Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lazaridis, N. K. , Jekel, M. and Zouboulis, A. I.(2003) 'Removal of Cr(VI), Mo(VI), and V(V) Ions from Single Metal Aqueous Solutions by Sorption or Nanofiltration', Separation Science and Technology, 38: 10, 2201 — 2219
To link to this Article: DOI: 10.1081/SS-120021620
URL: http://dx.doi.org/10.1081/SS-120021620

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 10, pp. 2201–2219, 2003

Removal of Cr(VI), Mo(VI), and V(V) Ions from Single Metal Aqueous Solutions by Sorption or Nanofiltration

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ABSTRACT

The removal of Cr(VI), Mo(VI), or V(V) anions from single metal aqueous solutions was studied. Two alternative treatment methods were applied: (1) sorption of these anions onto commercially available akaganeite (β-FeOOH) or (2) nanofiltration, using a commercial spiral-wound pilot-scale unit. During sorption experiments, kinetics and equilibrium were mainly studied. A modified second-order kinetic model was found to better fit the kinetic results. Freundlich isotherms better described (slightly) chromium and molybdenum equilibrium sorption experiments; whereas Langmuir isotherm better described vanadium equilibrium. During nanofiltration experiments, the influence of pH

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DOI: 10.1081/SS-120021620 0149-6395 (Print); 1520-5754 (Online)

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and of initial anion concentration was mainly studied, using a fixed background electrolyte concentration.

Key Words: Akaganeite; Removal; Anions; Sorption; Nanofiltration; Chromium; Molybdenum; Vanadium.

INTRODUCTION

The discharge of wastewaters polluted with toxic metal into the environment is strictly controlled by the respective legislation, among European countries. Therefore, the development and application of effective treatment processes is obligatory and several methods have been reported in use for the control of metal toxicants. The most commonly applied physicochemical treatment methods are: (1) precipitation as hydroxides, carbonates, or sulfides; (2) sorption (adsorption, ion exchange); (3) membrane processes; (4) electrolytic recovery; (5) evaporation; and (6) liquid–liquid extraction.[1] The present study focuses on the removal of chromium(VI), molybdenum(VI), and vanadium(V) anions from wastewaters by the application of two different treatment methods: (1) sorption or (2) nanofiltration.

Chromium is a naturally occurring element present in the environment with two main oxidation states, i.e., as a trivalent or hexavalent. Chromium(III) is an essential nutrient that can help the human body to use sugar, protein, and fat; an intake of 50 to 200 μg of Cr(III) per day is recommended for adults. On the contrary, Cr(VI) rarely occurs naturally; usually, it is produced from anthropogenic sources. The International Agency for Research on Cancer (IARC) determined that chromium(VI) is a carcinogenic element for humans and the Environmental Protection Agency (US EPA) set the maximum level of total chromium concentration allowed in drinking water at 100 μg/L.[2] According to the European Commission, the guide value for total chromium concentration in drinking water is 50 μg/L.[3] The remediation of Cr(VI)-contaminated water sources is gaining increasing importance due to the limited drinking water supply. Three strategies have been mainly applied for the removal of Cr(VI): (1) reduction of hexavalent chromium to trivalent, with subsequent precipitation of later as hydroxide[1]; (2) sorption onto various materials, including carbon,[4–13] whereas anion exchange, as well as biosorption, can be also included[14,15]; and (3) the use of membrane filtration has recently attracted increasing attention.[16–19] Nevertheless, sorption is perhaps the most conveniently applied treatment method for the removal of relatively small chromium concentrations from contaminated streams.

Molybdenum and vanadium occur in the earth crust in a mean concentration of about 0.0001% and 150 g/t, respectively.[20] Therefore, vanadium is one of the most commonly found metals. Since the 1980s, a new type of secondary raw materials has gained importance for the production of these metals, namely the molybdenum-containing catalysts, widely used in the petroleum refining industry. A typical catalyst uses molybdenum in combination with other metals on a porous alumina substrate. The usual composition range of spent catalysts is between 2 and 10% Mo, 0 and 12% V, 0.5 and 4% Co, and 0.5 and 10% Ni. Vanadium is also contained in most crude oils, in amounts ranging between 10 and 1400 mg/L. During petrochemical refining, vanadium is retained in boiler residues and incinerated fly ashes, with content between few percent and up to 40%.[20] Due to the fact that environmental legislation is becoming strict, emission and deposition of these residues has to be drastically reduced. Several methods dealing with the extraction of molybdenum and vanadium from different sources have been reported. Among them are liquid extraction, ion exchange, flotation, and sorption onto chitosan.[21–28]

