Investigation of Removal of Cr(VI), Mo(VI), W(VI), V(IV), and V(V) Oxy-ions from Industrial Waste-Waters by Adsorption and Electrosorption at High-Area Carbon Cloth

Abbas Afkhami[1] and Brian E. Conway[2]

Department of Chemistry, Ottawa University, 10 Marie Curie Streets, Ottawa, Ontario, K1N 6N5, Canada

Adsorption and electrosorption of Cr(VI), Mo(VI), W(VI), V(IV), and V(V) ions from water samples at low concentration were studied at high-area C-cloth electrodes. The concentrations of ions in the solution were monitored using *in situ* UV spectroscopy. All the investigated ions, except V(IV), showed better adsorption in acidic media. Positive polarization of the C-cloth caused increased adsorption of Cr(VI), Mo(VI), and V(V) ions. When previously adsorbed, Mo(VI) and V(V) ions were shown to be largely desorbable by negative polarization of the C-cloth. Since V(IV) does not become adsorbed significantly at the C-cloth in acidic media, the method provides an interesting means for separation of V(V) and V(IV) species in solution.   © 2002 Elsevier Science (USA)

Key Words: Adsorption and electrosorption; Cr(VI); Mo(VI); W(VI); V(IV); V(V); water purification

INTRODUCTION

The transition metals and their ions are of particular interest in many application areas. Hexavalent chromium exists in water as oxyanions such as chromate, $HCrO_4^-$, and dichromate, the speciation being dependent on pH. Such ions are toxic, carcinogenic, mutagenic, and teratogenic (1–4). Cr(VI) is used in various industries, including metallurgy, leather tanning, and electroplating, and has also been widely used as a corrosion-control agent (5, 6). Therefore, such ions can be major pollutants of the waste-waters of these industries. Also, because of their extensive use, chromium contamination of ground waters is unavoidable (7). The toxicity of vanadium is also well known (8). Water pollution by soluble compounds of toxic metals is not only a public health concern, but an economic one as well. Therefore, removal or modification of these ions from waste-waters and ground waters is of significant importance from an environmental point of view.

Several methods have been reported for the adsorption of Cr(VI) from water samples. Soil components, including Fe and Al oxides (9, 10), kaolinite (11), and sphagnum peat moss (12), have been used for the adsorption of chromate. There are also several reports on the application of activated carbon for the adsorption of Cr(VI) (13–17). Mikkonen and Tummavuori reported the adsorption of V(V), Mo(VI), and W(VI) by Finnish mineral soil (18). Adsorption of Mo(VI) on activated carbon (19), V(IV) on chitsona (20), and Mo(VI) and W(VI) on metal oxides (21) was also reported.

High-area carbon cloth, which has the advantage of having a very large specific surface area, e.g., $2500 \text{ m}^2 \text{ g}^{-1}$, has recently been used for the successful adsorptive removal of various S-containing inorganic anions (22), ethyl xanthate (23), and some phenolic compounds (24).

The extent of adsorption and reduction processes that take place depends on the nature and specific surface area of the adsorbent. Granular or powdered activated carbon materials having various origins and ranges of specific areas and pore distributions have been widely used as effective adsorbents for removal of a variety of contaminants in aqueous media. Such porous-activated carbon materials have specific surface areas of approximately $1000 \text{ m}^2 \text{ g}^{-1}$, e.g., see Ref. (15), depending on the source from which they are prepared.

A comparison of the specific surface areas of activated carbons and the C-cloth used in the present work indicates that it has about a 2.5 times larger specific area than commonly employed granular-activated carbons. One of the special advantages of the C-cloth material that we have used is that it is a woven matrix having excellent mechanical integrity, unlike granular or powdered carbon adsorbents which are difficult to handle in laboratory experiments or to form into convenient electrode structures.

In cases of most adsorbents, the "adsorption capacity" in the sense of attainable maximum coverage or maximum molar extents of sorption per gram of adsorbent is not a well-defined quantity; this is because it depends on molecular size, structure, functionality, and hydrophobicity of the adsorbate itself. Our previous work (23) using the C-cloth adsorbent shows that it adsorbs virtually all the adsorbent available in 10^{-4} M solutions at a module of approximately 0.04 g mass, and the adsorbate can be almost quantitatively desorbed by anodic or cathodic polarization of the C-cloth configured as a porous electrode. This provides a convenient procedure for *in situ* regeneration.

[1] To whom correspondence should be addressed. Fax: (613)562-5170.

[2] On sabbatical leave from Department of Chemistry, Bu-Ali Sina University, Hamadan, Iran.

In this paper we describe the adsorption and electrosorption of Cr(VI), Mo(VI), W(VI), V(IV), and V(V) ion species on high-area C-cloth for the purpose of development of procedures for purification of water and waste-waters where removal of such transition metal ions, which are often noxious, is desirable for environmental reasons. The solutions were monitored by means of *in situ* UV spectroscopy.

