



A recyclable adsorbent for salinized groundwater: Dual-adsorbent desalination and potassium-exchanged zeolite production

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HIGHLIGHTS

- CLDH and H-form zeolite remove Cl^- and Na^+ from potash brine-spiked groundwater.
- Na^+ -preconditioning and acid treatment of zeolites produce purer H-form zeolites.
- Synchrotron-based STXM showed dealumination and Na^+ abundance in H-form zeolites.
- It is feasible to regenerate the H-form zeolite for multiple Na^+ -removal cycles.
- H-form zeolite is converted to useful K-form zeolite after desalination cycles.

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ABSTRACT

This study focused on advancing the dual-adsorbent desalination technique that sequentially combines calcined layered double hydroxide (CLDH) and acid-treated zeolites (H-form zeolite) using groundwater spiked with potash mining effluent (brine). In sequential batch experiments, the CLDH adsorbent first reduced the high Cl^- concentration (4600 mg/L) of saline groundwater by 96%, the Ca^{2+} by 90%, and the Mg^{2+} by 92%, while transiently raising the pH to 12.80. H-form zeolites preconditioned with Na^+ then removed 92% of the Na^+ (2010 mg/L), while neutralizing the adsorption effluent pH to 7.7 and lowering the sodium adsorption ratio (SAR; 139.6 to 6.6) and the hardness (574 to 48.4 mg/L). In comparison, an equivalent amount of unmodified zeolite removed only 51% of the Na^+ and generated extremely hard water due to Ca^{2+} and Mg^{2+} release (1519 mg/L). Na^+ -conditioning the zeolites prior to acid treatment enhances native cation removal, forming H-form zeolites. Synchrotron-based X-ray scanning transmission microscopy (STXM) showed the occurrence of dealumination and visualized the sodium distribution associated with Si- and Al- sites in the H-form zeolites. Four consecutive desalination cycles were feasible for Na^+ and K^+ adsorption by regenerating the H-form zeolite. During regeneration, the Na^+ desorbed while the K^+ remained in the regenerated zeolites. Cumulative K^+ loading in the regenerated zeolites increased from 4.8 to 21.2 mg/g, producing K-form zeolites. These K-form zeolites released K^+ (2.15 mg/L for 24 h) in a leaching test and could potentially be considered as nutrient-supply media in other applications, thereby recycling the spent zeolites after multiple desalination treatments.

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1. Introduction

Accelerated natural weathering of geological materials, as well as the chronic and accidental discharges of salts (i.e., NaCl) from human activities such as de-icing roads and the production of industrial brine from oil, gas and mineral extractions, are recognized

as potential inputs of salts to water environments (Arocena and Rutherford, 2005; Kaushal et al., 2005; Klaustermeier et al., 2016). Excess sodium (Na^+) deteriorates water and soil quality, perturbs biogeochemical cycles, and inhibits plant growth (Bernstein, 1975; Belbase et al., 2013). Sodium-based salinization of water enhances the leaching of heavy metals from soils, sediments, and surface-aged waste pipes through ion exchange (Kaushal et al., 2005). Chronic inputs of chloride (Cl^-) are harmful to freshwater species, are not suitable for drinking, and cause corrosion in water distribution systems and steel infrastructure (Xu et al., 1999; White and

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Broadley, 2001; Kaushal, 2016).

Treatments for saline industrial produced water (e.g., coalbed methane produced water) that use strong acid chemical resins and natural or modified zeolites have received significant attention, mainly for Na^+ removal via ion exchange and adsorption (Huang and Natrajan, 2006; Ganjegunte et al., 2011; Wang et al., 2012; Belbase et al., 2013; Millar et al., 2015, 2016; Santiago et al., 2016; Wang and Nguyen, 2016). However, there are relatively fewer studies involving the removal of both Cl^- and Na^+ from industrial brine-impacted water using mineral adsorbents (Pless et al., 2006; Gibb et al., 2017). This study focuses on the removal of both Cl^- and Na^+ from potash brine-impacted groundwater using the dual-mineral adsorbent process suggested previously by our research group (Gibb et al., 2017). Potash brine produced by potash mining is largely composed of Na^+ and Cl^- at nearly saturated levels, as well as considerable amount of K^+ (Tallin et al., 1990). Briefly, we sequentially applied calcined layered double hydroxide (CLDH) and acid-treated (H-form) zeolite. The CLDH (anion adsorbent) was first used to remove Cl^- and transiently raise the pH. Acid-treated zeolite (cation adsorbent) was then used to remove Na^+ and neutralize the pH. The adsorption capacity of the H-form zeolite was significantly enhanced when used after the CLDH treatment.

Layered double hydroxide (LDH) has been considered as an anion exchanger for the removal of monoatomic anions, oxyanions, and metals (Allada et al., 2005; Lv et al., 2009; Liang et al., 2013; Theiss et al., 2014). The removal mechanism for Cl^- in CLDH is based on anion exchange followed by rehydration, which incorporates Cl^- into the layered framework of the CLDH and results in LDH reconstruction (also known as the memory effect) (Bontchev et al., 2003; Goh et al., 2008). On the other hand, researchers have modified zeolite-type mineral adsorbents using acid or other selected chemicals to augment its Na^+ adsorption capacity (Pless et al., 2005; Wang et al., 2012; Wang and Nguyen, 2016). With acid treatment, the surface area of the porous zeolite expands, and its pre-existing native cations are replaced by protons during the transition to an H-form zeolite (Wang et al., 2012; Gibb et al., 2017). These effects enhance Na^+/H^+ exchange (Gibb et al., 2017; Paul et al., 2017).

