Sorption mechanisms of metals to graphene oxide

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Abstract. Environmental toxic metal contamination remediation and prevention is an ongoing issue. Graphene oxide is highly sorptive for many heavy metals over a wide pH range under different ionic strength conditions. We present x-ray absorption fine structure (XAFS) spectroscopy results investigating the binding environment of Pb(II), Cd(II) and U(VI) ions onto multi-layered graphene oxide (MLGO). Analysis indicates that the dominant sorption mechanism of Pb to MLGO changes as a function of pH, with increasing inner sphere contribution as pH increases. In contrast, the sorption mechanism of Cd to MLGO remains constant under the studied pH range. This adsorption mechanism is an electrostatic attraction between the hydrated Cd²⁺ ion and the MLGO surface. The U(VI), present as the uranyl ion, changes only subtly as a function of pH and is bound to the surface via an inner sphere bond. Knowledge of the binding mechanism for each metal is necessary to help in optimizing environmental remediation or prevention in filtration systems.

1. Introduction

Graphene nanosheets are unique, 2-D systems with physical and chemical properties generating applications in a wide range of fields. One variation is graphene oxide, where oxidation of graphene's aromatic six-member carbon rings results in covalently bonded functional groups on both the basal planes and along the nanosheet edges, possibly including basal sites of epoxide (red), ketone (green), and hydroxyl (black) functional groups and edge site ester or lactol (blue) functional groups, including carboxylic/phenolic groups as shown in figure 1 [1]. The high surface area-to-mass ratio makes graphene oxide an ideal candidate for sorbing heavy metal ions from solution. In fact, multi-layered graphene oxide (MLGO) has exceptionally high reported sorption capacity for several toxic metals including lead (842 mg/g) [2], cadmium (106.3 mg/g) [3] and uranium (97.5 mg/g) [4]. These results also indicate that metal adsorption to MLGO depends strongly on the pH and ionic strength of the system. The high sorption capacity makes graphene oxide a promising new material for filtration systems and for in situ or ex situ remediation.

Effective use of graphene oxide in this capacity requires knowledge of how and why sorption occurs under environmental conditions. Possibilities for this adsorption include direct covalent inner-sphere bonds formed between de-protonated functional groups on the surface and the metal of interest or electrostatic outer sphere bonds formed between the surface and the metal of interest surrounded by a hydration sphere of water molecules, as shown in figure 1. X-ray absorption fine structure (XAFS)
spectroscopy provides the identity and distance of elements in the local environment surrounding a central atom [5]. XAFS can differentiate between elements, requires no long range order and is sensitive to small concentrations of the element of interest. These characteristics make XAFS an ideal technique to identify the sorption mechanisms of metals to surfaces in aqueous environments.

In a previous study, Pb adsorption onto MLGO was studied for the pH range of 4.9-8.3. The sorption mechanism of Pb onto MLGO is strongly dependent upon pH, with outer sphere electrostatic attraction being the dominant mechanism at low pH and inner sphere covalent bonding being the dominant mechanism at high pH. In contrast, Cd adsorption to MLGO over the pH range of 4.9-8.1 exhibited only a single mode of sorption. The spectra are all nearly identical to each other. The features of the samples closely resemble the hydrated free Cd$^{+2}$ ions in solution, but do not exactly replicate it. The best fit for the samples used only a Cd-O path with slightly larger Debye-Waller factors than the free Cd$^{+2}$ ions. This would be consistent with an electrostatic outer sphere adsorption since the close presence of the surface to the Cd would increase the disorder compared to the Cd$^{+2}$ ions in solution.

2. Materials and methods
The preparation, characterization and experimental methodologies are described in Duster et al. [6]. In brief, for the XAFS analysis, batch metal sorption experiments use 420 mg/L MLGO with 0.1 M NaClO$_4$ in ambient air (carbonate concentration < 0.6 ppm in solution) exposed to 10 ppm U before being centrifuged and the hydrated paste taken for XAFS analysis. Aqueous standards containing 10 mM U and 100 mM perchlorate salt, acetate salt, or ethylenediaminetetraacetate (EDTA) salt at appropriate pH values were also prepared to mimic the hydrated metal ion, bidentate inner spherically bound metal ion, and monodentate inner spherically bound metal ion, respectively. The hydrated paste was sealed in slotted Teflon holders using Kapton tape, and samples and standards were measured at the U L(III)-edge (17,166 eV) at the MRCAT 10-ID and 10-BM beamlines [7] at the Advanced Photon Source (APS) at Argonne National Laboratory near Chicago, IL, USA. Data analysis used the methodology of the UWXAFS package [8]. For the U fitting, a range of 1.15-3.5 Å with a Fourier transform range of 3.5-12.0 Å$^{-1}$ was used for pH values of 4.0, 5.8, 7.2 and 8.5.

