

SEPARATION OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS BY
CELLULOSE MODIFIED WITH D-GLUCOSE AND QUATERNARY
AMMONIUM GROUPS

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A novel method for D-glucose (D-Glu) and trimethylammonium chloride immobilization onto the surface of cellulose powder was studied. Cellulose powder was grafted with vinyl monomer glycidyl methacrylate (GMA), using ceric ammonium nitrate as an initiator, and further derived with quaternary ammonium groups to build the D-GluN⁺-type cellulose adsorbent (Cell-g-GMA-D-GluN⁺). Epoxy cellulose was found to contain 5.48 mmol/g epoxy groups. The adsorption process of modified cellulose was described by the Langmuir model of adsorption well, the maximum adsorption capacity of chromium (VI) reaching a value of 71.79 mg/g. Adsorption-desorption tests of the D-GluN⁺-type cellulose derivatives showed a good reproducibility of the adsorbent, so that the adsorbent could be reused for at least six times.

Keywords: chromium (VI), modified cellulose, D-glucose, trimethylammonium chloride

INTRODUCTION

Although chromium (VI) compounds are extensively used for electroplating and anodizing operations in the surface-finishing industry, corrosion control, oxidation, leather industry and various other industrial applications, they are known as toxic substances.^{1,2}

A long list of methods has been elaborated for the removal of chromium (VI), such as chemical precipitation, ion exchanger, membrane separation, solvent extraction and adsorption. Especially adsorption is considered as one of the

most popular techniques.³

Cellulose, considered as one of the most economic materials for the preparation of several types of adsorbent, is an abundant and renewable biopolymer in nature. Cellulose is not only renewable, biodegradable and inexpensive, but it also possesses numerous primary active hydroxyls, which easily trigger various reactions, such as the free radical reaction, esterification, halogenation, oxidation and etherification.⁴ Various cellulose derivatives were synthesized by

such reactions. Cation-exchange cellulose was modified by quaternary ammonium groups, as adsorption-desorption function groups, to uptake the heavy metal ions from aqueous solutions, and 2 mol/L NaCl or a mixture of 0.05 mol/L NaOH and 2 mol/L NaCl was used as a desorption agent, as due to the positive high charge density of adsorbent's surface.⁵ The N-methylglucamine-type cellulose derivatives were used for the treatment of arsenic (V) compounds aqueous solution.⁶

D-glucose is a natural polyhydroxyl compound with the β -D-glucoside, chain-D-glucose and α -D-glucoside forms in reversible balance system from aqueous solutions.

In this study, complex D-GluN⁺-type cellulose derivatives were synthesized to obtain a novel mixture adsorbent with high selectivity and excellent adsorption capacity for chromium (VI); also, the desorption behavior of chromium (VI) by batch and column methods was investigated.

EXPERIMENTAL

Materials

Regenerated cellulose powder was used as a form of cellulose. Ceric ammonium nitrate (CAN) and trimethylammonium (>33%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Glycidyl methacrylate (>99%, GMA), obtained from Shangqiu Shengyuan Industrial Assistant Co., Ltd., was further treated by the reduced pressure distillation method. D-glucose ($[\alpha]_D^{20} = +52.5^\circ \sim +53.0^\circ$) was obtained from Tianjin Kermel Co., Ltd. Potassium dichromate (K₂Cr₂O₇) was used as a source of chromium (VI). NaOH, HCl and all other chemicals and reagents were of an analytical grade.

Preparation of D-GluN⁺-type cellulose derivatives

Synthesis of epoxy cellulose

The poly(glycidyl methacrylate) [poly(GMA)] chains were grafted on the cellulose surface through GMA polymerization, using ceric ammonium nitrate as an initiator, epoxy cellulose being thus obtained. In a

500 mL round flask, cellulose (0.90 g) was initiated with CAN (0.12 mol) and 12 mL of 1 mol/L nitric acid in water (300 mL). The pH was adjusted to 1.3 with nitric acid and a sodium hydroxyl aqueous solution. Then, GMA (9 mL) was added, the content of the flask being heated at 35 °C for 2.5 h under stirring in N₂ atmosphere. The epoxy cellulose products were Soxhlet extracted with acetone for 12 h to remove the GMA homopolymer, then dried at 60 °C under vacuum. 6.21 g epoxy cellulose was obtained.