In this study, the removal of chromium(VI), molybdenum(VI), or vanadium(V) anions from aqueous solutions by sorption onto akaganeite (β-FeOOH, granulated ferric hydroxide), as well as by commercial spiral-wound nanofiltration pilot-scale equipment, was performed. The main parameters of Berlin city water are pH 7, turbidity <1 NTU, conductivity 1170 μS/cm, free of iron and manganese, containing natural organic matter concentration 2 to 3 mg/L (as TOC). The main objective of this research was the operation of both separation processes (sorption and membrane filtration) under similar experimental conditions and not the optimization of these processes. For this reason, we selected an experimental pH value of 7 (controlled); we did not change this value even though the pH is expected to highly influence the sorption experiments.

The major contribution of the present work to the body of knowledge, according to the authors' knowledge, can be stated as: (1) regarding the sorption process, there is no published information concerning the sorption of molybdenum and vanadium using GFH (akaganeite) as a sorbent material. For chromium, there is only a little information on this system, but these applied relatively different conditions. (2) regarding the membrane filtration process, there is no published information about molybdenum or vanadium removal. Even though chromium removal by membrane filtration has been studied, the experimental conditions were on the order of lab-scale (few L/h); whereas in this study, chromium filtration was investigated in a pilot-scale (feed rate 100 m^3/h).

Granular ferric hydroxide (GFH) is a specific commercially available sorbent developed especially for the removal of arsenic from contaminated water sources (mainly ground waters). It can be applied in simple fixed bed reactors, similar to those used for activated carbon applications. It is possible to ensure compliance with the drinking water standard of arsenic, even after treatment of more than 70,000 bed volumes. This is considered as a rather simple (technologically) process, requiring relatively low levels of plant investment.[29,30]

EXPERIMENTAL

Materials

Granulated ferric hydroxide was supplied by GEH-Wasserchemie (Osnabrück, Germany). The particle size of sorbent was in the range between 0.32 and 2 mm. The BET surface area was 280 m^2/g. GFH was initially sieved and the fraction lower than 63 μm was used for sorption experiments. Chromium(VI), molybdenum(VI), and vanadium(V) salts were used as pro-analysis reagents (Merck, Germany) in the forms of $K_2Cr_2O_7$, $(NH_4)Mo_7O_{24}$ $4H_2O$, and NH_4VO_3, respectively, for the preparation of stock solutions. Potassium chloride (KCl p.a) was used to regulate the ionic strength. Tap water from Berlin city (average conductivity 915 μS/cm) was used for all experimental runs for the preparation of contaminated water samples.

Sorption Experiments

Two main aspects of sorption were examined: kinetics and equilibrium. For each experimental series, a number of glass flasks containing a 200-mL solution of known metal concentration were prepared. A fixed quantity of GFH was added into them and the pH was adjusted at 7.0 ± 0.2 during the sorption time.[30] The bottles were shaken on a Gerhardt agitator (speed 200 rpm) to ensure appropriate mixing conditions. They were performed at room temperature (around 20°C). Samples were subsequently filtered through 0.45-μm Sartorius membranes and the filtrate was analyzed for the remaining metal concentrations by AAS. Metal uptake (sorption loading) by the sorbent was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

Nanofiltration Experiments

These experiments were carried out using a single stage DOW-Spiral wound, NF270-2540 module pilot-scale unit (Fig. 1) with a total membrane surface area of 2.60 m^2, operating with the recycling loop mode.[31] The feed flow was set to 100 m^3/h; whereas the permeate rate was 10 m^3/h, based on preliminary experiments.[31] The temperature was controlled by a cooler (Haake Kryothermat 140) and kept at 20 ± 1°C. The system was operated by applying a transmembrane pressure (Δp) of around 5 ($\pm$0.5) bar. Nanofiltration experiments were run for about 1 hour, until pH and temperature remained stable in the aqueous solution to be treated for at least half an hour. Following that, grab samples from concentrate and permeate streams were received. Rejection and permeate rates were kept constant during the membrane filtration. The rejection rate was calculated using the following equation:

$$R\% = \left(1 - C_p/C_f\right) \cdot 100 \tag{2}$$

Analysis

Atomic absorption spectrophotometry, using a Varian SpectrAA 300/400 (UK) equipment and following the usual procedure, determined residual metal concentrations.

