Removal of Chromium from Pantex Groundwater by Granular Activated Carbon

A Report to the Amarillo National Resource Center
for Plutonium (ANRCP) for the Project

Chemical Models and Redox Chemistry of Chromium

Mark Schlautman, Bill Batchelor and Ihnsup Han
Civil Engineering
Texas A&M University
College Station, Texas 77843-3136

RECEIVED
OCT 13 1999
OSTI

submitted as part of
the Higher Education Consortium
Chromium Remediation Task

submitted to
Department of Energy
Amarillo Area Office
Pantex Plant
P.O. Box 30020
Amarillo, Texas 79177

November 15, 1997

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Contents

Introduction	3
Materials and Methods	5
Materials	5
Experimental Methods	6
Batch Experiments	6
GAC Pretreatment	6
Rate Experiments	6
Isotherm Experiments	7
Column Experiments	7
GAC Extraction/Regeneration	7
Analytical Methods	8
Results and Discussion	9
pH Effects	9
Oxygen Effects	11
Pretreatment Effects	13
GAC Comparison	15
GAC Regeneration and Cycling	15
Summary and Conclusions	22
References	23
Appendix	24
Table 1. Column experiments with Virgin and Fe(II)-Pretreated ACs	24
Table 2. Cr(VI) Breakthrough with Virgin F-400 (first run)	26
Table 3. Cr(VI) Extraction with 0.01M K ₂ HPO ₄ (first extraction)	28
Table 4. Cr(VI) Breakthrough after First Extraction (second run)	29
Table 5. Cr(VI) Extraction (second extraction)	31
Table 6. Cr(VI) Breakthrough after Second Extraction (third run)	33

INTRODUCTION

The Pantex Plant, located approximately 17 miles northeast of downtown Amarillo, Texas, was first used by the U.S. Army Ordnance Corps for loading conventional ammunition shells and bombs during World War II. After operations ceased in 1945, the U.S. Atomic Energy Commission selected the site as the location for a nuclear weapons assembly facility in 1950. Currently, the site is being used for the development and fabrication of high explosive (HE) components for nuclear weapons, for assembly and disassembly of nuclear weapons, and for tests and disposal of HEs. Besides contamination problems with HEs such as TNT, RDX, and HMX, heavy metal contamination has resulted from weapon component tests. Chromium is one of the major contaminants in the groundwater under the Pantex Plant and exists at concentrations two or more orders of magnitude higher than the drinking water standard (forms of total and hexavalent chromium), particularly in the perched aquifer groundwater below Zones 11 and 12.

The most prevalent oxidation states of chromium are +3 and +6 under most conditions in natural water systems, although the oxidation state can range from -2 to +6 (Kaczynski et al, 1993; Krishnamurthy et al, 1994). While Cr(III) is an essential element for life to a certain level, Cr(VI) is toxic, carcinogenic, mutagenic, and teratogenic (Wittbrodt et al, 1995; Stollenwerk, 1985; Krishnamurthy et al, 1994; Goodgame et al, 1984; Anderson et al, 1994). Cr(VI) exists as anions such as chromate (CrO_4^{2-}), bichromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and is more mobile than Cr(III) because Cr(VI) is more soluble and less adsorbable to many soils under environmental conditions (Richard et al, 1991; James, 1996; Bartlett et al, 1979). In contrast, Cr(III) readily precipitates as forms of $\text{Cr}(\text{OH})_3$ or Cr-Fe hydroxides over pH ranges higher than 4 (Richard et al, 1991; Anderson et al, 1994; James, 1996; Fendorf et al, 1996). Reduction of Cr(VI) to Cr(III), therefore, is beneficial because a more toxic and mobile species is converted to a less toxic (even essential) and mobile form. As a result, two strategies for the treatment of Cr(VI) in a groundwater can be considered: (1) removal of Cr(VI) from aqueous solution by sorption or (2) precipitation and immobilization in the aqueous system by conversion to Cr(III). Because the conversion of Cr(VI) to Cr(III) may be reversible under some subsurface conditions (Eary and Rai, 1987; Vitale et al, 1994; Fendorf and Zasoski, 1992), complete removal of Cr(VI) from the aqueous system may be desirable. This latter approach could include reduction and precipitation steps after Cr(VI) sorption has occurred.

Sorption of Cr(VI) by various sorbents has been studied by several researchers. Chromate can be adsorbed by soil components including Fe and Al oxides (Zachara et al, 1987), kaolinite (Griffin et al, 1988), ferrihydrite (Schultz et al, 1987), goethite (Ainsworth et al, 1989), and sphagnum moss peat (Sharma and Forster, 1993). Chromate adsorption generally increases with decreasing pH due to the protonation of surface hydroxyl sites and chromate aqueous speciation (Zachara et al, 1989). Chromate binding in subsurface soils is reversible to pH increases and is hindered by sulfate (SO_4^{2-}) and dissolved organic carbon (Zachara et al, 1981) and by phosphate ($\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$) (Stollenwerk and Grove, 1985) due to the competition for sorption sites and electrostatic effects (Zachara et al, 1989, 1987). In addition to Cr(VI) adsorption on soils, reduction to Cr(III) with subsequent precipitation or adsorption of Cr(III) species may occur in the presence of reductive solids and dissolved Fe(II) species (Eary et al, 1988) and/or by readily oxidizable organic material (Mayer et al, 1981). Schultz et al. (1987) investigated the adsorption

and desorption of metals on ferrihydrite and concluded that Cr(III) is favorably sorbed on ferrihydrite at higher pH values; their interpretation, however, did not consider the possibility of Cr(III) precipitation at higher pH.

Activated carbon (AC) has been widely-used as an effective adsorbent for the removal of many aqueous contaminants, both organic and inorganic. High specific surface areas (e.g., $\sim 1000 \text{ m}^2/\text{g}$) and the presence of many different types of surface functional groups (e.g., oxygen-containing groups such as hydroxyl, carbonyl, lactone, and carboxylic acids) are well-known characteristics of ACs that make them excellent adsorbents. In particular, these favorable physicochemical surface properties enable AC to remove a variety of organic contaminants from aqueous solutions (e.g., Thakkar and Manes, 1987). In addition, select surface functionalities can react with aqueous contaminants by other chemical reactions, particularly in the presence of oxygen. For example, oxidative coupling or polymerization is believed to occur for some contaminants, particularly for phenolic compounds, in AC systems (Vidic et al., 1993). When AC is being used for removal of organic contaminants in natural waters and wastewaters, preloading effects by humic and fulvic acids or organic matter other than target contaminants must be considered for optimum treatment operations (Karanfil et al., 1994; Karanfil, 1995). In addition to preloading effects on the removal of organic contaminants, these background organic materials (BOMs) can form complexes with inorganic species and either improve or deteriorate the removal of those species in AC systems. Although the effect of BOMs on organic contaminant adsorption has been extensively researched, studies of their effect on inorganic compounds are rather rare.

In general, the adsorption capacity of AC for inorganic species (e.g., cadmium, arsenic, mercury(II), cobalt(II)) varies significantly with pH changes (Corapcioglu and Huang, 1987). For metal cations, the adsorption capacity increases abruptly at a specific pH value. Conversely, for inorganic anions removal is higher at lower pH. A limited number of studies are related to Cr(VI) removal by AC. Tan and Teo (1987) used powdered activated carbons for removing dissolved chromium and lead from water and observed that the adsorption showed a significant dependence on pH, carbon dosage and initial adsorbate concentration. They proposed empirical equations to describe the adsorption isotherms in terms of the mass ratio of carbon to the initial amount of adsorbate in solution. Ramos et al. (1994) reported that at pH values below 6, Cr(VI) was adsorbed and reduced to Cr(III) by the catalytic action of the carbon, although their methodologies were not adequate to prove this conclusively. Perez-Candela et al. (1995) observed that under very acidic conditions the amount of Cr(VI) removed decreased with decreasing pH when they used a leather-based AC. Above pH 3, however, the amount of Cr(VI) removed decreased with increasing pH. They explained their results by the adsorption of different Cr(VI) species (e.g., $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$) present at very low pH values. For lignin-based ACs, they obtained their highest Cr(VI) removal below pH 3 and described this trend as a reduction of Cr(VI) to Cr(III).

