Sorption of metals and metalloids from reverse osmosis concentrate on drinking water treatment solids

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ABSTRACT

Drinking water treatment solids (DWTS) from coagulation processes could be a low-cost sorbent for selective removal of certain metals and metalloids from brine. In this study, continuous-flow sorption processes and factors affecting sorption of boron (III), copper (II), chromium (VI), lead (II), and selenium (VI) from reverse osmosis (RO) concentrate were investigated using different types of iron-derived DWTS. DWTS was demonstrated to be very effective in removal of copper and lead from RO concentrate, attributed to formation of strong inner-sphere complexes between the metal cations and Fe/Al oxide surface sites in the DWTS, as well as attractive electrostatic interactions with the negatively charged DWTS surface. Sorption of boron and selenium on the DWTS was lower. Boron exists primarily as nonionic boric acid at operating pH of 5.5–7.8, while selenate is a weakly bonding anion typically assumed to form outer-sphere surface complexes with Fe/Al oxides, both resulting in low removal. Sorption of the metals and metalloids was affected by their speciation and electrostatic interactions with DWTS. Higher influent pH increased boron and copper sorption but inhibited removal of chromium. Water temperature, solid moisture content, and loading rate did not have significant impact on sorption to the DWTS.

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1. Introduction

The presence of metals and metalloids such as chromium (Cr), copper (Cu), lead (Pb), boron (B), and selenium (Se) in water can adversely impact microorganisms, plants, and animals [1]. More importantly, these contaminants bio-accumulate through food chains, leading to sub-lethal toxicity or death of humans and other animals [1]. Although trace amounts of these substances are ubiquitous in the environment, anthropogenic activities may release additional, harmful quantities of materials to the environment through industrial activities, mining, waste disposal, and agricultural use of pesticides and herbicides [1].

Because most metals and metalloids cannot be degraded in natural environment, it is important to reduce the quantity of these contaminants to a safe level prior to water use or discharge. Common treatment technologies include chemical precipitation [2], ion exchange [3], reverse osmosis (RO) [4], liquid–liquid extraction [5], and sorption [6]. Sorption is an effective method to transfer metals and metalloids from an aqueous solution to a solid phase. There is a growing effort to develop inexpensive sorbents for removal of metals and metalloids from water and wastewater, such as red

mud and steel slag [1], natural and modified kaolinite and montmorillonite [7,8], agricultural waste material [9], chemically modified plant wastes [10], clino-pyrrhotite [11], lignite [12], aragonite shells [13], kaolinite [14], peat [15], natural zeolites [16], lignin [17,18], diatomite [19], and clay [20]. The removal of metals and metalloids by different types of low-cost sorbents is summarized in Table S1 in the Supporting Information. Red mud, activated slag, and iron slag exhibited remarkable capacities for sorption of copper (II) and lead (II). Dry aluminum-derived water treatment solids also achieved good removal of chromium (VI) and selenium (VI), but sorption of boron (III) was low.

One of the most important factors controlling the sorption of metals and metalloids on amphoteric surfaces is pH [21]. Sorption of cations on amphoteric surfaces increases with increasing pH, whereas sorption of anions is typically a mirror image of the characteristic cation sorption behavior and decreases with increasing pH. The affinity of cations for amphoteric surfaces is correlated with the first hydrolysis constant of the metal cation, whereas the affinity of anions is related to the basicity constant of the anion considered as a base; stronger bases tend to have higher affinity for amphoteric surfaces [21].

The essential constituents of these sorbents are amorphous and crystalline iron and aluminum oxides. Electrolyte ions can form surface complexes of different strength and type on hydrous iron,

manganese, and aluminum oxide surfaces, including outer-sphere, ion pair complexes, as well as inner-sphere, covalent coordination complexes [22–27]. The high reactivity of hydrous metal oxides results from the fact that hydroxyl groups of the active surface sites form "bridges" for sorption of cation and anion metals and metalloids [27]. The OH–OH distances of the hydrous oxides match well with the geometry of the coordination polyhedral of metals and metalloids [27].

Drinking water treatment solids (DWTS) are produced during coagulation processes using iron or aluminum salts. It is reported that approximately 60% and 90% of total iron and aluminum, respectively, exist in the form of amorphous instead of crystalline oxides in DWTS [28]. These iron and aluminum precipitates can be active substances for sorption of cationic and anionic contaminants. Previous researches have shown that DWTS could remove phosphate [28,29], hydrogen sulfide [28], fluoride [30], and metals and metalloids, including arsenic, selenium, lead, chromium, and mercury from water [1,31–39]. DWTS has also been used for soil remediation to reduce the bioavailability and bioaccessibility of arsenic, barium, cadmium, chromium, copper, nickel, lead, and zinc in soil [31,33,34,37,38,40,41].

Although previous studies have demonstrated the potential use of DWTS to sorb metallic and metalloid contaminants from water, the majority of experiments were conducted in bench-scale, batch operations or using synthetic water (Table S1). More research is needed to understand sorption capacities and breakthrough volumes of DWTS under different operating conditions. Toxicity Characteristic Leaching Procedure (TCLP) tests indicate that DWTS is non-hazardous waste [42]; therefore, using DWTS as sorbent might be a suitable option to reduce disposal costs and an inexpensive method for removal of metals and metalloids from impaired waters. However, DWTS is laden with organic and inorganic substances sorbed or precipitated from surface water or groundwater. Therefore, desorption or leaching of these substances, even if nontoxic, may contaminate the treated water during reuse of DWTS. This concern can be alleviated if DWTS is used to treat another waste stream, such as desalination concentrate, when the production of high quality water is not critical.

In recent years, desalination technologies, such as RO, have been increasingly used to produce water from impaired streams such as brackish water, seawater, surface water, and wastewater [43–46]. While desalination processes generate high quality product water, dissolved salts and other contaminants are retained in the concentrate stream. Depending on water recovery, the concentration of dissolved solids in the retentate can be two to ten times higher than in the feed water. Therefore, naturally occurring minerals and anthropogenic contaminants such as boron, arsenic, chromium, selenium, lead, and copper, may be concentrated in the brine, exceed the discharge limits, and negatively impact the environment if they are not treated properly. Concentrate management and disposal is currently one of the most challenging issues associated with water desalination [47,48]. Conventional technologies for concentrate treatment are often energy intensive and cost-prohibitive, mainly because of high salinity and near saturation level of sparingly soluble salts.

