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Insights into the mechanisms of mercury sorption onto aluminum based drinking water treatment residuals☆

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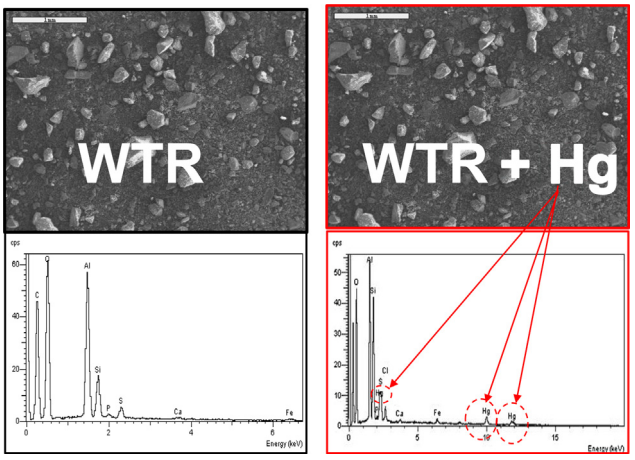
HIGHLIGHTS

- Mercury sorption by Al-WTRs involves electrostatic forces and chemisorption.
- Hg forms bonds with oxygen and sulfur atoms of Al-WTR's organic ligands.
- Mercury is incorporated into the residual fraction to form stable complexes.
- Mercury binds mainly to SiO_x species in the residual fraction.

GRAPHICAL ABSTRACT



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ABSTRACT

Several studies have demonstrated the ability of drinking water treatment residuals (WTRs) to efficiently sorb metal cations from aqueous solutions. Reported results have stimulated interest on the potential use of WTRs as sorbent for metal removal from contaminated aqueous effluents as well as in metal immobilization in contaminated soils. However, knowledge on mechanisms of metal sorption by WTRs remains very limited and data on the long-term stability of formed metal–WTR complexes as a function of changing key environmental parameters are lacking. In this study, chemical selective sequential extraction (SSE), scanning electron microscopy combined with X-ray energy dispersive spectrometer (SEM-EDS), and X-ray photoelectron spectroscopy (XPS) were used to gain insight into the different mechanisms of mercury (Hg) binding to aluminum based WTR (Al-WTRs). Results from sorption studies show that a significant portion of Hg becomes incorporated in the operationally defined residual fraction of Al-WTRs, and therefore, not prone to dissolution and mobility. The results of solid phase analyses suggested that Hg

☆ This paper reports on mechanistic sorption studies of mercury designed to add value to a readily available and abundant drinking water treatment residuals (WTR).

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immobilization by Al-WTR occurs largely through its binding to oxygen donor atoms of mineral ligands driven by a combination of electrostatic forces and covalent bonding.

1. Introduction

Past and current releases of mercury (Hg) from anthropogenic activities continue to raise concerns due to the well documented adverse effects of this metal on both human health and ecosystem functions. Lately, soil remediation technologies based on in situ immobilization of metals have regained heightened attention because of ease of application and relatively low costs. Accordingly, several sorbents are being tested for their abilities to immobilize metals within the contaminated soils. Overall, these studies have defined ideal sorbents for metal cation immobilization as fine particles, with large specific surface areas (SSA) and containing sulfur (S), nitrogen (N) and oxygen (O) as electron donors [1,2]. The ultimate goal of this study is to elucidate the potential role of drinking water treatment residuals (WTRs) as sorbent for the immobilization of metal cations in contaminated soils. However, the focus of this paper is limited to the understanding of the mechanisms of Hg sorption by aluminum based WTRs, to help predict the stability of formed metal–WTR complexes if formed within treated soils. In fact, WTRs have been used as sorbent for the immobilization of several pollutants including both negatively and positively charged ions [3–7]. WTRs are produced in abundance worldwide during drinking water treatment processes, and in the United States alone, >2 million metric tons of WTRs are produced daily [8]. However, large quantities of these produced WTRs are simply discarded in landfills, stored in onsite lagoons, or discharged into waterways [9]. We believe that one way to add value to this abundant and readily available waste material is to take advantage of its physicochemical reactivity and high sorption capacity for a wide variety of inorganic pollutants.

