Colloids and Surfaces B: Biointerfaces 116 (2014) 620–626

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

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

Novel composite films based on amidated pectin for cationic dye adsorption

Aleksandra R. Nesic[a,*], Sava J. Velickovic[b,1], Dusan G. Antonovic[b]

[a] Vinca Institute of Nuclear Sciences, University of Belgrade, PO Box 522, Belgrade, Serbia
[b] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia

ARTICLE INFO

Article history:
Received 14 August 2013
Accepted 22 October 2013
Available online 8 November 2013

Keywords:
Pectin
Biofilms
Dye adsorption

ABSTRACT

Pectin, with its tendency to gel in the presence of metal ions has become a widely used material for capturing the metal ions from wastewaters. Its dye-capturing properties have been much less investigated, and this paper is the first to show how films based on amidated pectin can be used for cationic dye adsorption. In the present study amidated pectin/montmorillonite composite films were synthesized by membrane casting, and they are stable in aqueous solution both below and above pectin pK_a. FTIR, thermogravimetry and SEM-EDAX have confirmed the presence of montmorillonite in the cast films and the interactions between the two constituents.

In order to evaluate the cationic dye adsorption of these films Basic Yellow 28 was used, showing that the films have higher adsorption capacity compared to the others reported in the literature. The results were fitted into Langmuir, Freundlich and Temkin isotherms indicating an exothermic process and setting the optimum amount of montmorillonite in the films to 30% of pectin mass. According to the Langmuir isotherm the maximum adsorption capacity is 571.4 mg/g.

1. Introduction

Pectin represents a family of polysaccharides that has in recent years been getting great attention due to its nontoxicity, biodegradability and biorenewability. Commercially, pectin can be easily obtained by extraction from citrus peel, apple pomace, sugar beets, mango and other plants [1]. Chemically, pectin is based on a galacturonic-rich backbone consisting of homogalacturonan (HG) and rhamnogalacturonan [2,3], but with at least 17 different monosaccharides in its structure [4]. The largest part of pectin polymer backbone consists of partially methyl esterified (1–4)-linked a-D-galacturonic acid (GalA) [5]. It can be modified by methylation or amidation of carboxylic groups. An important property that characterizes various types of pectin is its degree of esterification, as some of the carboxylic groups in pectin are methyl esterified.

As pectin has a tendency to form gel in presence of metal ions, that property is widely utilized for removal of metal ions from wastewaters [6–9]. The degree of esterification has big influence on adsorption properties and with decreasing the degree of esterification the adsorption capacity increases [10]. There are only few articles that present adsorption of dyes by pectin [11–13] and according to the literature there has been no investigation of amidated pectin as sorbent for metal ions and dyes before the one presented in this paper.

In our previous work we investigated the complexation between chitosan and montmorillonite [14] and application of these films in anionic dye adsorption. Therefore, in the present work, the idea was to try to replace the widely investigated chitosan with more biodegradable, more produced and cheaper material such as amidated pectin and to obtain new composite material based on amidated pectin (AP) in a form of thin film for wastewater application. Dye removing properties are tested for the removal of the cationic dye Basic Yellow 28.

Montmorillonite was chosen as the inorganic component due to its low cost, abundance and its layered structure which acts as a material with high sorption properties. The pristine sodium montmorillonite (MMT) is generally incompatible with hydrophobic polymers, since it is hydrophilic in nature. However, an advantage was taken to incorporate MMT particles into a hydrophilic polymer such as AP to develop novel hybrid composite membranes for dye adsorption. The hydroxide groups from amidated pectin can form hydrogen bonds with silicate layer from MMT and make films stable in aqueous solutions below pK_a of pectin.

2. Experimental

2.1. Materials

Amidated pectin (AP) LA-110, Mw = 15 kDa, with a degree of methylation of 35.9 and a degree of amidation 15.9 and 48.2% free

* Corresponding author at: Vinca Institute of Nuclear Sciences, University of Belgrade, PO Box 522, RS – 11001 Belgrade, Serbia. Tel.: +381 11 2455654; fax: +381 11 3370387.
E-mail address: anesic@vin.bg.ac.rs (A.R. Nesic).
[1] Unfortunetly Dr Sava Velickovic passed away few days ago.

0927-7765/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfb.2013.10.031

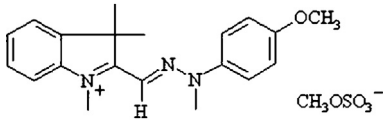

Fig. 1. Structure of Basic Yellow 28.

galacturonic acid residues (Danisco, Denmark) was used without any further purification. Cloisite Na^+ was a natural sodium-rich montmorillonite (MMT) was obtained from Southern Clay Products Inc. (USA). Basic Yellow 28 dye was a gift from Bezema AG.

