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A new chitosan biopolymer derivative as metal-complexing agent: synthesis, characterization, and metal(II) ion adsorption studies

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ABSTRACT

In this study, a new chitosan biopolymer derivative (CTSL) has been synthesized by anchoring a new vanillin-based complexing agent or ligand, namely 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1-yl)methyl] benzaldehyde, (L) with chitosan (CTS) by means of condensation. The new material was characterized by elemental (CHN), spectral (FTIR and solid state ^{13}C NMR), thermal (TG-DTA and DSC), structural (powder XRD), and morphological (SEM) analyses. The CTSL was employed to study the equilibrium adsorption of various metal ions, namely, Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II), as functions of pH of the solutions. Its kinetics of adsorption was evaluated utilizing the pseudo first order and pseudo second order equation models and the equilibrium data were analyzed by Langmuir isotherm model. The CTSL shows good adsorption capacity for metal ions studied in the order Cu(II) > Ni(II) > Cd(II) $\geqslant$ Co $\geqslant$ Mn(II) > Fe(II) > Pb(II) in all studied pH ranges due to the presence of many coordinating moieties present in it.

1. Introduction

Biosorption has recently received a great deal of attention due to the low cost of the materials used in these applications and for the environmentally friendly impact of the treatment of exhausted sorbents. Several types of biomass have been tested for the recovery of precious metals, including fungal biomass,[1,2] algal biomass but also polymers of biological origin.[3] Chitosan (CTS) (hetero polymer constituted of glucosamine and a fraction of acetylglucosamine residues) is a well-known biopolymer characterized by its high sorption properties due to its high nitrogen content. This biopolymer and its derivatives have great potential applications in the areas of biotechnology, biomedicine, food ingredients, and cosmetics because of their many useful features such as hydrophilicity, biocompatibility, biodegradability, anti-bacterial property, and remarkable affinity for many bio-macromolecules.[4–8] The presence of amino groups in the polymeric chain of chitosan leads to the possibility of several chemical modifications, including the preparation of Schiff bases by reaction with aldehydes and ketones.[9,10] The reaction of chitosan with aromatic aldehydes in acetic acid to produce the corresponding Schiff bases has been described by Tirkistani.[11] Its attractiveness as an analytical reagent arises from the fact that they enable simple and inexpensive determinations of various organic and inorganic substances.[12] The insertion of functional groups in the chitosan matrix may improve its capacity for interaction with metallic ions by complexation, thereby increasing their adsorption properties.[13,14] In this sense the modification of chitosan with aldehydes to produce Schiff bases may result in a potentially complexing material for metallic species with potential analytical and environmental applications.[15,16]

With growing interest in the chemical modification of chitosan,[17–21] a new chitosan derivative, CTSL, was synthesized using substituted vanillin namely 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1-yl)methyl] benzaldehyde (L). The complexing agent or ligand is anchored to chitosan in order to develop a new adsorbent for metal ions. The characterization of the product has been performed by elemental analysis, FTIR, and solid state ^{13}C NMR spectroscopy. This material was also employed to study the kinetics and the equilibrium adsorption of various metal ions such as Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II) as functions of the pH solution.

2. Experimental

2.1. Materials

Chitosan of low molecular weight was purchased from Aldrich (Cat. Number 44,8869) with a deacetylation percentage in the range of 75–85%, with Brookfield viscosity 20 cps, and used as received. Stock solutions (1000 mg L^{-1}) of Mn(II), Fe(II), Co(II), Cu(II), and Ni(II) were prepared by dissolving the appropriate amount of metal(II) sulfate (analytical grade) in double distilled water and

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were standardized with a standard solution of 0.01 mol L^{-1} EDTA.[22] Stock solutions (1000 mg L^{-1}) of Cd(II) and Pb(II) were prepared by dissolving the appropriate amount of their metal(II) nitrates (analytical grade) in double distilled water and their concentrations were estimated using Atomic Absorption Spectroscopy. Working standard solutions of all metal ions were prepared through the dilution of the respective 1000 mg L^{-1} stock solutions with distilled water. All other chemicals and solvents were of analytical grade and used as received.

2.2. Synthesis of the ligand: 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1-yl)methyl] benzaldehyde (L)

Formaldehyde solution (37%) (2 mL 0.025 mol) was added dropwise with stirring to *N*-methylpiperazine (2.0 g, 0.02 mol) in ethanol (20 mL) at 60 °C. Then, the stirring was further continued for an hour and a solution of 4-hydroxy-3-methoxy benzaldehyde (3.04 g, 0.02 mol) dissolved in 60 mL of ethanol was added to it and refluxed for 18 h. After refluxing, the solvent was removed by distillation under vacuum using rotary evaporator and the residue was extracted with chloroform. The white colored solid was recovered after removing the chloroform by distillation. It was then further purified by silica gel column chromatography using chloroform-light petroleum ether (bp 60–80 °C, 1:9 v/v) as the eluent. The product was obtained by slow evaporation of the eluted solvent as white colored crystals. Yield: 4.0 g (76%). mp: 118 °C. *Analytical data for* $C_{14}H_{20}N_2O_3$; Calcd: C, 63.62; H, 7.63; N, 10.60. Found: C, 63.60; H, 7.52; N, 10.56. Mass (EI) *m/z*: 264 (M^+). Selected FT-IR data (KBr, ν cm^{-1}): 3445, 1641, 1592, 1472. ^1H NMR ($CDCl_3$, δ ppm): 2.31 (s, NCH_3, 3H), 2.60 (br s, N–CH_2–CH_2–N, 8H), 3.82 (s, N–CH_2-Ar, 2H), 3.94 (s, CH_3O, 3H), 7.17 (s, Ar-*H*, 1H), 7.34 (s, Ar-*H*, 1H), 9.77 (s, C*H*O, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 45.7 (N–CH_3), 52.3, 54.6 (N–CH_2–CH_2 –N), 55.9 (N–CH_2-Ar), 60.6 (–OCH_3), 109.5, 120.6, 125.5, 128.2, 148.6, 153.9 (Ar*C*), 190.6 (CHO). Single Crystal Analysis CCDC No.: 673897.