RESULTS AND DISCUSSION

Figure 2 shows the kinetic study of anions sorption for 20 mg/L initial metal concentrations. It was found that this procedure is relatively fast for the case of chromium and molybdenum, which within 10 min of loading sorbent, was approaching an equilibrium plateau. In the case of vanadium, the respective time was extended to around 300 min. Due to the short contact time needed for equilibrium, a predominantly reaction kinetic model is a reasonable assumption for the interpretation of obtained results. The kinetics of Cr(VI) removal by the application of various sorbents have been reported to follow a first-order,[8] and second-order[9,12] rate equations. The following

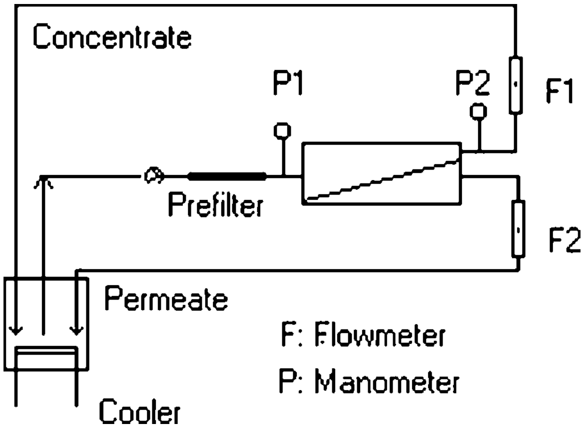

Figure 1. Schematic diagram of membrane nanofiltration equipment.

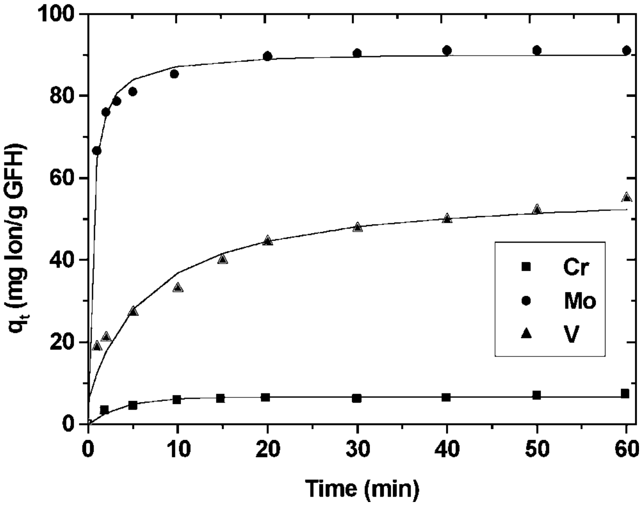

Figure 2. Influence of contact time, regarding GFH sorption loading for Cr(VI), Mo(VI), or V(V) anions; conditions: pH 7, [GFH] = 0.2 g/L for Mo, V and 3 g/L for Cr, [metal] = 20 mg/L.

pseudofirst-order equation, eq. (3), proposed by Lagergren, as well as the modified-second order eq. (4), were used to fit the experimental data[32]:

$$q_t = q_e\left[1 - \exp(-k_1 t)\right] \tag{3}$$

$$q_t = q_e\left(1 - \frac{1}{\beta_2 + k_2 t}\right) \tag{4}$$

The main kinetic parameters of sorption, such as the rate (k_1) and the predictive capacity (q_e), are presented in Table 1. The respective correlation coefficients are also presented in the same table, depicting that the second-order model shows a (slightly) better fit with the experimental data, as compared with the first-order one. The calculated sorption rates for the three examined anions are the following: 2.49 min^{-1} for Mo(VI), 0.41 min^{-1} for Cr(VI), and 0.17 min^{-1} for V(V).

Figures 3 through 5 present the equilibrium results in the presence of background electrolyte concentration 0.01 and 0.1 M KCl, respectively. The adsorption equilibrium models used to fit these results were the general-purpose relative equations of Langmuir (eq. 5), and Freundlich (eq. 6).

$$q_e = \frac{K_L C_e}{1 + a_L \cdot C_e} \tag{5}$$

$$q_e = K_F C_e^{1/n} \tag{6}$$

According to the calculated correlation coefficients (R^2), the Freundlich (F) equation was found to better fit the equilibrium sorption of Cr(VI) or Mo(VI) anions; whereas the Langmuir equation better represents the experimental results of V(V) (Table 2). The sorption of Cr(VI) onto various sorbent materials has been reported to follow either Langmuir[4,9] or Freundlich isotherms,[8,10,11] depending on the prevailing surface mechanisms; whereas

Table 1. Parameters and correlation coefficients for the examined kinetic models.

