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Co and Cr(VI) Adsorption on Maghemite, Quartz, and Maghemite-Quartz Mixtures

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ABSTRACT

In aquifers and other natural systems, single mineral systems are rare. Solids are commonly heterogeneous, containing multiple minerals, and mineral interactions are expected. Mineral interactions such as formation of coatings and physical blocking of adsorption sites have the potential to significantly change the adsorption of ions onto solids. To investigate such interactions, batch experiments using Co(II) or Cr(VI) were conducted to compare adsorption edges of these sorbates on pure and mixed mineral systems. Specifically, sorption of 10^{-5} or 10^{-6} M Co(II) and Cr(VI) was measured as a function of pH, with a background electrolyte concentration of 0.01 M NaNO₃ on 2 to 4 g/L of nanoparticulate (<50 nm) maghemite, quartz, maghemite-quartz physical mixtures, or maghemite-coated quartz. Changes in pH greatly influence adsorption behavior, but changes in sorbent concentration have little effect under the conditions of this study. A significant quantity of Co (up to 100%) sorbed onto maghemite and quartz in the pure mineral systems. In contrast, Cr(VI) only sorbed significantly onto maghemite and was insignificant on pure quartz. In mixed and coated mineral systems, the adsorption of Co and Cr(VI) was closer to that observed for the pure maghemite than the pure quartz systems. This study shows that maghemite is likely the dominant sorbent for Co and Cr(VI) in systems containing both quartz and maghemite.

1. INTRODUCTION:

Adsorption is defined as the adherence of molecules or ions in a solution to the surfaces of solids (Debrowski 2001). Adsorption of metals is particularly important in environmental systems and remediation processes. Groundwater is a primary source of fresh, potable water that continues to become scarcer as time goes on (Vaux 2011). The protection of this important source of freshwater is critical. Many ions, such as chromium, cobalt, and lead, have the potential to contaminate groundwater. Each of these contaminants has been found at elevated concentrations in the groundwater of areas influenced by industrial land use (Tariq et. al. 2007). A likely pathway of these contaminants into the groundwater is through dumping or leaching of industrial waste into surface or groundwater systems (Tariq et. al. 2007). The adsorption process may remove these ions from the groundwater, which has the potential, under certain circumstances, to affect the mobility and toxicity of contaminant plumes (Abulaban and Nieber 2000). Neglecting the process of binding of contaminant ions to mineral surfaces, or describing it poorly, could lead to an incorrect analysis of the severity and migration of contamination in reactive-transport models. Most adsorption models have been calibrated using relatively simple, single solid systems. Few models have been carefully tested for systems with mixtures of minerals, such as are present in natural systems. Discrepancies between experimental and theoretical results of adsorption in systems with mixed minerals could contribute to incorrect predictions of contaminant mobility and toxicity in natural or engineered systems (Stumm and Morgan 1996; Bethke and Brady 2005).

The chemical behavior of Co(II) and Cr(VI) is very different in earth systems. While both Cr and Co are electron donors, or metals, in oxic aqueous solutions, Cr(VI) forms the chromate anion (CrO_4^{-2}), whereas Co(II) is a cation (Faure 1991; Blowes 2002). Co, according to the Goldschmidt classification of elements, is a siderophile, meaning that it is often found in

association with iron. Cr is classified both as a chalcophile, found in association with sulfides, and a lithophile, found in association with silicates (Faure 1991). Thus, it might be expected that Co would be more strongly sorbed by the iron oxide, maghemite, while Cr would be more strongly sorbed by the quartz because it is a silicate

Co is typically found as Co(II) at the surface of the earth, and does not form Co(I) or Co(0), except under extremely reducing conditions. In contrast, in near-surface environments under slightly acidic conditions, or in anoxic environments, Cr(VI) is readily reduced to Cr(III). Both organic matter, and ferrous iron (Fe(II)) can reduce Cr(VI) to Cr(III), affecting the adsorption behavior of chromium in natural systems (Richard and Bourg 1991).