3. Results and discussion
U(VI) in solution generally appears as the uranyl ion, UO$_2^{+2}$, where the two oxygen atoms from the ion align axially and the bonding atoms coordinate in the equatorial plane. X-ray absorption near edge structure (XANES), which is sensitive to the oxidation state of the uranium, indicates that all uranium in this system remains as U(VI). The U-MLGO XANES data of the samples show only subtle differences from each other, especially when compared with the hydrated uranyl ion standard as seen in figure 2a. In the extended x-ray absorption fine structure (EXAFS) region, the U-MLGO data again shows only slight differences from each other. This suggests that there is one dominant type of adsorption mechanism across the studied pH range, similar to the Cd-MLGO system. In contrast though, the U-MLGO is clearly different from the hydrated uranyl ion and the precipitates formed at high pH, as shown in figure 2b. Subtle differences can be seen between the U-MLGO samples, with
these differences trending according to pH. This may be the result of increased disorder associated with varying aqueous speciation of the uranyl ion, as it forms several aqueous complexes with hydroxyl or carbonate ions in solution that change within the studied pH range. However, this effect seems to be small and does not change the dominant mode of sorption. As such, the binding mechanism of the U on the MLGO surface is most likely an inner sphere adsorption.

A comparison of the U-MLGO samples and precipitates formed by adding concentrated amounts of uranium (10 mM) to solution at pH 7.2 or 8.5 is shown in figure 3. Another study found a uranyl precipitate (similar to the one observed at pH 7.2 in figure 3) forming on a single-layer graphene oxide surface as low as pH 6.1 [9]. However, this study used a uranium concentration of 0.5 mM (119 ppm) on 0.4 g/L graphene oxide, which is a similar graphene oxide concentration to the current study, but an order of magnitude higher uranium concentration. At the lower uranium concentration used in this study, there does not seem to be any uranium precipitation occurring on the MLGO surface. The uranyl precipitate data show prominent differences to the data at low R (1.0-2.5 Å) and features between 3.5-4.0 Å that are lacking in the U-MLGO samples. Fitting is also inconsistent with a U-U bond for the U-MLGO data at this location, so there is no evidence that a significant amount of precipitate is forming on the U-MLGO samples in this study. As such, the sorption mechanism of U to MLGO in this study is determined to be inner sphere adsorption.

4. Conclusions
We have shown that different heavy metals have different adsorption mechanisms to MLGO in a moderate pH range that would be common in environmental remediation situations or in filtration
systems. XAFS has enabled us to identify the dominant adsorption mechanism for Pb, Cd and U to MLGO over this pH range. The Pb(II) adsorption mechanism is strongly dependent on the system pH, with adsorption controlled by a combination of outer sphere electrostatic attraction and inner sphere covalent bonding. At lower system pH, outer sphere adsorption dominates, while inner sphere adsorption takes over as the main sorption mechanism at higher pH values. In contrast, the adsorption mechanism for Cd and U is relatively independent of pH. For Cd, at all measured pH values adsorption is dominated by an electrostatic outer shell attraction between the Cd(II) and its coordinating water molecules and the MLGO surface. The U-MLGO systems show subtle variation across the measured pH range, but adsorption seems to be dominated by an inner sphere bond for all the samples. These slight differences may be attributable to aqueous complexation of the uranyl ion as it changes in pH. However, the U-MLGO samples are clearly unique from the hydrated uranyl ion in solution, indicating that attraction is not electrostatic. Similarly, the samples are inconsistent with appreciable precipitation, indicating that the U(VI) is bound to the MLGO surface via an inner sphere bond. Overall, metal adsorption to MLGO varies with the type of metal, indicating that it might be possible to tailor the material to best adsorb certain heavy metals, making it ideal for environmental remediation or filtration systems.

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