



Poly(methacrylic acid-co-maleic acid) grafted nanofibrillated cellulose as a reusable novel heavy metal ions adsorbent



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ABSTRACT

A poly(methacrylic acid-co-maleic acid) grafted nanofibrillated cellulose (NFC-MAA-MA) aerogel was prepared via radical polymerization in an aqueous solution using Fenton's reagent. The ensuing aerogel, in the form of a rigid porous material, was characterized by FTIR and NMR and used as an adsorbent for the removal of heavy metals from aqueous solutions. It showed an efficient adsorption, exceeding 95% toward Pb^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} when their concentration was lower than 10 ppm and ranged from 90% to 60% for a metal concentration higher than 10 ppm. Over 98% of the adsorbed metal ion was recovered using EDTA as a desorbing solution, and the subsequent washing allowed the aerogel to be reused repeatedly without noticeable loss of adsorption capacity. It was concluded that the (NFC-MAA-MA) aerogel may be used as a high capacity and reusable sorbent material in heavy-metal removing processes.

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1. Introduction

Water pollution by heavy metal ions is a worldwide issue and remains a topic of global concern, since wastewater collected from communities and industries must be drained back to the sea or land. Conventional methods for the removal of heavy metals from water are based on different approaches, such as adsorption, membrane, ion exchange and reverse osmosis, which are commonly applied to the treatment of industrial effluents (Fu & Wang, 2011). Among these techniques, adsorption offers the advantages of being easy to implement, flexible in design, and meeting requirements in terms of effluent standards (Babel & Kurniawan, 2003). In addition, owing to the reversible nature of most adsorption processes, the adsorbents can be regenerated by suitable desorption processes for multiple usage. Although activated carbon is the most widely used adsorbent material for wide ranges of pollutants including toxic heavy metals (Ioannidou & Zabaniotou, 2007), it is quite expensive to produce and its regeneration is time and energy consuming.

The use of bioadsorbents based on renewable resources as a low cost adsorbent for heavy metal ions has received increasing attention (Ioannidou & Zabaniotou, 2007; Varma, Deshpande, & Kennedy, 2004). Functional groups, such as carboxylate, hydroxyl, sulfate, amide, and amino groups appended on the bioadsorbents were responsible for metal binding (O'Connell et al., 2008).

However, since the density of these groups effective for metal binding is generally low, most lignocellulosic biosorbents do not show a high sorption capacity. The low available specific surface of the biopolymer and lignocellulosic biomass that does not exceed several $m^2 g^{-1}$ is another parameter limiting the adsorption capacity of the adsorbent. Different approaches have been explored to enhance the adsorption capacity and favor the widespread use of biopolymers for heavy metal remediation. The first of these methods involves a direct modification of the cellulose backbone with the introduction of chelating or metal binding functionalities producing a range of heavy metal adsorbents (Demirbas, 2008). Chemical grafting of selected monomers bearing metal binding moieties is another effective approach to improve the functional properties of natural biopolymers and boost their adsorption capacity. The combination of nanotechnology and chemical modification is an alternative approach offering a new technological platform to improve the metal binding efficiency of biobased adsorbents. As the size of biosorbents is reduced to nanoscale, the huge increase in the specific area is expected to provide an enhanced density of binding sites on the adsorbent.

Nanocelluloses are increasingly applied in purification technologies due to their high mechanical properties, high specific surface area and the capacity to undertake a wide possibility of surface modifications (Kalia, Boufi, Celli, & Kango, 2014; Maatar, Alila, & Boufi, 2013). Introducing carboxylate groups onto the surface of the nanofibers through TEMPO-mediated oxidation proved to be a facile functionalization route that enhanced considerably the adsorption of metal cations via coordination. This approach was successfully used by several authors to enhance the adsorption

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capacity of nanocellulose toward heavy metal cations (Saito & Isogai, 2005; Sehaqui et al., 2014). However, since the adsorption is driven by ion exchange processes and the surface charge density cannot exceed a critical threshold of 1.0–1.5 mmol g⁻¹, the adsorption capacity of the nanocellulose will be limited to a maximum of 500–700 μmol g⁻¹ for divalent cations. Accordingly, surface modification strategies of nanocelluloses were adopted to boost their adsorption capacity. For instance, aminosilane (APS) modified microfibrillated cellulose (MFC) was used to adsorb different divalent cations from aqueous solutions (Hokkanen et al., 2014). Succinic anhydride modified nanocellulose was found to effectively adsorb a wide range of divalent metal cations through an exchange process. The adsorbent could be regenerated after washing under ultrasonic conditions with an acid solution (Hokkanen, Repo, & Sillanpää, 2013).

In this study, NFC aerogels modified by graft copolymerization with methacrylic acid and maleic acid were used as heavy metal adsorbents. The evolution of the adsorption efficiency according to the metal concentration and metal type was investigated and a possible mechanism for the metal adsorption discussed.

