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Eco-Friendly Porous Biocomposites Based on Cellulose Nanocrystalline Hydrogels: Development and Application to the Elimination of Removal of Methyl Red Dye in Aqueous Solutions

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ABSTRACT

Cellulose nanocrystals (CNCs) which were extracted from industrial cotton waste was used to develop a new eco-friendly porous biocomposite sorbent based on cellulose nanocrystalline hydrogels (PCCNCsH). These new Nanocrystalline cellulose gelled beads is of interest in water purification technologies due to their high specific surface areas, excellent mechanical properties, biodegradability and non-toxicity. After bleaching, alkali and acid treatments of industrial waste cotton, the colloidal suspension of cellulose was freeze-dried for 24 hours to produce a white nanocrystalline cellulose powder. The obtained CNCs were immobilized in sodium alginate (NaAlg) gels to develop a new class of porous gelled biocomposite beads. Fourier Transform Infrared Spectroscopy (FTIR) as well as X-Ray Diffraction (XRD) analysis were used to characterize these novel porous hybrid sorbents. PCCNCsH were used as sorbents to remove methyl red (MR) batch wise and in aqueous solutions. The corresponding tests were conducted by examining the effects of sorbent dose, contact time, pH and initial dye concentration. The maximum sorption capacities of MR on the porous biocomposite based on cellulose nanocrystalline hydrogels was 21 mg/g for the optimum conditions were pH = 2, initial concentration of dye = 10 mg/L, contact time = 250 min and PCCNCsH dose = 0.2 (w/w). The kinetic sorption of methyl red on PCCNCsH sorbent best followed the pseudo-second order (PSO). The modeling of obtained sorption isotherms showed an appropriate fit for Langmuir model since the sorption isotherms are very closely ($R^2 = 0.977$).

Keywords: Nanoscale materials, cotton waste valorization, methyl red, sorption.

1 Introduction

A key natural resource in human life is water and in estimation, it covers about 70% of the earth's surface [1]. Due to the increase of water consumption, water quality is facing severe challenges. Industrialization, agricultural production, and urban life have resulted in the degradation and pollution of the environment, adversely affecting the water bodies (rivers and oceans) necessary for life, ultimately affecting human health and sustainable social development [2]. Common pollutants that affect water include very dangerous organic substances such as oil products, dyes and detergents, inorganic substances such as heavy metals and acids, radioactive substances and pathogenic organisms. Dyes are usually classified into anionic, cationic, or nonionic dyes. This classification is on the basis of the charge of the chromophore group when dissolved in the aqueous solution [3]. In this way, several different adsorbents such as activated carbon, zeolites, modified clays, biosorbent and nanomaterials have been used to their remove. Cellulose is the most important plant component to substitute synthetic polymers, due to its being an inexpensive, nontoxic, and biodegradable polymer [4]. Actually, a new area of cellulose nanocrystalline applications is still under examination in some fields, including surface modifications and nanocomposites. This research is then focused in the elaboration of new porous cellulose nanocrystalline particles based on industrial waste cotton. Then, prepared porous biocomposite powder were incorporated into sodium alginate to from a hydrogel beads using CaCl_2 as a cross linking agent. The PCCNCsH gelled beads were further used as sorbent to remove methyl red from aqueous solutions.



2 Experimental

Extraction of cellulose from industrial waste cotton: A mass of 100g of industrial waste cotton was grounded by high speed blender. The cellulose was extracted in the following two stages: i_1 : The first step is devoted to the blanching treatment, i_2 : The second step involves immersing the pretreated cellulose for 2 h in NaOH solution to remove the non-cellulosic components, such as lignin, hemicellulose and residue. Preparation of cellulose nanocrystals: A quantity of the initially extracted cellulose was mixed with 100 mL of 40% H_2SO_4 and stirred for 1 h at 45 °C. After centrifugation, the products thus obtained designated by CNCs were freezing dried. Preparation of porous biocomposite gelled beads based on cellulose nanocrystals: A mass of 3g of CNCs powder was dispersed in 100 mL of 2% sodium alginate. The gelled beads obtained using a micropipette were stored in a $CaCl_2$ solution for 24 h. The sorption tests of methyl red onto the PCCNCsH sorbent were investigated under varying conditions of pH (2–10), sorbent dose (0.1–0.5 g), equilibrium sorption time (5 – 480 minutes) and dye initial concentration (10–50 mg/L).

3 Results and Discussion

As confirmed by the obtained FTIR spectra, nanocrystalline cellulose was successfully cross-linked with sodium alginate hydrogels. It was found that the presence of the functional groups on the surface of these new gelled bead sorbents contributed favorably to the sorption of MR. From the XRD results, the crystallinity index (ICR) calculated using Seagal's equation was found to be around 73% indicating that nanocrystalline cellulose from industrial cotton waste is highly crystalline in nature. The sorption of MR dye by the sorbent PCCNCsH seems to be very influenced by the pH since the highest retention is obtained in a very acidic medium (pH = 2). Indeed, the corresponding results show a strong elimination of around 83% corresponding to a sorption capacity (9 mg/g) obtained for the following experimental conditions: Co = 10 mg/L, sorbent dose = 0.2 g, contact time = 250 min, stirring speed = 200 rpm.

The sorption abilities of PCCNCsH follow PSO rather than PFO. The applicability of the PSO model indicates the interaction between MR dye molecules and a large number of hydroxyl groups (O-H) groups. Hence, the sorption system is therefore chemical sorption. The regression correlation coefficient of the Langmuir isotherm ($R^2 = 0.977$) compared to the other isotherms implies that the sorption isotherm data well fit the Langmuir isotherm.

4 Conclusions

The removal of MR dye from aqueous solutions by sorption onto a novel porous cellulose nanocrystalline gelled beads (PCCNCsH) was experimentally investigated. The corresponding sorption process has been shown to strongly depend both on the initial concentration and pH solutions. The maximum sorption capacity reached under acidic conditions (pH 2) for an initial concentration 10 mg/L, sorbent dose = 0.2 g, contact time = 250 min, stirring speed = 200 rpm. This new generation of porous biocomposite gelled beads produced from nanocrystals cellulose could be used appropriately to eliminate water-soluble organic pollutants in aqueous environments.

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