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Integrating chloroethyl phosphate with biopolymer cellulose and assessing their potential for absorbing brilliant green dye

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ABSTRACT

Cellulose is vastly used in the adsorption of dyes. It can be used in its natural formor with modified surface. This present study aimed at integrating phosphate cellulose with chloroethyl phosphate, value their potential as adsorbents of brilliant green dye, and compare suchresults to those of pure cellulose (Pure-Cel). The phosphatic material (Phosp-Cel) was characterized by XRD, where it was found that the crystallinity of the material was kept; by IV, which showedtwo bands in 1059 and 1027 cm^{-1} that indicated the presence of the C—O—P link; by ^{31}P NMR, which showed a broad signal in 1.86 ppm indicating the presence of a single species of phosphorus in material (P—O—C); and by thermogravimetry, where Phosp-Cel proved to be more thermally stable than cellulose forerunner. A time of 20 and 120 min was obtained to reach the equilibrium, through the tests of adsorption, for Pure-Cel and Phosp-Cel, respectively. In both cases the system follows the pseudo second order model. The largest removal occurred at pH 10 and the maximum adsorption was 46.7, 58.42 and 90.5 mg $g^{-1}$for Pure-Cel, and 113.6, 114.2 and 112.1 mg g^{-1} for Phosp-Cel at 25 °C, 35 °C and 45 °C, respectively. Pure-Cel experimental isotherms were best fit to the Langmuir model, and Phosp-Cel at 25 °C best fit the Langmuir model; while at 35 °C and 45 °C it best fit the Freundlich model.

1. Introduction

Aquatic ecosystems are of utmost ecological importance, besides being used for various purposes, such as: leisure, recreation and fishing activities, it is an important livelihood activity of coastal communities [1].

The growths of industrial activity and population have contributed to significant increase of various pollutants in the aquatic environment [2,3].

Water is considered the universal solvent and, by its extraordinary ability to dissolve, it transports a large part of impurities, and if it does not receive the proper treatment, it will have its physical, chemical and ecological characteristics substantially modified [4].

The water used in textile industries serves as vehicle for dyes used in the dyeing process, generating highly colored effluents [5]. Discoloration of such effluents can be made by coagulation, precipitation, reverse osmosis, adsorption and many other techniques. However, the adsorption excels the other, because it is a simple technique, one of the most effective processes for the removal of color and textile effluent treatment, where low-cost materials are used, such as cellulose [6–9].

Cellulose is the most abundant modifiable and renewable biopolymerin nature. It is thus a promising raw material available, in terms of cost for adsorption and synthesis of new materials [10,11]. The presence of hydroxyl groups in cellulose surface can under go typical reactions of primary and secondary alcohols, which are the possible active sites for polymer modification [12–14].

Cellulose chemistry modification is an efficient method for the production of materials with properties improved in relation to precursor polymer [15].

Cellulose phosphorylation is under explored, but very promising in ion-exchange processes [16], inhibitor of the activation

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proteins in the blood that are harmful in hemodialysis after incorporation in the membranes in separation and purification of proteins, vitamins and other important natural products [16], in addition to being used in the adsorption of drugs, metals and dyes.

Adsorption can be defined as a process of transferring one or more constituents, which occurs at the interface between two phases. Compound (pollutant) that sticks or adheres to the solid surface is called an adsorbate and the solid surface is known as an adsorbent. When adsorption equilibrium is established, the concentrations of pollutants adsorbed and in the water become constant. The relationship, at a given temperature, between the equilibrium amounts of pollutant adsorbed and in the water is called an adsorption isotherm. Langmuir, Freundlich, Temkin and other models are well known and can explain the adsorption efficiency of a pollutant systematically and scientifically. Parameters as temperature, the nature of the adsorbate and adsorbent and atmospheric and experimental conditions (pH, concentration of pollutants, contact time) can affect the adsorption process. Thus, the adsorption parameters can be optimized in search for maximum decontamination capacity as well as having extensive knowledge of the system to possible large-scale extrapolations [17–21].

Thus, this work aimed at adding chloroethyl phosphate to cellulose phosphorylation to formulate a product with higher adsorption properties of precursor polymer, in order to compare both in brilliant green dye adsorption, by evaluating the parameters: time, pH, temperature and concentration.

