

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



Franco Ferrero^{a,*}, Cinzia Tonetti^b, Monica Periolatto^a

^a Politecnico di Torino, Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

^b CNR-ISMAR, Institute for Macromolecular Studies, Corso Pella 16, 13900 Biella, Italy

ARTICLE INFO

Article history:

Received 25 January 2014

Received in revised form 3 April 2014

Accepted 4 April 2014

Available online 18 April 2014

Keywords:

Chitosan
Cotton gauze
UV-curing
Adsorption
Copper
Chromium

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 satisfactorily described by the Langmuir isotherm, while that of Cu(II) ions showed a better agreement with the Freundlich model.

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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; Futral 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

* Corresponding author. Tel.: +39 011 0904653; fax: +39 011 0904699.
E-mail address: franco.ferrero@polito.it (F. Ferrero).

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• radicals can migrate within the chain and produce new radicals and macroradicals (Sionkowska, Płancka, 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/m² 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/cm², 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):

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

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):

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

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:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

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).

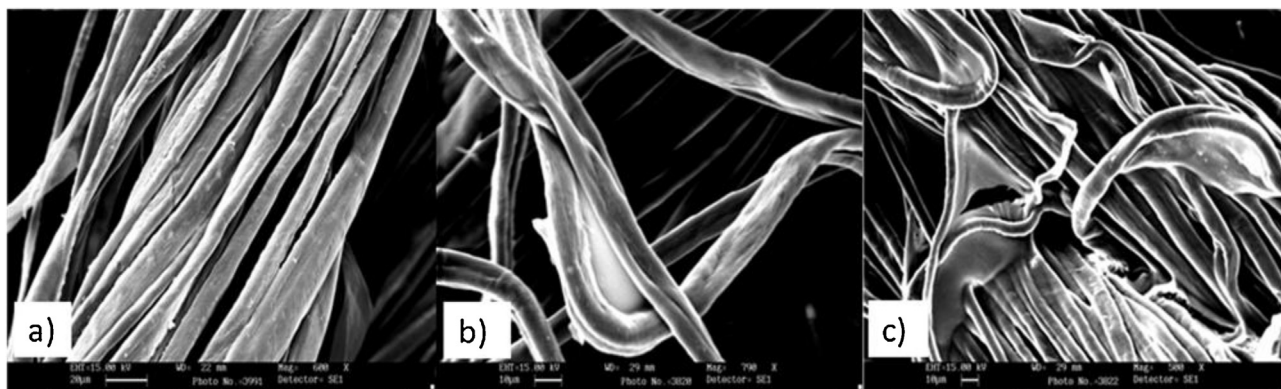


Fig. 1. SEM images of cotton gauze: (a) untreated (600×); (b) chitosan-coated 10 wt% gain (790×); (c) chitosan-coated after Cu(II) adsorption (500×).

The linear pseudo-second-order equation is given in the following form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where K_2 is the rate constant of the equation (g/mg min).

2.4. Adsorption isotherm models

The distribution of the metal ions between the liquid phase and the adsorbent is a measure of the equilibrium condition in the adsorption process and can generally be expressed in terms of the two most popular isotherm models: Langmuir and Freundlich isotherms.

The Langmuir isotherm model is based on the assumption of homogeneous adsorption and its equation can be written as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_m (mg/g) is the maximum adsorption capacity of the adsorbent, K_L (L/mg) is the Langmuir adsorption constant related to the free energy of adsorption and C_e (mg/L) is the equilibrium concentration.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L , defined by Eq. (6):

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where K_L is the Langmuir constant and C_0 is the initial metal concentration. The parameter R_L indicates if the adsorption is favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$).

The Freundlich isotherms model assumes a heterogeneous adsorption surface and its equation can be written in the form of Eq. (7):

$$q_e = K_f C_e^{1/n} \quad (7)$$

where K_f is a constant relating to the adsorption capacity and n is an empirical parameter relating to the adsorption intensity, which varies with the heterogeneity of the material.