Research on the potential use of WTRs as cost-effective sorbent focused initially on the immobilization of oxyanions such as PO_4^{3-}, AsO_4^{3-}, SeO_4^{2-} [4,7,10]. However, recent studies point to the ability of WTRs to also immobilize metal cations [5,6]. Our own preliminary investigations showed that aluminum based WTRs (*referred to herein as Al-WTRs*) can efficiently sorb Hg from aqueous solutions [6], which can be seen as an indication of the ability to potentially immobilize Hg from soil water. Prior to considering Al-WTRs as amendment for remediation of Hg contaminated soils, current knowledge gaps on the mechanisms of Hg sorption onto Al-WTR needs to be addressed to help predict the stability of formed Hg–Al-WTR complexes under changing soil's key parameters such as pH, dissolved organic carbon, and redox potential.

In this study, laboratory experiments were conducted to gain insight into the mechanisms of Hg binding to Al-WTRs using a combination of chemical fractionation and spectroscopic methods.

2. Materials and methods

2.1. Collection and characterization of used Al-WTR sample

The Al-WTR used in this study was collected from the Manatee County Drinking Water Treatment Plant in Bradenton, Florida, USA. The pH, cation exchange capacity (CEC), organic carbon (OC) content, and elemental composition of this Al-WTR have been published elsewhere [4]. The specific surface area (SSA) was determined on both air-dried non-spiked (control) and Hg-spiked Al-WTRs using the Brunauer–Emmett–Teller N_2 adsorption method at 77 K (BET-N_2) and the CO_2 adsorption method at 273 K (Quantachrome Autosorb-1 apparatus, Quantachrome Corp). BET-N_2 and CO_2 were both used in the determination of SSA to allow for the assessment of adsorption potential limited to surface sites and that of both surface and internal micropore sites, respectively.

2.2. Preparation of Hg-spiked Al-WTR samples

Hg spiked Al-WTR samples were prepared by using a flooding technique followed by wet and dry cycles. Briefly, a known amount of Al-WTR was brought into contact with a solution of $HgCl_2$ in a 1:4 ratio (mass/volume). For these Hg sorption experiments, two sets of Al-WTR samples prepared at different times were spiked using the flooding approach.

For the first set of Hg-spiked Al-WTR samples, an acidic aqueous solution of $HgCl_2$ containing 1% concentrated HNO_3 was added to the solid phase Al-WTR to produce a total Hg concentration >20,000 mg/kg. This high concentration was selected initially to facilitate detection with solid phase analytical methods. The Hg spiking experiments were conducted in triplicates and Hg–Al-WTR mixtures left to equilibrate for an initial period of 7 days in closed containers placed in a fume hood. At the end of the seven days, the lids of the containers were removed and the samples were allowed to dry at room temperature in the fume hood. Following this initial step, a series of flooding (wet) and drying (dry) cycles were conducted, except that this time, deionized water containing no Hg was added to pre-dried Al-WTR samples. This process was designed to facilitate the incorporation of Hg into the pores of Al-WTRs, and was performed for a period of 4 months. Aliquots from this first set of samples were used for measurements of changes in micropore volumes before and after Hg spiking, the chemical determination of Hg distribution among the different geochemical fractions of Al-WTR, and solid phase analyses. The remaining Hg spiked samples were left to age at room temperature and in the fume hood for 4 years.

The second set of Hg-spiked Al-WTR samples were prepared 4 years later. In this case, Hg as $HgCl_2$ was added to the Al-WTRs as described earlier, but to produce a lesser final total-Hg concentration of about 3000 mg/kg. This concentration reduction was driven by concerns raised with regard to the handling of samples with Hg levels >5 g/kg during solid phase analyses. The Hg incorporation process was similar to the one described above and the results presented for this second set of samples are based on 4-month old samples.

In summary, the Hg-spiking experiments resulted into 3 different types of Al-WTR samples. First, a 4-month old Hg-spiked Al-WTR with a total Hg (THg) concentration >20,000 mg/kg. Second, a 4-year old Hg-spiked Al-WTR with total Hg concentration >20,000 mg/kg. Finally, and third, a 4-month old Hg-spiked Al-WTR with a THg concentration >3000 mg/kg.

2.3. Determination of Hg concentrations in Al-WTR samples

After the completion of the above wet-dry cycles, aliquots of the dry and well homogenized Hg-spiked Al-WTR samples as well as samples of the non-spiked Al-WTR were used to determine THg concentrations following samples hot acid digestion. Briefly, 5 ml of aqua regia (mixture of concentrated HNO_3 and HCl) and