



Adsorption of chromium (VI) ion from aqueous solution by succinylated mercerized cellulose functionalized with quaternary ammonium groups

Leandro Vinícius Alves Gurgel^a, Júlio César Perin de Melo^c, Jorge Carvalho de Lena^b, Laurent Frédéric Gil^{a,*}

^a Departamento de Química, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto, Minas Gerais, Brazil

^b Departamento de Geologia, Escola de Minas, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto, Minas Gerais, Brazil

^c Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-971 Campinas, São Paulo, Brazil

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ABSTRACT

Succinylated mercerized cellulose (cell 1) was used to synthesize an anion exchange resin. Cell 1, containing carboxylic acid groups was reacted with triethylenetetramine to introduce amine functionality to this material to obtain cell 2. Cell 2 was reacted with methyl-iodide to quaternize the amine groups from this material to obtain cell 3. Cells 2 and 3 were characterized by mass percent gain, degree of amination and quaternization, FTIR and CHN. Cells 2 and 3 showed degrees of amination and quaternization of 2.8 and 0.9 mmol/g and nitrogen content of 6.07% and 2.13%, respectively. Cell 3 was used for Cr (VI) adsorption studies. Adsorption equilibrium time and optimum pH for Cr (VI) adsorption were found to be 300 min and 3.1, respectively. The Langmuir isotherm was used to model adsorption equilibrium data. The adsorption capacity of cell 3 was found to be 0.829 mmol/g. Kinetic studies showed that the rate of adsorption of Cr (VI) on cell 3 obeyed a pseudo-second-order kinetic model.

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1. Introduction

Removing pollutants from water and wastewater has grown with rapid industrialization. Industries including paint and pigment manufacturing, stainless steel production, corrosion control, leather tanning, chrome plating, wood preservation, fertilizers, textiles, and photography often discharge effluents containing hexavalent chromium, Cr (VI), to surface water (Gode and Pehlivan, 2005). Cr (VI) is toxic and a suspected carcinogenic material and it is quite soluble in aqueous phase almost over the entire pH range and mobile in the natural environment (Kotaš and Stasicka, 2000; Stasinakis et al., 2003; Gode and Pehlivan, 2005). Cr (VI) forms several species, the relative proportions of which depend on both pH and total Cr (VI) concentration. Within the normal pH range in natural waters, Cr (VI) exists mainly as CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$.

Among the various chemical treatment techniques available, commonly used in the removal of contaminants from wastewater: ion exchange, adsorption, reduction, and precipitation. In many cases, the environmentally most compatible and cost-effective technique comprises a combination of two or more of these processes. The main advantages of ion exchange are recovery of metal, selectivity, production of less sludge volume, and compliance with strict discharge specifications. Removal of Cr (VI) from cooling water and groundwater by various adsorbents has been investi-

gated by a number of researchers (Yoshitake et al., 2002; Demirbas et al., 2004; Gupta and Ali, 2004; Spinelli et al., 2004; Gode and Pehlivan, 2005; Karthikeyan et al., 2005; Khezami and Capart, 2005; Oliveira et al., 2005; Torres et al., 2005; Sarin and Pant, 2006; Namasivayam and Sureshkumar, 2008; Kuo and Bembenek, 2008).

Another adsorbent for removal of Cr (VI) from wastewater is activated carbon, which could be produced from various agricultural by-products and wastes. However, some of the adsorbents do not have good adsorption capabilities or need long adsorption equilibrium times. Hence, there is a need to search for more effective adsorbents (Namasivayam and Sureshkumar, 2008). One of the new developments in recent years for the removal of anionic Cr (VI) species from water and wastewater is to use surfactant modified adsorbents (Krishna et al., 2000; Li and Bowman, 2001; Bingol et al., 2004).

Cellulose is the most abundant and renewable biopolymer in nature, being considered one of the promising materials economically for the preparation of several types of adsorbents. Cellulose is more expensive than agricultural and agro-industrial by-products as sugarcane bagasse, sawdust, rice hulls, and coconut shells. However, cellulose has much more hydroxyl groups that can be modified than these by-products, which could improve synthesis yield and make its use economically feasible for some applications (Gurgel et al., 2008).

The quaternary ammonium halides have been synthesized and studied by Busi et al. (2005). These studies were based on their

* Corresponding author. Tel.: +55 31 3559 1717; fax: +55 31 3551 1707.
E-mail address: laurent@iceb.ufop.br (L.F. Gil).

properties as surfactants and catalysts. There is no data in literature about the synthesis in solid phase of adsorbents materials containing quaternary ammonium groups synthesized through the quaternization of amino-functionalized cellulose applied to oxyanions removal.