Adsorption is influenced by a variety of factors, including ionic strength, $p\text{CO}_2$, sorbate/sorbent ratio, and ion competition (Faure 1991; Richard and Bourg 1991; Waite et al. 2000). For example, a study of the adsorption of Cr(VI) on γ -alumina found that the adsorption of Cr(VI) is influenced by pH and the presence of carbonate anions. Specifically, a combination of low pH, a high ionic strength, and high $p\text{CO}_2$ represses sorption of Cr(VI) on this solid (Reich and Koretsky 2011). Adsorption of Pb was most influenced by pH, ionic strength and Pb loading on quartz and kaolinite surfaces (Reich et al. 2010). This conclusion concurs with that found by several other studies of ion adsorption on mineral surfaces at differing ionic strengths and pHs including those by Gu et al. (2010), Dyer et al. (2003) and Gu and Evans (2008). In contrast, adsorption of Pb on hydrous ferric oxide (HFO) was not significantly dependent on ionic strength for systems with 0.001 to 0.1 M NaNO_3 (Reich et al. 2010). This conclusion is supported by prior work (e.g., Roberston and Leckie 1997; Weisner et al. 2006) showing that the influence of ionic strength is dependent upon various factors including adsorption site type as defined by the mineral surface.

Sorbents in combination have the potential to influence the quantity of adsorption that occurs due to solid interactions. Such interactions include coating of a mineral by another or dissolution of one solid with subsequent precipitation of a new solid on the surface of another, blocking adsorption sites. Natural groundwater and sediment systems are rarely composed of a single mineral. The solid composition is typically heterogeneous, containing a variety of minerals and other solids. Thus, significant mineral interactions are probable. Understanding of how and if these interactions affect adsorption of ions will contribute to an understanding of the behavior of contaminant plumes in groundwater systems.

A study of a groundwater aquifer in the Cape Cod area has shown that coatings, mainly goethite, on aquifer minerals often dominate ion adsorption, in spite of the fact that other minerals comprised the majority of the sediment (Zhang et. al. 2011). Another study showed that iron oxide coatings on aquifer sediments are significant contributors to the adsorption of Pb and Zn ions (Coston et. al. 1995). Mixed mineral systems, not coated, also have the potential to affect adsorption because one solid may dominate ion sorption under a particular solution condition, as seen, for example, with Pb adsorption on physical mixtures of HFO and kaolinite (Reich et. al. 2010).

The hypotheses examined in this study are that adsorption of Co will be controlled by the presence of maghemite in solution and adsorption of Cr(VI) will be controlled by the presence of quartz. These hypotheses will be tested by measuring Co and Cr(VI) adsorption edges in slurries containing nanoparticulate maghemite, quartz, physical mixtures of these, or maghemite-coated quartz with NaNO₃ background electrolyte to determine whether the adsorption of Co and Cr(VI) are dominated by the maghemite or quartz, respectively.

2. MATERIALS AND METHODS

Quartz and maghemite were chosen as the sorbents for the experiments completed in this study. The quartz is Min-U-Sil 5, a natural, high purity, ground quartz with a median particle diameter of $\sim 1.4 \mu\text{m}$ (U.S. Silica, 2008), purchased from the U.S. Silica company in Berkeley Springs, WV. The maghemite was obtained as iron (III) oxide from the Aldrich Chemistry company. The maghemite is a nanopowder ($< 50 \text{ nm}$ in particle size). Quartz coated with the nanopowder maghemite (obtained from Michael Komarek) was also used in some experiments. The success of the coating process was verified using an electron microscope.

Hydroxylamine hydrochloride (HA-HCl) extractions were conducted to verify the coating of the quartz with maghemite. A solution of 100 mL of 0.5 M HA-HCl was made from HA-HCl powder. 0.5 g of solid, either coated quartz or pure maghemite, was added to 20 mL of the 0.5 M HA-HCl solution in 50 mL test tubes. Three replicates were carried out for each solid together with one no-solid control. The test tubes were placed on a rotator for 16 hours. After 16 hours, the samples were centrifuged at 8,000 rpm for 30 min or until the supernatant was visually separated from the solid. The supernatant was pipetted off and filtered using a $0.45 \mu\text{m}$ syringe-filter. The samples were then diluted by either 10 or 100 times. The concentration of iron was tested using the FerroZine method with a UV/Vis spectrophotometer.

BET analyses were conducted on the pure maghemite and coated quartz to determine surface area using a Quantachrome Instruments NOVA 2200e Surface Area & Pore Size Analyzer. Weighed samples of each solid were placed into short 9 mm Quantachrome tubes and degassed at 80°C for 16 hr, after which the samples were allowed to cool and then reweighed. The NOVA instrument calculates the density of the solid as well as the surface area using 99.9% purity

nitrogen gas as the adsorbate. Liquid nitrogen was used as the coolant for analysis. 11-point BET analysis was conducted and the resulting surface area was recorded.

