

PREPARATION OF ANION-EXCHANGE CELLULOSE FOR THE REMOVAL OF CHROMATE

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ABSTRACT

The quaternary ammonium group containing cellulose was prepared by the one-pot method and applied for the removal of chromate (CrO_4^{2-}) ions from aqueous solution. The prepared sorbent was characterized by using elemental analyzer and Fourier transform infrared (FTIR) spectroscopy. Its ion exchange behavior toward CrO_4^{2-} ions was investigated as a function of sorbent dose and initial solution pH. The kinetic and sorption equilibrium experiments were also carried out in a batch system. Equilibrium data were best fitted with the Langmuir model and the maximum ion exchange capacity of the sorbent was found as 3.8 mg of CrO_4^{2-} /g sorbent. Moreover, the removal of CrO_4^{2-} is achieved within 5 minutes. Furthermore, the calculated thermodynamic parameters disclosed that the ion exchange reaction is feasible, spontaneous and exothermic. In addition, the CrO_4^{2-} ions can be desorbed from the sorbent by 1.0 M HCl solution with 95% regeneration efficiency.

Keywords: Anion exchange, cellulose, chromate, quaternized cellulose, water treatment

1. INTRODUCTION

Chromium is primarily present in trivalent and hexavalent states as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in aqueous media [1,2]. Chromic acid is used in the plating and anodizing operations in the surface finishing industry and chromium salts has been used widely in metal plating, leather tanning, dye, printing inks, photography and wood preservatives [3–6].

The two common oxidation states, i.e. Cr(III) and Cr(VI), are drastically different in charge, physicochemical properties as well as chemical and biochemical reactivity. The distribution of compounds containing in trivalent and hexavalent states depends on the redox potential, pH of the media, the existence of substance which is oxidizer or reducer, the formation of chromium(III) insoluble salts or its complexes, and the total chromium concentration. Cr(III) is a trace essential element for the proper functioning of living organisms. It is responsible for the control of glucose and lipid metabolism in mammals. On the other hand, The Cr(VI) is acutely toxic, carcinogenic, it is also highly soluble and mobile in an aqueous environment. The World Health Organization has recommended that the maximum allowable concentration of Cr(VI) in drinking water be 0.05mg/L [2,7–9]. In order to reduce the Cr(VI) concentration to permissible level; adsorption, ion exchange, membrane processes, and polymeric sorbents were used [5,10–14]. It should be noted that such methods can be ineffective or too expensive to treat wastes having metal ions in concentrations of 100 mg/L or below. Hence, there is a constant need to search for an optimal technology while considering its cost, materials employed and its efficiency [15].

In respect of bio-sorption, development of a specific sorbent that is environmentally friendly, safe with high capacity and low cost is still a challenging task and biopolymers are used for this purpose [16,17]. Biopolymers are derived from plant, animal or microbial biomass that may be polysaccharides, lipopolysaccharides, glycolipids, proteins, or polyhydroxy alkanooates and are well amenable to environmental applications [18]. Cellulose is the most abundant organic raw material and finds applications in areas as diverse as composite materials, textiles, drug delivery systems, and personal care products [19]. Cellulosic materials have several advantages such as; biodegradable and CO_2 neutral; an abundant resource and has Low cost. Besides these advantages, it has High specific strength and modulus, high sound damping performance due to the hollow structure of fibers, low density and a relatively reactive surface, which can be used for surface modification [20]. The application, modification, advantages, and disadvantages of cellulose are already reviewed elsewhere [19–22].

In this work, quaternary ammonium group-containing cellulose was prepared via one-pot modification process and it was applied for the removal of CrO_4^{2-} ion from aqueous solution. Moreover, the Elemental analyzer and Fourier transform infrared (FT-IR) spectroscopy were made use of to characterize prepared anion exchange cellulose. Furthermore, the effect of sorbent dose, initial solution pH, initial CrO_4^{2-} concentration on ion exchange performance of modified cellulose were tested. In addition to this, sorption isotherms, kinetic performance and thermodynamic parameters for the CrO_4^{2-} were investigated. Finally, the regeneration of CrO_4^{2-} - loaded cellulose was evaluated by batch experiments.