Vitale et al. (1994) and James et al. (1995) have proposed methods for extracting chromium from soils that supposedly can maintain its speciation. They observed that prior methods utilizing alkaline digestion induced oxidation of Cr(III) to Cr(VI) when freshly

precipitated $\text{Cr}(\text{OH})_3$ was present in their soil samples. Whether their new extraction methods can be applied to ACs, however, has not been tested.

The objectives of this study are (i) to compare the performance of two ACs (LB830, currently used at the Pantex Plant, and F-400) for their ability to remove chromium from water, (ii) to determine if chemical pretreatment of the ACs can improve their adsorption/reduction capacity, (iii) to investigate potential adverse effects of dissolved oxygen (DO) on these reactions, and (iv) to evaluate potential regeneration methods after the AC capacity for chromium has been exhausted. These objectives were met by utilizing both batch (rate and isotherm) and continuous flow column experiments.

MATERIAL AND METHODS

Materials

Two types of granular activated carbon (GAC) were used as adsorbents for these experiments. Their physical properties and specifications as provided by the corresponding companies and Karanfil (1995) are shown in Table 1. To obtain consistent experimental results, two particle size fractions (U.S. standard sieve 80/100 (177/149 μm) and 230/325 (62/44 μm)) were prepared for the column and batch experiments, respectively, by crushing and sieving random samples from one lot of each GAC. The fractions were washed with distilled, deionized water (DDW; Barnstead Nanopure) to remove fines, dried in an oven at 105 °C for 48 hours, and stored in a vacuum desiccator until use. For experiments under anaerobic conditions, the crushed and sieved GACs were transferred to an anaerobic chamber (Coy Products Inc., MI) and washed with oxygen-free DDW, dried by the ambient gas of the chamber, and stored in a desiccator located in the anaerobic chamber. Oxygen-free DDW was prepared by purging with nitrogen gas for 12 hours outside of the chamber followed by its transfer into the anaerobic chamber and purging for an additional 12 hours with the gas mixture inside the chamber using an equivalent pump. The anaerobic chamber was filled with a 5% H_2 -95% N_2 gas mixture and two sets of catalysts were present inside the chamber to remove any oxygen that diffused inside through the PVC walls.

Artificial groundwater (AGW) was used to simulate concentrations of the major ions found in the perched aquifer below Zone 12 as observed from well PM-200 samples. Analytical-grade chemicals ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaHCO_3 , Alfa Chemical; K_2SO_4 and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, EM Chemical) and DDW were used to prepare the AGW; its composition was 45.5 mg/L Ca^{2+} , 9.1 mg/L K^+ , 51.9 mg/L Mg^{2+} , 75.9 mg/L Na^+ , 232.2 mg/L Cl^- , and 201.3 mg/L HCO_3^- . A Cr(VI) stock solution was prepared with K_2CrO_4 (Alfa, ACS grade). The majority of the Cr(VI) samples tested contained approximately 40 μM (≈ 2.083 mg/L) Cr(VI). $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ and $\text{Na}_2\text{S}_2\text{O}_4$ (both from Sigma, ACS grade) were used to pretreat the GACs. Depending on the particular experiment, the pH was adjusted with various concentrations of H_2SO_4 , HCl , or NaOH .

Table 1. Typical physical properties/specifications of granular activated carbons (GACs).

	LB830	F400
Total Surface Area [m ² /g]	950-1050	941 ^a
Iodine Number, min.	900	1000
Pore Volume [cm ³ /g]	0.85	0.536 ^a
Abrasion Number, min.	80	75
US Standard Sieve Size	8*30 (2.38*0.59 mm)	12*40 (1.68*0.42 mm)
Ash Content [%]	6	6.72 ^a
Base Material	Bituminous Coal	Bituminous Coal

a: from Karanfil, 1995.

Experimental Methods

Batch experiments. (a) GAC Pretreatment. Five grams (dry-weight) of oxygen-free (i.e., washed and dried in the anaerobic chamber) carbon was transferred to a 1-L Erlenmeyer flask wrapped with aluminum foil (to minimize photoreactions). Because these GACs were only dried by the atmosphere within the anaerobic chamber, moisture contents were determined for representative samples by drying in an oven at 105°C for 24 hours; these determinations revealed 18.3 and 16.7 % moisture contents for F400 and LB830, respectively. Oxygen-free DDW (175 mL) was added to the flask followed by 25 mL of a (anaerobically-prepared) 20-mM strong reductant (Fe(II) or dithionite) solution to obtain 0.1 mmole-reductant/g-AC. After contacting for 24 hours with intermittent agitation, the supernatant was poured out and the AC was washed with oxygen-free DDW (200 mL) for two hours. The supernatant was poured out again, and the washing procedure was repeated an additional four times. To check the remaining amount and the loss of reductants during washing, all aliquots from the supernatant washes were collected and analyzed. After the fifth wash, the wet AC was transferred to 40-mL amber vials with lead foil caps and centrifuged for 10 minutes at 1000 rpm. After removing the supernatant, a portion of the wet AC was taken to measure the dry-weight content. Although wet AC was used for rate and isotherm experiments, all pretreated AC amounts reported are on a dry-weight basis.

(b) Rate experiments. Rate experiments for AC adsorption of Cr(VI) were conducted in completely-mixed batch reactors (CMBRs). One-liter Erlenmeyer flasks wrapped with aluminum foil and mixed vigorously with a magnetic stirrer were used for the reactors. Initial Cr(VI) concentrations were $40 \pm 0.3 \mu\text{M}$ ($2.083 \pm 0.016 \text{ mg/L}$). GAC dosages were 0.500 and 1.000 g/L for pH 4 and pH 7.5, respectively, in the pH-controlled experiments using virgin AC and varying AC dosages for pretreated GAC experiments. Two-liter Erlenmeyer flasks were used in uncontrolled pH experiments which initially contained 1500 mL AGW, $40 \mu\text{M}$ Cr(VI) and 2 g GAC at initial pH values of 3.93 or 8.15. For initial pH values of 4 and 5, a 1-g GAC dose in 1000 mL AGW was used for equivalent experiments. Representative samples were collected periodically and filtered immediately through a 0.2- μm membrane filter to separate the GAC from the solution.

The pH was adjusted by periodic addition of acid or base as necessary from pH meter readings (controlled pH experiments) or was not adjusted at all (uncontrolled pH experiments). Blanks without GAC present were run to monitor Cr(VI) concentrations at corresponding pH values.

(c) **Isotherm experiments.** A bottle-point technique was used to investigate the adsorption capacity of virgin and pretreated GACs at different initial pH values. Forty-milliliter amber vials with Teflon-lined caps were used for the CMBRs. GAC doses ranged from 0.05-0.25 g/L and 1.6-3.5 g/L for initial pH values of 4 and 7.5, respectively. A Cr(VI) solution was transferred to the vials; the volume added was determined gravimetrically. The samples vials were tumbled for 3 days to ensure equilibration and then the samples were filtered through a 0.2- μ m membrane filter and analyzed for Cr(VI). For the anaerobic experiments, all preparation procedures were conducted in the anaerobic chamber. Before removing the vials from the chamber, lead-foil lined caps were used to seal them which prevented oxygen diffusion through the Teflon. These samples were also tumbled for 3 days, filtered and then analyzed. All pH values reported for the isotherm experiments are initial values.