Adsorption edges, as a function of pH, were measured for Co and Cr on systems containing 2 g/L of pure quartz, maghemite or maghemite-coated quartz as well as for systems with physical mixtures of quartz and maghemite. Each edge was measured with a NaNO_3 background electrolyte concentration of 0.01 M. The concentration of sorbates varied from 10^{-5} to 10^{-6} M. For each edge experiment, 500 mL solutions containing sorbent, sorbate, and background electrolyte were prepared in a 1 L nalgene bottle. Two 10 mL control samples were taken prior to the addition of the sorbent. The nalgene bottle containing the 500 mL slurry was capped and placed on a Lab Quake shaker for 24 hours at 200 rpm. The 500 mL slurry was then placed on a stir plate and titration was started immediately. The slurry was titrated to an initial pH of approximately 2.5 using drops of concentrated 0.001, 0.01, and 0.1 M HCl. Additional drops of concentrated 0.01, 0.1, and 1 M NaOH were used to increase the pH. 10-12 mL of the slurry was removed at approximately 0.5 pH intervals for a total of 15 samples spanning a pH range of ~2.5 to 10. These samples were then placed on the shaker with the controls for 24 hours to allow sorption reactions to reach equilibrium. After the equilibration period, the pH of each sample was measured. The samples were then centrifuged at the maximum speed on a Fisher Scientific Centrifuge for 10 min or until the solid and supernatant were visually separated. The supernatant was pipetted off and filtered using a 0.45 μm syringe-filter. The concentration of total Co or Cr remaining in the supernatant was tested using ICP-OES. For ICP analyses, samples were acidified using trace metal grade concentrated nitric acid (~5%) and spiked with an yttrium internal standard. Calibration standards were prepared using the yttrium internal standard and were matrix-matched to samples with the same NaNO_3 concentration. The

concentration of Cr(VI) was tested using the diphenylcarbazide method with a UV/Vis spectrophotometer. The concentration of adsorbed Co or Cr was calculated based on the difference between the concentration of added metal (verified with control samples) and the concentration measured in the supernatant.

4. RESULTS AND DISCUSSION

4.1 BET Surface Area Analyses

The surface area of the maghemite measured using 11-point BET analysis is $37.1 \text{ m}^2/\text{g}$ ($\pm 1\%$). The surface area of the maghemite-coated quartz from the BET analysis is $5.9 \text{ m}^2/\text{g}$ ($\pm 1\%$). A previous study found the surface area of the quartz to be $9.2 \text{ m}^2/\text{g}$ (Landry et. al. 2009). The surface area of the maghemite is large, which is as expected due to the nanoscale particle size ($<50 \text{ nm}$). The surface area of the coated quartz is much smaller than that of the pure maghemite. However, it seems that the addition of the maghemite coating onto the quartz decreases the surface area significantly. The results suggest that adsorption of ions should be greatest for the pure maghemite and least for the coated quartz if available surface area were the only major influencing factor.

Scanning electron microscopy images (courtesy of Sherine Obare and Clara Adams, Dept of Chemistry, WMU) show a minimal coating of maghemite on the quartz grains (Figure 1). The images also show that the quartz grains are larger than the maghemite grains.

