



Aluminum drinking water treatment residuals (Al-WTRs) as sorbent for mercury: Implications for soil remediation

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ABSTRACT

The potential of readily available and non-hazardous waste material, aluminum drinking water treatment residuals (Al-WTRs), to efficiently sorb and immobilize mercury (Hg) from aqueous solutions was evaluated. Al-WTR samples with average specific surface area of 48 m²/g and internal micropore surface area of 120 m²/g were used in a series of batch sorption experiments. Obtained sorption isotherms indicated a strong affinity of Hg for Al-WTRs. Using the Langmuir adsorption model, a relatively high maximum sorption capacity of 79 mg Hg/g Al-WTRs was determined. Sorption kinetic data was best fit to a pseudo-first-order model, while the use of the Weber–Morris and Bangham models suggested that the intraparticle diffusion could be the rate-limiting step. Also, Al-WTRs effectively immobilized Hg in the pH range of 3–8. The results from these short-term experiments demonstrate that Al-WTRs can be effectively used to remove Hg from aqueous solutions. This ability points to the potential of Al-WTRs as a sorbent in soil remediation techniques based on Hg-immobilization.

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1. Introduction

Mercury (Hg) is one of the 13 metals in the US-EPA priority pollutant list with known negative impacts on both human health and ecological functions. Its strong ability to bioaccumulate and biomagnify in food chains leads to toxicity in living organisms. The major sources of anthropogenic Hg in soils include chlor-alkali plants, mine wastes, and Hg from several diffuse sources such as coal-fired power plants [1,2]. Although much is now known on the biogeochemistry of Hg in sedimentary environments, research on the development of cost-effective and environment-friendly remediation techniques remains a challenge. So far, only a few remediation techniques (e.g., stabilization/solidification and soil washing/acid extraction) have been tested commercially. However, their widespread use remains limited due to several factors including their prohibitive costs [3]. In fact, the remediation of metal-contaminated soils remains one of the most intractable problems of environmental restoration, and this is both a national and international issue. It requires the development of cost-effective and efficient remedial approaches that render Hg and other metal contaminants harmless, while avoiding adverse effects on the treated systems.

Drinking water treatment residuals (WTRs), sometimes referred to as waterworks sludge, are waste by-products of the drinking water treatment processes produced daily and in large quantities in most municipalities worldwide. They are formed as a result of the addition of aluminum or iron salts to raw water in order to remove colloids, silt and clay-size particles, and color [4–6]. Accordingly, WTRs consist of particles that settle as a result of coagulation and flocculation processes [6,7]. Previous studies have focused primarily on the ability of WTRs to immobilize negatively charged ions such as phosphate [8], fluoride [9], and perchlorate [10]. Studies on the efficiency of WTRs in binding cations are still lacking. Some preliminary efforts, such as the work by Brown et al. [11] found that WTR amendments in soil reduce the NH₄NO₃-extractable Cd, Pb, and Zn, suggesting that WTRs might have the capacity to immobilize these metals.

In this study, we assessed the potential of WTRs, an inexpensive and readily available waste material, to sorb and immobilize Hg from aqueous solutions in a series of batch experiments. Although WTRs are found abundantly as either Al- or Fe-based materials, the limited choice to Al-WTRs in this study stems from the fact that Fe-based WTRs could be prone to redox driven changes. This could potentially lead to the dissolution of previously immobilized metals, and therefore negate the benefit for WTRs use in soil remediation. In this study, the maximum sorption capacities, sorption isotherms, as well as the effect of pH on Hg sorption by Al-WTRs were determined. Kinetic and intraparticle diffusion models were used to gain insight on the potential sorption mechanisms of Hg by Al-WTRs particles.

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2. Materials and methods

2.1. Collection and characterization of Al-WTRs

The Al-WTRs samples were collected from the Manatee County Drinking Water Treatment Plant in Bradenton, FL, USA. In this water treatment plant, Al-WTRs are produced following the addition of alum and a small amount of copolymers of sodium acrylate and acrylamide [6]. The Al-WTRs used in this study was a stabilized material, approximately 2-year old, and was collected from an open air disposal site located next to the water treatment plant. In the laboratory, Al-WTRs material was air-dried at room temperature for a period of 4 weeks. Relatively homogeneous material was obtained by passing Al-WTRs through a 2-mm screen.

The pH and the electrical conductivity (EC) of Al-WTRs were measured in 1:1 (mass/volume (m/v)) and 1:2 (m/v) Nanopure® water suspensions, respectively, after a 4-h equilibration period using a pH meter (model 240, Corning) and an EC meter (model 1054, Markson). The organic carbon content was measured according to the Walkley–Black method [12]. The effective cation exchange capacity (CEC_e) was determined as described by Sumner and Miller [13]. The toxicity of Al-WTRs was assayed after shaking Al-WTRs with Nanopure® water in a 1:2.5 solid to liquid ratio for 2 h at 200 rpm [14]. The supernatant was then analyzed via the MetPLATE™ toxicity test, which is specific to heavy metals [15]. For total metal analysis, about 1 g of dry Al-WTRs sample was digested overnight at 110 °C with 30 mL of HNO₃/H₂SO₄ mixture (7:3, v/v) in a closed Teflon® vessel. The mixture on cooling was diluted to 50 mL with Nanopure® water. The solution was then analyzed for total concentrations of Al, As, Fe, Ca, Cu, Cr, Pb, and Zn by inductively coupled plasma atomic emission spectrometry (ICP-AES) and Hg by cold vapor atomic fluorescence spectrometry (CV-AFS). In addition, Al-WTRs were examined via scanning electron microscopy (SEM), carried out in the JSM-6330F field emission scanning electron microscope unit equipped with an X-ray energy dispersive spectrometer (SEM-EDS).

