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CHROMATE ADSORPTION BY KAOLINITE

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Abstract—Chromate (CrO_4^{2-}) adsorption was investigated on kaolinite (0.2–2 μm) saturated with $NaClO_4$ over a range of pH. Adsorption increased with decreasing pH because of protonation of chromate and/or variable charge sites on kaolinite. Chemical pretreatment to remove noncrystalline and crystalline oxide contaminants affected the magnitude of CrO_4^{2-} adsorption, but not the pH range over which CrO_4^{2-} adsorbed. Chromate adsorption at different sorbate and sorbent concentrations increased below the pH_{zpc} for the kaolinite edge, suggesting the formation of weak surface complexes. If CrO_4^{2-} and SO_4^{2-} were present at equal concentration (5.0×10^{-7} M), the two solutes sorbed independently, suggesting binding to separate sites. The presence of excess SO_4^{2-} (5.0×10^{-4} M), however, unexplainably enhanced CrO_4^{2-} adsorption. The adsorption of both chromate and sulfate can be described in terms of a site-binding model of the kaolinite edge, in which the edge is viewed as composite layers of Al and Si oxide. Surface complexation constants for CrO_4^{2-} on kaolinite were similar to those for alumina, pointing to the importance of Al–OH edge sites in chromate adsorption.

Key Words—Adsorption, Chromate, Kaolinite, Sulfate, Surface complex.

INTRODUCTION

Chromate (CrO_4^{2-}) is an anionic contaminant often associated with industrial and power generation wastes that are disposed to the land surface. In domestic waters, chromate is a regulated constituent (U.S. Environmental Protection Agency, 1986), because it may be toxic to man and other organisms. Adequate protection of the terrestrial environment and subsurface water supplies and the mitigation of impacts where they occur require information on the chemical reactions between chromate and soil and subsurface materials that slow solute movement relative to the transporting water front.

Fe and Al oxides bind CrO_4^{2-} effectively at low to medium pHs (MacNaughton, 1977; Leckie *et al.*, 1980; Davis and Leckie, 1980; Mayer and Schick, 1981; Honeyman, 1984). Like other acid anions (e.g., SeO_4^{2-}, SO_4^{2-}, SeO_3^{2-}, AsO_4^{2-}), CrO_4^{2-} exhibits pH-dependent adsorption on these solids due to surface charging and aqueous solute speciation. Like oxides of Al and Fe, kaolinite also contains hydroxylated edge and defect sites, which may be important points for chromate adsorption in soils and subsurface materials. Kaolinite adsorbs acid anions, including SO_4^{2-} (Rao and Sridharan, 1984), MoO_4^{2-} (Phelan and Mattigod, 1984), PO_4^{3-} (Kafkafi *et al.*, 1967; Nagarajah *et al.*, 1968; Chen *et al.*, 1973), H_3BO_3 and $B(OH)_4^-$ (Mattigod *et al.*, 1985), and CrO_4^{2-} (Griffen *et al.*, 1977). The favored adsorption mechanism is surface complexation by aluminol groups (AlOH) exposed primarily on crystal edges (Chen *et al.*, 1973; Swartzen-Allen and Matijevic, 1974).

Because of the complex surface chemistry of kaolinite, few investigators have quantitatively linked its measured surface properties with its anion adsorption behavior. By applying chemical models of surface complexation, however, both Riese (1982) and Liechti (1983) succeeded in using surface-ionization and electrolyte-surface-complexation constants derived from titration data to simulate metallic cation adsorption on kaolinite. Their success in stimulating metal adsorption over ranges of pH and ionic strength suggests that a comparable approach may be tenable for anion adsorption on the kaolinite. Consideration of the surface charge-potential relationship as affected by the proton and strongly complexing solutes is particularly important for anion adsorption in which the electrostatic conditions at the solid-liquid interface exert a strong influence on adsorption (Bolan and Barrow, 1984; Zachara *et al.*, 1987).

In this paper, we extend earlier published work (Griffen *et al.*, 1987) on adsorption of CrO_4^{2-} by kaolinite. Chromate adsorption is measured as a function of pH and solution concentration on carefully sized and prepared kaolinite to elucidate the surface-complexation reaction. The effect of chemical pretreatment is demonstrated, as is the influence of SO_4^{2-} as a co-sorbing ion. The triple-layer model (TLM) and the chemical equilibrium program FITEQL, in combination with data from the literature on kaolinite surface properties, are used to simulate adsorption as a function of pH, and intrinsic adsorption constants calculated for the kaolinite surface are compared to those for aluminum oxide.

EXPERIMENTAL PROCEDURES

Clay preparation and analysis

A well-crystallized Georgia kaolinite (KGa-1, from the Source Clays Repository of the Clay Minerals Society) was used for the adsorption experiments. Ka-

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Table 1. Properties of 0.2–2.0-μm kaolinite.[1]

Property	Unit	Value
Surface area	m^2/g	15.64
Cation exchange capacity[2]	meq/100 g	1.5
Extractable constitutents	mole/g	
Al		
NaOH		7.17×10^{-4}
$NH_2OH \cdot HCl$		8.32×10^{-6}
DCB		2.08×10^{-5}
Si		
NaOH		6.69×10^{-4}
$NH_2OH \cdot HCl$		3.20×10^{-6}
DCB		1.52×10^{-5}
Fe		
$NH_2OH \cdot HCl$		1.50×10^{-8}
DCB		2.99×10^{-6}

[1] DCB indicates dithionite-citrate-bicarbonate extraction.
[2] Measured at pH = 6.2.

olinite saturated with sodium perchlorate ($NaClO_4$, 0.2–2.0-μm size) was prepared according to Schofield and Samson's (1953) procedure as modified by Mattigod *et al.* (1985) and Johnston *et al.* (1985). The procedure removes oxide and hydroxide coatings from the kaolinite surface by contact with 1 M $NaClO_4$ + 0.001 M $HClO_4$ after the desired clay-size fraction has been isolated by sedimentation and centrifugation. The final clay suspension (0.2–2.0 μm) was stored in 0.1 M $NaClO_4$ at about pH 6 under N_2. Kaolinite has been prepared in this way for adsorption experiments with B and Mo (Mattigod *et al.*, 1985; Phelan and Mattigod, 1984) and for a Raman spectroscopic investigation of the kaolinite surface (Johnston *et al.*, 1985).