2. Experimental part

2.1. Reagents

Cellulose microcrystalline (White powder, CAS: 9004-34-6, Fagron), chloroethyl phosphate ($(ClCH_2CH_2O)_3P(O)$, Molecular Weight: 285.49 g mol^{-1}, Dinâmica), acetone 99.5% (Isofar), brilliant green dye (Aldrich), NaOH (Impex), HCl (Impex), KNO_3 (Impex) and deionized water. All of which were analytical grade reagents and were usedwith no further purification.

2.2. Synthesis of cellulose with chloroethyl phosphate

The sample was prepared by reaction of 3.0 g of microcrystalline cellulose (Cel) with 7 mL of chloroethyl phosphate under mechanical stirring or 4 h at 95 °C. After reaction, the sample was filtered and washed with deionized water and acetone. The solid was dried at 60 °C for 48 h [22,23]. The final material, a dark yellow powder which has a yield of 11.0475 g, was labeled as Phosp-Cel (yellow powder).

2.3. Characterization

The techniques used to characterize the materials were X-ray diffraction, infrared, nuclear magnetic resonance ^{31}P and thermogravimetry.

The X-ray diffraction was performed on a diffractometer (Shimadzu XRD600A) in 2θ range between 5 and 75°. This rate was 5° min^{-1}, using the CuKα radiation source, with a wavelength of 154.06 p.m.

The infrared spectra were obtained using a Varian FTIR spectrophotometer by the method of the tablet, using 1% of sample in KBr, with 100 scans in the region between 4000 and 400 cm^{-1} with resolution of 4 cm^{-1}.

The ^{31}PNMR spectrum of the modified solid was obtained by cross-polarization (CP) with magic angle spin of rotation (MAS) technique in a Bruker AC300 spectrometer at room temperature. The relaxation time used was 3 s, with acquisition time of 50 ms, contact 3 ms, a rotation frequency of about 4 MHz and resonance frequence of 75 MHz.

Thermogravimetric analyzes were obtained on a TA instrument brand and SDTQ-600 V20.9 Build 20 model, at a temperature range of 25–1000 °C, at a heating rate of 10 °C min^{-1}, under constant flow of nitrogen.

Dye solution concentrations were determined on a Varian CARY300 spectrometer.

2.4. Adsorption

2.4.1. Adsorption kinetics

Kinetics equilibrium was carried out in batches using a range of contact time between 0 and 180 min, where 20 mL of dye solution at a concentration of 100.0 mg L^{-1}. They were then put in contact with 20.0 mg of adsorbent material under mechanical agitation to 150 rpm at different time intervals at 25 °C. Followed by centrifugation, dilution and the analysis of the final concentrations of solutions.

The concentration of the adsorbed dye in the adsorbent phase was quantified according to Eq. (1):

$$q = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

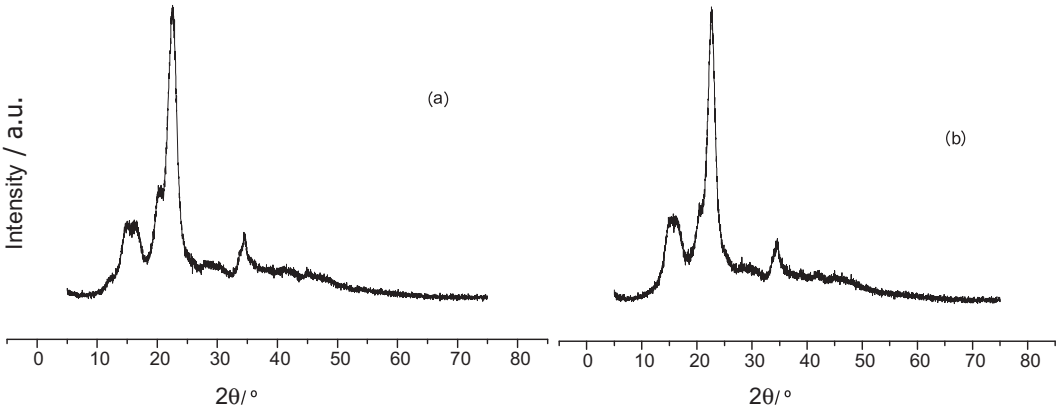

Fig. 1. X-Ray diffraction of Pure-Cel(a) and Phosp-Cel (b).