This work describes the preparation and evaluation of an anion exchange resin containing quaternary ammonium groups to adsorb Cr (VI) ions from an aqueous solution. For the preparation of this resin, cellulose was mercerized with an aqueous NaOH solution and reacted with succinic anhydride to introduce carboxylic acid functions according to the methodology described by Gurgel et al. (2008). The introduction of these functions opens the possibility for further derivatization as the introduction of amine functions (Mallon and Hill, 2002; Karnitz et al., 2007). Succinylated mercerized cellulose (cell 1) was reacted with diisopropylcarbodiimide and triethylenetetramine to introduce amine groups that can be transformed into quaternary ammonium groups by reaction of amino-functionalized succinylated mercerized cellulose (cell 2) with methyl-iodide to obtain ammonium-functionalized succinylated mercerized cellulose (cell 3). The adsorption capacity of chromium (VI) by cell 3 was evaluated by the Langmuir model (Ho et al., 2005; Karnitz et al., 2007; Gurgel et al., 2008).

2. Experimental

2.1. Materials

Grade 3 MM cellulose chromatography paper (Cat. No. 3030-861) was purchased from Whatman Company, Maidstone, England. Succinic anhydride, pyridine and methyl-iodide were purchased from VETEC (Brazil). *N,N'*-dimethylformamide (DMF) was purchased from TEDIA (CAS:68-12-2). 1,3-diisopropylcarbodiimide (DIC) and triethylenetetramine were purchased from Aldrich (Cat. No. D12,540-7 and 112-24-3, respectively). $K_2Cr_2O_7$ was purchased from ECIBRA (Brazil). Pyridine was refluxed with NaOH overnight and distilled. Dimethylformamide was treated with 4 Å molecular sieves (MERCK) and soon afterwards distilled under reduced pressure.

2.2. Synthesis of cellulose 2 (cell 2)

Succinylated mercerized cellulose (cell 1) was prepared and characterized according to the methodology described by Gurgel et al. (2008). Cell 1 (3.0 g, 7.2 mmol/g of carboxylic acid functions) was reacted with 10.2 mL (64.8 mmol) of 1,3-diisopropylcarbodiimide (DIC) in anhydrous dimethylformamide (DMF) (51 mL) at 25 °C for 1 h under constant magnetic stirring. Soon afterwards 16.1 mL (108 mmol) of triethylenetetramine was added to reaction media and the material was reacted for more 3 h in order to obtain cellulose 2 (cell 2). Cell 2 was separated by filtration in sintered filter, washed with DMF, ethanol 95%, distilled water, saturated sodium bicarbonate solution, distilled water, ethanol 95% and then with diethyl ether. After drying under vacuum, cell 2 was stored in a desiccator overnight and the mass percent gain (mpg) was calculated.

2.3. Synthesis of cellulose 3 (cell 3)

Cell 2 (3.0 g, 2.8 mmol/g of amine functions) was reacted with 5.2 mL (84 mmol) of methyl-iodide and 2.1 g (21 mmol) of anhydrous sodium carbonate in anhydrous dimethylformamide (DMF) (51 mL) at 50 °C for 24 h under constant magnetic stirring in order to obtain cellulose 3 (cell 3). Cell 3 was separated by filtration in sintered filter, washed with DMF, distilled water and then with diethyl ether. After drying under vacuum, cell 3 was stored in a

desiccator overnight and the mass percent gain (mpg) was calculated.

2.4. Characterization of celluloses 2 and 3

2.4.1. Mass percent gain

The mass percent gain (mpg) was calculated according to Eq. (1):

$$\text{mpg}(\%) = \left(\frac{m_{\text{mod}} - m_{\text{unmod}}}{m_{\text{unmod}}} \right) * 100, \quad (1)$$

where m_{mod} is the mass of modified material and m_{unmod} is the mass of unmodified material.

2.4.2. Degree of amination

The degree of amination of cellulose 2 was determined by measuring the quantity of introduced basic function. The concentration of amine functions per gram of modified cellulose 2 was determined by retro-titration. For this, 0.1000 g of cell 2 was treated with 100.0 mL of an aqueous HCl solution (0.01 mol/L) in a 250-mL Erlenmeyer for 1 h under constant stirring. Soon after the material was separated by single filtration and three aliquots (25.0 mL) of each obtained solution were titrated with aqueous NaOH solution (0.01 mol/L) (Karnitz et al., 2007). The concentration of amine functions was calculated by:

$$C_{\text{NH}_2} = \left[\frac{(C_{\text{HCl}} * V_{\text{HCl}}) - (4 * C_{\text{NaOH}} * V_{\text{NaOH}})}{m_{\text{cell 2}}} \right], \quad (2)$$

where C_{HCl} is the concentration of HCl solution (mmol/L), C_{NaOH} is the concentration of NaOH solution (mmol/L), V_{HCl} is the volume of HCl solution (L), V_{NaOH} is the volume of NaOH spent in the titration of non-reacted acid's excess (L) and $m_{\text{cell 2}}$ is the cellulose 2 mass (g).

