

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236136929>

Modified Poly(4-vinylpyridine) Coated Silica Gel. Fast Kinetics of Diffusion-Controlled Sorption of Chromium(VI)

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · FEBRUARY 2001

Impact Factor: 2.59 · DOI: 10.1021/ie000771b

CITATIONS

35

READS

54

4 AUTHORS, INCLUDING:



Daniel Dianchen Gang

University of Louisiana at Lafayette

59 PUBLICATIONS 593 CITATIONS

SEE PROFILE



Shankha Banerji

University of Missouri

51 PUBLICATIONS 664 CITATIONS

SEE PROFILE

SEPARATIONS

Modified Poly(4-vinylpyridine) Coated Silica Gel. Fast Kinetics of Diffusion-Controlled Sorption of Chromium(VI)**Dianchen Gang, Wenqing Hu, Shankha K. Banerji, and Thomas E. Clevenger****E 1511 Engineering Building East, Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, Missouri 65211*

A new sorbent has been prepared by coating alkyl quaternized poly(4-vinylpyridine) (PVP) on the high surface area of silica gel. The resulting granular sorbent was used to remove Cr(VI) from water. Batch experiments were conducted to determine the kinetics and sorption rate. The research demonstrated that the modified PVP coated silica gel (referred to as coated gel) could successfully remove chromium(VI) from solution and that the sorbent provided fast kinetics. A finite-bath diffusion-control model with changing bulk concentration was derived analytically for application to the coated gel sorption of Cr(VI). This model fitted the experimental data well. The sorption kinetics on modified PVP coated gel was found to be diffusion-controlled with a value of $5.8 \times 10^{-7} \text{ cm}^2/\text{s}$ for the product of the distribution coefficient and the effective diffusivity in the sorption of Cr(VI) on the coated silica gel.

Introduction

A wide range of technologies are available for the removal of hexavalent chromium from wastewaters, some of which are well-established methods that have been in practice for decades, such as precipitation, coprecipitation,¹ and concentration.² These processes simply remove chromium from wastewaters by reduction,³ coagulation, and filtration. Emphasis in recent years has been placed on methods for recovery and reuse of metals rather than disposal. These include activated carbon adsorption,⁴ liquid–liquid extraction,⁵ liquid membrane separation,⁶ ion exchange, biosorption,⁷ and chelating resin and reactive polymer methods.^{8,9}

Two important properties of ion-exchange resins that influence their application are resin capacity and rate behavior, in addition to sorption selectivity, which is basically an attribute of the functional groups of the resin. Although the equilibrium sorption capacity of a resin is dependent on the concentration of functional groups, often the equilibrium sorption capacity observed in practice is much less than the theoretical capacity calculated from the resin composition, especially for resins synthesized from functional groups bearing monomers as opposed to those produced by postfunctionalization of the resin. This is attributed to the inaccessibility of many sorption sites buried inside the resin matrix.¹⁰

In most cases of ion-exchange sorption, the rate-determining step of the process has been established to be diffusion of the sorbate species through either the resin bead (particle diffusion control) or the externally adherent liquid film (film diffusion control).¹¹ Whereas film diffusion resistance can be minimized by effective

agitation of the liquid, intraparticle diffusion is largely influenced by the pore structure of the resin bead. Diffusion in the resin is impaired by the presence of the matrix. Not only is part of the cross-sectional area of the resin bead blocked, but also diffusion around the matrix strands has to follow a tortuous and thus longer path.

Some of the practical examples of ion-exchange processes, which are limited by the slow kinetics within the resin phase, are the recovery of uranium from primary or byproduct sources and the removal of traces of transuranics from waste streams. The sorption of uranium on Duolite ES467 requires about 10–12 h, the sorption of cesium by potassium copper(II) cyanoferrate requires about 36 h, and the sorption of plutonium nitrate onto a weak-base anion-exchange resin requires in excess of 500 h to reach equilibrium.¹²

Because the slow rate of equilibrium sorption is related to the greater inaccessibility of sorption sites in the interior of resin beads and the longer diffusion path associated with progressive resin conversion, a significant improvement in rate would be expected to result from preparation of the sorbent as a thin layer on a high-surface-area substrate.