Synthesis of Cell-g-GMA-D-Glu

Cell-g-GMA-D-Glu was prepared by the ring-opening reaction of epoxy cellulose powder with a vinyl monomer. In a 250 mL flask, the epoxy cellulose powder (2.5 g) was added, then dissolved in 50 mL DMF for some time, after which D-glucose (0.3 g), NaCl (0.5 mol/L) and 50 mL H₂O solution were added, the reaction being heated at 75 °C for 16 h.⁷ The products were filtered off, washed with water, then dried at 50 °C for 12 h. 2.8 g Cell-g-GMA-D-Glu, the intermediate compound, were obtained.

Synthesis of trimethylammonium chloride

The quaternary ammonium compound was synthesized by trimethylammonium (0.12 mol) and hydrochloric acid (0.12 mol), as described by Levy *et al.*⁸ The trimethylammonium chloride aqueous solution was transferred into a 100 mL volumetric flask and the volume was filled to 100 mL by adding water, then the pH was adjusted to 9.0.

Synthesis of D-GluN⁺-type cellulose derivatives

In a 250 mL flask, Cell-g-GMA-D-Glu (2.5 g) was added, then dissolved in 50 mL DMF for some time, after which trimethylammonium chloride (60 mmol, 50 mL), NaCl (0.5 mol/L) and 50 mL H₂O solution were added and the reaction was heated at 75 °C for 20 h.⁹ The products were filtered off, washed with water and then dried at 50 °C for 12 h. 2.6 g Cell-g-GMA-D-GluN⁺ was obtained. The structure of D-GluN⁺-type cellulose derivatives is shown in Scheme 1.

Determination of epoxy cellulose and Cell-g-GMA-Glu

Graft percentage was determined by the percent increase in weight, as follows:¹⁰

$$G = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

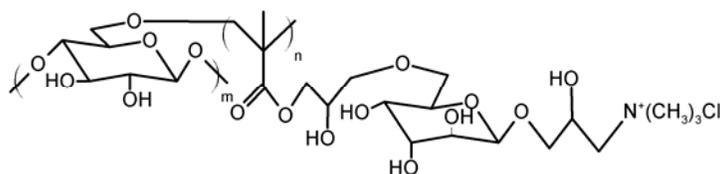
where W_o (g) and W_g (g) are the weights of the initial and epoxy cellulose, respectively, and G (%) is the graft percentage of epoxy cellulose.

The content of epoxy group in the epoxy cellulose was

determined by the HCl-acetone titration method. The content of the epoxy group in epoxy cellulose was expressed as follows:

$$E_{pv} = \frac{(V_0 - V_1)C_{NaOH}}{W_g} \quad (2)$$

where V_0 (mL) and V_1 (mL) are the titrimetric consumed volumes of both NaOH and blank sample, respectively; C_{NaOH} (mol/L) is the amount of NaOH standard solution; E_{pv} (mmol/g) is the content of epoxy group in the epoxy cellulose.



Scheme 1: Structure of D-GluN⁺-type cellulose derivatives

The Cell-g-GMA products opened the epoxy group and the Cell-hydro-g-GMA compound was obtained. The hydrolysis rate of the Cell-g-GMA was expressed as:

$$H = \frac{\frac{W_g - W_o - W_g \cdot E_{pv} \cdot M_{GMA} \times 10^{-3}}{M_{H_2O} + M_{GMA}} \times 100}{\frac{W_g - W_o - W_g \cdot E_{pv} \cdot M_{GMA} \times 10^{-3}}{M_{H_2O} + M_{GMA}} \times 10^3 + W_g \cdot E_{pv}} \times 100$$

where M_{H_2O} (g/mol) and M_{GMA} (g/mol) are the molecular weights of H₂O and GMA, respectively; H (%) is the hydrolysis rate of epoxy cellulose.

Epoxy cellulose is made up of Cell-g-GMA and Cell-hydro-g-GMA. Obviously, the amount of hydroxyl in epoxy cellulose can be transformed into the amount of hydroxyl of cellulose and hydro-g-GMA (part of Cell-hydro-g-GMA):

$$H_g = \frac{n_{before, OH}}{W_u} \quad (4)$$

$$n_{before, OH} = (2 \cdot n_{hydro-g-GMA} + b \cdot n_{cellulose}) \cdot \frac{W_u}{W_g} \quad (5)$$

$$n_{hydro-g-GMA} = \frac{W_g - W_o - W_g \cdot E_{pv} \cdot M_{GMA} \times 10^{-3}}{M_{H_2O} + M_{GMA}} \times 10^3 \quad (6)$$

where $n_{before, OH}$ (mmol) and $n_{hydro-g-GMA}$ (mmol) are the

amount of hydroxyl on epoxy cellulose and hydro-g-GMA, respectively; b is the amount of hydroxyl on glucose per unit of cellulose grafted by GMA, which could be selected in a range from 2 to 3; W_u (g) is the weight of the next step of epoxy cellulose intermediate compound; H_g (mmol/g) is the hydroxyl group content of epoxy cellulose.

