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Use of α-Cellulose Coated with Titanium(IV) Oxide in Separation of Cr^{VI}

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ABSTRACT

α-Cellulose reacted with $TiCl_4$ was hydrolyzed to obtain a TiO_2 coating on the biopolymer surface. Cr^{VI} in a concentration range between 10 and 50 ppb was separated from Cr^{III} using a column packed with this material. The presence of other ions such as Cu^{II}, Mn^{II}, Hg^{II}, and Fe^{III}, and the anions VO_3^{3-}, MoO_4^{2-}, PO_4^{3-}, and SO_4^{2-}, did not interfere significantly in the separation process.

Key Words. Chromium(VI) speciation; Chemically modified cellulose; Titanium oxide

INTRODUCTION

Hydrated titanium(IV) oxide has attracted considerable attention as an ion exchanger due to its high sorption capacity for some metal ions (1, 2). Of particular interest has been the selective sorption of chromium(VI) by the oxide from acid solution (3). However, metal oxides normally do not present sufficient mechanical resistance and are frequently in the form of a fine powder. Immobilization of the metal oxide on the surface of a matrix which, in turn, fulfills the conditions of chemical and mechanical resistance may be used (4, 5). Although silica gel has been widely used

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for such purposes, cellulose has also been used as a support for metal oxides (6–8). The structure of the biopolymer is held together by intra- and intermolecular hydrogen bonds and remains intact upon coating of the surface by the metal oxide (9, 10). Therefore, reaction of cellulose with a strong Lewis acid, followed by a hydrolysis reaction, gives a material in which only the surface is modified (7).

This work reports on the preparation of TiO_2 supported on an α-cellulose surface, Cel/TiO_2, and its utilization in Cr^{VI} and Cr^{III} separation. It is known that speciation of Cr^{VI} in natural water is very important from an environmental chemistry point of view. Since few processes for the specific separation of Cr^{VI} are available (11–13), Cel/TiO_2 packed in a microcolumn attached to a flow injection analysis (FIA), manifold for on-line preconcentration of Cr^{VI} and further analysis by spectrophotometry, was developed. The FIA technique for rapid inorganic speciation with spectrophotometric detection has been used for determination of Cr^{VI} (14–19).

EXPERIMENTAL

Preparation of Cellulose/TiO_2

Approximately 20 g of α-cellulose (Sigma, 99.5%) was immersed in 200 cm^3 of CCl_4, followed by the addition of 5 cm^3 of pure $TiCl_4$. The mixture was refluxed 5 hours at 343 K under nitrogen atmosphere, filtered in a Schlenck apparatus, and washed with CCl_4. The product was then immersed in ethanol and exposed to a current of ammonia gas and filtered. The resulting solid, Cel/TiO_2, was exhaustively washed with an ethanol–water solution (50%, v/v) and finally with bidistilled water. The amount of titanium(IV) oxide incorporated into the matrix, determined by calcination of the sample in air at 1173 K, was 10%.

In order to obtain the morphology of the untreated cellulose and of the composite, the samples were dispersed over a double-sided 3M tape fixed on a brass support. The material was then sputtered with a gold/palladium alloy using the Sputter Low Voltage LVC76 from Plasma Science Inc. A scanning electron microscope, (JEOL JSM T-300), connected to a secondary electron image (SEI) detector, was used.

Preparation of Stock Solutions

A stock solution of Cr^{VI} (1000 $\mu g \cdot cm^{-3}$) was prepared by dissolving 2.829 g of dry $K_2Cr_2O_7$ (Merck) in 1 dm^3 of 0.1 $mol \cdot dm^{-3}$ HNO_3 solution.

A solution of diphenylcarbazide (DPC) was prepared by dissolving 0.05 g of the reagent in 100 cm^3 of acetone–water (5%, v/v) solution.