2. EXPERIMENTAL

2.1 Reagents

The cellulose raw material was obtained from Denkim Kimya A.Ş. (Denizli, Turkey) and used without modification or any treatment. Glycidyltrimethylammonium chloride (GTMAC, 80% aqueous solution, TCI) and NaOH (Merck) was used for the modification of cellulose. The K_2CrO_4 (Merck) was used for the preparation of CrO_4^{2-} solutions. HCl (Merck) and NaOH (Merck) solutions were used for the pH adjustment.

2.2 Preparation of anion exchange cellulose

Cellulose was modified as explained in [23]. Briefly, 20 g NaOH dissolved in 250 g pure water and when the temperature of this solution reached 65 °C then, 30 g cellulose was added to NaOH solution. After ten minutes of adding cellulose, 25 g glycidyltrimethylammonium chloride solution (80% aqueous solution) was added to the suspension with stirring and the reaction was carried out at 65 °C for 270 minutes. Subsequently, 2 M HCl solution was added to the reaction medium to stop the modification reaction. The reaction mixture was filtered, washed with pure water and then dried in an oven at 50 °C. Dried anion exchange cellulose was milled and used in the experiments.

2.3 Characterization of ion-exchange cellulose

The functional groups of prepared cellulose were characterized by the Fourier transform infrared spectroscopy (FT-IR, PerkinElmer one-B, coupled with an ATR accessory) in the range of 600-4000 cm^{-1} . Leco CHNS-932 elemental analyzer was used for the compositional analysis of ion-exchange cellulose.

2.4 Experimental procedure for the removal of CrO_4^{2-}

In order to find obtain the highest removal rate of CrO_4^{2-} , different parameters were tested. The experimental conditions of batch sorption tests were summed up in Table 1. Standard diphenylcarbazide method [24] was utilized for the spectrophotometric determination of CrO_4^{2-} in aqueous samples by using PG T80+ spectrophotometer.

Table 1. Experimental parameters for removal of CrO_4^{2-}

Investigated parameter	CrO_4^{2-} concentration (mg/L)	Amount of sorbent (g)	Volume of solution (mL)	pH of solution	Temperature (°C)
Sorbent dose	5	0.02 - 0.3	25	7	25
Initial solution pH	5	0.2	25	2- 10	25
Equilibrium study	25 - 400	0.2	25	10	25
Temperature effect	25	0.2	25	10	30, 40 and 50
Kinetic study	5	8	1000	10	25

The percent removal (R %) of CrO₄²⁻ was calculated with Eqn. 1 and capacity of sorbent (q as mg- CrO₄²⁻/g-sorbent) was calculated with Eqn.2.

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \dots\dots\dots (1)$$

$$q = \frac{(C_0 - C_e) \times V}{m} \dots\dots\dots (2)$$

In these equations, C₀ is the initial concentration of CrO₄²⁻ (mg/L), C_e is the concentration of CrO₄²⁻ in the solution after sorption experiment (mg/L). V is the volume of solution (L) and m is the mass of the quaternized cellulose (g).

3 RESULTS AND DISCUSSIONS

3.1 Characterization of the anion exchange cellulose

The FTIR-ATR spectra of raw and quaternized cellulose is shown in Figure 1. Infrared spectra of raw and quaternized cellulose show many similarities. The peak at 3339 cm⁻¹ is due to stretching vibration frequencies of the -OH groups. The bands at 2898 and 1420 cm⁻¹ probably be attributed to deformation vibrations of CH₂ groups. The band at 1315 cm⁻¹ is the deformation vibrations of OH-groups. The peaks at 1159, 1051, and 1028 cm⁻¹ are involved C-O stretching of COH/C-O-C bonds. The band at 897 cm⁻¹ in the spectrum is attributed to stretching vibrations of the ring/semi-circle cellulose [25–27]. In addition to FTIR analysis, the elemental analysis was also used to confirm the presence of nitrogen (N) in the quaternized cellulose. The composition of the raw and modified cellulose is shown in Table 2.