Selective removal of metallic and metalloid contaminants from desalination concentrate using DWTS may offer a low-cost alternative to a major problem. Because high ionic strength and salt concentration could have a significant effect on sorption [24,25], the sorption capacity of DWTS for constituents found in desalination concentrate requires further investigation. Therefore, the objective of this study was to evaluate the sorption capacity of DWTS for various metal and metalloid contaminants, including boron (III), copper (II), chromium (VI), lead (II), and selenium (VI) from desalination concentrate in continuous-flow conditions. The impact of operating conditions on sorption, including pH, feed concentration, hydraulic and mass loading rates, and temperature were investigated. Two different types of DWTS were studied to determine their sorption capacity.

2. Materials and methods

2.1. RO concentrate and spiked metals and metalloids

RO concentrate was collected from the Kay Bailey Hutchison Desalination Plant in El Paso, Texas, that treats brackish groundwater. The total dissolved solids (TDS) concentration of the RO concentrate was approximately 10 ± 2.3 g L^{-1} with electrical conductivity of 18 ± 2.1 mS cm^{-1}. The major ions in the RO concentrate included Na$^+$ (2660 mg L^{-1}), Ca^{2+} (670 mg L^{-1}), Mg^{2+} (168 mg L^{-1}), K$^+$ (69 mg L^{-1}), Cl$^-$ (4990 mg L^{-1}) and SO$_4^{2-}$ (1272 mg L^{-1}) while minor elements included arsenic, boron, chromium, copper, iron, manganese, and selenium. The pH was 7.8 with alkalinity of 388 mg L^{-1} as CaCO$_3$. The total organic carbon (TOC) concentration in the RO concentrate varied between 0.5 and 7.7 mg L^{-1}. The physicochemical properties of the RO concentrate and the DWTS characteristics are summarized in Table 1.

To investigate the selective removal of metals and metalloids from desalination concentrate, metal salts of boron (III), copper (II), chromium (VI), lead (II), and selenium (VI) were spiked into the RO concentrate simultaneously (Table 2). These contaminants were selected because of their frequent occurrence in natural and industrially contaminated water, and their potential adverse impact on agricultural irrigation and human health [49–51]. The spiking concentrations of the contaminants were 2–6 times higher than the Maximum Contaminant Levels (MCLs) of the United States National Primary Drinking Water Regulations [52], or determined based on the recommended maximum concentrations of contaminants in irrigation water [53]. The spiked metal salt concentrations are within the typical concentration range of real RO concentrates. The metal salts spiked in the RO concentrate were of ACS grade or higher from Fisher Scientific Co. (Fair Lawn, NJ), J. T. Baker Chemical, Co. (Phillipsburg, NJ), and Sigma–Aldrich (St. Louis, MO).

Electrical conductivity and pH of the water samples were measured using a conductivity and pH meter (Model 431-61, Cole-Parmer, Vernon Hills, IL). TOC was quantified using a carbon analyzer (Shimadzu TOC-L, Kyoto, Japan). Common anions including chloride, phosphate, and sulfate were measured using an ion chromatograph (IC, ICS-2100, Dionex, Sunnyvale, CA, USA), and the concentrations of aluminum, arsenic, boron, calcium, chromium, copper, iron, potassium, magnesium, manganese, sodium, lead, and selenium were quantified using an inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC-e, PerkinElmer, Waltham, MA, USA). Alkalinity was measured using a digital titrator (Hach, Colorado, USA) and 1.6 N sulfuric acid standard solutions to an endpoint pH of 4.6. The TDS concentration was measured following evaporation method at 180 °C after filtering the RO concentrate sample using a 0.45 μm cellulose acetate membrane filter (Toyo Roshi Kaisha, Ltd., Japan).

2.2. DWTS and characterization

Two types of dewatered DWTS were studied to compare their selective sorption capacities for metals and metalloids in RO concentrate (Table 1). One DWTS (referred to as SDWTS) was obtained from a conventional surface water treatment plant in Colorado, USA, which uses coagulation, flocculation, sedimentation, and greensand filtration to treat the water diverted from a creek to produce potable water. Ferric sulfate is the coagulant used to remove turbidity, natural organic matter, and manganese from the surface

Table 1
Physicochemical properties of the RO concentrate and the DWTS used in this study.