	First order			Second order		
Anion	$k_1(\text{min}^{-1})$	q_e(mg/g)	R^2 –	$k_2(\text{min}^{-1})$	q_e(mg/g)	R^2 –
Cr(VI)	0.28	6.58	0.962	0.41	7.17	0.992
Mo(VI)	1.26	87.39	0.974	2.49	90.76	0.996
V(V)	0.19	47.18	0.897	0.17	57.42	0.963

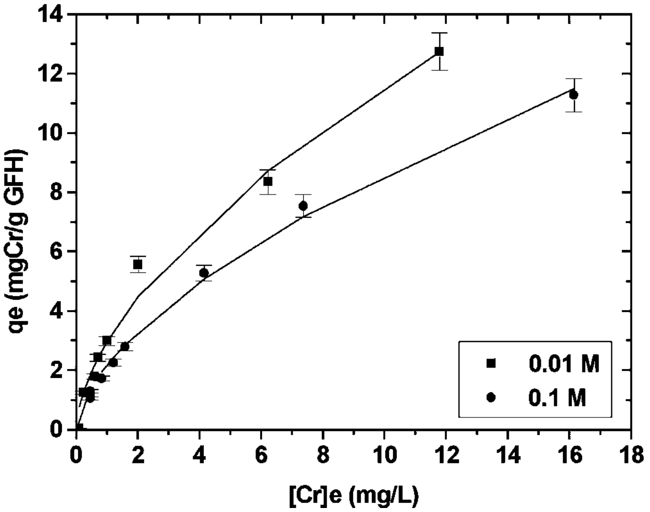

Figure 3. Sorption isotherms for Cr(VI) at two different ionic strength concentrations (0.01 M or 0.1 M); conditions: pH 7, [GFH] = 3 g/L.

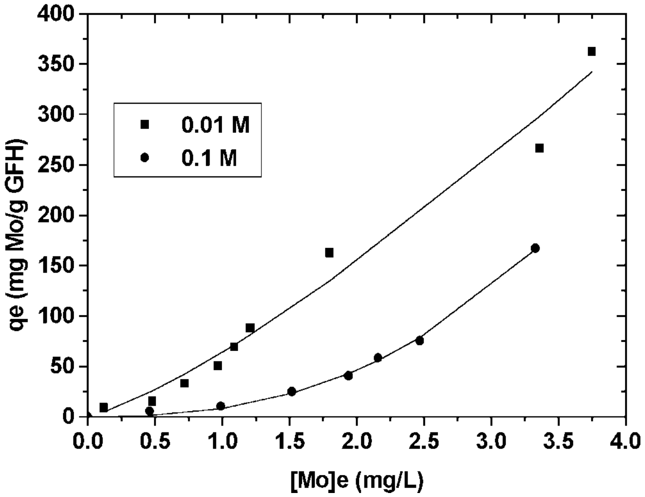

Figure 4. Sorption isotherms for Mo(VI) at two different ionic strength concentrations (0.01 M or 0.1 M); conditions: pH 7, [GFH] = 0.1 g/L.

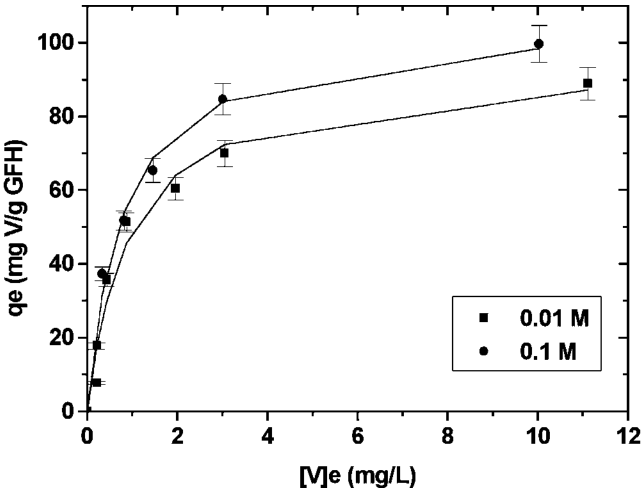

Figure 5. Sorption isotherms for V(V) at two different ionic strength concentrations (0.01 M or 0.1 M); conditions: pH 7, [GFH] = 0.1 g/L.