Column Experiments. Continuous flow experiments were conducted with glass columns (10 $\times$ 1 cm ID) as shown in Figure 1. Two columns were placed in series for each experiment; therefore, the empty bed contact time (EBCT) was 8.34 and 11.14 min for flowrates of 113.0 and 84.6 mL/hr, respectively. All column experiments utilized 5.20 g of the 80/100-size GAC. The apparent density and porosity of F400 GAC were 0.545 g/cm³ and 0.701, respectively, and those for LB830 were 0.548 g/cm³ and 0.670, respectively. A three-gallon polyethylene bottle was used for the influent reservoir and peristaltic pumps (Materflux) were used to feed the columns. The influent AGW contained 40 $\pm$ 0.1 μ M Cr(VI) and was maintained at a pH of 7.5 $\pm$ 0.1 throughout each run. Effluent samples were collected periodically for 10 min from the end of the second column and were analyzed for Cr(VI) without further treatment. The times reported here correspond to the end of each sampling period. Flowrates were monitored periodically during each run. Although the flowrates varied slightly between runs due to the packing conditions of each column, little variability was observed during any one run.

GAC Extraction/Regeneration. GAC extractions were conducted for both the batch and column systems. Batch extractions were performed in 40-mL amber vials or 100-mL amber bottles as appropriate. GAC samples containing adsorbed Cr(VI) were transferred to the extraction vials/bottles after first centrifuging them to reduce the water content. At each time point, a second GAC sample was collected, centrifuged and dried at 105°C for 24 hours to determine the moisture content of the wet carbon. DDW (30 mL) was added to the samples followed by spiking with concentrated K₂SO₄ or K₂HPO₄ solutions to obtain a final solution concentration of 0.1 M K₂SO₄ or 0.01 M K₂HPO₄. The samples were tumbled for 24 hours, filtered through 0.2- μ m membrane filters and analyzed for Cr(VI). Following these extractions, a DDW or acid (0.02 N H₂SO₄) wash followed. Column GAC regeneration was conducted *in situ* by feeding a 0.1 M K₂SO₄ or 0.01 M K₂HPO₄ solution through the exhausted carbon; washing immediately followed the extraction by feeding five bed volumes of water or 0.02 N H₂SO₄ through the columns.

Figure 1. GAC columns used for Cr(VI) adsorption experiments

Analytical Methods

Cr(VI) concentrations were determined colorimetrically by the diphenylcarbazide method (Standard Methods, 1995). The instrument used was a Hewlett Packard 8452A Diode-Array Spectrophotometer. Absorbance was measured at 542 nm. The method detection limit as determined by our laboratory is 0.04 mg/L and a linear range is observed for Cr(VI) concentrations up to 77 μM (~4.0 mg/L). Samples undergoing acid extraction were filtered and oxidized (batch) or directly oxidized (column) by KMnO_4 as recommended in Standard Methods (1995). Dissolved Fe(II) concentrations were determined colorimetrically by the ferrozine method using the same instrument. The method detection limit for Fe(II) is 0.02 mg/L at an absorbance wavelength of 562 nm.

RESULTS AND DISCUSSION

pH Effects

Solution pH significantly affected the removal of Cr(VI) by both GACs studied in this investigation (Figures 2 and 3), in agreement with the observations of previous researchers. Figure 2 shows LB830 sorption rates for experiments in which the pH was not controlled during the study (i.e., pH values shown are initial values prior to adding GAC). The sorption reactions were generally complete within 2 days, and blanks at pH 3.93 and 7.56 showed no significant changes in Cr(VI) concentration during this period. The sorption rate was relatively fast, with over 80 % of the equilibrium amount of Cr(VI) being removed within 8 hours. Initial sorption rates were faster at low pH than at higher pH values. For systems in which the pH was controlled, sorption rates were much faster than for the uncontrolled pH systems (Figures 3). Additionally, the amount of Cr(VI) removed by the GAC was greater in the pH-controlled experiments than in the uncontrolled experiments. These observations are consistent with the expectation that the GAC raises the solution pH up towards its PZC (pH > 9, Karanfil, 1995) in the uncontrolled systems and with the fact that inorganic anions such as HCrO_4^- and CrO_4^{2-} adsorb less at higher pH values (Zachra et al., 1989). Below the PZC, GAC surfaces have a net positive charge and above that point their surface carries a net negative charge.

The pH trends observed in the rate experiments are also seen in the adsorption isotherms, that is, an increase in adsorption capacity with decreasing pH. Representative Cr(VI) isotherms for F400 and LB830 are shown in Figure 4. Table 2 presents the results of isotherm experiments at several different initial pH values. All isotherm datasets were well-fit by the nonlinear Freundlich equation (R^2 values greater than 0.95). The decrease in sorption capacity with pH increase can be readily seen by the Freundlich capacity parameter, K_F , whose values rapidly decrease as the initial pH increases. Above pH 7, very little Cr(VI) can be removed from solution by either GAC, as evidenced by the very small K_F values. In contrast to K_F , there is no obvious trend with pH for the parameter $1/n$, which is a measure of the degree of isotherm nonlinearity and is commonly thought to represent the heterogeneity of GAC sorption sites.

Table 2. Freundlich constants of virgin ACs for Cr(VI) adsorption

	LB830		F400	
	K_F	$1/n$	K_F	$1/n$
PH 4	35.4	0.67	37.4	1.76
PH 5	25.4	1.34	18.8	2.38
PH 6	3.8	0.89	2.8	0.88
PH 7	0.1	3.27	0.1	3.21
pH 7.5	0.04	3.76	0.028	4.031
PH 8	0.1	0.79	0.04	2.42

Figure 4. Typical Cr(VI) isotherms on ACs

Oxygen Effects

Figures 5-1 and 5-2 show the effect of oxygen on Cr(VI) adsorption by F400 and LB830 at pH 4 and 7.5, respectively. The adsorption capacities of both carbons were greatly reduced when oxygen was effectively excluded from the chromium solutions. At pH 4, K_F values for experiments conducted under anaerobic conditions are three to four times larger than for those conducted under aerobic conditions (Figure 5-1). At pH 7.5, the effect is even greater (Figure 5-2). In addition, the degree of nonlinearity (i.e., slope of the isotherms) for the anaerobic isotherms was greater (i.e., less steep) than for aerobic isotherms.

The amount of Cr(VI) removed from solution (i.e., sorbed) was calculated by the difference between initial and final Cr(VI) concentrations. Whether this removal is only due to adsorption onto GAC or is due to a combination of adsorption plus chemical reaction (e.g., reduction of Cr(VI) to Cr(III)) cannot be determined conclusively from Figures 5-1 and 5-2. However, the experiments conducted under anaerobic conditions would be more favorable for promoting reduction reactions. For example, the carbon used in the aerobic experiments was washed with water containing ambient DO concentrations, dried in an oven in the presence of oxygen, and contacted again with oxygenated solutions during the Cr(VI) adsorption experiments. Conversely, in the anaerobic experiments oxygen was excluded at every stage from contacting the GAC (e.g., washing, drying, Cr(VI) adsorption). Contact between GAC and oxygen, both in

the gaseous and dissolved states, results in the sorption of oxygen at GAC surfaces and subsequent formation of carboxylic acid groups on the surface (Prober, et al., 1975), thereby changing its surface chemical properties. For example, many researchers have reported that catalytic oxidation reactions can occur at GAC surfaces in the presence of DO. Therefore, one plausible explanation for the higher Cr(VI) removal under anaerobic conditions is that reduction of Cr(VI) to Cr(III) occurs in the absence of oxygen.

Pretreatment Effects

The effects of different GAC pretreatments that were intended to increase its reduction capacity can be seen in Figures 6 and 7 and Table 3. The specific reductants investigated were dithionite and Fe(II); these were selected because of their excellent performance in our previously-reported tests with Pantex aquifer materials. The two GACs were contacted with dithionite and Fe(II) as described in the experimental section. After the 24-hr contact time, residual reductants in solution were removed by washing five times with DDW and the presence of reductants in the wash water were checked by reacting with Cr(VI) (for dithionite) or by direct measurement (for Fe(II)). The solution from the fifth washing after dithionite pretreatment showed that 0.26 mg Cr(VI) was reduced by 43.1 mL supernatant. Therefore, any reduction by residual dithionite on the wet GAC was negligible in our experiments because at the moisture levels measured, residual water on the carbon would be at most 0.26 mL (i.e., equivalent to 0.0016 mg of Cr(VI) reducing potential) for the isotherm experiments and 0.8 mL (0.0048 mg of Cr(VI) reducing potential) for the rate experiments. Fe(II) concentrations in the wash solutions were determined directly by the colorimetric ferrozine method; no Fe(II) was observed in any of the wash solutions nor was it observed in the supernatant of the solution used to initially contact the GAC.