EXPERIMENTAL

Reagents

The C-cloth used in this work was obtained from Spectra Corp., coded as Spectracarb 2225 having a specific area of $2500 \text{ m}^2 \text{ g}^{-1}$. $K_2Cr_2O_7$, $Na_2MoO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, NH_4VO_3, $VOSO_4$, and sulfuric acid were reagent grade materials. The high-purity water used for making up the test solutions from which adsorption at the C-cloth was measured was delivered from an 18.2-$M\Omega$ Milli-Q UV (Millipore) water preparation system. Sodium hydroxide and sulfuric acid solutions were used for pH adjustments.

Treatment of the C-Cloth

Previous work (22) from this laboratory had shown that Spectra Corp. C-cloth initially contained some traces of elutable ions as indicated by conductometric measurements. Hence, a C-cloth sample was first placed in a flow-through washing cup and eluted with a total of 5 L of warm (60°C) conductivity water in a kind of batch operation over 2 days. Nitrogen gas was bubbled continuously through the washing cup to avoid possible adsorption of CO_2 that might have been dissolved in the water. The outflow water from each batch was tested conductometrically for completeness of the washing procedure. The washed C-cloth modules were then dried under vacuum at 120°C and kept in a desiccator for further use. The C-cloth was cut in desired dimensions, weighed accurately, and attached to the electrode holder (Pt wire) for introduction into the adsorption cell. The C-cloth material had previously been electrochemically characterized by means of cyclic voltammetry to evaluate its double-layer capacitance and the form of its voltammogram (Fig. 1) as described and shown in Ref. (23). Specific details of its preparative and pretreatment conditioning are proprietary, but we were able to ascertain that it was prepared by pyrolysis of a phenolic C-film polymer between 800 and 900°C in N_2.

Electrolytic Cell

A V-shaped electrolytic cell was used for conducting the adsorption studies both under open-circuit conditions and upon electrochemical polarization Simultaneously *in situ* concentration measurements were made by means of UV absorption spectrophotometry (Fig. 2). One arm of the cell contained the working and the reference electrodes, while the other contained the counter-electrode and a thin tube for bubbling nitrogen gas through the solution for the dual purpose of mixing and elimi-
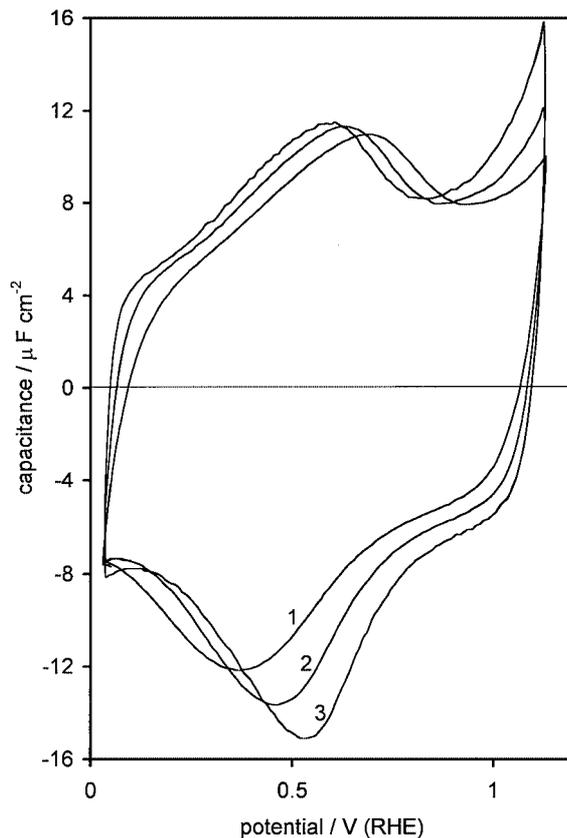

FIG. 1. Cyclic voltammetry response of the C-cloth electrode material recorded in terms of the capacitance derived as $C = i/s$, where i is the current response at sweep rates $s = 2$ (Curve 3), 5 (curve 2), and 10 (curve 1) mV s^{-1}.

nating any dissolved CO_2. The two arms were connected to a glass joint leading to a vacuum pump at the upper part of the V-shaped cell. A quartz spectrophotometer cuvette was sealed to the bottom of the electrolytic cell. The adsorbent electrode was a weighed piece of C-cloth serving as the working electrode and held in place by a short Pt wire; the counter electrode was a Pt wire. An Ag–Ag$_2$O electrode (22) was used as a reference electrode.

Absorbance Measurements

A Cary 1E-type UV/vis spectrophotometer, interfaced to a computer, was used for the absorbance measurements, which could be conducted *in situ* during study of the adsorption and electrosorption processes by the following procedure. An accurately weighed piece of the C-cloth was placed in one arm of the electrolytic cell. The sizes and weights of the C-cloth samples used were kept as constant as possible but their actual weights were accurately measured and recorded each time for calculation of the extents of adsorption per unit mass of the C-cloth.