After the epoxy cellulose reacted with glucose, the amount of hydroxyl was increased by hydroxyls of D-Glu and g-GMA (part of Cell-g-GMA):

$$n_{cellulose} = \frac{W_o}{M_{glucose}} \times 1000 \quad (7)$$

$$H_f = \frac{n_{after, OH}}{W_f} = \frac{n_{before, OH} + n_{f, OH}}{W_f} \quad (8)$$

$$n_{f, OH} = 3 \cdot n_{D-Glu} + 2 \cdot n_{g-GMA} = 5 \cdot n_{D-Glu} = 5 \cdot \frac{W_{D-Glu}}{M_{glucose}} \times 10^3$$

where n_{g-GMA} (mmol), n_{D-Glu} (mmol), $n_{before, OH}$ (mmol), $n_{after, OH}$ (mmol), $n_{f, OH}$ (mmol) and $n_{cellulose}$ (mmol) are the amount of hydroxyl on g-GMA (part of Cell-g-GMA), D-Glu, epoxy cellulose, Cell-g-GMA-D-Glu, g-GMA-D-Glu (part of Cell-g-GMA-D-Glu) and cellulose, respectively; $M_{glucose}$ (g/mol) is the molecular weight of D-glucose; W_{D-Glu} (g) is the weight D-Glu; H_f (mmol/g) is the

content of hydroxyl group in Cell-g-GMA-D-Glu.

FTIR characterization

The IR spectra of the samples prepared by mixing 1 mg of each material with 100 mg of spectroscopy grade KBr were recorded from 4000 cm^{-1} to 400 cm^{-1} using a Thermo Nicolet Avatar 360 FTIR Spectrometer.

SEM characterization

Scanning electron micrographs of the samples were recorded on a Jeol JSM5600LV scanning electron microscope.

Elemental analysis characterization

The epoxy cellulose and Cell-g-GMA- β -CDN⁺ were previously dried and analyzed using a Perkin-Elmer 2400II equipment.

Thermogravimetric and differential thermal analysis

Thermogravimetric (TGA) and differential thermal (DTA) analyses were performed with a Mettler-Toledo DTA/TGA instrument in the temperature range from 50 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$, at a rate of 10 $^{\circ}\text{C}/\text{min}$, under nitrogen flow.

Adsorption experiments

Batch adsorption studies were carried out by shaking 50 mg of Cell-g-GMA-D-GluN⁺ with 30 mL of the aqueous solution of chromium (VI), in different conical flasks, using a temperature-controlled shaker for some time. Then, the mixtures were filtered out and the chromium (VI) concentration of filtrate was analyzed by the 1,5-Diphenylcarbohydrazide spectrophotometric method, using a 7230G VIS recording spectrophotometer.

Desorption study

A glass column was used to pack 50 mg of adsorbent. A 25 mL of sample solution containing an appropriate amount of chromium (VI) was passed through the column at a flow rate of 0.5 mL/min after

the pH value was adjusted to 3.5. After washing the mixture with distilled water, the adsorbed chromium (VI) was stripped from the adsorbent, using a certain concentration of NaOH at a rate of 1 mL/min.

RESULTS AND DISCUSSION

Determination of epoxy cellulose and Cell-g-GMA-D-Glu

The graft percentage, epoxy content and hydrolysis rate of epoxy cellulose were determined with Eqs. (1-8). The results are shown in Table 1.

According to Table 1, the content of free epoxy groups in the epoxy cellulose intermediate material was of 72.19%. The hydroxyl group content of Cell-g-GMA-D-Glu increased obviously after the reaction of D-Glu with epoxy cellulose.

