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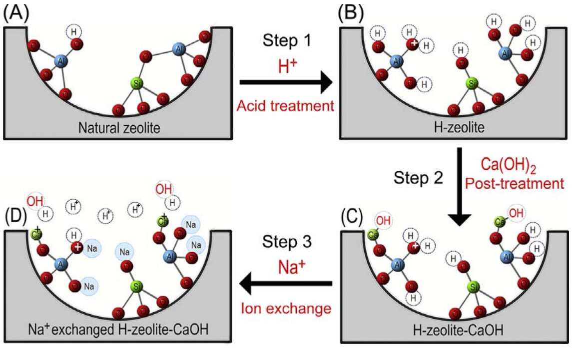
Modified zeolite adsorbents for the remediation of potash brine-impacted groundwater: Built-in dual functions for desalination and pH neutralization

Blain Paul[a], James J. Dynes[b], Wonjae Chang[a,*]

[a] *Department of Civil, Geological and Environmental Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada*
[b] *Canadian Light Source, 44 Innovation Boulevard, Saskatoon S7N 2V3, Saskatchewan, Canada*

GRAPHICAL ABSTRACT



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ABSTRACT

Clinoptilolite zeolites were modified through acid treatment followed by $Ca(OH)_2$ conditioning. The modified zeolite adsorbent (H-Zeo-CaOH) has built-in dual functions for desalination and pH neutralization. The modified zeolites were evaluated using synthetic saline water and groundwater spiked with brine produced during potash mining, and characterized using multiple instrumental techniques. Batch adsorption experiments were conducted for (1) zeolites treated with acids of varying strengths, (2) $Ca(OH)_2$-conditioned acid-treated zeolites, and (3) natural zeolites. Acid-treated zeolites, with or without $Ca(OH)_2$ conditioning, exhibited dramatically improved Na^+ removal. Na^+ removal from saline water (1000–5000 mg Na^+/L) using the modified zeolites ranged from 45 to 88%, whereas natural zeolites achieved approximately 25%. The modified zeolites desalinated the brine-impacted groundwater (73–87% Na^+ removal), despite abundant K^+ ions in the groundwater, which are highly competitive for adsorption sites. The acid treatment caused dealumination within the zeolites, generating acidified zeolites with a high affinity for Na^+ and a large porosity. Sodium adsorption sites, visualized by synchrotron-based scanning transmission X-ray microscopy, correlated with alumina (> Al-O-Na) in the modified zeolites. The effluent, which is normally highly acidic due to protonic exchanges in acid-treated zeolites, was neutralized by the concomitant release of hydroxyl ions only when using the H-Zeo-CaOH adsorbent.

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* Corresponding author at: 57 Campus Drive, Engineering Building, Department of Civil, Geological and Environmental Engineering, University of Saskatchewan, Saskatoon S7N 5A9, Saskatchewan, Canada.
E-mail address: wonjae.chang@usask.ca (W. Chang).

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1. Introduction

Potash is an important source of potassium-bearing minerals for fertilizer production, which ultimately contributes to food security for rapidly growing global populations [1]. Saskatchewan (Canada) is a world-leading potash producer, supplying one-third of the global demand in recent years [2]. However, conventional potash mining operations produce substantial quantities of solid tailings, composed mainly of sodium chloride (NaCl), potassium chloride (KCl), and insoluble substances (clays), as well as potash brine that is nearly saturated with NaCl (~10% w/w) [3]. Tailings are typically deposited in piles up to approximately 60 m high covering 200 ha in a tailings management area (TMA) on engineered grounds [4]. Potash brine is stored in containment facilities surrounded by earthen dykes in conjunction with geosynthetic clay liners, cut-off walls, drainage zones, leachate collection systems, and/or containment wells for seepage control and collection [5,6]. Stored brine is reclaimed for mining processes, and excess brine is injected into deep disposal wells in naturally saline formations [6,7].

Similar to potash mining, oil and gas extraction (including unconventional resources such as oil sands, shale gas, and coalbed methane) also produces large volumes of saline effluents [8–10]. Uncontrolled discharges and chronic infiltration of saline industrial effluents at brine-spill sites, abandoned mines, and decommissioned disposal wells, as well as malfunctioning containment facilities, can elevate the sodium salinity stress in surrounding soils, groundwater, surface water, and ecological systems [11]. For example, the number of industrial brine spills has increased along with intensified oil and gas exploration over recent decades in North Dakota, USA [12]. Kaushal et al. [13] also report increasing trends in the salinity of receiving fresh water bodies in some industrialized counties, such as the USA, Germany, France, and Japan, which may be due to intensified anthropogenic activities and raises concerns for drinking water safety. The detrimental effects of the salinity of industrial effluents on soil properties, water quality, plant growth, and the life of aquatic organisms are well known [14]. Due to planned expansions of potash mining operations, oil and gas production, and associated infrastructure development, the demand for cost-effective remediation technologies for sites affected by saline industrial effluents, including surrounding soils and shallow groundwater, has been rapidly growing in regions where such subsurface natural resource extraction has intensified [15,16].