The whole cell was first evacuated to remove all air in the pores of the C-cloth electrode. A known volume of water (15 mL) was transferred into the cell from a burette fitted to one of the arms of the cell. Further evacuation was applied after adding

the water to ensure removal of all air in the pores so that water had attained access to the whole C-cloth surface, except perhaps the finest fraction of the pore-size distribution. The vacuum was then released and the burette removed. Allowance was made for the fact that occupancy of the finest nanopore fraction of the structure requires considerable time.

The quartz cuvette fixed at the bottom of the cell (which now contained the C-cloth electrode and water) was inserted into the front sample compartment of the spectrophotometer. The reference and counterelectrodes were inserted into the appropriate arms of the electrolytic cell. A Teflon tube connected to the tip of a thin N_2-bubbling tube, to provide effective mixing, was lowered into the UV cell to a level just above the light path. The working, counter-, and reference electrodes were connected to a Hokuto Denko HA-301 potentiostat/galvanostat for control of voltage or current.

Finally, a calculated volume (0.15 mL) of relatively concentrated solution (∼0.01 M) of the desired ionic "impurity" for testing was accurately metered into the arm of the electrolytic cell containing the counterelectrode, using a micrometer burette.
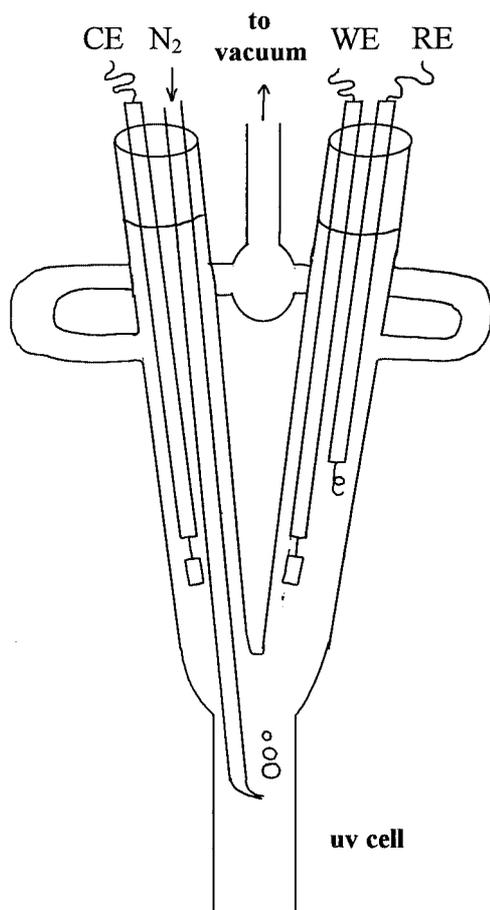
TABLE 1
Spectral and Calibration Data of Investigated Ions

Species	Solvent	λ (nm)	ε (cm^{-1} mM)	Correlation coefficient
$Cr_2O_7^{2-}$	0.1 M H_2SO_4	257	3.599	0.9991
		372	2.116	0.9998
CrO_4^{2-}	0.1 M NaOH	257	2.404	0.9992
		372	4.325	0.9995
Mo(VI)	H_2O	208	10.213	0.9982
	0.01 M H_2SO_4	218	7.553	0.9958
W(VI)	H_2O	193	9.542	0.9999
	0.01 M H_2SO_4	193	9.542	0.9963
V(V)	H_2O	203	6.128	0.9982
	0.01 M H_2SO_4	203	3.426	0.9996
V(IV)	H_2O	245	0.712	0.9995
	0.01 M H_2SO_4	245	0.712	0.9985

Then a black curtain was spread above the sample compartment of the spectrophotometer, over the cell, to prevent interference from external light.

Calibration and Beer's Law

The molar absorptivities of the investigated ions were measured, in order to monitor their adsorption by UV spectroscopy. After selection of an appropriate wavelength, the absorbances of a series of standard solutions were measured and the molar absorptivities were obtained from Beer's law. For determination of the molar absorptivities of chromate and dichromate, the absorbance of alkaline and acidic Cr(VI) standard solutions were measured. The regression coefficients were very close to a value of 1, which meant that Beer's law applied quantitatively over the concentration range (0.01–0.2 mM) employed in the experiments. The results are given in Table 1.

The quantity of ion adsorbed per unit mass of C-cloth was calculated from the equation

$$M = \frac{(c_o - c)V}{m},$$ [1]

where c_o and c are the concentration at the beginning and at the equilibrium adsorption state, respectively, V is the volume of the solution, and m is the mass of the C-cloth module.