Elemental analysis characterization

The percentage of Cell-g-GMA-D-Glu and Cell-g-GMA-D-GluN⁺ elements was determined by elemental analysis. The carbon and hydrogen percentages of Cell-g-GMA-D-Glu were 45.45 and 7.68%, respectively, while the carbon, hydrogen and nitrogen percentages of Cell-g-GMA-D-GluN⁺ were 44.26, 7.71 and 1.86%. The nitrogen percentage of Cell-g-GMA-D-GluN⁺ was 1.86%, which could prove that Cell-g-GMA-D-Glu was successfully derived with quaternary ammonium groups.

FTIR characterization

The FTIR spectra of cellulose, epoxy cellulose, Cell-g-GMA-D-Glu and Cell-g-GMA-D-GluN⁺ are presented in Figure 1. A wide absorption peak at 3417 cm^{-1} is assigned to the cellulose OH group, while the peak at 2900 cm^{-1} is related to the C-H vibration of the CH₂ groups. The epoxy cellulose spectrum is featured by a strong band at 1731 cm^{-1} due to the absorption of carbonyl group. The appearance of such bands at 907, 846 and 759 cm^{-1} , as due to the absorption of

the epoxy group, could explain why GMA was grafted onto the cellulose surface.¹¹ In curve (c), the bands of epoxy cellulose at 907, 846 and 759 cm^{-1} , caused by the absorption of the epoxy group, disappeared, which indicates that the epoxy group of epoxy cellulose reacted with D-Glu and trimethylammonium chloride.

SEM characterization

The scanning electron micrographs presented

in Figure 2 show the surface morphology of cellulose and epoxy cellulose.

Table 1
Determination of epoxy cellulose and
Cell-g-GMA-Glu

<i>G</i> (%)	<i>Epv</i> (mmol g^{-1})	<i>H</i> (%)	<i>H_g</i> (mmol g^{-1})	<i>H_f</i> (mmol g^{-1})
590	5.48	27.81	5.68–6.42	7.78–8.43

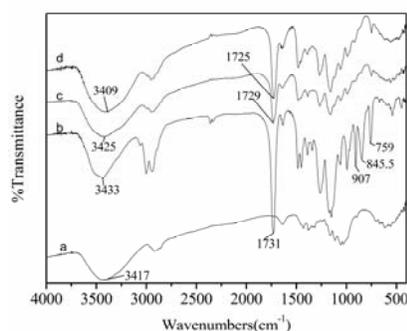


Figure 1: FTIR spectra of (a) cellulose; (b) epoxy cellulose; (c) Cell-g-GMA-D-Glu; (d) Cell-g-GMA-D-GluN⁺