3. Results and discussion

3.1. Characterization of the adsorbent

In Fig. 1 SEM images of untreated and 10% chitosan weighted gauze are reported, even after metal ions adsorptions by contact with 200 mg/L Cu^{2+} solution for 24 h at pH 5 and 20 °C. On treated

samples, chitosan is visible on and between cotton fibers as a coating or a slim membrane. Moreover in the previous work (Ferrero, Periolatto, Vineis, & Varesano, 2014) it was observed that chitosan is spread on the fabric in an homogeneous way, covering meshes without occluding them. Chitosan coating is still present on the gauze after the adsorption process of Cu(II) (Fig. 1c), hence it was not removed by the contact with the solution in the experimental conditions adopted.

The presence of metal ions was shown by a strong coloration of the gauze after adsorption tests, blue in the case of Cu(II), brown with Cr(VI) (Fig. 2). Moreover the EDX spectra reported in Fig. 3 showed the presence of Cu and Cr peaks in chitosan-coated gauze after adsorption in comparison with uncoated gauze. The gold peak present in every sample is due to preparation by sputter coating. Therefore the results confirm that the chitosan groups are able to function as adsorption sites for Cu(II) and Cr(VI) ions.

The comparison of FTIR-ATR spectra of untreated and 10% chitosan weighted cotton shows the evidence, in the spectrum of the treated fabric, of a typical peak of chitosan at 1560 cm^{-1} due to the bending of NH amide group. The other peaks can be due both to cotton and chitosan component of the sample while the band at 1644 cm^{-1} was due to the water adsorbed (Chung, Lee, & Choe, 2004). Considering the spectra related to the gauze after the adsorption process, no shift of any bands, ascribable to some chemical bond between chitosan and metal ions, can be seen. Hence it can

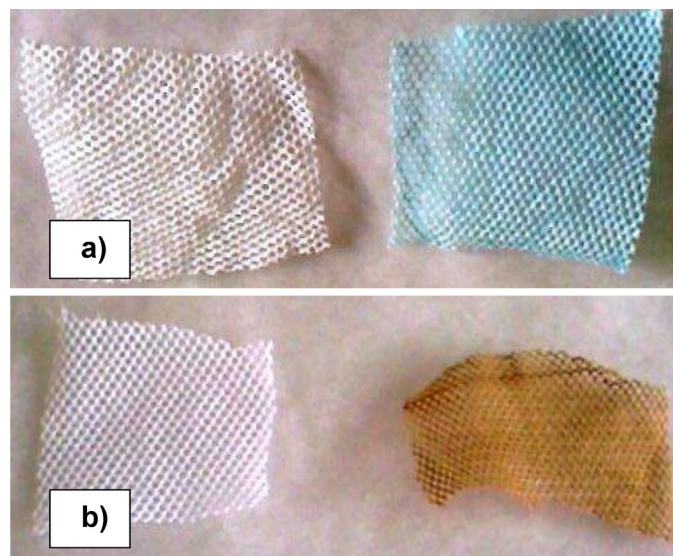


Fig. 2. Comparison between coloration of chitosan-coated gauze (10 wt% gain) before (on the left) and after adsorption (on the right) of: (a) Cu(II), (b) Cr(VI).