An emphasis in the characterization of used Al-WTRs was on the measurement of the specific surface area (SSA), a key parameter that strongly influences the sorption capacity of solid surfaces [16]. As a pretreatment to SSA characterization, a known amount of Al-WTRs was filled in a capillary glass tube and outgassed for 4 h under helium flow at 70 °C [17]. The SSA was then measured by nitrogen adsorption (SSA-N₂ at 77 K) and carbon dioxide (SSA-CO₂ at 273 K) methods using a Quantachrome Autosorb-1 (Quantachrome Corp.) apparatus. The SSA-N₂ was calculated using the Brunauer–Emmett–Teller or BET equation (Eq. (1)), where W is the weight of the gas adsorbed at a relative pressure P/P_0 , W_m is the monolayer capacity, and C is a BET constant.

$$\frac{1}{W((P_0/P) - 1)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C (P/P_0)} \quad (1)$$

The SSA-CO₂, which describes micropore specific surface area, was calculated using the Dubinin–Radushkevich–Kaganer (DRK) equation (Eq. (2)), where W is the amount of the gas adsorbed at relative pressure P/P_0 , W_m is the monolayer capacity, D is a constant that characterizes Gaussian distribution, P_0 is the vapor saturation pressure of CO₂ (26,140 mm Hg), and P is the equilibrium pressure (mm Hg) [18]. A plot of $\log W$ versus $[\log(P_0/P)]^2$ is used to determine the monolayer capacity W_m , from which the surface area can be calculated using Eq. (3).

$$\log W = \log W_m - D \left[\log \frac{P_0}{P} \right]^2 \quad (2)$$

$$S = \frac{W_m N A}{M} \quad (3)$$

where S is the specific surface area, A is the cross-sectional area, M is the molecular weight of the adsorbate, and N is the Avogadro number [19].

The BET-N₂ method is applied in the region of relative pressures from $P/P_0 = 0.05$ to $P/P_0 = 0.3$, while the SSA-CO₂ is carried out in the interval of relative pressures from $P/P_0 = 10^{-5}$ to $P/P_0 = 0.0029$ [18].

Finally, the zeta potential (ZP) of Al-WTRs as a function of pH was measured using the EKA electrokinetic analyzer (Anton–Paar). The EKA is used to determine the ZP of larger (non-colloidal) particles. The EKA automatically calculates the ZP by using the Helmholtz–Smoluchowski equation [20]. The pH of the electrolyte solution (1 mM KCl) was adjusted with 0.1 M HCl or 0.1 M NaOH to the desired value in the pH range of 3–11. The electrolyte solution was pumped through a cylindrical cell containing the Al-WTRs sample in between silver electrodes coated with AgCl. The ZP was then calculated based on the streaming potential. More detailed information about this methodology can be found elsewhere [21].

2.2. Determination of the maximum sorption capacity of Al-WTRs and sorption isotherms at pH 6.5

Maximum sorption capacity of Al-WTRs was determined in batch adsorption experiments. A commercial Hg(NO₃)₂ standard solution obtained from Fisher Scientific was used to prepare Hg solutions in Nanopure® water with final Hg concentrations of 10, 20, 40, and 80 ppm. Obtained solutions were put in contact with dry Al-WTRs material in a 3:5 ratio (mg Al-WTRs/mL of solution). All experiments were conducted at pH 6.5 and carried out in 50-mL capped and acid-cleaned polyethylene tubes which were continuously rotated at about 30 rpm on a Roto-Shake Genie® (Scientific Industries, Inc.). After 96 h of equilibration, the pH was measured and remained at 6.5 ± 0.05 . The Al-WTRs slurries were then centrifuged, the supernatant filtered (0.45 μm), and analyzed for total Hg. Total Hg concentration in solution was measured by CV-AFS, following sample digestion according to the EPA method 1631. Briefly, filtered samples were subjected to cold digestion using bromine monochloride and analyzed using the stannous chloride reduction method [22] and a Tekran Series 2600 system (Tekran, Ontario, Canada). The QA/QC criteria were met by running reagent blanks and standard solutions. All containers used in this study were acid washed and only Teflon® containers were used for storage of Hg containing solutions.

The Hg loading capacities of Al-WTRs (mg/g) were calculated using the following equation, where C_i and C_e are initial and equilibrium Hg concentrations in mg/L, M is the weight of used Al-WTRs in grams, and V is the volume of solution in liters.

$$\text{Hg loading capacity (mg/g)} = \frac{(C_i - C_e) V}{M} \quad (4)$$

The percentage of Hg sorbed was calculated from the difference between the initial Hg concentration and Hg concentration remaining in the solution at equilibrium. The sorption data was then fit to Langmuir and Freundlich models and the best fit was used to calculate the maximum sorption capacity.

The solid Al-WTRs material used in these sorption experiments was recovered and examined for sorbed Hg via SEM-EDS. To account for Hg mass balance, the solid Al-WTRs material was also analyzed for total Hg by CV-AFS.

