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Sorption of Arsenic from Desalination Concentrate onto Drinking Water Treatment Solids: Operating Conditions and Kinetics

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Abstract: Selective removal of arsenic from aqueous solutions with high salinity is required for safe disposal of the concentrate and protection of the environment. The use of drinking water treatment solids (DWTS) to remove arsenic from reverse osmosis (RO) concentrate was studied by batch sorption experiments. The impacts of solution chemistry, contact time, sorbent dosage, and arsenic concentration on sorption were investigated, and arsenic sorption kinetics and isotherms were modeled. The results indicated that DWTS were effective in removing arsenic from RO concentrate. The arsenic sorption process followed a pseudo-second-order kinetic model. Multilayer adsorption was simulated by Freundlich equation. The maximum sorption capacities were calculated to be 170 mg arsenic per gram of DWTS. Arsenic sorption was enhanced by surface precipitation onto the DWTS due to the high amount of calcium in the RO concentrate and the formation of ternary complexes between arsenic and natural organic matter (NOM) bound by the polyvalent cations in DWTS. The interactions between arsenic and NOM in the solid phase and aqueous phase exhibited two-sided effects on arsenic sorption onto DWTS. NOM in aqueous solution hindered the arsenic sorption onto DWTS, while the high organic matter content in solid DWTS phase enhanced arsenic sorption.

Keywords: arsenic removal; sorption; kinetics; desalination concentrate; drinking water treatment solids; natural organic matter (NOM)

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1. Introduction

Arsenic-contaminated water is a severe problem in many regions including Bangladesh, West Bengal in India, Pakistan, Vietnam, China, Spain, Mexico, Chile, Argentina, and the United States [1]. Arsenic in groundwater often originates from natural deposits in rocks, sediments, soils, and geothermal resources [2]. Arsenic in water may also be related to arsenic use in wood preservatives, pesticides, herbicides, alloys, pigments, and pharmaceuticals [3]. Arsenic exists in both inorganic and organic forms, while organoarsenic compounds are often absent or in very low concentrations in natural waters [4]. The most common oxidation states of inorganic arsenic are −3, 0, +3, and +5, which form various species. Arsenite (+3) and arsenate (+5) are the primary oxidation states in aqueous environments, with arsenate predominant in surface waters and arsenite prevalent under anaerobic conditions, e.g., groundwater [5]. Long-term exposure to low concentration of arsenic in drinking water could result in severe health effects and even cause cancer [6]. The United States Environmental Protection Agency (USEPA) has set an enforceable maximum contaminant level (MCL) for arsenic in drinking water at 10 μg/L (10 parts per billion, ppb).

Arsenic cannot be easily degraded in solutions, but can be separated from water or transformed into insoluble forms by a variety of physicochemical processes, such as coagulation [7,8], membrane separation [9,10], ion exchange [11], liquid–liquid extraction [12], and sorption [13]. Selection of

arsenic treatment methods is primarily determined by cost, operational complexity of the technology, and disposal of residuals containing arsenic [7]. The most common method for arsenic removal is coagulation and flocculation. Iron and aluminum salts are widely used as coagulants in conventional water treatment plants [14]. High removal efficiency was reported and up to 97% of arsenic removal can be achieved when using iron salts as coagulant [15].

Selective removal of arsenic from aqueous solutions with high salinity is required when membrane desalination processes, such as reverse osmosis [16], nanofiltration [17], and electrodialysis [10], are used to treat arsenic-contaminated water. Arsenic concentration in desalination concentrate increases with increasing water recovery (ratio of product to feed water). Disposal of the desalination concentrate with elevated concentrations of contaminants is an increasing challenge for the implementation of desalination techniques, especially for inland facilities that have limited disposal options [18–21]. Arsenic removal from desalination concentrate by the most common coagulation method using iron salts requires higher chemical demand than that in lower salinity water. In RO concentrate, Xu et al. found a Fe:As molar ratio of greater than 410 was required in order to achieve 80% arsenic removal using ferric chloride due to the high salinity and ion competition [22].

Sorption is a promising method that reduces chemical demand and the amount of sludge for disposal [23], and is attractive for small-scale treatment systems due to ease of operation [24]. A variety of sorbents have been utilized for arsenic removal, including ferrihydrite [25], hydrous zirconium oxides [26], hematite [27], and goethite [28]. For sorption processes, alternative sorbents that are cost-effective and environmentally friendly are needed. A low-cost and effective substitute for arsenic sorbents could be drinking water treatment solids (DWTS), the residuals produced from coagulation and flocculation processes during water treatment, which often utilize aluminum- or ferric-based coagulants [29].

More than two million tons of DWTS are produced every day in the United States [30], which are mainly disposed through landfills and can be used as a viable substitute to commercial sorbent for arsenic removal. Toxicity characteristic leaching procedure (TCLP) testing revealed a low risk of contaminants leaching from DWTS, indicating that most DWTS could be a safe sorbent [31,32]. Laboratory studies demonstrated that contaminants such as phosphorus [33], hydrogen sulfide [34], metals [35], fluoride [36], and arsenic [22] had a strong sorption affinity for DWTS. Equilibrium studies showed that both iron- and aluminum-based DWTS had a high capacity for arsenic, reaching a sorption capacity of about 15 grams arsenic per kilogram DWTS [37].

Although previous studies have demonstrated the feasibility of arsenic removal using DWTS, there is a substantial knowledge gap with respect to the removal efficiency of arsenic from desalination concentrate with high salinity. Therefore, the focus of this study was on investigating the DWTS sorption of arsenic from RO concentrate under different operating conditions, aiming to understand the kinetics and interactions between arsenic and DWTS. Batch experiments were conducted to elucidate the impact of contact time, pH, sorbent dosage, initial arsenic concentration, salinity, and natural organic matter on arsenic sorption from RO concentrate.