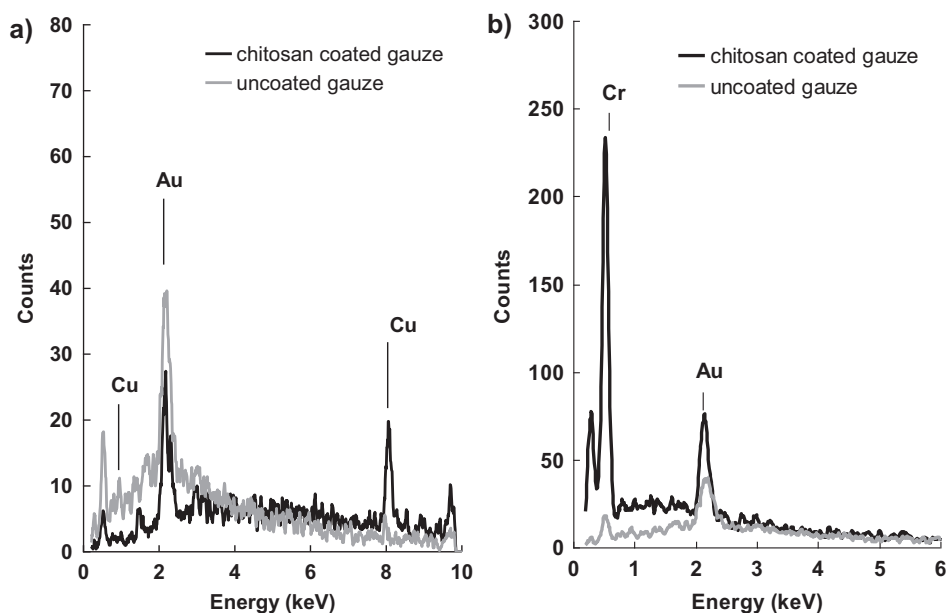


Fig. 3. Comparison between EDX spectra of uncoated and chitosan-coated gauze (10 wt% gain) after adsorption of: (a) Cu(II), (b) Cr(VI).

be concluded that the adsorption process was due only to physical interactions between chitosan and metal ions (Fig. 4).

As reported in the previous paper (Ferrero, Periolatto, Vineis, & Varesano, 2014) the comparison between the results of elemental and XPS analyses confirmed that almost all the chitosan fixed on the gauze was on the surface of cotton fibers, as desirable, rather than inside the bulk. In this way in fact, the whole amount of chitosan active sites is easily accessible to metal ions and the adsorption efficiency can be maximum.

3.2. Adsorption tests

3.2.1. Effect of pH

The pH is one of the most important parameters influencing the metal ion adsorption on chitosan (Chu, 2002). This is due to the

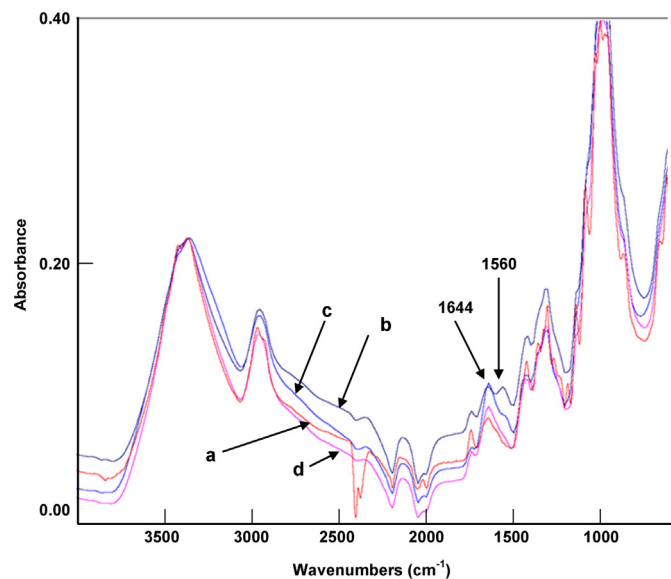


Fig. 4. FTIR-ATR spectra of cotton gauze: (a) untreated; (b) chitosan-coated (10 wt% gain); (c) chitosan-coated after Cu(II) adsorption; (d) chitosan-coated after Cr(VI) adsorption.

competition between the metal ion and the H⁺ ions for the active adsorption sites (Evans, Davids, MacRae, & Amirbahman, 2002). The effect of pH on the adsorption of Cu(II) and Cr(VI) on the chitosan-coated gauze was studied in the range of values from 1.5 to 5 for Cu(II) and from 1.5 to 10 for Cr(VI), using the gauze with chitosan amount of 10%, an equilibrium time of 24 h and an initial metal ion concentration of 100 mg/L for both the ions. Values of pH higher than 5 for Cu(II) were not investigated to avoid the formation of hydroxide.