Isotherms of Adsorption

The isotherms of adsorption were determined for Cr^{VI} at 298 K by the batch technique. In various flasks 50 cm^3 of 10^{-3} $mol \cdot dm^{-3}$ solutions of Cr^{VI} were shaken with 0.1 g of Cel/TiO_2 for 30 minutes at 298 K. The pH values of initial solutions were adjusted between 1 and 8 by adding HNO_3 or NaOH, and the pH values in the equilibrium were determined after the end of shaking. The quantity of Cr^{VI} in the supernatant solution was determined by spectrophotometry.

The quantity of adsorbed Cr^{VI} per gram of solid by the solid phase, N_f, was calculated by using the equation

$$N_f = (N_a - N_s)/w$$

where N_a is the initial mole number of Cr^{VI} in the solution phase, N_s is the equilibrium mole number of Cr^{VI} in the solution phase, and w is the mass of the adsorbent.

The adsorption capacity of the adsorbent was determined at pH 1 by shaking 0.1 g of the material with 50 cm^3 of Cr^{VI} solutions of variable concentrations.

Flow Injection Analysis (FIA)

The flow injection (FI) configuration used is shown in Fig. 1. Two injectors were used, one for the addition of Cr^{VI} and another for the addition of eluent (NaOH). Time-controlled injections of the samples were used.

The microcolumn C (length, 2 cm; i.d., 0.3 cm) was packed with 30 mg of Cel/TiO_2. The operation of the FI system was carried out in four steps:

1. Activation: 0.1 $mol \cdot dm^{-3}$ HNO_3 was passed through the column at a flow rate of 2.8 $cm^3 \cdot min^{-1}$ for 10 seconds (Fig. 1a).
2. Injection of Cr^{VI}: A Cr^{VI} solution (pH 1) was passed through the column at a flow rate of 3.2 $cm^3 \cdot min^{-1}$ for a predetermined time (10–100 seconds) (Fig. 1b).
3. Washing: The column was washed with 0.1 $mol \cdot dm^{-3}$ HNO_3 at a flow rate of 2.8 $cm^3 \cdot min^{-1}$ for 10 seconds (Fig. 1a).
4. Elution: Cr^{VI} was eluted from column C with 0.1 $mol \cdot dm^{-3}$ NaOH at a flow rate of 3.2 $cm^3 \cdot min^{-1}$ (Fig. 1c). A solution of DPC (0.05% m/v) was prepared earlier in the mixing coil (MC) with 0.8 $mol \cdot dm^{-3}$ HNO_3. The resulting solution was allowed to react in the reaction coil (RC) with Cr^{VI} carried by NaOH solution. The absorbance of the complex formed was measured at 540 nm in spectrophotometer P, and the signal was recorded at R.

