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Cr(VI) Removal from Aqueous Solution by Activated Carbon Coated with Quaternized Poly(4-vinylpyridine)

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A composite sorbent (GAC−QPVP) was prepared by coating poly(4-vinylpyridine) onto a granular activated carbon, followed by cross-linking and quaternization processes. The sorbent was characterized by scanning electron microscopy, point of zero charge measurement, and BET analysis. Batch experiments with variable pH, ionic strength, and concentrations of Cr(VI), sorbent, and competing anions were conducted to evaluate the selective sorption of Cr(VI) from aqueous solutions. The results showed that Cr(VI) sorption rates could be described by a reversible second-order kinetics, and equilibrium uptake of Cr(VI) increased with decreasing pH, decreasing ionic strength, and increasing sorbent concentration. The estimated maximum equilibrium uptake of chromium was 53.7 mg/g at pH = 2.25, 30.7 mg/g at pH = 3.65, and 18.9 mg/g at pH = 6.03, much higher than the maximum capacity of PVP-coated silica gel, an adsorbent for Cr examined previously. When compared with the untreated granular activated carbon, sorption onto GAC−QPVP resulted in much less Cr-(VI) reduction and subsequent release of Cr(III). The effect of phosphate, sulfate, and nitrate was minor on the selective sorption of Cr(VI). An ion exchange model that was linked with aqueous speciation chemistry described Cr-(VI) sorption reasonably well as a function of pH, ionic strength, and Cr(VI) concentration. Model simulations suggested that sorbed Cr(VI) was partially reduced to Cr-(III) on the sorbent when pH was less than 4. The presence of Cr(III) on the sorbent was confirmed by the X-ray photoelectron spectroscopic analysis. Overall, the study has demonstrated that GAC−QPVP can effectively remove Cr(VI) from aqueous solutions under a wide range of experimental conditions, without significant Cr(III) release associated with the virgin GAC treatment.

Introduction

Hexavalent chromium (Cr(VI)) exists in most aquatic environments as water soluble oxyanions, $HCrO_4^-$ or CrO_4^{2-}. Cr-(VI) species are known to be toxic and carcinogenic, and can cause health problems such as liver damage, pulmonary congestions, vomiting, and severe diarrhea (*2, 3*). Soil and water contamination of Cr arises from various industries including mining operation, metal plating, leather tanning, water cooling, and pigment manufacturing (*4*). Developing technologies to remediate past contamination and prevent further Cr discharge is needed.

The most common approach for Cr(VI) removal is through reduction of Cr(VI) to Cr(III), followed by Cr(III) precipitation under the alkaline condition (*5*). Other viable technologies include membrane separation, extraction, and sorption (*6*). To handle a large amount of aqueous solution with low concentration of Cr(VI), sorption-based processes are considered most cost-effective. Studies on Cr(VI) sorption by activated carbon (*7−12*), ion exchangers (*1, 13−15*), and biosorbents (*16−18*) have been reported. Of these, activated carbon is widely used because of its large specific surface area and multiple types of reactive surface sites. The interaction of Cr(VI) with activated carbon involves sorption of Cr(VI), reduction of Cr(VI) to Cr(III), and potential release of reduced Cr(III) back into the solution (*19*). At pH 5 or 6, sorption of Cr(VI) onto activated carbon dominates and reaches a maximum (*8, 20*). The apparent high sorption of Cr(VI) at lower pH (<3.0) is predominantly due to Cr(VI) reduction, and the produced Cr(III) species could be released back into solution (*7, 10*). Thus, the removal of chromium from waste streams will require subsequent pH adjustment and precipitation.

Recently, coating or grafting a synthetic or natural ion exchanger onto various sorbents, often followed by functionalization, has been used to improve the physical and chemical properties of a sorbent for contaminant removal (*21*). Common materials used as supports for composite sorbents include activated carbon (*22*), activated alumina (*17*), coconut husk (*23*), cellulose (*24*), and silica gel (*13*). Baes et al. (*25*) used modified coconut coir with secondary and tertiary amines for Cr(VI) removal from groundwater, though the efficiency was somewhat low. Quaternized poly-(4-vinylpyridine) has a higher affinity to metal anions since, after quaternization, the electron-deficient pyridine ring renders the pyridyl-N more attractive to anions than amine-N. Gang et al. (*1*) demonstrated that the quaternized poly-(4-vinylpyridine)-coated silica gel had a relatively high selectivity for Cr(VI) and the sorbent could be readily regenerated, but the maximum sorption, occurring at pH 5.0, was only 3.5 mg/g.