As it can be seen in Fig. 5, the maximum adsorption capacity was observed at pH 5 for Cu(II) and at pH 3 for Cr(VI). Furthermore at these pH the metal ions adsorption of the uncoated gauze was very low, hence such values were adopted in the other adsorption experiments.

The same trend of Cu(II) adsorption increasing pH was found with crosslinked chitosan beads (Juang & Shao, 2002; Wan Ngah, Endud, & Mayanar, 2002). This was ascribed to competitive adsorption of protons and Cu(II) ions onto chitosan. In fact the uptake of transition metal ions by chitosan takes place through coordination with unprotonated –NH₂ and –OH groups. Hence the concentration

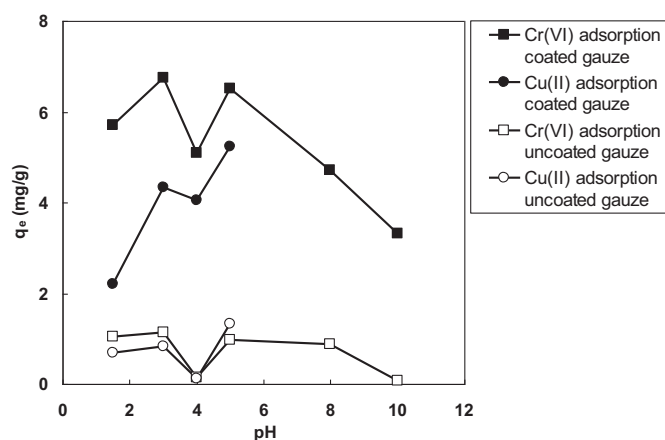


Fig. 5. pH effect on the adsorption capacity of Cu(II) and Cr(VI) by the chitosan-coated cotton gauze (10 wt% gain) at 20 °C for 24 h contact time; 100 mg/L initial metal concentration.

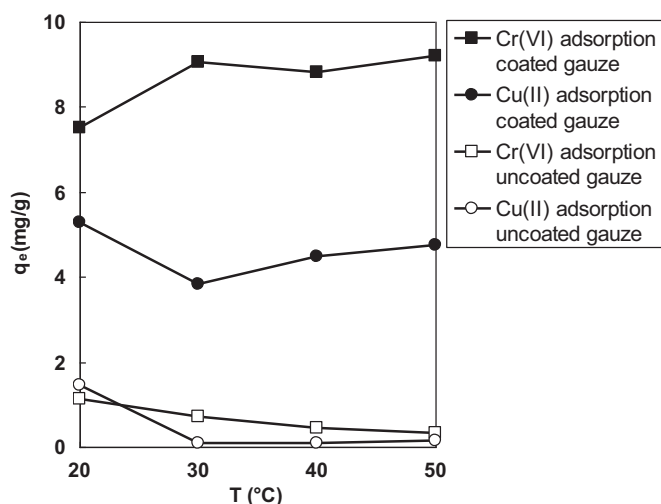


Fig. 6. Effect of the temperature on the adsorption capacity at pH 5 for Cu(II) and pH 3 for Cr(VI) respectively by the chitosan-coated cotton gauze (10 wt% gain); 100 mg/L initial metal concentration.

of protonated amino groups decreases as pH is increased, although it was observed that even at pH 7 still more than 20% of the amino groups of chitosan remain protonated.

On the other hand many authors (Aydin & Aksoy, 2009; Wan Ngah, Kamari, Fatinathan, & Ng, 2006) reported that the equilibrium uptake of Cr(VI) by crosslinked chitosan was maximum at pH 3 since the chromate ions are negatively charged while the amino groups are mainly protonated. In this case the adsorption is ascribed to electrostatic interaction between sorbent and sorbate.

Since Cr(VI) may undergo reduction due to oxidative action toward chitosan and cellulose, it was also verified that the total chromium in solution, determined by ICP analysis, was in agreement with Cr(VI) determined by spectrophotometry in the range of pH values studied. A good agreement was observed except for pH 1.5 and 8 where a significant lower Cr(VI) concentration than that of total chromium in solution indicated a partial reduction to Cr(III).