the pH-dependence equilibrium has been shown to follow double-layer, triple-layer or three-plane models.[5,13] Molybdenum and vanadium have been also cited to follow Langmuir or Freundlich isotherms, applying different sorbents.[26,27] From the obtained equilibrium results, a decrease in Mo(VI) uptake by increasing the ionic strength can be noticed, which could be attributed to the decrease of positive charge of sorbent surface, resulting in a lower attraction of molybdenum anions.[33]

EXAF spectroscopic evidence for inner-sphere complexation of CrO_4^{2-} on goethite surface has been reported. It was concluded that CrO_4^{2-} binding occurs

Table 2. Correlation coefficients of applied isotherm models for two different ionic strengths (KCl concentrations).

	0.01 M		0.1 M	
Anion	*L*	*F*	*L*	*F*
Cr(VI)	0.982	0.985	0.996	0.997
Mo(VI)	—	0.979	—	0.998
V(V)	0.972	0.905	0.992	0.978

inner spherically, forming three different surface complexes: a monodentate binuclear complex, a bidentate complex, and a bidentate-mononuclear one.[13] Accordingly, in the present study, the structural arrangements of the anions onto GFH surface can be: bidentate-mononuclear for Cr(VI), bidentate binuclear for V(V), and monodentate binuclear for Mo(VI), as presented in Fig. 6. This arrangement seems to be capable to interpret the sorption capacities of GFH for the studied anions.

Nanofiltration (NF) membranes may present a second separation mechanism (except the sieve effect) due to the charge effects after dissociation of membrane surface groups, such as sulfonated or carboxyl acids. Depending mainly on the pH value of solution to be treated and the concentration of feed solution, the surface charge can form an appropriate electrostatic potential, which could interact with the metal ions of solution.

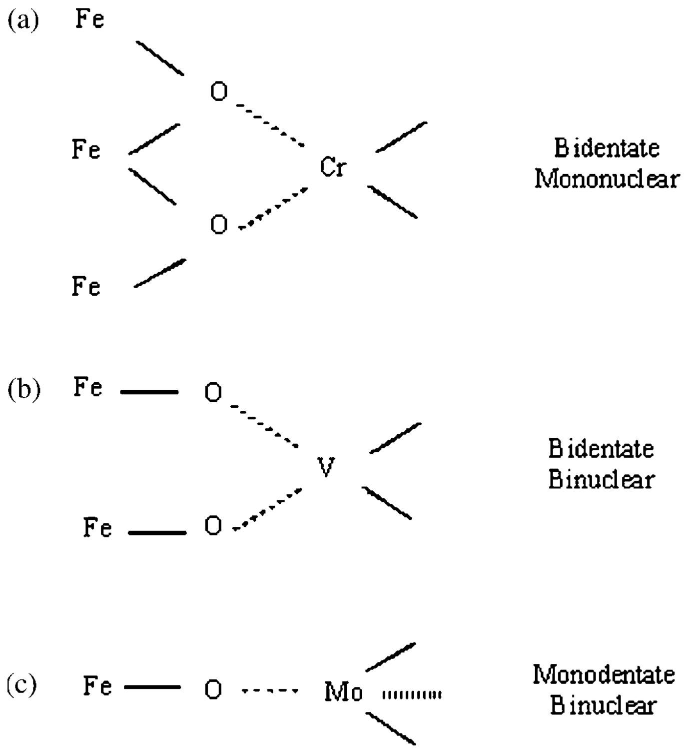

Figure 6. Structural arrangements of anion-GFH surface species. (a) Cr; (b) V; (c) Mo.

