

입상활성탄을 이용한 인공 조제 지하수내의 Cr(VI) 제거와 그 활성탄의 재생

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Cr(VI) Removal from Artificial Groundwater by Granular Activated Carbon and Regeneration of the Spent Carbon

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ABSTRACT

Removal of hexavalent chromium from artificial groundwater (AGW) by granular activated carbon (GAC) was investigated in batch and continuous-flow column studies. Experimental parameters that were examined included solution pH, presence of dissolved oxygen (DO), and GAC pretreatment with Fe(II). As the solution pH increased from 4 to 7.5, the amount of Cr(VI) removed by both GACs decreased significantly. Exclusion of DO from the experimental systems resulted in greater removal of Cr(VI) from solution, possibly as a result of reduction to Cr(III). However, pretreatment of the GAC with a reductant (Fe(II)) did not improve Cr(VI) removal. Equilibration with 0.01 M K_2HPO_4 [to extract adsorbed Cr(VI)] followed by a wash with 0.02 N H_2SO_4 [to remove precipitated/sorbed Cr(III)] proved to be a viable approach for the regeneration of carbons whose Cr(VI) removal capacities had been exhausted. The performance of the regenerated carbons exceeded that of the virgin carbons, primarily because of the favorable adsorption of Cr(VI) at lower pH values and the reduction of Cr(VI) to Cr(III). The presence of

Cr(III) in acid wash solutions provides direct evidence that Cr(VI) is reduced to Cr(III) in GAC systems under relatively acidic conditions. GAC performance over five complete cycles was consistently high, which suggests that such a system will be able to function over many operation cycles without deleterious effects.

Key words : adsorption, activated carbon, chromium, pH effects, pretreatment, dissolved oxygen, extraction, acid washing, reduction, regeneration

요 약 문

회분식 및 연속류 주상 실험을 통해 인공 조제 지하수로부터 입상활성탄에 의한 6가크롬 (Cr(VI)) 제거에 대한 연구를 수행하였다. 실험에 적용된 변수로는 용액의 pH, 용존산소의 존재여부를 사용하였고 2가철(Fe(II))로 활성탄을 전처리한 것을 처리하지 않은 활성탄과 그 결과를 비교하였다. 용액의 pH를 4.0에서 7.5로 증가 시킴에 따라 무처리 및 Fe(II)로 전처리한 활성탄 모두에 흡착된 Cr(VI)의 양이 현저히 감소하였다. 용존산소가 배제 (무산소조건) 되었을 경우 Cr(VI) 제거량이 증가하였는데, 이는 Cr(VI)의 Cr(III)로의 환원 때문으로 추측된다. 그러나, Fe(II)에 의한 활성탄의 전처리는 Cr(VI) 제거에 거의 영향을 미치지 않았다. 흡착된 Cr(VI)를 추출하기위해 0.01M K_2HPO_4 와 침전 또는 흡착된 Cr(III)를 제거하기위해 0.02N H_2SO_4 로 세척하였는데, 이는 Cr(VI)로 흡착능이 고갈된 활성탄 재생의 한 방법으로 고려될 수 있으리라 사료된다. 재생된 활성탄은 본래의 활성탄보다 큰 흡착능을 보였는데, 그 이유는 Cr(VI)가 낮은 pH에서 흡착이 잘되며 또 Cr(III)로 환원되기 때문으로 사료된다. 산 세척수중의 Cr(III)의 존재는 비교적 산성 조건하에서 Cr(VI)의 Cr(III)로의 환원을 보여주는 증거로 사료된다. 5회의 재생 및 재사용 실험에서 이 재생방법이 흡착능을 악화시키는 것 없이 지속적으로 사용될 수 있음을 알 수 있었다.

주제어 : 흡착, 활성탄, 크롬, pH의 영향, 전처리, 용존산소, 추출, 산세척, 환원, 재생

INTRODUCTION

Hexavalent chromium is commonly used in various industries including metallurgy, leather tanning, and electroplating, and has been widely used in the past as a corrosion control agent^{1, 2)}. Because of this extensive use, contamination of soils and groundwaters by chromium has become a

relatively-common occurrence³⁾. The oxidation state of chromium can range from -2 to +6; however, the most prevalent oxidation states of chromium in natural water systems are +3 and +6^{4, 5)}. Although Cr(III) is considered to be an essential trace element, Cr(VI) is toxic, carcinogenic, mutagenic, and teratogenic^{1, 5-8)}. Cr(VI) exists in water as anions such as chromate

(CrO_4^{2-}), bichromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and is more mobile in the environment than Cr(III) because it is more soluble and less adsorbable to soils under most environmental conditions^{2,9,10}. In contrast, Cr(III) readily precipitates as $\text{Cr}(\text{OH})_3$ or mixed Cr-Fe hydroxides at pH values higher than 4^{2,8,9,11}. Reduction of Cr(VI) to Cr(III), therefore, is beneficial because a more toxic and more mobile species is converted to a less toxic and less mobile form. Consequently, two strategies for the treatment of Cr(VI) in groundwater can be considered: (1) removal of Cr(VI) by sorption or (2) precipitation and immobilization *in situ* by reduction to Cr(III). Because the conversion of Cr(VI) to Cr(III) may be reversible under some subsurface conditions¹¹⁻¹³, complete removal of Cr(VI) from an aqueous system may be desirable. Note that this latter approach could still include reduction and precipitation steps after Cr(VI) sorption has occurred.

