Chemical Engineering and Processing 83 (2014) 43–48

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Introduction of copper nanoparticles in chitosan matrix as strategy to enhance chromate adsorption

Fernanda Condi de Godoi[a,*], Rodrigo Balloni Rabelo[a], Maria Aparecida Silva[a], Enrique Rodríguez-Castellón[b], Eric Guibal[c], Marisa Masumi Beppu[a]

[a] School of Chemical Engineering, University of Campinas, Av. Albert Einstein, 500, 13083-852 Campinas, Brazil
[b] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain
[c] Ecole des Mines d'Alès, 6 Avenue de Clavières, F-30319 Ales Cedex, France

ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 11 June 2014
Accepted 11 July 2014
Available online 19 July 2014

Keywords:
Chitosan
Copper nanoparticles
DXAS
Hygroscopic behavior
Cr(VI) adsorption

ABSTRACT

In this study, copper nanoparticles (CuNPs) were incorporated to chitosan (CHI) matrix as strategy to enhance the chromate adsorption by CHI membrane. The CuNPs were synthesized using $NaBH_4$ as the reducing agent. Dispersive X-ray Absorption Spectroscopy (DXAS) was used to monitor the *in situ* reduction of Cu(II). The influence of the presence of CuNPs on the hygroscopic behavior was also evaluated. DXAS technique showed that the adsorbed Cu(II) was reduced to Cu(I) (63%) and Cu(0) (37%) species, at the end of the reduction reaction (using $NaBH_4$, after ~30 min). The hygroscopic behavior of the proposed sorbent was more influenced by CuNPs when the water vapor adsorption was conducted under synthetic air atmosphere. A decrease in the energy of interaction among the water molecules adsorbed on the monolayer was observed. The chromate adsorption study has shown a higher equilibrium concentration of adsorbed chromium species when the CHI membrane containing CuNPs was used as sorbent. The CuNPs offered a second active adsorption site, which was characterized by a higher coefficient of affinity (12 $L\,mmol^{-1}$, against 0.18 $L\,mmol^{-1}$ reported for CHI). The enhanced adsorption of chromium in the presence of CuNPs was associated to the redox reaction between the CuNPs and chromate anions.

1. Introduction

Recently, considerable interest has been focused on metal nanoparticles due to their potential applications in diverse fields including catalysis, magnetic recording media, or microelectronics [1]. Several preparation methods of metallic nanoparticles were described, including wet and dry processes: (i) chemical reduction of metal salts, (ii) thermal, photochemical, or sonochemical decomposition, (iii) ligand reduction and displacement from organometallics, (iv) metal vapor synthesis, and (v) electrochemical reduction. The first cited method requires the use of stabilizers to prevent agglomeration of the resulting metal atoms as microscopic crystallites. Many studies reported the use of biopolymers as mediator during the reduction of the metallic salt solutions [2–5].

Chitosan (CHI) can be used as mediator due to its great ability to form metallic complexes [6–10]. According to Murugadoss et al. [11], CHI can act as both a reducing agent and a stabilizer of metal nanoparticles. CHI with supported metal nanoparticles can be applied in environmental uses [12,13], catalysis and for the development of biosensors [14].

In the field of Cr(VI) remediation, modified polymer structures recently retained a great attention [2,5,15–17]. Hexavalent chromium is considered by the United States Environmental Protection Agency (EPA) a carcinogenic and mutagenic agent [18]. It may cause damages to the kidney, lungs and ulcerations to the skin [19]. When in solution, the oxyanions $CrO_4{}^{2-}$ and $HCrO_4{}^{-}$ are predominant at $2 < pH < 6$. Hydrogendichromate ions ($HCr_2O_7{}^{-}$) are prevalent only in strong acidic solutions ($pH < 1$). In basic solutions ($pH > 8$), the main formed specimen is $CrO_4{}^{2-}$ [20,21].

Herein we report the introduction of copper nanoparticles on chitosan matrix as a strategy to enhance the chromate adsorption. Recently, using XPS technique, we have shown that the mechanism of Cr(VI) adsorption in CHI membrane containing CuNPs is governed by the redox reactions between CuNPs and Cr(VI) ions [22]. This research brings new insights into the development of modified polymeric sorbents. Our findings cover 3 important topics: (1) the synthesis and (2) the stability of the Cu-NPs into CHI matrix (hygroscopic behavior), moreover, (3) interpretation of the

---

* Corresponding author. Present address: Room 805, Chemistry Building #68, School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, QLD 4072, Australia. Tel.: +61 07 3365 3868.
E-mail address: f.condidegodoi@uq.edu.au (F.C. de Godoi).

http://dx.doi.org/10.1016/j.cep.2014.07.002
0255-2701/

mechanism involved in the enhancement of Cr(VI) removal regarding the incorporation of Cu(NP)s (in comparison to pristine chitosan).

The Dispersive X-ray Absorption Spectroscopy (DXAS) technique was employed as a novel way to monitor the formation of metallic nanoparticles into CHI polymeric matrix. It is a powerful tool to estimate the speciation of copper during Cu(II) reduction (with $NaBH_4$ as the reducing agent).

The hygroscopic behavior of the proposed sorbent was also studied by acquiring water vapor adsorption isotherms (dynamic method). The knowledge of how the CuNPs affect the hygroscopic behavior of the CHI membrane is a helpful data to support future studies about the corrosion of CuNPs into CHI polymeric matrix. As reported elsewhere [23], the ordinary corrosion of most common metals requires the presence of both water and oxygen, but the phenomena vary considerably according to whether the water or the oxygen is present in excess [23].

