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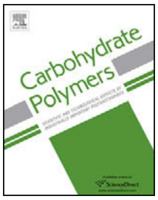

Adsorption of chromate and cupric ions onto chitosan-coated cotton gauze

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ABSTRACT

A chitosan-coated cotton gauze was prepared by UV-curing and tested as adsorbent to remove copper (II) and chromium (VI) ions from water solutions. The adsorbent characterization was carried out by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflection (FTIR-ATR).

Adsorption of copper and chromium ions onto the gauze was tested in batch process at different experimental conditions. The effects of pH, temperature, contact time and metal ion concentration were investigated. The optimum adsorption took place at pH 3 for Cr(VI) and pH 5 for Cu(II) ions respectively, while the temperature did not affect the adsorption process.

Pseudo-first and pseudo-second order models were used to investigate the adsorption kinetics which was found very fast and better described by the pseudo-second order model for both metal ions. The adsorption of Cr(VI) ions was satisfactory described by the Langmuir isotherm, while that of Cu(II) ions showed a better agreement with the Freundlich model.

1. Introduction

Heavy metals accumulation in the environment is hazardous to animals, plants, microorganisms and human beings, mainly because they are non-degradable, persistent and therefore they can accumulate in the body (Afridi et al., 2009; Arain et al., 2008).

On the other hand, metals like copper and chromium play important roles in most industries. Copper for instance is used in engine moving parts, brake linings, metal plating, fungicides, insecticides etc. Chromium is used for electroplating, leather tanning, cement preservation, paints, pigments, textile dyeing, steel fabrication and canning industries.

In order to remove metals from industrial wastewater, numerous techniques are currently available such as chemical precipitation and filtration, electrochemical treatments, ion exchange, reverse osmosis, adsorption and biosorption. Chemical precipitation produces great amount of muddy residues, while ion exchange and membrane separation require very high costs. Therefore, adsorption is considered an effective and economical method to remove heavy metals from wastewater, for the variety of adsorbent materials available to use and the high efficiency at a very low cost (Acosta, Rodriguez, Gutierrez, & Moctezuma, 2004; Dubey & Gopal, 2007; Hamadi, Chena, Farid, & Lub, 2001; Karthikeyan, Rajgopal, & Miranda, 2005; Mohan & Pittman Jr., 2006; Munagapati, Yarramuthi, Nadavala, Alla, & Abburi, 2010).

Among these materials, biopolymers such as chitin and chitosan are promising adsorbents for the removal of heavy metal ions. Chitin is the second most abundant polymer in nature after cellulose and can be extracted from crustacean shells, while chitosan is derived from the deacetylation of chitin. Chitosan chains are characterized by the presence of many hydroxyl and amino groups which can act as coordination sites for heavy metal ions (Bassi, Prasher, & Simpson, 2000; Delben & Muzzarelli, 1989; Muzzarelli, 2011; Nomanbhay & Palanisamy, 2005; Wan Ngah, Teong, & Hanafiah, 2011). This biopolymer was widely investigated for adsorption of copper and chromium ions (Aydin & Aksoy, 2009; Baroni, Vieira, Meneghetti, da Silva, & Beppu, 2008; Boddu, Abburi, Randolph, & Smith, 2008; Cheng, Liu, Han, & Ma, 2010; Chu, 2002; Ghaee, Shariaty-Niassar, Barzin, & Zarghan, 2012; Guibal, 2004; Futalan et al., 2011; Schmuhl, Krieg, & Keizer, 2001; Vieira, Guibal, Silva, & Beppu, 2007; Wan, Kan, Rogel, & Dalida, 2010). However, the chitosan degradation and release in acid environment limit its applications and crosslinking processes were studied to improve the chitosan stability (Chiou, Ho, & Li, 2004; Wan Ngah, Endud & Mayanar, 2002) even if the crosslinking reduces the density of the functional groups on the modified material. Nevertheless, chitosan

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grafted to polymers like cellulose showed good adsorption properties towards heavy metal ions (Li & Bai, 2005; Liu, Nishi, Tokura, & Sakairi, 2001; Zhang et al., 2008).

In this work we studied the batch adsorption of Cu(II) and Cr(VI) on a cotton gauze coated with chitosan by UV-curing at three content percentages (10, 20 and 30%), varying different process parameters, in order to apply this composite material to water treatment.

The choice of the support was due to its low cost and easy availability; moreover cellulose can also be involved in radical grafting (Roy, Semsarilar, Guthrie, & Perrier, 2009) and the open structure of the gauze is suitable to limit the pressure drop in continuous filtration system. Chitosan, in acetic acid solution, was applied on the gauze by padding, and grafted by UV radiation, in consequence of radical reactions promoted by a photoinitiator. The same composite was already experimented for antibacterial water filtration in our recent study (Ferrero, Periolatto, Vineis, & Varesano, 2014). Moreover the same chitosan functionalized gauze was tested as filter substrate for the removal of dyes from wastewater, with good performance also in continuous flow assessment (Periolatto & Ferrero, 2013).