Natural zeolites, primarily clinoptilolite-rich zeolites, have been considered as remedial agents for reducing sodium concentrations in saline water that is co-produced during the extraction of coalbed natural gas (CBNG), also known as coal seam gas (CSG), in Queensland, Australia and in Wyoming and Montana in the USA [8,14–17]. Zeolites are hydrated aluminosilicate minerals of alkali and alkaline earth elements with three-dimensional crystal structures composed of SiO_4 and AlO_4. Exchangeable hydrated cations are loosely bound to the negatively charged framework of natural zeolites, which is created by the isomorphous substitution of Al^{3+} for Si^{4+} in tetrahedral structural units. This is the basis for cation exchange reactions in zeolites [18]. Zeolites have cage-like microporous structures with regularly arranged cavities and pore channels, and they exhibit a high adsorption selectivity for metal cations that is related to their hydrated radii, abundance, and charge valences [19]. These are the crucial properties of zeolites that make them suitable as adsorbents and molecular sieves [20].

Ca-rich clinoptilolite zeolites have been employed as cation exchangers for treating saline and sodic CBNG-produced water due to their higher selectivity for Na^+ over Ca^{2+} [17]. The central mechanism for the removal of Na^+ from CBNG-produced water is the cation exchange reaction between Na^+ and Ca^{2+} in the Ca-clinoptilolites. The cation selectivity of clinoptilolites is expressed in the following order: Cs > Rb > K > NH_4 > Ba > Sr > Na > Ca > Fe > Al > Mg > Li [21]. The sodium adsorption ratio (SAR), a measure of the relative abundance of Na^+ compared to Ca^{2+} and Mg^{2+} in water, has been frequently used previously as an indicator of sodium salinity in CBNG-produced water treated by the zeolite-based adsorbents [8,14–17]. In previous studies involving CBNG-produced water with high SARs ranging from 30 to 34 (on a $mmol^{1/2}\,L^{-1/2}$ basis), Ca-clinoptilolites effectively decreased the SAR of the water to near or below 10 [14,15,17]. Acid-activated Australian zeolites (H-Zeolite) have also been used to reduce the SAR of CBNG-produced water from 70.3 to 18.5 [16].

The adsorption properties of zeolites are adjustable using surface modification techniques. In Zhao et al. [15], Na-clinoptilolite was modified using hard water (Ca^{2+}) to produce Ca-rich zeolite, which was then used to reduce the SAR of CBNG water to acceptable SARs for irrigation. In another study, the acid activation of zeolites to produce H-rich zeolites improved the sodium adsorption capacity by up to three times [16]. Pretreatment of clinoptilolites with acid causes dealumination through the hydrolysis of Al-O-Al and Si-O-Al bonds, forming numerous protonic exchange sites in clinoptilolites [22]. Acid treatment has consistently been reported to increase the particle porosity of silica-rich zeolites, thus improving their adsorption properties [16,23,24].

K^+ is present in potash brine at much smaller concentrations than Na^+. However, the adsorption affinity of natural clinoptilolites to K^+ is significantly higher than for Na^+ [25] and thus the presence of K^+ may reduce sodium uptake. The improved adsorption capacity of acid-activated zeolites may be advantageous for treating potash brine-impacted water that contains both Na^+ and K^+.

On the other hand, sodium removal using acid-activated zeolite relies on Na^+ replacing H^+ on exchange sites in the zeolite, which releases H^+ into the adsorption effluent and drastically decreases the pH. The application of acid-activated zeolites is then limited because the desalinated adsorption effluent is highly acidic. Unlike saline-sodic CBNG water, potash brine contains very low amounts of HCO_3^- and CO_3^{2-}, and the buffering capacity of the potash brine-impacted water is negligible.

The objective of the study was therefore to develop an improved modified zeolite adsorbent with built-in dual functions: improved sodium uptake and effluent pH neutralization. Natural clinoptilolite-rich zeolites were modified by direct acid treatment to increase their adsorption capacities, and are herein referred to as acid-activated or H-Zeolite adsorbents (H-Zeo). Some acid-activated zeolites were further conditioned with controlled doses of calcium hydroxide, and are referred to as H-Zeo-CaOH. The effectiveness of the modified zeolites for salinity mitigation (both H-Zeo and H-Zeo-CaOH adsorbents) was evaluated in a series of equilibrium batch adsorption experiments carried out using synthetic saline water and natural local groundwater spiked with actual potash brine from a mine in Saskatchewan. The dual-functions of the new modified zeolites were addressed using multiple instrumentation analyses including synchrotron-based scanning transmission X-ray microscopy (STXM) and powdered X-ray diffraction (XRD), X-ray fluorescence (XRF), and Fourier transform infrared spectroscopy (FT-IR). Conventionally, acidified zeolites have been known to be effective for sodium removal; however, the produced highly acidic adsorption effluent from the acidified zeolites has not been previously addressed. To the best of authors' knowledge, the acidified zeolite with $Ca(OH)_2$ post-conditioning, which exhibited built-in dual functions for desalination and pH neutralization, is a novel remedial agent.

2. Materials and methods

2.1. Natural zeolite

Zeolite from a natural zeolite tuff called Bromley Creek was obtained from Princeton, British Columbia, Canada (Canadian Mining Company, Inc., Vancouver). The Bromley Creek zeolite is naturally clinoptilolite-rich (66%, w/w; JCPDS card no. 04-013-6126), as