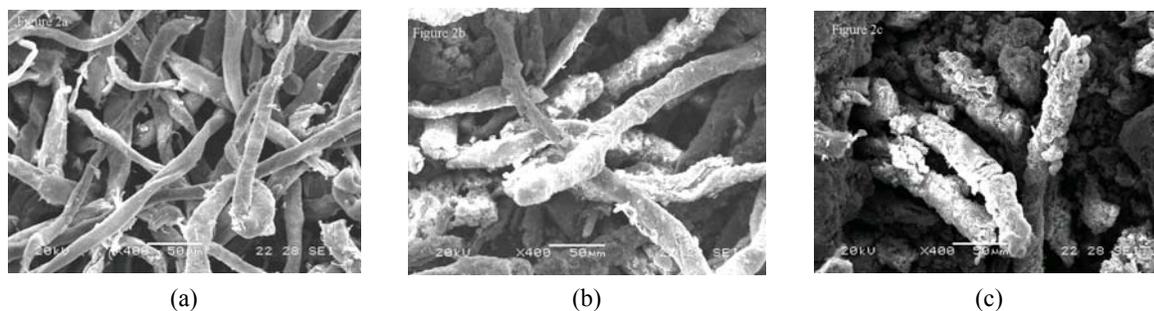


Figure 2: SEM of (a) cellulose (b) Cell-g-GMA; (c) Cell-g-GMA-D-GluN⁺

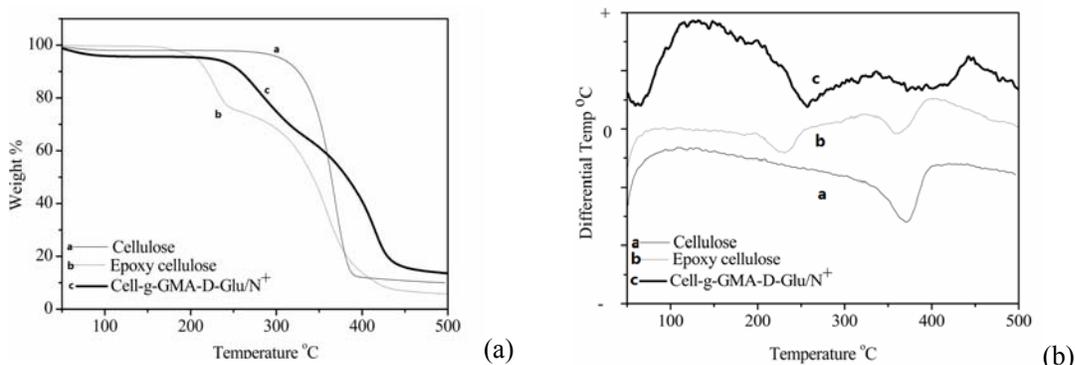


Figure 3: TGA (a) and DTA (b) curves for cellulose, epoxy cellulose and Cell-g-GMA-D-GluN⁺

According to Figures 2a and 2b, the surface of Cell-g-GMA was rougher than that of cellulose, as due to the swelling effect on cellulose and on the surface of cellulose grafted with GMA. The diameter of individual cellulose seemed thicker in epoxy cellulose. As shown in Figure 2c, the cross-linking structure of Cell-g-GMA-D-GluN⁺ was attributed to the crosslinking reaction between D-Glu and trimethylammonium chloride on the surface of epoxy cellulose.

TGA and DTA characterization

The TGA and DTA curves of cellulose powder, epoxy cellulose and Cell-g-GMA-D-GluN⁺ are presented in Figure 3. The differences in the thermal behavior of the three samples lie in (1) the temperatures of initial weight loss, (2) the rate of weight loss, (3) the extent of the enthalpy change, and (4) the temperature corresponding to the values of the DTA curve peak.¹² The endothermic peak at 120 °C is due to the evaporation of the water from the sample. The long endothermic process with a slow weight loss is due to dehydration and depolymerization–tar-forming processes occurring in cellulose.

The process from 240 to 370 °C is attributed to the thermal cleavage of the glucose units, and to the scission of other C-O bonds *via* a free radical reaction.¹³ Figure 3b shows an additional endothermic peak at 390 °C, caused by the degradation of poly(GMA) in the sample. The exothermic peak at 350 °C is due to some reactions of the epoxy group. The degradation process of poly(GMA) begins¹⁴ at 360 °C, and completes at 435 °C. The endothermic peak of the DTA curve at 250 °C is due to the fusion of the Cell-g-GMA-D-GluN⁺ and to the grafted epoxy group.^{15,16} The D-glucose units began to decompose¹⁷ into several organic compounds, over a temperature range from 300 to 450 °C. The

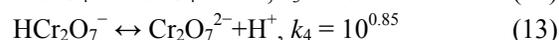
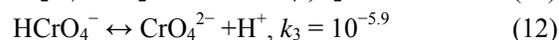
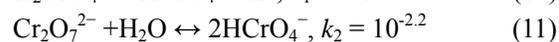
process from 250 to 425 °C can be interpreted as a decomposition of the new products with smaller chains, because of the reaction of the water molecule in the tight crosslink of the polymer network.¹⁸

The TGA curves show that the thermal stability of epoxy cellulose gets weaker, while the thermal stability of the epoxy group in Cell-g-GMA-D-GluN⁺ is much better than that of epoxy cellulose.

Adsorption studies of chromium (VI) onto Cell-g-GMA-D-GluN⁺

Effect of pH

The removal of pollutants from wastewaters through adsorption is highly dependent on the pH of solution. Variation of pH can affect the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate.¹⁹ The equilibrium equations of chromium in solution are known as:²⁰



The plot of the percentage of chromium (VI) removed by Cell-g-GMA-D-GluN⁺ at an initial pH range from 2.0 to 8.0 is shown in Figure 4.

The optimum pH range was between 4 and 6, while the adsorption rate of chromium (VI) decreased beyond this value, a possible explanation being the presence of mainly HCrO₄⁻ and Cr₂O₇²⁻ in solution over the 2.0-6.0 pH range. The quaternary ammonium groups of Cell-g-GMA-D-GluN⁺ have been protonated to N⁺(CH₃)₃ groups, which primarily acted as an active site, to form a Cell-g-GMA-D-GluN⁺-Cr complex compound. The HCrO₄⁻ and Cr₂O₇²⁻ with negative charge reacted with Cell-g-GMA-D-GluN⁺, and the Cell-g-GMA-D-GluN⁺-Cr complex compound was obtained in

aqueous solution at a pH range from 2.5 to 6.7.