In this study, we developed an activated carbon supported quaternized poly(4-vinylpyridine) sorbent (GAC−QPVP) for efficient Cr(VI) removal from aqueous solutions and investigated the sorption equilibrium and kinetics through batch experiments and modeling. The granular activated carbon was selected as the supporting medium because of its high chemical stability, mechanical robustness, large specific surface area, and easy availability. Polymeric molecules, with both hydrophobic groups and ionic moieties capable of ion-exchange and ion paring, are known to sorb contaminants such as perchlorate, chromate, and arsenate (*26, 27*). Coating of the quaternized poly(4-vinylpyridine) onto the activated carbon was therefore expected to remove Cr(VI) more efficiently than the silica-gel-based adsorbent. Because of the dominating ion exchange mechanism for Cr(VI) uptake by the quaternized poly(4-vinylpyridine) coating, there was less Cr(VI) reduction under acidic pH conditions, preventing releases of Cr(III) species back into solution.

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Experimental Section

Materials. All solutions were prepared with distilled and deionized water with 18 MΩ cm resistivity (DDW, Millipore Co.). Granular activated carbon (F400) was obtained from Calgon Carbon Corporation. Hydrochloric acid, sodium nitrate, sodium sulfate, sodium bicarbonate, sodium acetate, potassium dichromate, potassium chromate, dipotassium phosphate, potassium dihydrogen phosphate, diphenylcarbazide, and chloroform were obtained from Fisher Scientific, and 4-vinylpyridine (95%), cumene hydroperoxide (80% purity), 1,4-dibromobutane, 1-bromohexadecane, sodium azide (NaN$_3$), and potassium permanganate were purchased from Aldrich-Sigma Chemical. All chemicals were of ACS reagent grade and used as received, except 4-vinypyridine (95%) which was purified by vacuum distillation prior to use. The stock solution of 1000 mg/L Cr(VI) was prepared by dissolving potassium chromate in deionized water.

Preparation of the Quaternized Poly(4-vinylpyridine)-Coated Granular Activated Carbon (GAC−QPVP). The reactive polymer, poly(4-vinylpridine) (PVP), was synthesized by bulk polymerization of purified 4-vinylpyridine initiated by cumene hydroperoxide [0.5% (w/v)] at 55 °C, following a procedure previously used by Gang et al. (*1*; Figure S1 in the Supporting Information). PVP (15 g) was dissolved in 500 mL of chloroform and then mixed with 50 g of granular activated carbon (GAC) with a paddle stirrer for 12 h. The polymer-coated GAC (GAC−PVP) were collected and washed with methanol for several times, and dispersed in 300 mL of methanol. The cross-linking reagent, 1,4-dibromobutane, was then added to the extent of 50% the amount required for polymer cross-linking (15 g), and the mixture was stirred at 65 °C for 48 h in a slow current of nitrogen. After being washed with deionized water and methanol, the mixture reacted with 1-bromohexadecane in 300 mL of methanol at 65 °C for 48 h to obtain a long alkyl chain quaternary ammonium compound. The 1-bromohexadecane (87 g) was added to the extent of 200% the amount required for reaction with all ammonium atoms on the pyridine rings. The prepared quaternized poly(4-vinylpyridine) coated GAC (GAC−QPVP) was filtered, washed with methanol and deionized water, air-dried, then stored at room temperature prior to use.

Characterization of GAC−QPVP. The prepared GAC−QPVP sample and original GAC were characterized for surface morphology by scanning electron microscopy (SEM) using a field emission scanning electron microscope (Hitachi S-4700). Surface area, pore volume, and porosity of the sorbents were measured by sorption of ultrapure nitrogen at −196 °C on a PMI Automated Brunauer−Emmett−Teller (BET) Sorptometer (Porous Materials, Inc.). The pH values at the point of zero charge (pH$_{pzc}$) for both virgin GAC and GAC−QPVP samples were measured using the pH drift method (*28, 29*).

Batch Experimental Systems. All batch reactors were placed on a shaker at 200 rpm under controlled temperature of 24 ± 1 °C. Ionic strength was controlled at 0.10 M by NaCl unless otherwise noted.

Sorption kinetics were conducted to assess both the rate of Cr(VI) sorption and the equilibrium time required to obtain the sorption isotherm. The experiments were performed under conditions of variable pH (2.31−6.20) and initial Cr(VI) concentrations (4.50−18.12 mg/L). In each test, 20.0 mg of sorbent was weighed into 50-mL glass bottle, followed by addition of 20.00 mL of Cr(VI) solution, resulting in a sorbent loading of 1.00 g/L. At each predetermined time point, a 3 mL solution was collected, filtered (0.2 μm Nylon membrane, Fisher Scientific), and analyzed for Cr(VI).