X-ray powder diffraction analysis showed that the clay separate was well-crystallized kaolinite with a trace of 2:1 phyllosilicate contaminants. The surface area was measured by triple-point N_2(g) adsorption and is shown along with other properties of the kaolinite in Table 1. Cation-exchange capacity was measured by isotope dilution using ^{22}Na (Babcock and Schulz, 1970). Sodium hydroxide (Langston and Jenne, 1964), hydroxyl amine hydrochloride ($NH_2OH \cdot HCl$; Chao and Zhou, 1983), and dithionite-citrate-bicarbonate (DCB; Mehra and Jackson, 1960) extractions were performed on the pretreated kaolinite to assess the effectiveness of the $HClO_4$ washing in removing surface-active constituents. The properties defined by these extractions (Table 1) suggest that residual allophanic and Fe-oxide impurities were present, although the presence of octahedrally bound Fe^{3+} in the aluminum layer of kaolinite cannot be totally dismissed (Rengasamy, 1976).

Adsorption-edge experiments

Chromate adsorption at initial concentrations of 1.0×10^{-8}, 1.0×10^{-7}, 5.0×10^{-7}, 1.0×10^{-6}, and 5.0×10^{-6} M was measured on Na-saturated kaolinite (in 1:50 and 1:100 solid : solution ratios) in 0.1 M $NaClO_4$ over the initial pH range of 4.5 to 7.5. Because kaolinite solubility is at a minimum over this pH range (Liechti, 1983), complications arising from Si and Al dissolution, adsorption, and reprecipitation are minimized.

Sorption experiments were performed in a nitrogen atmosphere in a glovebox using a 250-ml jacketed glass flask maintained at 25°C by a circulating water bath. Reaction flasks were equilibrated with chromate solutions representing anticipated equilibrium concentrations. Electrolyte and radio-labeled chromate solutions and the kaolinite suspension were added in that order to the reaction vessel so that the initial chromate concentration and kaolinite mass were known precisely. An automatic titration system was used to maintain pH at 8.5 during this procedure. The pH of the suspension was sequentially lowered by the titrator to values of 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, and 4.5. The pH was maintained at each of these levels for 30 min, after which two, 10-ml aliquots of the suspension were removed, transferred to polycarbonate centrifuge tubes, and equilibrated under N_2 at 25°C in a constant-environment shaker. After 24 hr, the tubes were centrifuged (5000 × g for 10 min), and aliquots of known mass were removed for scintillation counting of the ^{51}Cr beta emission. Final pH was measured on each sample under N_2. The same procedure was used to measure SO_4^{2-} adsorption (at 1.0×10^{-7} and 5.0×10^{-7} M) on kaolinite at a 1:50 solids : solution ratio. Scintillation counting of the ^{35}S beta emission was used to quantify equilibrium SO_4^{2-} concentrations.

Na-saturated kaolinites (0.2–2.0 μm) following NaOH, $NH_2OH \cdot HCl$, and DCB extractions were used in pH-edge experiments to determine the effects of these treatments on CrO_4^{2-} adsorption. The kaolinite was pretreated with $NaClO_4/HClO_4$ as described above. The extracted clays were washed in deionized H_2O until their pH was near neutral (4–6 washings) and then washed four times with 0.1 M $NaClO_4$. Adsorption-edge experiments with these materials (1:100 solids : solution ratio) were performed with CrO_4^{2-} at 5.0×10^{-7} M.

Two dual-sorbate studies were performed with CrO_4^{2-} at 10^{-7} M and SO_4^{2-} at 10^{-7} and $10^{-3.3}$ M. These experiments were like the single-solute adsorption-edge experiments, except that the aqueous concentrations of both solutes at equilibrium (i.e., ^{51}Cr and ^{35}S) were quantified by counting. The activity of ^{51}Cr was determined by gamma counting. The activity of ^{35}S was determined by scintillation counting with a correction for the contribution of ^{51}Cr to the total beta activity.

Adsorption isotherm

An adsorption isotherm was determined by pipeting aliquots of a kaolinite suspension at pH 5.5 into rep-

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Table 2. Surface parameters and reactions used in adsorption modeling.

Parameter/reaction	Value	Source
Surface area (m^2/g)	15.6	This study
Surface site density (sites/nm^2)	6.0	Riese (1982)
	0.6	Sposito (1984)
Inner layer capacitance (C_1, $\mu F/cm^2$)	240	Riese (1982)
	120	
Outer layer capacitance (C_1, $\mu F/cm^2$)	20	Davis (1978)
$SiOH_2^+ \leftrightharpoons SiOH + H^+$	$\log K_{a1}^{int} = -1.75$[1]	Riese (1982)
$SiOH \leftrightharpoons SiO^- + H^+$	$\log K_{a2}^{int} = -6.25$[1]	Riese (1982)
$SiOH + Na^+ \leftrightharpoons (SiO^-\text{-}Na^+)^0 + H^+$	$\log^* K_{Na}^{int} = -3.50$[2]	Riese (1982)
$AlOH_2^+ \leftrightharpoons AlOH + H^+$	$\log K_{a1}^{int} = -5.7$[1]	Davis (1978)
$AlOH \leftrightharpoons AlOH + H^+$	$\log K_{a2}^{int} = -11.4$[1]	Davis (1978)
$AlOH + Na^+ \leftrightharpoons (AlO^-\text{-}Na^+)^0 + H^+$	$\log^* K_{Na}^{int} = -9.15$[2]	Davis (1978)
$AlOH + ClO_4^- + H^+ \leftrightharpoons (AlOH_2^+\text{-}ClO_4^-)^0$	$\log^* K_{ClO_4}^{int} = 7.9$[2]	Davis (1978)

[1] $K_{ai}^{int} = Q_{ai}\exp(-e\psi_s/k_BT)$ (i = 1 or 2).
[2] $^*K_{\alpha}^{int} = {}^*Q_{\alpha}\exp[-e(\psi_s - \psi_B)/k_BT]$ ($\alpha = Na^+$, ClO_4^-, $HCrO_4^-$, etc.) where Q_{ai} and $^*Q_{\alpha}$ are conditional equilibrium constants for the reactions, ψ_s and ψ_B are inner potentials, k_B is the Boltzman constant, and T is temperature (Sposito, 1984).

licate polycarbonate tubes, with the initial Cr concentrations ranging from 10^{-8} to 10^{-4} M. The reagent and clay were added gravimetrically, thereby yielding an accurate assessment of the initial Cr concentration and clay mass in each tube. The pH was adjusted back to pH 5.5, and the tubes were equilibrated for 24 hr in an incubator-shaker at 25°C under N_2. After centrifugation (5000 × g for 20 min), subsamples were transferred from each tube into scintillation vials for radioanalysis of ^{51}Cr. The final pH of the supernatant was determined after counting samples were removed.