2. Materials and Methods

2.1. RO Concentrate and Analysis

The RO concentrate was collected from the Kay Bailey Hutchison Brackish Groundwater Desalination Plant in El Paso, Texas. The total dissolved solids (TDS) concentration of the RO concentrate was 10 ± 2.3 g/L. The major ions in the RO concentrate included sodium (2660 ± 368 mg/L), calcium (673 ± 113 mg/L), potassium (69 ± 5.4 mg/L), magnesium (168 ± 22 mg/L), chloride (4993 ± 656 mg/L), and sulfate (1272 ± 226 mg/L), while minor ions included manganese (332 ± 8.6 µg/L), and arsenic (63 ± 11 µg/L). The pH of the RO concentrate was 7.8 ± 0.4, the alkalinity was 388 ± 6 mg/L as $CaCO_3$, and the dissolved organic carbon (DOC) concentration was 4.1 ± 2.6 mg/L. The brackish groundwater was chlorinated before RO process for biofouling control; therefore, the arsenic in the RO concentrate was oxidized to arsenate.

Electrical conductivity and pH of the water samples were measured using a conductivity and pH meter (Model 431-61, Cole-Parmer, Vernon Hills, IL, USA). DOC was quantified using a carbon analyzer (Shimadzu TOC-L, Kyoto, Japan). Common anions were measured using an ion chromatograph (IC, ICS-2100, Dionex, Sunnyvale, CA, USA), and the concentrations of trace metals and metalloids were quantified using inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC-e, PerkinElmer, Waltham, MA, USA). Alkalinity was measured using a digital titrator (Hach, Loveland, CO, USA) and 1.6 N sulfuric acid standard solutions to a pH 4.3 endpoint. The TDS concentration was measured following the evaporation method at 180 °C after filtering the RO concentrate sample using a 0.45 μm cellulose acetate membrane filter (Toyo Roshi Kaisha, Ltd., Tokyo, Japan). The fluorescence excitation-emission matrices (F-EEM) of filtered water samples were analyzed by a spectrofluorometer (Aqualog-UV-800C, HORIBA Jobin Yvon, Edison, NJ, USA).

2.2. DWTS and Characterization

The filter backwash DWTS used in the experiments were collected from the sand drying beds in a groundwater treatment plant in El Paso, Texas. The ground samples were then sieved into different particle sizes: <0.2, 0.2–0.4, 0.4–0.8, 0.8–2, and 2–5 mm. After microwave acid digestion of the solids, the elemental composition of the solids was analyzed by IC and ICP-MS [21]. The organic content was analyzed by calcining the DWTS at 550 °C for 8 h in a muffle furnace (Furnace Vulcan 3-550, Dentsply International Inc., York, PA, USA). The moisture content was measured by the standard thermal evaporation method in an oven (OF-01E, Jeio Tech, Daejeon, Korea) at 105 °C for 24 h. The specific surface area of the solids was quantitated by an extended pressure adsorption analyzer (ASAP 2050, Micromeritics Instrument Co., Norcross, GA, USA). The salt titration method was adopted to determine the pH at the point of zero charge (pH$_{PZC}$) to investigate the impact of DWTS surface charge on arsenic sorption [38].

The pH$_{PZC}$ of the DWTS was 6.9, indicating the transition point of net surface charge from positive to negative. The water and organic contents of the DWTS were approximately 7% and 10% of dry solid weight, respectively. The major metals in the DWTS included Al, Ca, Mg, K, Fe, and Mn. The detected trace inorganic constituents included Cu, Cr, Pb, As, Se, Ni, Zn, and Cd [21]. It should be noted that iron was not the dominant element in the DWTS, although the treatment plant uses ferric chloride as the coagulant. The higher amount of aluminum in the DWTS was attributed to aluminosilicate minerals (in silt, sand, and clay) retained during coagulation/flocculation, sedimentation, and filtration processes.

No significant differences were observed for the DWTS with different particle sizes in terms of the elemental composition, specific surface area, moisture content, and organic content. Therefore, DWTS with 0.2–0.4 mm size was used in the experiments.

Batch leaching tests were conducted to quantify leaching of constituents from the DWTS using deionized water and RO concentrate [21]. Trace amounts of As, Cr, Cu, Fe, Ni, and Se were detected in both deionized water and RO concentrate leaching solutions. Because of the high ionic strength in RO concentrate, more heavy metal cations desorbed or dissolved from the DWTS in RO concentrate than in deionized water. The high ionic strength in the RO concentrate decreased ion activity, which resulted in increased ion concentrations in the solution for a given activity in equilibrium with the DWTS, thereby facilitating the dissolution of the solids, and therefore higher heavy metal cation concentrations released from the DWTS in the RO concentrate. On the contrary, lower concentrations of oxyanions were released in RO concentrate, showing even increased net sorption of As and Se from RO concentrate, indicating the strong affinity of certain oxyanions for the DWTS. F-EEM spectra revealed the leaching of humics from the DWTS in deionized water, but the organic leaching in RO concentrate was one to two orders of magnitude less than in deionized water.

2.3. Sorption Experiments

Batch equilibrium experiments were conducted to investigate the arsenic sorption process at room temperature (23 ± 0.5 °C). The average arsenic concentration in the RO concentrate was 63 μg/L, six times higher than the arsenic MCL in the USEPA Primary Drinking Water Standards. To investigate

the impact of initial arsenic loading on DWTS sorption and to simulate a wide concentration range of desalination concentrate from arsenic contaminated groundwater (500 µg/L or 6.67 µM) to industrial wastewater (up to 300 mg/L or 4000 µM), arsenic with various concentrations was spiked into the RO concentrate. Arsenate stock solution was prepared weekly by the dissolution of $Na_2HAsO_4 \cdot 7H_2O$ (Reagent grade, Fisher Scientific Co., Fair Lawn, NJ, USA) in deionized water.

Arsenic solutions (200 mL) were added in 250 mL polyethylene bottles and 3 mL of sample from each bottle were removed for ICP-MS analysis to measure the initial arsenic concentration before adding DWTS. Different amounts of DWTS were added into each bottle to obtain the sorbent dosages from 1 g solids per liter solution (g/L) to 40 g/L. After adjusting the samples to the desired pH using small amounts of HCl or NaOH solution, the bottles were shaken in a shaker for 24 h to reach sorption equilibrium (Model 3500, VWR, Radnor, PA, USA). Supernatants were taken and analyzed to determine the arsenic sorption under various operating conditions.