Sorption of Cr(VI) by various materials has been studied by previous researchers. Chromate can be adsorbed by soil components including Fe and Al (hydr)oxides¹⁴⁻¹⁶, kaolinite¹⁷, and spagnum moss peat¹⁸. Chromate adsorption generally increases with decreasing pH due to the protonation of surface hydroxyl sites and chromate aqueous speciation¹⁹. Chromate binding to subsurface soils is reversible upon pH increase and is hindered by sulfate (SO_4^{2-}), phosphate ($\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$) and dissolved organic carbon because of

competition for sorption sites and electrostatic effects^{6,14,19}. 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, dissolved Fe(II) species, and/or readily-oxidizable organic materials^{12,20}. Schultz et al. (1987)¹⁵ 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., ~1000 m²/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^{21,22}. In general, the adsorption of inorganic species (e.g., cadmium, arsenic, mercury(II), cobalt(II)) on AC is highly dependent on the pH²¹. For metal cations, adsorption increases abruptly from 0 to 100% over a narrow pH range as the solution pH increases (i.e., adsorption edge). Conversely, for inorganic anions, removal is higher at lower pH values (i.e., adsorption envelope).

A limited number of studies are relevant to the removal of Cr(VI) from water in AC

treatment systems; in general, the studies report AC as behaving similarly to other sorbents (i.e., Cr(VI) removal increases with decreasing solution pH except under very acidic conditions)²³⁻²⁷. Removal of Cr(VI) species from aqueous solution is believed to result from a combination of Cr(VI) adsorption onto AC surfaces and Cr(VI) reduction to Cr(III) in the presence of AC²³⁻²⁶. However, experimental shortcomings in many of these studies confound our understanding of the relative importance of the two proposed removal mechanisms. For example, several researchers reporting Cr(VI) reduction in their experimental systems presented no data whatsoever to support this claim (i.e., no Cr(III) determinations were made)^{24,25}. Others measured aqueous Cr(III) concentrations but did not attempt to desorb/dissolve any Cr(III) that may have been present on AC surfaces;²⁶ in other words, they assumed that the Cr(III) produced by the reduction of Cr(VI) was present only in the aqueous phase. This assumption might be valid for some systems, but clearly cannot be true for all experimental conditions. For example, Leyva-Ramos et al. (1995)²⁸ reported that their AC adsorbed over 99% of the Cr(III) initially present in a pH 5 solution and that significant removal also occurred at higher and lower pH values: above pH 6.4, Cr(III) precipitated from solution in their systems. In addition, Leyva-Ramos et al.²⁸ reported that the adsorbed Cr(III) appeared to be

irreversibly bound to the AC. Clearly then, quantifying Cr(VI) reduction by only measuring Cr(III) solution concentrations can lead to a large underestimation of the true importance of reduction in some AC systems.

The objectives of this study were to (i) determine if chemical pretreatment of the GAC can improve its adsorption/reduction capacity, (ii) investigate potential adverse effects of dissolved oxygen (DO) on these reactions, and (iii) evaluate potential regeneration methods after the AC capacity for chromium has been exhausted.

METHODOLOGY

Materials

Granular activated carbon (GAC), F400 (Calgon Corp.), was used in this study. The physical properties and specifications as reported by Karanfil (1995)³⁰ are shown in Table 1. To obtain consistent experimental

Table 1. Typical physical properties/ specifications of granular activated carbon (GAC).

Name and Manufacturer	Filtrisorb 400/ Calgon Carbon
Total Surface Area [m ² /g]	941
Iodine Number, min.	1000
Pore Volume [cm ³ /g]	0.536
Abrasion Number, min.	75
US Standard Sieve Size	12*40 (1.68*0.42 mm)
Ash Content [%]	6.72
Base Material	Bituminous Coal

a: from Karanfil, 1995.

results, two particle size fractions (U.S. standard sieve 80/100 (177/149 μm) and 230/325 (62/44 μm : only to increase the adsorption rate)) were prepared for the column and batch experiments, respectively, by crushing and sieving random samples from one lot of F400 GAC. The fractions were washed with distilled, deionized water (DDW; Barnstead Nanopure) to remove fines, dried in an oven at 105 $^{\circ}\text{C}$ for 48 hours, and stored in a vacuum desiccator until use. For experiments under oxygen-limited conditions, the crushed and sieved GAC were transferred to an anaerobic chamber (Coy Products Inc., MI), 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 ultra-pure 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 aquarium 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 might have diffused through the PVC walls.

Artificial groundwater (AGW) solutions were prepared to simulate the concentrations of major ions expected in a typical aquifer. 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): initial Cr(VI) concentrations in the samples were nominally 2.083 mg/L (40 μM). $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (from Sigma, ACS grade) solution, prepared with oxygen-free DDW in the anaerobic chamber, were used to pretreat selected GAC samples. All other chemicals were reagent grade or better. Depending on the particular experiment, the pH was adjusted with various concentrations of H_2SO_4 , HCl , or NaOH .