The effect of exposure to UV light of chitosan films or blends, forming macroradicals, has been widely studied (Sionkowska, Wisniewski, Skopinska, Vicini, & Marsano, 2005; Sionkowska et al., 2006) and the same radicals can be involved for example in photopolymerization process of chitosan with acrylates (Alam, Khan, Khan, Ghoshal, & Mondal, 2008). During UV exposure of chitosan main chain scissions were evidenced, but free radicals formed may interact with each other to form additional crosslinkages between the chains. Moreover, the very active HO$^{\bullet}$ radicals can migrate within the chain and produce new radicals and macroradicals (Sionkowska, Płanecka, Lewandowska, Kaczmarek, & Szarszewska, 2013) which may interact even with the groups of the substrate to give graft bonding. However radicals involving amino groups of chitosan were not evidenced by ESR (Saiki et al., 2010) and even an increase of amine content by UV irradiation was found probably due to photolysis of the residual acetamide groups of chitin with the consequent hydrogen abstraction to form primary amines (Andrady, Torikay, & Kobatake, 1996). Therefore the UV-curing should not reduce the content of free amines of chitosan unlike other chemical crosslinking methods, e.g. with dialdehydes, and these groups should remain available for coordination with metal ions.

2. Materials and methods

2.1. Materials

A pure cotton gauze fabric, 49 g/m^2 with hexagonal holes 2 mm opening, already used in the previous studies on water filtration was chosen as support.

Low viscosity chitosan, 75–85% deacetylation degree (Fluka) was used for gauze coating. It was dissolved in aqueous solution of 2% (v/v) glacial acetic acid, by ripening for 24 h followed by magnetic stirring at ambient temperature for further 24 h. A chitosan concentration of 5 wt% was used while 2% on chitosan weight of 2-hydroxy-2-methylphenylpropane-1-one (Darocur 1173, Ciba Specialty Chemicals) was added as photoinitiator. A proper amount of the solution was spread on the gauze with 12 h impregnation time and the same was dried for about 20 min at 80–100 °C. Then the coated fabric was exposed for 60 s to UV radiation under a medium pressure mercury lamp, with irradiance on the fabric of about 60 mW/cm^2, at a distance of about 20 cm in a small box equipped with a quartz window flushed by nitrogen (oxygen content lower than 20 ppm). To assure the complete curing of the chitosan on the fabric, it was radiated on both the sides.

The weight gain of fabrics was calculated as in Eq. (1):

$$\text{Weight gain}\,(\%) = \frac{(w - w_0) \times 100}{w_0} \tag{1}$$

where w is the weight of grafted fabric and w_0 that of the original fabric.

The gauzes coated with chitosan weight gain in the range between 10 and 30 wt% were characterized by SEM and FTIR-ATR analyses as reported in the previous study (Ferrero, Periolatto, Vineis, & Varesano, 2014). Both characterizations were carried out on untreated gauze and on chitosan-coated gauze before and after metal adsorption. Copper and chromium presence on the gauze surface after adsorption were evidenced by Energy Dispersive X-ray Spectroscopy (EDX) performed by an Oxford Instrument Model 7060 Link ISIS.

2.2. Adsorption tests

Stock solutions of Cu(II) and Cr(VI) containing 1.000 g/L and 0.500 g/L respectively were prepared by dissolving proper amounts of analytical grade copper sulfate or potassium dichromate in distilled water.

Cotton gauzes coated with chitosan at three different percentages (10, 20 and 30%) were dried in oven at 50 °C for 4 h and conditioned in standard atmosphere at 20 °C and 65% R.H. for 24 h. The adsorption tests were carried out in batch by shaking, in sealed test tubes, 0.100 g of adsorbent material in 10 mL of the metal solution (estimated volume ratio: 6 mL of swollen chitosan-coated gauze to 100 mL of solution) by varying concentration, pH value, temperature and contact time.

The effects of these variables on the adsorption capacity of gauze coated and uncoated with chitosan were studied. After the adsorption, the adsorbent was settled and the metal ion residual concentration in the supernatant was analyzed by an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES, Optima 7000 DV PerkinElmer) for Cu(II) and total Cr determination, while Cr(VI) was determined by 1,5-diphenylcarbazide method using UV-Visible Spectrometer (Lambda 35 PerkinElmer).

The adsorption tests were repeated three times and the results reported were averaged.

The adsorption capacity was evaluated using Eq. (2):

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

where q_t (mg/g) is the adsorption capacity of the adsorbent at a given time t; C_0 and C_t (mg/L) are the initial metal concentration and at time t, respectively; V (L) is the volume of the metal solutions; and m (g) is the mass of the adsorbent.

2.3. Adsorption kinetics

In order to clarify the adsorption kinetics of Cu(II) and Cr(VI) on the cotton gauze with chitosan weight gain of about 10, 20 and 30%, the experimental data were fitted to the Lagergren's pseudo-first-order and Ho's pseudo-second-order models respectively.

The linear pseudo-first-order equation according to Lagergren model can be written in the following form:

$$\log(q_e - qt) = \log q_e - \frac{K_1}{2.303}t \tag{3}$$

where q_e (mg/g) is the amount of metal ion adsorbed at the equilibrium time and K_1 is the rate constant of the equation (min^{-1}).