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Lead adsorption with sulfonated wheat pulp nanocelluloses

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ABSTRACT

Low-cost sorbents derived from abundant natural resources, industrial by-products, or waste materials are considered amongst the most viable novel materials for heavy metal removal. In this study, wheat straw pulp fine cellulosics were used as a biosorbent for the removal of Pb(II) in aqueous solutions after nanofibrillation and sulfonation pretreatments. The effect of the initial lead concentration, sorption time, and solution pH were studied, and the isothermal data were modeled with the Langmuir and Freundlich isotherm models. Pb(II) was adsorbed efficiently (1.2 mmol/g) from the model solution by sulfonated nanocelluloses which had a width between 5 and 50 nm and a sulfonic acid content of 0.45 mmol g^{-1}. This adsorption capacity is comparable to those of commercial adsorbents. The Pb(II) adsorption onto nanofibrillated and sulfonated cellulosics followed the Langmuir isotherm model and showed rapid initial kinetics. Thus, nanofibrillated and sulfonated cellulosics are promising green alternatives for the recovery of metals from aqueous solutions.

1. Introduction

Environmental toxins, including heavy metals, enter the food chain through drinking water and crop irrigation, which is an extensive problem in several countries [1]. Additionally, industrial activities produce wastewaters that are contaminated by toxic heavy metals. The mining, metallurgical, electroplating, electronic, nuclear and other water-intensive industries are major causes of ground water contamination by heavy metals [2]. Commonly, dissolved metal ions are removed from dilute wastewaters using conventional physicochemical methods, such as chemical reduction, an electrochemical treatment, ion exchange, precipitation, evaporative recovery, or adsorption onto activated carbon [3–5]. However, in many cases, these methods are expensive and inefficient [2–4]. Consequently, low-cost sorbents derived from abundant renewable resources, industrial by-products, or waste materials are considered amongst the most viable novel alternatives for heavy metal removal [1,3,6,7]. Cellulosic waste materials, such as sugarcane bagasse [8,9], cotton linters [10], and wheat straw [11,12] have been investigated for the adsorption of, for example, Cd(II), Cu(II), Mn(II), Mg(II), Sr(II) and Pb(II) ions. Wheat straw pulp is produced from the agricultural residues of food production and, therefore, is a potential sustainable renewable cellulosic source. The fine material fraction (usually <200 μm) of wheat straw pulp in particular is a potential cellulosic raw material for use as a biosorbent because it decreases the feasibility of using wheat pulp for papermaking. However, fine fractions of fractionated wheat straw pulps have not yet been investigated as a heavy metal adsorbent.

Nanofibrillation, i.e., the liberation of nanosized constituents from the cell wall matrix of plant fibers, produces a cellulosic material with a very high surface area of 170–246 m^2/g (as measured for a nanocellulose and polypyrrole aerogel composite [13]) that is covered with anionic hydroxyl groups, the latter assumed to be beneficial for adsorption. Cellulose can be easily chemically modified, which enables the addition of various functional groups to the cellulose backbone [14]. In turn, this addition enhances the uptake of specific metal ions [15] and improves the adsorption capacity of cellulosics. One potential, environmentally sustainable method for introducing reactive aldehyde functionalities into cellulose is aqueous periodate oxidation [16,17]. Aldehyde groups of 2,3-dialdehyde cellulose (DAC) can be further converted easily and selectively with various functionalities, such as carboxylic acids [18,19], sulfonates [20–22] or imines [23]. Therefore, periodate-oxidized and selectively functionalized nanocellulose from the cellulosics of wheat pulp fines may be a suitable material for metal ion adsorption in water. Sulfur containing ligands are known to act as soft acids that have high affinity toward Pb(II) ions with high selectivity and reversibility [24,25]. Our recent studies have shown that the periodate-sulfonation reaction is a potentially green method to

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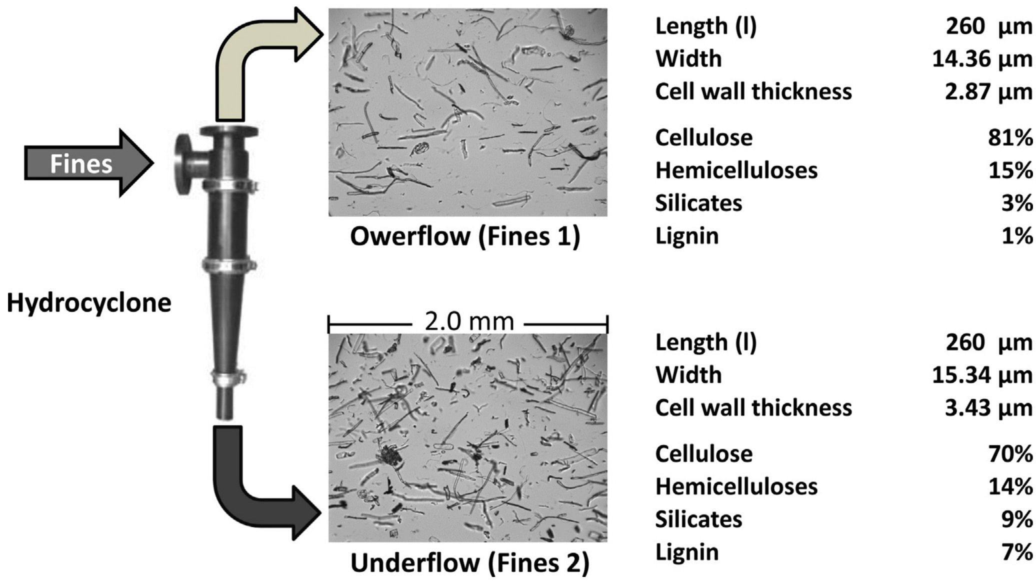