Sorption isotherms were measured at various pHs and GAC−QPVP loadings of 1−10 g/L. The solution pH was controlled at 2.25 by HCl but higher pHs were controlled by acetate buffer (0.01 M [Ac$^-$]$_T$). Preliminary tests showed that acetate buffer could slightly decrease Cr(VI) sorption, but the change was always less than 4%. After 24 h of equilibrium, the suspension was sampled and filtered, and the filtrate was analyzed for Cr(VI). The sorption density of Cr(VI) onto the sorbent, q_e, was calculated by

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where C_i and C_e are initial and equilibrium concentrations (mg/L), respectively; M is the dry mass of the GAC−QPVP (g); and V is volume of the solution (L).

Effects of pH and ionic strength on Cr(VI) sorption by GAC−QPVP were evaluated in comparison with its sorption onto virgin GAC. The solution pH was controlled with HCl or NaOH and the final pH was recorded as the equilibrium pH. Ionic strength was maintained at desired values using sodium chloride solutions. Initial Cr(VI) (10.0 mg/L), sorbent loading (1.00 g/L), and temperature (24 ± 1°C) were kept constant.

Effects of sorbent loading and competing anions were also examined. The sorbent loading varied from 1.00 to 7.00 g/L. Competing anions included nitrate, sulfate, and phosphate at concentrations of 0.100, 1.00, or 10.0 mM, while initial Cr(VI) concentration was set at 0.19 mM (10 mg/L), ionic strength at 0.10 M (by NaCl), and pH at 3.70 (by 0.01 M acetate buffer).

Analytical Methods. Cr(VI) was determined by a modified diphenylcarbazide colorimetric method (*30*) with a detection limit of 0.10 μM (or 0.005 mg/L as Cr). Total Cr, including
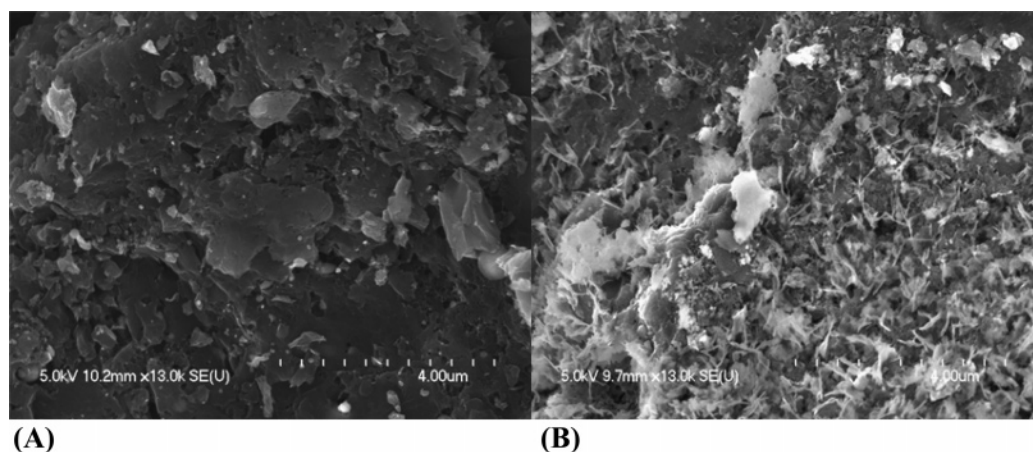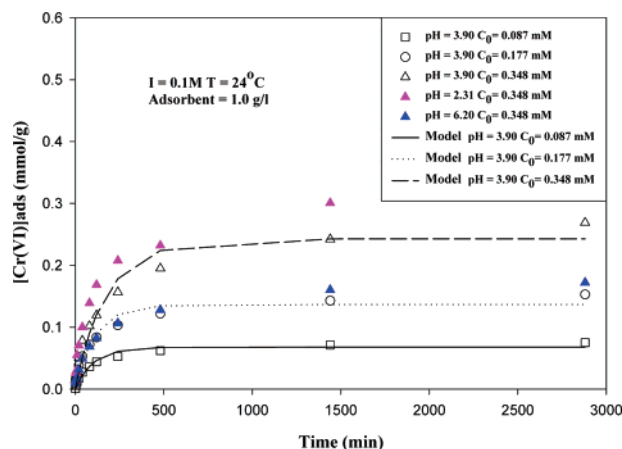

FIGURE 1. SEM micrographs of the virgin GAC (A) and GAC−QPVP (B).