This surface charge is usually negatively charged, therefore, producing a repulsive force to anions. Hence, the specific electrostatic interaction is expected to be the main reason for the observed higher rejection rates of divalent anions; whereas single-charged ions can usually permeate the NF membranes.[34]

Figures 7 through 9 present the combined influence of pH values and of initial metal concentration (1 or 10 mg/L) on the rejection for the three metal anions, applying fixed (background) ionic strength of 0.01 M KCl. For all examined anions it was found that their rejection is rather independent from the initial concentration at fixed ionic strength. For the case of Cr(VI), the rejection was found to be increased by pH elevation, which can be attributed to the change of chromium speciation from the monovalent specie ($HCrO_4^-$) to the divalent form (CrO_4^{2-}). This occurs at a pH value around 7.5.[19] It is worth noting that for lower chromium concentrations (i.e., lower than $0.19.10^{-3}$ M as studied in this research) and in the acidic region, this metal exists mainly in the form of $HCrO_4^-$; dimerization of $HCrO_4^-$ to the $Cr_2O_7^{2-}$ form may also occur, but for substantially higher concentrations, i.e., greater than 0.01 M Cr(VI) in acidic media (Fig. 10, according to ref.[35]).

The highest rejection between the three metals was found for the case of Mo(VI) anions, which are always present in the form of divalent form (MoO_4^{2-}). Vanadium at pH values higher than 7.5 exists mainly as a mixture of

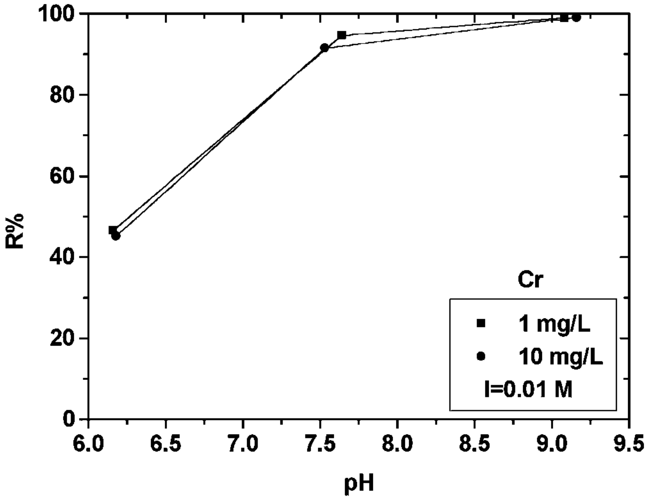

Figure 7. Nanofiltration rejection of Cr(VI) at constant ionic strength of 0.01 M and for two different initial metal concentrations (1 or 10 mg/L).

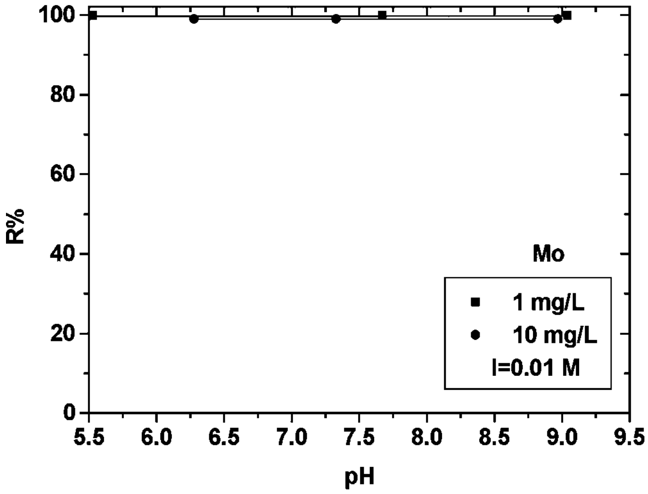

Figure 8. Nanofiltration rejection of Mo(VI) at constant ionic strength of 0.01 M and for two different initial metal concentrations (1 or 10 mg/L).

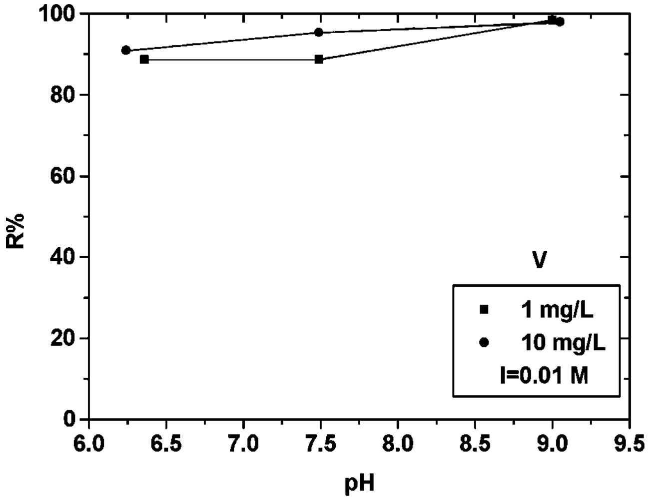

Figure 9. Nanofiltration rejection of V(V) at constant ionic strength of 0.01 M and for two different initial metal concentrations (1 or 10 mg/L).