Experimental Methods

Batch experiments, (a) GAC point of zero charge (PZC) determination. Carbon PZC values were determined by an equilibration method^{22,30}. One hundred-milligram GAC (230/325) samples were contacted with 20 mL of a 0.1 M KCl solution at different initial pH values in 30-mL polyethylene bottles for 60 hours. The PZC was determined from the solution whose initial pH did not change after this time.

(b) GAC pretreatment. Five grams (dry-weight) of oxygen-free (i.e., washed and dried in the anaerobic chamber) 230/325 carbon were transferred to a 1-L Erlenmeyer flask wrapped with aluminum

foil (to minimize photoreactions) for batch experiments. Because this GAC was only dried by the atmosphere within the anaerobic chamber, moisture contents were determined for representative subsamples by drying in an oven at 105°C for 24 hours; this determination gave a moisture content of 18.3 for F400. Oxygen-free DDW (175 mL) was added to the flask followed by 25 mL of a 20-mM reductant (Fe(II)) solution to obtain 0.1 mmole-reductant/g-AC. After contacting for 24 hours with intermittent agitation, the supernatant was removed and the AC was rinsed with oxygen-free DDW (200 mL) for two hours. The supernatant rinse was then removed and the washing procedure was repeated an additional four times. To check the remaining amount and the loss of the reductant during this procedure, all decanted aliquots were collected and analyzed. After the fifth wash, the wet AC was transferred to 40-mL amber vials with lead foil-lined 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 the rate experiments, all pretreated AC amounts are reported on a dry-weight basis. For column experiments, 80/100 carbon samples (prepared and stored in the anaerobic chamber) were transferred to 1-L Erlenmeyer flasks and corresponding oxygen-free DDW and reductant solutions were added to obtain 0.1 mmole-reductant/g-AC. All other procedures were

identical to those for the batch experiments.

(c) Rate experiments. Cr(VI) removal by AC was studied 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 2.083 ± 0.016 mg/L ($40.0 \pm 0.3 \mu\text{M}$). The GAC dose was 1.000 g/L for the pH-controlled (pH 4 and 7.5) experiments using virgin AC and varying AC doses were used in the pretreated GAC experiments. In addition, 2-L Erlenmeyer flasks were used in uncontrolled pH experiments which initially contained 1500 mL AGW, $40 \mu\text{M}$ Cr(VI) and 2.000 g GAC at initial pH values of 3.93 or 8.15. For initial pH values of 4 and 5, a 1.000-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.

(d) Isotherm experiments. A bottle-point technique was used to investigate the Cr(VI) removal capacity of virgin GAC at two initial pH values (pH 4 and 7.5) in the presence and absence of DO. Forty-milliliter

amber glass vials with Teflon-lined caps were used for the CMBRs. GAC doses ranged from 0.01-0.25 g/L and 1.6-3.5 g/L for initial pH values of 4 and 7.5, respectively. A Cr(VI) solution was then transferred to the vials: the volume added was determined gravimetrically. The vials were tumbled for 3 days to ensure equilibration before filtering the samples through 0.2- μ m membrane filters and analyzing for Cr(VI). For oxygen-limited experiments, all preparation procedures were conducted in the anaerobic chamber. Before removing the vials from the chamber, lead foil tape was used to line the caps, which minimized oxygen diffusion through the caps. These samples were also tumbled for 3 days before returning them to the anaerobic chamber where they were opened, filtered and prepared for analysis. Note that all pH values reported for the isotherm experiments are initial values only.

Column Experiments. Continuous flow experiments were conducted using glass columns (10 \times 1cm ID). For each experiment, two columns were placed in series which provided for empty bed contact times (EBCTs) of 8.34 and 11.14 min for flowrates of 113.0 and 84.6 mL/hr, respectively. All columns were packed with 5.20 g of the appropriate 80/100 GAC. The apparent density and porosity of F400 GAC were determined to be 0.545 g/cm³ and 0.701, respectively. A three-gallon polyethylene bottle was used as the influent reservoir and peristaltic pumps (Masterflux) were

used to feed the columns. The influent AGW contained 2.083 ± 0.005 mg/L (40.0 ± 0.1 μ M) Cr(VI) and was maintained at a pH of 7.5 ± 0.1 throughout each run. Effluent samples were collected periodically for 10 min from the end of the second column and analyzed for Cr(VI); 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 extraction methodologies were developed in batch reactor systems. To extract Cr(VI) sorbed on GAC, the extractions were performed in 40-mL amber glass vials or 100-mL amber bottles as appropriate. Chromium-containing GAC samples were centrifuged to reduce their water content and then transferred to extraction vials/bottles. 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. Each sample was tumbled for 24 hours before filtering the extract solution through a 0.2- μ m membrane filter and analyzing for Cr(VI) and total dissolved chromium. 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.

