Removal of Hexavalent Chromium from Estuarine Waters by Model Substrates and Natural Sediments

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■ Chromate removal from waters with a range of salinities (0–32‰) was studied by using both model substrates, alumina and kaolinite, and natural estuarine sediments in order to determine possible effects of sediment on dissolved chromate in estuarine systems. The dependence of chromate removal on sediment concentration shows that typical estuarine suspended sediment concentrations (<1 g L^{-1}) will be ineffective in removing dissolved chromate from the water column, though the reaction will be important in deposited sediments. Chromate removal is more effective in low- than high-salinity regimes. Removal by model substrates decreases monotonically with increasing salinity but shows a peak in the 0.1–1.0‰ range with estuarine sediments. This latter behavior shows similarity with the salinity dependence of chromate reduction by gallic acid, suggesting reductive adsorption by the estuarine sediments. Naturally occurring levels of phosphate and silicate show negligible effect on chromate removal.

Introduction

Chromium is widely used in industry. The element occurs primarily in two valence states in nature—the relatively toxic hexavalent form and the relatively benign trivalent form. Removal of dangerous levels of the hexavalent form from water can be accomplished by either reduction or adsorption.

A number of workers have examined hexavalent-chromium removal onto soils and commercial adsorbents. Chromate has been found to exhibit sorption behavior similar to that of other tetraoxo anions such as phosphate (1, 2). Adsorption is enhanced by low-pH conditions (1, 3, 4) and can be further enhanced by reduction to the trivalent form in certain soil types (2, 5). A significant chemisorption component in the total adsorption free energy has been noted (1, 4), allowing adsorption onto negatively charged surfaces.

Sediments are thought to strongly control the estuarine geochemistry of trace metals. The nature and extent of such a control for hexavalent chromium in estuarine systems has received little attention. We report here an experimental study of the removal of hexavalent chromium from estuarine waters by both model substrates and natural estuarine sediments, with a determination of the effects of sediment concentration, salinity, and interferences by naturally occurring levels of phosphate and silicate.

Materials and Methods

Removal experiments were carried out by equilibrating 1 μM solutions of K_2CrO_4 with a variety of substrates. Chromatographic-grade alumina (80–200 mesh) showed trace chromate contamination and was therefore washed alternately with pH 2 HCl, pH 11 NaOH, and distilled water until no contamination was detected. The alumina was heated to 204 °C overnight to activate it; tests showed that this treatment enhanced removal. Kaolin from Washington County, GA (A.P.I. KGa-1 from the University of Missouri source clay collection) was used as received. Estuarine sediments were collected from the oxidized layer in intertidal zones of the Saco, Damariscotta, and Sheepscot River estuaries, Maine,

wet sieved at 63 μm to remove the coarse fraction, and washed repeatedly with 1 mM $NaHCO_3$ solutions. These washings initially removed yellow colloidal material, presumably organic substances, which caused serious blanking problems. Washing was continued until the yellow color was no longer removed, as determined by visual inspection of the supernatants. Experiments indicated that removal of these yellow substances decreased chromate removal by as much as 40%. Centrifugations between washings were timed so that particles <0.35 μm in size may have been discarded with the supernatants.

Estuarine waters of varying salinities were made by mixing an artificial river water of 1 mM $NaHCO_3$ with varying proportions of filtered seawater (Gelman A/E) freshly collected from the Damariscotta estuary. Before spiking with chromium, we titrated sediment–water suspensions to pH 8 with HCl or NaOH, recording the amount of titrant for salinity calculations. Equilibration of 50- or 60-mL suspensions of sediments and chromium-spiked waters was carried out for 16 ± 1 h at room temperatuare (18–24 °C) on a reciprocating shaker. Polycarbonate centrifuge tubes were used, which were found to minimize wall adsorption of chromium. Control tubes without sediment were run to account for wall adsorption, and control tubes without K_2CrO_4 spikes were run to account for other color-producing effects. Suspensions were clarified by centrifugation and 0.22-μm filtration. Experiments to test for the effects of silicate or phosphate on chromate removal used spikes of K_2HPO_4 or Na_2SiO_3 solutions. $HgCl_2$ was added to a concentration of 3 mg L^{-1} to retard bacterial activity during the P–Si spike experiments.

Experiments to examine the reduction of hexavalent chromium by organic material were performed by spiking waters of various salinities, buffered at pH 8 with a 5 mM phosphate buffer, to 2 μM K_2CrO_4 and 20 μM gallic acid. These solutions were allowed to equilibrate at 40 °C for 4 h, cooled, and analyzed for hexavalent chromium. Controls without gallic acid were run at each salinity.

Hexavalent chromium was analyzed by a modified diphenylcarbazide technique, with the analytical coefficient of variation ranging from ±1.5% at 0.2 μM Cr to ±0.7% at 1 μM Cr (6). Phosphate and silicate were analyzed colorimetrically by standard techniques (7).