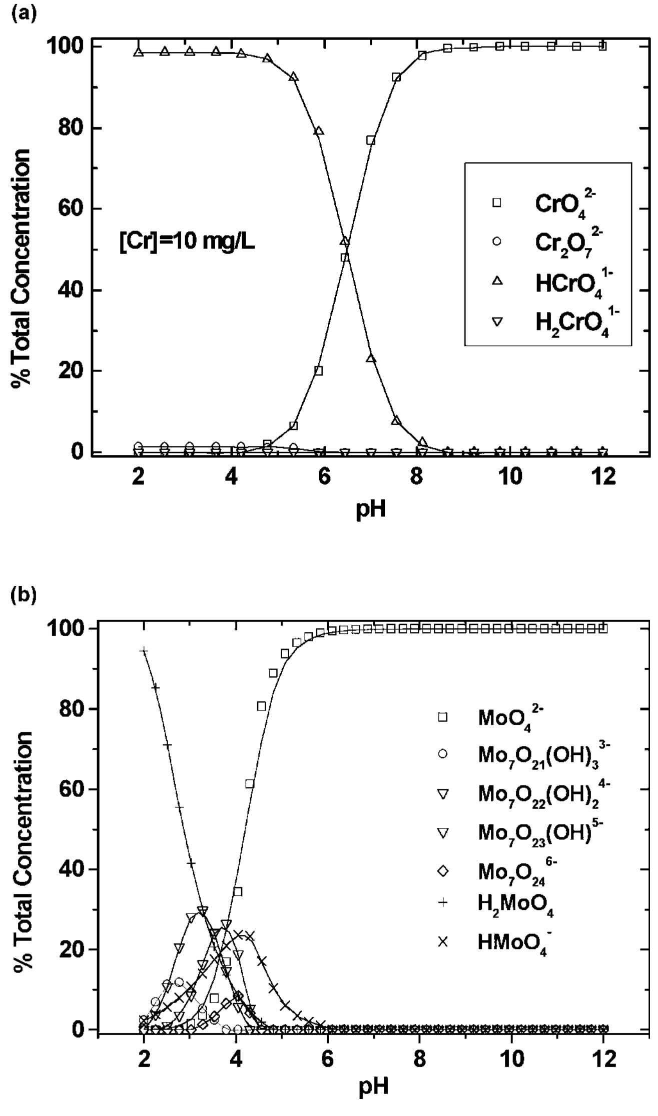

Figure 10. Speciation diagrams for the examined metal anions, at 25°C and 10 mg/L anion content: (a) Cr, (b) Mo, (c) V.

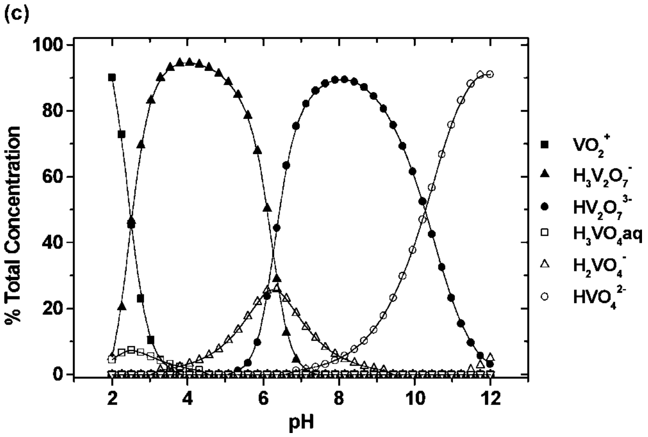

Figure 10. Continued.

$HV_2O_7^{3-}$ and HVO_4^{2-}, hence, stipulating the higher rejection of this metal in the elevated pH range (see Fig. 10, according to ref.[35]).

Although NF membranes are finding increased applications in various fields, especially regarding environmental protection, the respective transport mechanisms are not yet well understood. Several studies applied different models to understand the rejection behavior of NF membranes as a function of pore size distribution, of diffusion coefficients, and/or of concentration polarization. In these studies, the Donnan equation and the extended Nerst–Planck equation have been often applied to describe the influence of electrical properties of membrane surface. It was also shown that the fitting parameters of these equations are not only a function of metal/electrolyte concentrations, but also of the pH-value of solution.[33]

The examined concentrations of metals are closely related to those found in actual environmental situations, such as in the following cases.