Adsorption modeling

The chemical equilibrium program FITEQL (Westall, 1982) was used to calculate surface-equilibrium constants for CrO_4^{2-} on the kaolinite. The titration data on which the surface acidity and electrolyte complexation constants for kaolinite are based may be suspect because of clay dissolution and reprecipitation of Si and Al. The ideal structure of kaolinite without ionic substitution was assumed, with the ionization of SiOH and AlOH sites (Table 2) controlling surface charge. Chromate was allowed to adsorb to both AlOH and SiOH sites and to cover four sites per adsorbed molecule. This site coverage is consistent with that used in Davis and Leckie's (1980) simulation of chromate adsorption by oxide surfaces. The total site density (n_s) has been assumed here to arise from a combination of AlOH and SiOH edge sites in equal proportions (i.e., n_s = AlOH + SiOH and AlOH = SiOH), based on the experimental data of Williams and Williams (1978).

The surface parameters, surface ionization, and electrolyte complexation constants for the component oxides of kaolinite that were used in the calculations are given in Table 2. Constants for the SiOH sites on kaolinite (sample KGa-1) were determined by Riese (1982) using the double extrapolation technique and assuming that kaolinite charge development arises only from surface ionization and electrolyte complexation. These constants were developed for a different size fraction of sample KGa-1 (>0.1 μm) which had received stronger pretreatment (acid ammonium oxalate and hot 0.5 M NaOH) than used in this work. The intrinsic constants for the aluminol sites (AlOH) were taken from Davis (1978) who used the data of Anderson *et al.* (1976). The constants of Davis (1978) were more rigorously defined than those of Riese (1982), who used K_{al}^{int} of AlOH on kaolinite as a fitting parameter. The aluminol constants from $Al(OH)_3$ (Davis, 1978) have been assumed here to be relevant to the kaolinite surface. No attempt was made to verify whether the surface ionization constants used in this study describe the surface charging of kaolinite as determined by Riese (1982). Solution equilibrium constants are given in Table 3.

RESULTS AND DISCUSSION

Influence of kaolinite pretreatment

In adsorption and surface chemistry studies, kaolinite is often pretreated to remove gel-like coatings and to expose gibbsite and silica layers (Ferris and Jepson, 1975; Hawthorne and Solomon, 1972). These pretreatments significantly influenced CrO_4^{2-} adsorption by kaolinite (Figure 1). With all pretreatments, chromate adsorption increased with decreasing pH, as observed for a CrO_4^{2-} adsorption on Fe and Al oxides (Davis and Leckie, 1980; Honeyman, 1984) and for indifferent anion adsorption on kaolinite (Ferris and Jepson, 1975; Bolland *et al.*, 1976). The amount of CrO_4^{2-} adsorbed, however, varied as much as four-fold depending on the pretreatment method. The most abrupt adsorption edge occurred on the DCB-treated kaolinite. The DCB-treated kaolinite adsorbed the most CrO_4^{2-}, whereas the kaolinite treated with acidified $NaClO_4$ adsorbed the least. Analyses of the equilibrium solutions from

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Table 3. Aqueous speciation reactions and equilibrium constants.

Reaction	Log K	Source
$H^+ + SO_4^{2-} \leftrightharpoons HSO_4^-$	1.99	Truesdell and Jones (1974)
$Na^+ + SO_4^{2-} \leftrightharpoons NaSO_4^-$	0.70	Truesdell and Jones (1974)
$H^+ + CrO_4^{2-} \leftrightharpoons HCrO_4^-$	6.51	Ball *et al.* (1980)
$2H^+ + CrO_4^{2-} \leftrightharpoons H_2CrO_4^0$	5.65	Schmidt (1984)
$Na^+ + CrO_4^{2-} \leftrightharpoons NaCrO_4^-$	0.70	Schmidt (1984)
$2H^+ + 2CrO_4^{2-} \leftrightharpoons Cr_2O_7^{2-} + H_2O$	14.56	Schmidt (1984)

these experiments provided no explanation for this behavior. Silica, however, was present at approximately $10^{-3.5}$ M concentration in all pretreatment solutions; this concentration decreased with pH, suggesting that Si was adsorbed on the kaolinite.

By effectively removing the free iron and noncrystalline aluminosilicate coatings that may adsorb CrO_4^{2-}, the DCB, $NH_2OH \cdot HCl$, and NaOH treatments should have decreased CrO_4^{2-} adsorption by kaolinite. Residual specifically adsorbed citrate and sulfate from the DCB extraction should also have further reduced the adsorption of CrO_4^{2-}. The data, however, negated these hypotheses and suggested instead that the stronger extractants (i.e., DCB and NaOH) induced changes in the surface properties of kaolinite that affected CrO_4^{2-} adsorption. These results contrast with Sumner's (1962) findings that DCB extraction has little effect on the surface properties of phyllosilicates. The net effect of the pretreatment appears to have been either an increase in the number of reactive surface groups responsible for CrO_4^{2-} complexation by exposure of more edges and defects, or an enhanced positive charge caused by adsorption of Al^{3+} or Al-SO_4^+ complexes (in the DCB treatment) or by desorption of adsorbed silica (in the NaOH treatment). The large increase in CrO_4^{2-} adsorption following DCB extraction may have been due to reduction and removal of structural Fe^{3+} in the AlOH layer, to the exposure of new AlOH sites for reaction, or possibly to the reduction of hexavalent Cr to trivalent Cr by residual reduced-sulfur species.