Throughout the study, all RO concentrate and treated samples were diluted to levels suitable for analysis using each analytical instrument. Sample collection and handling followed the guidelines in Section 1060 of Standard Methods [39]. Water samples were filtered through 0.45 µm cellulose acetate filters (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) when applicable.

3. Results and Discussion

3.1. Effect of DWTS Dosage

The impact of the DWTS dosage on arsenic sorption in deionized water and RO concentrate was investigated by testing a series of solids/solution ratios ranging from 1 to 40 g/L, with an initial arsenic concentration of 700 µg/L and 20 mg/L at pH 7 (Figure 1). It was evident that the fractional uptake of arsenic significantly increased with the increasing DWTS dosage (Figure 1a,c), and reached a complete removal at high sorbent dosage with an abundant surface area and number of available sorption sites [31].

For an initial arsenic concentration of ~700 µg/L, the arsenic uptake capacity in deionized water was higher than that in RO concentrate, but the difference almost disappeared at higher DWTS loadings (Figure 1d). At a DWTS dosage of 10 g/L, more than 95% arsenic removal from RO concentrate or deionized water was achieved (Figure 1c). At the DWTS dosage of 1 g/L, DWTS still exhibited noticeable arsenic sorption efficiency in both RO concentrate (39% removal) and deionized water (43% removal). For high initial arsenic concentrations (~20 mg/L), the trend of arsenic sorption in deionized water was highly analogous with that in RO concentrate (Figure 1a,b). The arsenic sorption capacity decreased with increasing DWTS dosage due to the decrease of available DWTS surface area per unit mass resulting from overlapping and aggregation of sorption sites [40]. Based on the DWTS dosage experiments, 1–2 g/L and 20 g/L of DWTS dosages were selected to represent the low and high sorbent dosage for the subsequent experiments, respectively.

3.2. Kinetics of Arsenic Sorption onto DWTS

In an arsenic treatment system, the hydraulic retention time or contact time is mainly determined by arsenic uptake rate [41], which is an important factor that defines sorption efficiency. The effect of contact time on arsenic sorption by DWTS was investigated using deionized water and RO concentrate at low (2 g/L prepared with initial arsenic concentration of 0.60–0.65 mg/L) and high sorbent dosage (20 g/L prepared with initial arsenic concentration of 20 mg/L) (Figure 2).
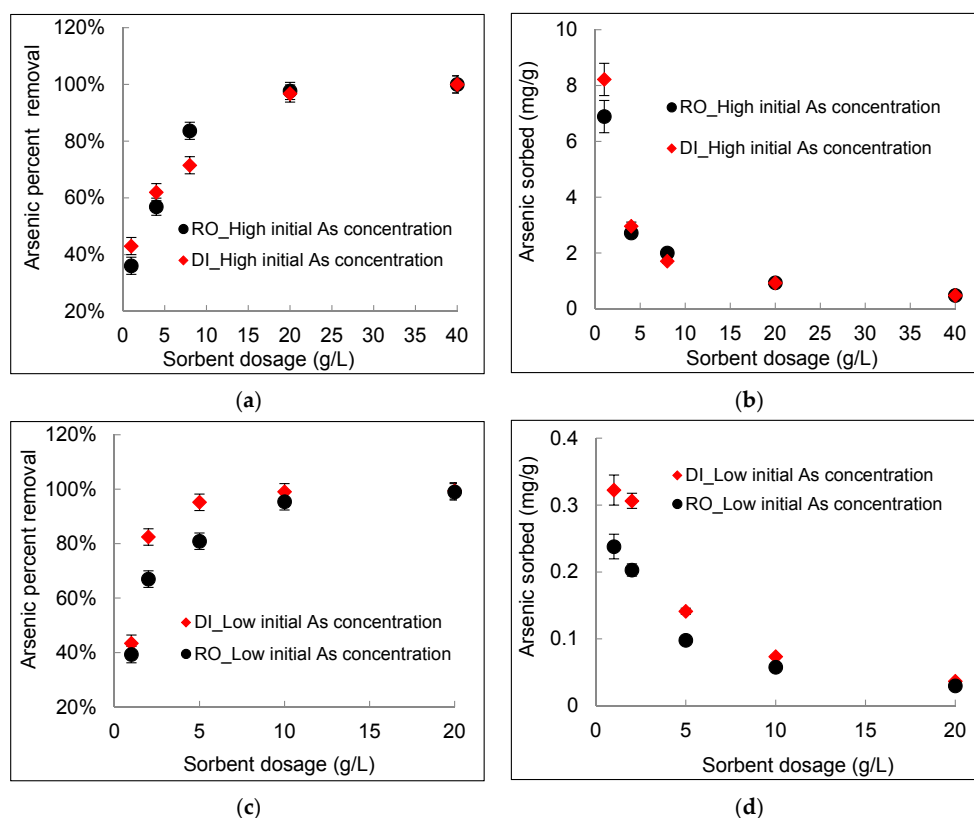
Figure 1. Effect of DWTS dosage on arsenic sorption at pH 7 and 23 °C. (**a**) Arsenic percent removal at high initial arsenic concentration (~20 mg/L); (**b**) Amount of arsenic sorbed at high initial arsenic concentration (~20 mg/L); (**c**) Arsenic percent removal at low initial arsenic concentration (~700 µg/L); (**d**) Amount of arsenic sorbed at low initial arsenic concentration (~700 µg/L). The error bars represent the standard deviation of duplicate or triplicate testing results.
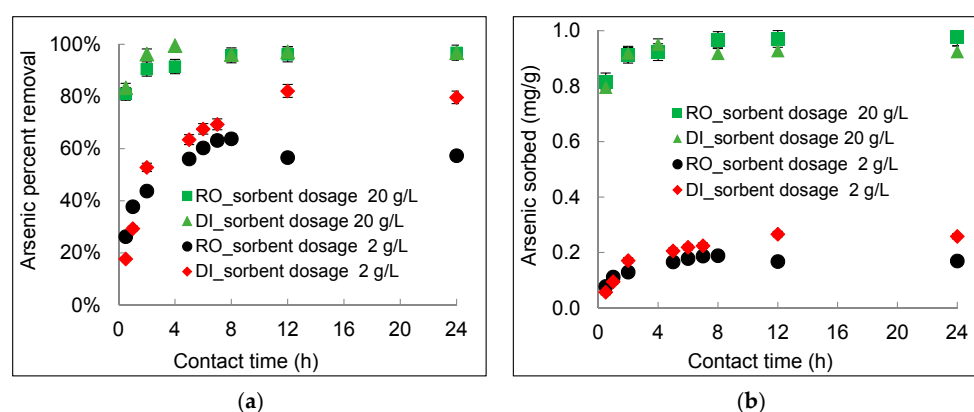