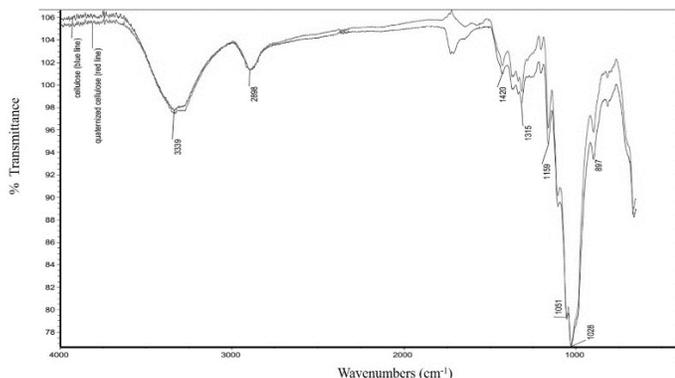


Figure 1. FTIR spectrum of raw and quaternized cellulose

Table 2. Elemental composition of the raw and quaternized cellulose

Material	C %	H %	N %
Raw cellulose	41.89	6.21	-
Quaternized cellulose	42.92	6.49	0.23

As can be seen from Table 2, raw cellulose does not contain Nitrogen element. The amount of nitrogen in the quaternized cellulose was 0.23 %. Moreover, after attaching the quarter groups to the cellulose, the percentage C and H in the sorbent increased. The quaternary ammonium groups also contain CH₃ groups and this leads to increment on C and H percentage.

3.2 Effect of sorbent dose on CrO₄²⁻ removal.

The percent removal of CrO₄²⁻ versus sorbent dose is shown in Figure 2. The curve indicates that removal of CrO₄²⁻ increases with increase in the sorbent dose due to the greater availability of the sorption sites [28]. The optimal amount of sorbent for CrO₄²⁻ removal was 0.2 g sorbent/25 mL solution and such sorbent dose used in subsequent experiments. Prepared sorbent removed 99 % of CrO₄²⁻ from solution.

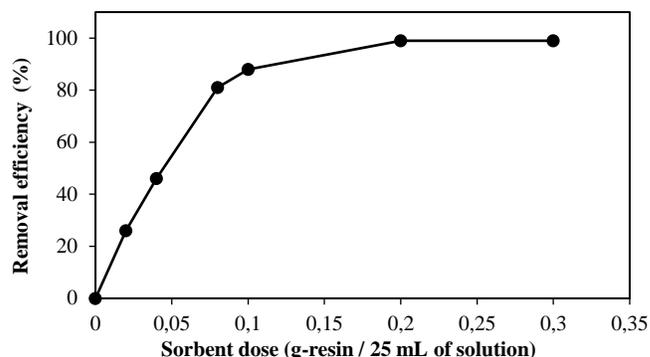


Figure 2. Removal of CrO₄²⁻ versus sorbent dose.

3.3 Effect of initial solution pH

The uptake of CrO₄²⁻ by quaternized cellulose at different pH is shown in Figure 3. When the pH of the solution was adjusted to 2, only 36% of CrO₄²⁻ removed from the solution. Increment on solution pH leads to enhancement on CrO₄²⁻ removal. It was reached maximum at pH 8 and 10 (99% removal).

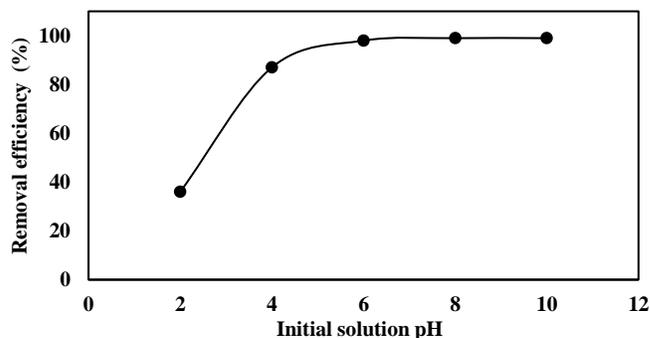
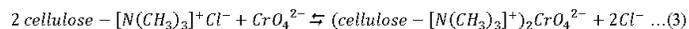


Figure 3. Effect of initial solution pH on the uptake of chromate

Such results can be explained as follows. The ion exchange reaction between CrO₄²⁻ and quaternized cellulose is shown in Eqn. 3



In order to adjust the pH of the solution to 2 and 3, the HCl solution was added to the solution. When the HCl solution was added the Cl⁻ concentration in the solution increased and according to Le Chatelier's principle reaction shifted to the left-hand side thus percent removal of CrO₄²⁻ decreased.

As can be seen from Figure 3 the optimum pH values found as pH ≥ 6.