2.4.3. Degree of quaternization

The degree of quaternization of the cellulose 3 was determined by measuring the quantity of iodide ions. The concentration of ammonium groups per gram of modified cellulose 3 was determined by conductimetric titration. For this, 0.1000 g of cell 3 was suspended in a 250-mL Erlenmeyer containing 100.0 mL of bidistilled water and titrated with aqueous standard $AgNO_3$ solution (0.1 mol/L). This procedure was accomplished in triplicate (Spinelli et al., 2004). The concentration of ammonium groups was calculated by:

$$C_{-\text{NH}_3} = \frac{(C_{\text{AgNO}_3} * V_{\text{AgNO}_3})}{m_{\text{cell 3}}}, \quad (3)$$

where C_{AgNO_3} is the concentration of $AgNO_3$ solution (mmol/L), V_{AgNO_3} is the volume of $AgNO_3$ solution (L) and $m_{\text{cell 3}}$ is the mass of cellulose 3 (g).

2.4.4. FTIR analysis

Samples were prepared mixing 1 mg of material with 100 mg of spectroscopy grade KBr. The FTIR spectra were recorded using Nicolet Impact 410 equipment with detector at 4 cm^{-1} resolution from 500 to 4000 cm^{-1} and 32 scans per sample.

2.4.5. Elemental analysis

The samples were previously dried and analyzed with a CHNS/O Perkin Elmer Series II equipment.

2.4.6. Scanning electron microscopy and energy dispersive X-ray (SEM/EDX)

The map of adsorbed chromium (VI) on the surface of cell 3 was made using scanning electron microscopy and energy dispersive

X-ray (SEM/EDX) model JEOL JSM-5510 equipments. The sample was pressed to make its surface perfectly flat and metallized with graphite using an evaporate-to-vacuum equipment model JEE-4C to make the surface conductive. The analysis was made using potential difference of 20 kV for the tungsten filament.

2.5. Kinetic study of Cr (VI) adsorption

Experiments with cell 3 and Cr (VI) ion were performed to determine the adsorption equilibrium time. The time intervals used were: 10, 20, 30, 45, 60, 120, 180, 240, 300 and 1440 min, respectively. Masses of 50 mg of cell 3 were placed in a 250-mL Erlenmeyer with 50.0 mL of Cr (VI) ion solution at 1.92 mmol/L. The adsorption experiments were made under constant mechanic stirring at 25 °C. The pH of Cr (VI) solution with cell 3 was found to be 3. There were not significant pH variations at the end of each experiment.

After single filtration, the concentration of Cr (VI) ion was determined by atomic absorption spectroscopy (Varian Spectra AA475).

2.6. Effect of pH on Cr (VI) adsorption

A study on the pH dependency of Cr (VI) adsorption by cell 3 was carried out. The range of pH used was 1.0–10.0. Masses of 50 mg of cell 3 were placed in a 250-mL Erlenmeyer with 50.0 mL of Cr (VI) ion solution at 1.92 mmol/L. The adsorption experiments were made under constant mechanic stirring at 25 °C and the pHs of solutions were adjusted with an aqueous HCl and NaOH solution at 0.01–1.0 mol/L. The reaction time used was obtained from the kinetic study. Significant pH variations were observed during each experiment, but pH values were kept constant by adjusting it with NaOH solution (0.01–0.1 mol/L).

2.7. Adsorption isotherm of Cr (VI)

Experiments with cell 3 and Cr (VI) ion were performed to determine the adsorption equilibrium isotherm. Masses of 50 mg of cell 3 were placed in a 250-mL Erlenmeyer with 50.0 mL of Cr (VI) ion solution at specific concentrations from 0.67 to 1.64 mmol/L. Each experiment was performed at pH 3.1, optimum pH for Cr (VI) ion adsorption obtained from pH study and a period of 300 min was adopted. Significant pH variations were observed during each experiment, but pH values were kept constant by adjusting it with NaOH solution (0.01–0.1 mol/L).

3. Results and discussion

3.1. Characterization of cells 2 and 3

Fig. 1 illustrates the synthesis route used to prepare cells 2 and 3 and adsorption mechanism of HCrO_4^- on cell 3. According to the Cr (VI) speciation diagram (Leyva-Ramos et al., 1994), the predominant Cr (VI) species in an aqueous solution at pH 3.1 is HCrO_4^- . The results of mass percent gains, concentration of amine and ammonium functions and percentage of nitrogen are presented in Table 1.

The carboxylic acid functions introduced in cell 1 were used to anchor the triethylenetetramine to cellulosic matrix. Cell 2 was obtained with a mass percent gain of 33.6%, amination degree of 2.8 mmol/g and nitrogen content of 6.07%. These results show that the utilization of succinylated mercerized cellulose (cell 1) is an excellent alternative to prepare chelating materials containing amine ligands.

In the synthesis of cell 2, the formation of crosslinking was observed as mentioned by Navarro et al. (1999), decreasing the amount of immobilized triethylenetetramine. Various studies were performed in our laboratory to reduce the formation of crosslinking. It was concluded through our studies that the use of an excess amount of triethylenetetramine is one of the possible ways to reduce the formation of crosslinking.