Based on the batch extraction results, a 0.01M K_2HPO_4 solution was selected for extracting the GAC in column tests. GAC regeneration was conducted *in situ* by feeding extract solutions through the exhausted carbon columns. Washing of the GAC, to remove precipitated/sorbed Cr(III), immediately followed the extraction by feeding five bed volumes (BVs) of DDW or 0.02 N H_2SO_4 through the columns at the end of each regeneration and before the next sorption run. Filtering of the column extract and wash solutions before analyzing for Cr(VI) and total dissolved chromium proved to be unnecessary.

Analytical Methods

Aqueous Cr(VI) concentrations were determined by the diphenylcarbazide method³⁶⁾. 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 μ M (~4.0 mg/L). For the GAC samples that were extracted, Cr(VI) determinations were performed on the extract and wash solutions before and after oxidation with $KMnO_4$ as recommended in Standard Methods (1995)³⁶⁾ for determining total dissolved chromium concentrations. Dissolved Fe(II) concentrations were determined by the ferrozine method²⁹⁾ 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 GAC studied in this investigation (Fig. 1), in agreement with the observations of previous researchers²³⁻²⁷⁾. Fig. 1 shows Cr(VI) concentration profiles with time for experiments in which the pH was controlled (shadowed triangles and circles) or not controlled (filled triangles and circles) during the study (i.e., pH values shown are initial values prior to adding GAC). In controlled pH conditions, Cr(VI) removal generally reached its limit within 1.5 days, and blank solutions without GAC at pH 3.93 and 7.56 showed no significant changes in Cr(VI) concentration over this time period. Cr(VI) removal rates were relatively fast, with over 80% of the total

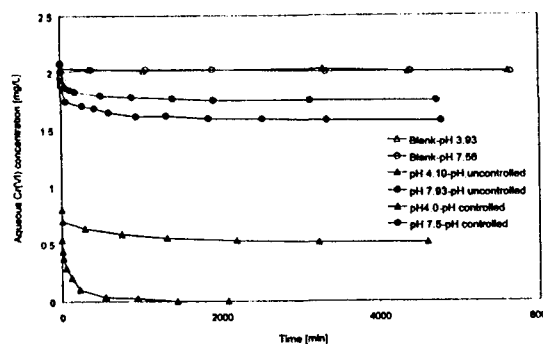


Fig. 1. Rate experiments in oxygenated system

amount of Cr(VI) being removed within 8 hours. In addition, removal rates at lower pH values appeared faster than those at higher pH values. Most importantly, it is readily apparent that the total amount of Cr(VI) removed by GAC increased as the initial solution pH decreased.

For the systems in which the pH was controlled, overall removal rates were faster than for the uncontrolled pH systems. For example, although the respective Cr(VI) concentrations at the first observation points appear to be similar at pH 4, the times to reach 75% removal (i.e., 0.5 mg/L residual Cr(VI)) were approximately 5 and 1000 minutes for the pH-controlled and pH-uncontrolled systems, respectively (Fig. 1). Even more importantly, the total amount of Cr(VI) removed by the GACs was greater in the pH-controlled experiments than in the uncontrolled experiments for similar starting pH values. This observation is consistent with the fact that inorganic anions such as HCrO_4^- and CrO_4^{2-} adsorb less as pH values increase¹⁹⁾ and with the expectation that an AC will raise solution pH values up toward its PZC in systems that have relatively-low buffering capacities. In fact, this latter expectation was confirmed in the pH-controlled experiments which required periodic additions of acid to maintain the values. All experiments conducted in this study utilized pH values below the PZCs of the carbon, which it was measured to be approximately pH 9.5 to 9.6, comparable with previous reports^{21, 22, 30)}.

The pH trends observed in the rate experiments were confirmed in select isotherm studies, as shown in Fig. 2 for representative Cr(VI) isotherms with F400. To create the isotherms shown, the amount of Cr(VI) removed from solution (i.e., typically referred to as the *sorbed* amount) was calculated from the difference between initial and final Cr(VI) solution concentrations. It is important to note that this type of analysis cannot be used to determine unambiguously whether the removal is only due to adsorption onto GAC surfaces or instead results from a combination of adsorption plus chemical reaction (e.g., reduction of Cr(VI) to Cr(III)). Table 2 reports the quantitative isotherm results for initial pH values of 4 and 7.5. All isotherm datasets were relatively well-fit ($R^2 > 0.95$) by the nonlinear Freundlich equation $q_e = K_F C_e^{1/n}$, where q_e (mg/g) is the GAC-normalized mass of Cr(VI) removed from solution at equilibrium; C_e (mg/L) is the Cr(VI) concentration remaining in solution at

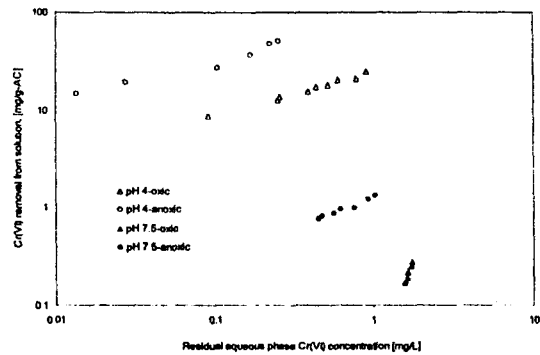


Fig. 2. Cr(VI) removal in the presence/absence of DO.