3.4 Kinetic study

Another set of experiments was also performed in order to clarify the kinetics of CrO₄²⁻ removal by quaternized cellulose and obtained results are depicted in Figure 4.

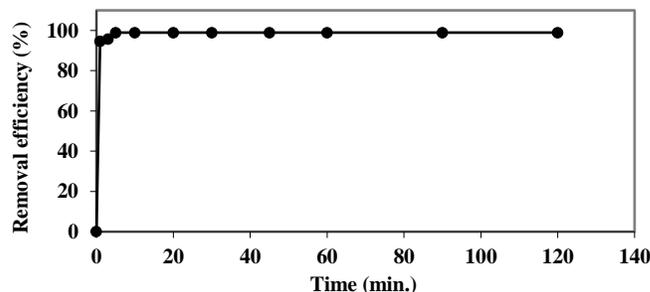


Figure 4. Change of percent removal of CrO₄²⁻ as a function of time

It is clear from Figure 4 that, kinetic of the sorbent is quite fast and 99% of CrO₄²⁻ removed in 5 minutes.

3.5 Sorption isotherm

Isotherm studies give information about the capacity of the prepared sorbent. The sorption isotherm for CrO₄²⁻ is represented in Figure 5.

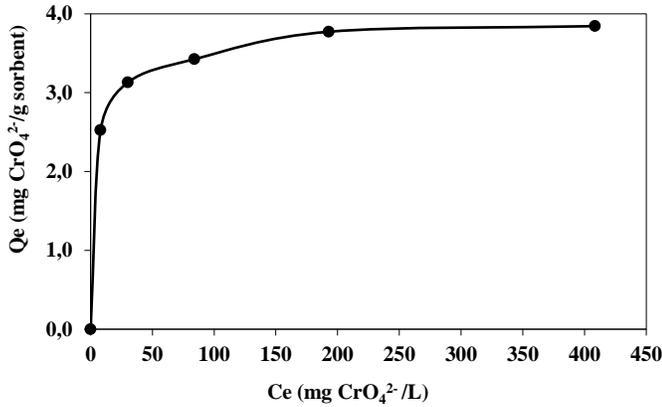


Figure 5. Sorption isotherm for CrO₄²⁻

Figure 5 represents that, when the initial CrO₄²⁻ concentration in the solution was increased, the capacity of sorbent increased and then reached to its maximum sorption capacity. In order to obtain the theoretical sorption capacity, experimental results were fitted to the two most common isotherm models, i.e., the Langmuir and Freundlich models. The Langmuir equation is valid for monolayer sorption onto a surface is given as follows [29,30]

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \dots\dots\dots (4)$$

C_e is equilibrium concentration (mg/L), Q_e is the amount sorbed ion under equilibrium (mg/g), Q₀ is the theoretical maximum sorption capacity, and b (L/mg) is a Langmuir constant, which indicates the affinity of the CrO₄²⁻ toward the quaternized cellulose.

The Freundlich equation, indicative of surface heterogeneity of the adsorbent, is given as follows

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \dots\dots\dots (5)$$

1/n and K_F are Freundlich constants, related to sorption capacity and sorption intensity (heterogeneity factor), respectively, Q_e is the amount of CrO₄²⁻ sorbed per unit weight of the sorbent (mg/g-sorbent), and C_e is the equilibrium concentration of sorbate in solution (mg/L). The obtained and calculated parameters were summarized in Table 3.

It can be seen that the correlation coefficient (R²) values of Langmuir model is significantly higher than that of Freundlich model for CrO₄²⁻ removal. According to the Langmuir isotherm model, the sorption occurs at the surface of the sorbent in a homogeneous way and the CrO₄²⁻ ions form a monolayer, having no mutual interactions on the sorbent surface.

Table 3. Isotherm constants for CrO₄²⁻ sorption on the quaternized cellulose

Langmuir Isotherm Constants			Freundlich Isotherm Constants		
Q ₀ (mg·g ⁻¹)	b (L/mg)	R ²	K _F (mg/g)	n	R ²
3.91	0.13	0.9997	2.09	9.23	0.9575

The theoretical capacity of the prepared sorbent is compared with others reported in literature and results are summed up in Table 4.

