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Adsorption of Co(II) and Ni(II) by EDTA- and/or DTPA-modified chitosan: Kinetic and equilibrium modeling

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ABSTRACT

The aim of the present study was to investigate the adsorption properties of surface modified chitosans in the aqueous solutions containing Co(II) and/or Ni(II) ions. For this purpose, the ligands of ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) were immobilized onto polymer matrices of chitosan. Adsorption of Co(II) and Ni(II) by prepared adsorbents was investigated in batch techniques. The effects of pH, functional group, contact time, and the concentration of metals were studied. Metal uptake by EDTA-chitosan was 63.0 mg g^{-1} for Co(II) and 71.0 mg g^{-1} for Ni(II) and by DTPA-chitosan 49.1 mg g^{-1} for Co(II) and 53.1 mg g^{-1} for Ni(II). The adsorption efficiency of studied adsorbents ranged from 93.6% to 99.5% from 100 mg L^{-1} Co(II) and/or Ni(II) solution, when the adsorbent dose was 2 g L^{-1} and solution pH 2.1. The kinetics of Co(II) and Ni(II) on both of the modified chitosans followed the pseudo-second-order model but the adsorption rate was also influenced by intraparticle diffusion. The equilibrium data was best described by the Sips isotherm and its extended form was also well fitted to the two-component data obtained for systems containing different ratios of Co(II) and Ni(II). Nevertheless, the obtained modeling results indicated relatively homogenous system for Co(II) and heterogeneous system for Ni(II) adsorption.

1. Introduction

The increasing level of toxic metals such as Co(II) and Ni(II) that are discharged into the environment as industrial wastes, represent a serious threat to human health, living resources, and ecological systems [1]. Co(II) is present in the wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments, and electro-engineering [2]. Ni(II) is widely used in silver refineries, electroplating, zinc base casting, and storage battery industries [3].

Various technologies have been applied to remove Co(II) and Ni(II) from waste streams. These include chemical precipitation [4], chemical oxidation/reduction [5], and electrochemical treatment [6]. However, all of the above methods have disadvantages making them less technically appealing in wastewater treatment. Precipitation is ineffective and produces a lot of sludge, chemical reduction/oxidation requires extra chemicals and electrochemical treatment has high operating costs [7,8].

One of the most effective methods for the removal of Co(II) and Ni(II) from wastewater streams is adsorption. Activated carbon has been the most popular material in wastewater treatment for heavy metal removal. However, the high cost of this material makes its application less economically attractive in industrial scale [9]. Cation-exchange resins used for Co(II) and Ni(II) removal can produce treated effluents that contain metals less than the required discharge limits [10]. However, commercial resins remain expensive materials [7]. To reduce the operational costs, the search for alternative adsorbents has intensified in recent years. For example, natural bentonite [2], orange peel [11], chitosan [12–15], and anaerobic granular sludges [16,17] have been tested for heavy metal removal. However, these materials have usually low adsorption capacities in as-received forms. To improve their performance, non-conventional materials such as chitosan needs to be modified chemically.

Due to the reactivity of amine groups and stable chelation, chitosan can be functionalized to improve its adsorption properties [15]. Chemical modification of chitosan with chelating agents such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), which form very strong chelates with metal ions [18,19] may produce adsorbents with excellent metal binding properties. The environmental fate of these chelating agents has received attention, but, when immobilized, EDTA and

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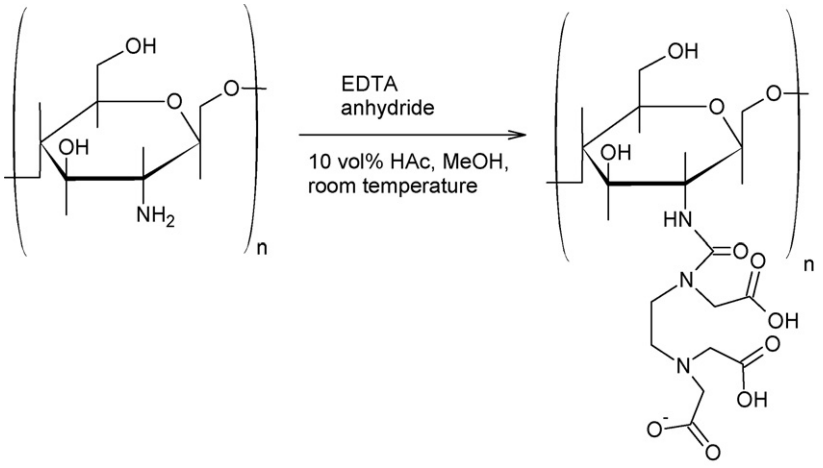

Fig. 1. Synthesis of EDTA-chitosan.

