Regular Article

An X-ray absorption fine structure spectroscopy study of metal sorption to graphene oxide

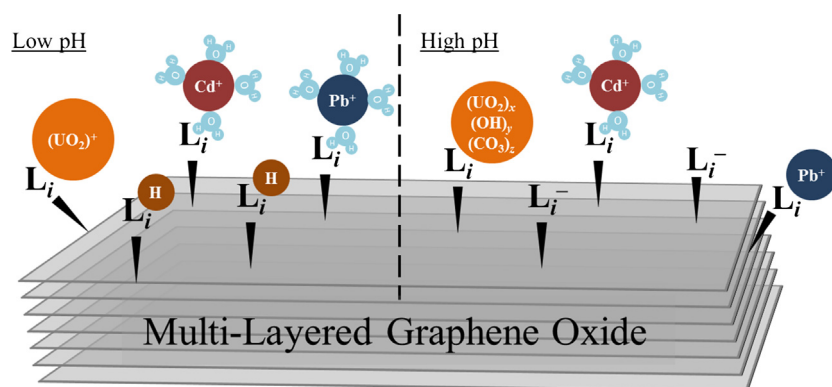Allison R. Showalter [a], Thomas A. Duster [b], Jennifer E.S. Szymanowski [b], Chongzheng Na [b], Jeremy B. Fein [b,*], Bruce A. Bunker [a]

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GRAPHICAL ABSTRACT

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Remediation and prevention of environmental contamination by toxic metals is an ongoing issue. Additionally, improving water filtration systems is necessary to prevent toxic metals from circulating through the water supply. Graphene oxide (GO) is a highly sorptive material for a variety of heavy metals under different ionic strength conditions over a wide pH range, making it a promising candidate for use in metal adsorption from contaminated sites or in filtration systems. We present X-ray absorption fine structure (XAFS) spectroscopy results investigating the binding environment of Cd (II), U(VI) and Pb(II) ions onto multi-layered graphene oxide (MLGO).

This study shows that the binding environment of each metal onto the MLGO is unique, with different behaviors governing the sorption as a function of pH. For Cd sorption to MLGO, the same mechanism of electrostatic attraction between the MLGO and the Cd^{+2} ions surrounded by water molecules prevails over the entire pH range studied. The U(VI), present in solution as the uranyl ion, shows only subtle changes as a function of pH, likely due to the varied speciation of uranium in solution. The adsorption of the U to the MLGO is through a covalent, inner-sphere bond. The only metal from this study where the dominant adsorption mechanism to the MLGO changes with pH is Pb. In this case, under lower pH conditions, Pb is bound onto the MLGO through dominantly outer-sphere, electrostatic adsorption, while under higher pH conditions, the bonding changes to be dominated by inner-sphere, covalent adsorption.

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Since each of the metals in this study show unique binding properties, it is possible that MLGO could be engineered to effectively adsorb specific metal ions from solution and optimize environmental remediation or filtration for each metal.

1. Introduction

Graphene, a single-atomic-layer 2D sheet of carbon, is an exciting material with a multitude of active research areas [1], including variations of the basic material such as graphene oxide (GO) and reduced graphene oxide [2]. Active areas of research for graphene derivatives, especially multi-layered graphene oxide (MLGO), include electronics [3], energy storage [4], biosensing [5,6] and other biomedical applications [7,8], water desalination [9] and environmental remediation [10,11]. In MLGO, oxygen-containing functional groups, including carboxyl, hydroxyl and epoxyl groups, are attached to the aromatic six-member carbon rings that compose graphene [10]. In addition, MLGO boasts an exceptionally large surface-area-to-mass ratio of hundreds of m^2/g [12]. These characteristics allow graphene to adsorb significant concentrations of a wide range of aqueous environmental toxins, from charged metal ions [11] and dyes [13,14], to organic materials [15] including pesticides [16] and antibiotics [17]. MLGO is also being developed for environmental contamination remediation and wastewater treatment [18,19] because it can readily absorb magnetic materials along with aqueous environmental contaminants, allowing easy magnetic extraction from solution [20,21] and can be recovered for reuse [22]. Experimentation is ongoing to optimize the sorbent for heavy metals through addition of amino acid functional groups to the MLGO surface [23]. MLGO exhibits one of the highest sorption capacities of any solid for metal ions of environmental concern such as Zn(II) [24], As(III/V) [25], Cd(II) [26], Pb(II) [22,27] and U(VI) [28,29].