Maghemite

Maghemite Coated Quartz

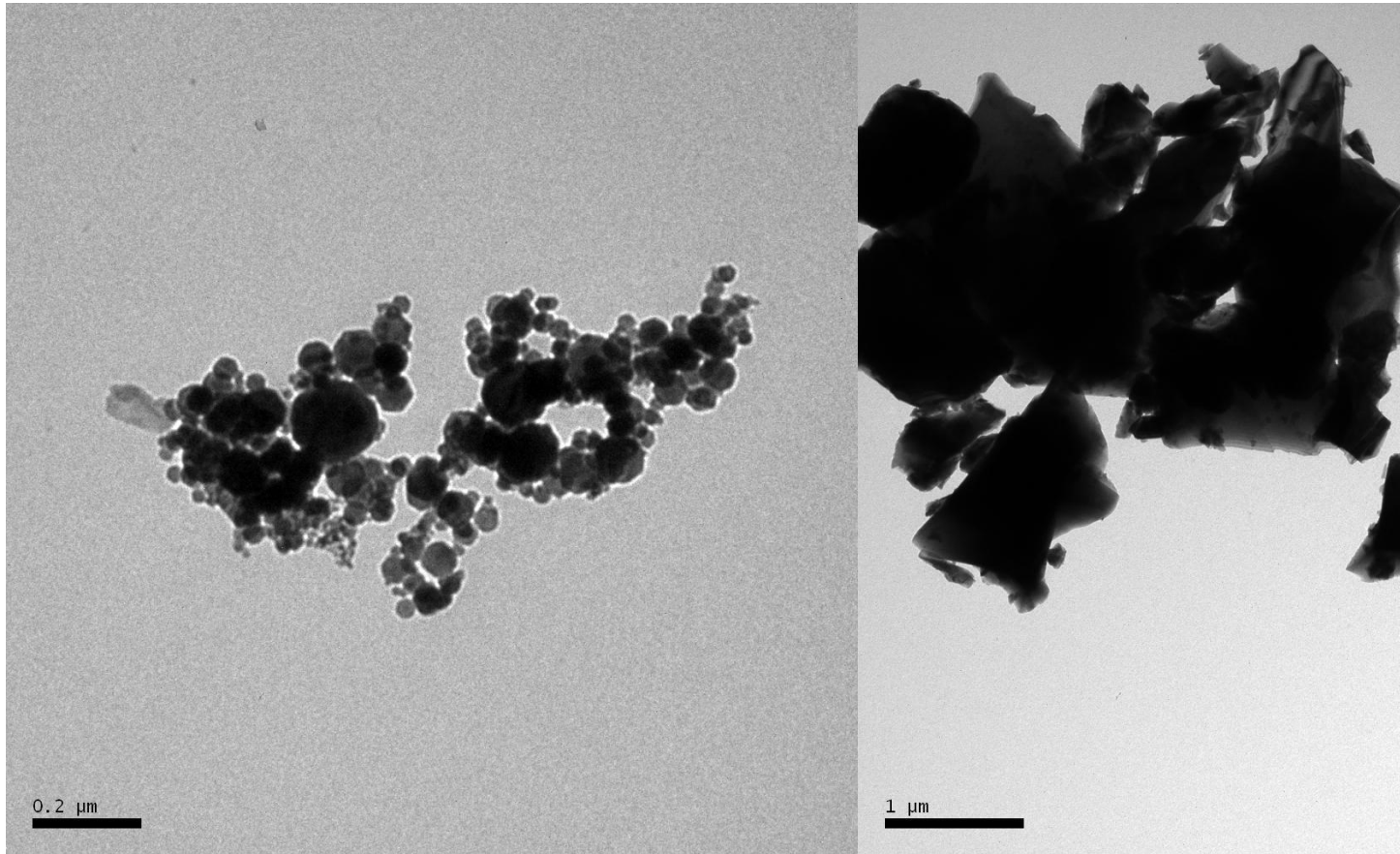


Figure 1. Scanning electron microscopy images (from Sherine Obare and Clara Adams, Department of Chemistry, WMU) of maghemite (left) and maghemite coated quartz (right). Rounded grains are maghemite and angular grains are quartz.

4.2 Hydroxylamine HCl Extractions

The hydroxylamine-hydrochloric acid (HA-HCl) extractions were used to assess the amount of maghemite that coated the quartz. During the extractions, Fe is reductively dissolved into solution by the HA-HCl, and the concentration of released Fe is measured. The concentration of Fe in solutions extracted from the maghemite-coated quartz was approximately 545 μM , which converts to approximately 22 moles of Fe per g solid. The concentration of Fe in extracted solutions from the pure maghemite was approximately 5830 μM , which converts to

approximately 230 moles of Fe per g solid. Thus, a given mass of maghemite-coated quartz contains approximately 10 times less Fe than the same mass of pure maghemite. As stated in previous studies, small amounts of coatings on mineral surfaces can dominate the adsorption of ions (Zhang et. al. 2011 and Coston et. al. 1995), thus, even this small quantity of maghemite may have a large effect on ion adsorption.

4.3 Adsorption Edge Experiments

4.3.1 Co adsorption

Adsorption of Co was measured as a function of pH on pure maghemite and physical mixtures of maghemite and quartz. These experiments were done using a Co concentration of 10^{-5} M and NaNO_3 background electrolyte concentration of 0.01 M. An initial experiment was conducted to analyze the adsorption of Co on 2 g/L of maghemite. The edge is typical of that of cations, with maximum sorption at high pH and minimum sorption at low pH (Figure 2). The adsorption “edge” spanned a pH range of approximately 4 to 7. The pH_{50} , the pH value at which 50% of the total Co is sorbed on the maghemite is 5.7 ± 0.1 . This value differs from the pH_{50} of approximately 8 for experiments using 0.01 M NaNO_3 , 10^{-5} M Co, and 2 g/L of quartz (Landry et al. 2009).