Figure 2. Effect of contact time on arsenic removal using DWTS. (**a**) Arsenic percentage removal; (**b**) Amount of arsenic sorbed. The error bars represent the standard deviation of duplicate testing results.

At a DWTS dosage of 20 g/L, high arsenic sorption was observed, reaching more than 80% removal in 0.5 h, and 96% removal within 2 h of contact time. Pseudo-equilibrium was attained in approximately 4 h, demonstrating a fast arsenic uptake. The difference of sorption kinetics was negligible between deionized water and RO concentrate because of the abundant sorption sites at high sorbent dosage and the strong affinity of arsenic for DWTS. However, at a low DWTS dosage of 2 g/L, arsenic sorption was lower in the beginning, reaching less than 18% removal in deionized water

and 26% in RO concentrate in 0.5 h. After reaching equilibrium at 12 h of contact time, no significant changes of arsenic concentrations in the solutions were observed.

The high DWTS dosage experiments would not be appropriate to evaluate kinetics because of the high arsenic sorption under these conditions. The results from the 2 g/L experiments were used to compute the arsenic sorption kinetics using the pseudo-second-order equation [41]:

$$q = \frac{K_{ad}q_e^2 t}{1 + K_{ad}q_e t} \tag{1}$$

where K_{ad} (h^{-1}) is the sorption rate constant of pseudo-second-order model; q (mg/g) is the amount of arsenic sorbed at time t; and q_e (mg/g) is the amount sorbed at equilibrium.

The q_e values derived from pseudo-second-order model (Figure 3a) were consistent with the measured arsenic sorption values in the experiments (Table 1), demonstrating that the pseudo-second-order model is suitable to predict the kinetic behavior of arsenic sorption onto DWTS. Meanwhile, it infers that the chemisorption is the rate-limiting step of a multiple sorption process, primarily contributing to the arsenic sorption onto DWTS [41,42]. The linear trend with high correlation coefficients ($R^2 > 0.99$) also indicated that arsenic sorption depends on both the arsenic concentration and the available sorption sites in DWTS [24].
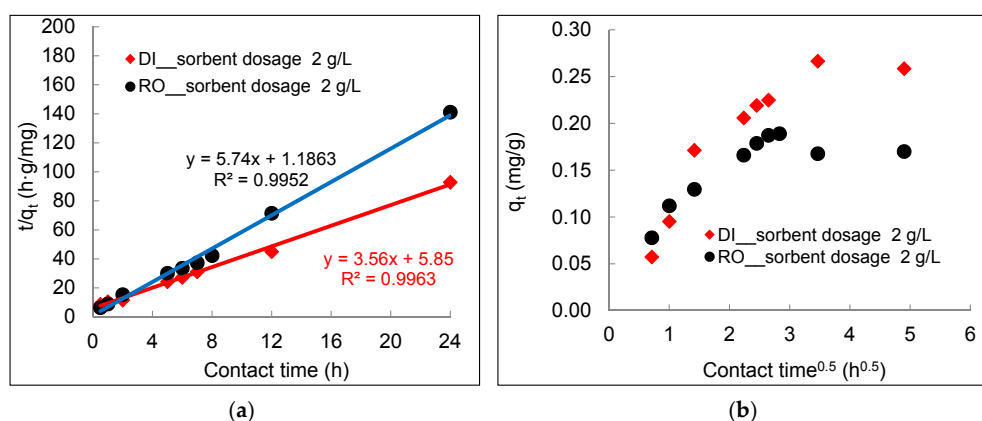

Figure 3. Kinetic studies of arsenic sorption at DWTS dosage of 2 g/L at pH 7 and 23 °C. (**a**) Pseudo-second-order sorption model; (**b**) Intra-particle diffusion kinetic model.

Table 1. Pseudo-second-order sorption constants of arsenic onto DWTS.

Water Type	DWTS Dosage	Arsenic Conc.	Arsenic Loading	K_{ad}	q_e (Experiment)	q_e (model) *	R^2
	g/L	mg/L	mg/g	(h^{-1})	(mg/g)	(mg/g)	
RO concentrate	2	0.65	0.30	27.8	0.170	0.174	0.995
Deionized water	2	0.60	0.32	2.17	0.260	0.281	0.996

Note: * Calculated from Equation (1).

The intra-particle diffusion kinetic model was applied by plotting q_t (mg/g) versus $t^{0.5}$ (h$^{0.5}$), which presented a multi-linear trend with three distinct sorption steps (Figure 3b). The initial sharp increase was attributed to arsenic sorption to the external, easily accessible surface of the DWTS or the boundary diffusion of the arsenic [43]. When the exterior surface was gradually saturated, arsenic ions started to diffuse into the interior of the DWTS via pores within the particles, where the intra-particle diffusion was a rate-limiting step, leading to the decrease of diffusion rate with the increase in diffusion resistance [44]. The third step was attributed to the final equilibrium stage because of the low arsenic concentration remaining in the solution [45].

Although the intra-particle diffusion kinetic model was used to describe the mechanisms of arsenic sorption onto the DWTS, more research is needed to elucidate the modeling results. For example, the quantitative characterization of the DWTS to measure the fraction of the internal versus external surface area would be required to support the hypothesis of the intra-particle diffusion of arsenic to the DWTS.