In order to optimize the use of MLGO for environmental remediation or in wastewater treatment, it is necessary to develop quantitative predictive models that enable estimations of the extent of adsorption that occurs in complex geologic or engineered systems. The accuracy of these predictive models depends on a precise understanding of the binding mechanisms between metal ions and the MLGO surface. Sorption of the metal cations onto MLGO can occur in a variety of ways, including direct, covalent inner-sphere bonds between the metal and de-protonated functional groups on the MLGO surface, or via weaker electrostatic outer-sphere bonds where the metal ion with its surrounding shell of hydrating water molecules is held on the surface by electrostatic attraction. X-ray absorption fine structure (XAFS) spectroscopy provides constraints on the identity and distance of elements in the local environment surrounding a central atom of interest [30], and the approach can be used even with relatively low adsorbed metal concentrations, making XAFS ideal for determination of the sorption mechanism of metals to surfaces of environmental relevance.

Although a number of studies have measured metal adsorption onto MLGO [e.g., 13,22,28,31,32–38], the binding mechanisms of many metals onto MLGO remain poorly constrained. Cd(II) adsorption to MLGO has been attributed to outer- or inner-sphere adsorption in different studies. Zeta potential measurements of the MLGO surface and measurements of bulk Cd adsorption onto MLGO suggested electrostatic attraction [13], in addition to batch adsorption studies of Cd to MLGO in a 1:200 Cd:MLGO ratio where Cd adsorption was found to be strongly dependent on solution ionic strength [31] suggesting outer-sphere adsorption. In contrast, a different study on batch adsorption of Cd to MLGO in a 1:120 Cd:MLGO ratio where Cd adsorption was found to be independent of solution ionic strength [32] concluded inner-sphere adsorption. Various studies of U(VI) adsorption to MLGO using surface complexation modeling and batch adsorption studies determined uranium adsorbs in an inner-sphere bond to the MLGO surface under lower pH conditions (around 4.0–5.0) and precipitates on the surface under higher pH conditions (around 7.0–8.0) [34,35]. Pb(II) has been suggested to adsorb to the MLGO surface, especially on edge sites, based on transmission electron microscopy images and Fourier transform infrared spectroscopy [22,37]. Batch adsorption studies show conflicting results for different ratios of Pb:MLGO, with one study at a Pb:MLGO ratio of 1:25 showing that Pb adsorption to MLGO was independent of solution ionic strength, suggesting inner-sphere adsorption [39], while a different study at a Pb:MLGO ratio of 1:20 found that Pb adsorption to MLGO was dependent upon solution ionic strength, indicating the presence of outer-sphere adsorption [31]. Since conflicting results exist in the literature, this XAFS study can contribute spectroscopic determination of the binding mechanisms of Cd, U and Pb to MLGO.

Previous studies have used XAFS analysis of U-GO systems to demonstrate that the binding mechanism is inner-sphere under low pH conditions (around 4.0) and that U precipitation occurs under higher pH conditions (around 8.0) [e.g., 28,36,40], but the conditions for these studies are significantly different than those used in the current study. Li et al. [28] performed XAFS measurements on a U-GO system at pH 3.9, 6.1 and 7.6 with a U:GO ratio of 119:400. Only qualitative information can be gleaned from the data treatment, as insufficient XAFS fitting details were provided and only the lowest pH condition sample was fitted. In addition, the U-precipitate described in this study matched a solubility-limiting phase standard prepared under the same conditions. Li et al. present no evidence that the surface was involved, so the uranium may have precipitated from solution without any surface interaction. Sun et al. [36] performed XAFS measurements on a U-GO system at pH 4.0 and 8.0 with a U:GO ratio of 6:25 under carbonate-free conditions. The authors concluded that the U adsorbs in inner-sphere adsorption at pH 4.0 and forms a U precipitate at pH 8.0, but the XAFS analysis does not include σ^2 uncertainties, making it difficult to assess the fitting reliability. In addition, the present study was performed under atmospheric conditions, making it more applicable to environmental systems. This XAFS study seeks to determine the local environment of cadmium, uranium and lead atoms bound to the graphene oxide surface as a function of pH using environmentally relevant metal:MLGO ratios. The experiments reported here were conducted under similar metal loading, pH, and ionic strength conditions to those of our previous studies of the extent of bulk adsorption of U(VI), Cd(II), and Pb (II) onto MLGO [31,41]. In each case, metal adsorption is strongly pH dependent due to progressive deprotonation of binding sites with increasing pH; Cd(II) and Pb(II) exhibit a strong ionic strength dependence to the adsorption behavior, but the ionic strength dependence to adsorption is much weaker for U(VI) [31,41].