Table 2. Freundlich constants for Cr(VI) removal by virgin GACs in the presence/absence of DO

Conditions		N	K_F	1/n	R^2
oxic	pH 4	9	24.5 (23.2-26.0)	0.444 (0.394-0.494)	0.99
	pH 7.5	6	0.028 (0.018-0.044)	4.031 (3.131-4.911)	0.97
anoxic	pH 4	6	80.9 (57.0-115.0)	0.405 (0.275-0.534)	0.95
	pH 7.5	6	1.25 (1.16-1.37)	0.646 (0.490-0.860)	0.96

N equals number of data points.

Units of K_F are [(mg/g)(mg/L)^{-1/n}] and 1/n is dimensionless.

Values in parentheses are 95% confidence intervals.

equilibrium: and K_F [(mg/g)(mg/L)^{-1/n}] and 1/n (dimensionless) are empirical Freundlich isotherm parameters. The decrease in Cr(VI) removal with increasing pH can be readily seen by the location of the curves in Fig. 2: this trend is also evident when comparing the Freundlich capacity parameter, K_F , whose values at pH 7.5 are much smaller than at pH 4 for the respective GACs (Table 2). In contrast to K_F , 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^{31,32}, had higher values at pH 7.5 than at pH 4, particularly for the oxygenated systems.

Dissolved Oxygen Effects

Fig. 2 and Table 2 also show the effects of DO on Cr(VI) removal from solution by F400. In all cases, Cr(VI) removal was greatly enhanced when oxygen was effectively excluded from the GAC systems. For example, K_F values for the experiments

conducted under oxygen-limited conditions are three to four times larger than for those conducted under oxygenated conditions at pH 4 (Table 2 and Fig. 2). At pH 7.5, the presence of DO has an even larger effect on K_F values. Upon examining the other Freundlich parameter, 1/n, it is readily apparent that the oxygenated isotherms have larger values than the respective anoxic ones, particularly at pH 7.5.

As discussed above, it is not possible to determine whether the removal of Cr(VI) as shown in Fig. 2 results from a combination of reactions or only from its adsorption onto GAC surfaces. However, the experiments conducted under anoxic conditions would have been more favorable for promoting reduction reactions. For example, the carbon used in the oxygenated 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 anoxic 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 surface³³, 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 oxygen-limited conditions is that reduction of Cr(VI) to Cr(III) occurs in the absence of oxygen (i.e., Karanfil et al., 1994; Vidic et al., 1993)³⁰⁻³⁷. Alternatively, the observed reduction in Cr(VI) removal in oxygenated systems may merely be a result of oxygen sorbing to GAC surfaces and lowering their effective PZC values, thus making the overall electrostatic attractions between the surfaces and Cr(VI) anions less favorable.

Pretreatment Effects

The effects of different pretreatments that were intended to increase the reduction capacities of the GAC were evaluated. The specific reductants investigated were dithionite and Fe(II); these were selected because of their excellent performance for Cr(VI) removal in Batchelor and his coworkers' previous tests with soils and aquifer materials³¹. The GAC 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 anaerobic DDW and the presence of reductants in the wash water was 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 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.

Fig. 3 shows 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

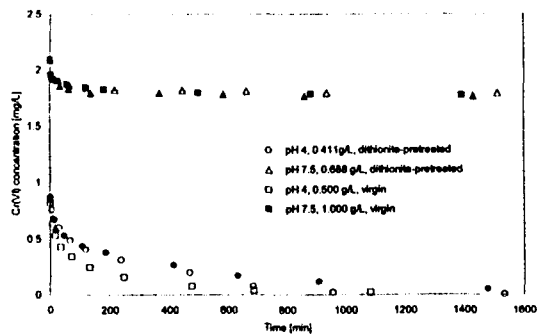


Fig. 3. Cr(VI) removal rates for virgin and dithionite-pretreated ACs

Cr(VI) reaction vessels after the centrifuged pretreatment vials (lined with lead foil tape) 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 dithionite-pretreated carbons, Cr(VI) concentrations initially decreased very rapidly and thereafter continued to decrease slowly over times longer than 1 day (1440 min, Fig. 3). The pH effects were similar to those observed for the virgin carbons: although the dosages at pH 4 were approximately one-third those at pH 7.5, the amount of Cr(VI) removed from solution was much greater. Similar results were observed for the carbon pretreated with Fe(II). Upon comparison with the virgin GAC, however, pretreatment by Fe(II) or dithionite did not significantly improve the sorption properties. In fact, pretreatment generally hindered Cr(VI) removal.