Analytes	RO concentrate	SDWTS	GDWTS
Al	BDL ($<0.05\ \mu g\ L^{-1}$)	$17 \pm 0.4\ mg\ g^{-1}$	$53 \pm 1.4\ mg\ g^{-1}$
As	$63 \pm 11\ \mu g\ L^{-1}$	$22 \pm 0.6\ \mu g\ g^{-1}$	$43 \pm 1.3\ \mu g\ g^{-1}$
B	$158.9 \pm 2\ \mu g\ L^{-1}$	BDL ($<0.5\ \mu g\ g^{-1}$)	BDL ($<0.5\ \mu g\ g^{-1}$)
Ca	$673 \pm 113\ mg\ L^{-1}$	$2.5 \pm 0.8\ mg\ g^{-1}$	$17 \pm 0.9\ mg\ g^{-1}$
Cl	$4993 \pm 656\ mg\ L^{-1}$	–	–
Cr	$7.3 \pm 3.6\ \mu g\ L^{-1}$	$45 \pm 5.2\ \mu g\ g^{-1}$	$119 \pm 2.1\ \mu g\ g^{-1}$
Cu	BDL ($<0.05\ \mu g\ L^{-1}$)	$360 \pm 71\ \mu g\ g^{-1}$	$288 \pm 0\ \mu g\ g^{-1}$
F	$154 \pm 18\ \mu g\ L^{-1}$	–	–
Fe	BDL ($<0.2\ \mu g\ L^{-1}$)	$3.3 \pm 0.2\ mg\ g^{-1}$	$1.1 \pm 0\ mg\ g^{-1}$
K	$69 \pm 5.4\ mg\ L^{-1}$	$3.9 \pm 0.3\ mg\ g^{-1}$	$9.6 \pm 0.3\ mg\ g^{-1}$
Mg	$168 \pm 22\ mg\ L^{-1}$	$2.4 \pm 0.2\ mg\ g^{-1}$	$13 \pm 0.5\ mg\ g^{-1}$
Mn	$332 \pm 8.6\ \mu g\ L^{-1}$	$30 \pm 0.2\ mg\ g^{-1}$	$1.0 \pm 0\ mg\ g^{-1}$
Na	$2660 \pm 368\ mg\ L^{-1}$	–	–
Pb	BDL ($<0.05\ \mu g\ L^{-1}$)	$27 \pm 1.6\ \mu g\ g^{-1}$	$2.8 \pm 0.2\ \mu g\ g^{-1}$
Se	$11.5 \pm 0.9\ \mu g\ L^{-1}$	$4.4 \pm 0\ \mu g\ g^{-1}$	$1.6 \pm 0\ \mu g\ g^{-1}$
SO_4^{2-}	$1272 \pm 226\ mg\ L^{-1}$	–	–
TOC	$4.1 \pm 3.6\ mg\ L^{-1}$	–	–
EC	$18 \pm 2.1\ mS\ cm^{-1}$	–	–
TDS	$10 \pm 2.3\ g\ L^{-1}$	–	–
pH	7.8	–	–
PZC (pH)	–	Dry solids: 4.8 Wet solids: 5.4	Dry solids: 6.9
Total alkalinity	$388 \pm 6\ mg\ L^{-1}$ as $CaCO_3$	Dry solids: $1.0\ mg\ g^{-1}$ (DI); $1.2\ mg\ g^{-1}$ (NaCl) as $CaCO_3$ Wet solids: $1.7\ mg\ g^{-1}$ (DI); $1.2\ mg\ g^{-1}$ (NaCl) as $CaCO_3$	Dry solids: $4.9\ mg\ g^{-1}$ (DI); $6.9\ mg\ g^{-1}$ (NaCl) as $CaCO_3$
Organic matter	–	22%	14%
Bulk density	–	Dry solids: $1206\ kg\ m^{-3}$; Wet solids: $1212\ kg\ m^{-3}$	Dry solids: $1206\ kg\ m^{-3}$

Note: BDL – below detection limit. The elemental data were obtained from dry solids except as noted otherwise.

Table 2
Metals and metalloids spiked in the RO concentrate.

Metals and metalloids	Concentration (as the element)	Spiked salts	Drinking water MCLs [52]	Agriculture irrigation requirements [53]
Boron	$5\ mg\ L^{-1}$ (0.45 mM)	Sodium borate		$<0.7\ mg\ L^{-1}$ for no restriction on use; $0.7 \sim 3\ mg\ L^{-1}$ for slight to moderate restriction on use
Chromium	$0.4\ mg\ L^{-1}$ (7.7 µM)	Potassium dichromate	$0.1\ mg\ L^{-1}$	$0.1\ mg\ L^{-1}$
Copper	$5\ mg\ L^{-1}$ (78 µM)	Copper chloride	$1.3\ mg\ L^{-1}$	$0.2\ mg\ L^{-1}$
Lead	$0.1\ mg\ L^{-1}$ (0.48 µM)	Lead chloride	$0–0.015\ mg\ L^{-1}$	$5.0\ mg\ L^{-1}$
Selenium	$0.2\ mg\ L^{-1}$ (2.5 µM)	Sodium selenate	$0.05\ mg\ L^{-1}$	$0.02\ mg\ L^{-1}$

water. The SDWTS was collected from the dewatering filter press of the treatment plant. The second DWTS (referred to as GDWTS) was obtained from a groundwater treatment plant in Texas, USA. This plant removes naturally occurring arsenic with chlorination and coagulation using ferric chloride followed by sand filtration. The filter backwash iron-derived GDWTS was collected from the sand drying beds in the treatment plant. Even though the DWTS did not come from a process that used aluminum salt as a coagulant, a significant amount of aluminum was measured in the DWTS as discussed later.

To compare the impact of moisture content (i.e., the level of hydration of iron oxide) on sorption capacity, wet SDWTS (dewatered SDWTS collected from filter press) and dry SDWTS (dried at 105 °C for 48 h) were studied in the experiments. The water content of the DWTS was measured by standard thermal evaporation method in an oven (OF-01E, Jeio Tech, Korea) at 105 °C for 24 h. Organic content was measured using ignition test by heating the DWTS at 550 °C for 8 h (Furnace Vulcan 3-550, Dentsply International Inc., PA, USA). The inorganic composition of the DWTS was analyzed by acid digestion method, mixing 0.2 g DWTS with 12 mL concentrated nitric acid and digested in a microwave (Multiwave 3000, Anton Paar, Austria), then analyzed by ICP-MS and IC. To identify the contribution of the DWTS to the alkalinity of the water, the alkalinity of a solution equilibrating with the DWTS was determined. Deionized (DI) water or a $10\ g\ L^{-1}$ NaCl solution was used to simulate the leaching of alkalinity from DWTS to water or RO concentrate, respectively. Two grams of DWTS were mixed with the solution and stirred for 24 h, and the supernatant was used for measuring alkalinity. The pH value at the point of zero charge (PZC) was determined to investigate the impact of DWTS charge on sorption. The salt titration approach was modified in the study based on the methods developed by Sakurai et al. [54] and Jain et al. [55]. For each DWTS, the PZC was determined based on triplicate measurements. Two grams of DWTS were mixed with 20 mL of 0.02 M or 0.2 M NaCl solution. Then 0.3 mL of 1 N HCl solution was added in each DWTS solution. The DWTS aqueous solutions were stirred for 1 h each day and equilibrated for 4 d. The equilibrium pH values of the DWTS solutions were measured every 24 h (pH_1 for 0.02 N NaCl solution and pH_2 for 0.2 N NaCl solution). The value of $\Delta pH = pH_2 - pH_1$ was calculated, and the graph of ΔpH *versus* pH_1 was plotted to determine the PZC value at which $\Delta pH = 0$.