Figures 6 and 7 show the results of rate experiments using Fe(II)- and dithionite-pretreated GACs, respectively. A direct comparison of the relative amounts of Cr(VI) removed from solution is somewhat complicated because of the varying GAC doses as shown in the figure legends. Wet carbon was used in these experiments and, because dithionite and Fe(II) are both easily oxidized by oxygen, the pretreated carbon was transferred as quickly as possible to the Cr(VI) reaction vessels after the centrifuged pretreatment vials (capped with lead-foil) were opened. Therefore, the exact same amount of carbon on a dry-weight basis could not be transferred because of the slightly varying moisture content of the wet GAC. For the Fe(II)-pretreated carbons, Cr(VI) concentrations initially decreased very rapidly and thereafter continued to decrease slowly over times longer than 1 day (Figure 6). The pH effects were similar to those observed for the virgin carbons; although the dosages at pH 4 were approximately one-third that at pH 7.5, the amount of Cr(VI) removed was much greater. Similar results were observed for the carbon pretreated with dithionite (Figure 7). Upon comparison with the virgin GACs, pretreatment by Fe(II) or dithionite did not significantly improve the adsorption properties. In fact, pretreatment generally hindered Cr(VI) removal except for some select cases (i.e., compare K_F in Tables 2 and 3). These results contrast greatly with our previous observations for the Pantex soils and aquifer materials; for those sorbents pretreatment with dithionite and, particularly, Fe(II) greatly enhanced Cr(VI) removal from solution. Evidently, pretreatment of GAC with these reductants results in very different reactions than those that occur for Pantex

Table3. Freundlich constants of pretreated ACs for Cr(VI) adsorption

		LB830		F400	
		K _F	1/n	K _F	1/n
With Dithionite	pH 4	-	-	30.54	0.86
	pH 5	21.4	2.68	12.12	0.32
	pH 6	6.7	0.92	6.33	0.55
	pH 7	0.05	4.87	0.49	1.99
	pH 8	7.5E-4	7.78	0.06	1.94
With Fe(II) ion	pH 4	14.0	5.62	48.30	0.36
	pH 7.5	0.14	1.83	0.27	1.34

soils/aquifer materials (i.e., an enhancement of the soil reduction capacity). It is possible that the pretreatment with strong reductants is somehow altering the carbon surface chemistry in a way that adversely affects its ability to react with Cr(VI). Alternatively, the GAC surfaces may have very large buffering capacities that make them resistant to reduction (i.e., GAC oxidizes the reductants without being significantly changed itself). In any case, GAC pretreatment will be more difficult and may not prove to be as beneficial as it is for Pantex soils and aquifer materials.

GAC Comparison

The two GACs investigated showed similar removal efficiencies for Cr(VI), in both the virgin carbon studies as well as those that utilized pretreatment. Overall GAC differences were relatively small, particularly when compared to the effects of pH and DO. Because the two carbons have the same base material and similar physical properties (Table 1), it should not be too surprising that they showed similar behaviors. Only one major physical property difference was evident, that being the inferior hardness of LB 830 relative to that of the F400. This difference became noticeable upon washing the carbons and during pretreatment experiments. No quantitative hardness measurements were made, but it was readily apparent that the LB830 produced more nonsettleable particle fines than did the F400.

GAC Regeneration and Cycling

Based on our previous results for Pantex soils and aquifer materials, we first studied the feasibility of extracting Cr(VI) from the GAC surfaces using 0.1 M K₂SO₄. Without making any pH adjustments, we observed that only 4 to 6% of the Cr(VI) removed from solution at pH 4 could be extracted (results not shown). Extraction efficiencies using 0.01M K₂HPO₄ were much higher (e.g., 18 to 20% for the same GAC sample and conditions). These rather low efficiencies were expected because the carbon was in contact with the Cr(VI) solution (i.e., aged) for 10 days and because no pH adjustment was made. Based on these results, K₂HPO₄ was selected as the extractant to be used for all subsequent regeneration experiments. Extraction by concentrated NaOH solutions (i.e., pH > 12) was not attempted because of the potential for Cr(III) oxidization to Cr(VI) in the presence of oxygen.

Figure 8. Column experiments with virgin and Fe(II)-pretreated ACs

Figure 8 shows Cr(VI) breakthrough curves from column experiments using virgin and Fe(II)-pretreated GACs. In all cases, the influent solution pH was maintained at 7.5. Initial Cr(VI) breakthrough began at approximately 23 bed volumes and complete breakthrough occurred at 60 to 70 bed volumes. The amounts of Cr(VI) removed by virgin and Fe(II)-pretreated LB830 were 0.1625 and 0.1477 mg/g, respectively, and were 0.1520 and 0.1423 mg/g by virgin and Fe(II)-pretreated F400, respectively. Similarly to the results obtained in batch rate and isotherm experiments, pretreatment with Fe(II) did not improve the performance of either GAC in the column studies, both on a Cr(VI) removal basis and on a Cr(VI) breakthrough basis.

To test the cycling and performance of regenerated GACs (i.e., those previously saturated with Cr(VI) and then extracted and washed), F400 carbon with no pretreatment was used. Figure 9 shows the Cr(VI) breakthrough for the first run (i.e., virgin F400). As was observed in Figure 8, Cr(VI) breakthrough began at approximately 23 bed volumes and the carbon was completely saturated within 55 bed volumes. The small differences between the two breakthrough curves are a result of the slightly different flowrates utilized. After the carbon was exhausted, the influent was switched to a 0.01M K_2HPO_4 solution in order to extract the Cr(VI). Figure 10 shows the results of the Cr(VI) extraction. The first Cr(VI) extraction peak appeared within 10 bed volumes, peaking at a concentration of approximately 12 mg/L and then rapidly decreasing. Flow interruptions at approximately 13 to 14 bed volumes and then again at approximately 20 to 25 bed volumes showed that the extraction (i.e., the combination of Cr(VI) desorption and resorption) were rate-limited at the flowrates used here, as observed by the small peaks that

appeared when the flow was reinitiated. The amount of Cr(VI) removed from solution during the first run was 0.1067 and 0.1144 mg/g for column 1 and column 2, respectively (Table 4). The measured Cr(VI) extracted from the columns in the first extraction was 0.0947 and 0.0999 mg/g for columns 1 and 2, respectively (i.e., extraction efficiencies of 88.8 and 87.8%, respectively). Before the subsequent runs, column 1 underwent an acid wash and column 2 underwent a water wash as described in the experimental section. Cr(VI) concentrations in all wash solutions (0.02N H₂SO₄ and water, respectively) were below the detection limit. For the water wash, this result indicated that water alone was not an effective extractant for Cr(VI), as expected. In fact, because the wash water had a pH of approximately 5.6 to 6, the water may have actually decreased the GAC surface pH slightly with respect to the Cr(VI) influent solution (i.e., solution pH of 7.5±0.1). As shown previously, lower pH values actually favor Cr(VI) adsorption by GAC. For the acid wash, this pH difference would have a much more dramatic effect on Cr(VI) adsorption. However, the lack of chromium in the acid solution would appear to indicate that no Cr(VI) reduction to Cr(III) occurred in the columns or that 0.02N H₂SO₄ is not an effective extractant for Cr(III) in our systems.