3.2.2. Effect of temperature

In order to determine the effect of temperature on the adsorption of Cu(II) and Cr(VI), experiments were carried out at different temperature (20, 30, 40, 50 °C), using an initial metal ion concentration of 100 mg/L for both the metal ions, pH 5 for Cu(II), pH 3 for Cr(VI) and equilibrium time of 24 h.

As shown in Fig. 6, the temperature did not affect significantly the metal ions adsorption process and also in this case the adsorption of metal ions onto uncoated gauze was unimportant. Moreover it was verified that the temperature variation did not cause Cr(VI) reduction.

3.3. Adsorption kinetics

The effect of the contact time on the Cu(II) adsorption on the gauze with chitosan weighting of 10, 20 and 30% was studied using an initial metal concentration of 100 mg/L, a pH value of 5 at 20 °C. As shown in Fig. 7, the adsorption capacity considerably increased with increasing the contact time and reached about a constant value after 2 h. It is worth of note that the highest chitosan percentage (30%) shows lower adsorption rate than the lower weight gains. This fact can be justified by a thicker chitosan coating which slows down the metal ion diffusion toward the adsorption sites.

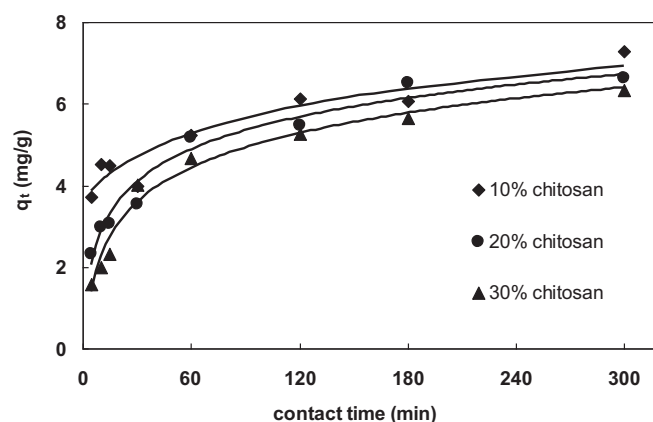


Fig. 7. Kinetics of Cu(II) adsorption on the chitosan-coated gauze at pH 5, 20 °C, 100 mg/L initial Cu(II) concentration.

The relationship between contact time and Cr(VI) adsorption capacity of the chitosan-coated gauze was studied using an initial metal concentration of 50 and 100 mg/L, a pH value of 3 at 20 °C.

As shown in Fig. 8, the Cr(VI) adsorption kinetics is very fast for both initial metal ion concentrations: the equilibrium condition is reached already after 10 min. Unlike Cu(II), with 100 mg/L the adsorption capacity of Cr(VI) is lower with 10% chitosan, while with 50 mg/L it is practically unaffected by chitosan percentage. These results are in agreement with the hypothesis of a faster Cr(VI) diffusion than Cu(II) into chitosan coating which enables to exploit a larger number of adsorption sites. Hence with the highest metal concentration the capacity is limited by the number of available sites in dependence on chitosan content.

Applying the pseudo-first and pseudo-second order kinetic models to the results, the kinetic parameters obtained (Table 1) indicate that the adsorption kinetics of both Cu(II) and Cr(VI) ions on the adsorbent is better represented by the pseudo-second order kinetic model.

3.4. Adsorption isotherm models

After verifying that the Cu(II) and Cr(VI) adsorption of uncoated cotton gauze from solutions at different metal ions concentration was negligible, the 10% coated gauze was used to perform the equilibrium adsorption tests.