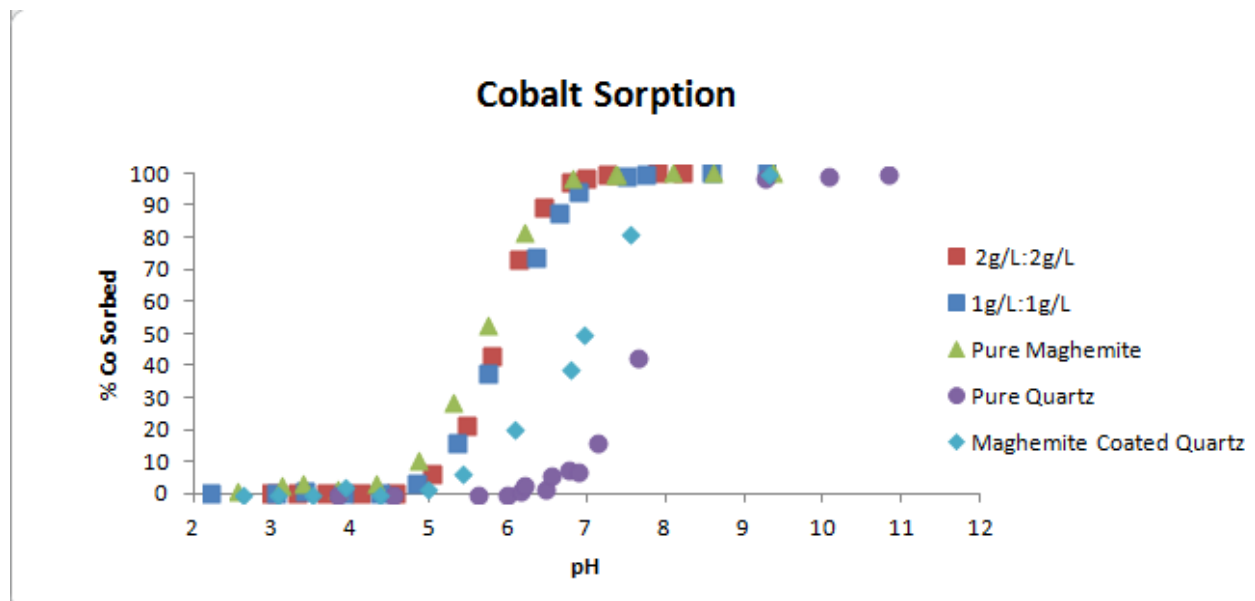


Figure 2. Adsorption of 10^{-5} M Co on equal masses of physically mixed quartz and maghemite (1 or 2 g/L of each) and 2 g/L of pure maghemite, maghemite coated quartz, and pure quartz in a background electrolyte of 0.01 M NaNO_3 .

Two experiments with physical mixtures of quartz and maghemite were conducted to study possible mineral interactions. Each experiment had a Co concentration of 10^{-5} M and a NaNO_3 background electrolyte concentration of 0.01 M. The concentrations of quartz and maghemite differed in the two experiments. In the first experiment, the total concentration of solids was kept at 2 g/L. Thus, the concentration of quartz was 1 g/L and the concentration of maghemite was 1 g/L. In the second experiment, each solid had a concentration of 2 g/L for a total solid concentration of 4 g/L. This was done in order to more readily compare the edge with the edges measured on pure quartz and pure maghemite. Surprisingly, the concentration of solids had no significant effect on the sorption pH edges (Figure 2). The pH range over which cation sorption increases with increasing pH spanned a range of approximately 4.5 to 7 for both of the experiments, and the pH_{50} of both mixed mineral systems is approximately 6 ± 0.1 . However, at the upper portions, pH range of 6 to 7, the adsorption edges of the physical mixtures shift slightly to the right, closer to the adsorption edge of pure quartz. This maghemite-like edge

for the mineral mixtures suggests that the maghemite (or Fe released from dissolving maghemite) may block the quartz sites, even in these physical mixtures. Alternatively, the stronger sorption of Co on maghemite, as demonstrated by the lower pH_{50} compared to the pure quartz system, may dominate Co adsorption in the physical mixtures.

Experiments using a concentration of 2 g/L maghemite coated quartz, 0.01 M NaNO_3 , and 10^{-5} M Co were conducted to assess the influence of coatings on adsorption. The coated quartz was also used because it is a good analog for natural systems because natural systems often contain minerals coated with iron oxides or other minerals. The pH_{50} of the coated quartz is 7 ± 0.1 with Co sorption increasing over a pH range of ~ 5 to 9 (Figure 2). Prior studies of Co on pure quartz found a pH_{50} for 10^{-5} M Co sorption on 2 g/L quartz with 0.01 M NaNO_3 of $\sim 8 \pm 0.2$, with Co sorption increasing over a pH range of approximately 7 to 9 (Landry et. al. 2009; Figure 2). The adsorption edge of the coated quartz falls approximately halfway between that of the pure maghemite and pure quartz. This suggests that much of the Co sorption is dominated by the presence of maghemite coating the quartz, in spite of the fact that there is less total maghemite present in these systems.