RESULTS AND DISCUSSION

Open-Circuit Adsorption of Cr(VI) Species

Ions from a 1.0×10^{-4} M dichromate solution were allowed to become adsorbed on the C-cloth. Figure 3 shows the variation of the absorption spectrum of Cr(VI) ions with time. As this figure shows, the absorbance of the solution decreased at 257 nm but increased at 372 nm with time, then remained nearly constant after about 100 min. In neutral solutions, chromate and dichromate ions are in equilibrium (25). The individual absorption spectra of chromate and dichromate are shown in Fig. 4. As
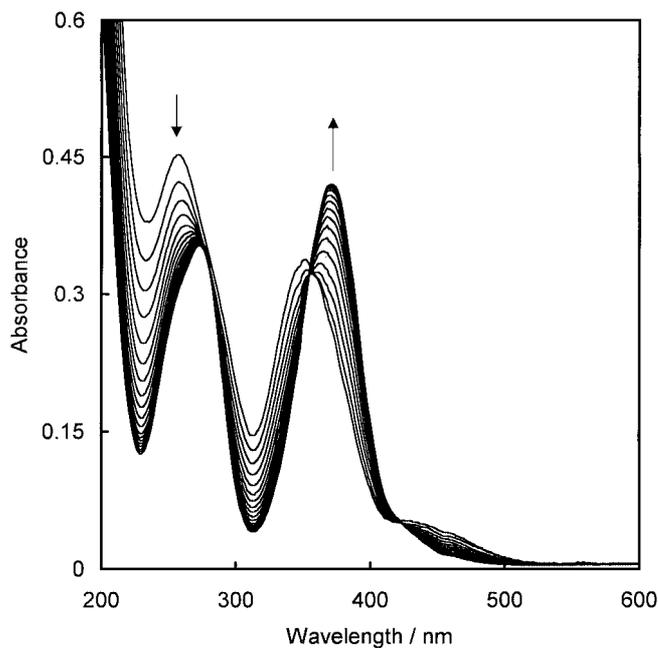

FIG. 2. Cell for *in situ* spectroanalysis at high-area C-cloth modules. The diagram also shows connections for electrodes, when required, as for cyclic voltammetry characterization (WE = working electrode, CE = counter electrode, and RE = reference electrode).

FIG. 3. Variation of the absorption spectra of a nearly neutral 2.0×10^{-4} M Cr(VI) solution with time in the presence of 0.0220 g of C-cloth. Time intervals 7 min.

can be deduced from Fig. 4, the decrease in the absorbance of the solution at 257 nm seen in Fig. 3 is due to the decrease in dichromate concentration while the increase in the absorbance at 372 nm is due to the increase in the concentration of chromate. Note the appearance of isosbestic points in the series of curves in Fig. 3, indicating the complementarity of the increases and
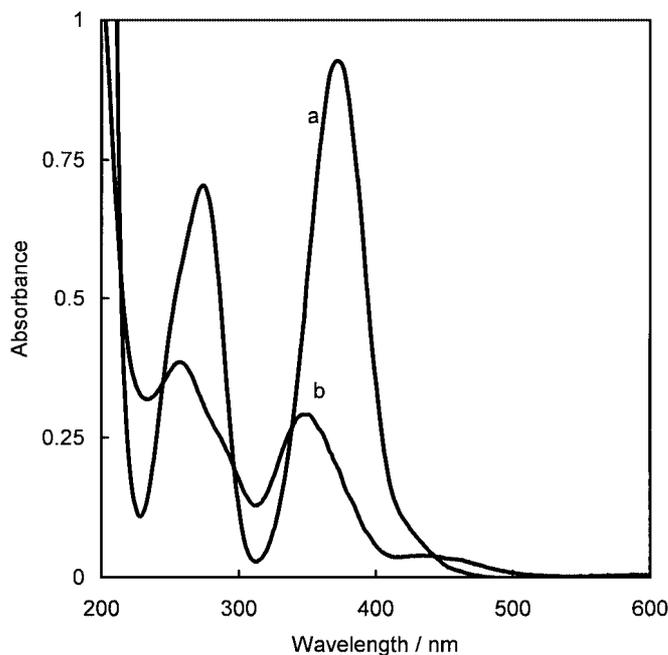
decreases of the two Cr(VI) species in solution. Examination of the kinetics of these decreases and increases of absorbance in Fig. 3 showed them to be of first order as previously found (23) for adsorption of ethyl xanthate at the same C-fiber material. The first-order rate constant was evaluated as 0.0256 min^{-1}. The increase in the absorbance of the solution at 372 nm shows that hydroxyl ion is produced by the adsorption of Cr(IV) on the C-cloth as will be explained below in the next section.

The amount of adsorbed Cr(IV) could be readily calculated from Beer's law using the proportional equation method

$$\Delta A^{257} = \Delta A_1 - \Delta A_2 \qquad [2]$$

and

$$\Delta A^{372} = \Delta A_3 + \Delta A_4, \qquad [3]$$

where ΔA^{257} and ΔA^{372} are the total absorbance changes at 257 and 372 nm, respectively, ΔA_1 and ΔA_3 are the decreases in absorbance at 257 and 372 nm, respectively, due to the decrease in dichromate concentration while ΔA_2 and ΔA_4 are increases in absorbance at 257 and 372 nm due to the increase in chromate concentration. Therefore,

$$\Delta A^{257} = \varepsilon_{\text{dichromate}}^{257} b \Delta c - \varepsilon_{\text{chromate}}^{257} b \Delta c' \qquad [4]$$

$$\Delta A^{372} = \varepsilon_{\text{dichromate}}^{372} b \Delta c + \varepsilon_{\text{chromate}}^{372} b \Delta c', \qquad [5]$$

where Δc and $\Delta c'$ are the decrease in dichromate concentration and increase in chromate concentration, respectively.

