



Synergistic desalination of potash brine-impacted groundwater using a dual adsorbent



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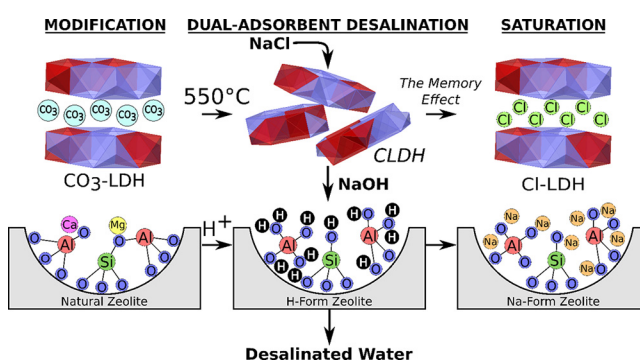
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HIGHLIGHTS

- CLDH and acid-treated zeolites were sequentially applied for desalination.
- Adsorption experiments were performed with NaCl solutions and saline groundwater.
- Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and S were removed and the effluent pH was neutral.
- Memory effect, dealumination, proton exchange, and zeolite porosity were addressed.
- STXM visualized Na⁺ adsorption related to silanol groups in acid-treated zeolite.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact of saline mining effluent has been a significant environmental concern. Natural and modified clay-mineral adsorbents have been receiving increasing attention for salinity reduction of brine-impacted water, especially for natural resource extraction sites and surrounding environments. In this study, a dual-adsorbent treatment based on the sequential application of calcined layered double hydroxide (CLDH) and acid-treated zeolite was developed, evaluated and characterized for the desalination of potash brine-impacted groundwater. Potash brine produced by conventional potash mining in Saskatchewan (Canada) contains a large amount of Na⁺, K⁺ and Cl⁻. The CLDH and acid-treated clinoptilolite zeolites were combined to sequentially remove Cl⁻ and Na⁺. A series of batch adsorption experiments were conducted for synthetic saline water and potash brine-spiked groundwater using various combinations of adsorbents: natural zeolites (NZ) or acid-treated zeolites (AZ) with or without the CLDH pretreatment. The experiment revealed that the Na⁺ removal percentage was synergistically increased by the dechlorination pretreatment using CLDH, and further improved by AZ. The CLDH-AZ dual adsorbent achieved a Langmuir Na⁺ adsorption capacity of 24.4 mg/g, a significant improvement over conventional approaches to zeolite-based desalination. Using the brine-impacted groundwater with a high sodium adsorption ratio (SAR) of 13.3 ± 0.1, the CLDH-AZ dual adsorbent decreased the concentrations of Na⁺, K⁺, and Cl⁻ by 87, 97, and 87%, respectively (below drinking water standards). It also exhibited the additional advantages of neutralizing the effluent pH and decreasing the hardness, SAR, and total dissolved sulfur concentration. This study addresses the removal mechanisms, which are associated with the structural memory effect, dealumination, protonic exchanges, and zeolite porosity changes. Synchrotron-based scanning transmission X-

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ray microscopy analyses provided visual evidence of sodium adsorption sites (Si—O—Na and Al—O—Na) associated with dealumination in the acid-treated zeolites. This study is the first report that demonstrates the synergy of the CLDH-AZ dual adsorbent treatment for potash brine-impacted water.

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1. Introduction

Recent studies have consistently reported that amplified industrial activities have greatly increased the concentration of salts in receiving freshwater bodies in various regions of the world (Kaushal et al., 2005; Kelly et al., 2007). The elevated salinity of water bodies has led to growing concerns over water security, particularly in developed regions (Kelly et al., 2007; Kaushal, 2016). Inputs include road deicing salts, sewage and water softeners, accelerated geological weathering, as well as tailings and saline industrial effluents (e.g., brine) from mining, oil, and gas operations (Kaushal et al., 2005; Kaushal et al., 2013; Lauer et al., 2016). Improper containment or uncontrolled discharges of salts and brines, including chronic and accidental releases, can salinize proximate soils and shallow aquifers (Tallin et al., 1990). High sodium (Na^+) concentrations may degrade soils, disturb biogeochemical cycling, and mobilize contaminants (Barbour and Yang, 1993; Gabbasova et al., 2013; Keren, 2012; Levy, 2012). Chloride (Cl^-) is toxic to plants and freshwater species at high concentrations (White and Broadley, 2001; Xu et al., 1999), and Cl-induced infrastructure corrosion (e.g., water distribution pipes) can have serious health, economic, and engineering repercussions (Revie and Uhlig, 2011). High salinity can ultimately render groundwater unsuitable for beneficial uses, including drinking water, irrigation, and feedlot watering (Kaushal et al., 2005; Kaushal, 2016; Barbour and Yang, 1993).

Widespread attention has focused on the saline water originating from mining, and oil and gas production (Belbase et al., 2013; Ganjegunte et al., 2011; Huang and Natrajan, 2006; Millar et al., 2016a; Santiago et al., 2016; Wang and Nguyen, 2016; Wang et al., 2012; Zhao et al., 2008; Wang, 2004; Shaffer et al., 2013). For example, due to intensified coal seam gas (CSG) gas extraction in North Dakota (USA), the reported number of saline effluent spills has greatly increased over the last two decades (Lauer et al., 2016). In Australia, the burgeoning CSG industry produces large quantities of saline-sodic water with total dissolved solids (TDS) concentrations generally ranging from 200 to 10,000 mg/L (Nghiem et al., 2011). Similarly, in Saskatchewan (Canada), potash (KCl) mining generates large quantities of hypersaline tailings and brine (Tallin et al., 1990). Preventing brine migration from the mine site to proximate soils and aquifers is a continual challenge for the potash industry (Reid and Getzlaf, 2004). Overall, there is a strong and growing demand within the mining, and oil and gas industries for effective technologies to remediate salt-impacted sites (e.g., abandoned mines, spill sites, and waste disposal sites) or to contain or treat saline produced water (Shaffer et al., 2013).