3.3. Effect of Initial Arsenic Concentration

The effect of the initial arsenic concentration on sorption was studied at different arsenic concentrations using deionized water and RO concentrate at low (2 g/L) and high (20 g/L) sorbent dosages. For a low sorbent dosage of 2 g/L, up to 3 mg/L arsenic (arsenic loading 1.5 mg/g) was spiked into solutions to investigate the sorption isotherms (Figure 4). In comparison, up to 100 mg/L arsenic (arsenic loading 5 mg/g) was spiked into solutions for high sorbent dosage of 20 g/L (Figure 5). The Freundlich and Langmuir equations were used to analyze the experimental data. The Freundlich equation is expressed as:

$$\log(q_e) = \log\left(K_f\right) + \frac{1}{n}\log(C_e) \tag{2}$$

where q_e is the amount of arsenic sorbed onto DWTS at equilibrium (mg/g); C_e is the arsenic concentration in solution at equilibrium (mg/L); and K_f and n are Freundlich constants.

The Langmuir model is described as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}\,k_L} \tag{3}$$

where k_L is Langmuir constant (L/mg).

The amounts of arsenic sorbed to the DWTS increased with the increasing arsenic concentration in both RO concentrate and deionized water (Figures 4b and 5c), indicating enhanced interactions between arsenic and the DWTS at the solid–liquid interface [46]. At the lower sorbent dosage of 2 g/L, DWTS exhibited higher arsenic sorption capacity in RO concentrate than that in deionized water with initial arsenic concentration above 1 mg/L and arsenic loading of ~0.5 mg/g (Figure 4b). At higher initial arsenic concentrations, calcium cations in RO concentrate (673 mg/L) likely interacted with arsenic anions with elevated concentration causing surface precipitation and resulting in higher sorption than that in deionized water. For the higher sorbent dosage of 20 g/L, the normalized arsenic sorption behavior was identical in both RO concentrate and deionized water for arsenic loading from 0.05 mg/g to 5 mg/g, exhibiting a highly linear increase in sorption with increasing arsenic loading (Figure 5c).

Langmuir and Freundlich equations were applied to simulate the arsenic sorption isotherm (Table 2). The Freundlich isotherm was found to describe arsenic sorption generally better with correlation coefficients greater than 0.95, for the DWTS dosage of 2 to 20 g/L, than the Langmuir model. At low to intermediate arsenic concentrations (<3 mg/L), the sorption isotherm of arsenic onto DWTS fitted poorly to the Langmuir equation with correlation coefficients of 0.60–0.69. The isotherms suggest multilayer sorption due to the surface precipitation of arsenic onto the DWTS.

Table 2. Isotherm parameters of arsenic sorption onto DWTS.

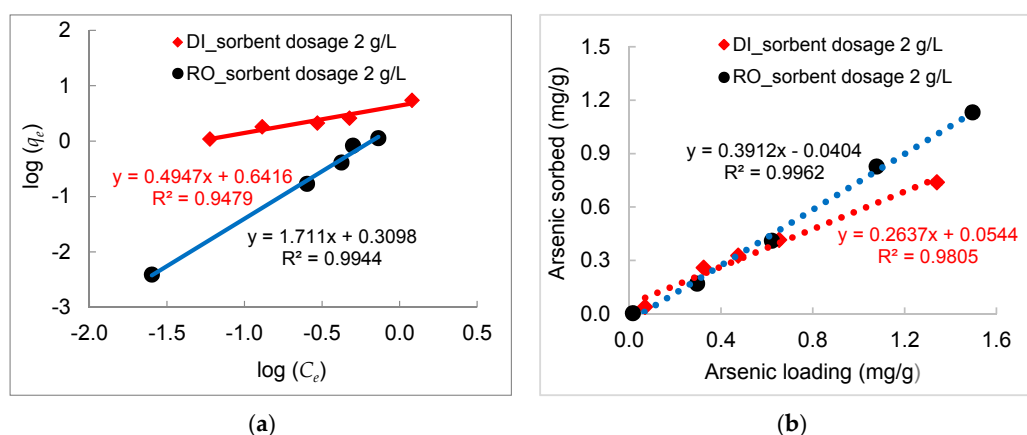| Water Type	DWTS Dosage	Arsenic conc.	Arsenic Loading	Freundlich	Langmuir	Langmuir q_{max}
	g/L	mg/L	mg/g	R^2	R^2	mg/g
RO concentrate	20	1–100	0.05–5	0.96	0.98	5.07
Deionized water	20	1–100	0.05–5	0.98	0.99	4.44
RO concentrate	2	0.1–3	0.05–1.3	0.99	0.69	/
Deionized water	2	0.075–3	0.04–1.5	0.95	0.60	/