Results and Discussion

The capacity of a variety of substrates to remove chromate is shown in Figure 1. These data indicate that sediment concentrations of considerably more than 1 g L^{-1} are necessary to remove significant amounts of chromate from a 1 μM solution. Experiments were also carried out with Saco estuary sediment without pH adjustment; these runs showed greater removal than the substrates in Figure 1, which probably resulted from lower pH (1, 2) during the runs, ~6–6.5, and higher organic loadings in the Saco sediments (4, 8). Nevertheless, even these sediments required concentrations of several g L^{-1} to significantly remove chromate from solution. Suspended sediment levels greater than 1 g L^{-1} are rare in estuarine systems—levels of <200 mg L^{-1} are more common—and so removal of chromate from solution by suspended

sediment is not likely to occur in most estuaries. Sediments can, however, serve as a significant sink for chromate from interstitial waters, and, to the extent that the removal mechanism is adsorptive in nature, the diffusion coefficient of chromate in pore waters will be decreased (9). Figure 1 also shows that removal occurs to a greater extent in freshwater than in seawater.

Removal of chromate onto the model sedimentary substrates, alumina and kaolinite, as a function of salinity is shown in Figure 2. A monotonic decrease of removal with increasing salinity is evident. An experiment with 0.5 M NaCl showed a similar inhibition of removal, ruling out non-chloride anions in seawater as the primary inhibition factor. These results contrast with those of Griffin et al. (3), who found no effect of 0.028 M NaCl on chromate removal from a 172 μM Cr^{VI} solution. MacNaughton (1) observed a decrease in chromate removal onto alumina with increasing strength KNO$_3$ solutions (10^{-3}–10^{-1} M), at somewhat lower pH values than our experiments. He ascribed this decrease to a shrinkage of the electrical double layer, and consequently the electrical potential and Coulombic attraction, at the oxide surface. This hypothesis has increased validity at pH values well below the zero point of charge (ZPC), which is ~9.1 for Al$_2$O$_3$ (10, p 478), because of the increasing importance of Coulombic attraction for adsorption at lower pH. Above the ZPC, shrinkage of the double layer would be expected to cause an increase in adsorption with increasing electrolyte content because of decreased negative–negative repulsion. Such increases have been found for phosphate adsorption onto alumina (1) and kaolinite (11) at pHs above their respective ZPC's. The decrease in chromate removal onto kaolinite with increasing salinity that we observed at pH 8—kaolinite's ZPC is 4.6 (10, p 478)—suggests that other factors are important in this case. Two alternative hypotheses may assist in explaining our chromate data. First, simple competition at the oxide–water interface by the electrolyte anions may reduce chromate adsorption. Second, the decrease in the activity coefficient of the divalent chromate ion with increasing salinity may lower its reactivity. The magnitude of this decrease, calculated from the Davies equation (10, p 83) $-\log \gamma(CrO_4^{2-}) = AZ^2[I^{1/2}/(1 + I^{1/2}) - 0.3I]$, is ~70% and thus similar to that of the inhibition of chromate removal. Complexation or ion-pair formation with seawater cations may also reduce the activity of the chromate ion. While any of the three hypotheses may be used to explain the removal vs. salinity trend for alumina, only the last two hypotheses are consistent with the trend found for kaolinite. That these last two factors can inhibit chromate removal more strongly than that of phosphate is consistent
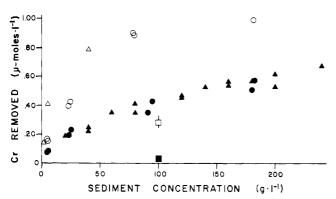
with the stronger chemisorption tendency of phosphate (1); chemisorption has been found to be relatively insensitive to ionic strength effects (12, 13).

Chromate removal by estuarine sediments (Figure 3) showed a slightly different response to salinity. Removal invariably showed an increase proceeding from the freshwater end-member to a maximum in the 0.1–1.0‰ range and thereafter decreased with increasing salinity to a value at the seawater end-member of $\frac{1}{3}$–$\frac{1}{2}$ of its peak in the low-salinity regime. On the hypothesis that a principal difference between the model substrates and the estuarine sediments was the presence of organic matter associated with the latter, we examined the effect of salinity on the reduction of chromate by organic compounds.