1. Motiva Enterprises refinery was discharging more than 1200 μg V/L into the Delaware River. The concentration level considered normal for local waters is only 19 μg/L (03/31/2002, http://www.delawareonline).
2. The U.S. EPA estimated metal loadings from centralized biological waste water treatment plants for chromium, molybdenum, and vanadium as 0.387, 3.4, and 0.037 mg/L, respectively, after primary precipitation treatment. These values are close to the studied ones, 1 or 10 mg/L, for each metal ion (www.epa.gov/guide/cwt).

Finally, comparing the experimental results with other published results, the following can be said.

- Both methods, sorption and nanofiltration, seem to be effective in the removal of Cr(VI), Mo(VI), and V(V) from aqueous solutions.
- GFH presents a low capacity (16 mg/g) for chromium. The later is close to the capacities presented by microoganisms, 3 to 40 mg/g,[15] ion exchange resins, 40 mg/g,[14] and zeolite.[4,11] The only material that presents a high sorption capacity, 120 mg/g, is the double-layer hydroxides.[7,8]
- GFH presents a high sorption capacity for molybdenum (400 mg/g) and vanadium (100 mg/g). This value was determined as the maximum (although indicative) sorption capacity, under the applied experimental conditions. The respective values of chitosan are 679 and 400 mg/g, but at very low pH values.[26,27]
- Sorption experiments were conducted at natural pH value without any change that could improve the removal of anions.
- In nanofiltration, chromium presents the same behavior as shown in previous studies. In this work, the permeate flux was very high at 3846 L/m^2 h, in comparison with other study results.[16,19]
- The estimated sorbent quantity for the reduction of metal concentration from 10 mg/L initially down to 0.1 mg/L, considering a 1 m^3 of aqueous solution, was found to be approximately: 2.7 kg GFH for V, 1.6 kg GFH for Mo, and 12.5 kg GFH for Cr. In the same manner, the estimated membrane filter size required is approximately 0.011 m^2 for each metal ion.

CONCLUSION

The following conclusions can be drawn from the experimental data.

- Akaganeite is a promising low-cost and low-risk sorbent material.
- The sorption behavior of Cr(VI), Mo(VI), or V(V) anions under equilibrium conditions follows, in most cases, the Freundlich isotherm model, presenting maximum sorption capacities of around 16 mg Cr(VI), 400 mg Mo(VI), or 100 mg V(V) per g of GFH, respectively.
- The sorption behavior of Cr(VI) or V(V) is not affected by increasing the ionic strength. On the contrary, Mo(VI) sorption capacity was found to decrease significantly.
- The sorption kinetics can be satisfactory represented by a modified second-order equation.

- In nanofiltration experiments, the rejection of examined anions was found to be very high ($>80\%$). Cr(VI) behavior was strongly influenced by the pH value of solution; whereas the behavior of other examined anions was found to be pH independent.

NOMENCLATURE

a_L	Langmuir constant, L/mg
C_0	Initial metal concentration, mg/L
C_t	Metal concentration at time t, mg/L
C_e	Equilibrium metal concentration, mg/L
C_f	Metal concentration in the feed (initial), mg/L
C_p	Metal concentration in the permeate, mg/L
k_i	Kinetic rate constant, min^{-1}
K_F	Freundlich constant, $(\text{mg/g})\cdot(\text{L/mg})^{1/n}$
K_L	Langmuir constant, L/g
m	Quantity of akaganeite, g
n	Freundlich constant
q_t	Metal quantity adsorbed at time t (sorption loading), mg/g
q_e	Metal quantity adsorbed at equilibrium (sorption capacity), mg/g
t	Time (min)
V	Volume of solution (L)
β_2	Constant of modified second-order kinetic equation: $1/(1-\theta_0)$
θ_0	Initial accomplished surface coverage ($\theta_0 = q_0/q_t$)

ACKNOWLEDGMENTS

Thanks are due to the Greek State Scholarship Organization (IKY) for financing this common research in the framework of Greek–German cooperation project (IKYDA), as well as to Dr. Ernst for experimental collaboration with the membrane experiments.

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Received August 2002
Revised December 2002