The adverse effects of carbon

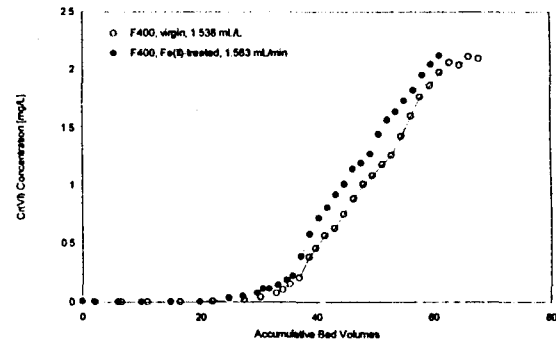


Fig. 4. Column experiments with virgin and Fe(II)-pretreated GACs

pretreatment can also be observed in Fig. 4, which 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 (BVs) and complete breakthrough occurred at 60 to 70 BVs. The amounts of Cr(VI) removed by virgin and Fe(II)-pretreated GACs were 0.1520 and 0.1423 mg/g, respectively. Similarly to the results obtained in batch rate 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

The GAC pretreatment results observed here contrast greatly with Batchelor and his coworkers' previous observations for soils and aquifer materials:³⁴⁾ pretreatment of the materials with dithionite and, particularly, Fe(II) greatly enhanced Cr(VI) removal from solution. Evidently, pretreatment of

GAC with these reductants does not result in the same reactions that occurred with the 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 redox 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 soils and aquifer materials.

GAC Regeneration and Cycling

Based on Batchelor and his coworkers' previous results for soils and aquifer materials³⁴, the feasibility of extracting Cr(VI) from GAC surfaces was first studied using 0.1 M K₂SO₄ in batch systems. Without any pH adjustments, it was observed that only 4 to 6% of the Cr(VI) removed from solution at pH 4 could be extracted (results not shown). Extraction recoveries with 0.01 M K₂HPO₄ were much higher (e.g., 18 to 20% for the same GAC sample and conditions). These rather low recoveries were not too surprising because of the long contact time used (i.e., 10 days) and because the pH of the extract solutions was not adjusted; it was first expected that

these contact conditions would promote reduction of Cr(VI) to Cr(III), and that Cr(III) would only be effectively removed from the GAC surface by contacting with an acidic solution. Based on these batch results, K₂HPO₄ was selected as the extractant to be used for all subsequent column regeneration experiments. Extraction by concentrated NaOH solutions (i.e., pH > 12) was not attempted because of the potential for Cr(III) oxidation to Cr(VI) in the presence of oxygen^{13,35}.

To test the cycling and performance of regenerated GAC (i.e., those previously saturated with Cr(VI) and then extracted and washed), virgin GAC with no pretreatment was used. Stage A in Fig. 5 shows the Cr(VI) breakthrough for the first run (i.e., virgin F400). As was observed in Fig. 4, Cr(VI) breakthrough began at approximately 23 BVs and the carbon was completely saturated within 55 BVs. The small differences between the two

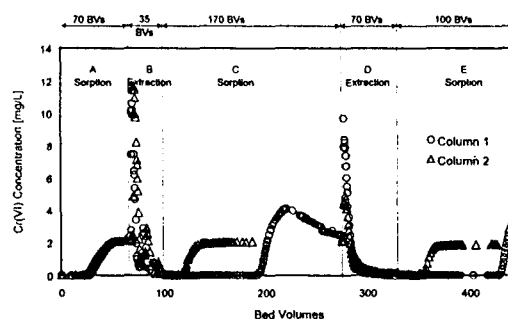


Fig. 5. Column experiments for sorption/extraction: A-1st sorption; B-1st extraction; C-2nd sorption; D-2nd extraction; E-3rd sorption

Table 3. Cr(VI) amounts [all in mg/g-AC] removed from solution and recovered during column runs with F400 GAC (Figures 5(a)-(e))

Column		Total Cr(VI) removed from solution	Cr(VI) extracted w/ K ₂ HPO ₄	Cr(VI) ^a in acid wash	Cr(VI) ^a in water wash	Extraction recovery [%]
1 st run	Column 1 (virgin GAC)	0.1067	0.0947	< MDL ^b	—	88.8
	Column 2 (virgin GAC)	0.1144	0.0999	—	< MDL	87.3
2 nd run	Column 1 (acid washed)	0.1650 (0.2930) ^c	0.0841	0.0006 ^d	—	51.3
	Column 2 (water washed)	0.0714	0.0562	—	< MDL	78.7
3 rd run	Column 1 (acid washed)	0.2813 (0.2930) ^c	—	—	—	—
	Column 2 (water washed)	0.0752	—	—	—	—

^a After oxidation with KMnO₄ (Standard Methods, 1995). ^b Below method detection limit.

^c Value shown in parentheses is for initial carbon exhaustion (see text).

^d Coefficient of variation from multiple measurements was 16.7%.