The advantages of surface-coated adsorbents have led to their use in several practical applications. For example, ion exchange coated silica has been used not only in high-performance liquid chromatography (HPLC) but also in purification of human albumin.^{13,14} Chanda and Rempel¹⁰ reported a new anionic granular sorbent for uranyl sulfate (UO_2SO_4) recovery, which was developed by gel-coating the weak-base resin poly(4-vinylpyridine) (PVP) as a lightly cross-linked thin layer on high-surface-area silica gel. The gel coating of the resin afforded nearly 80% attainment of its theoretical capacity and provided fast sorption kinetics and nearly

* Author to whom correspondence should be addressed.
Phone (573) 882-7564, (573) 882-3132. Fax: (573) 882-4784.
E-mail: clevengert@missouri.edu.

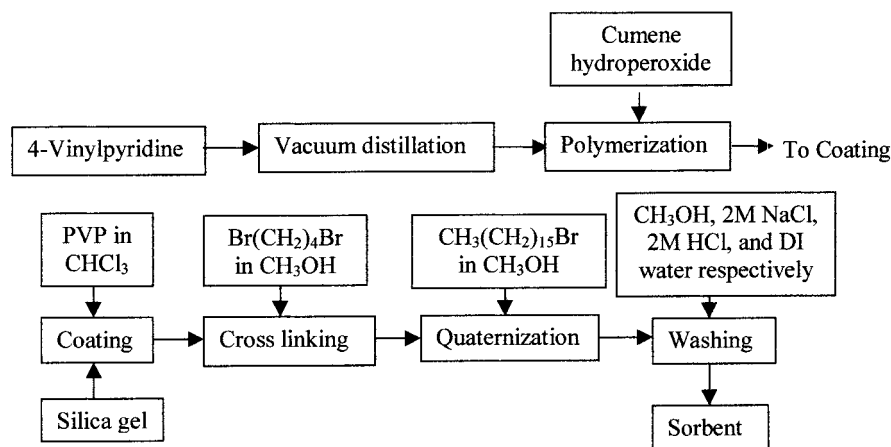


Figure 1. Steps for preparing reactive polymer coated gel.

instantaneous stripping as compared to conventional weak- and strong-base resins at a relatively high pH (>4).

Because of the success of the polymer developed by Chanda and Rempel,¹⁰ the polymer was modified and coated onto a high-surface-area silica gel to promote Cr(VI) sorption.¹⁵

For a comparison with conventional anionic sorbents, rate measurements were needed with Cr(VI). In this study, a diffusion-controlled sorption model was used to fit the experimental data. The results of the study are presented herein.

Materials and Experimental Procedures

Materials and Reagents. A chromium(VI) solution of 1000 ppm concentration was obtained from Fisher Scientific Co. and used as a reference standard solution. The standard Cr(VI) solution was diluted to the desired concentration using distilled water (DW) when needed. DW was obtained from the College of Engineering at University of Missouri-Columbia (MU) centralized purified water system.

All glassware and plasticware were washed with soap and water, followed by a tap water rinse, an acid rinse with 1 N HCl, and three final rinses with distilled water.

Preparation of Reactive Polymer. The polymer used, poly(4-vinylpyridine) (PVP), had an average molecular weight of about 1.4×10^6 (Chanda and Rempel¹⁰) and was prepared by bulk polymerization of 4-vinylpyridine using cumene hydroperoxide as an initiator [0.5% (w/v)] at 55 °C. This process is similar to the process described by Chanda and Rempel.¹⁰ Silica gel (100 g) was soaked in 250 mL of 2% (w/v) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution and evaporated to dryness in a water bath with continuous mixing (I). PVP (12 g) was dissolved in 1000 mL of chloroform (II). Reagent I was added to reagent II, and the mixture was agitated with a paddle stirrer for 6 h. Chloroform was decanted, and the polymer-impregnated gel (III) was washed several times with methanol. The gel (III) was dispersed in 300 mL of methanol to which the cross-linking reagent 1,4-dibromobutane was added (in steps) to the extent of 50% of the theoretical amount required for cross-linking of the pyridine. The mixture was vigorously stirred at 65 °C for 96 h in a slow current of nitrogen. To synthesize the long alkyl chain quaternary ammonium compound, 1-bromohexadecane was used as a quaternization agent. The above mixture was washed successively with 2 M NH_4OH and 2 M NaCl, which gave the lightly cross-