Another cation, Cd, has been analyzed under the same sorbate (10^{-5} M Cd), sorbent (2 g/L pure quartz, pure maghemite or maghemite-coated quartz), and background electrolyte (0.01 M NaNO_3) conditions (Michael Komarek, personal communication). The Cd adsorption edge on coated quartz falls between the pure maghemite and pure quartz, similar to the Co edges measured in this study (Figure 3). This suggests that, as for Co, the adsorption of Cd is dominated by relatively small quantities of maghemite. However, the difference between the three Cd edges is much smaller than observed for Co.

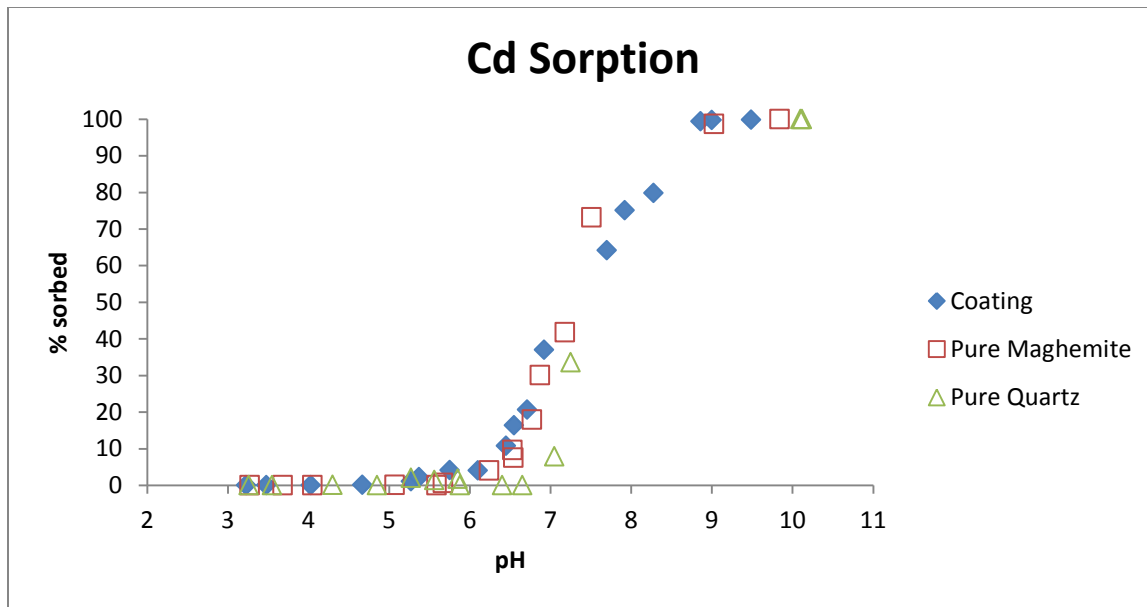


Figure 3. Adsorption of 10^{-5} M Cd on equal masses of coatings, pure maghemite, and pure quartz at 2 g/L with a background electrolyte of 0.01 M NaNO_3 (data from Dr. Michael Komarek, Czech University of Life Sciences Prague, personal communication).

4.3.2 Cr(VI) adsorption

Adsorption edge experiments for Cr(VI) on quartz were completed using 2 g/L quartz, 0.01 M NaNO_3 and either 10^{-5} or 10^{-6} M Cr(VI). For these conditions, an insignificant (below detection limits) quantity of Cr(VI) is sorbed by the quartz (Figure 4). A comparison of UV/Vis data and ICP-OES data to measure Cr(VI) and total Cr in solution, respectively, shows that insignificant amounts of Cr are present in solution. The 10^{-6} M Cr(VI) UV/Vis data is elevated, likely due to a systematic error because the total Cr analyzed with the ICP-OES should not be lower than that of just the Cr(VI).