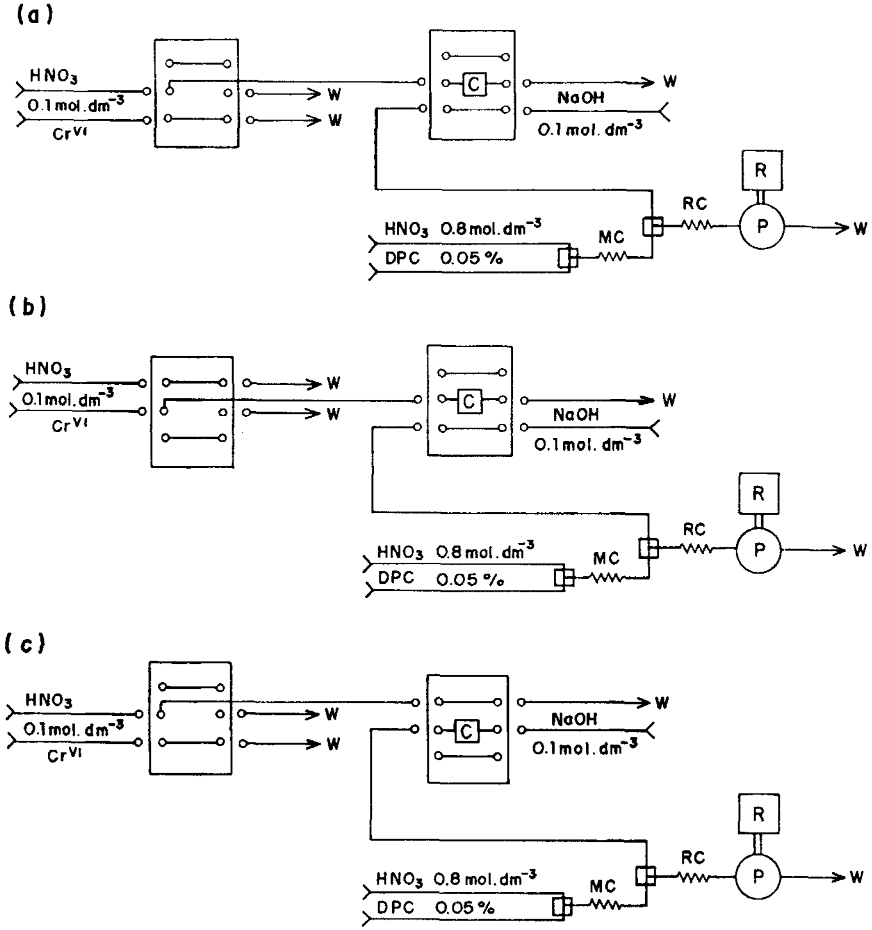

FIG. 1 Flow injection configurations: (a) activation and washing, (b) injection, and (c) elution. *W = waste, MC = mixing coil, RC = reaction coil,* P = *spectrophotometer, and* R = recorder.

RESULTS AND DISCUSSION

Characteristics of the Material

Figure 2 shows micrographies of cellulose, cellulose–titanium(IV) oxide composite, and cellulose–titanium(IV) oxide with adsorbed chromium(VI). Figure 2(A) shows the image of cellulose, and Fig. 2(B) shows the cellulose–titanium(IV) oxide composite. The fibers were not destroyed under chemical treatment with $TiCl_4$ followed by hydrolysis of the metal. Upon mapping the composite Cel/TiO_2 surface by the energy dispersive microanalysis image technique, it was observed that the fibers are totally covered by the metal oxide. Adsorbed Cr(VI) appears on small agglomerate particles nearly homogeneously dispersed throughout the surface (Fig. 2C).

Isotherms of Adsorption

Figure 3 shows the plot of N_f against solution pH. As the solution pH decreases, the adsorption of Cr^{VI} by the solid phase increases. Above pH 5, no adsorption is observed. The change of N_f with solution pH can be explained by the following reaction (3):

$$\equiv TiOH + H^+ + Cr_2O_7^{2-} \rightarrow \equiv Ti^+ \, Cr_2O_7^{2-} + H_2O$$

where $\equiv$TiOH stands for attached hydrated metal oxide. At lower pH, the surface is positively charged due to the reaction of attached hydroxyl groups (3). In such conditions the reaction is shifted toward the right with the formation of the ion paired $\equiv Ti^+ \, Cr_2O_7^{2-}$ species. It has been observed that TiO_2 is very selective to Cr^{VI} (3, 4).

In the present case, Cr^{VI} adsorption on the surface takes, about 15 minutes to achieve equilibrium conditions (Fig. 4). The process is very fast in comparison with the 24–96 hours required for hydrated TiO_2 (3, 20) to achieve equilibrium for the same reaction. This characteristic makes the composite Cel/TiO_2 a suitable sorbent material to be used in a microcolumn inserted in an FIA system.

The adsorption capacity of this material, determined from the isotherm of Fig. 5 at pH 1, was 40 $\mu mol \cdot g^{-1}$. Adsorption of Cr^{VI} by pure cellulose is much smaller under these same conditions, i.e., 5 $\mu mol \cdot g^{-1}$, as illustrated in Fig. 5.