After the extractions and washes were performed, the regenerated GACs were used in a second run (Figure 11). The column containing the water-washed GAC (i.e., column 2) showed a Cr(VI) breakthrough that initiated at approximately 8 bed volumes. This breakthrough was much earlier than that observed for the virgin carbon (~23 bed volumes). The amount of Cr(VI) removed from solution in column 2 at the end of the run was 0.0714 mg/g, a decrease of approximately 40% from the virgin GAC. This decrease in performance was most likely due to

Table 4. Cr(VI) amount sorbed and desorbed during the runs (F400) [mg/g-AC]

		Cr(VI) sorbed	Cr(VI) desorbed w/ K ₂ HPO ₄	Cr(VI) desorbed w/ Acid Washing	Cr(VI) desorbed w/ Water Washing	Extraction Efficiency
1st run	Column 1	0.1067	0.0947	0	-	0.888
	Column 2	0.1144	0.0999	-	0	0.878
2nd run	Column 1	0.1650 (0.2930)	0.0841	0.0006	-	0.514
	Column 2	0.0714	0.0562	-	0	0.788
3rd run	Column 1	0.2813 (0.2930)	-	-	-	-
	Column 2	0.0752	-	-	-	-

the occupation of sorption sites by Cr(VI) or Cr(III). In contrast, the column washed with 0.02 N H_2SO_4 (i.e., column 1) showed a significantly-increased delay in Cr(VI) breakthrough (~ 84 bed volumes). A comparison of the acid-washed GAC to the virgin GAC shows an enhancement in performance of approximately 3.6-fold based on the amount of water treated before initial Cr(VI) breakthrough (i.e., 86 versus 23 bed volumes) or of approximately 2.7-fold based on the amount of Cr(VI) removed from solution before the carbon capacity has been exhausted. For this latter calculation, the GAC in column 1 was considered to be exhausted at 96 bed volumes (i.e., when the effluent Cr(VI) concentration was the same as the influent concentration). In Table 4, the values in parentheses are the Cr(VI) amounts removed from solution at the point where effluent concentrations equaled influent concentrations, whereas the values beside those in parentheses are the integrated amounts at the end of the run. The appearance of effluent Cr(VI) concentrations above the influent concentration results from the gradual increase in pH that occurs in the column as the solution passes through it. This pH increase results in release of some previously-adsorbed Cr(VI), consistent with our pH results previously shown.

Figure 12 shows the effluent Cr(VI) concentrations during the second extraction. The relative amounts of Cr(VI) extracted by K_2HPO_4 after the second run provides for an interesting contrast between columns 1 and 2 (Table 4). The decrease in extraction efficiency for the acid-washed versus the water-washed GAC would appear to indicate that Cr(VI) reduction has occurred in column 1 or that a stronger (i.e., more resistant to extraction) adsorption of Cr(VI) has occurred at the acidic GAC surface. The presence of a slight amount of chromium in the acid

Figure 12. The second Cr(VI) extraction from water- and acid-washed columns by continuous flow of extractants(0.01M K₂HPO₄)

wash solution would be consistent with the first scenario (i.e., Cr(III) extraction by acid and quantification following oxidation back to Cr(VI) using the diphenylcarbazide method).

Figure 13 shows the third GAC column runs. Initial Cr(VI) breakthrough in the water-washed column was even earlier than was observed in the second run; this earlier breakthrough appears to show a continuing degradation of GAC performance due to additional loss of available adsorption sites for Cr(VI). Breakthrough for the acid-washed column began at 82 bed volumes which was only a slight decrease with respect to the second run. The amount of Cr(VI) removed from solution was still much larger than that observed for the virgin carbon, suggesting that many cycles could be completed with this operation before the GAC performance would suffer deleterious effects.

SUMMARY AND CONCLUSIONS

Cr(VI) removal from solution by granular activated carbon (GAC) was investigated in studies pertinent to the ongoing remediation efforts at the Pantex Plant. Batch and continuous-flow column experiments were utilized to elucidate potential benefits/effects of pH, dissolved oxygen, and various GAC pretreatment schemes. The artificial groundwater (AGW) utilized in these studies was chemically-equivalent to the Pantex groundwater under Zone 12 as sampled by Well PM-200. Two different GACs were tested; LB830 is the carbon currently being used at Pantex in groundwater treatability studies and F400 is a widely-used carbon in water/wastewater treatment operations.

The effect of pH on Cr(VI) removal that we observed in this study agreed well with previous studies, namely that the removal is favored at lower pH values. Over the pH range investigated here, the best performance occurred at pH 4 whereas the performance at pH 8 was significantly lower. Both carbons tested showed similar effects on pH changes.

Dissolved oxygen proved to play an important role in the removal of Cr(VI) by GAC. For those studies performed in an anaerobic chamber to limit oxygen concentrations, the ability of the two GACs to remove Cr(VI) from solution was greatly enhanced relative to oxygenated solutions. This improvement may have resulted from enhanced reduction of Cr(VI) to Cr(III) that would be favored under the more reducing (i.e., oxygen-limited) conditions obtained in the chamber or possibly because of a deterioration in the GAC surface brought about by the presence of dissolved oxygen.

Pretreatment of the two GACs with dithionite and dissolved Fe(II) did not improve their ability to remove Cr(VI) from AGW. These results are in contrast with our previous observations for Pantex soils and aquifer materials. For those materials, we observed that these pretreatments significantly enhanced their ability to remove Cr(VI) via reduction reactions.

GAC regeneration and cycling experiments provide promising alternatives for operations that could possibly enhance the Cr(VI) removal from Pantex groundwaters in GAC treatment systems. Using 0.01M K_2HPO_4 solutions, approximately 88% of the Cr(VI) initially removed in columns packed with virgin F400 could be extracted. After following the extraction with an acid wash the GAC performance was greatly enhanced (~3-fold increase in Cr(VI) removal); however, the subsequent extraction efficiency dropped to approximately 50%. The presence of chromium in the following acid wash solution suggests that this decrease in extraction efficiency resulted from reactions in addition to adsorption. This observation provides indirect evidence to suggest that Cr(VI) can be reduced to Cr(III) in GAC systems under relatively acidic conditions. After the second acid wash, the GAC performance in the third run was approximately the same as that observed in the second run. These results suggest that a GAC treatment system utilizing K_2HPO_4 extraction and acid washes to regenerate the spent carbon will observe enhanced removal of Cr(VI) from solution and will be able to reuse the regenerated carbon over many operation cycles without suffering adverse performance effects.

REFERENCES

- Ainsworth, C.C., Girvin, D.C., Zachara, J.M. and Smith, S.C. *Soil Sci. Soc. Am. J.* **1989**, 53, 411-418
- Anderson, L.D., Kent, D.B., and Pavis J.A., *Environ. Sci. Technol.* **1994**, 178-185
- Bartlett, R. and James, B., *J. Environ. Qual.* **1979**, 8, 31-35
- Corapcioglu, M.O., and Huang, C.P. *Carbons*, **1987**, 25, 569-578
- Eary, L.E. and Rai, D. *Environ. Sci. Technol.* **1988**, 22, 972-977
- Fendorf, S.E. and Zasoski, R.J. *Environ. Sci. Technol.* **1992**, 26, 79-85
- Goodgame, D.M.L. and Hayman, P.B., *Inorg. Chimi. Acta*, **1984**, 91, 113-115
- Griffin, R.A., Au, A.K., and Frost, R.R. *J. Environ. Sci. Health*, **1977**, A12, 431-449
- James, B.R., *Environ. Sci. Technol.* **1996**, 30 248A-251A
- Kaczynski, S. E. and Kieber, R. J., *Environ. Sci. Technol.* **1993**, 27, 1572 - 1576
- Kararfil, T, Schlautman, M.A. and Weber, W.J.Jr. *Wat. Res.* **1994**, 28, 1673-1678
- Karanfil, T. *Oxygen Sensitivity of Natural and Synthetic organic Macromolecule sorption by Activated Carbon*, Ph.D. dissertation, U. of Mich., 1995
- Krishnamurthy, S. and Wilkens, M.M. *Northeastern Geology*, **1994**, 16, 14-17
- Mayer, L.M. and Schick, L.L. *Environ. Sci. Technol.* **1981**, 15, 1482-1484
- Prober, R., Pyeha, J.J. and Kidon, W.E. *AIChE Jour.*, **1975**, 21, 1200-1203
- Ramos, R.L., Martinez, A.J. and Coronado, R.M.G. *Wat. Sci. Tech.* **1994**, 30, 191-197
- Perez-Candela, M., Martin-Martinez, J.M. and Torregrosa-Macia, R. *Wat. Res.*, **1995**, 29, 2174-2180
- Richard, F.C. and Bourge, A.C.M., *Wat. Res.* **1991**, 25, 807-816
- Schultz, M.F., Benjamin, M.M, and Ferguson, J.F. *Environ. Sci. Technol.* **1987**, 21, 863-869
- Schwarzenbach, R.P. Gschwend, P.M, and Imboden, D.M. *Environmental Organic Chemistry*, John Wiley and Sons, Inc., 1993, NY
- Sharma, D.C. and Forster, C.F. *Water Res.* **1993**, 27, 1201-1208
- *Standard Methods*, 19th ed., 1995
- Stollenwerk, K. CT. and Grove, D.B., *J. Environ. Qual.* **1985**, 14, 396-399
- Tan, T.C. and Teo, W.K. *Wat. Res.* **1987**, 21, 1183-1188
- Thankkar, S, and Manes, M., *Environ. Sci. Technol.* **1987**, 21, 546-549
- Vidic, R.D., Suidan., and Brenner, R.C., *Environ. Sci. Technol.* **1993**, 27, 2079-2085
- Wittbrodt, P.R. and Palmer, C.D., *Environ. Sci. Technol.* **1995**, 29, 255-263
- Zachara, J.M., Girvin, D.C., Schmidt, R.L., and Resch, C.T., *Environ. Sci. Technol.* **1987**, 21, 589-594
- Zachara, J.M., Ainsworth, C.C., Cowan, C.E. and Resch, C.T., *Soil Sci, Soc. Am. J.* **1989**, 53, 418-428