To determine the maximum metal adsorption capacities of the chitosan-coated cotton gauze with 10% chitosan, equilibrium adsorption studies were carried out in the range of metal ions initial concentration between 10 and 200 mg/L, at pH 5 for Cu(II) and

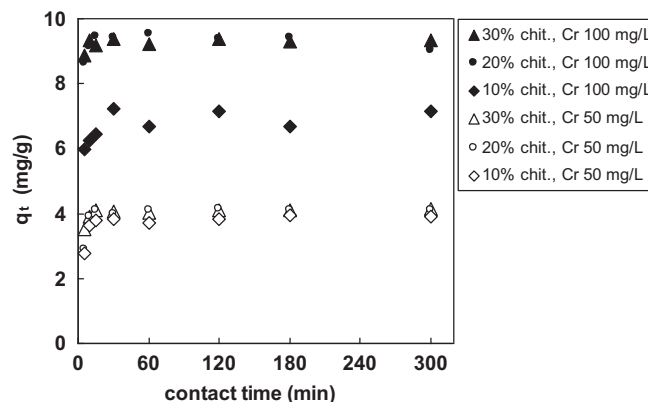


Fig. 8. Kinetics of Cr(VI) adsorption on the chitosan-coated gauze at pH 3, 20 °C.

Table 1
Kinetic parameters according to pseudo-first and pseudo-second order models.

Metal	Chitosan add-on (%)	Pseudo-first order			Pseudo-second order		
		K_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2	K_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
Cu(II) 100 mg/L	10	0.005527	4.093	0.9492	0.008771	7.267	0.9860
	20	0.009212	4.178	0.9318	0.007181	7.022	0.9940
	30	0.014279	4.032	0.9624	0.006117	6.689	0.9960
Cr(VI) 100 mg/L	10	0.002073	1.471	0.3216	0.077976	7.097	0.9985
	20	0.000921	0.165	0.0111	0.073735	9.083	0.9993
	30	0.000691	0.788	0.1708	0.063725	9.337	0.9999
Cr(VI) 50 mg/L	10	0.006910	0.363	0.4965	0.298578	3.700	0.9998
	20	0.002303	0.617	0.2151	0.373042	4.120	0.9999
	30	0.001842	0.565	0.3271	0.332647	4.131	0.9999

Table 2
Adsorption coefficients of Langmuir and Freundlich isotherm models applied to Cu(II) and Cr(VI) adsorption on chitosan-coated gauze (10% add-on). Experimental conditions: pH 5 for Cu(II) and pH 3 for Cr(VI), 24 h contact time at 20 °C.

Metal	Langmuir			Freundlich		
	q_m	K_L (L/mg)	R^2	K_f	n	R^2
Cu(II)	14.1	0.058	0.9501	1.12	1.74	0.9732
Cr(VI)	12.4	12.78	0.8618	3.42	3.69	0.2619

pH 3 for Cr(VI), with equilibrium time of 24 h at 20 °C. As it can be seen in Fig. 9, the adsorption capacities increased with increasing metal ion concentration.

Langmuir and Freundlich adsorption constants evaluated from the isotherms along with the correlation coefficients are reported in Table 2. According to the values of squared correlation coefficient (R^2), the adsorption results of Cu(II) by chitosan-coated cotton gauze fitted better the Freundlich isotherm model than the Langmuir one. On the contrary, the Cr(VI) adsorption might be better described by Langmuir model.

The maximum adsorption capacity of the gauze coated with chitosan (10 wt% gain) was calculated as 14.1 mg/g for Cu(II) and 12.4 mg/g for Cr(VI). The value of R_L calculated for the 10 mg/L initial concentration, i.e. the lowest initial metal ion concentration considered, was 0.63 for Cu(II) and 1.00 for Cr(VI), indicating a favourable adsorption on the chitosan-coated gauze in both cases.

Taking into account the chitosan content of the gauze, the adsorption capacity found for Cu(II) (i.e. 2.4 mmol/g of chitosan grafted) is even higher than that reported by Vieira et al. (2007) in the same experimental conditions with a membrane of

natural chitosan (2.0 mmol/g). This confirms that the crosslinking and grafting reactions induced by UV-curing do not reduce the availability of $-NH_2$ and $-OH$ groups to coordinate Cu(II) ions.