Flow Injection Analysis

The rate of analysis is illustrated in Fig. 6, and the data of the calibration curve are presented in Table 1. The injection times were 10, 40, 70, and 100 seconds. Plotting the absorbance (A) against the mass (m) of Cr^{VI} gave a straight line, corresponding to the equation $A = 0.002 + 1.304m$, with a correlation coefficient of 0.999. The precision of the method for different Cr^{VI} concentrations was evaluated by carrying out 10 replicate measurements for each solution. Solution concentrations of 10, 30, and 50 ppb were injected into the column at a flow rate of 3.2 $cm^3 \cdot min^{-1}$. The relative standard deviations (rsd) values were 6.4, 2.4, and 3.4%, respectively (Table 2). Below 10 ppb, the rsd value could not be deter-

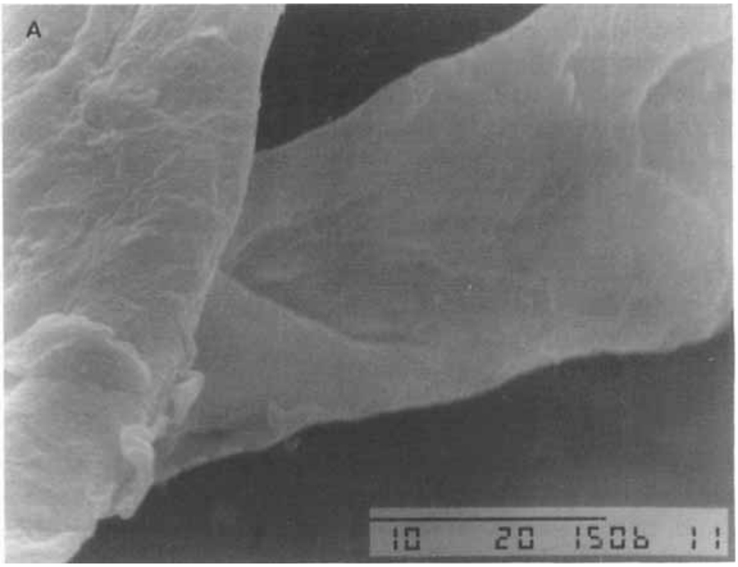

FIG. 2 Scanning electron microscopy with secondary electrons. Image: (A) α-cellulose (2000×), (B) Cel/TiO_2 (3500×), (C) Cel/$Ti^+Cr_2O_7^{2-}$ (3500×).

mined because of a large error at this low level of metal ion concentration. The values of rsd at the higher concentrations are reasonable in comparison with the results obtained by the alternative on-line separation and preconcentration of Cr^{VI} in a microcolumn packed with zirconium(IV) oxide coated on a silica gel surface and inserted into the FIA system (19). The alkali solution used as the eluent for Cr^{VI} did not attack the cellulose matrix in the column, contrary to the attack observed when silica gel was used as the supporting matrix.

Selectivity of the Material

In order to study the selectivity of the present material for Cr^{VI} detection/separation, an interference study was carried out by passing a binary mixture of 0.1 ppm Cr^{VI} and varying concentrations of the interfering ions through the column. The results are presented in Table 3. The interference factor was calculated from the ratio of the absorbance of Cr^{VI} in the binary solution to that of a pure solution of Cr^{VI}. The interfering cations studied were Cr^{III}, Cu^{II}, Mn^{II}, Hg^{II}, and Fe^{III} with concentrations of the interfer-