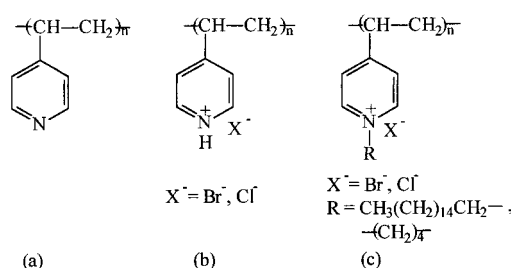


Figure 2. Possible structures of the modified PVP.

linked polymer (IV). The mixture (IV) was dispersed in 250 mL of methanol to which 1-bromohexadecane was added to the extent of 200% in excess of the theoretical amount required for reaction with all of the residual pyridine units. The mixture was agitated at 68 °C for 72 h in a slow current of nitrogen. The product was filtered and washed with methanol, 2 M NaCl solution, 2 M HCl, and water to obtain the final polymer (modified PVP), following the method of Chanda and Rempel.¹¹ Figure 1 presents the flowchart of the preparation processes.

Figure 2 shows the possible structures of the reactive polymer: the structures of (a) PVP formed in the polymerization process, (b) protonated PVP under acidic conditions, and (c) 1,4-dibromobutane cross-linked or 1-bromohexadecane quaternized PVP.

Chromium Sorption Experiments. The sorption studies were performed at room temperature (25 °C). In an earlier paper,¹⁵ it was reported that the maximum chromium(VI) sorption on the coated silica gel occurred at about pH 4.5–5.5 under the test conditions. Thus, in the present study, the pH of the solution containing the desired quantity of chromium(VI) was adjusted to 5.0 by adding 0.1 M HCl. A desired quantity of the long alkyl quaternized poly(4-vinylpyridine) (modified PVP) coated gel was placed in a separate test tube with the pH-adjusted Cr(VI) solution (pH = 5.0). One sample of the same concentration solution without the sorbent was also prepared and treated under the same conditions as the tube containing sorbent (control). This control was used as a reference to establish the initial concentration for the tube containing the sorbent. The test tubes were capped and placed on a Thermolyne Maxi-Mix mixer (manufactured by Barnstead Thermolyne Corporation) for the kinetics studies. The test tubes were then removed periodically, and the solutions were filtered using a vacuum filtration device and a clean test-tube receiver through a filter paper (Whatman 5,

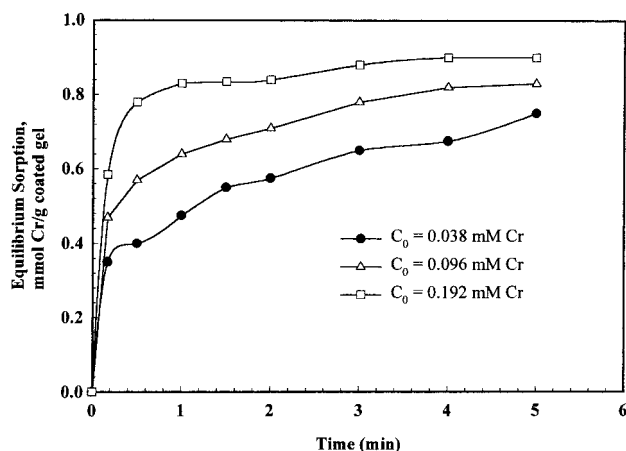


Figure 3. Rate of Cr(VI) sorption on coated gel of particle size 0.008–0.012 cm for different initial concentrations C_0 at pH 5.0 and a temperature of 25 °C.