The amine functions anchored to cell 2 were used to synthesize a new chelating material containing ammonium quaternary groups capable of adsorbing oxyanions through anion exchange (cell 3). Cell 3 was obtained with a mass percent gain of 144.6%, quaternization degree of 0.9 mmol/g and nitrogen content of 2.13%. These results showed the success of the synthesis methodology applied in this work.

3.1.1. FTIR characterization

The characterization of the cells 2 and 3 was accomplished by FTIR spectroscopy. The FTIR spectra of cell 1–cell 2 and cell 2–cell 3 are presented in Figs. 2 and 3, respectively.

As depicted in Fig. 2, the most relevant change observed in the FTIR spectra of cell 2 in relation to cell 1 is the appearance of bands at 1699, 1647, 1635, 1576, 1410, 1259, 1159 and 1055 cm^{-1} . The bands at 1699 and 1647 cm^{-1} correspond to stretching of carbonyl group (C=O) of primary amide (amide I). The band at 1635 cm^{-1} corresponds to deformation vibration of $-\text{NH}_x$ in plane. The band at 1576 cm^{-1} corresponds to deformation vibration of groups $-\text{NH}-$ of amines. The bands at 1410, 1259 and 1159 cm^{-1}

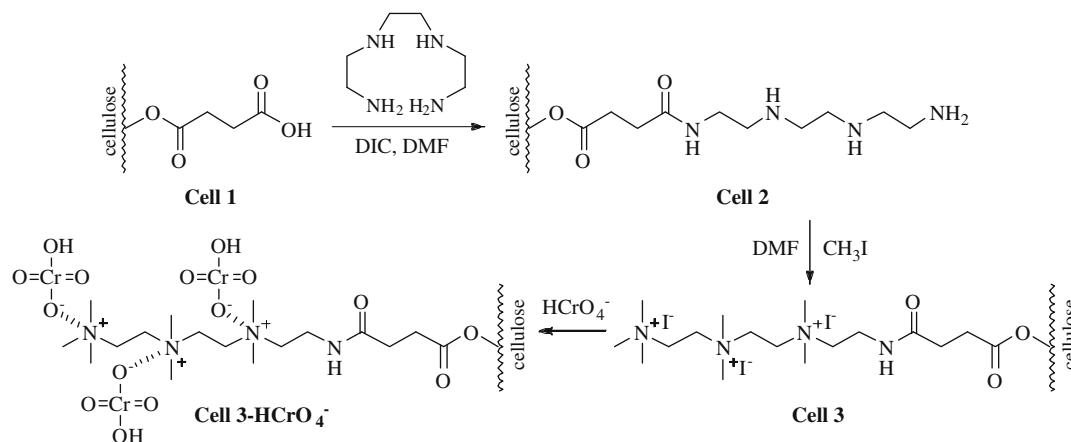
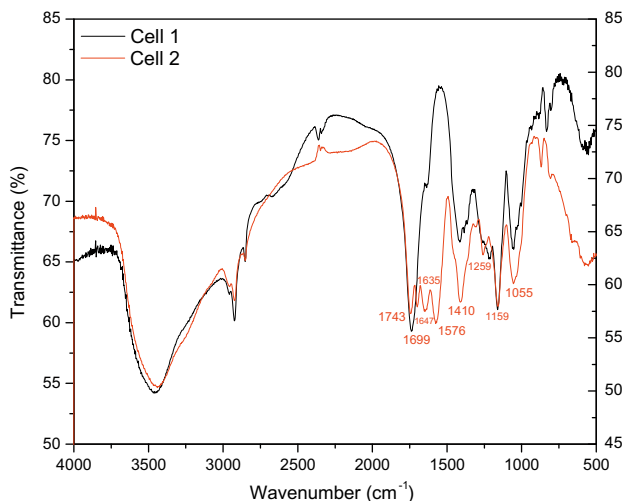
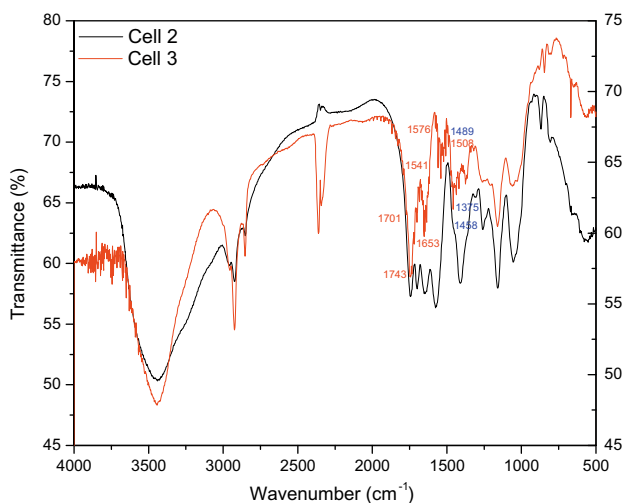


Fig. 1. Synthesis route used to prepare cells 2 and 3, and adsorption mechanism of HCrO_4^- on cell 3.