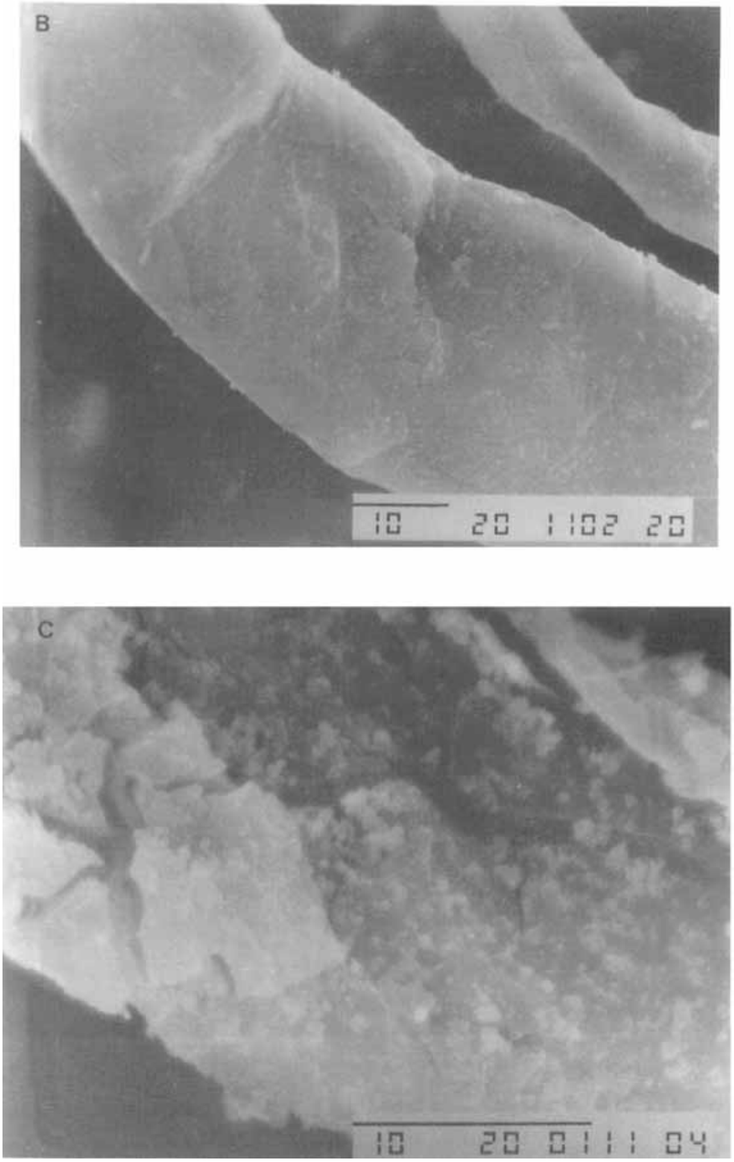

FIG. 2 Continued.

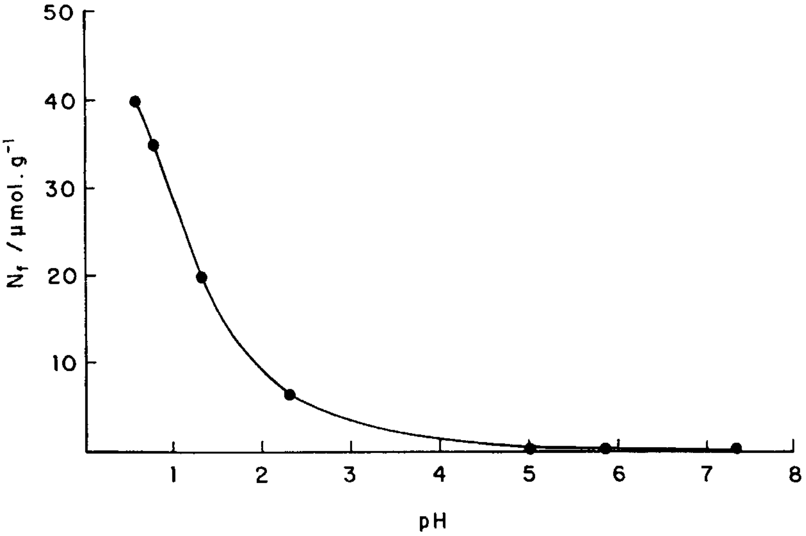

FIG. 3 Plot of Cr^{VI} adsorption versus pH of the solution.