2.2. Synthesis of amidated pectin/montmorillonite membranes

Amidated pectin/montmorillonite films were prepared by mixing solutions of AP and dispersions of MMT in water in different ratios. The montmorillonite amount was 10, 30 and 50% by mass of pectin. The general procedure of synthesis is as follows: firstly, AP (1 wt%) was dissolved in distilled water with constant stirring at the temperature of 50 °C. Montmorillonite was dispersed in 0.2 M acetic acid with constant stirring 30 min at the temperature of 50 °C. These solutions were mixed with constant stirring for 30 min. The mixed solutions in different ratios of MMT were cast on Petri dishes and dried at room temperature for 24 h and the films were obtained.

Pure amidated pectin film was used as a reference sample. Amidated pectin film was obtained by dissolving 1% wt AP in distilled at 60 °C and casting on Petri dish.

2.3. Characterization of films

FTIR spectra of amidated pectin/montmorillonite films before and after adsorption of Basic Yellow 28 dye were recorded on a Bomem MB 100 FTIR spectrophotometer from KBr pellets.

Thermogravimetric analysis (TG) was performed by a SDT Q-600 TG instrument (TA Instruments). All analyses were performed with 5 mg samples in ceramic pans under nitrogen atmosphere between 0 and 600 °C at heating rate 10 °C/min.

SEM-EDAX was used to determine morphology of membranes before and after adsorption azo dyes. Measurements were taken on a JEOL JSM-5800 scanning electron microscope.

The dye concentrations for the adsorption experiments were measured at a wavelength $\lambda = 439$ nm by UV/VIS Shimadzu 1700 spectrophotometer.

2.4. Model cationic dye

In this investigation Basic Yellow 28 was used as a model cationic dye. Basic Yellow 28 dye is a hazardous azo dye and according to the European regulation is proposed for ban as a hair dying substance due to eye and skin irritation and carcinogenic effects [15]. Despite the prohibition, this dye is widely used in less-developed countries for dyeing of acrylic fibers, but also in paper, textile, leather and cosmetic industries. The structure of BY28 is given in Fig. 1.

2.5. Adsorption

Experiments were carried out by adding approximately 15 mg of films into 50 mL of dye solution with desired concentration, temperature of solution and appropriate pH. The effect of dye concentration was investigated at pH = 2, at 20 °C and from 30–80 mg/L. In order to investigate the effect of temperature and pH, the equilibrium sorption measurements were carried out in solutions with dye concentration of 80 mg/L, at 8, 20, 37 and 55 °C, and pH of solution within the range 2–7.4, respectively. The sorption kinetic experiments were conducted by varying the initial concentration of dye from 30 to 80 mg/L. At predetermined time intervals approximately 3 mL of dye solution was used for UV–vis measurements and afterwards returned into the flask. This was repeated until equilibrium was reached.

The capacity of adsorbed dye was calculated according to the following equation:

$$q_e = (C_0 - C_e)\frac{V}{m} \quad (1)$$

where q_e (mg/g) is the amount of dye adsorbed on the membrane, C_0 (mg/L) is the initial concentration of dye in solution, C_e is the equilibrium concentration of dye in solution, V (L) is volume of the used dye solution and m (g) is weight of the used membrane. Each experiment was repeated three times under the same controlled conditions.

In order to determine sorption kinetic parameters, four kinetic models were applied to fit the obtained experimental data: the pseudo-first order kinetic model of Lagergren, the pseudo-second order kinetic model of Ho. The linear forms of listed models are presented by Eqs. (2)–(4):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \quad (3)$$

$$q_t = K_p \times t^{0.5} + C \quad (4)$$

2.6. Adsorption isotherms

The most common way to investigate the type of established interactions between an adsorbent and the given adsorbate is through sorption isotherms which present sorption capacities as a function of the equilibrium adsorbate concentration at constant temperature. The initial dye concentration was varied from 30 to 80 mg/L while the mass of adsorbent was constant, 15 mg.

Adsorption data were fitted to the Langmuir, Freundlich and Temkin isotherms. The theoretical Langmuir sorption isotherm is based on assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface and the energy of adsorption is constant [16]. Langmuir equation can be applied to describe chemisorptions. The following equation was used:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} K_L}\right)\frac{1}{C_e} \quad (5)$$

where q_e is the equilibrium dye concentration (mg/g), C_e the equilibrium dye concentration in solution (mg/L), $q_{\max}$ the monolayer adsorption capacity (mg/g) and K_L Langmuir adsorption constant related to the free energy constant. According to Hall et al. [17], the favorable adsorption of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L. This factor can indicate whether the sorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$), and is given by following equation:

$$R_L = \frac{1}{1 + K_L \times c_0} \quad (6)$$

The Freundlich isotherm is employed to describe heterogeneous system [18]. A linear form of Freundlich equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$