FIGURE 2. Observed kinetics of Cr(VI) sorption onto GAC−QPVP at different initial Cr(VI) concentrations and pH values (dots) and modeling results based on a reversible second-order kinetics (lines).

both Cr(VI) and any produced Cr(III) species, was determined by first converting all chromium to Cr(VI) with potassium permanganate (KMnO$_4$) at high temperature (130−140 °C). Extra KMnO$_4$ was eliminated by adding NaN$_3$ to just disappearance of the purple color prior to total Cr analysis (*31*). X-ray photoelectron spectroscopy (XPS) analysis was conducted for the composite GAC−QPVP sorbent after exposure to Cr(VI) solution, using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe at Pacific Northwest National Laboratory.

Results and Discussion

Characterization of the GAC−QPVP. The measured BET surface area of virgin GAC (F400, H type) was 902 m^2/g, similar to the value reported by Karanfil (*32*), but lower than 1236 m^2/g reported by Corapcioglu and Huang (*33*). The quaternization and coating of poly(4-pyridine) on the activated carbon reduced the surface area to 68 m^2/g. Decreases in pore volume (from 0.684 to 0.082 cm^3/g) and porosity (from 0.406 to 0.076) were also observed. The SEM micrographs (Figure 1) show that there are considerable small cavities and attached fine particles over the virgin activated carbon surface, forming a system of complicated pore networks. After the coating and quaternization process, the polymers have deposited on the carbon surface and filled or covered most of the cavities. Changes in the pore volumes are therefore attributed to the successful coating of the poly-(4-pyridine) polymer onto the GAC surfaces, which filled/blocked most micropores. The average pore diameter increased slightly from 3.04 to 4.85 nm after coating, consistent with preferential blocking of micropores.

The pH$_{pzc}$ values were determined by plotting pHs of filtered solutions after equilibration (pH$_f$) with virgin GAC or GAC−QPVP versus initial solution pH (pH$_i$) (Supporting Information Figure S2). Previous studies showed that pH$_{pzc}$ of virgin GAC (F-400) was around 10.50 (*34*), therefore, the initial pH range to determine the pH$_{pzc}$ of virgin GAC in this study was set between 5.5 and 11.0. It was found that the pH$_{pzc}$ of virgin GAC was 9.8, comparable to the reported value (*34*). The pH$_{pzc}$ of GAC−QPVP in 0.10 M NaCl solution was 5.65. Such a decrease in pH$_{pzc}$ after the coating process indicated that protonated surface functional groups on the carbon were neutralized or blocked by the coated polymer layer.

Sorption Kinetics. As demonstrated by the observed Cr-(VI) uptake vs *t* profiles (Figure 2), under the same pH of 3.90, the rate and extent of Cr(VI) sorption onto GAC−QPVP increased with increasing initial Cr(VI) concentration from 0.087 to 0.348 mM. In systems with the same initial Cr(VI)
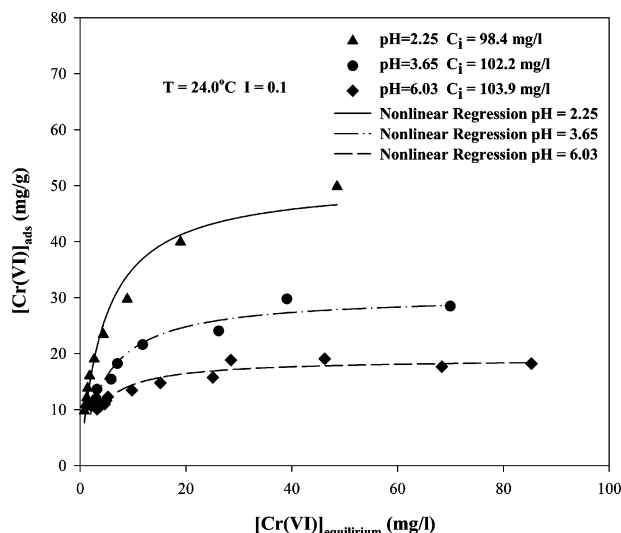
FIGURE 3. Comparison of the experimental results (symbols) and the model fits using Langmuir isotherms for the sorption of Cr(VI) on the GAC−QPVP at different pHs at 24 °C.

concentration of 0.348 mM, increasing pH values from 2.31 to 6.20 decreased the sorption rates and extents. The observed Cr(VI) sorption progressed and plateaued within 24 h. The sorption rate of Cr(VI) onto GAC−QPVP was somewhat slower than that onto the PVP-coated silica gel (*35*). Many characteristics of the sorbent might contribute to the slightly slower kinetics, including the particle size distribution, percentage of coated QPVP, and the more porous structure of GAC−QPVP compared to silica gel that might require a longer time scale for mass transfer.