At a high initial pH, adsorption was reduced, as the competitive adsorption of hydroxyl reacted with chromium (VI), while the competitive adsorption of Cl^- reacted with chromium (VI) at low initial pH would reduce the percentage of chromium (VI) removal. Consequently, the optimum initial pH was 3.5.

Effect of shaking time

The batch technique was used to determine the effect of shaking time on chromium (VI) uptake by Cell-g-GMA-D-GluN⁺. The adsorption rate reached up to 97.6% when shaking for 10 min, while maximum adsorption was 99% when shaking for 60 min or more. The rate of chromium (VI) uptake by Cell-g-GMA-D-GluN⁺ indicated that the adsorption process was quite rapid. The rapid sorption of the metal ions by the Cell-g-GMA-D-GluN⁺-type adsorbent was highly probable, as due to the hydrophilicity of the adsorbent and to the conformational flexibility of the functional groups.²¹

Effect of adsorbent amount

The percentage of chromium (VI) removal was studied by changing the amount of adsorbent from 20 to 105 mg, while the concentration of chromium (VI) was 50 mg/L without change. The

total chromium removal efficiency increased with the amount of adsorbent up to an optimum dosage, beyond which the efficiency did not change significantly. The adsorption was of 99.3% at an adsorbent amount of 50 mg. Also, adsorption did not change significantly when changing the amount of adsorbent from 50 to 105 mg. This could be explained as follows: although an increased adsorbent dosage could provide larger surface areas (or more adsorption sites), the initial concentration of chromium (VI) was fixed and the adsorbent was excessive when the amount of adsorbent overran the optimum dosage. Consequently, the optimum dosage was determined to be 50 mg.

Effect of various ions

Various kinds of ions are present in waste water, therefore the effects of various ions of Cd^{2+} , F^- , H_2PO_4^- , Ca^{2+} , Co^{2+} , NH_4^+ , Zn^{2+} , Mg^{2+} , Mn^{2+} , SO_4^{2-} on the chromium (VI) adsorbed in the batch method were also studied. The experimental results are shown in Table 2. It could be seen that 25 mL 50 mg/L of chromium (VI) in the solution were effectively absorbed by the Cell-g-GMA-D-GluN⁺-type adsorbent, when the solution also contained other ions. In other words, the adsorbent could selectively and effectively adsorb chromium (VI) from the mixed solution.

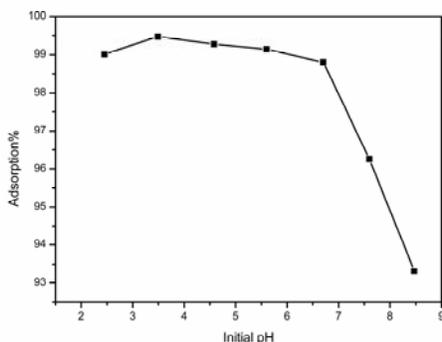


Figure 4: Effect of pH on Cr (VI) adsorption at 18 °C

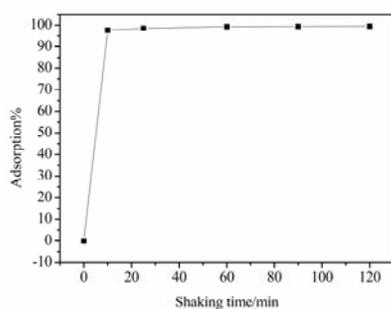


Figure 5: Effect of shaking time on the adsorption of Cr (VI) at 18 °C

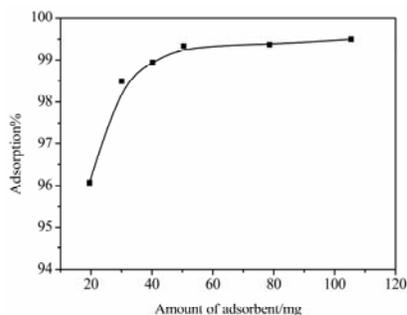


Figure 6: Effect of adsorbent amount on adsorption of Cr (VI) at 18 °C

Table 2
Effect of various ions

Ion	Concentration of ion, (mg L ⁻¹)	Cr (VI) found, (mg L ⁻¹)	Adsorption, (%)
Cd ²⁺	100	0.76	98.5
F ⁻	100	1.15	97.7
H ₂ PO ₄ ⁻	100	0.95	98.1
Ca ²⁺	100	1.41	97.2
Co ²⁺	100	1.47	97.0
NH ₄ ⁺	100	1.61	96.8
Zn ²⁺	100	0.95	98.1
Mg ²⁺	100	2.16	95.7
Mn ²⁺	40	1.74	96.5