The dual-adsorbent desalination showed potential for treating coalbed methane brackish water (Pless et al., 2006), cooling tower water (Sasan et al., 2017a, 2017b), and potash brine-impacted groundwater (Gibb et al., 2017). However, it is not yet a mature technology and there are several research gaps. Specifically, it is necessary to improve the adsorbent modification and regeneration techniques to achieve multiple desalination cycles and expand the reusability of the spent adsorbents for various purposes. This study aims to (1) assess the effects of pre-conditioning zeolites with Na^+ prior to the acid treatment, (2) further characterize the dual-adsorbent performance for chloride and sodium adsorption from industrial-brine-spiked groundwater using multiple instruments, (3) investigate the feasibility of multiple desalination cycles for brine-impacted groundwater by regenerating the H-form zeolite, and finally (4) explore the potential reusability of the spent potassium-loaded zeolites (K-form zeolites). To the best of our knowledge, the study is the first study to show the production of K-form zeolites resulting from desalination treatment and shed light on the feasibility of producing low-cost slow-release fertilizers (valuables) from the desalination of groundwater salinized with potash mining effluent (brine).

2. Materials and methods

2.1. Adsorbent pre-conditioning and modification

Natural zeolite (denoted as NZ) was obtained from Bear River

Zeolite Company (Preston, Idaho) and the LDH was obtained from Kyowa Chemical Industry (Sakaide, Japan). The zeolite was determined by quantitative X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyzers to be 85.4% clinoptilolite (Table S1). The LDH, represented by the formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$, contained Mg^{2+} and Al^{3+} as constituent cations (Mg/Al molar ratio of 3.0 according to the manufacturer) and CO_3^{2-} as the interlayer anion. The average particle size of the LDH and ground zeolite were 30 μm and 80 μm , respectively. The detailed properties of the zeolite and LDH are described in Gibb et al. (2017).

The LDH sample was calcined at 500 °C for 6 h to produce Mg–Al oxide (CLDH). The zeolite sample was converted to its Na-form (NaZ) by putting it in contact with a 1-M NaCl solution (1:5 wt ratio), which is referred to in this study as the Na^+ pre-conditioning prior to acid treatment. After 24 h of agitation (200 rpm), the NaZ was separated from the solution by vacuum filtration, rinsed with deionized (DI) water until the Cl^- concentration of the filtrate was less than 10 mg/L, and then oven-dried at 103 °C overnight. Both NZ and NaZ were then acid treated with 1.0-M HCl (1:5 wt ratio). After 30 min of agitation (200 rpm), the zeolite was again separated by vacuum filtration, rinsed with DI water until no significant difference was observed in the pHs of two sequential washing steps, and oven-dried at 103 °C overnight. Acid-treated NZ is denoted as AZ, and acid-treated NaZ is denoted as ANaZ.

2.2. Dual-adsorbent sequential desalination experiment

Adsorption experiments were conducted by placing a specified mass of adsorbent (CLDH, NZ, AZ, and ANaZ) in a 50-mL screw-cap centrifuge tube with 30 mL of saline solutions. Two solutions were used: GB and GB_{dc} . The first, denoted as GB, was prepared using natural groundwater spiked with potash brine (2% by volume). The detailed chemistry of the GB and GB_{dc} solutions for the series of experiments conducted in this study is presented in Table 1. The GB solution is classified as highly saline groundwater (Moir, 1994; Huang and Natrajan, 2006; Isa and Aris, 2015). Varying amounts of CLDH (0–3 g in 0.5-g increments) and NZ (0–10 g in 2.5-g increments) were equilibrated with 30 mL of GB solution at room temperature.

The CLDH amount that reduced the Cl^- concentration below 250 mg/L (the World Health Organization and Canadian drinking water standard) was determined and used to remove Cl^- from 2 L of GB solution (World Health Organization, 2004; Health Canada, 2014). After 24 h of contact time, the CLDH was separated from solution using vacuum filtration, and the filtrate was recovered. This resultant solution is denoted as GB_{dc} , with the “dc” subscript indicating that the initial groundwater-brine solution has been treated with CLDH to remove Cl^- ions. Varying masses of AZ and ANaZ (0–10 g in 2.5-g increments) were equilibrated with 30 mL of GB_{dc} solution. An equilibrium isotherm for Cl^- adsorption onto

Table 1

Key analytes for groundwater-brine (GB) and GB_{dc} solution after CLDH treatment (2.5 g/30 mL). GB_{dc} is the GB solution treated with CLDH for Cl^- removal.

Analyte	GB	GB_{dc} (after CLDH treatment)
Cl^- (mg/L)	4600	193 ± 22
Ca^{2+} (mg/L)	67.1	6.9 ± 8.9
Mg^{2+} (mg/L)	98.8	7.6 ± 1.5
Na^+ (mg/L)	2010	2190 ± 85
K^+ (mg/L)	1119	1267 ± 180
Hardness (mg/L as CaCO_3)	574	48.4 ± 16.2
SAR	36.5	139.6 ± 18.3
pH	8.23	12.80 ± 0.03

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