Fig. 1. Obtained wheat straw pulp fine fractions using a hydrocyclone, and the physical and chemical parameters of the fractions.

produce nanocellulose, as it avoids the production of halogenated wastes, because the periodate used can be efficiently regenerated and recycled back to the oxidation reaction [26].

The objective of the present study was to use the fine fractions of wheat straw as a biosorbent after nanofibrillation and subsequent periodate-sulfonation pretreatments for the removal of Pb(II) in aqueous model solutions. The effects of the initial lead concentration, sorption time, and solution pH were studied. Moreover, the adsorption isotherms of lead were determined in order to study the adsorption mechanism.

2. Materials and methods

2.1. Raw material and chemicals

Dry sheets of bleached wheat straw pulp (*Triticum aestivum* L.) were used as a cellulosic raw material for the experiments. The pulp was fractionated into fines and fiber fractions using a pressure screen after disintegration in deionized water. The fine fractions (39% w/w from the whole pulp) were fractionated further into two fractions, according to density and size differences, using a hydrocyclone (Fig. 1). These two fractions, i.e., the hydrocyclone overflow (Fines 1) and underflow (Fines 2), were thickened by settling and were used as raw materials in the homogenization and sulfonation pretreatments. The silicate, hemicellulose and lignin contents of the pulp were determined using the ISO 1762, TAPPI-T-212 and TAPPI-T-222 standards, respectively. The physical parameters of the fine fractions were measured by a Metso FiberLab image analyzer (Finland). The chemical compositions and physical parameters of the wheat pulp fine fractions are shown in Fig. 1.

The fine fractions were suspended in deionized water with a 0.5% consistency and converted into nanofibrils using a two-chamber high-pressure homogenizer (Invensys APV-2000, Denmark) with a pressure of 400–900 bar. The suspensions were passed through the homogenizer eight times to obtain nanofibrillar cellulose gels (NFC 1 and NFC 2).

All of the chemicals that were used in the adsorbent synthesis and characterization were obtained as p.a. grade from Sigma–Aldrich, Germany and were used without further purification. Deionized water was used throughout this work.

2.2. Synthesis of the sulfonated nanofibrillar cellulose adsorbents

Anionic sulfonated cellulose derivatives (SNFC 1 and SNFC 2) were synthesized by consecutive periodate oxidation and sodium metabisulfite sulfonation using NFC 1 and NFC 2 as the starting materials. The synthesis was conducted as reported previously for chemical bleached birch pulp [20] with small modifications. In brief, the vicinal hydroxyl groups at positions 2 and 3 of the homogenized cellulose fines (NFC 1 and NFC 2) were first oxidized using sodium metaperiodate to produce aldehyde groups (1.31 mmol/g), and the aldehyde groups were then sulfonated using sodium metabisulfite (NaS_2O_5 which reacts with water to form $NaHSO_3$) (Fig. 2).

The suspensions were centrifuged after 72 h of the sulfonation reaction, which was conducted at room temperature in an aqueous solution, and were washed until the conductivity of the suspensions was <20 μS/cm. The anionic charge density of the samples was analyzed by conductometric titration using a procedure that was described by Katz et al. [27] and by Rattaz et al. [28]. The mass yields of the reactions were measured by weighing the obtained products on an analytical balance.

2.3. Characterization of the sulfonated nanofibrillar cellulose adsorbents

2.3.1. Size fractions of the adsorbents

A fractional size analysis of the nanocellulose adsorbents was conducted with a chromatographic washer using a continuous water flow in a long tube. The nanocelluloses were washed in a long plastic tube (diameter of 4 mm) with 1000 ml of deionized water for 108 s at a flow rate of 7.5 ml/s. In this tube, the particles flow with different average velocities according to their size such that the largest particles tend to stay in the middle of the tube, i.e., in the faster flow, longer. Thus, these particles emerge first from the end of the long tube [29]. A 5 ml sample was injected into the washer with a 0.1% consistency in a constant water flow, and four different size categories were obtained by taking samples after separation times of 60, 77, 86 and 95 s. The largest particles were visualized with a CCD camera (resolution of 1.6 μm), and the amounts of material in the different fractions were measured by filtering the samples on a membrane (retention of 0.2 μm), followed by weighing. Fractions were also collected for further analysis with FESEM.