2.3. Continuous-flow column sorption tests

Continuous-flow column experiments were conducted using the RO concentrate spiked with five metal salts. The column reactors are 5 cm in diameter and 30 cm long, packed with 200 g wet DWTS or 42 g dry DWTS (with the same amount of dry solids mass). Washed small gravels were installed at the bottom of the

columns for water to perforate through (approximately 3 cm thickness). Wet DWTS were packed directly to the columns. Dry solids were crushed and sieved to particle sizes between 0.8 and 2.0 mm before packing.

RO concentrate was pumped to the bottom of the columns by peristaltic pumps with Masterflex L/S Variable-Speed Drives (Cole-Parmer, Illinois, USA) at flow rates of 11–33 mL/min. The effects of operating conditions on sorption processes, including influent pH, moisture content, different DWTS, columns-in-series, and temperature, were investigated. Effluent samples were collected at 0, 0.5, 2, 4, 8, 12, 18, and 24 h, and once a day for the following 15 days, aiming at monitoring long-term removal efficiency.

Number of bed volumes (dimensionless), hydraulic loading rate (HLR, $m^3 m^{-3} h^{-1}$), mass loading rate (MLR, $L kg^{-1} h^{-1}$), and hydraulic retention time (HRT, min) were calculated as follows:

Bed volumes = Volume of water processed/solids volume.
Hydraulic loading rate, HLR = Water flow rate/solids volume.
Mass loading rate, MLR = Water flow rate/mass of dry solids.
Hydraulic retention time, HRT = Solids volume/water flow rate.

3. Results and discussion

The experimental conditions, sorption capacity and removal efficiency of DWTS are summarized in Table 3. To compare the sorption under equal basis, the sorption capacity and percent removal were calculated at 85 bed volumes of treated RO concentrate.

3.1. Characteristics of DWTS

The water content of the wet SDWTS was 78.9%, and the organic content of the dry SDWTS was 22% (i.e., 4.6% of the wet DWTS). The water content of the dry GDWTS was 4%, and the organic content was 14% (Table 1). The alkalinity of the supernatant equilibrated with dry and wet SDWTS was similar (1.0–1.7 mg $CaCO_3$ per gram of DWTS), but the alkalinity of GDWTS supernatant was approximately 4–5 times higher than that of SDWTS (4.9–6.9 mg $CaCO_3$ per gram of DWTS). The major metals in the DWTS were manganese (30 mg g^{-1}), aluminum (17 mg g^{-1}), iron (3.3 mg g^{-1}), calcium (2.5 mg g^{-1}) and magnesium (2.4 mg g^{-1}) for SDWTS; and aluminum (53 mg g^{-1}), calcium (17 mg g^{-1}), magnesium (13 mg g^{-1}), iron (1.1 mg g^{-1}) and manganese (1.0 mg g^{-1}) for GDWTS. It should

be noted that iron is not the dominant element in the DWTS although both treatment plants use ferric salt as primary coagulant. The higher amount of aluminum in the DWTS was attributed to the acid digestion of aluminosilicate particles in the silt and clay fraction that were retained from the source water during the coagulation process. The high amount of manganese in the SDWTS was due to manganese precipitation from surface water that has manganese concentration of 0.3–1.0 mg L^{-1}. For trace inorganic contaminants detected in the solids, GDWTS had higher amount of arsenic and chromium while SDWTS contained higher amount of selenium, copper, and lead. Boron was not detected in DWTS samples.

The PZC values of the DWTS varied depending on the source and hydration degree of the solids. The dry GDWTS had the highest PZC value (6.9), followed by the wet SDWTS (5.4) and dry SDWTS (4.8), which is consistent with the analytical results of alkalinity contribution from the DWTS samples (Table 1). The PZC values are similar to those reported by Zhou et al. [32], 5.6–5.7 for aluminum-derived DWTS. As the major constituents of DWTS are organic matter and aluminosilicate particles, the PZC of the DWTS is lower than that expected for iron oxide precipitates.

3.2. Effect of pH

The impact of pH on sorption of metals and metalloids to the DWTS was investigated at pH values of 5.5 (adjusted with chloric acid solution) and 7.8 (ambient pH of RO concentrate). Many RO systems operate at acidic pH to prevent membrane scaling. The testing pH values of 5.5 and 7.8 represent the operating pH range of RO concentrate in desalination facilities. In addition, these two pH values were chosen because the measured PZC values of the DWTS are in the range of 4.8–6.9. At pH 5.5, the dry SDWTS were slightly negatively charged, wet SDWTS neutral, and GDWTS slightly positively charged; whereas at pH 7.8, all the DWTS were negatively charged. The charge of DWTS is expected to affect the electrostatic interactions between the solutes and solids.

3.2.1. Effect of pH on sorption of metal cations
The impact of pH on sorption of copper and lead was studied with wet SDWTS at RO concentrate pH of 5.5 and 7.8 (Fig. 1). Specific sorption of copper is strongly pH-dependent. The SDWTS could remove over 98% of copper at pH 7.8, but the percent removal declined markedly to 50% at pH 5.5. The sorption capacities of

Table 3
Summary of experimental conditions, and sorption capacity ($\mu g g^{-1}$ of dry solids mass) and percent removal of DWTS after treating 85 bed volumes of RO concentrate.