On the other hand the adsorption capacity found for Cr(VI) (i.e. 136 mg/g of chitosan grafted) is strongly higher than that reported by Schmuhi et al. (2001) for non crosslinked chitosan (78 mg/g). Moreover these authors observed the same different behavior of the two ions towards the fitting of isotherm models, i.e. better fitting of Freundlich isotherm for Cu(II) and Langmuir for Cr(VI). This can be justified by the different ionic character: cationic for Cu(II) and anionic for Cr(VI). Therefore the first should mainly be adsorbed by coordination due to amino and hydroxyl groups (Delben & Muzarelli, 1989) while the other should be linked by electrostatic interaction between Cr(VI) anions and cationized amino groups. Such hypothesis is in agreement with the different pH values of maximum adsorption: strongly acid for Cr(VI), less for Cu(II). As a consequence, the cationic sites for Cr(VI) adsorption should be more uniformly spread, in agreement with the Langmuir isotherm, than those for Cu(II), heterogeneously distributed on the adsorbent surface, in agreement with the better fitting of Freundlich isotherm.

4. Conclusions

A chitosan functionalized gauze was tested as adsorbent for the removal of copper(II) and chromium(VI) ions from water solution in batch process. The adsorption capacity of this material was evaluated varying pH, temperature, contact time and initial metal ion concentration.

The copper adsorption capacity increased with contact time increasing and reached a constant value after 2 h. The kinetic parameters obtained indicate that the adsorption of Cu(II) follows the pseudo-second order rate. The maximum adsorption capacity (14.1 mg/g) was reached at pH 5 and the data obtained fitted better the Freundlich isotherm model.

The equilibrium time of Cr(VI) adsorption was reached already after 10 min and the kinetic experiments demonstrated that the Cr(VI) adsorption is better represented by the pseudo-second order kinetic model. The maximum adsorption capacity (12.4 mg/g) was reached at pH 3 and the Langmuir isotherm model described better the Cr(VI) adsorption process.

In both cases, the value of R_L calculated for the 10 mg/L initial concentration indicated a favourable adsorption on the chitosan-coated gauze.

For both the metal ions studied, the adsorption capacities increased with increasing metal ion concentration while the temperature did not affect significantly the adsorption process of the metal ions. Furthermore the maximum adsorption capacities obtained with regard to chitosan content were higher than that reported in literature articles for non-crosslinked chitosan

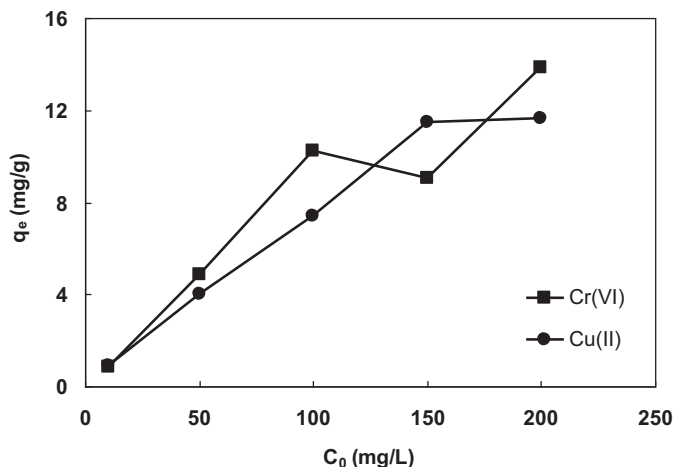


Fig. 9. Effect of the initial metal ion concentration (C_0) on the adsorption capacity of the chitosan-coated gauze (10 wt% gain) at 20 °C; pH 5 for Cu(II) and pH 3 for Cr(VI).

confirming that UV-grafting treatment does not reduce the availability of the amino and hydroxyl groups to coordinate metal ions.

Thus, the chitosan-coated cotton gauze studied can be considered as a good adsorbent for application in treatment of water solutions containing metal ions, like copper(II) and chromium(VI). Moreover its physical structure should enable the use in continuous flow filters owing to low pressure drop.

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