Figure 4. Effect of initial arsenic concentration in RO concentrate and deionized water at low sorbent dosage (2 g/L) with pH 7 and 23 °C. (**a**) Freundlich isotherm; (**b**) Amount of arsenic sorbed.
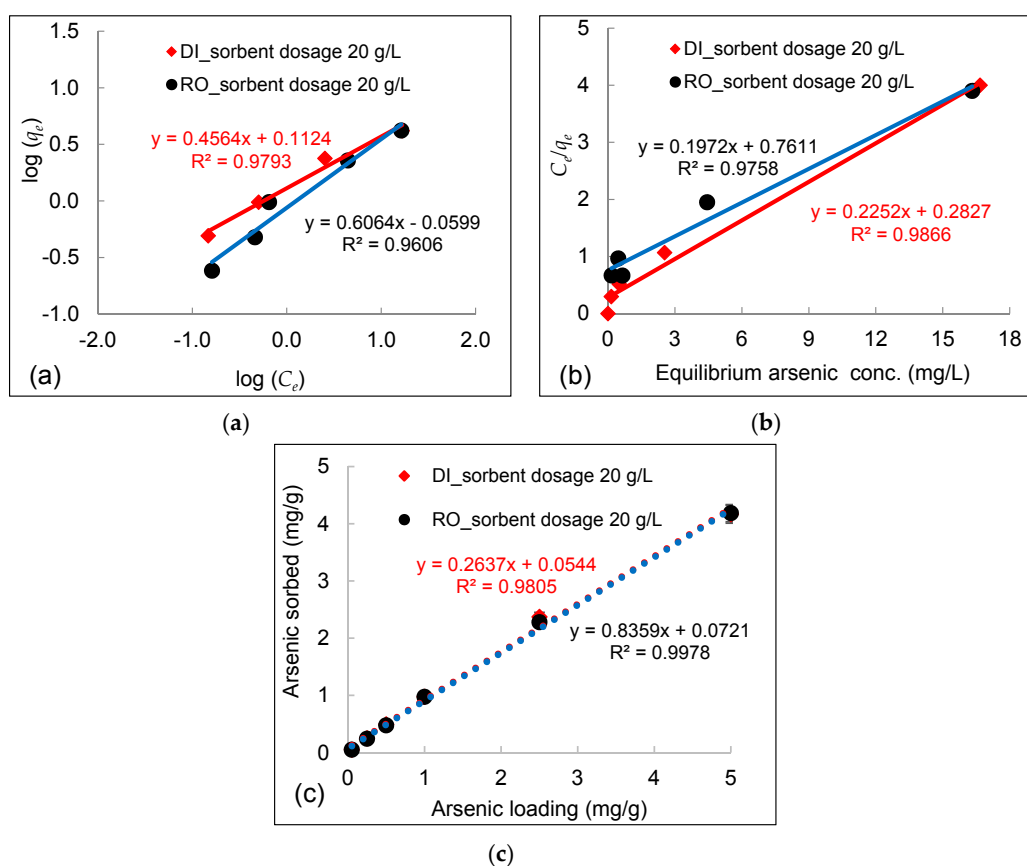

Figure 5. Effect of initial arsenic concentration in RO concentrate and deionized water at high sorbent dosage (20 g/L) with pH 7 and 23 °C. (**a**) Freundlich isotherm; (**b**) Langmuir isotherm; (**c**) Amount of arsenic sorbed. The error bars represent the standard deviation of duplicate or triplicate testing results.

Based on the Langmuir isotherm model, the 100 mg/L arsenic spike concentration was still not high enough to approach the maximum arsenic sorption capacity of the DWTS, revealing potentially high arsenic uptake by DWTS. Because the Langmuir model assumes a maximum amount of arsenic that could sorb on the DWTS, it is worth determining the maximum arsenic removal capacity of the DWTS. Therefore, a sorbent dosage of 1 g/L was prepared to determine the maximum arsenic sorption capacity of the DWTS with arsenic spiked from 1 to 300 mg/L. The maximum sorption capacities

calculated based on the Langmuir isotherm in RO concentrate and deionized water were 169 mg/g and 172 mg/g, respectively. The maximum arsenic sorption capacity of DWTS in this study was much higher compared to other unconventional adsorbents reported (Table 3) due to different water chemistry and sorbent properties, as discussed later in this paper.

The remarkable amount of arsenic sorbed to the DWTS could be attributed to the fact that intra-particle diffusion played a key role in arsenic sorption, instead of the Donnan effect which impeded the sorption due to electrostatic repulsion of the sorbed arsenic against arsenic ions in a solution with same charge [45]. The chemisorption of arsenic onto DWTS could encompass the specific sorption and surface precipitation at high arsenic concentrations, significantly enhancing the level of arsenic sorption [31].

Meanwhile, the high natural organic matter (NOM) content in DWTS (~10%) could also enhance the arsenic sorption from solution [47]. Arsenic binding to NOM was reported previously [48], and the mechanism involves the formation of ternary complexes: arsenic and NOM bound by bridge forming with polyvalent cations (e.g., Fe, Al) in DWTS [49]. The quantities of organic carbon leached from the DWTS were lower by two orders of magnitude than the organic matter in DWTS particles, which enabled high arsenic retention with NOM in DWTS, while a relatively small amount of arsenic bound with dissolved NOM in aqueous solutions.

Table 3. Sorption capacity of unconventional adsorbents under different testing conditions.

Adsorbents	Adsorption Capacity (mg/g)	Water Type	As Conc. (μM)	pH	Temp. (°C)	Langmuir R^2	Ref.
DWTS	172	RO concentrate	17.7~4004	7.0	23	0.99	This study
Fe-based DWTS	42.9	Groundwater (fresh)	0.58~	8.1	22	0.98	[50]
Al-based DWTS	47.4	Synthetic water	125~6250	6.0	20	0.95	[47]
Red mud	0.51	Synthetic water (0.1 M NaCl)	33.3~400	3.2	25	0.99	[51]
Goethite	12.4	Synthetic water	133~13,348	5.5	25	-	[52]
Chitosan bead	39.1	Synthetic water	66.7~800	7.0	25	0.91	[53]
Mesoporous alumina	121	Synthetic water	100~20,000	5.0	25	0.98	[44]

3.4. Effect of NOM

NOM is a mixture of acidic organic compounds, which is ubiquitous in aquatic environments. NOM molecules (e.g., fulvic and humic acids) were found to have the ability of binding with arsenic to form As-NOM complexes [54], a process that can affect arsenic sorption in two ways. When arsenic is sorbed by NOM in the DWTS, the arsenic sorption capacity of DWTS is enhanced. On the other hand, when arsenic is bound with NOM in solution, the retention of arsenic in the aqueous phase would inhibit the arsenic uptake by DWTS.

Humic substances were major components of NOM. The macro-molecular humic substances, with the main fraction as humic acid, consist of a large number of functional groups such as carboxylic, amines, esteric, and phenolic groups [55]. In this study, humic acid was selected to represent humic substances in natural water to investigate the impact of NOM on arsenic sorption onto DWTS. The arsenic sorption onto DWTS as a function of humic acid concentration at a sorbent dosage of 1 g/L was carried out using deionized water and RO concentrate at initial arsenic concentration of 20 mg/L, pH 7, and 23 °C (Figure 6). With the addition of humic acid in deionized water, arsenic sorption capacity significantly decreased from 8.2 mg/g to 2.5–3.5 mg/g. Similarly, the addition of humic acid to RO concentrate resulted in a decreased arsenic sorption capacity from 6.9 mg/g to 2.4–3.5 mg/g.