| Test no.	pH	Solid type	Mass of solids (g)	Temperature (°C)	MLR (L kg^{-1} h^{-1})	HRT (min)	Contaminant initial concentration ($\mu g L^{-1}$)	B (III) 5000	Cr (VI) 400	Se (VI) 200	Cu (II) 5000	Pb (II)100
1	7.8	Wet SDWTS	200	23	14	17	Sorption capacity ($\mu g g^{-1}$)	–	–	–	>1800	>22
							Percent removal	–	–	–	100–99%	~100%
2	5.5	Wet SDWTS	200	23	14	17	Sorption capacity ($\mu g g^{-1}$)	125	>141	>3.1	>1300	>33
							Percent removal	50–3%	99–93%	38–4%	98–55%	100–88%
3	5.5	Dry SDWTS	42.2	23	24	2	Sorption capacity ($\mu g g^{-1}$)	>113	>23	3.8	>300	>7.1
							Percent removal	41–10%	89–58%	23–3%	84–63%	~100%
4	7.8	Dry SDWTS	42.2	23	24	2	Sorption capacity ($\mu g g^{-1}$)	>87	>15	1.4	–	–
							Percent removal	47–18%	94–30%	22–2%	–	–
5	5.5	Wet SDWTS	200	35	14	17	Sorption capacity ($\mu g g^{-1}$)	>454	>126	17	>1430	–
							Percent removal	37–19%	100–93%	34–25%	92–77%	–
6	5.5	Dry GDWTS	42.2	23	24	2	Sorption capacity ($\mu g g^{-1}$)	29	>6.6	0.11	>320	–
							Percent removal	56–3%	71–60%	14–4%	90–84%	–
7	5.5	Dry GDWTS	126.6	23	6	8	Sorption capacity ($\mu g g^{-1}$)	26	>8.0	0.077	>310	–
							Percent removal	48–3%	95–43%	4–2%	90–85%	–
8	5.5	Dry SDWTS	126.6	23	6	8	Sorption capacity ($\mu g g^{-1}$)	34	>15	0.085	>300	–
							Percent removal	42–3%	100–87%	10–0%	84–73%	–
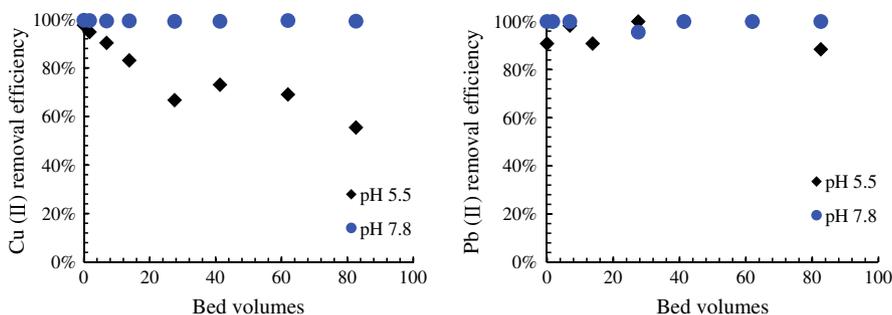
Fig. 1. Effect of pH 5.5 and 7.8 on copper and lead sorption using wet SDWTS at MLR of 14 L kg^{-1} h^{-1}, HRT of 17 min, and 23 °C.

copper were greater than 1800 µg g^{-1} and 1300 µg g^{-1} at pH 7.8 and 5.5, respectively (Tests 1 and 2 in Table 3), and the sorption was far from saturation after 85 bed volumes of treatment. Compared to other sorbents (Table S1 in Supporting Information), the copper removal capacity of the DWTS was higher than fly ash and kaolinite clay, but lower than iron slag of which Langmuir isotherm calculated 89 mg g^{-1} maximum sorption capacity. This difference is likely caused by the high iron composition in the slag as compared to 0.3% in the DWTS.

The removal of lead exceeded 90% at pH 5.5, and it was almost completely removed (~100%) at pH 7.8. Electrostatic interactions between the surface of the solids and metals/metalloids strongly affect the sorption. As pH increases, the solid surface becomes increasingly negatively charged (given the PZC of wet SDWTS 5.4), resulting in attractive interactions between the surface of the wet SDWTS and the positively charged copper and lead ions. Previous studies showed that the first hydrolysis constant of metal cations correlates well with the affinity of metal ions for amphoteric oxide surfaces [1], thus copper and lead would tend to bind considerably stronger to iron and aluminum oxide surfaces compared to alkali metals and alkaline earth metals.

It should be noted that at higher surface coverage, metal ions have been known to form surface precipitates [56], and the tendency to form surface precipitates generally increases with increasing pH. Although distinguishing between sorption complexes and surface precipitates requires spectroscopic evidence [57], the

observation of blue copper precipitates on the solid surface during later period of the experiments is a clear indication of surface precipitation, as would be expected, given the high surface loading during these experiments. In addition, the water used in this study was RO concentrate that had high concentration of bicarbonate (388 mg L^{-1} as CaCO$_3$), potentially leading to the formation of either lead carbonate ($K_{spPbCO3}$ 3.3 × 10^{-14}) or lead hydroxide ($K_{spPb(OH)2}$ 1.43 × 10^{-20}) precipitates, both sparingly soluble solids. As stated above, metal cations tend to form surface precipitates on oxide surfaces at higher surface coverage, even before the thermodynamic solubility product of a bulk precipitate is reached. Thus, the observed lead removal during these experiments was most likely due to the formation of bulk or surface precipitates.

3.2.2. Effect of pH on sorption of anions

Just like cations, anions display selectivity with respect to sorption on amphoteric oxide surfaces, with the strength of a base correlated to the affinity of the anion for oxide surfaces. Meanwhile, the pH of the RO concentrate has strong impact on the speciation of anions, thus affecting their sorption to DWTS due to electrostatic interactions and chemical bonding with metal oxides in the DWTS. Therefore, the sorption of chromium to SDWTS was considerably higher compared to boron and selenium because of its stronger complexation with DWTS (Fig. 2). For example, at pH 5.5, removal efficiency of chromium was approximately 3 times higher than boron and selenium. However, because the initial
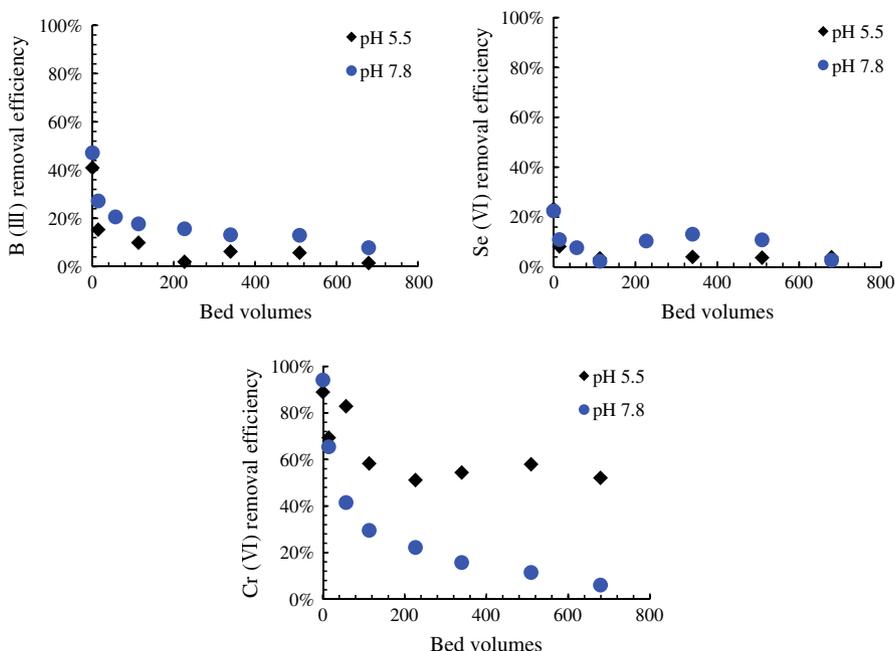