Molar absorptivities of chromate and dichromate were evaluated in separate experiments as described earlier. The overall variation of adsorbed Cr(VI) species with time is shown in Fig. 5.
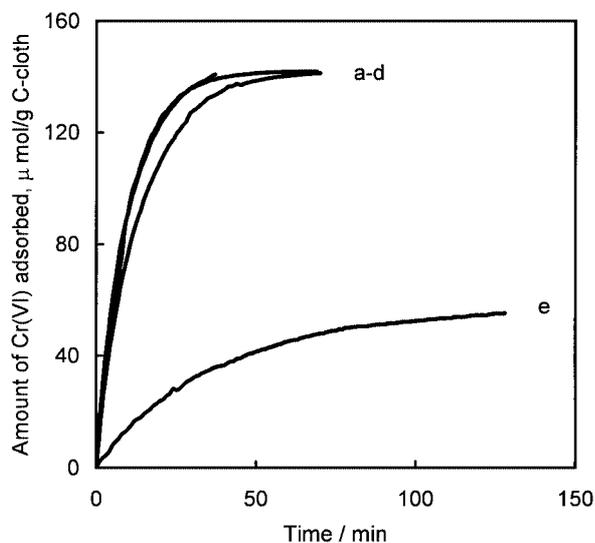

FIG. 4. The absorption spectra of (a) chromate and (b) dichromate.

FIG. 5. Adsorption of Cr(VI) with time on C-cloth in (a) 0.001, (b) 0.005, (c) 0.01, and (d) 0.05 M sulfuric acid solution. Initial Cr(VI) concentration is 2.0×10^{-4} M, volume of solution is 15 mL, and amount of C-cloth used is 0.0220 g. Curve e is for pH 6.

Effect of pH on Adsorption of Cr(VI) Species

Adsorption of Cr(VI) on C-cloth in both acidic and alkaline solutions was also investigated. The results show that Cr(VI) is not adsorbed from alkaline media (pH 12), even after 100 min. Adsorption of Cr(VI) at initial pHs of 2.7, 2.1, 1.2, and 1.1 was also studied. The results are shown in Fig. 5. The extents of adsorption were significantly greater in the more acidic solutions than in nearly neutral media around pH 6.

In basic solutions, Cr(VI) species are in the form of chromate ions while in acidic media chromate and dichromate are in equilibrium. The adsorption behavior is expected to be closely related to the state of hydration of the ions, as described in Ref. (26). Therefore, it is probable that dichromate is being adsorbed at the two O-bridged Cr atoms but this is not possible for chromate ions where the Cr center is monomeric and screened by four O atom ligands. This kind of effect has been reported for the adsorption of sulfate ions too (22, 26). Therefore, the extent of adsorption of Cr(VI) species increases when the ratio of dichromate to chromate ions is increased in the solution. Another reason for the increase of the adsorption of Cr(VI) in acidic media is that Cr(VI) removal by the C-cloth is a result of a combination of physicochemical adsorption and chemical reduction by surface functionalities (27) on the C-cloth. Since reduction of Cr(VI) in acidic media is more favored than in nearly neutral media, removal of Cr(VI) from the solution therefore increases by acidification of the solution. Production of hydroxide ions during the course of open-circuit adsorption and electrosorption of Cr(VI) in nearly neutral solutions provides additional evidence for reduction of Cr(VI). This has also been reported for the removal of Cr(VI) from water solutions by active carbon (14, 15).

Electrosorption of Cr(VI)