Table 1

Type of material, mass gain percent, concentration of amine and ammonium functions and percentage of nitrogen.

Material	Mpg (%)	C _{NH-NH₂} (mmol/g)	C _{-NH₃⁺} (mmol/g)	N (%)
Cell 2	33.6	2.8 ± 0.0	–	6.07 ± 0.01
Cell 3	144.6	–	0.9 ± 0.1	2.13 ± 0.01

**Fig. 2.** FTIR spectra of cell 1 and cell 2.**Fig. 3.** FTIR spectra of the cell 2 and cell 3.

correspond to deformation vibration of C–N and the band at 1055 cm⁻¹ corresponds to asymmetric stretching of C–N–C.

As depicted in Fig. 3, the most relevant change observed in the FTIR spectra of cell 3 in relation to cell 2 is the appearance of bands at 1576, 1508, 1489, 1458 and 1375 cm⁻¹. The bands at 1576 and 1508 cm⁻¹ correspond to asymmetric and symmetric deformation of –N⁺(CH₃)₃. The bands marked in blue are present in FTIR spectra of tetramethylammonium iodide and also in cell 3 which has dimethyl and trimethylammonium groups. Therefore, the bands at 1489 and 1458 cm⁻¹ correspond to symmetric deformation of –CH₃.

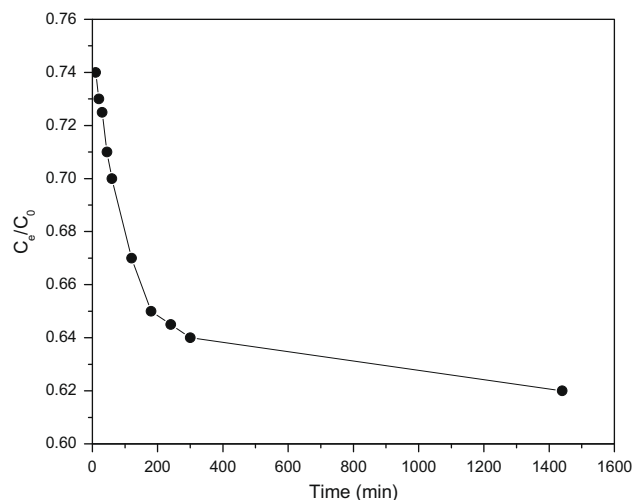
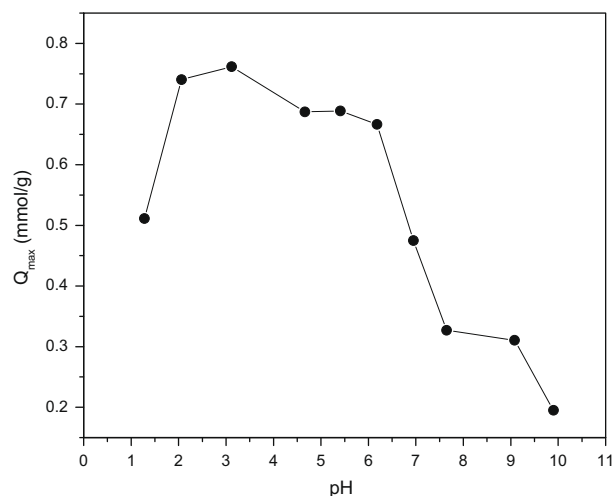
3.2. Adsorption of Cr (VI) onto cell 3

3.2.1. Effect of contact time

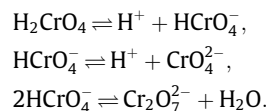
The effect of contact time on the adsorption of Cr (VI) on cell 3 for fixed initial Cr (VI) concentration (1.92 mmol/L) at pH 3 and 25 °C is shown in Fig. 4. The adsorption equilibrium of Cr (VI) was attained in 300 min. C_e and C₀ are the equilibrium and initial metal ion concentrations (mmol/L), respectively. There was not significant change in equilibrium concentration after 300 min up to 1440 min within detection limit of the atomic absorption equipment used.

