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Commodifying a Carcinogen: Critical Raw Materials from Arsenic-laden Groundwater

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Arsenic (As) is a potent carcinogen whose presence in groundwater has created a continuing global public health catastrophe. Groundwater treatment minimizes health impacts from As, but generates As-rich groundwater treatment sludge that is universally viewed as an environmental burden. At the same time, As is experiencing a renaissance. Both the European Union and the United States have classified As as a Critical Raw Material (CRM) due to the role of metallic arsenic (As(0)) in materials needed for digital infrastructure and to transition to clean energy systems, such as batteries and high speed electronics.

Bringing these two material flows together, this presentation reports a process to form valuable metallic As(0) from As-laden groundwater treatment sludges collected from several treatment plants around the world. The two-stage upcycling process consists of extracting As(V) from the sludge using alkali solution (*extraction*) followed by selective reduction of extracted As(V) (*refinement*) via thiourea dioxide (TDO), yielding upcycled As(0) solids.

Alkali extraction with 1 M NaOH lead to As extraction efficiencies reaching 98-99% for almost all sludges at the sludge/liquid (S/L) ratio of 13 g/L. At increasing S/L ratios, the extraction efficiency decreased to 72-94%, but high As concentrations exceeding 100 mg/L could be obtained. The addition of TDO to the extraction solutions reduced >99% of aqueous As(V) to form upcycled As(0) solids in optimum conditions. As K-edge XAS and TEM data (Figure 1) indicated that the upcycled As(0) solids were pure amorphous As(0) consisting of a single As-As path with coordination number ($CN_{As\text{-}As}$) near 4 and interatomic distance ($R_{As\text{-}As}$) of 2.46 Å. These structural properties contrast with the crystalline structure of commercial As(0), which has a different local bonding environment ($CN_{As\text{-}As}$ = 3, $R_{As\text{-}As}$ = 2.52 Å) and requires several As-As paths to fit longer-ranged atomic shells (Figure 1c).

Our results show that CRMs can be created from carcinogenic water treatment waste, which is a potentially disruptive technology for the water sector that can alter global As(0) supply chains. Furthermore, through the sale of recovered materials, As-rich waste upcycling can improve the challenging economics of water treatment in rural areas affected most by As-contaminated groundwater.

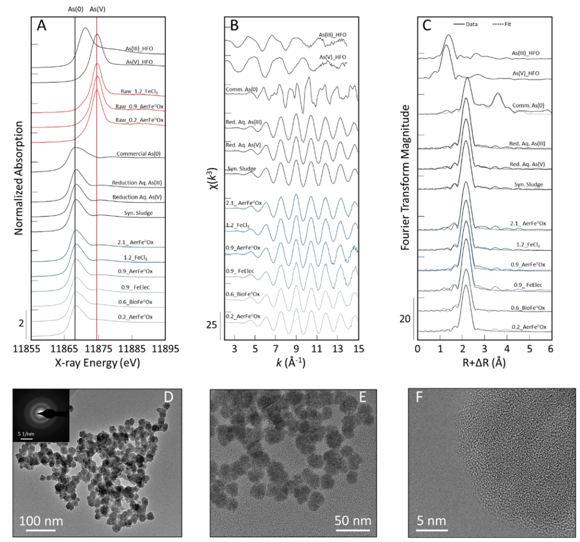

Figure 1. As K-edge XAS data (A-C) and TEM images (D-F) of upcycled As(0) solids. In Panel A, the As K-edge XANES spectra for a subset of initial raw sludges (red spectra) are provided to compare with upcycled As(0). We adopt a naming convention in this figure to identify the sludge samples that includes the As mass fraction in g/kg followed by the treatment process employed by plant. Panels A-C also include As K-edge XAS data for standards of As(III) and As(V) adsorbed to hydrous ferric oxide (As(III)_HFO, As(V)_HFO), commercial As(0) and the products of reductive As precipitation in control experiments using aqueous As(III) (Reduction Aq, As(III)), aqueous As(V) (Reduction Aq. As(V)) and synthetic sludge (Syn. Sludge). Panels D-F show the TEM data for the upcycled 0.9_AerFe^{II}Ox sample.