Positive polarization of the C-cloth electrode, in nearly neutral solutions, by passing a current of +0.1 mA galvanostatically, caused a rapid increase in the absorbance of the solution at 372 nm up to an adsorption period of about 20 min and then decreased. As on open-circuit, the increase in the adsorption appears to be due to the production of hydroxide ions from the C-cloth surface by adsorption of Cr(VI). The electrostatic attraction of dichromate by the C-cloth, polarized in the positive direction, results in a decrease in Cr(VI) concentration in the solution and therefore a decrease in the absorbance of the solution. However, reversal of the direction of the resulting polarization at 155 min, by passing −0.1 mA current galvanostatically, results in desorption of electrosorbed Cr(VI) during the next 20 min. These results are shown in Fig. 6. It was also determined that the small area wires, Ag and Pt, used as counter and reference electrodes, or as the holder of the C-cloth, do not have any effect on the adsorption behavior of Cr(VI) on C-cloth. The above experiment was repeated using just the wire (without the C-cloth) previously used to hold the C-cloth: under such conditions, no detectable changes were observable in the absorbance of the Cr(VI) solution during the whole course of
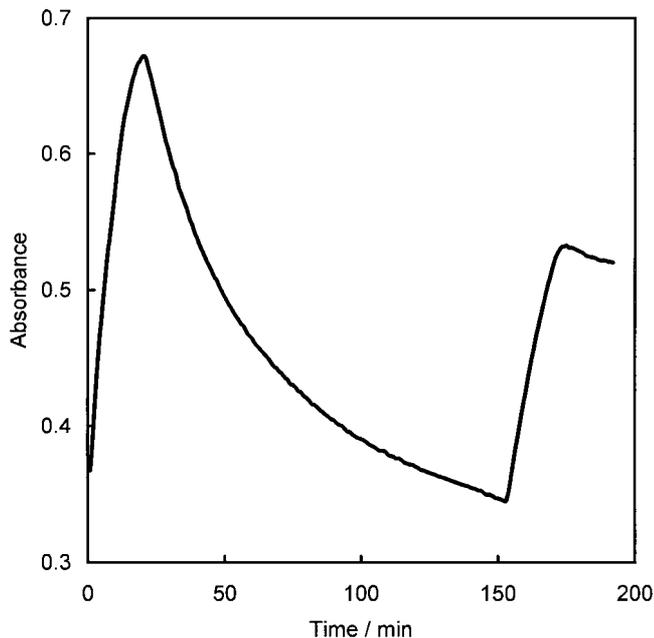

FIG. 6. Variation with time in absorbance at 372 nm for a 2.0×10^{-4} M nearly neutral solution of Cr(VI) resulting from polarization of the C-cloth electrode. (See details in the text.) The volume of the solution is 15 mL, and the amount of C-cloth used is 0.0223 g.

an experiment, including the positive and negative polarization stages.

It must be noted that polarization of the C-cloth had no effect on the adsorption of Cr(VI) at C-cloth electrodes in buffered acidic and alkaline media at well-defined pH's.

Adsorption and Electrosorption of Mo(VI) Species

The adsorption of Mo(VI) in nearly neutral solution and at initial pH's of 1.2, 2.1, 2.7, and 3.2 and also its electrosorption are shown in Fig. 7. As before, a thin Pt wire was used to hold the C-cloth as well as to connect it to the potentiostat/galvanostat and a Pt wire was again used as the counterelectrode. The open-circuit adsorption of Mo(VI) in a nearly neutral solution is very small but is significantly increased in acidic media. Figure 8 shows the variation of Mo(VI) absorption spectra with time under the latter conditions. A Mo(VI) solution contains, in fact, a variety of condensed molybdates. As the acidity of the solution increases, the oxygen : metal ratio decreases by removal of the oxide ion ligands by protonation (28). The dramatic increase in the adsorption of Mo(VI) observed in acidic solutions could arise for the following reasons. At acidic pH's, the preferentially adsorbing molybdate ($Mo_xO_y^{2-}$) is present but not in nearly neutral solution where its concentration is only quite small. The addition of acid also tends to produce positive sites on the C-cloth, by protonation of surface -OH groups (27, 29) that would cause an increase in electrostatic adsorption of molybdate ions. The adsorption of Mo(VI) decreases again with increasing acid concentration, probably due to formation of other condensed molybdates. Under open-circuit conditions for adsorption of
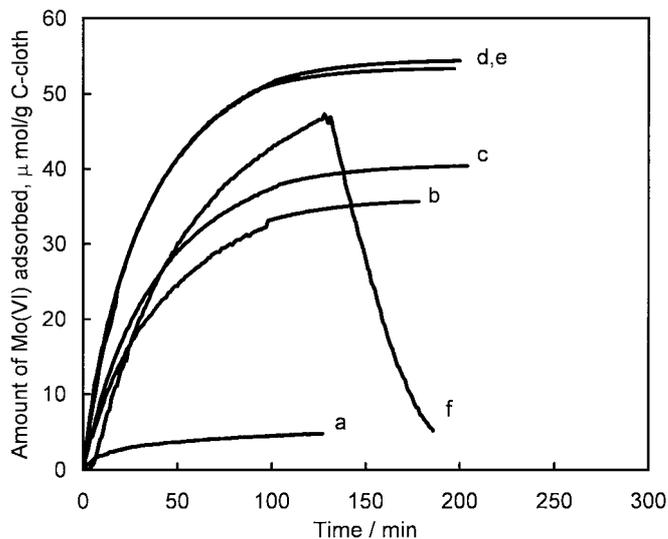
FIG. 7. Adsorption of Mo(VI) on C-cloth in (a) a nearly neutral solution, (b) 0.01 M, (c) 0.005 M, (d) 0.001 M, and (e) 0.0005 M sulfuric acid and (f) electrosorption in a nearly neutral solution. (See detailes in text.) The volume of the solution is 15 mL, and the amount of C-cloth used is 0.0227 g.

Mo(VI), liberation of OH^- was not observed. This shows that the mechanism of adsorption of Mo(VI) differs from that of Cr(VI).