Considering the low DOC concentration in deionized water at a sorbent dosage of 1 g/L, the addition of 2 mg/L humic acid would at least triple the organic content in the solution and cause the decrease of arsenic sorption onto DWTS, suggesting a high reactivity of NOM with arsenic. When the humic acid concentration increased from 2 to 10 mg/L, the change of arsenic removal was not significant. This study confirmed the strong complexation between NOM and arsenic as reported in previous research [56].

3.5. Effect of pH

The pH was found to be a primary factor affecting the arsenic sorption processes. The impact of pH on arsenic sorption using DWTS was investigated over the pH range of 2 to 10 in deionized water and RO concentrate at low (2 g/L) and high DWTS dosages (20 g/L), under initial low arsenic concentration (~700 μg/L) and high arsenic concentration (20 mg/L). The pH affects the speciation of arsenic in aqueous solutions (governed by the arsenic acid dissociation constants, pKa) and the surface charge of the DWTS. Arsenate species exist primarily as $H_2AsO_4^-$ (~3 < pH < ~7) or $HAsO_4^{2-}$ (~7 < pH < ~11). The increase of the negative surface charge of DWTS caused by increasing pH may inhibit arsenic sorption because of electrostatic repulsion [31].
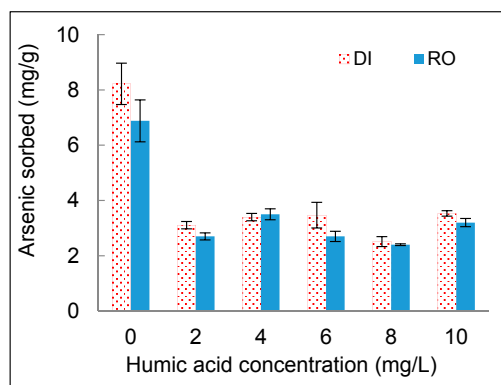

Figure 6. Effect of humic acid on arsenic sorption onto the DWTS at sorbent dosage of 1 g/L, initial arsenic concentration of 20 mg/L, pH 7 and 23 °C. The error bars represent the standard deviation of duplicate testing results.

Due to the large amount of available sorption sites, pH has little impact on arsenic uptake in both deionized water and RO concentrate at DWTS dosage of 20 g/L with initial arsenic concentration of 20 mg/L (Figure 7). Moreover, DWTS is a complex mixture of different minerals with different respective pH_{PZC}. Therefore, DWTS components could potentially have different surface charges at a given pH, thereby maintaining arsenic removal over a wide pH range. Arsenic removal up to 100% was achieved with DWTS (Figure 7a), associated with sorption capacity approximately 1 mg/g throughout the entire pH range (Figure 7b). The impact of pH became more pronounced at a low sorbent dosage (Figure 7). At a DWTS dosage of 2 g/L, the sorption of arsenic onto DWTS gradually increased from 0.28 to 0.35 mg/g as the pH of the deionized water decreased from 10 to 2. For RO concentrate, arsenic removal was reduced from 0.31 to 0.11 mg/g as the pH increased from 2 to 9, except at pH 10 (0.26 mg/g). Although an overall downward trend was observed in the deionized water, the arsenic removal remained relatively high throughout the entire pH range (>78%), showing overlapping trends with RO concentrate before pH 6 (near pH_{PZC} of the DWTS).

In order to explore the difference of sorption behavior with a pH lower than the pH_{PZC}, a DWTS dosage of 1 g/L was used to further investigate the pH effect with high initial arsenic concentration (20 mg/L), because of the pronounced pH effect on arsenic removal at low sorbent dosage [57]. The sorption process was significantly pH-dependent in both deionized water and RO concentrate, with a relatively stable sorption plateau between pH 4 and pH_{PZC} (Figure 7c,d). Enhanced arsenic removal was also observed in RO concentrate at pH 10. The above results clearly demonstrate the favorable arsenic sorption into DWTS in the acidic pH range.

The elevated arsenic removal at pH 10 in RO concentrate was attributed to the interaction of arsenic with the high concentration of calcium (673 ± 113 mg/L) in the RO concentrate. At pH 10, the main arsenic species ($HAsO_4^{2-}$) could react with Ca^{2+} by following equation [58]:

$$HAsO_4^{2-} + Ca^{2+} + nH_2O \rightarrow CaHAsO_4 \cdot nH_2O \tag{4}$$

The low solubility of the calcium arsenate compounds under high pH may cause the elevated arsenic removal due to surface precipitation, in addition to the sorption of arsenic onto DWTS [58]. The result was in good agreement with the study of Nagar et al. on arsenic sorption at different molar ratio of As:Ca by DWTS and synergistic behavior of calcium on arsenic sorption onto DWTS at pH 10 [57].
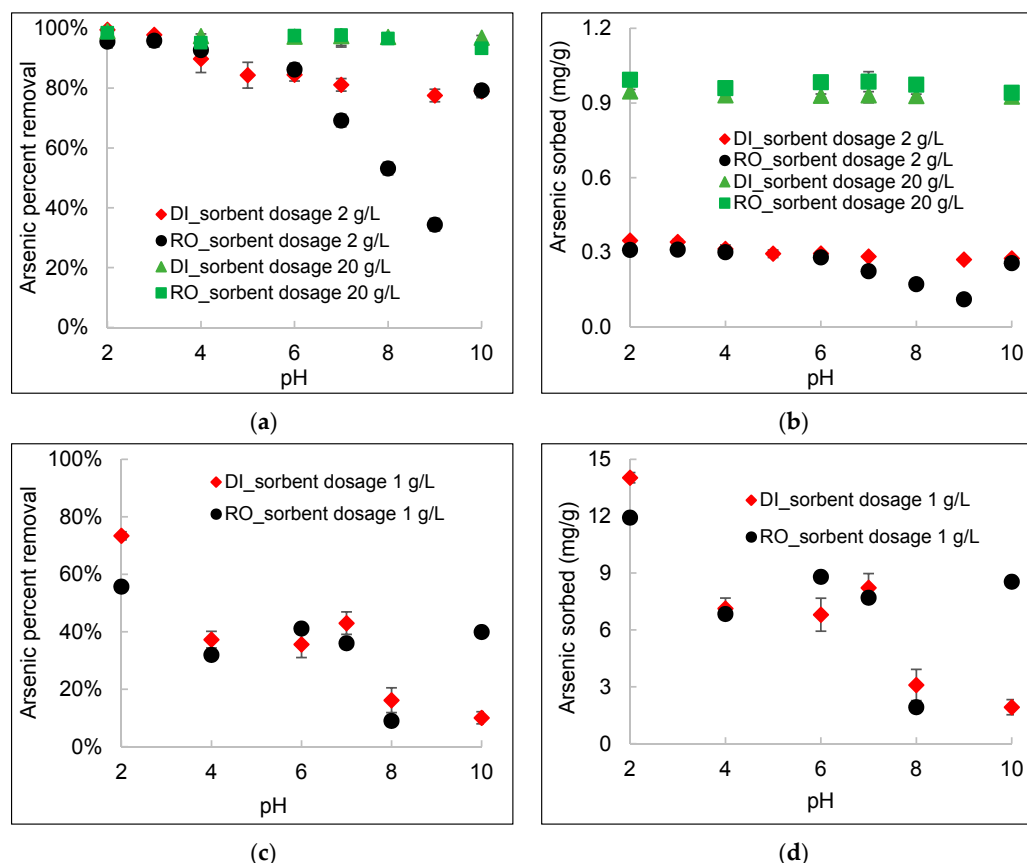