Conditions: temperature 18 °C; shaking time- 90 min; adsorbent - 50 mg; initial pH 3.5; Cr (VI)- 25 mL 50 mg L⁻¹

Table 3
Pseudo-first-order and pseudo-second-order constants for Cr (VI) adsorption on Cell-g-GMA-D-GluN⁺

Kinetic models	q _e (mg g ⁻¹)	k ₁ (g mg ⁻¹ min ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	h (mg g ⁻¹ min ⁻¹)	R ²
Pseudo-first-order	24.87	5.54×10 ⁻²	-	-	0.9700
Pseudo-second-order	24.89	-	2.68×10 ⁻¹	165.84	0.9999

Conditions: 50 mg L⁻¹ Cr (VI) solution; temperature 18 °C; adsorbent- 50 mg; initial pH 3.5

Kinetic parameters

Two important physico-chemical aspects of the process, the kinetics and the equilibrium of adsorption were used to evaluate adsorption. Two rate equations were used to analyze the adsorption kinetics, pseudo-first-order kinetics and pseudo-second-order reaction kinetics.²² The

results are presented in Table 3.

Lagergren's pseudo-first-order kinetics – Eq. (14) – can be represented in non-linearized form – Eq. (15), and in linear form – Eq. (16):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (14)$$

$$q_t = q_e(1 - e^{-k_1 t}) \quad (15)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (16)$$

where k_1 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-first-order rate constant of the adsorption process. The values of q_e and k_1 are calculated by the non-linearized form – Eq. (15), while the value of R^2 is carried out by the linearized form – Eq. (16). The results are presented in Table 3.

Pseudo-second-order kinetics – Eq. (17) – can be used to assess the concentration of chromium (VI) adsorbed. The linearized form of the pseudo-second-order kinetics is represented by Eq. (18):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (17)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (18)$$

where k_2 ($\text{dm}^3 \text{mg}^{-1} \text{min}^{-1}$) is the rate constant of the adsorption process, q_e (mg/g) is the equilibrium amount of adsorbed chromium (VI), and q_t (mg/g) is the amount of chromium (VI) adsorbed at any time, t .

When $t \rightarrow 0$, the initial sorption rate, h , can be defined as:

$$h = k_2 q_e^2 \quad (19)$$

where q_e is the equilibrium sorption capacity, k_2 , the pseudo-second-order rate constant, which can be determined experimentally from the slope and intercept by plotting t/q_t against t .

Some results could be obtained by analyzing the parameters listed in Table 3.

The kinetics of chromium (VI) adsorption on Cell-g-GMA-D-GluN⁺ agrees with the pseudo-second-order kinetic process. In addition, the plot shows an exact coefficient (R^2), coherent with the pseudo-second-order equation proposed.

Adsorption isotherms

An adsorption isotherm can be used to characterize the interaction of metal ions with adsorbents. The isotherm provides a relationship between the concentration of metal ions in solution and the amount of metal ions adsorbed on the solid phase, when both phases are in

equilibrium.²³ When the equilibrium concentration of chromium (VI) was changed from 0 to 12.8 mg/L, the adsorption quantity of chromium (VI) sharply increased, after which the adsorption quantity of chromium (VI) did not change significantly. This is because the initial concentration of adsorbent was fixed and the adsorption sites were not sufficient for chromium (VI), when its concentration (VI) increased.

