Mercury sorption on a thiocarbamoyl derivative of chitosan

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ABSTRACT

The grafting of thiourea on chitosan backbone allows synthesizing a thiocarbamoyl derivative that was very efficient for mercury sorption in acidic solutions. Though the sorption capacity is not increased compared to raw chitosan in near neutral solutions, this modification allowed maintaining high sorption capacity (close to 2.3 mmol Hg g^{-1}) at pH 2. Mercury sorption in acidic solutions is not affected by the presence of competitor metals (such as Zn(II), Pb(II), Cu(II), Cd(II), Ni(II)) or the presence of nitrate anions (even at concentration as high as 0.8 M)). The presence of chloride or sulfate anions (0.8 M) decreased Hg(II) sorption capacity to 1 mmol Hg g^{-1}. Kinetics are controlled by a combination of pseudo second-order reaction rate and resistance to intraparticle diffusion. Mercury desorption reached about 75% using thiourea (in HCl solution).

1. Introduction

Due to the toxicity and accumulation effects of metals ions in the food chain, these micro-pollutants are extensively surveyed and the national and international regulations are becoming more and more drastic. The dramatic example of contamination in Minamata (Japan) showed the potential impact of the accumulation of mercury in the food chain on population health. Conventional processes for the recovery of mercury from industrial effluents consist in precipitation [1–4], cementation [5], ion exchange [6–9], solvent extraction [10–13] and adsorption [6,14–21]. Sorption processes may use synthetic resins but an increasing interest has been focused on biosorbents for the last decades. Biosorbents may consist of biomass [22–24], agriculture waste [22,25], biopolymers such as chitosan [26–30]. Chitosan (β-(1–4)-linked D-glucosamine) is obtained by the deacetylation of chitin (β-(1–4)-linked N-acetyl-D-glucosamine), one of the biopolymers the most abundant in nature. This biopolymer is characterized by its high ratio of amine groups, it is very efficient for metal binding through different mechanisms [31]. The binding of metal cations may occur by complexation on amine groups in near neutral solutions [32,33], while metal anions can bind to protonated amine groups in acidic solutions [34–36]. The intrinsic pK of amine groups in chitosan strongly depends on

the degree of acetylation and the degree of neutralization of amine groups. However, it is close to 6.5 with commercial samples (degree of acetylation close to 15%). The presence of chloride ions in the solution may induce the formation of chloro-anionic species that can bind to protonated amine groups [37,38]. Chitosan is soluble in acidic solution, except in sulfuric acid media; the biopolymer is thus frequently cross-linked for improving its stability in acidic solutions. Glutaraldehyde is a dialdehyde that contributes to establish supplementary linkages (Schiff's base reaction between aldehyde functions and amine groups) between the polymer chains and to stabilize the polymer in acidic media [32,33,39]. The cross-linking may reduce the availability and reactivity of amine functions for chelation [40], and in the case of ion exchange/electrostatic attraction mechanism the presence of anions strongly decreases sorption performance (competition effect) [41]. To prevent these limiting effects, a number of chitosan derivatives have been synthesized [38,42–45], with the objectives of increasing the density of reactive groups (aminated chitosan) [44,46,47], or to improve sorption selectivity (grafting of sulfur compounds for example). Different strategies have been developed including (a) the grafting of thiourea or other sulfur compounds (dithioxamide, for example) through reaction with glutaraldehyde (as a linking agent) [48,49], http://www.lwr.kth.se/English/OurSoftware/vminteq, (b) the grafting of cysteine on chitosan backbone [50–52], and (c) the grafting of mercaptoacetamide [53]. The main drawback of these procedures is the limited pH range for efficient use or the lack of stability of the sulfur compounds (degradation of sulfur

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groups). Though most of the mercury-containing effluents at industrial scale are alkaline solutions (for example chlor-alkali industry), the recovery of mercury from acidic solutions is retaining attention in hydrometallurgy for example (processing of copper ores, for example) [54,55]. The present work describes a new procedure for the synthesis of a series of thiocarbamoyl derivatives of chitosan (including a cross-linking treatment with glutaraldehyde) and investigates their sorption properties for mercury. The reaction pathway is different to the procedures described in the literature (cysteine grafting, thiourea grafting through glutaraldehyde linkage, the grafting of mercaptoacetamide, etc.) and the procedure allows reaching high substitution degree. Apart of sorption isotherms, the influence of several parameters on sorption has been tested: pH (and effect of the acid used for pH control), presence of competitor ions on equilibrium (sorption isotherms) and influence of metal concentration, agitation speed and sorbent dosage (uptake kinetics). Finally the possibility to desorb mercury from loaded resin is investigated.

2. Materials and methods

2.1. Material

Chitosan was purchased from JSC "Sonat" (Moscow, Russia). Degree of acetylation (DA) was determined by ^1H NMR spectroscopy to be 0.16; while the average molecular mass of $2.5 \times 10^5 \, g \, mol^{-1}$ was established using viscometry [56]. All other chemicals for sorbent synthesis were of analytical grade and were used without further purification.

For sorption experiments, metal salts were supplied by Fluka (Switzerland) as analytical grade salts (under the form of chloride salts).