Table 1. Operation Parameters of Atomic Absorption Spectrophotometer for Chromium Analysis

type of lamp	hollow cathode
current, mA	10
spectral bandwidth, nm	0.7
wavelength, nm	357.9
flame gases	air–acetylene
acetylene flow rate, L/min	4.0
standard solutions, mM Cr	0.019, 0.058, 0.096

pore size = 2.5 μm). Filtration was rapid (less than 2 s). The concentration of chromium(VI) in aqueous phase was determined by a Perkin-Elmer atomic absorption spectrophotometer model 2380. The operational parameters of the atomic absorption spectrophotometer are summarized in Table 1. The amount of chromium adsorbed was determined by subtracting the final concentration from the initial concentrations. If the chromium concentration in the solution was smaller than 0.096 mM, the solution was measured directly using the atomic adsorption spectrophotometer; if the concentration was greater than 0.096 mM, the solution was diluted with distilled water to 0.0096–0.038 mM before measurement by the spectrophotometer.

Results and Discussion

Sorption Capacity and the Sorbent Stability.

The sorption capacity, sorption isotherm, desorption behavior, and comparison results of Cr(VI) on modified PVP were presented in an earlier paper.¹⁵

The advantages of surface-coated adsorbents have led to their use in several applications. For example, ion exchange coated silica has been used not only in high-performance liquid chromatography (HPLC) but also in purification of human albumin.^{13,14} These successful applications have shown that the surface-coated polymer has a good stability and constant sorbent capacity. It has previously been reported¹⁶ that the modified PVP coated silica gel is stable and can be regenerated.

Kinetic Experiments. To evaluate the sorption behavior and establish the kinetic diffusion model, the sorption rates of different initial concentrations of Cr(VI) (0.038, 0.096, and 0.192 mM) were measured. Forty milliliters of the 0.038, 0.096, or 0.192 mM chromium solution with pH = 5.0 and 0.048–0.24 g of coated gel sorbent were added to the test tubes. Tests were run at pH 5.0 because it was found that the optimum sorption of Cr(VI) on PVP coated gel sorbent was at pH 4.5–

5.5.¹⁵ The test tubes were capped and placed on a mixer (Thermolyne Maxi-Mix) for 0–5 min. Then, the test tubes were periodically removed, and the solutions were filtered to determine the rate of sorption.

The observed data are shown in Figure 3. It can be seen that the Cr(VI) concentration in this experiment had a pronounced effect on the rate of sorption. When the Cr(VI) concentration increased, the sorption rate also increased. Such a concentration effect has also been reported by Chanda and Rempel¹⁰ for the sorption of uranyl sulfate on a similar reactive polymer-coated gel. Such a concentration effect is not consistent with predictions from the ordinary particle diffusion control (pdc) model,¹⁷ but it is in accord with the shell-core or reacted-layer diffusion control model.¹⁰

The $t_{1/2}$ (the time needed for 50% of the chromium to be removed) value calculated from the data in Figure 3 for the 0.192 mM Cr concentration was 10 s, while the $t_{1/2}$ values for the 0.096 and 0.038 mM Cr solutions were 20 and 70 s, respectively. The $t_{1/2}$ value decreased as the concentration of Cr(VI) increased. When the Cr(VI) concentration increased, the collision numbers between the sorption site and the Cr(VI) species increased; this increased the sorption rate. As a result, the time needed to reach equilibrium was shortened. Chanda and Rempel¹⁰ also reported a similar concentration effect for the removal of uranyl sulfate on a PVP coated gel.

To examine the applicability of the shell-core hypothesis employing finite-bath data (Figure 3) obtained from the experiments, rate model equations that could be applied to a finite-bath system under reacted-layer diffusion control were derived following the approach of Adams et al.¹⁸

Finite-Bath Diffusion-Control Model. Assuming a linear change of concentration of sorbate species across the shell from a value \bar{C} on the surface of the sorbent particle to zero at the surface of the inner core of the unconverted form of the resin layer, one can write from Fick's first law

$$\bar{J} = \bar{D}\bar{C}(\bar{r} - \bar{r}_i) \quad (1)$$

where \bar{J} is the flux per unit area in the resin layer, \bar{r}_i is the radius of the inner core comprising the unconverted resin layer on silica, \bar{r} is the initial radius of the sorbent particle, and \bar{D} is the diffusion coefficient of the sorbent species within the converted form of the resin layer.