Because the DCB, $NH_2OH \cdot HCl$, and NaOH extractions affected the surface properties of kaolinite in ways that were not resolved, all additional experiments were performed with kaolinites pretreated with $NaClO_4$-$HClO_4$ (referred to as H-treated in Figure 1). Such kaolinites are presumed to be more representative of the natural environment and less influenced by the complex physicochemical effects (dissolution, specific adsorption, or chromate reduction) that apparently accompanied the other extraction procedures. This treatment may have preferentially solubilized alumina, leaving the surface enriched in silica or adsorbed Al^{3+}.

Concentration-dependent adsorption

At pH = 5.5, chromate adsorption yielded a curvilinear isotherm that has been linearized on a log-log or Freundlich-type plot (Figure 2). When plotted according to the Langmuir isotherm (Sposito, 1984), the data conformed to a two-series Langmuir equation, $q = b_1K_1c/(1 + K_1c) + b_2K_2c/(1 + K_2c)$ (Figure 3), where b_1, b_2, K_1, and K_2 are adjustable parameters. The x intercept equals $b_1 + b_2$ or an estimate of the adsorption capacity of kaolinite for chromate at pH = 5.5. This value (3.33×10^{-7} mole/g, 2.13×10^{-8} mole/m^2, or 4.26×10^{-8} eq/m^2) is considerably below the densities of hydroxylated surface sites estimated from crystallographic considerations (1.0×10^{-6} mole/m^2; Sposito, 1984), tritium exchange (1.0×10^{-5} mole/m^2;

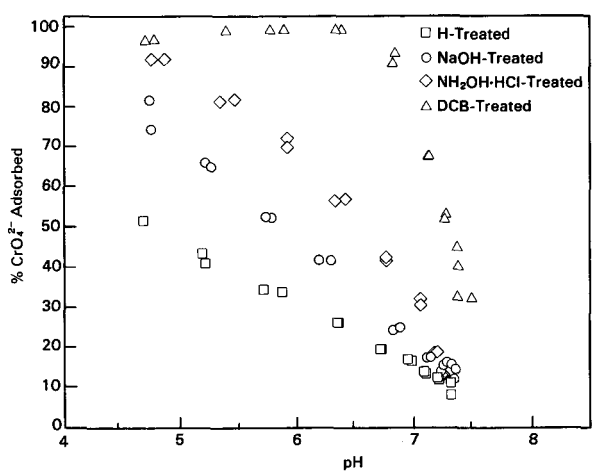


Figure 1. Fractional adsorption of 5.0×10^{-7} M CrO_4^{2-} on chemically treated 0.2–2 μm Na-kaolinite.

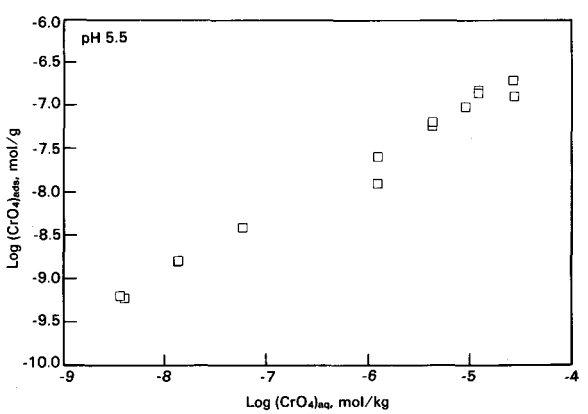


Figure 2. Adsorption isotherm of CrO_4^{2-} on kaolinite at pH 5.5 in 0.01 M $NaClO_4$.

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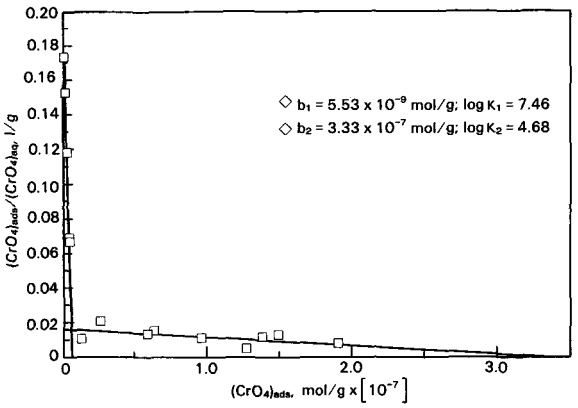


Figure 3. Langmuir plot for CrO_4^{2-} adsorption on Na-kaolinite at pH 5.5.

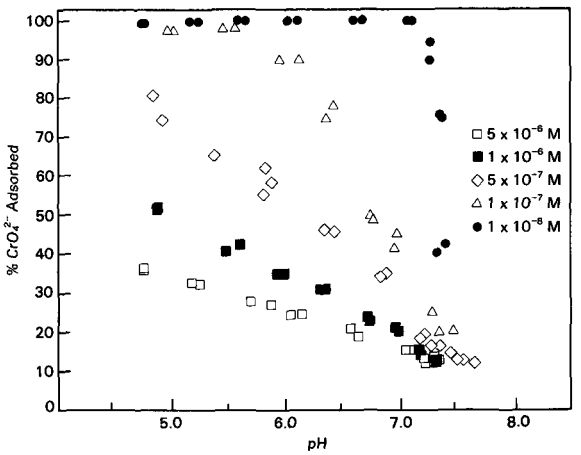


Figure 4. Influence of CrO_4^{2-} concentration and pH on the fractional adsorption of CrO_4^{2-} by Na-kaolinite.

Riese, 1982), or titration (3.92 × 10^{-6} mole/m^2; Liechti, 1983), and anion-exchange capacity measured by Cl^- and NO_3^- adsorption (~2.5–5.0 × 10^{-7} eq/m^2; Bolland *et al.*, 1976; Sumner and Reeve, 1966; Ferris and Jepson, 1975). As Posner and Bowden (1980) noted, adherence to a two-series Langmuir equation yields no mechanistic information and does not necessarily imply adsorption to two distinct types of surface sites.