2.2. Sorbent synthesis

Previous investigations at the I. Ya. Postovsky Institute of Organic Synthesis (U.D.R.A.S.) have contributed to select optimum conditions for thiol grafting. Varying the reaction temperature it appeared that below 110 °C, the kinetics of the conversion was substantially reduced, while at temperature greater than 150 °C, the partial degradation of the polymer matrix limited the efficiency of the synthesis. A temperature in the range 110–130 °C appeared optimum. The reaction time was also varied: when the reaction time was lower than 4 h the substitution degree was low (less than 0.3); when the reaction time exceeded 6 h the substitution yields remained constant. A reaction time of 5 h was considered as the optimum. Actually, under optimal conditions the substitution yield varied between 0.5 and 1.1 depending on the ratio of reagents.

The modification of chitosan (thiocarbamoylation) was operated using the following procedure:

(a) 20 g (0.12 mol) of chitosan was mixed with 25.6 g (0.34 mol) of ammonium thiocyanate and 12.2 g (0.16 mol) of thiourea.
(b) The mixture was heated below 130 °C for 10 min (formation of a gel-like mass).
(c) The gel was heated at 130 °C for 4 h before being cooled.
(d) The gel was finally rinsed with water until the reaction of the water phase with ferric ions became negative (complete removal of unreacted SCN^-), and air-dried.

The synthesis yield reached 22.8 g.

The cross-linking treatment was operated by contact of the thiocarbamoyl derivative with glutaraldehyde [57]. 16 g of thiocarbamoyl chitosan (10.6 mmol amine groups, degree of substitution DS: 0.68) were dispersed in 90 mL of water. The cross-linking solu-

tion was prepared by mixing 1.7 g of glutaraldehyde (25% solution, 4.48 mmol) with 30 mL of water. The cross-linking solution was mixed with the slurry (thiocarbamoyl chitosan) for 24 h at 24 °C. The solid was thus filtered and dried at 50 °C.

Two lots of sulfur derivative of chitosan have been prepared following the same procedure. They will be called S1 and S2 sorbents. These materials have been separated in two fractions: the first fraction has been used as synthesized; the second fraction of the sulfur derivative was chemically cross-linked with glutaraldehyde. Cross-linked materials have been called S1C and S2C, respectively.

2.3. Sorbent characterization

Element analysis was performed using an Elemental Analyzer Perkin Elmer. FT-IR spectra were recorded on a "Spectrum One" FT-IR spectrometer (Perkin Elmer) using (a) a Diffuse Reflectance Sampling Accessory (DRA); or (b) a Smart Orbit Accessory for Single-Reflection Attenuated Total Reflectance (ATR) (see Additional material). Solid-state ^{13}C NMR spectra were registered on a spectrometer Bruker Avance AV-300 at 300 MHz.

2.4. Sorption and desorption experiments

The pH of initial solutions was controlled using NaOH and either H_2SO_4 or HCl. The acid was changed to verify if the acid used can impact metal speciation and thus its sorption. The pH was not controlled during the sorption but it was measured at the end of each experiment.

Sorption isotherms were obtained by contact of a given amount of sorbent (i.e., 20 mg) with 150 mL of solution containing increasing concentrations of mercury (in the range 0–100 or 0–200 mg Hg L^{-1}) at target pH (pH 2, 5 and 7). A sample was collected after 4 days of agitation and filtered before being analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES JY 2000, Jobin Yvon, Longjumeau, France). The mass balance equation was used for the calculation of sorption capacity (metal concentration in the sorbent). The equilibrium pH was systematically measured at equilibrium. For the isotherm at pH 2, the equilibrium pH varied by less than 0.1 unit (between 1.9 and 2.1). For the isotherm at pH 5, the equilibrium systematically decreased in the range 3.7–4.3 when pH was controlled with sulfuric acid and in the range 3.3–4 when hydrochloric acid was used for initial pH control. Similar experimental procedures were used for the determination of sorption performance at equilibrium when investigating the effect of pH, the influence of the presence of competitor ions (metal salts or anions, which were directly added to metal solution as solid-state salts).

Kinetics was performed in batch reactor; the sorbent, at the appropriate sorbent dosage (SD), was added to 1 L of solution with known initial concentration. Samples were regularly collected, filtered and analyzed for plotting the relative metal concentration (residual concentration divided by the initial concentration) versus time. Experimental conditions (SD, metal concentration, sorbent type, etc.) were varied and the values of the parameters will be systematically reported in the caption of the figures.

The desorption of mercury from loaded sorbents has been studied in two steps: (a) the mass balance equation was used to evaluate the amount of mercury adsorbed on the sorbent (SD: 0.2 g L^{-1}; C_0: 70 mg L^{-1}, pH 2 controlled with sulfuric acid; contact time: 4 days); and (b) the loaded sorbent (after being rinsed with water) was mixed with the eluent solutions (SD: 0.4 g L^{-1}; contact time 2 h). The eluate was filtered and analyzed using ICP-AES. The comparison of the amounts of metal successively adsorbed and desorbed was used for the calculation of desorption efficiency.