2.3. Hg desorption from Al-WTRs

For the desorption study, Hg-loaded Al-WTRs were prepared by bringing Al-WTRs into contact with Hg solution to achieve a Hg concentration of 30,000 mg/kg and were equilibrated for 7 days. The amount of Hg sorbed was determined by analyzing the dried

Hg-loaded Al-WTRs for total Hg concentration. Desorption of Hg was studied by adding dried Hg-loaded Al-WTRs in a 1:20 (m/v) to an extracting solution with a final pH of 4.22. The extracting solution was prepared according to the US-EPA Synthetic Precipitation Leaching Procedure (SPLP) [23] and was used to simulate the leaching effect of acid rain. Next, the samples were rotated in capped centrifuge tubes at about 30 rpm for 18 h on a Roto-Shake Genie® and the supernatant analyzed for total Hg as described in Section 2.2. The percentage of Hg desorbed was calculated using Eq. (5), where C_{des} is the desorbed Hg concentration in SPLP extracting solution (mg/L), C_{ads} is the Hg sorbed concentration on Al-WTRs (mg/kg), V is the volume of extracting solution (mL), and M is the weight of Al-WTRs (g).

$$\% \text{Hg desorbed} = \frac{C_{des} V}{M C_{ads}} \times 100 \quad (5)$$

2.4. Kinetics of Hg sorption on Al-WTRs at pH 6.5

Batch kinetic studies were performed to obtain data on Hg sorption behavior versus time. Mercury solution with an initial concentration of 40 ppm was used for this experiment. Mercury solution and Al-WTRs were mixed in a 2:5 ratio (m/v) and the pH was adjusted to 6.5 ± 0.05 and monitored throughout the experiment. The mixture was agitated by continuous stirring for the duration of the experiment. The contact time and sampling intervals were selected based on preliminary experiments. Thus, at pre-decided time intervals, the supernatant was withdrawn, filtered (0.45 μm), and analyzed for total Hg as described in Section 2.2. To investigate possible mechanisms of sorption, obtained data were fit into two different kinetic (first- and second-order) and intraparticle diffusion models.

2.5. Effect of pH on Hg sorption on Al-WTRs

Finally, in addition to the above experiments at fixed pH, batch studies were conducted to investigate the effect of changing pH (3–8) on Hg sorption by Al-WTRs. In these sorption experiments, 40 ppm Hg solutions were used and the pH of Al-WTRs slurries (3:5 ratio, m/v) adjusted with either 0.1N HCl or 0.1N NaOH. These slurries were then equilibrated for 96 h. After the equilibration period, the pH of each solution was verified to be at ± 0.05 of the initial pH value. The Al-WTRs slurries were then centrifuged, the supernatant filtered (0.45 μm), and analyzed for total Hg as described in Section 2.2. In addition, the supernatant was analyzed for other metals too (Al, As, Cu, Cr, Fe, Pb, and Zn).

3. Results and discussion

3.1. Characterization of Al-WTRs

Images obtained from scanning electron microscopy showed that collected Al-WTRs are heterogeneous mixtures of particles with irregular shape and variable sizes (Fig. 1). The EDS elemental spectra analysis showed that Al-WTRs are predominantly composed of Al, Si, P, S, Ca, and Fe (Fig. 2a). Other measured physicochemical characteristics of Al-WTRs are presented in Table 1. Overall, these parameters are similar to Al-WTRs composition reported by others in previous studies (e.g., [4,6,8,17,24]). Although not regulated by the US-EPA 40 CFR Part 503 for sewage sludge [25], the concentration of Hg (0.02 mg Hg/kg Al-WTR) and of other metals present in these Al-WTR samples were lower than the US-EPA regulatory limits for land application of sewage sludge (Table 1; US-EPA 40 CFR Part 503). With regard to high Al levels and its potential toxicity, the MetPLATE™ bioassay showed no measurable toxic

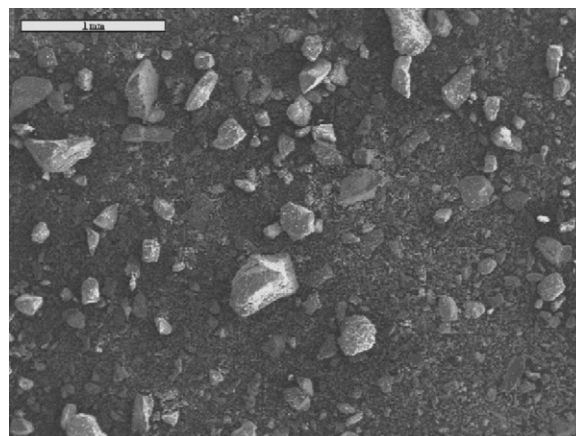


Fig. 1. SEM micrographs of the original Al-WTRs collected from the Bradenton Drinking Water Treatment Facility (Florida, USA) showing irregular size and non-homogeneity of particles.

effect of Al-WTRs extracts. This observation is in line with previous studies where no aluminum toxicity was found in tomatoes [4] and broad beans [26] when grown in Al-WTRs used as a soil substitute.

The SSA-N₂ characterization based on the BET method (BET-N₂) revealed a rather high surface area averaging 48 m²/g. The BET-N₂ is applicable mostly to non-porous or mesoporous materials and tends to underestimate the SSA of internal micropores when present [19]. CO₂ is a preferred adsorbent in micropore analysis despite the fact that CO₂ and N₂ have similar molecular dimensions (3.0 Å for N₂ and 2.8 Å for CO₂) [17,19]. This is because CO₂ analysis is performed at a higher temperature compared to N₂ ($T = 273 \text{ K}$ for CO₂ and $T = 77 \text{ K}$ for N₂), as a result CO₂ passage through micropores is less constricted [17,19,27]. Our measured SSA-CO₂ of 120 m²/g Al-WTR suggests that Al-WTRs have a large internal surface area that is not accounted by the BET-N₂ (Table 1). The values for SSA-N₂ and SSA-CO₂ compare quite well with those reported for Al-WTRs