Fig. 2. Effect of pH on anions sorption using dry SDWTS as sorbent at MLR of 24 L kg^{-1} h^{-1}, HRT of 2 min, and 23 °C.

boron concentration was 25 times higher than chromium, the sorption capacity for boron ($>113\ \mu g\ g^{-1}$) was higher, even though percent removal was lower (<41%) (Test 3 in Table 3). Besides, the sorption capacity of DWTS for boron was similar to illite and kaolinite, while lower than other sorbents for chromium due to low initial concentration and ion competition in RO concentrate (Table S1 in Supporting Information).

The effect of pH on boron and selenium sorption was largely marginal, given that very little sorption was observed for boron and selenium under either operating pH value. The most pronounced pH-dependence effect was observed for chromium sorption, where increase in pH from 5.5 to 7.8 reduced the removal efficiency by approximately 40%. At pH 5.5, the initial removal of chromium achieved 89%, and stabilized at approximately 50% between 110 and 680 bed volumes of RO concentrate, whereas at pH 7.8 the sorption of chromium declined gradually from 94% to 6%. As pH increases, the surface of the solids becomes increasingly negatively charged, resulting in greater electrostatic repulsion between anions and solids sorption sites. At pH 5.5, chromium exists mainly as $HCrO_4^-$, whereas at pH 7.8 CrO_4^{2-} is the predominant species. $HCrO_4^-$ is a weaker acid compared to CrO_4^{2-}, forming stronger inner-sphere complexes with DWTS at low pH values.

The selenium anion (SeO_4^{2-}), the conjugate base of the strong selenic acid (pK_a 1.9) is expected to form mostly outer-sphere complexes. Due to the similar behavior of sulfate and selenate anions, selenium sorption to DWTS is expected to be affected substantially by sulfate in RO concentrate. In RO concentrate, the molar ratio of S:Se and S:Cr is 10,500 and 3350, respectively. At such high concentration, sulfate ions certainly compete with chromium and selenium ions for sorption sites. Our bench-scale DWTS sorption experiments achieved 16% sulfate removal from RO concentrate, indicating strong ionic competition of sulfate with anions such as chromium and selenium. Even though SO_4^{2-} ions are expected to form only weak outer-sphere complexes, the substantial amount of these anions in RO concentrate increases their competition with target anions for the sorption sites, thus reducing the selective sorption capacity of DWTS.

In this study, selenate was selected as representative of selenium ions in water. For groundwater, selenium may exist as selenite in a reducing environment. Selenite is a much stronger base than selenate, and can therefore bind strongly with DWTS, resulting in higher removal.

The percent removal of boron exhibited the same trend for both wet and dry SDWTS at pH 5.5, while sorption at pH 7.8 was slightly higher than sorption at pH 5.5. At the operating pH of 5.5 and 7.8, borate exists primarily as the nonionic boric acid (pK_a 9.2) in RO concentrate, resulting in low sorption. It was previously reported that the sorption of boron was pH-dependent and the sorption curve was bell-shaped, where the maximum sorption occurred near the pK_a of 9.2 [49], which might explain the slightly higher percent removal (less than 10%) of boron at pH 7.8 by the DWTS. Interestingly, boron sorption might be enhanced at high ionic strength compared to low ionic strength [49]. The surface charge of dry SDWTS (PZC 4.8) could be reduced by non-specific sorption of cations at higher ionic strength, thereby compressing the electrical double layer, and potentially enhancing boron sorption at high ionic strength solutions [49].

3.3. Effect of solid moisture content

The moisture content of DWTS may change over time or depending on the dewatering/drying process in a water treatment plant. Dry DWTS may be preferred to reduce solid volume for transportation. The impact of DWTS moisture content on sorption of metals and metalloids was evaluated with wet and dry SDWTS at pH 5.5 (Fig. S1 in Supporting Information, and Tests 2 and 3 in

Table 3). Both wet and dry SDWTS sorbed chromium and copper effectively from the RO concentrate, while the sorption of boron and selenium was low due to their weak bonding or electrostatic repulsion by the negatively charged solid surface.

DWTS moisture content had negligible impact on the removal of copper; removal efficiencies of both wet and dry SDWTS began with over 80%, and then gradually declined to 60%. The relative affinity of cations for sorption sites is a function of the stability of surface-cations bonds [1]. Iron, aluminum, and manganese oxides in the DWTS provide substantial sorption sites, resulting in the high cations sorption capacity of DWTS. Similar to sorption on ferrihydrite, the mechanism of SDWTS sorption involves the formation of cation-oxygen complexes on the surface of iron, manganese, and aluminum oxy-hydroxides. Although the SDWTS are iron-derived solids, the iron mass percentage was only 0.33%. The sorption of metals and metalloids on DWTS involves the synergistic effects of metal oxides, organic matter, particles, and surface properties of the solids. Organic matter in DWTS possesses a variety of ligands, including carboxyl, amine, hydroxyl, and sulfhydryl groups. Polyvalent cations, such as copper and lead, could bind to these groups by ion exchange, covalent bonding, and chelation [1]. They preferentially coordinate directly with functional groups to form inner-sphere complexes, which are strong and rapidly forming bonds [58]. SDWTS also contains substantial amount of clay, silt, and sand, in general aluminosilicate particles, which play a beneficial role in metal sorption [59]. In addition, SDWTS with PZC of 4.8 and 5.4 carry a slightly negative charge at pH 5.5, and therefore attractive electrostatic interactions exist between the DWTS surface and metal cations.