APPENDIX

Table-1. Column experiments with virgin and Fe(II)-pretreated ACs

LB830-Virgin			LB830-Fe(II) treated	
Time [min]	bed vol.	Cr(VI) Conc. [mg/L]	bed vol.	Cr(VI) Conc. [mg/L]
0	0	0	0	0
20	2.14668	0	2.06137	0
70	7.51337	0	7.2148	0
120	12.8801	0	12.3682	0
143	15.3487	0	14.7388	0
186	19.9641	0	19.1707	0
215	23.0768	0	22.1597	0
223	23.9354	0.00194	22.9843	0.02439
295	31.6635	0.02224	30.4052	0.08704
335	35.9568	0.03436	34.5279	0.12426
350	37.5668	0.05182	36.074	0.17114
357	38.3182	0.06951	36.7955	0.22236
365	39.1769	0.0918	37.62	0.28145
372	39.9282	0.13465	38.3415	0.37453
380	40.7869	0.2036	39.166	0.5016
395	42.3969	0.28947	40.7121	0.6342
410	44.0069	0.38788	42.2581	0.7658
425	45.6169	0.50237	43.8041	0.89579
440	47.2269	0.62534	45.3501	1.0064
455	48.8369	0.75299	46.8962	1.1138
470	50.4469	0.88842	48.4422	1.2201
485	52.0569	1.0139	49.9882	1.3135
500	53.6669	1.1458	51.5343	1.3994
515	55.2769	1.3342	53.0803	1.532
530	56.8869	1.5104	54.6263	1.6412
555	59.5703	1.6522	57.203	1.7373
580	62.2536	1.8336	59.7797	1.8522
605	64.937	1.959	62.3564	1.9482
635	68.157	2.0653	65.4485	2.0254
670	71.9137	2.1293	69.0559	2.0687
720	77.2804	2.1497	74.2093	2.0931
755	81.0371	2.1348	77.8167	2.0816
780	83.7204	2.1346	80.3934	2.1042

Table-1. Column experiments with virgin and Fe(II)-pretreated ACs (continued)

F400, virgin			F400, Fe(II) treated	
Time [min]	bed vol.	Cr(VI) Conc [mg/L]	bed vol.	Cr(VI) Conc [mg/L]
0	0	0	0	0
20	2.20659	0	1.99007	0
60	6.61977	0	5.97021	0
100	11.0329	0	9.95034	0
150	16.5494	0	14.9255	0
200	22.0659	0.0045	19.9007	0
250	27.5824	0.01815	24.8759	0.0342
275	30.3406	0.04081	27.3634	0.0443
300	33.0988	0.07592	29.851	0.0749
310	34.2021	0.105	30.8461	0.1084
320	35.3054	0.1477	31.8411	0.1064
335	36.9604	0.2047	33.3337	0.1465
350	38.6153	0.3784	34.8262	0.1837
360	39.7186	0.4519	35.8212	0.217
375	41.3735	0.56493	37.3138	0.387
390	43.0285	0.6288	38.8063	0.577
405	44.6834	0.7458	40.2989	0.715
420	46.3384	0.8878	41.7914	0.805
435	47.9933	1.0034	43.284	0.922
450	49.6483	1.0803	44.7765	1.006
465	51.3032	1.1779	46.2691	1.139
480	52.9581	1.257	47.7617	1.192
495	54.6131	1.426	49.2542	1.271
510	56.268	1.6	50.7468	1.441
525	57.923	1.767	52.2393	1.563
540	59.5779	1.862	53.7319	1.631
555	61.2329	1.971	55.2244	1.732
570	62.8878	2.055	56.717	1.822
585	64.5427	2.036	58.2095	1.949
600	66.1977	2.111	59.7021	2.039
615	67.8526	2.092	61.1946	2.113

Table-2. Cr(VI) breakthrough with virgin F400 (1st run)

Time [min]	Bed Vol.	Cr(VI), column-1	Bed Vol.	Cr(VI), Column-2
0	0	0	0	0
10	1.1032946	0	1.1459494	0
85	9.3780041	0	9.7405698	0
121	13.349865	0	13.865988	0
161	17.763043	0	18.449785	0
171	18.866338	0	19.595735	0
181	19.969632	0	20.741684	0
186	20.52128	0	21.314659	0
191	21.072927	0	21.887633	0
198	21.845233	0	22.689798	0
204	22.50721	0.0045	23.377367	0
209	23.058857	0.01815	23.950342	0.008395
212	23.389846	0.01768	24.294127	0.03102
215	23.720834	0.04081	24.637912	0.028321
218	24.051822	0.05707	24.981697	0.04104
221	24.382811	0.07592	25.325481	0.0533
224	24.713799	0.0859	25.669266	0.07095
227	25.044788	0.105	26.013051	0.0879
230	25.375776	0.1269	26.356836	0.1093
233	25.706764	0.1477	26.700621	0.129
236	26.037753	0.173	27.044406	0.1546
239	26.368741	0.2033	27.38819	0.1798
242	26.699729	0.2259	27.731975	0.2109
245	27.030718	0.2607	28.07576	0.241
248	27.361706	0.2899	28.419545	0.2758
251	27.692695	0.3178	28.76333	0.3067
254	28.023683	0.3469	29.107114	0.3894
257	28.354671	0.3878	29.450899	0.3766
260	28.68566	0.4341	29.794684	0.4204
263	29.016648	0.4519	30.138469	0.4894
269	29.678625	0.5235	30.826039	0.5328
272	30.009613	0.56493	31.169823	0.5828
275	30.340602	0.58459	31.513608	0.6197
278	30.67159	0.6288	31.857393	0.6624
281	31.002578	0.6513	32.201178	0.7019
284	31.333567	0.697	32.544963	0.7457
289	31.885214	0.7458	33.117937	0.8001
295	32.547191	0.8199	33.805507	0.8652
299	32.988509	0.8878	34.263887	0.9305
304	33.540156	0.9336	34.836861	0.995
309	34.091803	1.0034	35.409836	1.0477
314	34.643451	1.0373	35.982811	1.1022
319	35.195098	1.0803	36.555785	1.1313

Table-2. Cr(VI) breakthrough with virgin F400 (1st run)
(continued)