breakthrough curves are most likely a result of experimental variability (e.g., small differences in column packings, slightly different flowrates). After the carbon was exhausted, the influent was switched to a 0.01 M K₂HPO₄ solution to extract adsorbed Cr(VI). Stage B in Fig. 5 shows the results of the Cr(VI) extraction. The first Cr(VI) extraction peak appeared within 10 BVs, reaching a maximum concentration of approximately 12 mg/L at 3 BVs, and then rapidly decreasing. Flow interruptions at approximately 13 to 14 BVs and then again at approximately 20 to 25 BVs showed that the extractions (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 by the GAC during the first run was 0.1067 and 0.1144 mg/g for columns 1 and 2, respectively (Table 3). The measured Cr(VI) extracted from the GAC in the first extraction was 0.0947 and 0.0999 mg/g for columns 1 and 2, respectively (i.e., extraction recoveries of 88.8 and 87.3%, respectively). Before the subsequent runs, column 1 underwent an acid wash and column 2 underwent a wash with DDW as described in the experimental section. Cr(VI) concentrations in all wash solutions (0.02 N H₂SO₄ and water, respectively)

before and after oxidation with KMnO_4 were below the detection limit. For the water wash, this result indicated that DDW 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, it may have actually promoted some additional Cr(VI) removal from solution with respect to the Cr(VI) influent solution (i.e., pH of 7.5 ± 0.1). As shown previously, lower pH values favor Cr(VI) removal by GAC. For the acid wash, this pH difference would have had an even more dramatic effect on Cr(VI) removal. However, the lack of chromium in the acid solution after oxidation with KMnO_4 would appear to indicate that no Cr(VI) reduction to Cr(III) occurred in the columns during the initial run. Alternatively, it could indicate that 0.02 N H_2SO_4 is not an effective extractant for Cr(III) in our systems (however, see discussion below).

After the extractions and washes were performed, the regenerated GACs were used in a second run (Stage C in Fig. 5). The column containing the water-washed GAC (i.e., column 2) showed a Cr(VI) breakthrough that initiated at approximately 8 BVs. This breakthrough was much earlier than that observed for the virgin carbon (~23 BVs). The amount of Cr(VI) removed from solution by the GAC 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 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 BVs). 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 BVs) and of approximately 2.7-fold based on the amount of Cr(VI) removed from solution before the carbon capacity had been exhausted. For this latter calculation, the GAC in column 1 was considered to be exhausted at 96 BVs (i.e., when the effluent Cr(VI) concentration first reached the same concentration as the influent solution). In Table 3, the values in parentheses are the Cr(VI) amounts removed from solution at this point, whereas the first values shown are the integrated amounts at the end of the run. The appearance of effluent Cr(VI) concentrations above the influent solution concentration results from the gradual increase in pH that occurs in the column as the solution passes through it. This pH increase results in the release of some previously-adsorbed Cr(VI), consistent with our pH results previously shown.

Stage D in Fig. 5 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 an interesting contrast between

columns 1 and 2 (Table 3). The decrease in extraction recoveries 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 on the acidic GAC surface. The presence of a slight amount of chromium in the acid wash solution after oxidation would be consistent with the first scenario (i.e., Cr(III) extraction by acid, oxidation to Cr(VI) by KMnO_4 and measurement as Cr(VI) by the diphenylcarbazide method).

Stage E in Fig. 5 shows the third GAC column runs. Initial Cr(VI) breakthrough in the water-washed column (~ 3 BVs) was even earlier than that 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). However, it should be noted that the total amount of Cr(VI) removed before the GAC capacity was exhausted was similar to that observed in the second run (Table 3). Breakthrough for the acid-washed column began at approximately 83 BVs 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 can be completed with this operation before the GAC performance would suffer deleterious effects.

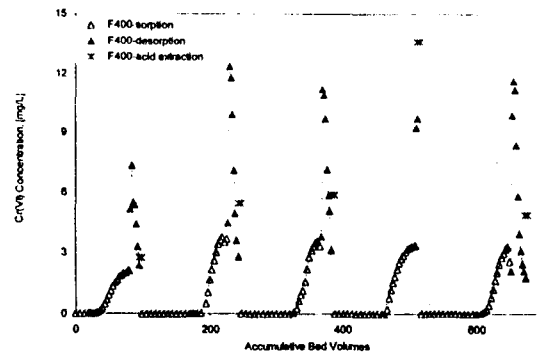


Fig. 6. GAC column regeneration and cycling

Fig. 6 and Table 4 show the results of five cyclings of sorption, phosphate extraction, and acid washes to validate the results in Fig. 5. Flowrates were 1.651 to 1.719 mL/min for F400. To better simulate an actual regeneration scheme, because the volume of extractant was somewhat large (about half of treated water volume to extract almost completely) as were shown in Fig. 5, phosphate extractions were performed only until the Cr(VI) concentrations fell below 2 mg/L, with the exception of the fourth extraction which was stopped even earlier. After all

Table 4. Cr(VI) amounts [all in mg/g-AC] removed from water, extracted and present in acid washes during cycling tests

	Cr(VI) _{removed}	Cr(VI) _{extracted}	Cr(VI) _{acid wash}
Run 1	0.1752	0.1064	0.0174 ± 0.0005
Run 2	0.2875	0.1782	0.0346 ± 0.0014
Run 3	0.2715	0.1701	0.0372 ± 0.0017
Run 4	0.2513	0.0563	0.0864 ± 0.0023
Run 5	0.3307	0.1947	0.0318 ± 0.0065

* Cr(VI) concentration after oxidation

extractions, the GACs were washed with 4.2 to 4.3 BVs of 0.02 N H₂SO₄. Because chromium determinations were only made for the combined acid washings, they are shown as single data points in Fig. 6. In general, about 70% of the total amount of Cr(VI) removed from solution in a run was recovered in the extract and/or wash solutions (Table 4); recoveries were slightly lower (50 to 60%) for the fourth run when the extractions were stopped earlier, which suggests that errors in our recovery calculations may actually be underreporting the true recoveries. From Fig. 6 and Table 4, it is readily evident that regeneration of the GACs using a phosphate extraction followed by acid washing enhances subsequent removal of Cr(VI) from water. In addition, it is also apparent that GAC performance remains relatively stable, as observed from a comparison of Cr(VI) removal in the last four cycles.