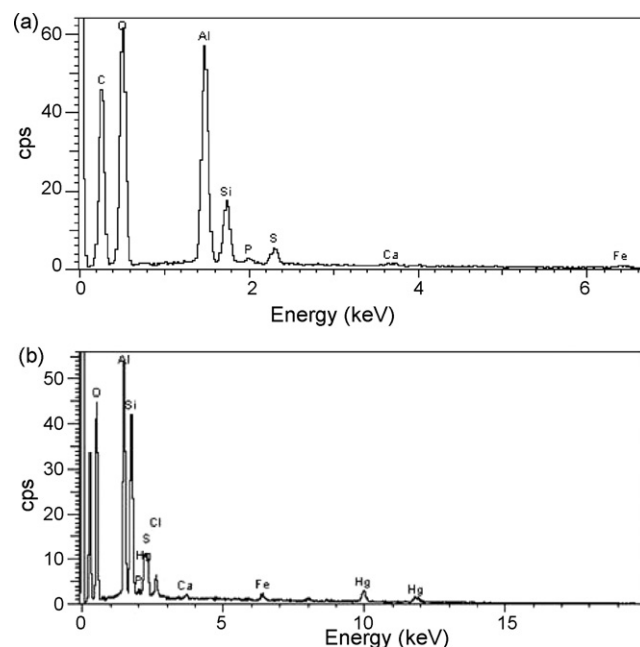


Fig. 2. (a) Elemental spectra (EDS) of the original Al-WTRs before use in Hg sorption experiments. (2b) Elemental spectra (EDS) of the recovered Al-WTRs sample after the sorption experiments confirming Hg sorption on Al-WTRs.

Table 1
Physicochemical properties of Al-WTRs

Parameter	Mean value ^a	Units	Regulatory limit ^b (mg/kg)
pH ^c	5.6 ± 0.01 ^d	–	–
EC ^e	0.36 ± 0.01	dS/m	–
CEC ^f	45.80 ± 0.09	cmol/kg	–
SSA-N ₂ (BET)	48 ± 0.3	m ² /g	–
SSA-CO ₂ (micropore)	120 ± 0.3	m ² /g	–
Organic carbon	12.7 ± 0.08	%	–
Al	73,816 ± 3278	mg/kg	nd ^g
As	8.01 ± 1.1	mg/kg	41
Ca	2263 ± 50	mg/kg	nd
Cu	141 ± 3.4	mg/kg	1500
Cr	81.1 ± 1.3	mg/kg	1200
Hg	0.02 ± 0.003	mg/kg	17
Fe	3728 ± 116	mg/kg	nd
Pb	1.99 ± 0.4	mg/kg	300
Zn	14.37 ± 1.3	mg/kg	2800

^a All the values are means of triplicates.

^b US-EPA 40 CFR Part 503, pollutant limits for meeting land exceptional quality criteria.

^c At a soil/water ratio of 1:1 (m/v).

^d ±Values represent standard errors of the mean.

^e At a soil/water ratio of 1:2 (m/v).

^f Effective cation exchange capacity.

^g Not defined.

collected from the same water treatment plant by Makris et al. [6,17].

3.2. Determination of the maximum sorption capacity of Al-WTRs and sorption isotherms at pH 6.5

Table 2 summarizes the results obtained from these experiments. The Hg loading capacities and the percentage of Hg adsorbed onto Al-WTRs calculated for each treatment show that these specific Al-WTRs can efficiently remove dissolved Hg. Samples with 10 mg/L of initial Hg concentration had Hg levels reduced by almost 100%, while solutions with initial Hg levels of 20 mg/L were reduced by about 90%. The maximum sorption capacity of 75.4 mg/g was obtained based on experiments with an initial Hg dissolved concentration of 80 mg/L. The EDS elemental spectra analysis of used Al-WTR particles recovered at the end of the Hg sorption experiments verified the presence of sorbed Hg on Al-WTR-particles (Fig. 2b), and the mass balance calculation on the distribution of Hg between the aqueous and solid phases accounted for 99 ± 10% of the initial Hg concentrations. Additionally, the shape of the obtained sorption isotherm (Fig. 3) suggests that sorption sites with high affinity for Hg are present on Al-WTRs, leading to very low aqueous Hg equilibrium concentrations for samples with 10 and 20 mg/L initial Hg concentrations [28]. Also, the analysis of supernatant resulted in concentrations of Al, As, Cr, Cu, Fe, and Pb below their respective detection limits (3, 50, 0.4, 2, and 10 µg/L).

The sorption data was best fit to a Langmuir model ($R^2 = 0.98$, $p = 0.007$). Based on the following equation, a plot of C_e/q versus

Table 2
Determination of Hg maximum sorption capacity (mg/g) at pH 6.5

Initial Hg (mg/L)	Mean equilibrium concentration (mg/L) ^a	Loading capacity (mg/g)	%Hg adsorbed
10	0.03 ± 0.01 ^b	16.6	99.7
20	2.01 ± 0.33	29.9	90.0
40	8.72 ± 0.37	52.1	78.2
80	45 ± 8.13	75.4	56.6

^a All the values are means of four replicates.

^b ±Values represent standard errors of the mean.

