Efficent removal of nickel(II) salts from aqueous solution using carboxymethylchitosan-coated silica particles as adsorbent

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ABSTRACT

Three types of organo-mineral composites have been probed as adsorbents for the removal of Ni(II) ions from aqueous solution. Native Aerosil 200 silica particles have been encapsulated with carboxymethyl-chitosan (**CM-CS**) providing $SiO_2 + CM – CS$, surface-silanized silica particles $SiO_2NH_2 + CM – CS$ were obtained by treatment with APTES and subsequent encapsulation by **CM-CS**. Alternatively, surface-carboxylated Aerosil 200 was coated by **CM-CS** affording $SiO_2CO_2H + CM – CS$. The materials have been characterized by various techniques. The effects of counter ions (Cl^-, Br^-, CH_3COO^-, NO_3^- and SO_4^{2-}), pH and initial Ni(II) concentration on the adsorption capacities have been systematically investigated. The maximum adsorption capacity q_m of **CM-CS**-coated silica was determined using the Langmuir adsorption isotherm. For $SiO_2CO_2H + CM – CS$, $SiO_2 + CM – CS$ and $SiO_2NH_2 + CM – CS$, they decrease at pH 7 in the order 256 mg/g > 140 mg/g > 105 mg/g. The adsorption kinetic fits well with a pseudo-second order model. These carbohydrate-derived biosorbents are excellent adsorbents with capacities superior to most other adsorbents reported in the literature.

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1. Introduction

Water contamination by heavy metals has emerged as a critical issue for environmental considerations. Effluents containing significant amounts of toxic heavy metal ions influence ecological systems as well as human health (Giller, Witter, & Mcgrath, 1998). The heavy metal Nickel is widely used in various industrial sectors such as the refining industry, textile and painting industry, foundries and metal processing industries. Therefore, the challenge associated with nickel contaminated wastewater treatment is important because of its environmental impact and threat to human health (Kocaoba & Akyuz, 2005).

Several techniques are used to remove heavy metal ions from wastewater effluent, including but not limited to ion exchange, chemical precipitation and coagulation (Charerntanyarak, 1999), membrane processes, electro-dialysis, osmosis, electrochemical treatment and adsorption on organic-inorganic hybrid materials (Feng et al., 2010), (Karidakis, Agatzini-Leonardou, &Neou-Syngouna, 2005), (Papadopoulos et al., 2004), (Choksi & Joshi,

2007), (Ho & McKay, 1998), (Vijaya, Popuri, Boddu, & Krishnaiah, 2008a). However, these methods present some drawbacks such as their lack of selectivity, incomplete retention of metal ions, in addition to the production of wastes during their production (Vijaya, Popuri, Boddu, & Krishnaiah, 2008b). Biosorption of heavy metals from aqueous solutions is an alternative and promising process for the removal of contaminants. Numerous studies have been carried out to elaborate and to screen various biosorbents as suitable as alternative adsorbents for heavy metal removal from aqueous solution (Gerente, Lee, Cloirec, & McKay, 2007), (Crini & Badot, 2008), (Wang et al., 2013) and (Gerente et al., 2007). There are some review articles on chitosan and its derivatives as biosorbents for the removal of heavy metal ions and organic pollutant in the field of adsorption (Kyzas & Bikiaris, 2015), (Alves & Mano, 2008), (Muzzarelli, 2011) (Muzzarelli et al., 2012), (Wan Ngah, Teong, & Hanafiah, 2011), (Todorova, Chernev, Okolie, & Salvado, 2015), (Boamah et al., 2015), (Boamah et al., 2016). In recent years, researchers have also examined inorganic–organic hybrid materials as adsorbents. Many studies have been undertaken to evaluate the potential of adsorption of heavy metals and organic pollutant on inorganic–organic compounds because of the specific chemical reactivity and flexibility of the organic functional groups, their attractive mechanical properties, combined with thermally stable inorganic backbone. (Da'na & Sayari, 2012) studied the abil-

ity of SBA-15 functionalized with 3-aminopropyltrimethoxysilane to adsorb Cr^{3+}, Al^{3+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+} from single-metal solutions with different concentrations. (Li, Du, Chen, & Zhang, 2007) prepared a new silica gel-supported porous sorbent by organic–inorganic hybridization for removal of toxic metal ions. (Tran, Tran, & Nguyen, 2010) prepared chitosan/magnetite nanocomposite beads for the removal Pb(II), Ni(II) in the pH range from 4 to 6. We and others have used in the past native (Aerosil 200) and surface-functionalized silica materials as supports to design composite material combining the intrinsic properties and advantages of SiO_2 (large surface area, high mass exchange characteristics, non-swelling, mechanical resistance) with those of chitosan (Singhon, Husson, Knorr, Lakard, & Euvrard, 2012). Some preliminary studies on the adsorption of Cu(II) indicated that the efficiency of our composites could be still raised replacing the chitosan layer by its derived polymer carboxymethylchitosan **CM-CS** (Escoda et al., 2013). The use of **CM-CS** as an encapsulation agent is very interesting, since a polymer modification can significantly affect the properties. For example, carboxymethylation permits the creation of new materials enriched with carboxylate groups (Muzzarelli, Tanfani, Emanuelli, & Mariotti, 1982), (Muzzarelli, 1988). CM-CS is an amphoteric polyelectrolyte containing both $-NH_2$ and $-CO_2H$ groups thus reinforcing the complexation properties towards heavy metals ions. These amino, hydroxyl and carboxyl groups can be regarded as binding sites for the chelation of metal ions. Unsurprisingly, there are more and more reports of the complexation of metal ions by **CS** and **CM-CS** (Da Sacco & Masotti, 2010), (Liu, Hu, Fang, Zhang, & Zhang, 2009), (Sun & Wang, 2006), (Varma, Deshpande, & Kennedy, 2004), (Levitskaia, Chen, Fulton, & Sinkov, 2011). The actuality of this topic is witnessed by a very recent report on the design of a Zirconium-based CS-MOF (Metal-Organic Framework prepared by treatment of $ZrCl_4$ and 1,4-benzenedicarboxylic acid) composite for the removal of heavy metal ions (Wang, Tao, Xu, & Yin, 2016).