3.2.2. Effect of pH

The effect of pH on the adsorption of Cr (VI) at a fixed initial Cr (VI) concentration (1.92 mmol/L) at 25 °C is shown in Fig. 5. In aqueous solutions, Cr (VI) exists in the form of chromic acid (H₂CrO₄) and in the form of dichromate (Cr₂O₇²⁻). In this process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The chromate may be represented in various forms such as H₂CrO₄, HCrO₄⁻, CrO₄²⁻, HCr₂O₇⁻, and Cr₂O₇²⁻ in the solution phase as a function of pH and concentration. At pH 1, chromium ions exist in the form of HCrO₄⁻, while in the pH range 2–6 different

**Fig. 4.** Effect of contact time on the adsorption of Cr (VI) ion onto cell 3.**Fig. 5.** Effect of pH on the adsorption of Cr (VI) onto cell 3.

forms of chromium ions such as HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ coexist, being HCrO_4^- predominant. As the pH increases, this form shifts to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. At pH greater than 7.5, CrO_4^{2-} is the only chromate species in aqueous phase (Mallick et al, 2006). The existing balance among different ionic species of chromium is as follows:



The charges of the ammonium groups of cell 3 are not pH-dependent, i.e., they come from positively charged nitrogen atoms joined by single bonds to methyl groups as can be seen in Fig. 1. Besides, iodide ions are bonded to ammonium groups through electrostatic interactions and the Cr (VI) adsorption on cell 3 could be based on ion-exchange process in which Cr (VI) ions are adsorbed while iodide ions are released to the solution (Fig. 1). Therefore, amount of positive charges on cell 3 is fixed, and then quantity of Cr (VI) adsorbed is only dependent on the forms of chromium species present in solution.

The maximum adsorption capacity (Q_{max}) of Cr (VI) ions was obtained at pH 3.1 while the adsorption decreased when the pH increased, as can be observed in Fig. 5. At pH 3.1, the specie of chromium that predominates is HCrO_4^- (Leyva-Ramos et al., 1994; Yusof and Malek, 2008). As described above, at lower pH, the Cr (VI) species are mostly univalent forms (HCrO_4^-) and thus this specie requires only one exchange site. At pH greater than 3.5, the adsorption of chromium decreased due to an increase in the concentration of divalent chromium species as CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ that require two exchange sites to occur the adsorption. At pH greater than 7.0, OH^- ions concentration is higher and these ions could be adsorbed by cell 3. At the pH range of 6.5–10, the adsorption decreased significantly. According to Yusof and Malek (2008), this behavior might be explained considering the lower affinity of the exchange sites for Cr (VI) sorption at pH 10 and thus the adsorption capacity may then be influenced by the strong competition of OH^- with I^- or CrO_4^{2-} for the sorption sites since more OH^- ions are present at high pH. Li (2004) and Yusof and Malek (2008) also found similar observations.

3.2.3. Adsorption kinetics

The kinetics of adsorption describes the adsorption rate of chromium ions onto the cell 3 and this rate controls the equilibrium time. These models are important in water treatment process projects. The kinetics of adsorption of Cr (VI) onto cell 3 was analyzed by pseudo-first-order and pseudo-second-order mechanism 25 °C temperature.

3.2.3.1. Pseudo-first-order model. The adsorption kinetics data of Cr (VI) were analyzed using the Lagergren rate equation (Lagergren, 1898). The linearized form of the pseudo-first-order equation (Ho and McKay, 1998) is illustrated by:

$$\log(q_e - q_t) = \log q_e - \frac{k'_1}{2.303} t, \quad (4)$$

where q_e and q_t are the amounts of Cr (VI) adsorbed (mmol/g) at equilibrium and at time t (min), respectively, and k'_1 is the Lagergren rate constant of first-order adsorption time (min^{-1}). Values of q_e

and k'_1 were calculated from the slope and intercept of plot of $\log(q_e - q_t)$ versus t (figure not shown). As can be seen in Table 2, the R^2 value of the pseudo-first-order model was found to be lower than pseudo-second-order model. Based on these results it can be concluded that the adsorption of Cr (VI) on cell 3 did not fit a pseudo-first-order kinetic model. Moreover, from Table 2, it can be seen that the experimental value of $q_{e,\text{exp}}$ is not in good agreement with the theoretical value calculated ($q_{e1,\text{cal}}$) from Eq. (4). Therefore, this suggests that the pseudo-first-order model was not suitable for modeling the adsorption of Cr (VI) on cell 3. Experimental data were also tested by the pseudo-second-order kinetic model, which is described by Eq. (5).

3.2.3.2. Pseudo-second-order model. A pseudo-second-order model can be used to describe the sorption kinetics. The linearized form of the pseudo-second-order equation (Ho and McKay, 1998) is illustrated by:

$$\frac{t}{q_t} = \frac{1}{k'_2 q_e^2} + \frac{1}{q_e} t, \quad (5)$$

where q_e (mmol/g) and q_t (mmol/g) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium time, t is the time (min) and k'_2 is the pseudo-second-order rate constant ($\text{g mmol}^{-1} \text{min}^{-1}$). The equilibrium constants of pseudo-second-order model, k'_2 and q_e can be obtained by plotting t/q_t versus t (Fig. 6).