2. Materials and methods

2.1. Materials

Methacrylic acid (MAA) and maleic acid (MA) were used as monomers. H₂O₂ (30% in water) and ferrous ammonium sulphate (FAS) were used as initiators. [Cd(NO₃)₂·4H₂O], [Pb(CH₃COO)₂·3H₂O], [NiSO₄·6H₂O], Zn(CH₃COO)₂ and disodium salt of ethylenediaminetetraacetic acid (EDTA) were used in sorption experiments. All the products were purchased from Aldrich.

2.2. Preparation of nanofibrillated cellulose

Nanofibrillated cellulose (NFC) was prepared from bleached eucalyptus pulp (*Eucalyptus globulus*) using a high pressure homogenizer (NS1001L PANDA 2K-GEA) following the procedure described elsewhere (Besbes, Rei Vilar, & Boufi, 2011). Briefly, the bleached cellulose fibers were first oxidized to a level of 500 μmol g⁻¹. Then fibrillation was carried out by passing the fiber suspension (2 wt%) through the homogenizer 10 times at a pressure of 600 bars. The ensuing product was a high viscosity translucent gel. The cellulose nanofibrils had a cross-sectional diameter of 5–20 nm and lengths of a few micrometers.

2.3. Adsorbent preparation

The modified NFC aerogel was prepared in two steps. In the first step, an NFC-aerogel was prepared by freeze-drying and then subjected to surface modification by graft copolymerization.

2.3.1. NFC-aerogel preparation

The NFC gel was packed in a glass cylindrical tube (h/D: 20/20 mm) and kept at -20 °C for 24 h to freeze the gel. Thereafter, the frozen sample was transferred to a vacuum chamber at -20 °C and freeze dried at a pressure of 0.05–0.02 mbar for 20–24 h until complete water sublimation.

2.3.2. Graft copolymerization

The graft copolymerization of NFC aerogel was achieved by the radical copolymerization of methacrylic acid and maleic acid using the Fe²⁺/H₂O₂ redox system. In a typical reaction, 10 pellets of NFC aerogel (with a total weight of about 1 g) were introduced in 100 ml of water and a mixture of MAA and MA (5 g/5 g in 50 ml water) was added. The reaction flask was bubbled with nitrogen

for 15 min to remove atmospheric oxygen and a continuous supply of nitrogen was maintained throughout the reaction period. Then, the reaction flask was placed in a water bath at 50 °C and the initiator, comprising 10 ml of H₂O₂ (10⁻² M) and 10 ml of freshly prepared FAS (10⁻³ M), was added dropwise for 2 h to initiate the polymerization. Afterwards, the aerogel foam was removed and subjected to Soxhlet extraction with water for 24 h to remove the homopolymers likely to be formed. Then the aerogel was freeze dried at a pressure of 0.05–0.02 mbar for 24 h for complete water sublimation.

The grafting yield *G* was calculated from the increase in weight of NFC aerogel after grafting in the following manner:

$$G(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where *W*₁ and *W*₂, denote, respectively, the weights of the original NFC aerogel, the G-NFC (grafted-NFC) after water extraction and drying.

2.4. Characterization of the aerogel

The specific surface areas were determined by N₂ adsorption/desorption measurements at the temperature of liquid nitrogen (ASAP, 2020, Micromeritics, USA). The surface area was determined from the adsorption results using the Brunauer-Emmet-Teller (BET) method.

Observation of the morphology of the NFC aerogel was performed by scanning electron microscopy (SEM) using a (JEOL JSM-6390LV) operating at 5–10 kV. Prior to the analysis by SEM, the surface was coated with a gold/palladium layer. For higher magnification observation of the cell wall of the aerogel, Field-effect SEM microscopy was used by depositing a thin sample on a carbon tape followed by a coating with a thin platinum layer.

Densities of the samples were determined by weighing the aerogel and measuring their dimensions. Dimensions for each aerogel were taken at least at three different positions, and a minimum of two samples were used for density determination.

The porosity *P* of the aerogel is defined as $P = (1 - d_a/d_b) \times 100$, where *d*_a and *d*_b (1.56 g cm⁻³) are the densities of the aerogel and the density of the bulk cellulose fibril, respectively.

2.5. Adsorption experiments

The weighted NFC-aerogels were added to a flask containing 50 ml of metal solution, and the flask placed in a thermostated water bath shaker operated at 150 rpm at the desired temperature for 3 h. In all the experiments, the amount of dried gel sorbents was kept at around 200 mg. To obtain the equilibrium data, the initial concentration of the metal solutions was varied, while the amount of the adsorbent was kept constant. The initial pH values of the solutions had been previously adjusted with diluted HCl (0.01 M) using a pH meter. The concentration of the residual metal remaining in the aqueous solution was then analyzed, after suitable dilution, by atomic absorption using a Perkin-Elmer 560 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

The amount of adsorption, *q* (mg g⁻¹) was calculated as follows:

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

where *C*₀ (mg/l) and *C*_e (mg/l) are the initial and final metal concentrations of the solution, respectively, *V* (ml) is the volume of the metal solution, and *m* (g) the weight of the aerogel.

Each aerogel pellet has a weight of about 0.2 g and exhibited a hydrophilic property. It was immediately wetted with the solution without any change in its volume.

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