DTPA are not expected to be environmentally critical compounds [20]. Inoue et al. studied quite extensively adsorption of metals such as Cd, Fe, Cu, Ni, Co, and Zn by EDTA- and DTPA-chitosans [21,22]. However, their work lacked of simulation modeling of adsorption kinetics and isotherms of the adsorbents as well as adsorption mechanism and regeneration studies. Therefore, the aim of this study was to investigate the adsorption properties of these promising materials in more detail.

In the previous study, we investigated the applicability of EDTA- and/or DTPA-modified silica gels to remove Co(II) and Ni(II) from contaminated water at optimized conditions [23]. In this work, EDTA- and DTPA-chitosans were used to adsorb Co(II) and Ni(II) from aqueous solutions. The effects of variables including the type of chelating agent, metal concentration, and pH on the adsorption capacity, selectivity and desorption properties of the modified chitosan were considered. To investigate the mechanism of adsorption the gathered experimental data was fitted to kinetic and equilibrium models. Furthermore, equilibrium behavior of modified chitosans was investigated in Co(II)/Ni(II) two-component systems and obtained data modeled using binary isotherm selected based on the modeling results of one-component systems.

2. Methods

2.1. Materials

Chitosan flakes >85% deacetylated supplied by Sigma–Aldrich had molecular weight ranging from 190,000 to 375,000 g mol^{-1} and viscosity of 200–2000 MPa. All other chemicals used in this study were of analytical grade and supplied by Merck (Finland). Stock solutions of 1000 mg L^{-1} were prepared by dissolving appropriate amounts of Co(II) and Ni(II) nitrate salts in double deionized water. Working solutions ranging from 1 to 200 mg L^{-1} of Co(II) or Ni(II) were prepared by diluting the stock solutions. Adjustment of pH was carried out using 0.1 M NaOH and 0.1 M HNO_3.

2.2. Synthesis of EDTA- and/or DTPA-modified chitosan

To improve its reactivity, chitosan was functionalized with EDTA and/or DTPA according to Nagib et al. [22] (Fig. 1). About 10 g of chitosan was dissolved in 200 mL of 10% (v/v) acetic acid and then diluted five times with methanol. Afterwards, approximately 60 g of EDTA anhydride synthesized according to Tülü and Geckeler [24] suspended in methanol was added and the mixture was stirred vigorously for 24 h in room temperature. After filtration the precipitation was mixed with ethanol (AA) and subsequently stirred for another 16 h. Then the precipitation was washed with NaOH solution (pH 11) to remove unreacted EDTA. Finally, EDTA-modified chitosan was washed with deionized water, 0.1 M HCl, again deionized water, and ethanol. The final product was dried in an oven at 40 °C for 48 h and stored in a desiccator. Using the same method, the chitosan was functionalized with DTPA.

2.3. Characterization of modified chitosans

The formation of additional functional groups on chitosan surface after modification with EDTA and/or DTPA was studied using a FTIR-spectroscope type Nicolet Nexus 8700 (USA). Kjeldahl method was employed to determine the amount of nitrogen in the modified chitosans [25] and the results were used to determine the surface coverage of EDTA and DTPA on the adsorbents. The specific surface area and total pore volume of modified chitosans were measured with Autosorb-1-C surface area and pore size analyzer (Quantachrome, the UK).

2.4. Batch adsorption tests

Applicability of modified chitosans for Co(II) and Ni(II) removal was studied using batch experiments in a reaction mixture of 0.01 g of adsorbent and 0.005 L of metal solution containing Co^{2+} and/or Ni^2 at concentrations ranging from 1 to 200 mg L^{-1}. To study adsorption equilibrium in binary systems, solutions containing Co(II) and Ni(II) at ratios of 1:1, 2:1, and 1:2, where total concentration of metals varied from 1 to 500 mg L^{-1}, were used. The effect of pH was studied at metal concentration of 100 mg L^{-1} in the pH range of 1–7. Alkalic solutions were not used to avoid the hydroxide formation (Visual MINTEQ ver. 2.53). The effect of contact time was studied at metal concentrations of 20 and 100 mg L^{-1}. Agitation was undertaken using a rotary shaker type ST5 (CAT M.Zipperer GmbH, Staufen, Germany). At designated contact time, the adsorbent was separated from the solution using 0.45 μm polypropylene syringe filter. After dilution with 2% HNO_3, the metal concentrations in the filtrates were analyzed by an inductively coupled plasma optical atomic emission spectrometry (ICP-OES) model iCAP 6300 (Thermo Electron Corporation, USA). Co(II) was analyzed at a wavelength of 228.616 nm, while Ni(II) was detected at 231.605 nm. The detection limits for Co(II) and Ni(II) were 0.4 and 0.8 μg L^{-1}, respectively. The adsorption capacities (mg g^{-1}) of modified chitosans were calculated as follows:

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