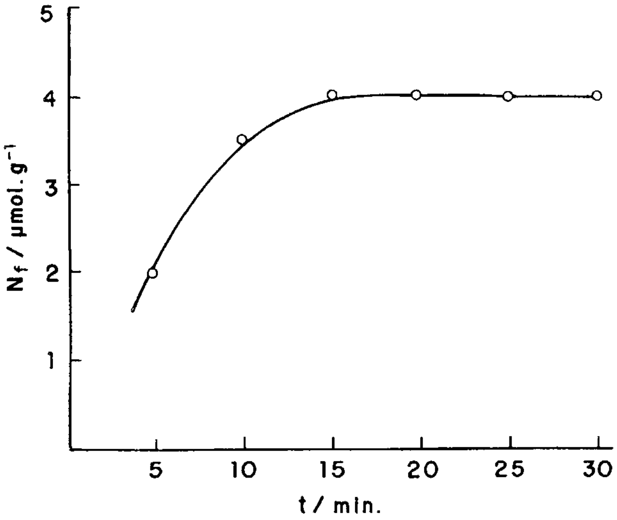

FIG. 4 Rate of Cr^{VI} adsorption by Cel/TiO_2 at pH 1.

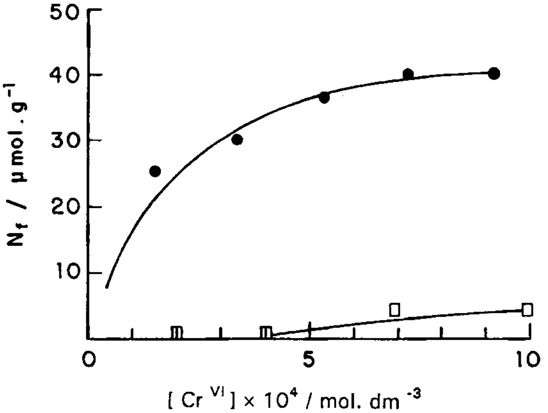

FIG. 5 Adsorption isotherms of Cr^{VI} on (●) Cel/TiO$_2$ and (☐) pure cellulose at pH 1.

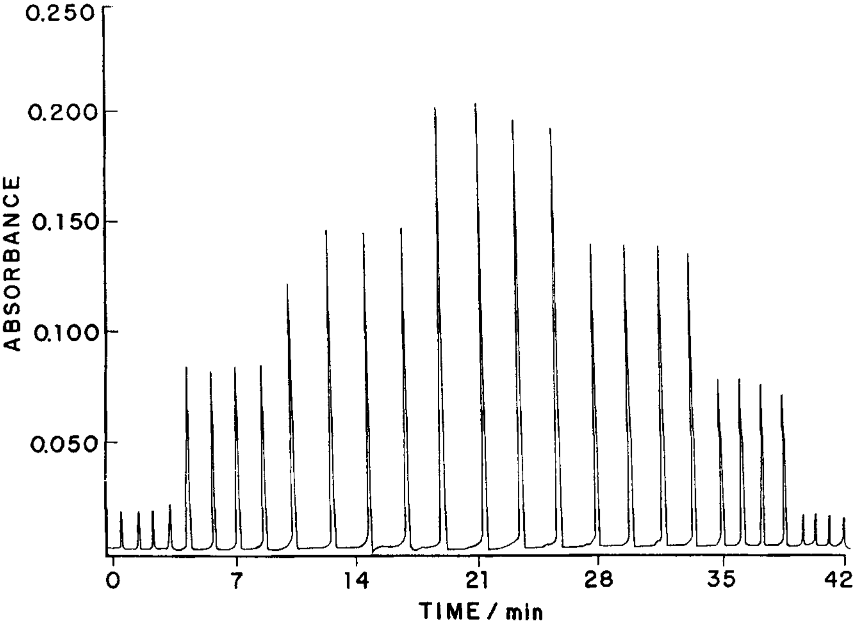

FIG. 6 Determination of Cr^{VI} using the manifold configuration shown in Fig. 1. From left to right: replicate of four injections of Cr^{VI} 50 ppb solutions with injections times of 10, 40, 70, 100, 70, 40, and 10 seconds.