The removal efficiency of wet SDWTS for chromium was approximately 10% higher than that of dry SDWTS, and the sorption capacity was greater than $141\ \mu g\ g^{-1}$ and $23\ \mu g\ g^{-1}$ for wet and dry SDWTS (Tests 2 and 3 in Table 3). The charge on iron and aluminum oxy-hydroxides surface determines the speciation of $M-OH_2^{0.5+}$ and $M-OH^{0.5-}$ groups [32]. Water in wet SDWTS accelerates hydrolysis of iron, aluminum, and cations on the sorbent surface, resulting in higher sorption. Likewise, dry SDWTS was being hydrated during the sorption process, thereby enhancing metal sorption. For example, at pH 5.5, the removal efficiency of chromium increased by 7% after treating 230 bed volumes of RO concentrate. However, no change of volume or color was observed for the dry SDWTS after wetting. In addition, because the PZC of dry SDWTS (4.8) is lower compared to wet SDWTS (5.4), the surface of dry SDWTS is more negatively charged at pH 5.5; thus, anions (such as $HCrO_4^-$) sorb preferably to the wet SDWTS as a result of electrostatic interactions.

The removal efficiencies for boron and selenium were initially over 40% but declined quickly with bed volumes of processed RO concentrate. The complete breakthrough of these ions occurred with wet SDWTS after 80–100 bed volumes, indicating the poor sorption capacity of boron and selenium by DWTS.

3.4. Sorption by different DWTS

The impact of different types of DWTS on sorption of metals and metalloids was studied with dry SDWTS and GDWTS at pH 5.5 and HLR of 6 and $24\ L\ kg^{-1}\ h^{-1}$ (Tests 3 and 6 in Table 3). The GDWTS was more efficient than the SDWTS in sorbing copper by 10%. The sorption capacity for copper was greater than $300\ \mu g\ g^{-1}$ for SDWTS, and $320\ \mu g\ g^{-1}$ for GDWTS after treating 85 bed volumes of RO concentrate. The sorption difference might be attributed to the elemental composition of DWTS. SDWTS contains more copper than GDWTS (Table 1: 360 *versus* $288\ \mu g\ g^{-1}$), influencing the sorption of copper on DWTS. In addition, the alkalinity of the solution in equilibrium with GDWTS was approximately 5 times higher
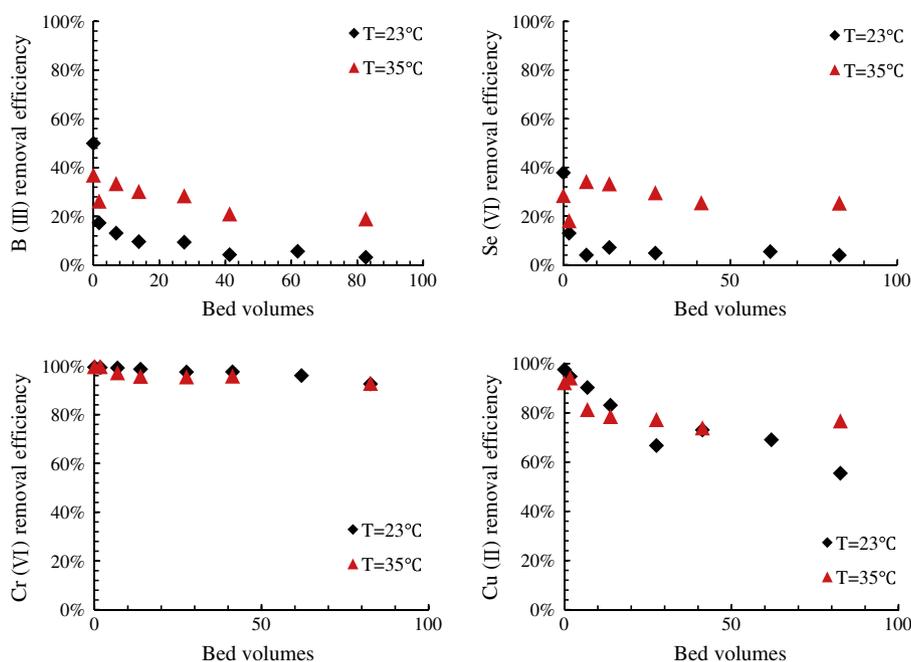
Fig. 3. Effect of temperature on metals and metalloids sorption using wet SDWTS at MLR of 14 L kg^{-1} h^{-1} and pH 5.5.

than with SDWTS; thus, copper (II) is more likely to form mixed precipitates with HCO$_3^-$ in GDWTS.

For anions, the sorption capacity of SDWTS (boron: 113 µg g^{-1}, chromium: 23 µg g^{-1}, selenium: 3.8 µg g^{-1}) was higher than GDWTS (boron: 29 µg g^{-1}, chromium: 6.6 µg g^{-1}, selenium: 0.11 µg g^{-1}) after treating 85 bed volumes of RO concentrate (Table 3). GDWTS contained higher alkalinity than in SDWTS, suggesting increased competition effects on the surface of GDWTS.

As shown in Table 3 (Tests 6 and 7 *versus* Tests 3 and 8), higher MLR resulted in higher sorption capacity for both types of DWTS, whereas the MLR impact on SDWTS was more discernable than on GDWTS. For example, the removal efficiency of boron was in the range of 0–56% for both types of DWTS, but the sorption capacity at 24 L kg^{-1} h^{-1} (29 µg g^{-1}) for GDWTS was 12% greater than at 6 L kg^{-1} h^{-1} (26 µg g^{-1}), and the sorption capacity at 24 L kg^{-1} h^{-1} (113 µg g^{-1}) for SDWTS was 3 times more than at 6 L kg^{-1} h^{-1} (34 µg g^{-1}). Dry DWTS is likely to clump when wetting, so sorption sites might be overlapping or aggregation might occur with increasing DWTS mass, causing the decrease in effective total sorbent surface area and the increase in diffusion path length [60]. On the other hand, the sorption of different DWTS for copper was similar in the range of 300–320 µg g^{-1}; high sorption capacity of both DWTS could not make significant difference in copper removal.