Figure 7. Effect of pH on arsenic removal in RO concentrate and deionized water. (**a**) Arsenic percentage removal at sorbent dosage of 2 and 20 g/L; (**b**) Amount of arsenic sorbed at sorbent dosage of 2 and 20 g/L; (**c**) Arsenic percentage removal at sorbent dosage of 1 g/L; (**d**) Amount of arsenic sorbed at sorbent dosage of 1 g/L. The error bars represent the standard deviation of duplicate or triplicate testing results.

The data of the three experimental conditions confirmed the previous finding that arsenic sorption depends on both the arsenic concentration and the available sorption sites. For high DWTS dosage (20 g/L), abundant sorption sites guaranteed high arsenic removal, minimizing other positive or negative mechanisms affecting arsenic sorption. For a sorbent dosage of 2 g/L with low initial arsenic concentration, sorption behavior was similar, with a slightly decreasing trend as the pH increased in both deionized water and RO concentrate at a pH lower than pH_{PZC}, because a positively charged surface favors strong arsenic sorption onto DWTS. At a pH above the pH_{PZC}, with a gradual increase of the negative charge, arsenic affinity for DWTS was weakened and other mechanisms affecting arsenic removal needed to be considered, especially in RO concentrate where silica competition and high ionic strength may result in more pronounced decrease of arsenic uptake than in deionized water. For a sorbent dosage of 1 g/L with high initial arsenic concentration, the high arsenic concentration driving force was the dominant factor determining the sorption capacity, enabling similar behavior in deionized water and RO concentrate below pH 10, when the precipitation of arsenic with calcium could become influential. The significant decrease of arsenic sorption onto DWTS with increasing pH was a result of the deprotonation of the sorbent surface, resulting in an increasingly negative surface

of DWTS. The increase of soluble organic matter from DWTS at high pH could also attribute to the decrease of arsenic uptake because of the formation of arsenic–NOM complexes [59].

4. Conclusions

This study investigated the impact of water chemistry, operating conditions, and kinetics on the arsenic sorption process to DWTS. The primary conclusions are summarized below:

- The percent removal of arsenic increased significantly with an increasing DWTS dosage from ~40% removal at a 1 g/L sorbent dosage to greater than 95% removal at a sorbent dosage of 20 g/L. However, the sorption capacity decreased with an increasing DWTS dosage. For example, for a high arsenic concentration of 20 mg/L, the amount of arsenic sorbed decreased from 6.8 mg/g in RO concentrate and 8.2 mg/g in deionized water at 1 g/L sorbent dosage to 0.92 mg/g at sorbent dosage of 20 g/L for both water matrices. For a lower arsenic concentration of 0.7 mg/L, the amount of arsenic sorbed decreased from 0.32 mg/g in deionized water and 0.24 mg/g in RO concentrate at 1 g/L sorbent dosage to 0.03 mg/g at a sorbent dosage of 20 g/L for both deionized water and RO concentrate.
- At a high DWTS dosage of 20 g/L, no pH-dependent behavior was observed within the pH range of 2–10 because of the abundant sorption sites in DWTS. For a low DWTS dosage of 1–2 g/L, the sorption of arsenic increased substantially as the pH decreased, except at pH 10, in RO concentrate. Precipitation of calcium arsenate at a higher pH (>10) increased arsenic sorption onto DWTS in the presence of a high concentration of calcium in RO concentrate.
- The arsenic sorption kinetics was best described by the pseudo-second-order kinetic model. The intra-particle diffusion kinetics model depicted by plotting q_t (mg/g) versus $t^{0.5}$ ($h^{0.5}$) showed three distinct sorption steps including boundary diffusion, intra-particle diffusion, and the equilibrium of arsenic to the DWTS.
- Experimental data fitted well to the Freundlich equation, demonstrating a multilayer adsorption process between arsenic in water and DWTS due to surface precipitation of calcium arsenate and the formation of ternary complexes between arsenic and NOM bounded by polyvalent cations (e.g., Fe, Al) in DWTS. The maximum sorption capacities calculated from the Langmuir isotherm in RO concentrate and deionized water were 169 mg/g and 172 mg/g, respectively.
- The presence of NOM in an aqueous phase or a solid phase had significant effects on arsenic sorption onto DWTS. NOM in the aqueous phase hindered the sorption of arsenic to DWTS. The high organic matter content in DWTS enhanced the arsenic sorption from the aqueous phase to the solid phase.
- This study demonstrated that DWTS is effective in removing arsenic from desalination concentrate. The experimental data indicated that the DWTS used in this study has a promising potential for arsenic removal as a low-cost alternative sorbent.

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