pH-dependent adsorption

The initial CrO_4^{2-} concentration significantly influenced the slope of the pH adsorption edges, lowering the pH at the point of 50% adsorption (pH_{50}) (Figure 4). With the exception of the lowest concentration that displayed highly selective adsorption (10^{-8} M), the edges showed less pH dependence than has been observed for CrO_4^{2-} adsorption on aluminum oxide (Honeyman, 1984). For all concentrations, adsorption increased at pH <7.5, in agreement with the pattern noted for Cl^- and NO_3^- anions bound to kaolinite by coulombic forces (Ferris and Jepson, 1975; Bolland *et al.*, 1976). Rand and Melton (1975) suggested pH 7.3 as the apparent isoelectric point of the kaolinite edge. Significantly, all CrO_4^{2-} concentrations in Figure 4 and the adsorption edges for all treated kaolinites (Figure 1) converged on this value. Although this observation does not necessarily support strict, indifferent anion exchange, it does suggest weak adsorption and probably outer-sphere complex formation between chromium species and the kaolinite surface. Although adsorption increased steadily with decreasing pH, the experimental data were not influenced by the change in chromate speciation that occurred at pH <6.51 ($HCrO_4^- = CrO_4^{2-} + H^+$, pK_a = 6.51). Decreasing the solids concentration of kaolinite at a fixed initial CrO_4^{2-} concentration reduced the number of reactive surface sites and, hence, chromate adsorption (Figure 5). The twofold reduction in kaolinite concentration decreased fractional adsorption of chromate by a factor of about 1.8.

The pH adsorption-edge data were modeled with the computer program FITEQL using the triple-layer surface complexation model and the data in Tables 2 and 3. Because the site density and inner-layer capacitance were uncertain, these parameters were varied to identify their influence on the resulting surface complexation constants. Using the outer-sphere surface reactions expressed in Eqs. (1–3):

$$AlOH + CrO_4^{2-} + H^+ \rightleftharpoons AlOH_2^+\text{-}CrO_4^{2-}, \quad (1)$$

$$AlOH + CrO_4^{2-} + 2H^+ \rightleftharpoons AlOH_2^+\text{-}HCrO_4^-, \text{ and} \quad (2)$$

$$SiOH + CrO_4^{2-} + 2H^+ \rightleftharpoons SiOH\text{-}H_2CrO_4 \quad (3)$$

FITEQL converged readily on all the adsorption edges, except for the 10^{-8} M data. Figure 6 shows an optimized fit to the 1.0 × 10^{-7} and 1 × 10^{-6} M adsorption data; best-fit equilibrium constants for a site

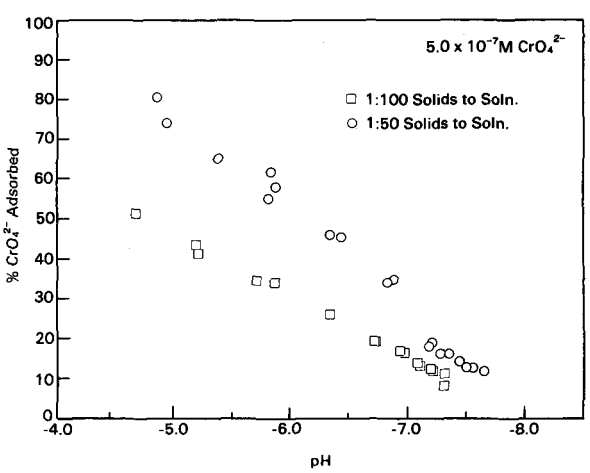


Figure 5. Influence of kaolinite solids concentration on the fractional adsorption of 5.0 × 10^{-7} M CrO_4^{2-}.

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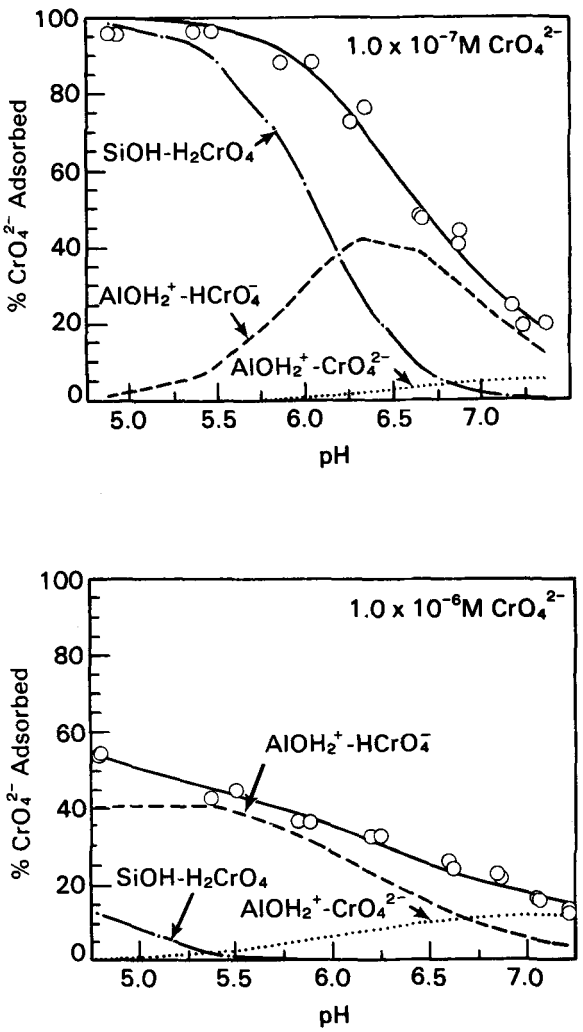


Figure 6. Adsorption modeling of two CrO_4^{2-} concentrations on Na-kaolinite. Open circles are data points; dot-dashed, dotted, and dashed lines represent simulated species contributed to adsorption; solid lines represent summation of species.

density of 6.0 sites/nm² are summarized in Table 4. The inner-layer capacitance was varied from 240 μF/cm² as suggested by Riese (1982) to 110 μF/cm² as used by Davis (1978) for modeling chromate adsorption by α-Al_2O_3. This had minimal influence on the magnitude of the intrinsic constants (<5%, data not shown).

In support of the outer sphere complexation mechanism for CrO_4^{2-}, direct spectroscopic measurements indicated that SeO_4^{2-} formed an outer-sphere complex on goethite (Hayes *et al.*, 1987). Sulfate and SeO_4^{2-} sorbed identically on noncrystalline iron oxyhydroxide, binding to the same group of surface sites (Leckie *et al.*, 1980). Both SO_4^{2-} and SeO_4^{2-} compete with CrO_4^{2-} for surface sites on noncrystalline iron oxyhydroxide (Leckie *et al.*, 1980; Zachara *et al.*, 1987) implying that all three of these anions form outer-sphere

Table 4. Surface complexation constants[1] for CrO_4^{2-} and SO_4^{2-} on kaolinite.