3.5. Sorption in columns-in-series

Sorption of the metals and metalloids in two-columns-in-series was studied at pH 5.5 with wet SDWTS (Fig. S2 in Supporting Information). Each column was operated at MLR of 14 L kg^{-1} h^{-1}.

In the 1st column the percent removal of boron and selenium dropped quickly to zero with increasing bed volumes. The complete breakthrough occurred at bed volumes of 250 and 120 for boron and selenium, respectively, achieving maximum sorption capacities of 183 and 3 µg g^{-1} of dry DWTS mass, respectively. The removal efficiency of boron and selenium was not improved in the 2nd column.

However, there was remaining sorption capacity for chromium and copper in the 1st column after treating 1330 bed volumes of RO concentrate. The percent removal of chromium began at 99% and then gradually declined to 11%, while the percent removal of

copper declined to 15% after treating 770 bed volumes of RO concentrate, then increased to 76% after treating 1020 bed volumes of RO concentrate, and gradually declined afterwards. The total sorption capacities were greater than 0.48 and 8.01 mg g^{-1} for chromium and copper, respectively. Other materials, such as activated blast furnace slag [61] and mixture of brine sediments and sawdust [62], achieved maximum sorption capacities of 38 and 0.31 mg g^{-1} for copper using low salinity solutions in column tests (Table S1 in Supporting Information). This suggests that the sorption capacity of DWTS is comparable to these sorbents and effective at removing chromium and copper in RO concentrate.

The overall percent removal of chromium and copper increased through the two-columns-in-series, but removal efficiency was higher in the 1st column. In both stages, the percent removal of copper and chromium fluctuated over time, which suggests the existence of sorption and desorption processes. Sorption of chromium and copper on the DWTS surface might have become increasingly difficult when the sorption sites were saturated, resulting in desorption of ions.

3.6. Effect of temperature

Effect of temperature on metals and metalloids sorption to DWTS was investigated using wet SDWTS at MLR of 14 L kg^{-1} h^{-1} and pH 5.5 (Fig. 3). Increase in temperature from 23 to 35 °C enhanced the sorption of boron and selenium by over 20%. Temperature had negligible influence on the sorption of chromium, where over 93% removal was achieved under both temperatures. This result is consistent with the study of Zhou et al. who observed chromium sorption increased by less than 5% between 20 and 60 °C [32]. The impact of temperature on copper removal fluctuated with slightly better removal at 23 °C in the beginning of the sorption experiments, and then declined at a faster rate compared to the sorption at 35 °C.

Temperature can enhance sorption processes through two mechanisms. First, higher temperature can accelerate physicochemical processes such as ion diffusion, co-precipitation, and slow-rate reactions such as ion bonding with sites that have low activation energy at first and then gradually form stronger bonds with high activation energy [1]. Second, increased temperature

may lead to increased breaking of internal bonds near the edge of the particle surfaces, thereby effectively increasing the number of sorption sites [61] .

4. Conclusion

This study demonstrated that DWTS, a residual of water treatment plant that is often disposed of in landfill, could be reused as an effective sorbent to selectively remove certain metals and metalloid contaminants from saline water. The DWTS collected from a surface water, and a groundwater treatment plant were characterized thoroughly to investigate the sorption processes and impact of operating conditions on sorption in continuous-flow columns.

The DWTSs derived from iron coagulants were comprised of mainly organic matter, clay and silt-size particles; the mass ratio of iron was between 0.1% and 0.3% of dry solids mass. Organic matter in DWTS possesses a variety of ligands such as carboxyl, amine, hydroxyl and sulfhydryl groups that can bind with polyvalent cations, such as copper and lead, by ion exchange, covalent bonding, and chelation. The sorption mechanisms of metals and metalloids involve the electrostatic interactions between the metals and metalloids ions and DWTS, and the strong inner- or weak outer-sphere complexes formed between metal and metalloid ions with Fe/Al oxide surface sites.

The pH of RO concentrate played a critical role in DWTS sorption of metals and metalloids in RO concentrate. Copper and lead exhibited high removal due to their strong affinity for Fe/Al oxide surfaces and the electrostatic attraction to negatively charged DWTS surface at ambient pH (7.8) of RO concentrate. However, at higher pH, the removal of chromium decreased because of the electrostatic repulsion between anions and the more negatively charged solids surface. The removal of boron and selenium by DWTS was low. Boron existed primarily as the nonionic boric acid (H_3BO_3) at the operating pH of 5.5–7.8, while SeO_4^{2-} is a weakly bonding anion that is expected to form outer-sphere (ion-pair) surface complexes with solids, resulting in low sorption. High concentration of major anions in RO concentrate, such as sulfate ions, can compete with chromium and selenium for sorption sites, thus reducing the sorption capacity of DWTS for target anions.

Solids moisture content did not have significant impact on the sorption of copper, boron and selenium, but wet DWTS with higher moisture content showed higher sorption capacity for chromium than dry DWTS due to solids hydrolysis. Both surface water and groundwater DWTS exhibited similar sorption trends, however SDWTS showed higher anion sorption capacity, while GDWTS was more efficient in copper removal due to their property difference in DWTS.

In summary, DWTS is a suitable material for development of a low-cost sorbent for the selective removal of metals and metalloids from RO concentrate, which could also apply to other high salinity wastewaters, such as acid mine and agricultural drainage. The selectivity can be controlled by adjusting the pH of feed solution; high pH favors the sorption of copper and lead while low pH facilitates the removal of chromium. Although the characteristics of DWTS are unique to the type of coagulant and the feed water, the results showed that there were no significant differences in sorption capacities of the two types of iron-derived DWTS with iron mass percentage of 0.1–0.3%. Further research work should consider disposal options of DWTS after sorption of metals and metalloids, which is an important aspect of risk evaluation.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2014.07.008.

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