The current paper combined with our previous mechanism study using the XPS technique [22] represent an important contribution to further studies concerning the chromate anions adsorption by modified polymeric sorbents.

2. Experimental

2.1. Preparation of the CHI-RED membrane

CHI-membrane containing Cu-NPs (CHI-RED membrane) was prepared as described elsewhere [22]. Firstly, Cu(II) was adsorbed to CHI membrane. Thus, the CHI-Cu(II) membrane (discs of $d = 4.5$ cm) was set into a container with 80 mL of ultra-pure water under constant magnetic stirring and under N_2 atmosphere (ambient temperature, pH = 8). After approximately 2 min, a freshly prepared a $NaBH_4$ aqueous solution (20 mL $[NaBH_4] = 26$ mmol L^{-1}) was added to the recipient until the CHI-Cu(II) membrane turns its color from light-blue to dark-brown (the process usually takes about 90 s). The CHI-RED membrane was then quickly rinsed with Milli-Q® water and immediately submitted to chromate adsorption batch experiments.

2.2. Dispersive X-ray Absorption Spectroscopy (DXAS)

The chemical reduction of the CHI-Cu(II) membrane using $NaBH_4$ was monitored by the Dispersive X-ray Absorption Spectroscopy (DXAS) technique at the DXAS beam line of the LNLS (National Synchrotron Light Source), in Campinas (Brazil). A Si(1 1 1) monochromator was used to select the energy. The experimental setup applied to the DXAS experiment consisted of a sample chamber connected to a recipient containing $NaBH_4$ aqueous solution ($[NaBH_4] = 26$ mmol L^{-1}). The sample chamber was a compact circle with ends closed and with aluminum flanges sealed by Kapton windows. A piece of the CHI-membrane with diameter equal to 1 cm was fixed in the center of the chamber. The $NaBH_4$ aqueous solution was pushed into the sample chamber through a N_2 gas flow. The Cu K-edge spectra started to record in transmission mode with 15 ms of time exposure and 150 accumulations for each measure. The equipment was set to record 120 spectra. The acquisition of each spectrum took around 1 min.

2.3. Dynamic vapor sorption isotherms

Dynamic vapor sorption system (DVS) is a well-established method for the determination of water vapor sorption isotherms. DVS-2 instrument (London, UK) was employed to measure gravimetrically the uptake and loss of water vapor by using a recording ultra-microbalance. For the DVS experiments, samples of CHI and CHI-RED membranes were placed in a quartz sample pan, which was firstly placed in the DVS equipment at 25 °C and water activity (a_w) equal to zero until reaching the equilibrium of mass. After, the sample was exposed to over an input a_w ranging from 0.11 to 0.95. The mass equilibrium was established at each a_w level by measuring the mass variation against time. The values of the water content at equilibrium were used to plot the water vapor sorption isotherms. The experiments were performed under N_2 (CHI and CHI-RED) and synthetic air (CHI-RED) atmospheres.

2.4. Chromate batch adsorption experiments

Kinetic uptake and isotherm curves were obtained using CHI and CHI-RED membranes as chromate sorbents from aqueous solution at 20 °C. The chromate solutions were prepared using a potassium dichromate salt ($K_2Cr_2O_7$). The initial pH of the metal solution was adjusted to 4 before the sorbent immersion and it was not corrected along the adsorption tests. All the collected samples of chromate solution were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES JY 2000, Jobin Yvon, Longjumeau, France).

For the adsorption kinetic test, aliquots were withdrawn from 650 mL of chromate aqueous solution containing 1.3 g of sorbent, under constant magnetic stirring for 48 h. The initial concentration of Cr(VI) was 1.92 mmol L^{-1}. The equilibrium adsorption tests were carried out by mixing the sorbent (0.1 g) with a series of Cr(VI) solution for 48 h (initial concentration varied in the range: 0.6–60 mmol L^{-1}). The mass balance equation (Eq. (1)) was used to calculate the sorption capacity of the sorbent (q):

$$q = \frac{V(C_0 - C_{eq})}{m} \tag{1}$$

where, V is the volume of chromate solution and m is the mass of sorbent. C_0 and C_{eq} are the initial and equilibrium concentrations, respectively.

3. Results and discussion

3.1. Kinetics of Cu(II) reduction monitored by DXAS technique

The Cu(II) reduction was monitored using DXAS technique (to obtain the X-ray absorption spectra) in the course of the reduction reaction of Cu(II) from CHI-Cu(II) membrane (using $NaBH_4$, as the reducing agent, Fig. 1). Each spectrum was studied over a photon energy ranging from 8960 to 9020 eV, XANES region (X-ray absorption near-edge structure), for getting information on the oxidation

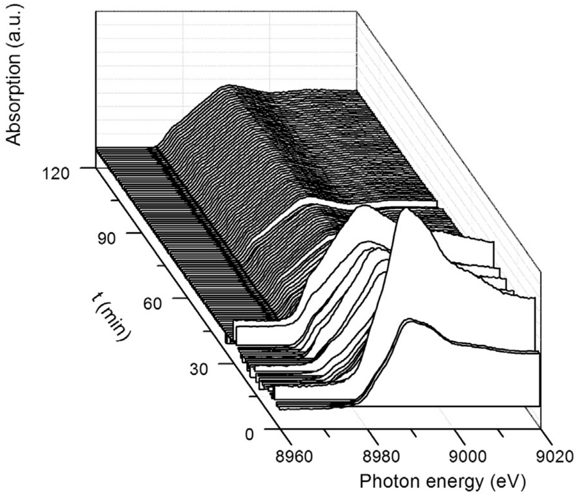

Fig. 1. XANES spectra recorded during DXAS experiment.