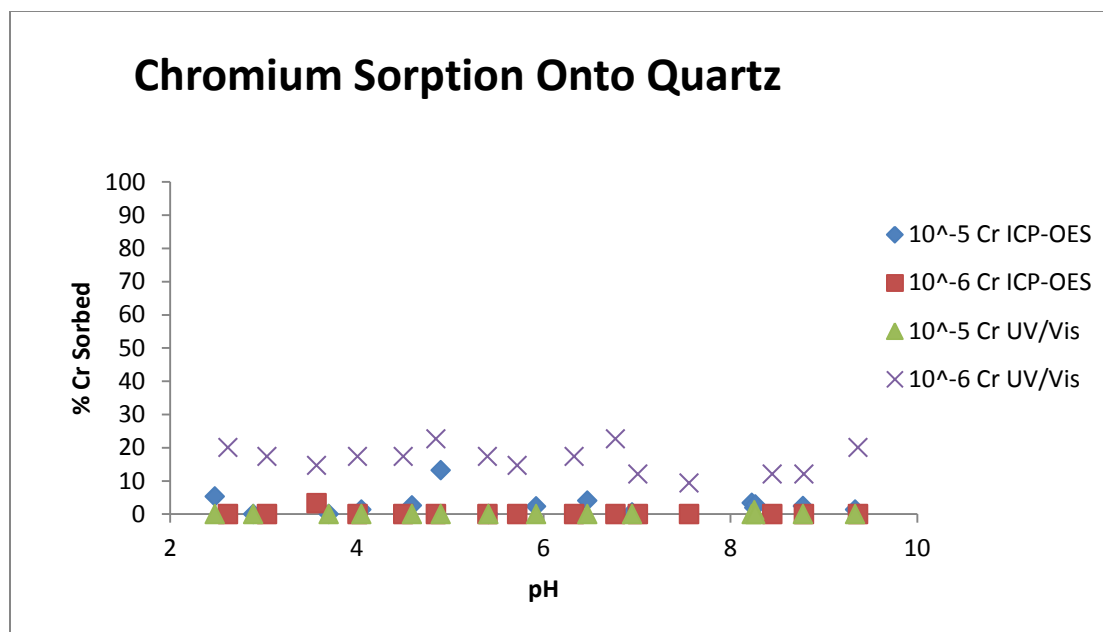


Figure 4. Adsorption of 10^{-5} and 10^{-6} M Cr on 2 g/L of pure quartz in a background electrolyte of 0.01 M NaNO_3 . UV/Vis and ICP-OES were used to analyze for Cr(VI) and total Cr in solution, respectively.

In contrast to quartz, Cr(VI) is readily adsorbed on nanosized maghemite. This has been noted in previous studies as well. For example, Hu et al. (2005) proposed a method using nanosized maghemite to remove Cr(VI) from waste water. They found that Cr(VI) was significantly adsorbed by the maghemite, with optimal adsorption occurring at a pH of 2.5. An adsorption edge measuring 10^{-5} Cr(VI) on 2 g/L pure maghemite with 0.01 M NaNO_3 showed that Cr is significantly sorbed onto maghemite (Figure 5; Krishna Stephen, Western Michigan University, personal communication). An adsorption edge for Cr(VI) on maghemite-coated quartz was intermediate between edges measured for the same mass of pure quartz or pure maghemite (Figure 5). This suggests that the adsorption of Cr(VI) in the maghemite-coated quartz system is dominated by the presence of maghemite.