2.3. Synthesis of the chitosan biopolymer derivative (CTSL)

Chitosan powder 1.0 g (0.0048 mol of glucosamine residue) was dissolved in 25 mL of 1 wt % acetic acid and diluted with methanol (150 mL). Then 1.6 g of 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1-yl)methyl] benzaldehyde (L) (0.006 mol) dissolved in chloroform (20 mL) was added slowly to it. The mixture was stirred at room temperature for 16 h, followed by refluxing for 18 h, which resulted in a brown colored gel. It was then decanted and thoroughly washed with chloroform to remove any unreacted L and then dried in vacuum at 60 °C to give CTSL as a brown colored powder. Yield: 1.87 g (72%). *Analytical data for CTSL* ($C_{20}H_{29}N_2O_6$): Found: C, 46.52; H, 6.01; N, 6.55. ^{13}C NMR (Solid State, δ ppm): 23.1, 59.0, 73.9, 81.9, 102.8, 126.1, 159.0. Selected FT-IR data (KBr, ν cm^{-1}): 3431, 1638, 1404, 1033, 750, 649.

2.4. Preparation of metal-CTSL

The metal complexes of the chitosan derivative were prepared by the addition of 50.0 mL of 100 mg L^{-1} of metal ion (Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II)) solutions buffered at pH 7.5 to 50 mg sample of chitosan derivative (CTSL) for a period of 4 h by agitation. After 4 h the shaking was turned off and immediately thereafter the adsorbent material was decanted and dried at 60 °C.

2.5. Instrumentation

Elemental analyses were carried out on a Carlo Erba model 1106 elemental analyzer. Fourier transform infrared spectra (FTIR) were recorded on a Perkin–Elmer RX1 model spectrophotometer on KBr disks in the wavenumber range 4000–250 cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded using a model FX-80-Q Fourier transform nuclear magnetic resonance spectrometer. TG and DTG analyses were carried out with TG-50 Shimadzu Model Thermogravimetric analyzer with a heating rate of 10 °C min^{-1}, under a nitrogen atmosphere. Powder X-ray diffraction studies were carried out using a scientific high-resolution Guinier X-ray Powder diffractometer using Cu Kα1 radiation with a quartz monochromator. Micrographs of CTSL before and after metal(II) ion adsorption were taken by using a JSM-5600LV, JEOL model scanning electron microscope. The metal(II) ion concentration was measured by using a Perkin Elmer AAnalyst-750 Model atomic absorption spectrophotometer (AAS).

2.6. Adsorption experiments

2.6.1. Effect of pH on adsorption

The adsorption properties of chitosan derivative and the effect of the pH on adsorption were studied from pH 3 to 10 utilizing various buffer solutions (KCl/HCl for pH 2 and 3; acetic acid/sodium acetate for pH 4, 5, and 6; tris(hydroxymethyl) aminomethane/HCl for pH 7.5 and 8.5; and ammonia/ammonium chloride for pH 9.5 and 10). Aliquots (50.0 mL) of 100 mg L^{-1} of metal ion solutions buffered at different pH values were placed in contact with 50 mg samples of chitosan derivative for a period of 2 h by agitation. After 4 h the shaking was turned off, and immediately thereafter the adsorbent material was decanted, and 2 mL of the filtrate was removed and diluted in volumetric flasks to determine the metal ion concentration by atomic absorption spectrophotometry (AAS). Each run was duplicated under identical conditions. The quantity of metal (II) ions adsorbed at different pH values was calculated with the following Eq. 1:[23,24]

$$Q_e = \frac{(C_0 - C_e)V}{W}, \tag{1}$$

where Q_e is the equilibrium adsorption capacity of the vanillin-based chitosan derivative CTSL (mg g^{-1} adsorbent), V is the volume of solution (mL), C_0 and C_e are the initial and equilibrium concentration of the solute in (mg L^{-1}), respectively, and W is the weight of the sorbent (g).

The amount of metal ions adsorbed by the adsorbent can also be calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{WM}, \tag{2}$$

where q_e is the adsorption capacity of the adsorbent at equilibrium in mmol metal ion/g adsorbent and M is the atomic weight of the corresponding metal ion.

2.6.2. Adsorption kinetics

The adsorption kinetics of the new chitosan material was determined at pH 8.5. A 50 mg of chitosan derivative and 50.0 mL of Cu(II) ion solutions buffered at 8.5 were shaken using an orbital shaker at 200 rpm for 2 h. After pre-determined time periods, 2 mL aliquots were removed and the concentrations of Cu(II) ions in solutions were measured.

2.6.3. Adsorption equilibrium isotherms

Samples of the chitosan derivative (50.0 mg) were added to 25.0 mL of Cu(II) ion solution in several concentrations and previously buffered to the optimum adsorption pH. After this procedure, they were kept under stirring until the adsorption equilibrium was reached. Aliquots were taken and diluted in order to determine metal ion concentration by AAS. It was observed that the adsorption process was fast and reached equilibrium after 2 h and remained constant for 24 h.