The equilibrium amount of chromium (VI) adsorbed per unit mass of adsorbent, q_e (mg/g), and its final concentration in solution, C_e (mg/L), are related to the adsorption isotherm. The adsorption isotherm models of Langmuir (Eq. 20) and Freundlich (Eq. 22) were used to evaluate the adsorption experiments as a function of the initial metal ion concentration in aqueous single solutions. The adsorption isotherm models of Langmuir and Freundlich can be represented in the linearized form of Eqs. (21) and (23), respectively:

$$q_e = \frac{Q^o b_L C_e}{1 + b_L C_e} \quad (20)$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q^o} + \frac{1}{Q^o b_L} \quad (21)$$

$$q_e = K_F C_e^{1/n_F} \quad (22)$$

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (23)$$

where Q^o , b_L represent the adsorption and binding energies of adsorption of Langmuir; K_F and $1/n_F$ are the adsorption capacity and the heterogeneity factor of Freundlich adsorption isotherm, respectively; q_e (mg/g) is the amount of solute adsorbed, and C_e (mg/L) is the equilibrium concentration in solution. The values of $1/Q^o b_L$ (intercept) and $1/Q^o$ (slope) were determined by Eq. (21). Eq. (23) shows a logarithmic relationship between the adsorption quantity and equilibrium concentration. Figure 7 plots the Langmuir adsorption isotherm. The Langmuir and Freundlich model correlation coefficient values (R^2), of 0.9999 and 0.9092 respectively, were

calculated by Eqs. (21) and (13). Obviously, the adsorption process was correctly described by the Langmuir isotherm model. The Langmuir constants, calculated by Eq. (21), are shown in

Table 4. The calculated value of Q^o was 71.79 mg/g.

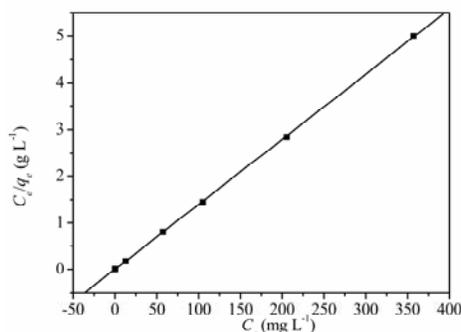


Figure 7: Langmuir isotherm for Cr (VI) adsorption on Cell-g-GMA-D-GluN⁺ at 18 °C

Table 4

Langmuir and Freundlich constants for Cr (VI) adsorption on Cell-g-GMA-D-GluN⁺

Isotherm models	b_L (L mg ⁻¹)	K_F (L g ⁻¹)	Q^o (mg g ⁻¹)	n_F	R^2
Langmuir	1.0000	-	71.79	-	0.9999
Freundlich	-	18.1023	-	3.263	0.9092

Conditions: temperature 18 °C; shaking time- 90 min; adsorbent- 50 mg; initial pH 3.5

Desorption

One of the important characteristics of chelating copolymers is their ability to be regenerated and reused.

As shown in Figure 4, the competitive adsorption of the hydroxyl reacted with chromium (VI) was more efficient under alkaline conditions. Thus, sodium hydroxide may be viewed as a desorption agent to obtain Cell-g-GMA-D-GluN⁺-type adsorbents. The relationship between the desorption percentage and the concentration of sodium hydroxide was studied. At a sodium hydroxide concentration of 0.05 mol/L, the desorption percentage was the maximum (99.7%), which makes this value the optimum concentration of sodium hydroxide.

The adsorbent could be reused five times at least in the adsorption-desorption-adsorption cycle,

without modifying the efficiency of chromium (VI) removed from solution, which proves that the Cell-g-GMA-D-GluN⁺-type adsorbent had excellent ability for reuse and regeneration.

CONCLUSIONS

A new type of adsorbent, Cell-g-GMA-D-GluN⁺, was synthesized, characterized and applied to uptake chromium (VI) in water samples. A series of characterizations suggested that the free radical polymerization and subsequent functionalization were successful. The adsorption process fits the assumptions of the Langmuir isotherm and of the pseudo-second-order kinetics model, as determined by the values of the correlation coefficient (R^2). In adsorption-desorption experiments, the desorption percentage of

chromium (VI) could reach up to 99.7% with D-GluN⁺-type cellulose derivatives, with 0.05 mol/L NaOH as a desorption agent.

The experimental data suggested that Cell-g-GMA-D-GluN⁺ selectivity and adsorbability were good, as due to the positive charge density of adsorbent supplied by trimethylammonium chloride on the surface.

The Cell-g-GMA-D-GluN⁺-type adsorbent has been proven as one of the most efficient adsorbents for the removal of toxic chromium (VI) from aqueous media. Also, the adsorbent may be used to adsorb heavy metal ions from industrial wastewaters.

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