Ion-exchange media, including resins and mineral adsorbents, show great potential for salinity mitigation (Millar et al., 2016b; Millar et al., 2016c; Pless et al., 2006). Layered double hydroxide (LDH) minerals, such as hydrotalcite, consist of positively charged brucite-like sheets with anions occupying the interlayers and can be used to remove anions and divalent cations. For example, through calcination and reconstruction (i.e., *the memory effect*) LDHs have been used to remove a range of anions (e.g., Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-}) from solution (Goh et al., 2008; Lv et al., 2006).

Zeolite minerals can be used to remove a wide range of cations, including monovalent cations (e.g. Na^+ and K^+). Zeolites consist of SiO_4 and AlO_4^- tetrahedra joined by shared oxygen atoms to form a cage-like, three-dimensional framework (Zhao et al., 2009). The AlO_4^- bears a negative charge, which is neutralized by weakly held, exchangeable cations (varying amounts of Ca^{2+} , K^+ , Na^+ , and Mg^{2+}) (Zhao et al., 2008; Ćurković et al., 1997; Inglezakis, 2005). Zeolites can be modified

using heat and/or chemical treatments (alkali, acids, surfactants, or salts of alkali and alkaline earth metals) to augment their adsorption capacity. Acid treatment is particularly useful; it removes pore-blocking impurities, increases the surface area and porosity, and strips away sorbed cations by replacing them with H^+ ions (conversion to a near-homoionic H-form zeolite) (Wang et al., 2016; Rivera et al., 2013). Acid-treated zeolites have recently garnered attention for Na^+ removal from saline industrial produced water (Wang et al., 2012; Santiago et al., 2016).

By using CLDH and acid-treated zeolite in combination, both anions and cations can be removed while achieving a neutral effluent pH (Pless et al., 2006). Yet, this combined application of acid-treated zeolite and CLDH has not been extensively investigated despite numerous studies on their independent uses (Goh et al., 2008; Theiss et al., 2014; Misaelides, 2011; Cejka et al., 2007). In a lone study by Pless and co-workers, permutite (a synthetic, weak acid-treated zeolite) was combined with CLDH to desalinate CSG produced water, which is dominated by Na^+ , Cl^- , and HCO_3^- (Pless et al., 2006). After this dual-adsorbent treatment, the TDS content decreased from 11,000 to 600 ppm and the effluent pH was 5.0.

The objectives of this study are to develop, evaluate, and characterize a dual adsorbent as a potential remedial agent that sequentially combines CLDH and acid-treated zeolites for the purpose of mitigating the salinity of groundwater impacted by potash brine (both Na^+ and Cl^-). This dual-adsorbent treatment, initially developed by Pless et al. (2006), is applied in the present study with several distinctive elements. First, natural clinoptilolite zeolite is used and converted to its H-form by strong acid (up to 2 M) treatment. The application of CLDH and acid-treated clinoptilolite zeolite in combination, and the associated effects and mechanisms for salinity mitigation, have not been extensively addressed in previous studies. Second, the potential synergies that result from the combination of CLDH and the acid-treated zeolite treatments are investigated. Dechlorination (i.e., solution pretreatment using CLDH) is hypothesized to synergistically improve subsequent Na^+ removal using acid-treated zeolite due to its basicity, while at the same time ensuring that the treated water is of neutral pH. Therefore, the proposed dual-adsorbent treatment to remove both Na^+ and Cl^- may overcome problems associated with the typically very low pH of adsorption effluents generated by conventional salinity mitigation treatments using acid-treated zeolites. Third, natural groundwater spiked with potash brine is used as the adsorbate solution, mimicking real-world problems. Brine-impacted groundwater is dominated by Na^+ , but also contains a considerable amount of K^+ and other competitive ions. Given clinoptilolite's selectivity sequence ($\text{Cs} > \text{Rb} > \text{K} > \text{NH}_4 > \text{Ba} > \text{Sr} > \text{Na} > \text{Ca} > \text{Fe} > \text{Al} > \text{Mg} > \text{Li}$), the presence of K^+ is expected to reduce the Na^+ adsorption (Mumpton, 1999). To determine the effects of K^+ and other co-existing competitive ions, the complete solution chemistry is characterized at each step of the dual-adsorbent treatment using natural groundwater spiked with actual potash brine.

Batch adsorption experiments were conducted for synthetic saline water (NaCl solution) and potash brine-spiked groundwater using various combinations of the adsorbents: natural zeolites (NZ) or acid-treated zeolites (AZ) with or without the CLDH pretreatment. The acidified zeolites were prepared using varying acid types and strengths. The developed dual adsorbents are characterized through porosimetry, X-ray diffraction (XRD), X-ray fluorescence (XRF), and synchrotron-based scanning transmission X-ray microscopy (STXM).

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