Concentration (M)	Log*K^{int}	Log*K^{int}	Log*K^{int}
CrO_4^{2-}	$AlOH_2^+$-CrO_4^{2-}	$AlOH_2^+$-$HCrO_4$	SiOH-H_2CrO_4
1.0×10^{-4}	9.19	17.1	17.8
5.0×10^{-7}	9.42	16.9	14.9
1.0×10^{-6}	9.42	16.3	14.5
5.0×10^{-6}	9.48	16.2	13.9
SO_4^{2-}	$AlOH_2^+$-SO_4^{2-}	$AlOH_2^+$-HSO_4^-	
1.0×10^{-7}	9.49	15.6	
5.0×10^{-7}	9.37	15.9	

[1] Constants derived from experiments at 1:50 solids:solution ratio, the complexation constants for the Cr surface species refer to Eqs. (1–3).

complexes on Fe oxide. Inasmuch as CrO_4^{2-} is more weakly adsorbed on Al oxide than on Fe oxide (Honeyman, 1984; Rai *et al.*, 1988), the CrO_4^{2-} surface complex on both Al oxide and kaolinite is probably outer sphere as well. Without spectroscopic evidence, others have suggested that SO_4^{2-} forms an inner-sphere complex on alumina (Rajan, 1978) and kaolinite (Rao and Sridharan, 1984).

As has been observed for iron oxide (Davis and Leckie, 1980; Zachara *et al.*, 1987) and Al oxide (Zachara and Cowan, unpublished data), bichromate ($HCrO_4^-$) calculated to be more strongly adsorbed and to be the dominant surface species, accounting for much of the increase in adsorption with decreasing pH. The enhanced surface stability of the bichromate species can be understood by considering the solvent properties of adsorbed or interfacial water, which may promote both hydrolysis of adsorbed hydrated cations and protonation of protolyzeable anions (Davis and Leckie, 1979; Davis and Leckie, 1980). The protonated forms of other weakly adsorbing anions, bisulfate and biselenate, also compute to be dominant adsorbed species on iron oxides (Davis and Leckie, 1980). Proton-consumption measurements in association with adsorption experiments provide some support for the importance of the protonated surface species (Balistrieri and Murray, 1979).

The CrO_4^{2-} adsorption data could not be modeled without considering the surface ionization of both the alumina and silica edge sites and the neutral SiOH-H_2CrO_4 surface complex, which contributed significantly at lower pH and lower chromate concentrations. The neutral complex was, in effect, a fitting parameter. A chemical justification for the formation of this complex is not evident. Although the calculated ionization of SiOH sites over the pH range of the experiments was low, it was not insignificant and had to be included for electrostatic reasons to simulate CrO_4^{2-} adsorption adequately.

The complexation constants for CrO_4^{2-} on AlOH sites varied by as much as one log unit (Table 4); a similar concentration-dependent variation in the sur-

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Table 5. Average intrinsic binding constants for chromate adsorption on alumina and kaolinite.

Solid	log $K^{int}_{CrO_4}$[1]	log $K^{int}_{HCrO_4}$[1]
α-Al_2O_3[2]	5.84	5.70
Kaolinite		
6 sites/nm^2	3.68	4.42
0.6 sites/nm^2	5.21	5.36

[1] Surface reactions:
$AlOH_2^+ + CrO_4^{2-} \leftrightharpoons AlOH_2^+\text{-}CrO_4^{2-}$ ($K^{int}_{CrO_4}$)
$AlOH_2^+ + HCrO_4^- \leftrightharpoons AlOH_2^+\text{-}HCrO_4^-$ ($K^{int}_{HCrO_4}$).

[2] Data from Honeyman (1984).

face complexation constants was observed for CrO_4^{2-} adsorption on α-Al_2O_3. The complexation constant for the neutral $SiOH\text{-}H_2CrO_4$ species varied more significantly with surface coverage. Changing the surface-site density of the kaolinite by an order of magnitude also changed the surface complexation constants by 0.94 to 1.53 log units (Table 5). The intrinsic constants for the AlOH sites calculated with site concentrations estimated from crystallographic parameters (1.0×10^{-6} mole of sites/m^2) were similar to, but slightly lower in magnitude than those for aluminum oxide (Table 5). These results affirm the proposed importance of AlOH groups in binding chromate to the kaolinite surface.

Because the chemical interaction between CrO_4^{2-} and hydroxylated Al surface sites is relatively weak (Davis, 1978; see also Table 4), the variation in the computed complexation constants may reflect (1) an inadequate description of surface electrostatics or (2) the presence of other surface reactions that have not been accounted for. The influence of ionic substitution on total surface potential has been ignored here, and adsorption on ionizable edge sites has been assumed to be totally responsible for charge development. It must also be re-emphasized that the applicability of the surface ionization, electrolyte complexation, and site density parameters in Table 2 to the kaolinite used in this study has not been established. The effect of pretreatment on the surface properties of kaolinite was apparently significant, as shown by the chromate adsorption data in Figure 1, which brings into question the relevance of the constants of Riese (1982) to sample KGa-1 pretreated in a different way.

Kaolinite is a complex sorbent, and the data in Figures 3 and 4 suggest highly selective CrO_4^{2-} adsorption at low aqueous concentrations. Successful modeling of these data required inclusion of the neutral surface complex $SiOH\text{-}H_2CrO_4$ that dominated at low aqueous concentrations and contributed to the steep adsorption edge. Alternatively, a small number of strongly adsorbing sites may have accounted for this selectivity. A sensitivity calculation using the triple-layer model, the complexation constants and surface properties of noncrystalline iron oxyhydroxides reported by Zachara