Time [min]	Bed Vol.	Cr(VI), column-1	Bed Vol.	Cr(VI), Column-2
324	35.746745	1.1321	37.12876	1.1881
329	36.298392	1.1779	37.701735	1.2554
339	37.401687	1.257	38.847684	1.32
349	38.504982	1.361	39.993634	1.421
359	39.608276	1.426	41.139583	1.508
369	40.711571	1.5	42.285532	1.642
379	41.814866	1.6	43.431482	1.709
389	42.91816	1.689	44.577431	1.81
399	44.021455	1.767	45.723381	1.875
409	45.124749	1.841	46.86933	1.922
419	46.228044	1.862	48.015279	1.984
434	47.882986	1.933	49.734203	2.004
449	49.537928	1.971	51.453127	2.044
464	51.19287	2.017	53.172052	2.071
479	52.847812	2.055	54.890976	2.038
494	54.502753	2.074	56.6099	2.091
509	56.157695	2.036	58.328824	2.051
524	57.812637	2.044	60.047748	2.064
539	59.467579	2.111	61.766672	2.111
559	61.674168	2.1	64.058571	2.058
579	63.880758	2.092	66.35047	2.105
599	66.087347	2.084	68.642368	2.084

Table-3. Cr(VI) extraction from the columns with 0.01M K₂HPO₄ (1st extraction)

	Bed Vol.	Cr(VI)-col. 1	Bed Vol.	Cr(VI)-col. 2
0	0	2.3279	0	2.3724
6	0.7364635	2.3755	0.7949069	2.4199
9	1.1046952	2.3468	1.1923603	2.4525
12	1.4729269	2.3749	1.5898138	2.4219
15	1.8411587	2.7288	1.9872672	4.8393
18	2.2093904	7.4496	2.3847207	10.01423
21	2.5776222	10.0817	2.7821741	11.634
24	2.9458539	11.6134	3.1796276	11.4831
27	3.3140856	11.3812	3.577081	10.94013
30	3.6823174	10.568	3.9745345	9.9712
33	4.0505491	10.159	4.3719879	9.7632
36	4.4187808	9.8702	4.7694413	8.1942
39	4.7870126	7.4563	5.1668948	7.1106
42	5.1552443	6.432	5.5643482	6.8043
45	5.523476	6.1893	5.9618017	5.9641
48	5.8917078	5.3428	6.3592551	5.1604
51	6.2599395	4.6513	6.7567086	3.8477
54	6.6281713	3.3938	7.154162	2.18
57	6.996403	1.9049	7.5516155	1.5713
60	7.3646347	1.1241	7.9490689	0.85293
63	7.7328665	0.9609	8.3465224	0.73582
69	8.4693299	0.71374	9.1414293	0.55568
75	9.2057934	0.54289	9.9363361	0.7619
80	9.819513	0.47257	10.598759	0.731506
85	10.433233	0.86031	11.261181	1.2164
90	11.046952	0.91382	11.923603	1.2102
95	11.660672	1.0655	12.586026	1.2543
100	12.274391	1.3243	13.248448	1.38
105	12.888111	2.4388	13.910871	2.3934
110	13.50183	2.8715	14.573293	2.845
115	14.11555	2.5641	15.235715	2.5249
120	14.729269	2.5541	15.898138	2.0852
135	16.570428	1.6566	17.885405	1.3936
150	18.411587	0.8161	19.872672	0.59349
165	20.252746	0.33852	21.85994	0.24109
180	22.093904	0.13568	23.847207	0.10471
185	22.707624	0.75113	24.509629	0.70206
196	24.057807	0.77322	25.966958	0.79102
201	24.671526	0.6424	26.629381	0.64513
208	25.530734	0.54498	27.556772	0.52529
216	26.512685	0.45264	28.616648	0.39323
231	28.353844	0.25832	30.603915	0.19545

Table-3. Cr(VI) extraction from the columns with 0.01M K_2HPO_4

(1st extraction) (continued)

	Bed Vol.	Cr(VI)-col. 1	Bed Vol.	Cr(VI)-col. 2
246	30.195002	0.059457	32.591183	0.081669
256	31.422442	0.035322	33.916027	0.031313
266	32.649881	0.029909	35.240872	0.024156

Table -4. Cr(VI) breakthrough with washed AC(2nd run)

Time [min]	bed vol.	Cr(VI)-water- washed	Time [min]	bed vol.	Cr(VI)-acid- washed
0	0	0	0	0	0
5	0.59938	0	5	0.53062	0
10	1.19875	0	10	1.06124	0
15	1.79813	0	15	1.59186	0
20	2.3975	0	20	2.12249	0
25	2.99688	0	25	2.65311	0
30	3.59626	0	30	3.18373	0
45	5.39439	0	45	4.77559	0
60	7.19251	0	60	6.36746	0
75	8.99064	0.04899	75	7.95932	0
100	11.9875	0.08652	100	10.6124	0
120	14.385	0.25555	130	13.7962	0
123	14.7447	0.32154	145	15.388	0
128	15.344	0.39158	160	16.9799	0
133	15.9434	0.50148	175	18.5717	0
137	16.4229	0.60167	190	20.1636	0
142	17.0223	0.71365	205	21.7555	0
149	17.8614	0.98964	220	23.3473	0
154	18.4608	1.0001	235	24.9392	0
159	19.0602	1.1185	265	28.1229	0
166	19.8993	1.2271	280	29.7148	0
175	20.9782	1.37	295	31.3067	0
182	21.8173	1.4784	310	32.8985	0
190	22.7763	1.5381	325	34.4904	0
198	23.7353	1.6149	340	36.0823	0
205	24.5744	1.7032	355	37.6741	0
214	25.6533	1.7115	370	39.266	0
220	26.3725	1.773	385	40.8578	0
235	28.1707	1.8295	400	42.4497	0
258	30.9278	1.8489	415	44.0416	0
265	31.7669	1.8857	430	45.6334	0
272	32.6061	1.8904	445	47.2253	0
280	33.5651	1.9074	460	48.8172	0

Table-4. Cr(VI) breakthrough with washed AC(2nd run)

(continued)

Time [min]	bed vol.	Cr(VI)-water-washed	Time [min]	bed vol.	Cr(VI)-acid-washed
288	34.5241	1.9141	475	50.409	0
295	35.3632	1.9039	490	52.0009	0
302	36.2023	1.8974	513	54.4417	0
310	37.1613	1.9391	531	56.352	0
325	38.9594	1.9106	556	59.0051	0
340	40.7576	1.9104	601	63.7807	0
355	42.5557	1.9338	631	66.9644	0
370	44.3538	1.9397	682	72.3768	0
385	46.152	1.9396	713	75.6666	0
400	47.9501	1.9529	728	77.2585	0
415	49.7482	1.9678	743	78.8503	0
430	51.5463	1.939	758	80.4422	0
445	53.3445	1.9834	773	82.0341	0
460	55.1426	1.9953	788	83.6259	0
475	56.9407	1.9918	803	85.2178	0
490	58.7389	1.9949	818	86.8097	0.01552
513	61.496	1.9869	831	88.1893	0.18198
531	63.6537	1.9802	846	89.7811	0.22917
556	66.6506	2.0108	851	90.3118	0.3292
601	72.045	2.0062	856	90.8424	0.42217
631	75.6413	1.9933	861	91.373	0.54746
682	81.7549	2.0324	866	91.9036	0.6768
			871	92.4342	0.82751
			876	92.9649	0.99381
			881	93.4955	1.1689
			886	94.0261	1.3431
			891	94.5567	1.495
			896	95.0873	1.6204
			901	95.618	1.8492
			906	96.1486	1.9959
			911	96.6792	2.1458
			926	98.2711	2.444
			941	99.8629	2.7687
			956	101.455	3.0456
			971	103.047	3.2317
			986	104.639	3.4322
			1001	106.23	3.5322
			1016	107.822	3.6508
			1031	109.414	3.8075
			1046	111.006	3.8357
			1061	112.598	4.004
			1076	114.19	4.0134