Table 4. Comparison of the sorption capacity of biomass and other biomaterials

Sorbent	Capacity (mg/g)	Reference
Succinylated mercerized cellulose functionalized with quaternary ammonium groups	96.16	[31]
Chitosan	7.94	[32]
Iron (III) hydroxide-loaded sugar beet pulp	5.12	[33]
Cellulose-Clay Composite Biosorbent	22.20	[34]
Polyethylenimine Facilitated Ethyl Cellulose	36.80	[35]
Amine-crosslinked cotton stalk peel	129.0	[2]
Coconut tree sawdust	3.46	[36]
Quaternary ammonium groups functionalized cellulose	3.91	This work

The capacity of prepared sorbents varies from 3.46 to 129 mg/g. The modification way, its duration and modification materials strongly affect sorption capacity.

3.6 Thermodynamic parameters

To analyze the effect of temperature on the sorption of sorption CrO₄²⁻ onto ion-exchange cellulose, experiments were conducted at different temperatures and thermodynamic parameters were calculated from the Van't Hoff's plot. Changes in standard free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were estimated by the following Eq. 6-8 [37,38]

$$\Delta G^\circ = -RT \ln K_c^\circ \dots\dots\dots (6)$$

$$\ln K_c^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots\dots\dots (7)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \dots\dots\dots (8)$$

In these equations, K_c is the equilibrium constant and it was calculated by q_e/C_e, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the temperature (K). Parameters change in enthalpy (ΔH°) and change in entropy (ΔS°) are calculated from the slope and the intercept of the linear plot of ln K_c vs. 1/T. The calculated values are summarized in Table 5.

Table 5. Thermodynamic parameters for CrO₄²⁻ sorption

ΔS° / J mol ⁻¹ K ⁻¹	ΔH° / kJ mol ⁻¹	ΔG° / kJ mol ⁻¹
4.62	-5.63	-7.08 /313 K
		-7.13 /323 K
		-7.17 /333 K

The negative values of ΔG° at all temperatures studied are due to the fact that the ion-exchange reaction is spontaneous. The negative value of ΔH° suggests the exothermic nature of the ion-exchange reaction. The positive value of ΔS° suggests increased randomness at the quaternized cellulose/solution interface during the sorption of CrO₄²⁻ onto the cellulose.

3.7 Regeneration of the sorbent

1.0 grams of quaternized cellulose was contacted 50 ml of CrO₄²⁻ solution (500 mg- CrO₄²⁻ /L) for one hour. Later, the sorbent was separated from the solution by decantation and washed with deionized water then dried in an oven at 40 °C. The CrO₄²⁻ concentration in feed and effluent was analyzed and loaded amount of CrO₄²⁻ on quaternized cellulose was calculated. An 0.025 g of dry CrO₄²⁻-loaded sorbent was contacted with 25 mL regeneration solutions, then the mixture was shaken at room temperature for 24 hours and after this period CrO₄²⁻ concentration in the solution was determined. Regeneration efficiency (RE,%) was calculated using the Equation Eq. (9) and the obtained results were summarized in Table 6.

$$RE (\%) = \frac{\text{Amount of eluated } CrO_4^{2-}}{\text{Amount of loaded } CrO_4^{2-}} \times 100 \dots\dots\dots (9)$$

Table 6. Percentage recovery of CrO_4^{2-} by different regeneration solution

Regenerated by	Regeneration efficiency
0.1 M HCl	85
0.5 M HCl	88
1.0 M HCl	95

As can be seen from Table 6, when the HCl concentration was increased the regeneration efficiency increased. 1.0 M HCl solution can regenerate the CrO_4^{2-} -loaded cellulose with 95 % efficiency.

4. CONCLUSIONS

The anion exchange cellulose was synthesized and applied for the removal of CrO_4^{2-} ions from aqueous solutions. The removal of CrO_4^{2-} ions from aqueous solution by prepared cellulose was found to be effective with 99% removal efficiency. The kinetic of CrO_4^{2-} removal is quite fast and in 5 minutes it reached equilibrium. Removal of CrO_4^{2-} is pH depended and removal rate increased with increment on initial solution pH. Optimum pH for CrO_4^{2-} removal was found to be ≥ 6 . Equilibrium data fitted to the Langmuir model very well which means that CrO_4^{2-} might be sorbed in the formation of a monolayer coverage on the surface of anion-exchange cellulose. The CrO_4^{2-} -loaded cellulose can be regenerated with 1.0 M HCl solution.

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