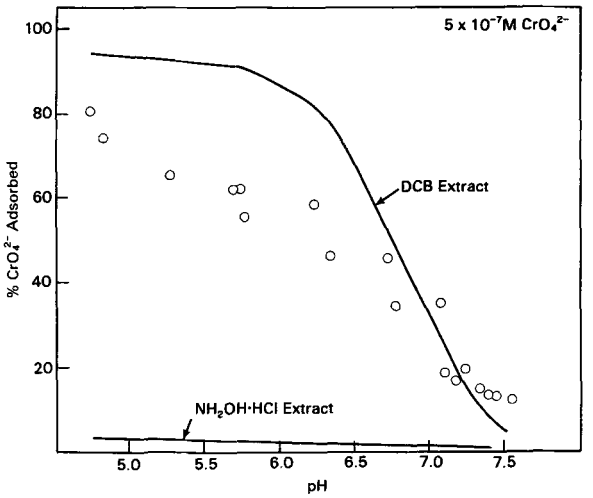


Figure 7. Calculated contributions of extractable iron to CrO_4^{2-} adsorption. Open circles are data points; solid lines are model simulations.

et al. (1987), and the extractable-Fe concentrations given in Table 1 was performed to assess whether Fe oxide impurities could be responsible for this selectivity. The calculations indicated that Fe in the kaolinite was important to adsorption *if* the DCB-extractable Fe had a site density approaching that of freshly precipitated noncrystalline iron oxyhydroxide (Figure 7). Although this site concentration of Fe oxide impurities is unlikely, the calculations affirm that Fe may have contributed to CrO_4^{2-} adsorption in sample KGa-1 treated with $NaClO_4$-$HClO_4$.

Adsorption of SO_4^{2-} and dual sorbate mixtures

Sulfate adsorption on kaolinite also varied with pH (Figure 8); however, the dependency on pH was not as strong as for chromate, and highly selective adsorption at the lower concentration was not observed. The two concentrations of SO_4^{2-} investigated produced similar adsorption edges. At low concentrations ($<5.0 \times 10^{-7}$

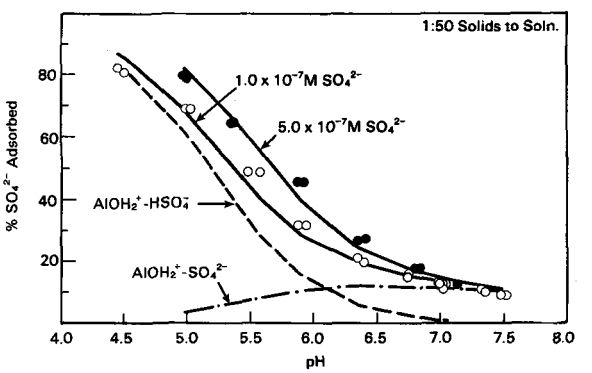


Figure 8. Fractional adsorption of two concentrations of SO_4^{2-} on Na-kaolinite as a function of pH. Circles are data points; solid lines are model simulations. Dashed lines and species contributions for 1×10^{-7} M data only.

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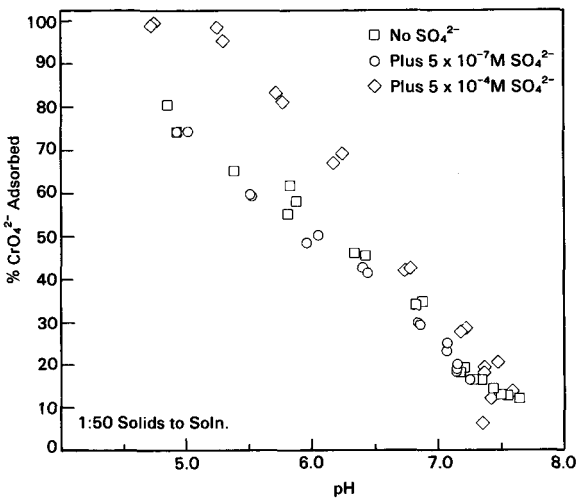


Figure 9. Influence of two concentrations of SO_4^{2-} on the fractional adsorption of 5.0 × 10^{-7} M CrO_4^{2-} by Na-kaolinite.

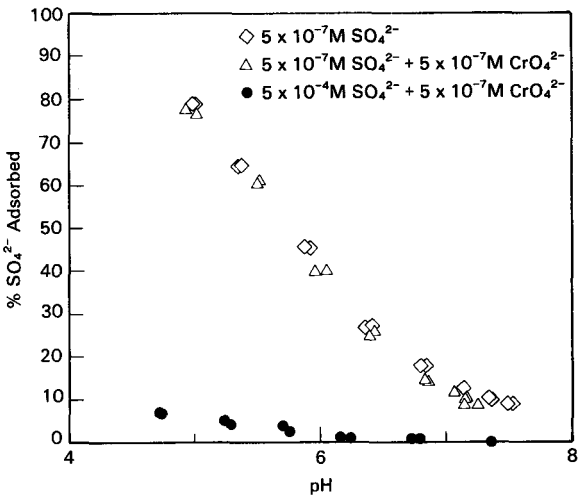


Figure 10. Influence of CrO_4^{2-} on the fractional adsorption of SO_4^{2-} by Na-kaolinite.

M), chromate was more strongly adsorbed than sulfate, in agreement with the selectivity sequence noted on noncrystalline iron oxyhydroxide (Leckie *et al.*, 1980; Zachara *et al.*, 1987). The adsorption of the two anions was comparable at higher initial anion concentrations. As for CrO_4^{2-}, the increase in SO_4^{2-} adsorption with decreasing pH reflected both protonation of AlOH groups on the surface of kaolinite and protonation of the divalent SO_4^{2-} ion in solution. The univalent bisulfate and bichromate have also been calculated to be more stable surface species on oxides (Davis and Leckie, 1980), and the weaker adsorption of sulfate may reflect its pK_{a2} (1.99) being lower than that of chromate (6.51). The concave adsorption edge and pH_{50} for sulfate on kaolinite are similar to those observed for SO_4^{2-} (Davis, 1978) and SeO_4^{2-} (Davis and Leckie, 1980) on noncrystalline iron oxyhydroxide at comparable ratios of total anion concentration to surface site concentration.

Assuming that three AlOH sites were occupied per adsorbed molecule, SO_4^{2-} adsorption is well described by the triple-layer model (solid lines in Figure 8) using outer-sphere complexation reactions (Table 4). The surface complexation constants for SO_4^{2-} indicated that HSO_4^- was bound less strongly than $HCrO_4^-$ (Table 4). The sulfate species ($AlOH_2^+$-SO_4^{2-}) predominated only at low surface saturations and pHs >6.25 (Figure 8), in accord with the experimental observations of Rao and Sridharan (1984).