Positive polarization of the C-cloth by passing +0.1 mA current galvanostatically caused an increase in the adsorption of Mo(VI). The electrostatic attraction of molybdate ions by the C-cloth polarized in the pos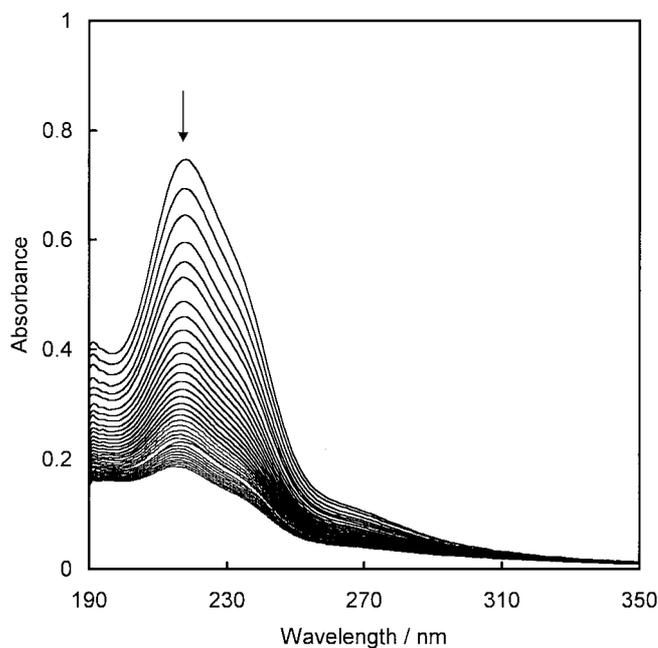itive direction results in a decrease in Mo(VI) concentration in the solution. However, reversal of the direction of polarization at 130 min, by passing −0.1 mA current galvanostatically, results in desorption of most of the electrosorbed Mo(VI) ions from the C-cloth, leading to an increase in the concentration of Mo(VI) in solution during the next 120 min (Fig. 7). This reversibility of adsorption/desorption is of significance for the development of practical applications, e.g., for accumulation of the noxious ions from a dilute-solution environment followed by discharge desorption into a small rejection volume.

Adsorption and Electrosorption of W(VI) Species

The variation in the concentration of W(VI) during the course of adsorption in nearly neutral and acidic solutions at pH's of 1.1, 1.2, 2.1, and 2.7 on C-cloth is shown in Fig. 9. However, for this species, the decrease in the concentration of W(VI) in nearly neutral solution was less than 10%, even after 100 min, while for acidic solutions this decrease was about 80%. As for the case of Mo(VI), the solution of W(VI) contains a wide range of tungstates. As the acidity of the solution increases, again the oxygen : metal ratio decreases by protonation of the oxide ligands (28). Therefore, acid not only increases the adsorption of W(VI) by the formation of positive sites on C-cloth surface by the protonation of -OH groups but also by the production of suitable tungstate species more suceptible to adsorption.

The electrosorption of W(VI) species was also studied. Positive polarization of the C-cloth by passing a current of +0.1 mA galvanostatically, caused a slight decrease in pH, probably by electrolysis. This caused a blue shift in the λ_{max} and a small decrease in the absorbance of the solution. Reversal of the direction of polarization after 105 min, by passing a current of −0.1 mA

FIG. 8. Variation of the absorption spectra of a 1.0×10^{-4} M Mo(VI) in 0.001 M sulfuric acid solution with time in the presence of 0.0225 g of C-cloth. Time intervals 3 min.
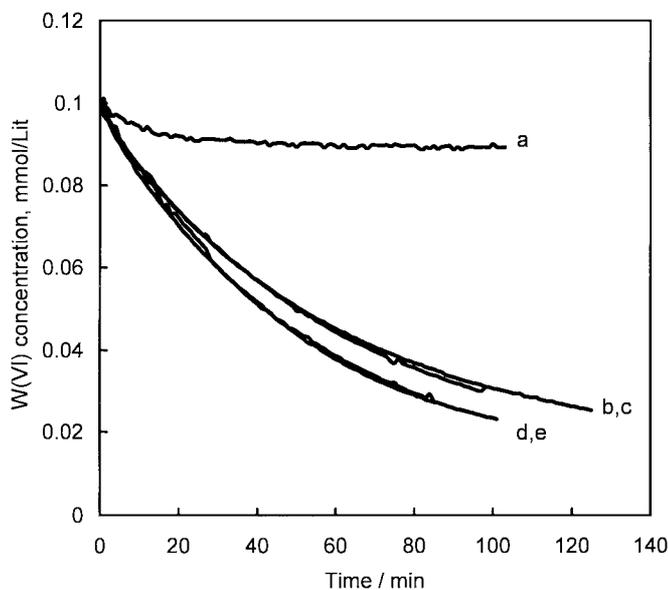