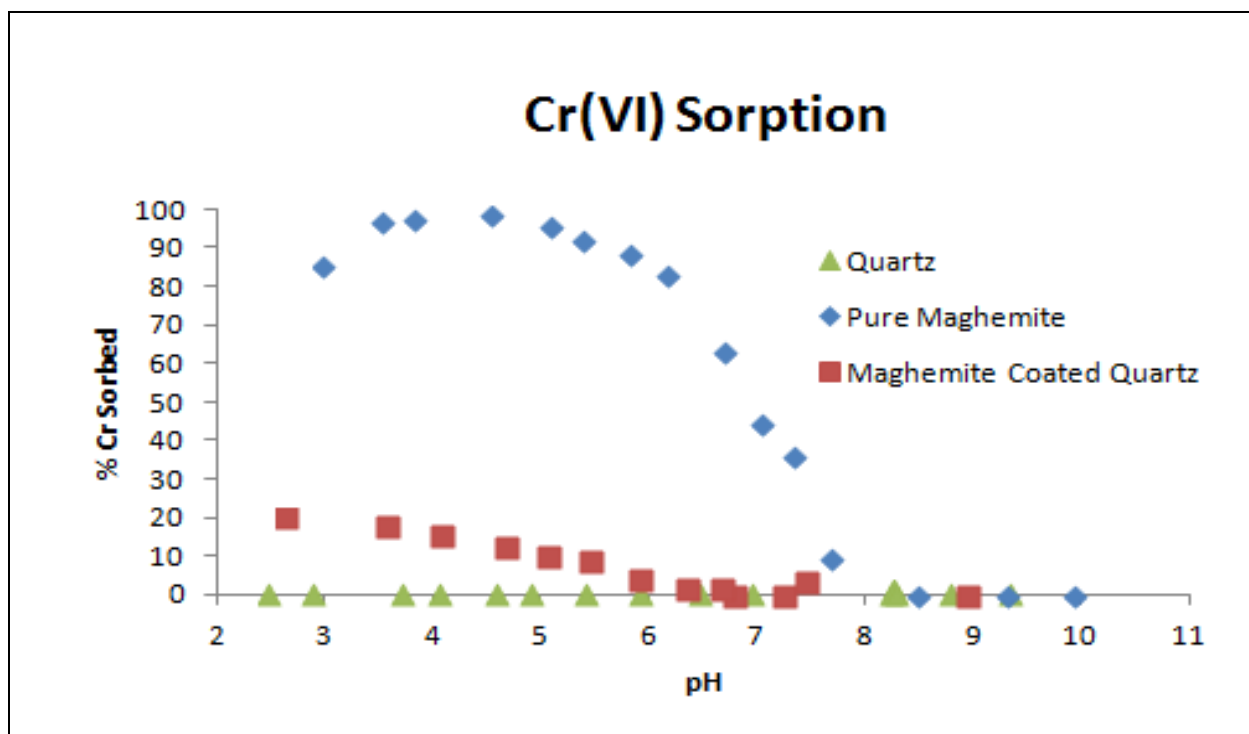


Figure 5. Adsorption of 10^{-5} M Cr on 2 g/L of pure quartz, pure maghemite, and maghemite coated quartz in a background electrolyte of 0.01 M NaNO_3 . Pure maghemite data from Krishna Stephen, Western Michigan University, personal communication.

5. CONCLUSIONS

Cobalt sorbed strongly onto pure maghemite and pure quartz. The adsorption of Co in physical mixtures of maghemite and quartz closely resembled adsorption on pure maghemite, with a slight shift to more alkaline pH at ~6 to 7. The similarity of the edge to that measured for pure maghemite suggests that maghemite controls most of the Co adsorption in the physically mixed system. Changes in concentrations of sorbents in the mixed systems resulted in insignificant changes in adsorption edges. The adsorption edge for Co on maghemite-coated quartz also lay between those of pure quartz and pure maghemite, with the edge slightly closer to the pure maghemite. This indicates that in natural systems, the adsorption of Co will likely be

controlled by the presence of maghemite rather than quartz. The Cd data gathered by Michael Komerak showed similar trends to those observed for Co. The Cd adsorption edge in the pure maghemite system is at a slightly lower pH than the edge for maghemite-coated quartz and the pure quartz edge is at a slightly higher pH.

It is important to note that while Co and Cd significantly sorb onto quartz and maghemite, Cr(VI) does not sorb appreciably onto quartz under the conditions assessed in this study. Cr(VI) does, however, significantly sorb onto maghemite, as shown by Krishna Stephen. In the maghemite-coated quartz systems, the sorption of Cr(VI) was likely dominated by the maghemite, as shown by the significant increase of Cr(VI) adsorption at low pH compared to the pure quartz system.

5.1 Suggestions for Future Work

Adsorption experiments for Co and Cr(VI) on maghemite-coated quartz could be used to determine how small amounts of maghemite influence adsorption of these ions on quartz. This could be done by measuring adsorption edges with Cr(VI), Co, and NaNO₃ concentrations comparable to those used in this study (10^{-5} M Co, 10^{-5} and 10^{-6} M Cr, and 0.01 M NaNO₃), but with varying concentrations of the maghemite coatings. One set of experiments should be done using less than 2 g/L of maghemite-coated quartz in order to determine if small amounts of maghemite can dominate the adsorption of ions. Cr(VI) would be best to use in this situation due to the insignificance of sorption on quartz. A second set of experiments should be done by calculating the mass of maghemite-coated quartz needed for a total maghemite concentration of 2 g/L. This would enable the possible mineral interaction effects to be compared to the adsorption on pure maghemite. X-ray absorption spectroscopy or XAS could be used to confirm

whether the Co and Cr ions are associating with the iron or silicon sites. The remaining solid from the samples could be analyzed using this technique.

Kinetics of adsorption on each of the mineral assemblages would also provide useful information. Adsorption edges could be measured at 1 hr, 4 hr, 24 hr, 48 hr, 1 week, and 2 week intervals. The kinetics would give a better idea whether mineral interactions are actually causing the difference in adsorption edges between sorbents. This is because with a longer equilibration time, mineral interactions are assumed to be greater. Thus, it would be hypothesized that the 1 week and 2 week intervals would have adsorption edges that are significantly influenced by mineral interactions in comparison to the 1 or 4 hour intervals.

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