The sorbate concentration at the surface of the resin layer \bar{C} can be related to the external concentration C by the expression¹⁹

$$\bar{C} = KC^{2-z} \quad (2)$$

where K and z are characteristic constants. Substituting eq 2 into eq 1 and expressing \bar{J} (in moles per unit area of resin layer within the volume \bar{V} of sorbent particles) in terms of the change in concentration of the volume V of the external solution, according to Chanda and Rempel,¹⁰ we can obtain

$$\frac{d(CV)}{dt} = \frac{-3\bar{V}\bar{D}KC^{2-z}}{\bar{r}(\bar{r} - \bar{r}_i)} \quad (2.1)$$

The fractional conversion of the resin layer (\bar{X}) can be represented by

$$\bar{X} = 1 - \frac{\bar{r}_i^3 - \bar{r}_s^3}{\bar{r}^3 - \bar{r}_s^3} \quad (2.2)$$

From eq 2.2, we obtain

$$\bar{r}_i/\bar{r} = \left[(1 - \bar{X}) + \bar{X} \left(\frac{\bar{r}_s}{\bar{r}} \right)^3 \right]^{1/3} \quad (2.3)$$

where \bar{r}_s is the radius of the solid core of the sorbent particle, and the sorbate concentration (C) is given by

$$C = C_0(1 - \omega\bar{X}) \quad (2.4)$$

where C_0 is the initial sorbate concentration in solution and ω is the equivalent ratio, defined as the ratio of the total sorption capacity of the resin to the total sorbate content of the external solution. Substituting eq 2.4 into eq 2.1, we obtain

$$\frac{d[C_0 V(1 - \omega\bar{X})]}{dt} = \frac{-3\bar{V}DK[C_0(1 - \omega\bar{X})]^{2-z}}{\bar{r}(\bar{r} - \bar{r}_i)} \quad (2.5)$$

where \bar{X} is the fractional conversion of the resin layer, \bar{r}_s is the radius of the solid core of the sorbent particle, and C_0 is the initial sorbate concentration in solution. By substituting eq 2.3 into eq 2.5, eq 3 was obtained.

$$\frac{d(1 - \omega\bar{X})}{dt} = \frac{-3\bar{V}DKC_0^{1-z}(1 - \omega\bar{X})^{2-z}}{V\bar{r}^2 \left\{ 1 - \left[(1 - \bar{X}) + \bar{X} \left(\frac{\bar{r}_s}{\bar{r}} \right)^3 \right]^{1/3} \right\}} \quad (3)$$

To simplify the equation, Chanda and Rempel¹⁰ ignored the $(\bar{r}_s/\bar{r})^3$ term in the above eq 3 and let $\omega = 1$ for the special case when $\bar{r}_s/\bar{r} < 1$ and for small values of \bar{X} . Thus, Chanda and Rempel's¹⁰ approximation was only applicable for low values of \bar{X} . In practice, \bar{X} can reach 0.8–0.9, so the $\bar{X}(\bar{r}_s/\bar{r})^3$ term cannot be ignored. In our study, a constant (\bar{X}_0) was introduced into the equation to consider this effect. \bar{X}_0 is a constant related to \bar{r}_s and the fractional attainment of equilibrium sorption (\bar{X}), which is defined as $\bar{r}_0 = (\bar{r}_s/\bar{r})^3 \bar{X}$. Based on the definition of ω and the high value of \bar{X} conditions, ω can be approximately expressed as $(\bar{r}^3 - \bar{r}_s^3)/\bar{r}^3$, that is, $\omega = [1 - (\bar{r}_s/\bar{r})^3]$. Thus, eq 3 becomes

$$\frac{d(1 - \omega\bar{X})}{dt} = \frac{-3\bar{V}DKC_0^{1-z}(1 - \omega\bar{X})^{2-z}}{V\bar{r}^2[1 - (1 - \omega\bar{X})^{1/3}]} \quad (4)$$

According to the same simplification procedures as used by Chanda and Rempel,¹⁰ eq 4 can be rewritten, with $U = 1 - \omega\bar{X}$ and $\lambda = KC_0^{1-z}$, as

$$\frac{dU}{dt} = \frac{-3\bar{V}D\lambda U^{2-z}}{V\bar{r}^2[1 - U^{1/3}]} \quad (5)$$

$$\int \frac{1 - U^{1/3}}{U^{2-z}} dU = \int \frac{-3\bar{V}D\lambda}{V\bar{r}^2} dt + \text{const} \quad (6)$$

$$\frac{U^{z-1}}{1-z} - \frac{3U^{z-2/3}}{2-3z} = \left(\frac{3\bar{V}D\lambda}{V\bar{r}^2} \right) t + \text{const} \quad (7)$$