Fig. 7 shows Cr(VI) concentrations in the acid wash solutions before and after treatment with KMnO₄. Any Cr(VI)

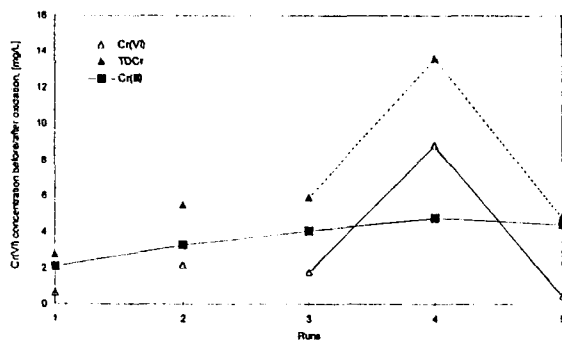


Fig. 7. Chromium concentrations in the extraction acid

observed before treatment with the oxidant is merely a result of the incomplete phosphate extraction procedure used in the cycling studies as discussed above. These values tended to be less than 2 mg/L, with the exception of the fourth acid wash which had almost 10 mg/L Cr(VI) present; this latter concentration resulted because the fourth phosphate extraction was halted earlier than the other extractions. Differences in Cr(VI) concentrations measured before and after oxidation, however, clearly indicate that some reduction of Cr(VI) occurred in the GAC columns. Assuming that the differences in Cr(VI) concentrations before and after oxidation are due to the presence of Cr(III) species³⁶, it can then be seen that Cr(III) concentrations slowly increase as the number of cycles increase (Fig. 7, Table 5), probably due to an increasing contact time with the GAC surfaces. To our knowledge this is the first report of Cr(III) determinations in regenerated GAC systems, which provides convincing evidence that Cr(VI) reduction to Cr(III) has occurred in the presence of GAC. The presence of Cr(III) in the first acid wash solution (which followed the first phosphate extraction) lends credible evidence that Cr(VI) reduction is occurring prior to and/or during the acid introduction. Because Cr(III) concentrations in the acid wash solutions only increase slightly thereafter, it does not appear that the Cr(VI) reduction to Cr(III) is significantly impacted by any acid-

Table 5. Measured amounts [mg/g-AC] of Cr(VI) reduced to Cr(III) in cycling tests

	Reduced amounts of Cr(VI)
Run 1	0.013 ± 0.0011
Run 2	0.021 ± 0.0019
Run 3	0.026 ± 0.0026
Run 4	0.030 ± 0.0030
Run 5	0.029 ± 0.0064

catalyzed reactions at GAC surfaces.

SUMMARY AND CONCLUSIONS

Cr(VI) removal from an artificial groundwater (AGW) solution by granular activated carbon (GAC) was investigated as a potential remediation method for contaminated aquifers. Batch and continuous-flow column experiments were utilized to elucidate potential benefits and/or effects of pH, dissolved oxygen, and two GAC pretreatment schemes.

The effects of pH on Cr(VI) removal agreed well with previous studies, namely, that the removal is favored at lower pH values. Over the pH range investigated here, better performance occurred at pH 4 whereas the performance at pH 7.5 was significantly worse. Dissolved oxygen also played an important role in the removal of Cr(VI). For those studies performed in an anaerobic chamber to limit oxygen concentrations, the ability of the GAC to remove Cr(VI) from solution was greatly enhanced relative to oxygenated systems. It

is believed that this improvement resulted from the 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. Pretreatment of GAC with dithionite and dissolved Fe(II), however, did not improve its ability to remove Cr(VI) from AGW. These results are in contrast with Batchelor and his coworkers' previous observations³⁵ for soils and aquifer materials. For those materials, pretreatment with these reductants significantly enhanced their ability to remove Cr(VI) from AGW via reduction reactions.

The regeneration and cycling experiments conducted here provide promising alternatives to enhance the removal of Cr(VI) from groundwaters in GAC treatment systems. Approximately 88% of the Cr(VI) initially removed in columns could be extracted with 0.01 M K₂HPO₄ solutions. Following phosphate extractions with an acid wash (0.02 N H₂SO₄) enhanced the performance of GAC relative to that of the virgin carbons (~3-fold increase in Cr(VI) removal). It is believed that this increased performance results from two different phenomena: (1) the more favorable adsorption of Cr(VI) at lower pH values and (2) the reduction of Cr(VI) to Cr(III). The presence of Cr(III) in acid wash solutions provides direct evidence that Cr(VI) can be reduced to Cr(III) in GAC systems under relatively acidic conditions. Results from the cycling experiments

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 contaminated waters and that such a system will be able to reuse the regenerated carbon over many operation cycles without suffering adverse performance effects.

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