Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose

Sanna Hokkanen [*], Eveliina Repo [1], Mika Sillanpää [1]

Laboratory of Green Chemistry, Department of Energy and Environmental Technology, Faculty of Technology, Lappeenranta University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland

HIGHLIGHTS

▶ Novel adsorbents combined beneficial properties of modified nanocellulose.
▶ Succinic anhydride modified merzerated nanocellulose were effective adsorbents for heavy metals.
▶ Modified nanocellulose could be regenerated after ultrasonic treatment.
▶ Porosity of the hybrid adsorbents affected the kinetics of the metal adsorption.
▶ Adsorption isotherms depended on the type of metal.

ARTICLE INFO

ABSTRACT

In this study, the removal of Zn(II), Ni(II), Cu(II), Co(II), and Cd(II) ions from aqueous solutions was investigated using succinic anhydride modified mercerized nanocellulose. The modified adsorbents were characterized using FTIR and SEM analyses. FTIR results showed the bands related to carboxyl groups and SEM-images clear increase in crystallinity after modification of nanocellulose. The effects of pH, contact time, regeneration, and the concentration of metals were studied in batch mode. The maximum metal uptakes ranged from 0.72 to 1.95 mmol/g following the order of: Cd > Cu > Zn > Co > Ni. Adsorption isotherms were demonstrated using Langmuir and Sips models with wet and dry weight of adsorbent. Both models were representative to simulate adsorption isotherms. Regeneration of the modified nanocellulose was accomplished using nitric acid and ultrasonic treatment.

1. Introduction

Investigation of heavy metals contaminated water has become essential focus of environmental scientists in recent years. The heavy metals in water could be derived from natural sources like volcanoes, weathering and erosion of bed rocks and ore deposits but also numerous anthropogenic activities, such as mining, industries, wastewater irrigation, and agriculture activities [1–3].

Heavy metals are essential to living organisms at low concentrations, but many of them are toxic at elevated concentrations [4]. Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, autoimmunity, and even death in extreme cases [5]. Therefore, their removal from contaminated, water is required prior to discharge. Metal removal from the waste streams is of relevance not only due to their toxicity but also due to the possibility to reuse metals in various industrial applications.

Conventional methods employed for the removal of heavy metal ions from industrial effluents include chemical precipitation, flocculation, membrane separation, ion exchange, evaporation, and electrolysis. Most of these methods are often costly or ineffective, especially in removing heavy metal ions from dilute solutions [6–8].

Adsorption has been shown to be one of the most efficient and technically feasible methods for the metal removal from aqueous solutions. Activated carbon is the most widely used adsorbent throughout the world for this purpose. However, it possesses disadvantages related to high operating costs, low selectivity, and its complex thermal regeneration requirements. Therefore, development of alternative adsorption materials is constantly under an intensive study. For example, natural bentonite [9,10], combination of natural zeolite–kaolin–bentonite [11], fruit peel [12,13], chitosan [14–16], and anaerobic granular sludge [17,18] have been tested for heavy metal removal. Heavy metal adsorption by inherently formed iron-based water treatment residuals (WTRs) and a boron processing waste (BW) has also seldom studied [19,20]. Promising materials for metal recovery are adsorbents functionalized with different

chelating agents. This is due to the strong affinity of chelate forming groups towards metal ions, selectivity, and the possibility to regenerate the metal loaded adsorbent by a simple acid treatment [21,22].

Cellulose is regarded as the most abundant and renewable biopolymer in nature. The ongoing global trend to promote the production and usage of sustainable and biodegradable materials from natural resources have increased interest towards novel, high-value cellulose-based products and it is one of the most affordable raw materials available for the preparation of various functional materials. Moreover, nano- and microcelluloses are considered to be amongst the most potential bio-based materials for future high-end applications [23,24]. There are very few functional groups in cellulose fiber that are able to capture metals. Hence, many methods have been used to utilize cellulose as a metal scavenger through some derivatizations. Some of these methods are based on using carboxylate and amine groups as chelating agents [25–27] or catalytic and selective oxidation of primary hydroxyl groups of cellulose [28,29]. Succinylation reaction has also shown to be an alternative in cellulose modification [24,30–32].

Gurgel proposed the mercerization treatment as a way of increasing the fibers specific surface area and to make the hydroxyl groups of cellulose macromolecules more easily accessible for the modification with succinic anhydride (succinylation) and as continuation of that study they have described the preparation of two new chelating materials containing amine groups from succinylated mercerized cellulose [8,33].