TABLE 1
Calibration Curve of Cr^{VI} Adsorption by Cel/TiO_2

Inject time (s)	Inject volume (cm^3)	Mass of Cr^{VI} (μg)	Absorbance
10	0.53	0.027	0.019
40	2.12	0.106	0.080
70	3.71	0.186	0.140
100	5.30	0.265	0.202

ing ions up to 50 times the Cr^{VI} concentration. No significant interference was observed up to a 10:1 ratio. Fe^{III}, for which the tendency of hydrolysis is great, presents a significant interference factor at a 50:1 ratio, considerably larger in comparison to that observed for the other cations (21).

Anions interfere more because the surface is positively charged at pH 1 and they can therefore compete with $Cr_2O_7^{2-}$ for the adsorption sites by a simple ion exchange reaction. Larger interferences were observed for SO_4^{2-} and PO_4^{3-} (0.85 and 0.76, respectively) for the molar ratio [interferent]:[Cr^{VI}] = 10:1. However, no significant interference was observed for a 1:1 ratio.

Cr^{VI} in Natural Water

To determine the potential use of this material as an adsorbent specific for Cr^{VI}, natural water samples were collected from a city lake (sample A) and the University campus lake (sample B), and their pHs were adjusted to 1. Since no Cr^{VI} was detected in either sample using a previously described method (19), they were spiked with Cr^{VI} and allowed to stand for 12

TABLE 2
Relative Standard Deviations in Determining Cr^{VI} [a]

Injection time (s)	Cr^{VI} concentration (ppb)	Relative standard deviations (%)
20	50	3.37
33	30	2.44
100	10	6.44

[a] Flow rate = 3.2 $cm^3 \cdot min^{-1}$; replicate of 10 injections for each time.

TABLE 3
Study of the Interference of Ions on the Adsorption of Cr^{VI} by Cel/TiO_2[a]

Ion	Added as	[Interferent]:[Cr^{VI}]	Interference factor
Cr^{III}	$Cr(NO_3)_3$	50	0.93
		10	1.07
Cu^{II}	$CuCl_2$	50	1.01
Mn^{II}	$MnCl_2$	50	0.85
		10	1.13
		1	1.10
Hg^{II}	$HgCl_2$	50	0.83
		10	1.08
		1	0.99
Fe^{III}	$FeCl_3$	50	—
		10	0.94
		1	1.00
V^{V}	NH_4VO_3	50	1.28
		10	1.10
		1	1.00
Mo^{VI}	Na_2MoO_4	50	1.16
		1	0.99
SO_4^{3-}	H_2SO_4	10	0.85
		1	1.00
PO_4^{3-}	Na_2HPO_4	10	0.76
		1	0.99

[a] [Cr^{VI}] = 0.1 ppm.

hours and then the metal ion was analyzed by the FI technique. The same samples were analyzed by spectrophotometry using the DPC reagent. The results are summarized in Table 4. The agreement between the results obtained by the two procedures is very reasonable and indicate that Cel/TiO_2 can be used in determining Cr^{VI} in natural water.

TABLE 4
Comparison of the Results Obtained for the Analysis of Natural Water Spiked with Cr^{VI}

	Cr^{VI}/ppm	
Samples	DPC method	FI method
A	0.076	0.072
B	0.028	0.027

CONCLUSIONS

Titanium(IV) oxide supported on cellulose is very selective for Cr^{VI}, and the advantage in comparison with the previously described method (19) is that the composite is easier to prepare and cellulose is an abundant natural polymer. The solutions of NaOH used as the eluant did not attack the cellulose fiber, thus avoiding clogging of the column during operations. The composite is very selectivity to Cr^{VI} and does not suffer significant interference from Cr^{III}, Cu^{II}, Fe^{III}, V^{V}, and Mo^{VI}.

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