When $t = 0$ and $U = 1$

$$\text{const} = (1-z)^{-1} - 3(2-3z)^{-1} \frac{(1-\omega\bar{X})^{z-1}}{1-z} - \frac{3(1-\omega\bar{X})^{z-2/3}}{2-3z} = \left(\frac{3\bar{V}D\lambda}{V\bar{r}^2} \right) t + \frac{1}{1-z} - \frac{3}{2-3z} \quad (8)$$

Expanding in a Taylor series and ignoring terms that are higher than quadratic in \bar{X} , we have the following approximation:

$$\frac{1}{6}(\omega\bar{X})^2 = \left(\frac{3\bar{V}D\lambda}{V\bar{r}^2} \right) t \quad (9)$$

From $\omega = [1 - (\bar{r}_s/\bar{r})^3]$ and $\bar{X}_0 = (\bar{r}_s/\bar{r})^3 \bar{X}$, we obtain $\omega = (1 - \bar{X}_0/\bar{X})$; then, replacing ω with $(1 - \bar{X}_0/\bar{X})$ yields

$$\bar{X} = \left(\frac{18\bar{V}D\lambda}{V\bar{r}^2} \right)^{1/2} t^{1/2} + \bar{X}_0 \quad (10)$$

Hence, the plot of \bar{X} versus $t^{1/2}$ should be linear, with the constant \bar{X}_0 able to be determined from the intercept of the straight line.

The fractional attainment data measured in the experiment is plotted in Figure 4 according to eq 10. The good linearity of the plots shows the validity of the model. The values of $\lambda\bar{D}$ were calculated from the slopes in Figure 4 and recorded in Table 2. Because the sorbent used for rate measurement was a mixture of particles of different shapes, but with a narrow size range, the average radius was used for the calculation of $\lambda\bar{D}$. According to the Chanda and Rempel¹⁰ simplification, for $z \approx 1$, the integration of eq 5 becomes

$$\ln U - 3U^{1/3} = -\frac{3\bar{V}D\lambda}{V\bar{r}^2} t + \text{const} \quad (11)$$

When $t = 0$ and $U = 1$, $\text{const} = -3$. After U is substituted by $1 - \omega\bar{X}$, eq 11 becomes

$$\ln(1 - \omega\bar{X}) - 3(1 - \omega\bar{X})^{1/3} = -\frac{3\bar{V}D\lambda}{V\bar{r}^2} t - 3 \quad (12)$$

$$\ln[1/(1 - \bar{X} + \bar{X}_0)] - 3[1 - (1 - \bar{X} + \bar{X}_0)^{1/3}] = \frac{3\bar{V}D\lambda}{V\bar{r}^2} t \quad (13)$$

According to this model, a plot of $\ln[1/(1 - \bar{X} + \bar{X}_0)] - 3[1 - (1 - \bar{X} + \bar{X}_0)^{1/3}]$ vs t should be linear. The data in Figure 3 are again plotted in Figure 5 according to eq 13. The good linearity of the plots seems to indicate the validity of the assumption of $z \approx 1$ in the derivation of eq 13. The values of $\lambda\bar{D}$ calculated from the slopes of the linear plots of Figure 5 and given in Table 2 are found to be close to those obtained from eq 10. An average value of $\lambda\bar{D}$ for the coated gel sorbent is $5.8 \times 10^{-7} \text{ cm}^2/\text{s}$. Chanda and Rempel¹⁰ also found that the sorption of uranyl sulfate on a similar coated gel correlated well with this model. The $\lambda\bar{D}$ value reported by them was $5.4 \times 10^{-6} \text{ cm}^2/\text{s}$. The difference between the two $\lambda\bar{D}$ values can be attributed to the different thicknesses of the reactive polymer layer and the use of different sorbates.