FIG. 9. Adsorption of W(VI) on C-cloth in (a) a nearly neutral solution, (b) 0.05 M, (c) 0.001 M, (d) 0.005 M, and (e) 0.01 M sulfuric acid. The volume of the solution is 15 mL and amount of C-cloth used is 0.0224 g.
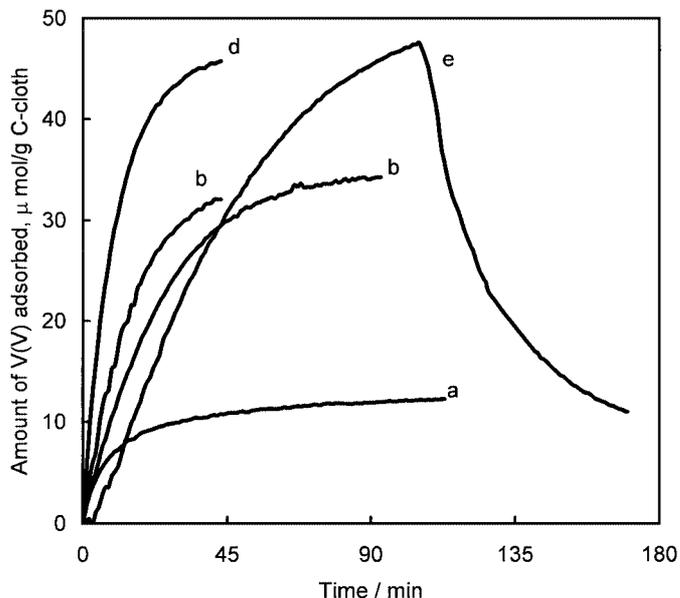
FIG. 10. Adsorption of V(V) on C-cloth in (a) a nearly neutral solution, (b) 0.01 M, (c) 0.005 M and (d) 0.001 M sulfuric acid and (e) electrosorption in a nearly neutral solution. (See details in text.) Volume of the solution is 15 mL and amount of C-cloth used in 0.0225 g.

caused a red shift in λ_{max}, this time with a small increase in the adsorbance of the solution. Overall, it could be said that polarization had no appreciable systematic effect on the adsorption of W(VI) species.

Adsorption and Electrosorption of V(V) and V(IV) Species

The adsorption of V(V) in nearly neutral and acidic solutions at pH's of 1.2, 2.1, and 2.7 and its electrosorption were also studied. The results are shown in Fig. 10. The concentration of V(V) in a nearly neutral solution decreased by 20% of its initial value after 110 min while it was decreased by about 80% after 45 min in 0.001 M sulfuric acid solution. This shows that the adsorption of V(V) at C-cloth in acidic solutions is significantly greater than that in nearly neutral solutions. However, an increase of the concentration of acid decreased the adsorption. It is well known that in V(V) solutions a wide range of vanadates can exist. Again the principal species depend upon the hydrogen ion concentration (28). As various vanadates adsorb differently, the effect of acid on the adsorption of V(V) can be discussed as in the case of Mo(VI) species.

Positive polarization of the C-cloth electrode by passing a current of +0.1 mA galvanostatically in a nearly neutral solution caused an increase in the adsorption of V(V) relative to that on open-circuit. The concentration of V(V) decreased to about 20% of its initial value after 105 min. The electrostatic attraction of vanadate ions by the C-cloth polarized in the positive direction results in a decrease in V(V) concentration in the solution. However, reversal of the direction of polarization at 105 min, by passing −0.1 mA current galvanostatically, results in desorption of most of the electrosorbed V(V) ions from the C-cloth, leading

to an increase in the concentration of V(V) in solution during the next 65 min. Again, this is a favorable effect for applications.

Investigation of open-circuit adsorption of V(IV) in a nearly neutral solution showed that its concentration decreases only by about 5% after 100 min. Negative polarization of the C-cloth electrode by passing a current of −0.1 mA galvanostatically, and reversal of polarization by passing a +0.1 mA current after 60 min did not improve the extent of adsorption. These results show that V(IV) does not become adsorbed at C-cloth in acidic media, even after 100 min adsorption time. However as mentioned above, V(V) becomes adsorbed very well in acidic media; therefore this procedure could be used for separation of V(V) and V(IV) in water samples or in other chemical operations.

CONCLUSIONS

High-area C-cloth in a proprietary form, designated "Spectracarb 2225," is an effective sorbent for Cr(VI), Mo(VI), W(VI), and V(V) ions, thus providing a procedure for clean-up of various industrial waste-waters. Procedures based on adsorption and electrosorption of these species at high-area C-cloth are shown to be effective for removal of them from aqueous solutions. *In situ* optical absorbance measurements were found to provide quantitative information for the adsorption studies. Polarization of the C-cloth increases the rate of adsorption of the various oxyanions. Reversing the polarization of the C-cloth electrodes caused desorption of previously adsorbed Mo(VI) and V(V) species. Acidification of the solution significantly increases adsorption of the investigated ions, except V(IV). Adsorption of Cr(VI) is a result of a combination of physicochemical adsorption and chemical reduction at the C surface. V(IV) does not become adsorbed significantly at high-area C-cloth in acidic media, and therefore the method provides an interesting means for separation of V(IV) and V(V) species in solution.

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