A reversible second-order rate expression developed by Dzombak and Morel (*36*) was adopted here to describe the kinetics of Cr(VI) sorption onto the GAC−QPVP

$$\frac{d(\rho q_t)}{dt} = k_f[\rho(q_M - q_t)](C_0 - \rho q_t) - k_b(\rho q_t) \qquad (2)$$

where k_f (mM^{-1}min^{-1}) and k_b (min^{-1}) are the forward and reverse kinetic constants of sorption, ρ (g/L) is the ratio of sorbent and sorbate, C_0 is the initial Cr(VI) concentration, q_M (mmol/g) is the amount of binding sites on surface, which could be estimated from the maximum Cr(VI) uptake by sorbent using higher initial Cr(VI) concentration, and q_t is the amount of anion on the surface at time *t*. After some algebraic manipulation, eq 2 could be rewritten as

$$\frac{dq_t}{dt} = k_f q_M C_0 - [k_f(\rho q_M + C_0) + k_b]q_t + k_f \rho q_t^2 \qquad (3)$$

This differential equation was solved using a fourth-order Runge−Kutta method through a program, Scientist 2.01 (MicroMath Research), and k_f and k_b were determined by trial and error to enable the fits of data in Figure 2. The calculated rate constants at pH 3.90 fell within narrow ranges (4.0×10^{-3} to 7.5×10^{-3} for k_f; 1.4×10^{-3} to 2.0×10^{-3} for k_b) as the initial Cr(VI) concentration was increased from 0.0866 to 0.348 mM (Table S1).

Sorption Isotherms. As shown by Cr(VI) sorption isotherms onto GAC−QPVP (q_e versus C_e plots) at different pHs (Figure 3), sorption densities of Cr(VI) increased with increasing equilibrium Cr(VI) concentration and decreasing pH values. The Langmuir equation was applied to fit the experimental data using nonlinear regression. The estimated maximum uptake of chromium was 53.7 mg/g (1.03×10^{-3} mol/g), 30.7 mg/g (5.90×10^{-4} mol/g), and 18.9 mg/g (3.64×10^{-4} mol/g) at pH 2.25, 3.65, and 6.03, respectively (Table
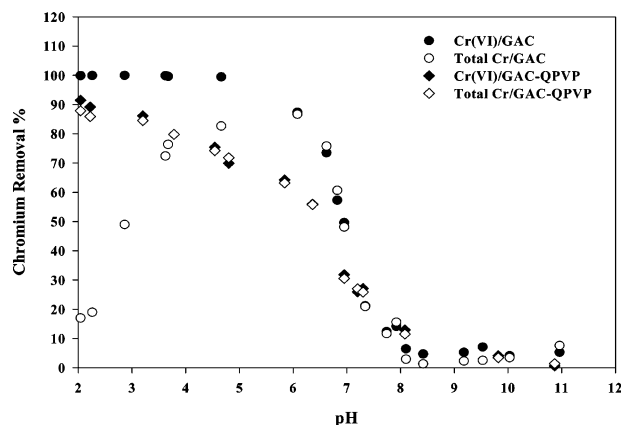
FIGURE 4. Effect of pH on the removal of Cr(VI) and total Cr on GAC and GAC−QPVP (Sorbent = 1 g/L; I = 0.1 M; Initial Cr(VI) = 10 mg/L).

S2). These values were significantly higher than the maximum sorption capacity of 3.5 mg/g (6.73 × 10⁻⁵ mol/g) for the PVP-coated silica gel at pH = 5.0 (optimal pH for Cr(VI) sorption onto this material) (1). Higher Cr(VI) sorption onto GAC−QPVP was observed at lower pH, so it was particularly suitable for Cr(VI) removal from acid solutions.

Effect of pH. Cr(VI) removal by GAC−QPVP and virgin GAC was measured in batch systems with pH values from 2 to 11 (Figure 4). Total soluble Cr, which includes not only Cr(VI) but also Cr(III) that could potentially be generated from Cr(VI) reduction, was also analyzed. As shown in Figure 4, for GAC−QPVP, the percentage removal of Cr(VI) was around 90% at pH = 2 but decreased with increasing pH. The sharpest decline occurred when pH increased from 6 to 8, and no apparent sorption was observed when pH was above 9. The total Cr removal was only slightly lower than that of Cr(VI), even in solutions of pH 2 in which Cr(III) was quite soluble, indicating that either no Cr(VI) was reduced or reduced Cr(III) was kept in the solid phase. Gang et al. (1) reported a similar pH dependence for Cr(VI) sorption onto PVP-coated silica gel.