Conclusions

This research demonstrated that the designed and synthesized long alkyl quaternized PVP coated silica gel

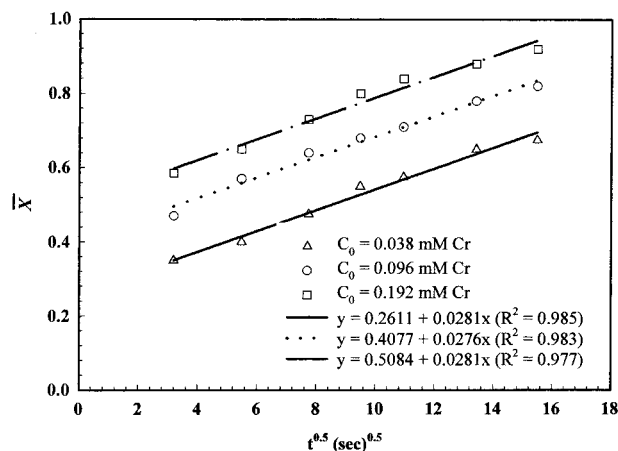


Figure 4. Test of eq 10.

Table 2. Values of $\lambda\bar{D}$ for Sorption of Cr(VI) on Modified PVP Coated Silica Gel at Different Concentrations

concentration of Cr(VI) in solution (mM)	$\lambda\bar{D}$ (cm ² /s) calculated from	
	eq 10	eq 13
0.038	7.95×10^{-7}	1.17×10^{-6}
0.096	4.60×10^{-7}	6.70×10^{-7}
0.192	1.59×10^{-7}	2.30×10^{-7}

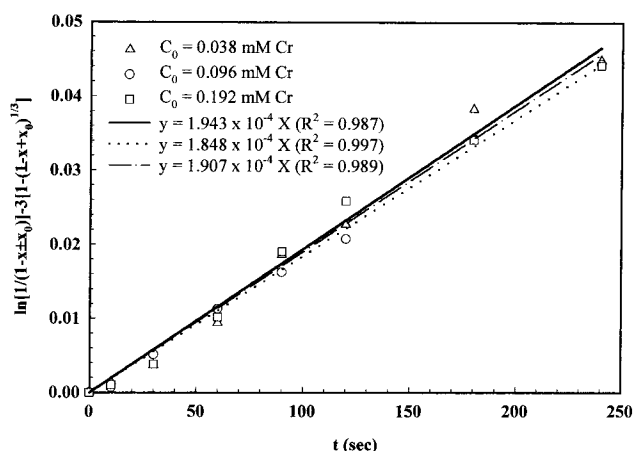


Figure 5. Test of eq 13.

could remove chromium(VI) from solution. The sorbent provides fast kinetics. Finite-bath diffusion-control models fit the experimental loading data well. The sorption kinetics on modified PVP coated gel is found to be diffusion-controlled with average value of 5.8×10^{-7} cm²/s for the product of the distribution coefficient and the effective diffusivity in the sorption of Cr(VI) on the modified PVP coated silica gel.

Nomenclature

C = sorbate concentration in solution, mmol L⁻¹
 \bar{C} = sorbate concentration in resin at the surface, mmol L⁻¹
 C_0 = initial sorbate concentration in solution, mmol L⁻¹
 \bar{D} = effective diffusivity in reacted layer, cm² s⁻¹
 K = characteristic constant, (mmol L⁻¹)^{z-1}
 \bar{r} = initial radius of sorbent particle, cm
 \bar{r}_1 = radius of inner core including unreacted resin layer, cm
 \bar{r}_s = radius of silica core of sorbent particle, cm
 t = time, s
 $U = 1 - \bar{X}$
 V = volume of external solution, L

\bar{V} = volume of sorbent particles, L
 \bar{X} = fractional attainment of equilibrium sorption
 \bar{X}_0 = fractional attainment constant
 z = constant of nonuniformity

Greek Symbols

ω = ratio of equilibrium sorption capacity of resin to initial sorbate content of solution
 λ = distribution coefficient