As noted above, there are a few studies of modified cellulose as adsorbent for heavy metals, but, to the best of our knowledge, there are no studies on modification of nano- and microcellulose for this purpose. Modification of nano- and microcellulose can provide effective, stable, and regenerable adsorbents for metal recovery from various kinds of wastewaters. This study describes the preparation and evaluation of mercerized and succinic anhydride modified micro/nano cellulose to adsorb Zn(II), Ni(II), Cu(II), Co(II) and Cd(II) ions in aqueous solutions. Studies on pH dependence, adsorption kinetics and isotherms were investigated. Regeneration studies, using different acids at different concentrations, were also examined.

2. Materials and methods

2.1. Materials

Microfibrillated cellulose (MFC) was purchased from University of Oulu, Finland. All chemicals used in this study were of analytical grade and supplied by Sigma–Aldrich. Stock solutions of 1000 mg/L were prepared by dissolving appropriate amounts of Zn(II), Ni(II), Cu(II), Co(II) and Cd(II) nitrate salts in deionized water. Adjustment of pH was accomplished using 0.1 M NaOH or 0.1 M HNO$_3$.

2.2. Cellulose mercerization

Microfibrillated cellulose (MFC) (30 g) was treated with 0.20 L of NaOH solution (20 wt.%) at room temperature at least 16 h with magnetic stirring. The alkali-cellulose was separated from the solution using centrifuge and washed with distilled water down to pH 7.

2.3. Synthesis of celluloses

Mercerized cellulose (20 g) was reacted with succinic anhydride (35 g) under pyridine reflux (0.17 L) for 24 h. The modified cellulose was centrifugated and filtered, washed in sequence with dimethylformamide (DMF), ethanol 95%, distilled water, HNO$_3$ (0.01 mol/L), distilled water and finally with acetone. In order to liberate carboxylate functions for a better chelating function than the carboxylic group, succinylated cellulose was treated with a saturated sodium bicarbonate solution for 30 min under constant stirring and afterwards filtered and finally washed with distilled water and then acetone.

2.4. Characterization of celluloses

Fourier transform infrared spectroscopy (FTIR) type Vertex 70 by B Bruker Optics (Germany) was used to identify the surface groups of the synthesized nanocellulose. Attenuated Total Reflectance (ATR) technique was used. The FTIR spectra were recorded at 4 cm^{-1} resolution from 400 to 4000 cm^{-1} and 100 scans per sample. The surface morphology of the different treatment phases was examined using a Hitachi S-4100 scanning electron microscope (SEM).

2.5. Batch adsorption studies

Applicability of modified cellulose for Zn(II), Ni(II), Cu(II), Co(II) and Cd(II) removal was studied using batch experiments in a reaction mixture of 0.02 g of adsorbent and 0.004 L of metal solution containing each metals at concentrations ranging from 0.1 to 10.0 mmol/L. using own decanter glass for each metal reaction mixture. The kinetic study was carried out using five different containers for each metal solution (0.05 L) and 5 g of adsorbent was weighted in each container. 0.002 L samples were pipetted from the reaction mixtures according to schedule. The contact time was varied from 5 to 1140 min resulting overall 90 samples. Implementation under the same conditions as in the other adsorption tests (0.02 g adsorbent and 0.004 L metal solution, reacting in own sample container) would been very difficult because of large number of samples. Agitation was conducted under magnetic stirring and measurements conducted at the room temperature and temperature of 10 °C.

After centrifugation metal concentrations were analyzed by an inductively coupled plasma optical atomic emission spectrometry (ICP-OES) model iCAP 6300 (Thermo Electron Corporation, USA). Zn(II) was analyzed at a wavelength of 202.548 nm, Ni(II) at 231.605 nm, Cu(II) at 324.754 nm, Co(II) at 228.616 nm, and Cd(II) at 226.502 nm.

The amount of metal ions adsorbed per unit mass of modified nanocellulose (mmol/g) was calculated as follows:

$$q_e = \frac{(C_i - C_e)}{M} V \tag{1}$$

where C_i and C_e are the initial and the equilibrium concentrations (mmol/L), while M and V are the weight of the adsorbent (g) and the volume of the solution (L), respectively.

2.6. Regeneration studies

The regeneration of the modified nanocellulose was studied in Zn(II), Ni(II), Cu(II), Co(II) and Cd(II) solutions. At first adsorbents were loaded by metal ions by mixing 5 g of the adsorbent with 0.015 L of 1.8–3.4 mmol/L metal solution. Bigger dose was used in order to make separation of the adsorbent easier. After attaining equilibrium, the spent adsorbent was separated from the solution by centrifuge. Metal ions were eluted using 1 M HNO$_3$. The effect of different acids for the regeneration was tested with Zn(II) ions using 0.1 M formic acid, ascorbic acid, and acetic acid. The regeneration efficiency (%RE) of the adsorbent was calculated as follows:

$$(\%RE) = \frac{q_r}{q_0} \times 100 \tag{2}$$