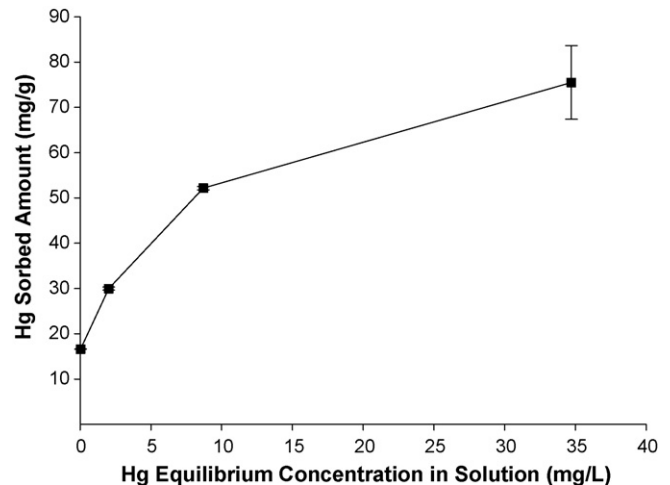


Fig. 3. Mercury sorption isotherm with initial Hg concentrations of 10, 20, 40, and 80 mg/L and pH 6.5. Plotted values are averages ($n = 4$) and error bars represent standard errors of the mean. Error bars for 10, 20, and 40 mg/L are very small and overlap with the point.

C_e allowed the determination of the maximum sorption capacity (q_m), the binding constant (K_{ads}) from the slope, and the intercept of the linear regression. In this equation, q is the adsorption density (mg/g), C_e is the equilibrium Hg concentrations (mg/L), q_m is the maximum sorption capacity (mg/g), and K_{ads} is the binding constant that measures the affinity of adsorbate for adsorbent (L/mg) [29].

$$\frac{C_e}{q} = \frac{1}{K_{ads}q_m} + \frac{C_e}{q_m} \quad (6)$$

The maximum sorption capacity determined from the Langmuir model was 79.3 mg/g, which compares well with the maximum sorption capacity of 75.4 mg/g determined experimentally (Table 3). This sorption capacity is considerably larger than that of some of the previously tested waste adsorbents such as used tire rubber with a maximum sorption capacity of 14.6 mg Hg/g [30].

Additionally, the favorable nature of sorption processes can be expressed in terms of a dimensionless constant separation factor (r) defined as: $r = 1/(1 + K_{ads}C_0)$, where C_0 is the initial Hg concentration (mg/L) and K_{ads} is the binding constant from Eq. (6). For this study, the calculated (r) values were less than 1 and greater than 0, indicating a favorable sorption [31].

It is worth noting that the Langmuir model assumes that the adsorption is limited to a single monolayer coverage and that all surface sites on the adsorbent have the same affinity for the adsorbate [29]. Accordingly, this model applies well to these short-term sorption experiments, dominated primarily by sorption of Hg to the external surface sites of Al-WTRs [32]. However, for microporous adsorbents such as Al-WTRs, there is also a possibility for the intraparticle diffusion of Hg into the micropores. Therefore, it is likely that the true sorption capacity of Al-WTRs is even greater than the value obtained in these short-term sorption experiments. Intraparticle diffusion is a much slower sorption process and is

Table 3
Sorption isotherm parameters for Hg sorption on Al-WTRs at pH 6.5

Parameter	Value
K_{ads} (L/mg)	0.4
q_m Langmuir (mg/g)	79.3
q_m Experimental (mg/g)	75.4
R^2 (Langmuir)	0.9858
p -Value	0.007

observed by maintaining a constant boundary condition of a metal in the bulk aqueous phase [33]. Further long-term experiments are therefore needed to study the potential diffusion mechanisms of Hg into Al-WTRs micropores.

Finally, Hg desorption studied by leaching of formed Hg-[Al-WTRs] complexes with synthetic acid rainwater solution (SPLP) led to the release of just 1.5% of Hg previously sorbed onto Al-WTRs particles. Although preliminary, these results suggest that the leaching potential of Hg from Al-WTRs could be very low. In addition, the analysis of the SPLP leachate showed Al values below the Florida Groundwater Guidance Concentration (FGGC) regulatory limit of 0.2 mg/L. Concentrations of other metals (As, Cr, Cu, Fe, and Pb) were below their respective detection limits (50, 0.4, 2, and 10 $\mu\text{g/L}$). This is in partial agreement with Jain et al. [34] who reported similar results for As, Fe, Cr, and Cu. However, they reported that Al and Pb concentrations exceeded the FGGC regulatory limit in some of the Al-WTRs.

3.3. Kinetics of Hg sorption by Al-WTRs at pH 6.5

Fig. 4 shows the effect of contact time on Hg adsorption on Al-WTRs in a series of sorption experiments with initial Hg concentration of 40 mg/L and pH 6.5. Equilibrium was attained in about 32 h, with nearly all initial dissolved Hg (~99%) sorbed onto Al-WTRs particles. To gain insight on the potential mechanisms of Hg sorption and fixation on Al-WTRs based on these kinetic studies, we used kinetic and intraparticle diffusion models.