Table-4. Cr(VI) breakthrough with washed AC(2nd run)

(continued)

Time [min]	bed vol.	Cr(VI)-water-washed	Time [min]	bed vol.	Cr(VI)-acid-washed
			1091	115.782	4.0913
			1144	121.406	3.9747
			1211	128.516	3.6687
			1226	130.108	3.6128
			1241	131.7	3.6057
			1256	133.292	3.4563
			1271	134.884	3.4985
			1286	136.476	3.3743
			1301	138.068	3.3064
			1316	139.66	3.2904
			1331	141.251	3.2423
			1346	142.843	3.1555
			1361	144.435	3.1125
			1376	146.027	3.0529
			1391	147.619	3.0045
			1406	149.211	2.9662
			1421	150.803	2.6881
			1436	152.394	2.6978
			1451	153.986	2.654
			1466	155.578	2.6062
			1481	157.17	2.604
			1496	158.762	2.5641
			1511	160.354	2.7171
			1526	161.946	2.5082
			1541	163.537	2.5057
			1556	165.129	2.4338
			1571	166.721	2.4613
			1586	168.313	2.4346
			1601	169.905	2.4254

Table-5. Cr(VI) extraction (2nd extraction)

Time [min]	Bed Vol.	Cr(VI)-water-washed col.	Bed Vol.	Cr(VI)-acid-washed col.
0	0	2.083	0	2.0504
8	0.9080723	2.0423	0.7170868	2.0917
16	1.8161446	2.0413	1.4341737	2.2847
22	2.4971989	4.38	1.9719888	7.9239

Table-5. Cr(VI) extraction (2nd extraction)
(continued)

Time [min]	Bed Vol.	Cr(VI)- water- washed col.	Bed Vol.	Cr(VI)- acid- washed col.
26	2.951235	4.55	2.3305322	9.6949
32	3.6322893	4.89	2.8683473	8.368
36	4.0863254	4.67	3.2268908	8.1751
41	4.6538706	4.34	3.67507	7.8696
46	5.2214158	4.1116	4.1232493	7.3869
51	5.788961	3.6039	4.5714286	6.7325
56	6.3565062	3.0906	5.0196078	6.007
61	6.9240514	2.7459	5.4677871	5.4497
66	7.4915966	2.3386	5.9159664	5.08
71	8.0591418	1.9452	6.3641457	4.1962
76	8.626687	1.6195	6.8123249	3.5551
81	9.1942322	1.3455	7.2605042	3.0219
91	10.329323	1.0691	8.1568627	2.4003
96	10.896868	0.8631	8.605042	1.9309
101	11.464413	0.83903	9.0532213	1.7305
106	12.031958	0.69131	9.5014006	1.545
111	12.599503	0.62722	9.9495798	1.4672
116	13.167049	0.56839	10.397759	1.3702
121	13.734594	0.52149	10.845938	1.2648
126	14.302139	0.48164	11.294118	1.1851
131	14.869684	0.446	11.742297	1.1205
136	15.437229	0.41256	12.190476	1.0678
141	16.004775	0.49098	12.638655	1.0515
146	16.57232	0.46621	13.086835	0.98246
151	17.139865	0.44373	13.535014	0.92333
156	17.70741	0.42308	13.983193	0.88269
161	18.274955	0.40388	14.431373	0.83456
166	18.842501	0.38323	14.879552	0.81159
171	19.410046	0.3675	15.327731	0.78205
176	19.977591	0.34308	15.77591	0.74777
181	20.545136	0.31047	16.22409	0.70726
186	21.112681	0.28842	16.672269	0.65615
191	21.680227	0.28018	17.120448	0.59623
196	22.247772	0.27851	17.568627	0.56427
201	22.815317	0.27338	18.016807	0.558
206	23.382862	0.26882	18.464986	0.54275
211	23.950407	0.16695	18.913165	0.54174
246	27.923224	0.13539	22.05042	0.43886
296	33.598676	0.10185	26.532213	0.34615
311	35.301311	0.090938	27.876751	0.33094
326	37.003947	0.077656	29.221289	0.29635

Table-5. Cr(VI) extraction (2nd extraction)
(continued)

Time [min]	Bed Vol.	Cr(VI)- water- washed col.	Bed Vol.	Cr(VI)- acid- washed col.
341	38.706583	0.070642	30.565826	0.26176
356	40.409218	0.076384	31.910364	0.26233
371	42.111854	0.066214	33.254902	0.25729
381	43.246944	0.05096	34.151261	0.20802
406	46.08467	0.041623	36.392157	0.16708
448	50.85205	0.029393	40.156863	0.1591
511	58.003119	0.027639	45.803922	0.15963
526	59.705755	0.026894	47.148459	0.16099
541	61.408391	0.025184	48.492997	0.15704
556	63.111026	0.022028	49.837535	0.15511
571	64.813662	0.020494	51.182073	0.15362
586	66.516297	0.0201	52.526611	0.14968
601	68.218933	0.017426	53.871148	0.14543
616	69.921569	0.016549		

Table-6. Cr(VI) breakthrough after 2nd extraction (3rd run)

Time [min]	bed vol.	Cr(VI)- water- washed	Time [min]	bed vol.	Cr(VI)- acid- washed
0	0	0	0	0	0
20	2.083015	0	20	1.9964349	0
40	4.16603	0.02081	40	3.9928699	0
50	5.2075376	0.0843	60	5.9893048	0
60	6.2490451	0.10006	70	6.9875223	0
70	7.2905526	0.12193	85	8.4848485	0
80	8.3320601	0.099705	100	9.9821747	0
90	9.3735676	0.11597	115	11.479501	0
100	10.415075	0.17843	130	12.976827	0
107	11.14413	0.28649	145	14.474153	0
115	11.977336	0.44193	160	15.97148	0
130	13.539598	0.73339	175	17.468806	0
145	15.101859	1.1206	190	18.966132	0
160	16.66412	1.3757	205	20.463458	0
175	18.226381	1.5625	220	21.960784	0
190	19.788643	1.6616	235	23.458111	0
205	21.350904	1.7164	250	24.955437	0
220	22.913165	1.7417	265	26.452763	0
235	24.475427	1.7483	280	27.950089	0
250	26.037688	1.7643	295	29.447415	0
265	27.599949	1.7675	310	30.944742	0

Table-6. Cr(VI) breakthrough after 2nd extraction (3rd run) (continued)					
Time [min]	bed vol.	Cr(VI)- water- washed	Time [min]	bed vol.	Cr(VI)- acid- washed
280	29.16221	1.7748	325	32.442068	0
295	30.724472	1.7868	340	33.939394	0
310	32.286733	1.79	355	35.43672	0
325	33.848994	1.7948	370	36.934046	0
340	35.411255	1.8019	385	38.431373	0
355	36.973517	1.8037	400	39.928699	0
370	38.535778	1.7819	415	41.426025	0
385	40.098039	1.8151	430	42.923351	0
400	41.6603	1.8211	445	44.420677	0
415	43.222562	1.8013	460	45.918004	0
430	44.784823	1.819	585	58.395722	0
445	46.347084	1.8104	725	72.370766	0
460	47.909346	1.8171	740	73.868093	0
585	60.928189	1.8417	755	75.365419	0
725	75.509295	1.8536	770	76.862745	0
740	77.071556	1.8538	785	78.360071	0
755	78.633817	1.8544	800	79.857398	0
770	80.196078	1.857	815	81.354724	0
785	81.75834	1.8343	830	82.85205	0
			845	84.349376	0.038554
			853	85.14795	0.20447
			860	85.846702	0.34944
			868	86.645276	0.55073
			875	87.344029	0.78735
			883	88.142602	1.0689
			890	88.841355	1.3416
			898	89.639929	1.642
			905	90.338681	1.8942
			913	91.137255	2.1494
			920	91.836007	2.3427
			928	92.634581	2.5715
			935	93.333333	2.716
			950	94.83066	2.9548
			965	96.327986	3.1902
			980	97.825312	3.3782
			995	99.322638	3.4963