In comparison, the apparent removal of Cr(VI) by virgin GAC was almost 100% at pH <5.0 and decreased dramatically to near zero at pH >8.0. However, the removal of total Cr in solution was identical to Cr(VI) removal only at pH >6.0. When pH <5.0, the percentage removal of total Cr was much less than that of Cr(VI) and decreased to approximately 17% at pH 2.0. Assuming that total Cr determined in the solution was the sum of Cr(VI) and Cr(III), the results indicated that the Cr removal was not completely due to Cr(VI) sorption; instead, a significant fraction of Cr(VI) was reduced to Cr-(III), which was then released into the solution at lower pH. A similar behavior for Cr(VI) removal by GAC was observed by Huang and Wu (7) and Imai and Gloyna (37).

Effects of Co-Existing Anions. The effects of nitrate, sulfate, and phosphate on Cr(VI) sorption were examined at three concentration levels (0.10, 1.0, and 10.0 mM) for each anion (Figure S3), where the molar ratios of the competing anions to Cr(VI), denoted as R_i, were 0.53, 5.3, and 53, respectively. At R_i = 0.53, the observed Cr(VI) sorption densities in the presence of NO_3^-, SO_4^{2-} and PO_4^{3-} were 7.72, 7.48, and 7.55 mg/g, respectively. Compared with the sorption density of 7.83 mg/g in the control, the anions demonstrated no significant effect. At R_i = 53, the sorption densities of Cr(VI) decreased to 6.94, 6.50, and 5.45 mg/g, respectively. It was therefore concluded that the anions could slightly reduce Cr(VI) sorption at high concentrations in the following order: PO_4^{3-} > SO_4^{2-} > NO_3^-.

Effects of Ionic Strength. The effects of ionic strength (I) on Cr(VI) sorption on GAC−QPVP is illustrated in Figure 5a. Two different I values, 0.1 and 1.0 M NaCl were used, and
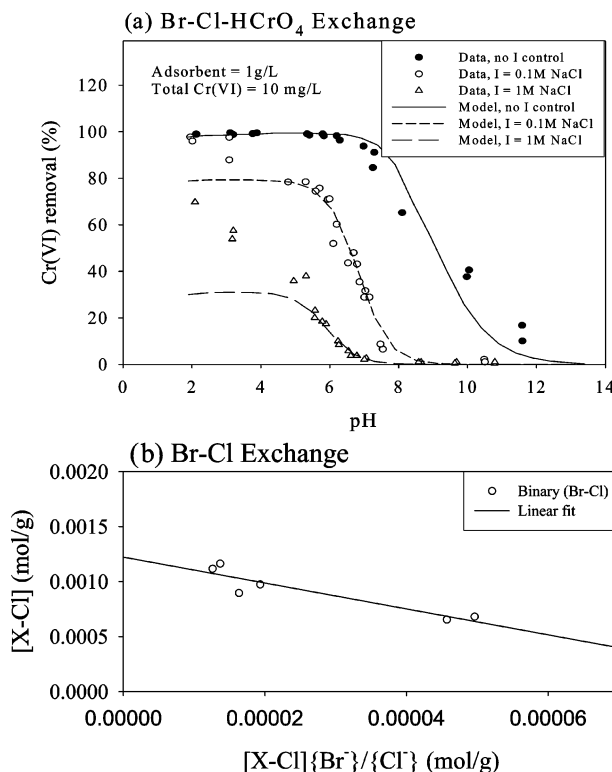

FIGURE 5. (a) Experimental data and model prediction of sorption behavior of Cr(VI) on GAC−QPVP as a function of ionic strength, and (b) ion exchange behavior in binary system between Br−Cl.

the results were compared with those obtained for GAC−QPVP with no I control (where ionic strength varied from 0 to 0.01 due to the addition of HCl and NaOH for pH control). An increase in ionic strength markedly lowered Cr(VI) sorption and shifted the position of pH edge to lower pH values (Figure 5a). The results indicated that Cr(VI) sorption was affected by ion exchange processes. The fixed charges on the sorbent were most likely contributed from the electron-deficient pyridine rings (1). Independent experiments were performed to investigate the exchange of Cl⁻ for Br on the sorbent (Figure 5b) and results were consistent with the following ion exchange reaction:

$$Cl^- + X{-}Br = Br^- + X{-}Cl \quad K_v(Br{-}Cl) \quad (4)$$
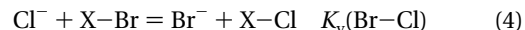
where X− denotes the sorbent site and K_v is the Vanselow selectivity coefficient.