3.3.1. Pseudo-first-order Lagergren model

Lagergren's pseudo-first-order equation [35] is widely used for modeling sorption of metals from solutions [36–38]. In linear form it is expressed as follows:

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_1 t}{2.303} \quad (7)$$

where q_e is the Hg concentration at equilibrium per unit mass of Al-WTRs (mg/g), q_t is the amount of Hg adsorbed at time (t) per unit mass of Al-WTRs (mg/g), and k_1 is the sorption rate constant of the pseudo-first order (h^{-1}). By plotting $\log(q_e - q_t)$ versus time (t), a straight line with a correlation coefficient of $R^2 = 0.9944$ ($p < 0.005$) was obtained. The parameters k_1 and q_e determined from the slope and the intercept of the plot are presented in Table 4. Based on the heterogeneous composition of used Al-WTRs, it is likely that

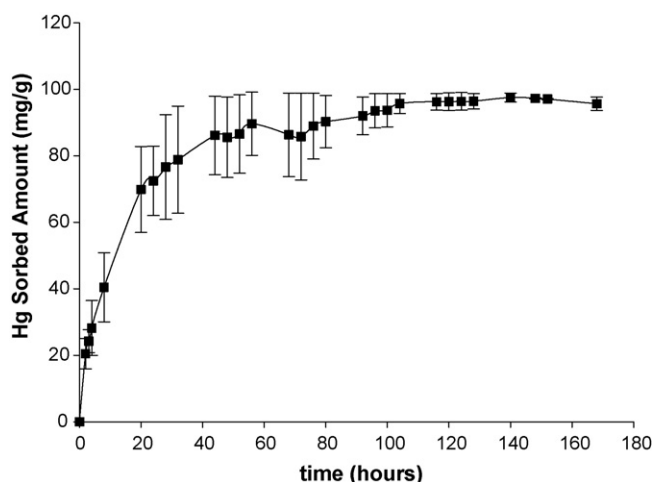


Fig. 4. Effect of treatment time on Hg sorption on Al-WTRs at 40 mg/L initial Hg concentration and pH 6.5. The values are averages ($n=2$) and error bars represent standard errors of the mean.

Table 4

Kinetic parameters for Hg sorption on Al-WTRs at pH 6.5 and initial Hg concentration of 40 mg/L

Parameter	Value	Parameter	Value
Pseudo-first order		Pseudo-second order	
K_1 (h^{-1})	0.057	k_2 ($\text{g}/(\text{mg h})$)	9.12×10^{-4}
q_e (mg/g)	80.2	q_{e_2} (mg/g)	103
R^2	0.9944	R^2	0.9901
p -Value	<0.005	p -Value	<0.005
Weber and Morris model ^a		Bangham model ^a	
k_i ($\text{mg}/(\text{g h})$)	0.0677	k_b ($\text{mL}/(\text{g L})$)	297
C	0.1328	A	0.7375
R^2	0.9915	R^2	0.9948
p -Value	<0.005	p -Value	<0.005

^a Intraparticle diffusion.

several reaction types/mechanisms are involved in the fixation of Hg on the tested Al-WTRs. However, the use of Eq. (7) tends to suggest that the rates of these reactions could be approximated by a pseudo-first-order kinetic model.

3.3.2. Pseudo-second-order model

Parameters describing the pseudo-second-order model were obtained by plotting t/q_t versus time (t), based on Eq. (8) [39], where q_{e_2} is the Hg concentration at equilibrium per unit mass of Al-WTRs (mg/g), q_t is the amount of Hg adsorbed at time (t) per unit mass of Al-WTRs (mg/g), and k_2 is the sorption rate constant ($\text{g}/(\text{mg h})$).

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e_2}^2} + \frac{t}{q_{e_2}} \quad (8)$$

The parameters q_{e_2} and k_2 obtained from the intercept and the slope of the plot are listed in Table 4. The correlation coefficient for this pseudo-second-order model ($R^2 = 0.9901$, $p < 0.005$) is slightly lower when compared to the pseudo-first-order model ($R^2 = 0.9944$, $p < 0.005$), suggesting that pseudo-first-order model fits data slightly better.

3.3.3. Intraparticle diffusion

The potential role of intraparticle diffusion on Hg sorption process was first explored by using the Weber–Morris intraparticle diffusion model shown in the following equation [40,41], and where q_t is the amount of Hg adsorbed at time (t) per unit mass of Al-WTRs (mg/g), k_i is the intraparticle diffusion rate constant ($\text{mg}/(\text{g } \sqrt{\text{h}})$), and C is the sorption constant, which describes the thickness of the boundary layer.

$$q_t = k_i \sqrt{t} + C \quad (9)$$

Fig. 5 was obtained by plotting q_t versus \sqrt{t} and the obtained relationship ($R^2 = 0.9915$, $p < 0.005$), seems to indicate that intraparticle diffusion may play a role in the sorption process. Indeed, Fig. 5 can be divided in two distinct linear portions. The first portion could be attributed to either boundary layer diffusion effects or the mass transfer effects on external surfaces, while the second portion tends to suggest an additional slower and gradual sorption stage during which intraparticle diffusion would likely dominate [42]. The role of intraparticle diffusion as the rate-limiting step on the sorption process was further investigated by use of Bangham's model shown in the following equation [43,44], where C_0 is the initial concentration of adsorbate in solution (mg/L), V is the volume of solution (mL), m is the weight of adsorbent used per liter of solution (g/L), q_t is the amount of Hg adsorbed at time (t) per unit mass of Al-WTRs (mg/g), and α (< 1) and k_b are constants.

$$\log \log \left(\frac{C_0}{C_0 - q_t m} \right) = \log \left(\frac{k_b m}{2.303 V} \right) + \alpha \log(t) \quad (10)$$

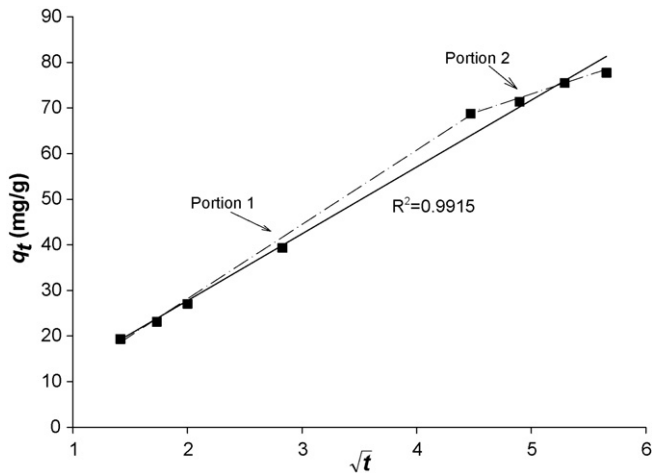


Fig. 5. Weber and Morris intraparticle diffusion plot for Hg sorption on Al-WTRs at initial Hg concentration of 40 mg/L and pH 6.5. q_t is the amount of Hg adsorbed at time (t) per unit mass of Al-WTRs (mg/g).

