminosity of the object and it varies from 100 (white) to 0 (black); a^* varies from red