In the dual-sorbate experiments, SO_4^{2-} had a variable influence on CrO_4^{2-} adsorption, ranging from no effect if the solutes were in equal concentration (5.0 × 10^{-7} M) to enhanced CrO_4^{2-} adsorption if the SO_4^{2-} concentration was higher (5.0 × 10^{-4} M) (Figure 9). The lack of influence of SO_4^{2-} (5.0 × 10^{-7} M) on 5.0 × 10^{-7} M CrO_4^{2-} adsorption suggests that the two solutes accessed different site populations on the kaolinite. In a similar manner, metallic cations apparently bind to different groups of surface sites on noncrystalline iron oxyhydroxide because competitive effects are absent (Benjamin, 1978; Benjamin and Leckie, 1980; Leckie *et al.*, 1980). The multisite hypothesis for kaolinite is substantiated by the observation that increasing the CrO_4^{2-} concentration from 5.0 × 10^{-7} M to 1.0 × 10^{-6} M in a single solute experiment induced an approximate 20–30% reduction in the CrO_4^{2-} adsorption at pH 6.0 to 4.5 (Figure 4). No comparable reduction in CrO_4^{2-} adsorption (at 5.0 × 10^{-7} M) was observed at a total anion concentration (SO_4^{2-} + CrO_4^{2-}) of 1.0 × 10^{-6} M (Figure 9). Although the increase in CrO_4^{2-} adsorption that occurred in the presence of 5.0 × 10^{-4} M SO_4^{2-} was unexpected, it was proven reproducible.

Sulfate and SeO_4^{2-} compete with CrO_4^{2-} for adsorption sites on noncrystalline iron oxyhydroxide (Leckie *et al.*, 1980; Zachara *et al.*, 1987) and share some but not all of the same adsorption sites (Leckie *et al.*, 1980). In contrast to the results shown in Figure 9, a concentration of 5.0 × 10^{-4} M SO_4^{2-} significantly reduces CrO_4^{2-} (10^{-6} M) adsorption on noncrystalline iron oxyhydroxide by inducing site saturation and decreasing positive interfacial potential (Zachara *et al.*, 1987). Binding of aqueous $AlSO_4^+$ complexes to kaolinite in the CrO_4^{2-}/SO_4^{2-} dual sorbate experiment may have increased interfacial potential and CrO_4^{2-} adsorption. Direct analysis of the equilibrium solution, however, suggests that Al^{3+} (aq) was not present in sufficient concentration to induce this effect.

^{35}S was used along with ^{51}Cr as a tracer in the dual-sorbate experiments to show that SO_4^{2-} adsorption (at 5.0 × 10^{-7} M) was unaffected by the presence of chromate at an equal concentration (Figure 10). This lack of effect was anticipated because fractional adsorption

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of SO_4^{2-} (Figure 8) decreased less with increasing initial concentration of SO_4^{2-} than did chromate (Figure 4). Thus, an increase in the total anion concentration (CrO_4^{2-} + SO_4^{2-}) from 5.0×10^{-7} to 1.0×10^{-6} M was not expected to decrease SO_4^{2-} adsorption even if the two anions adsorbed to the same population of sites. The apparent independence of SO_4^{2-} adsorption from CrO_4^{2-} in the dual-sorbate experiments therefore cannot confirm the existence of multisite adsorption that was implied from CrO_4^{2-} adsorption in the dual sorbate experiments (Figure 9). Detectable adsorption of SO_4^{2-} at a high concentration (5.0×10^{-4} M, Figure 10) occurred at about the same pH (~6.25) that enhanced adsorption of CrO_4^{2-} began in the dual-sorbate experiment (Figure 9). A linkage between enhanced CrO_4^{2-} adsorption and SO_4^{2-} adsorption in the dual sorbate experiments is therefore implied.

SUMMARY AND CONCLUSIONS

The abrupt increase in adsorption for all kaolinite treatments and adsorbate concentrations near the proposed pH_{zpc} for the kaolinite edge suggest that weak outer-sphere complexes formed between CrO_4^{2-} and the kaolinite surface. The effects of chromate adsorption of chemically pretreating kaolinite were significant. Although designed to remove iron oxides that may bind CrO_4^{2-}, pretreatment with certain reducing agents (in this investigation, $NH_2OH \cdot HCl$ and DCB) may have enhanced adsorption by exposing new edge or defect sites or by reducing CrO_4^{2-} and precipitating $Cr(OH)_3$ on the surface. The weak-acid pretreatment of Schofield and Samson (1953) and Mattigod *et al.* (1985) was the mildest of the procedures and, for this reason, was used for most of the CrO_4^{2-} adsorption experiments reported in this paper.

Chromate adsorption was simulated with a site-binding model of the kaolinite edge, using surface ionization and electrolyte complexation constants from the literature. The edge was viewed as composite layers of Al and Si oxide. The triple layer model was used for these calculations with CrO_4^{2-} forming outer-sphere complexes with AlOH and SiOH sites on the kaolinite edge. Variation in the binding constants and highly selective adsorption at low chromate concentrations suggest the presence of a limited number of high-energy sites which may have been associated with iron oxides or kink structures on the alumina sheet. Quantitative calculations regarding the role of Fe oxides could not be made without knowledge of their site concentration in the kaolinite.

Analogous to multiple-site adsorption of metals on iron oxide (Benjamin and Leckie, 1981), dual-sorbate experiments suggest that CrO_4^{2-} and SO_4^{2-} bound to different sites on kaolinite. This was unexpected because SO_4^{2-} and CrO_4^{2-} compete for adsorption sites on noncrystalline iron oxyhydroxide, and the two anions are thought to adsorb to the kaolinite edge via a similar mechanism. The kaolinite edge or comparable defect structures are therefore inferred to be a complex, nonhomogeneous array of ligands that differ in the physical and electrical structure of their microenvironment and, hence, ion selectivity. The enhanced adsorption of CrO_4^{2-} that occurred with $10^{-3.3}$ M sulfate addition is not currently explainable.

Carefully performed charge titrations, designed to minimize dissolution and reprecipitation, and other surface characterizations of kaolinite are needed on treated and untreated specimens to interpret, model, and predict anion adsorption. Experiments in this paper indirectly affirm the importance of edge sites in chromate adsorption. A minor contribution from contaminating adsorbents, specifically Fe, is suspected but unverified.

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