The linearity of the plot ($R^2 = 0.9948$, $p < 0.005$) confirms the applicability of Bangham's equation and indicates that intraparticle diffusion is a likely rate-limiting step of Hg sorption on Al-WTRs [45]. The mechanism of intraparticle diffusion is also supported by the fact that Al-WTR particles have a large internal network of micropores as mentioned in earlier sections.

In general, the amorphous structure of Al-WTRs is believed to be caused by the formation of amorphous Al oxides and hydroxides [6,46]. The concentrations of amorphous aluminum oxides in Al-WTRs have been found to range from 50 to 150 g/kg [4]. Theoretically, the prevalence of such geochemical phases in Al-WTRs would make them behave like aluminum oxyhydroxides. Results from previous studies tend to suggest that sorption of heavy metals to oxyhydroxides is usually a two-step process with a rapid sorption of the metal first to the external surface, followed by a slow intraparticle diffusion along the oxide micropore walls [47]. For remediation purposes, it is the long-term slow process which might play the most significant role in the sorption of the Hg fraction that becomes non-exchangeable, and therefore fully immobilized. Long-term studies appear necessary to validate these observations and to help determine surface diffusivities.

3.4. Effect of pH on Hg sorption on Al-WTRs

The pH is a key parameter governing the surface charge of solid materials [48]. Although Al-WTR is a heterogeneous material, its reactivity has been found to be similar to that of amorphous aluminum oxyhydroxides. The reported point of zero charge (PZC) of aluminum oxyhydroxides is usually greater than 7.7 [16,49]. Theoretically, the affinity of Hg and other metal cations for oxyhydroxides and therefore Al-WTRs should increase for pH greater than pH_{pzc} and decrease at $pH < pH_{pzc}$, based on electrostatic interactions. The effect of the pH of the solution on the sorption of Hg on Al-WTRs is presented in Fig. 6. These results show the highest Hg removal from aqueous phase at the highly acidic pH of 3, while the lowest Hg removal level was observed at pH 5. Overall, Hg sorption decreased first from pH 3 to 5, and then increased gradually with increasing pH from 5 to 8. This trend is not supported by the empirical PZC concept described above. Therefore, behavior of Al-WTRs deviates from the normal behavior indicative of oxyhydroxides.

We measured the ZP of the Al-WTRs across a wide range of pH (3–11) to tentatively explain the unusual sorption trend shown in Fig. 6. Usually, the ZP should become more positive with the

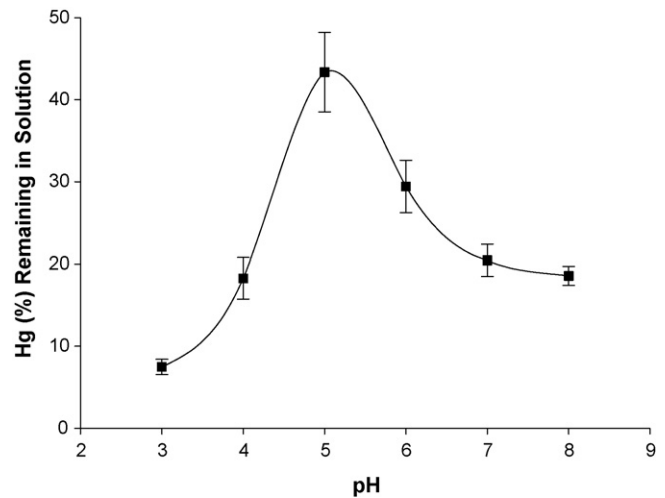


Fig. 6. Effect of pH on Hg sorption on Al-WTRs at 40 mg/L initial Hg concentration. The values are averages ($n = 3$) and error bars represent standard errors of the mean.

decrease in pH because of the build up of positively charged protons. The experimental data show that as the pH decreases from about 5.5 to 3, the ZP of Al-WTRs becomes more negative. This trend could explain the high Hg sorption at pH 3. Similar ZP trends have been reported for several organic polymers such as cellulose and lignin, the most abundant organic polymers in nature [50,51]. The organic carbon content of used Al-WTRs averaged 13%, and besides the anthropogenic inputs due to the addition of organo-compounds during the treatment process, it also originates from natural raw waters that undergo the treatment process. This high organic carbon content and the chemical composition of these organics may be influencing the ZP versus pH trend of Al-WTRs. The fact that Hg removal was very efficient at low pH values is significant from remediation standpoint, because often times contaminated soils may have a very low pH and, if left untreated, may leach out Hg.