Literature Cited

- (1) Patterson, J. W.; Passino, R. Metals Separation and Recovery. In *Metal Speciation Separation and Recovery*; Lewis Publishing: Chelsea, MI, 1987.
- (2) EPA Control and Treatment Technology for the Metal Finishing Industry. *Sulfide Precipitation*; EPA-625/8-80-003; U.S. Environmental Protection Agency: Cincinnati, OH, 1980.
- (3) Shen, H.; Wang, Y. T. Hexavalent chromium removal in two-stage bioreactor system. *J. Environ. Eng.* **1995**, 121 (11), 798–804.
- (4) Ouki, S. K.; Neufeld, R. D. Use of activated carbon for the recovery of chromium from industrial wastewater. *J. Chem. Technol. Biotechnol.* **1997**, 70 (1), 3–8.
- (5) Clevenger, T.; Novak, J. T. The recovery of metals from electroplating wastes using liquid–liquid extraction. *J. Water Pollut. Control Fed.* **1983**, 55 (7), 984–989.
- (6) Fraser, B. G.; Pritzker, M. D. Removal and recovery of chromium from aqueous effluents. *Sep. Sci. Technol.* **1994**, 29 (16), 2097–2116.
- (7) Petruzzelli, D.; Tiravanti, G. Ion Exchange Process for Chromium Removal and Recovery from Tannery Wastewater. *Ind. Eng. Chem. Res.* **1995**, 34 (8), 2612–2617.
- (8) Chen, C. A new Cr(VI) adsorbing agent. *Huanjing Wuran Yu Fangzhi* **1995**, 16 (2), 27–28.
- (9) Tiravanti, G.; Petruzzelli, D. Low and non waste technologies for metals recovery by reactive polymers. *Waste Manage.* **1996**, 16 (7), 597–605.
- (10) Chanda, M.; Rempel, G. L. Poly(4-vinylpyridine) Gel Coated on Silica. High Capacity and Fast Kinetics in Uranyl Sulfate Recovery. *Ind. Eng. Chem. Res.* **1993**, 32 (4), 726–732.
- (11) Chanda, M.; Rempel, G. L. Quaternized Poly(4-vinylpyridine) Gel Coated on Silica. Fast Kinetics of Diffusion-Controlled Sorption of Organic Sulfonates. *Ind. Eng. Chem. Res.* **1994**, 33 (3), 623–630.
- (12) Streat, M. Kinetics of slow diffusing species in ion exchangers. *React. Polym.* **1984**, 2, 79–91.
- (13) Tayot, J. L.; Tardy, M.; Gattel, P.; Plan, R.; Roumiantzeff, M. Industrial ion exchange chromatography of proteins on DEAE dextran derivatives of porous silica beds. In *Chromatography of Synthetic and Biological Polymers*; Epton, R., Ed.; Ellis Horwood: Chichester, U.K., 1978; Vol. 2, pp 95–110.
- (14) Van der Wiel, J. P.; Wesselingh, J. A. Continuous Adsorption in Biotechnology. In *Adsorption: Science and Technology*; Rodrigues, A. E., Le Van, M. D., Tondeur, D., Eds.; NATO ASI Series, Series E: Applied Sciences, 158; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; pp 427–496.
- (15) Gang, D.; Banerji, S. K.; Clevenger, T. E. Chromium (VI) removal by modified PVP coated silica gel. *Pract. Period. Hazard., Toxic, Radioact. Waste Manage.* **2000**, 4 (3), 105–110.
- (16) Gang, D.; Banerji, S. K.; Clevenger, T. E. Factors affecting chromium(VI) removal by modified poly(4-vinylpyridine) coated silica gel. *Pract. Period. Hazard., Toxic, Radioact. Waste Manage.* **2001**, 4 (2), in press.
- (17) Helfferich, F. G.; Hwang, Y.-L. Ion Exchange Kinetics. In *Ion Exchangers*; Dorfner, K., Ed.; Walter de Gruyter: Berlin, 1991; pp 1277–1309.
- (18) Adams, G.; Jones, P. M.; Millar, J. R. Kinetics of acid uptake by weak-base anion exchangers. *J. Chem. Soc. A* **1969**, 2543–1551.
- (19) Glueckauf, E. A new approach to ion exchange polymers. *Proc. R. Soc.* **1962**, A268, 350–370.

Received for review August 22, 2000

Revised manuscript received December 13, 2000

Accepted December 19, 2000

IE000771B