Modeling Cr(VI) Sorption. Cr(VI) sorption, similar to other metals, could usually be attributed to ion exchange, surface complexation, and precipitation (38). Our experimental observations that ionic strength significantly affected Cr(VI) sorption (Figure 5a), Br⁻ release accompanied with the sorption of Cl⁻ (Figure 5b) and Cr(VI), and electron-deficient properties of the pyridine rings on the QPVP polymers (1), led us to construct an ionic exchange model to describe Cr-(VI) sorption to GAC−QPVP. Cr(VI) exists in several species such as $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ with dominant species depending on Cr(VI) concentration and pH values (12). These species could all participate in the ion exchange process. To simplify the ion exchange model and minimize the number of model parameters, we assumed the following reaction to represent the Cr(VI) exchange process:

$$X{-}Br + HCrO_4^- = X{-}HCrO_4 + Br^- \quad K_v(Br{-}HCrO_4) \quad (5)$$
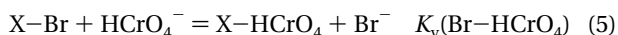
The Vanselow exchange coefficient (K_v) in reactions 4 and 5 can be expressed as

$$\frac{N_{\text{Cl}}\{\text{Br}^-\}}{N_{\text{Br}}\{\text{Cl}^-\}} = K_v(\text{Br} - \text{Cl}) \tag{6}$$

$$\frac{N_{\text{HCrO}_4}\{\text{Br}^-\}}{N_{\text{Br}}\{\text{HCrO}_4^-\}} = K_v(\text{Br} - \text{HCrO}_4) \tag{7}$$

where bracket {} denotes the activity in aqueous phase and N_A is the molar fraction of anion A in the exchange phase. The molar fraction was defined as

$$N_A = \frac{[X - A]}{AEC} \tag{8}$$

where $[X-A]$ is the molar concentration of A on the exchanger; and AEC is the anion exchange capacity. The reactions 4 and 5 were then built into an equilibrium speciation program, Minteqa2 (39), and were linked with aqueous Cr(VI) speciation reactions built in the Minteqa2 database to formulate an ion exchange model to describe Cr(VI) sorption.

We first used the model to fit the binary exchange data between Cl$^-$ and Br$^-$ (Figure 5b) to determine K_v(Cl−Br) and AEC. For the Cl−Br binary system, we have

$$[X - \text{Cl}] + [X - \text{Br}] = \text{AEC} \tag{9}$$

Combining eq 9 with eq 6 and after some algebraic manipulation, we obtain

$$[X - \text{Cl}] = \text{AEC} - \frac{1}{K_v(\text{Cl} - \text{Br})} \frac{[X - \text{Cl}]\{\text{Br}^-\}}{\{\text{Cl}^-\}} \tag{10}$$

Parameters AEC and K_v(Cl−Br) were then estimated by linear regression between [X−Cl] and [X−Cl]/{Cl$^-$} (Figure 5b). The best fitted log K_v (Cl−Br) was −1.07 and AEC 1.22×10^{-3} mol/g. The estimated AEC was close to, but slightly larger than, a value of 1.03×10^{-3} mol/g (Table S2), which was estimated from the Langmuir fit of the sorption isotherm at pH 2.25. The Cr sorption profile as a function of pH without ionic strength control (Figure 5a) was used to estimate parameter K_v(HCrO$_4$−Br). Because HCl or NaOH was used to adjust the pH in this experiment, a ternary exchange system (HCrO$_4$, Br, and Cl) was used to determine K_v(HCrO$_4$−Br). Parameters K_v(Cl−Br) and AEC that were determined from the binary Cl−Br exchange were fixed. A trial-and-error approach was used to fit K_v(HCrO$_4$−Br). Specifically, we tried a value for K_v(HCrO$_4$−Br), ran the Minteqa2 program to calculate Cr(VI) sorption, and estimated the errors between the calculated and measured Cr(VI) sorption. This process was repeated until the calculated best matched with the measured Cr(VI) sorption. The model well described the Cr(VI) sorption as a function of pH with a best fitted log K_v-(HCrO$_4$−Br) = 8.04.