This model is more likely to predict kinetic behavior of adsorption of Cr (VI) on cell 3. The linear plot of t/q_t versus t (Fig. 6) showed R^2 value greater than 0.999 as can be seen in Table 2. In addition, the theoretical $q_{e2,\text{cal}}$ value is closer to the experimental $q_{e,\text{exp}}$ value. Considering these results, it can be said that pseudo-second-order kinetic model provided a good correlation for adsorption of Cr (VI) on cell 3 in contrast to pseudo-first-order model. A similar result was observed in the adsorption of Cr (VI) onto quarternary chitosan salt (Spinelli et al., 2004).

3.2.4. Adsorption isotherm

Factors influencing the adsorption rate are mainly, among others, the nature and concentration of competing ions, pH, resin amount, shaking speed and temperature (Gode and Pehlivan, 2005). According to Gode and Pehlivan (2005), three individual composition variables (nature of polymer matrix, basicity and steric property of the exchanger's functional group) were found to have significant impact on chromium sorption.

Adsorption isotherms describe how adsorbates interact with adsorbents and are important in optimizing the use of the latter. The widely used Langmuir isotherm (Langmuir, 1918) has found successful application in many real adsorption processes and its linearized form is expressed by:

$$\frac{C_e}{q_e} = \frac{1}{Q_{\text{max}} b} + \frac{C_e}{Q_{\text{max}}}, \quad (6)$$

where q_e (mmol/g) is the equilibrium adsorption capacity, Q_{max} (mmol/g) is the maximum amount of metal ion per weight unit of cell 3 to form a complete monolayer coverage on the surface bound at high equilibrium metal ion concentration C_e (mmol/L) and b (L/mmol) is the Langmuir constant related to the affinity of binding sites. Q_{max} represents the practical limiting adsorption capacity when the surface is fully covered with metal ions, assisting in the

Table 2
Comparison of pseudo-first-order and pseudo-second-order adsorption rate constant and calculated and experimental q_e values for Cr (VI) adsorption.

Parameter	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k'_1 (min^{-1})	$q_{e1,\text{cal}}$ (mmol/g)	R^2	k'_2 (g/mmol min)	$q_{e2,\text{cal}}$ (mmol/g)	R^2
$q_{e,\text{exp}}$ (mmol/g)						
0.829	2.67×10^{-1}	0.248	0.9834	7.20×10^{-2}	0.754	0.9996

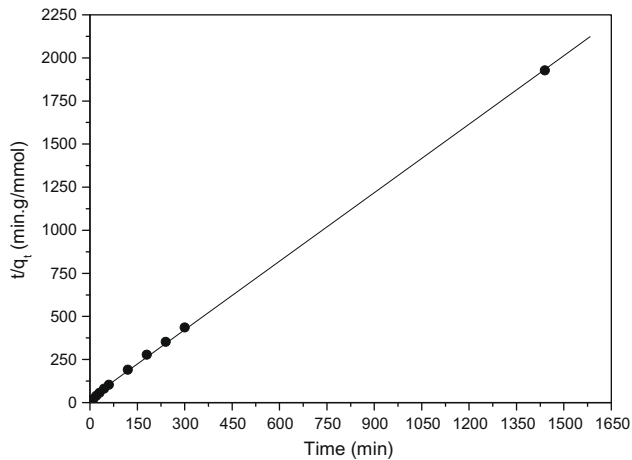


Fig. 6. Pseudo-second-order kinetic plot for the adsorption of Cr (VI) onto cell 3.

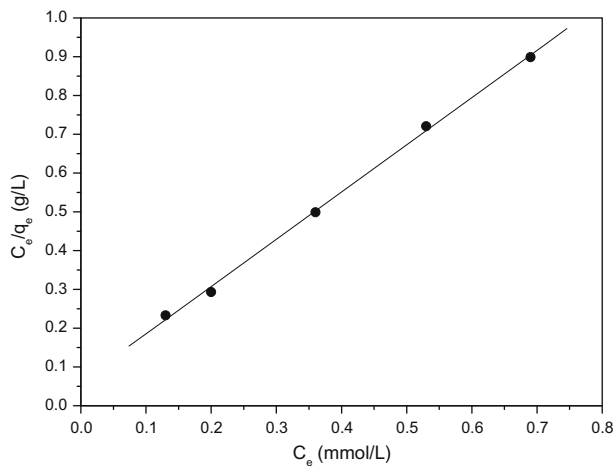


Fig. 7. Langmuir plot for the adsorption of Cr (VI) onto cell 3.

Table 3
Langmuir parameters for Cr (VI) adsorption onto cell 3.

Q_{\max} (mmol/g)	b (L/mmol)	R^2
0.829	18.0	0.9985

comparison of adsorption performance, and b indicates the bond energy of the adsorption reaction between metal and material.

A linearized plot of C_e/q_e versus C_e was obtained from the model and is shown in Fig. 7. Q_{\max} and b were computed from the slope and intercept of straight line. Table 3 lists the results calculated.

The high correlation coefficient obtained by the Langmuir model indicated that it described the adsorption of Cr (VI) by cell 3 very well.