In the present study, the elaboration of series of new composites based on an Aerosil 200 silica core encapsulated by a polymeric **CM**-**CS** matrix is presented. Theses composites ($SiO_2 + CM - CS$), silica amine encapsulated by CM-CS ($SiO_2NH_2 + CM - CS$) and silica carboxyl encapsulated by CM-CS ($SiO_2CO_2H + CM - CS$) were obtained by deposition of CM-CS on native Aerosil particles or surface-silanized silica. Their adsorption capacity for nickel ions in aqueous solutions was then evaluated. We furthermore determined the adsorption kinetics providing complementary pieces of information on the adsorption process of Ni(II). The study focuses also on the effect of using different types of Ni(II) counterion such as chloride, bromide, nitrate, sulphate and acetate on the Ni(II) removal from aqueous solutions using the biocomposite $SiO_2CO_2H + CM - CS$ and a critical comparision with other literature-known chitosan-derived adsorbents is provided.

2. Experimental

2.1. Materials and methods

The degree of deacetylation and viscosity average molecular weight of Chitosan LMW (**CS**) (Sigma Aldrich) are 77% and 150 kDa, respectively. Monochloroacetic acid (99.3%), 3-aminopropyltriethoxysilane (APTES), 4-(triethoxysilyl)-butyronitrile (CPTES) (98%) and glacial acetic acid (99.9%) were purchased from Aldrich. Fumed silica (Aerosil 200) was obtained from Evonik Industries, Japan. Analytical grade $NiCl_2 \cdot 6H_2O$ was purchased from Merck, Germany. The pH of the solutions was adjusted by addition of 0.1 M NaOH or HCl solutions. All solutions were prepared using deionized water (DI).

2.2. Instruments

FT-IR measurements were performed using a VERTEX 70 Spectrometer equipped with a DTGS detector (BRUKER). Elemental analyses were carried out by the Service d'Analyse Elementaire at UMR 7565 Vandoeuvre-les-Nancy. Zeta potentials were obtained by means of a Zetasizer Nano Z from Malvern. The morphology of the composites was examined using Scanning Electron Microscopy (SEM, JEOL JSM-7600F). For the determination of the Ni(II) concentration, samples were analyzed by Atomic Absorption Spectrometry (Spectra AA50 B Varian). The EDX analysis of the nickel adsorbed on **CM-CS + SiO₂CO₂H** was performed using an Oxford Instrument SDD X-MAX 80.

2.3. Preparation of carboxyl/amine groups-functionalized silica particles SiO_2CO_2H/SiO_2NH_2

The functionalization of the Aerosil 200 surface with carboxyl and amine groups was carried out according to procedures described in the literature (Ponvel, Kim, & Lee, 2010) and (Goswami & Singh, 2002).

2.4. Preparation and characterization of the carboxymethyl chitosan (**CM-CS**)

10 g of CS was dispersed in 100 ml of isopropanol and stirred for 30 min at room temperature, then 25 ml of 10 N aqueous NaOH solution was added in six equal portions at 4 min intervals. After stirring the alkaline slurry for an additional 45 min, solid monochloroacetic acid (24.0 g, 0.25 mol) was added in five portions at 5 min intervals over a period of 20 min. The reaction mixture was then stirred continuously for 3 h at a temperature of 60 °C. The reaction mixture was then filtered and the residue poured into 300 ml of a stirred 70% (v/v) methanol/water mixture. The solid product was filtered of, and then dispersed in 300 ml of anhydrous MeOH to wash it again. The purified product was collected and dried overnight in an oven at 60 °C to yield 8.1 g.

2.4.1. Potentiometric titration of **CM-CS**

The degree of ionization was estimated by a method described in literature (Wang, Chen, Liu, Li, & Zhou, 2008). **CM-CS** (0.20 g) was dissolved in 40 ml of hydrochloric acid solution (0.1 M). A standard aqueous solution of NaOH (0.1 M) was used as the titrant. Alkalimetric curves were recorded by titrimetry. The titration was terminated when the pH of the solution reached a value of 12.0. For accuracy, the measurements were repeated 3 times.

2.4.2. Water solubility of CM-CS

A solubility pH profile of **CM-CS** was obtained from turbidity measurement (Chen & Park, 2003). The pH dependence of the water solubility of **CM-CS** was estimated by measuring the transmittance at 550 nm. The sample concentration was 2 g/l. The pH values of CM-**CS** are adjusted down with aqueous solution HCl (0.1 M).

2.5. Preparation of the composites

0.5 g of native and/or grafted silica was added to 100 ml of 2% **CM-CS** before adjusting the pH to 4 with glacial acetic acid. The mixture was then magnetically stirred for 24 h leading to the formation of a CM-CS/Silica suspension. The pH of this suspension was adjusted to 7 with NaOH (0.1 M) solution to neutralize excess acid. After centrifugation (12.000 rpm for 10 min), the materials were washed with DI water. This operation was repeated 10 times until the water conductivity was below 40 uS/cm. The composites were then dried in an oven at 100 °C for 24 h before use as adsorbent.