The model with the estimated parameters was then used to predict Cr sorption as a function of pH in 0.1 and 1 M NaCl solutions (Figure 5a). The predictions matched data well above pH 5 at both ionic strength 0.1 and 1 M (Figure 5a). Below pH 4, however, the model under-predicted the observed uptake of Cr(VI) by the sorbent. The under-prediction increased with decreasing pH and increasing ionic strength with a maximum value of 18% at $I = 0.1$ M, and 35% at $I = 1$ M. The under-predictions suggested that the reactions other than reactions 4 and 5 on the sorbent also affected the Cr(VI) uptake.

To further understand the processes affecting the Cr(VI) sorption, the GAC−QPVP samples after reaction with Cr(VI) solution at pH around 2.0 for 24 h were analyzed with X-ray photoelectron spectroscopy (XPS). XPS results (Figure 6) showed two Cr2p$_{3/2}$ intensity peaks at 577.1 and 579.3 eV,
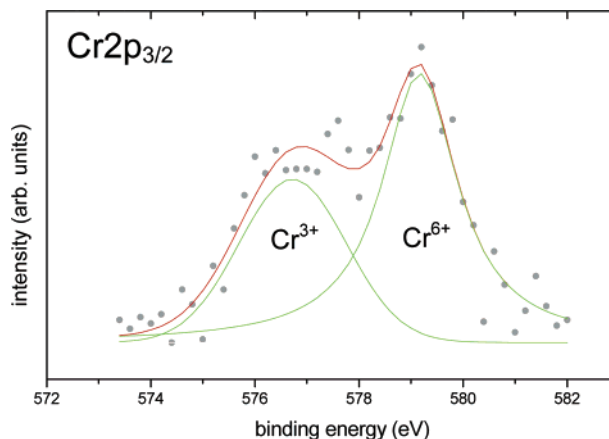
FIGURE 6. XPS spectra of GAC−QPVP sample after exposure to Cr(VI) solution for 24 h. Green lines represent the Cr(III) and Cr(VI) components. The red line is the fit envelope, and the solid circles show the data.

which are consistent with Cr(III) and Cr(VI), respectively. Best fits to the data were obtained by using a Gaussian for Cr(III) and a Voigt for Cr(VI). Slow reduction of Cr(VI) occurred under the beam, where minor but noticeable reduction occurred after about 5−10 min of beam exposure. The mole fraction, Cr(III)/Cr(total), was calculated from spectra that were only exposed to the beam for 45 s. Curve fitting showed 37% of the sorbed chromium on the GAC−QPVP existed in its trivalent form.

The presence of Cr(III) on the sorbent was consistent with the under-predictions of Cr(VI) sorption (Figure 5a) because the ion exchange model only considers Cr(VI) species. The increasing differences between the model predictions and measurements with decreasing pH (Figure 5a) suggested Cr-(VI) reduction was more favored at low pH. This agreed with the facts that the rates of chromate reduction to Cr(III) increased with decreasing pH by many inorganic and organic reductants (30, 40). The presence of Cr(III) also indicated that the activated carbon sites that were able to reduce Cr-(VI) (Figure 4) were not completely blocked by the QPVP process, suggesting that the small pores in the polymer on the surface of GAC−QPVP (Figure 1) were conduits for Cr-(VI) to diffuse to the underneath reduction sites. After reduction, Cr was occluded in the solid phase or slow to diffuse back to aqueous phase so that aqueous Cr(III) was undetectable within 24 h equilibration time (Figure 4). The Cr(III) was thermodynamically stable in aqueous phase below pH 4. This diffusion-reduction mechanism also explained the increasing under-predictions of Cr(VI) sorption with increasing ionic strength (Figure 5a) because in solutions with high ionic strength, Cr(VI) was less adsorbed and more available for diffusion into reduction sites.

Overall, under a wide range of experimental conditions examined in this study, GAC−QPVP is found to remove Cr-(VI) efficiently from pH 2 to 6 and in the presence of strong competing anions such as phosphate, sulfate, and nitrate. Its sorption capacity for Cr is much higher than that of PVP-coated silica gel. An ion exchange model is developed that well explains the dependence of Cr(VI) uptake on pH, ionic strength, and Cr(VI) concentrations. Further studies are needed to define the conditions for the sorbent regeneration and to assess its potential for the removal of other contaminants.

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Supporting Information Available

Constants of reversible second-order kinetics, constants of Langmuir sorption isotherms, schematic of procedures of GAC−QPVP preparation, determination of pH_{pzc} of virgin GAC and GAC−QPVP, and effect of anions on the sorption of chromium (VI) on the GAC−QPVP. This material is available free of charge via the Internet at http://pubs.acs.org.

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