As shown in Table 3, cell 3 presented a maximum adsorption capacity (Q_{\max}) of 0.829 mmol/g and bond energy (b) in relation to chromium species of 18.0 L/mmol. This Q_{\max} for Cr (VI) adsorption by cell 3 was smaller than activated carbon prepared from agricultural wastes such as cornelian cherry (CC), apricot stone (AS), and almond shell (ASC) (Demirbas et al., 2004) that adsorbed 1.142, 1.132, and 1.147 mmol/g of Cr (VI), respectively (pH 1 and adsorption equilibrium at 72 h) and much higher than impregnated Fe or Al oxide-shavings (Kuo and Bembenek, 2008) that adsorbed 0.0194 and 0.0186 mmol/g (pH 6 and adsorption equilibrium at 4 h). In contrast, the rate constant k_2 for cell 3 (0.072 g/mmol min) was smaller than impregnated Fe or Al oxide-shavings (Kuo and Bembenek, 2008), which was equal to 2.95 and 3.77 g/mmol min and (CC), (AS), and (ASC) (Demirbas et al., 2004), whose rate constant k_2 ranged from 0.0260 to 3.026 g/mmol min, depending on type of activated carbon and initial concentration of Cr (VI) used.

Compared to CC, AS, ASC, and impregnated Fe or Al oxide-shavings, cell 3 was the most expensive material to be prepared by considering the biopolymer matrix, reagents and preparation techniques used. Therefore, the preparation cost of cell 3 is a disadvantage in relation to the compared materials, however cell 3 showed a good adsorption capacity as discussed previously and this could be an advantage of this material.

An advantage of impregnated Fe or Al oxide-shavings demonstrated by Kuo and Bembenek (2008) was the rapid desorption rate of sorbed Cr (VI). However, after nine weeks of contact, more than 50% of sorbed Cr on Fe oxide-shavings was transformed into stable form not extractable by 0.1 mol/L NaOH and 1 mol/L HNO₃. This transformation did not happen to Al oxide-shavings system.

On the other hand, cell 3 was resistant to acid and basic pHs and this could make possible successive desorption processes to recover sorbed Cr (VI) without significant loss of adsorption capacity.

3.3. Scanning electron microscopy (SEM/EDX)

Cell 3 surface was analyzed by SEM/EDX after adsorption studies of Cr (VI). Fig. 8 shows cell 3 map containing adsorbed chromium (VI). As can be observed from cell 3 map, the adsorbed Cr (VI) appeared to be uniformly distributed onto the surface indicat-

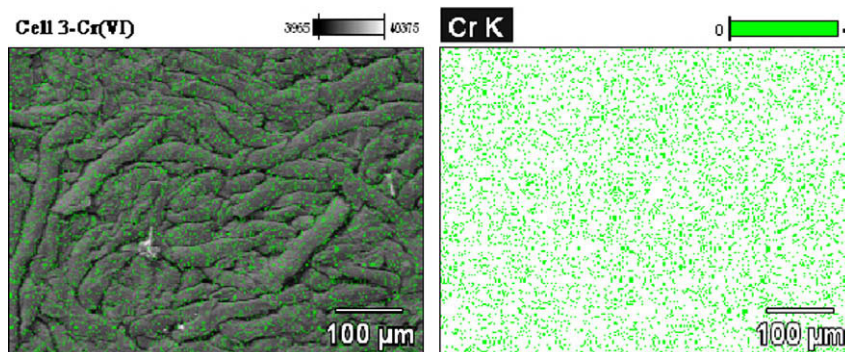


Fig. 8. Scanning electron micrograph of cell 3-Cr (VI) sample.

ing that the adsorption sites were uniformly distributed and that chemical modification occurred in all extension of material.

4. Conclusions

Cell 2, containing ligands groups amine was synthesized with success through the reaction between succinylated mercerized cellulose (cell 1) and triethylenetetramine, a polydentate ligand. Cell 2 was obtained with a mass percent gain of 33.6%, a concentration of ammonium function of 2.8 mmol/g and nitrogen content of 6.07%. Cell 3, a surfactant containing ammonium groups, was synthesized by reaction of cell 2 with methyl-iodide, an alkylating agent. Cell 3 was obtained with a mass percent gain of 144.6%, a concentration of ammonium function of 0.9 mmol/g and nitrogen content of 2.13%.

The removal of chromium ions from aqueous solution by cell 3 was found to be effective. Equilibrium adsorption time was found to be 300 min and optimum pH for chromium removal was found to be 3.1. Equilibrium adsorption data fitted to the Langmuir model very well, the adsorption maximum capacity of Cr (VI) was found to be 0.829 mmol/g and the Langmuir constant related to the affinity of binding sites by Cr (VI) species was found to be 18.0 L/mmol. The adsorption process of Cr (VI) on cell 3 followed the pseudo-second-order kinetic model and the adsorption rate was found to be 7.2×10^{-2} g/mmol min.

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