Figure 4 shows the extent of chromate reduction in a 2 μM Cr^{VI} solution by the 20 μM gallic acid solution at pH 8. The variability between experiments conducted on separate days probably resulted from variable autoxidation of the gallic acid stocks before the reduction experiment. The salinity dependence of reduction in this one-phase system is very similar to that of the chromate removal found for the two-phase estuarine sediment–water system, implying that the removal onto estuarine sediments, detected by lowered reactivity of the
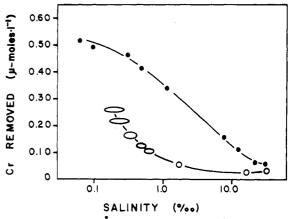

Figure 2. Removal of Cr^{VI} from a 1 μM solution by 10 g L^{-1} of alumina (solid circles) and 83 g L^{-1} of kaolinite (open ovals) as a function of salinity. Horizontal width of ovals represents range of uncertainty in salinity determination. All points represent means of duplicate determinations.
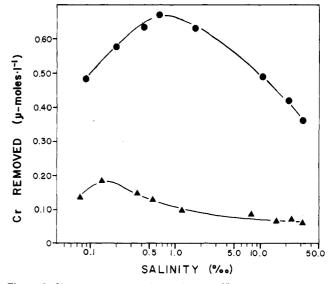

Figure 1. Chromate removal from a 1 μM solution of K$_2$CrO$_4$ vs. suspended substrate concentration. Substrates are as follows: triangles, alumina; squares, kaolinite; circles, Sheepscot estuarine sediment. Hollow symbols refer to experiments in freshwater; solid symbols refer to experiments in seawater. Alumina data are from single determinations; all others are means of duplicate determinations.

Figure 3. Chromium removed from a 1 μM Cr^{VI} solution vs. salinity. Triangles represent a 58.2 g L^{-1} suspension of estuarine sediment collected from the Damariscotta estuary; circles represent a 48.6 g L^{-1} suspension of estuarine sediment collected from the Sheepscot estuary. All points are means of duplicates.
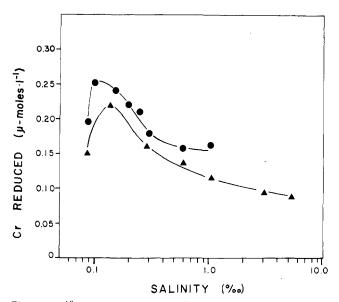
Figure 4. Cr^{VI} reduced from a 1 μM Cr^{VI} solution by a 20 μM gallic acid solution as a function of salinity. Circles and triangles refer to experiments run on different days. All points are means of triplicates.

supernatant with diphenylcarbazide, involved the reduction of hexavalent to trivalent chromium. However, the resultant levels of highly reactive trivalent chromium would become rapidly adsorbed by suspended sediment levels of ca. 50 g L^{-1} (unpublished data). We suggest, therefore, that the removal of hexavalent chromium resulted from such a two-step sequence of reduction followed by adsorption, a process that may be termed reductive adsorption. Bartlett and Kimble (2) found reductive adsorption in soils to be favored by low pH and high organic content, although the reaction was demonstrable in low organic content soils at pH values as high as 7.4. It thus appears that, although the salinity dependence of chromate removal by estuarine sediments mimics that of inorganic oxides, the cause of this salinity dependence may be very different for the two different types of substrates.

It should be noted that the peak in removal by sediments was usually reached at a salinity within the range of world river compositions, and so, in many estuarine situations, only a monotonic decrease in adsorption with salinity would be expected.

Chromate adsorption onto oxide surfaces has been shown to be specifically inhibited by anions such as cyanide and phosphate (1, 2, 4). We therefore examined this inhibition by naturally occurring levels of phosphate and silicate. Figure 5 shows the results of a freshwater experiment in which 1 μM solutions of Cr^{VI} with various phosphate and silicate concentrations were equilibrated with 100 g of kaolinite per liter at pH 8. Initial phosphate concentrations ranged from 0 to 16 μM. Two initial silicate concentrations were used—0 and 0.71 mM. The no-silicate experiment resulted in a small but real reduction of chromate removal by increasing phosphate adsorption. The high-silicate experiment showed no significant effect of silicate on the average amount of chromate removed. However, the high silicate level removed the effect of phos-
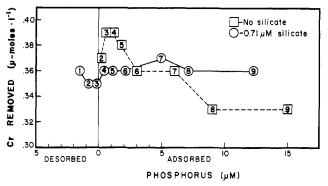

Figure 5. Effect of phosphate sorption on Cr^{VI} removal at 0 and 0.71 mM silicate concentrations. Substrate was 100 g L^{-1} kaolinite in distilled water buffered to pH 8.0. Initial phosphate concentrations were (1) 0, (2) 0.32, (3) 0.65, (4) 1.29, (5) 1.94, (6) 3.23, (7) 6.46, (8) 9.69, and (9) 16.14 μM. All points are means of duplicates.

phate on chromate removal. Although the silicate addition did reduce phosphate adsorption, this reduction alone was not sufficient in magnitude to account for the removal of the effect of phosphate on chromate removal. Presumably this last effect resulted from a strong competition of silicate with phosphate for those sites in which phosphate and chromate compete (14). Similar effects of phosphate additions on chromate removal were found in experiments with alumina in seawater and a forest soil sample in freshwater. It is concluded that natural levels of phosphate and silicate will have negligible effect on the removal of chromate.

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