As the pH increases from about 5.5 to 11, the ZP becomes more negative, because of the build up of negatively charged hydroxyl ions. Fig. 6 and Fig. 7 show correlation between Hg sorption behavior versus pH and the measured ZP versus pH, indicating that electrostatic attractions play a role in Hg sorption onto Al-WTRs. However, as the pH increases above about pH 4, Hg occurs primarily as $Hg(OH)_{2(aq)}^0$ as calculated by the MINEQL⁺ chemical equilibrium modeling system [52]. Studies suggest that adsorption of $Hg(OH)_{2(aq)}^0$ is generally limited because of the loss of

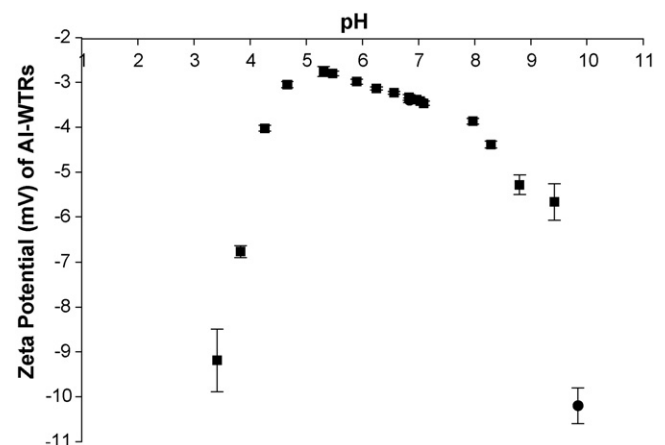


Fig. 7. Effect of pH on zeta potential of Al-WTRs.

exchangeable ligands from the surface [53]. Therefore, it is likely that electrostatic attraction is not the only force that governs the sorption of Hg onto Al-WTRs. These data suggest that additional forces are involved in Hg sorption. One could speculate on the role of steric and hydrophobic interactions as well as the intraparticle diffusion in the Hg sorption process on Al-WTRs. However, further investigations are needed to study the mechanism of Hg sorption on Al-WTRs.

In addition to Hg, the supernatant was analyzed for concentrations of Al, As, Cr, Cu, Fe, and Pb. The dissolution of Al was significant at pH 3 (~7 mg/L), and at pH ≥ 4 concentrations of Al were either lower than the 0.2 mg/L FGGC or below the detection limit (3 $\mu\text{g/L}$). The concentrations of other metals (As, Cr, Cu, Fe, and Pb) were below their respective detection limits (50, 0.4, 2, and 10 $\mu\text{g/L}$).

3.5. Implications for soil remediation

The speciation of Hg in soils is rather complex and depends on various factors including pH and redox conditions [54]. In natural systems, rain is the dominant source of water in the soil, and the decrease in soil pH as a result of acid rain could increase the mobility and bioavailability of Hg [55,56]. Our results show the potential of Al-WTRs used in this study to reduce/eliminate dissolved and mobile Hg, which is the most toxic and bioavailable form of Hg in the soil. Current remediation methods of Hg-polluted soils are rather expensive and have several other disadvantages. Use of Al-WTRs as soil amendments to immobilize Hg would not only provide environmental benefits as a result of the reclamation of Hg-contaminated soils but will also provide a cost-effective alternative for the disposal of Al-WTRs. However, the risks associated with relatively high total Al and As concentrations in some Al-WTRs should be considered in land application.

Even though metal concentrations of Al-WTRs are not regulated by the US-EPA 40 CFR Part 503 for sewage sludge disposal [57], most states in the US have guidelines that regulate the application of solid waste materials to the land [34]. In our study, total metal concentrations of tested Al-WTRs were below the regulatory limit for sewage sludge disposal (US-EPA 40 CFR Part 503, Table 1). However, the Al (73,816 mg/kg) and As (8 mg/kg) concentrations of tested Al-WTRs were above the Florida soil cleanup target levels of 72,000 mg/kg for Al and 0.8 mg/kg for As. However, the leachable Al and As concentrations obtained using the SPLP test were below the Florida Groundwater Guidance Concentration of 0.2 mg/L for Al and below the detection limit for As (DL=0.05 mg/L). This is in partial agreement with Jain et al. [34] who reported similar results for As, but, the Al concentrations exceeded the FGGC regulatory limit in some of the Al-WTRs.

It is important to note that these guidelines were developed with the assumption that waste materials replace the soil [34]. Therefore, the application rate of Al-WTRs to soil should be considered when assessing the risk of land application of Al-WTRs. In addition, soils contaminated with Hg are generally hazardous waste superfund sites. The background metal concentrations in these soils are usually above most soil cleanup target levels. Therefore, application of Al-WTRs to these soils is not likely to pose a risk.

4. Conclusions

In this study we demonstrated the ability of Al-WTRs collected from the drinking water treatment plant in Bradenton, FL to sorb Hg from aqueous solutions. Sorption isotherms indicated a strong affinity of Hg for Al-WTRs and a relatively high maximum sorption capacity of 79 mg Hg/g Al-WTRs. Also, Al-WTRs effectively immobilized Hg in the pH range of 3–8. Sorption kinetic data was best fit to a pseudo-first-order model, while the use of the

Weber–Morris and Bangham models suggested that the intraparticle diffusion could be the rate-limiting step for Hg immobilization onto Al-WTRs particles. However, further studies are needed for more in depth evaluation of Hg sorption mechanisms and the long-term stability of formed Hg-[Al-WTRs] complexes.

Overall, the results from these short-term experiments demonstrate that tested Al-WTRs can be effectively used to remove Hg from aqueous solutions. This ability points to the potential of Al-WTRs as sorbent in soil remediation techniques based on Hg-immobilization. However, future studies are needed to validate the ability of Al-WTRs from different facilities around the nation to sorb Hg. Finally, the ideal soil/Al-WTRs ratios for the control of Hg mobility in soils should also be evaluated.

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