

Removal of dissolved silica from industrial waters using inorganic ion exchangers



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ABSTRACT

Dissolved silica is ubiquitous in impaired waters, a fouling agent in desalination membranes, resistant to existing antiscalants, and difficult to remove from power plant feed waters, thereby inhibiting long term reuse of industrial water. Herein we report a systematic materials study of an inorganic anion exchanger, hydrotalcite (HTC, $(Mg_6Al_2(OH)_{16}(CO_3)_4 \cdot 4H_2O)$), for the highly selective removal of silica from aqueous solutions. HTCs exist in two different forms: crystalline uncalcined and calcined (550 °C) phases. Variables studied in ion-exchange studies include pH, HTC concentration, duration and selectivity with competing anions. Results indicate calcined HTC effectively removes silicate anion from different waters including simulated concentrated cooling tower water (CCTW), and waters with high concentration of competing ions, such as SO_4^{2-} and Cl^- . The non-optimized HTC can be easily regenerated and recycled. Calcined HTC has a silica adsorption capacity of 45 mg SiO_2/g HTC. The single path flow through (SPFT) studies indicate that using ~ 1.1 g/L calcined HTC effectively removes >90% of the dissolved silica from the CCTW. A pseudo-second order kinetic model was fit the experimental data of calcined HTC. Data is supported by Fourier transform infrared (FTIR), Thermogravimetric-Mass analyses (TGA-MS), Energy dispersive spectroscopy (EDS) and powder X-ray diffraction (XRD).

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1. Introduction

Fresh water scarcity is becoming a great global challenge. Water resources are limited and, hence, water treatment and recycling methods are vital alternatives for fresh water procurement in the upcoming decades [1]. These methods serve to remove harmful or problematic constituents from ground, surface and waste waters prior to their consumption, industrial utilization, or other uses [2].

About half of all fresh water withdrawn daily in the US, ~ 500 billion gal/day, is used by thermoelectric power generation plants [3]. The recovery cost for the impaired waters produced by the inland power generation sites is estimated to be 1.5–2 times the cost of freshwater, often because of the high cost of silica removal process [4]. A key solution to limited availability and high cost is reducing freshwater use and replacement of it with reclaimed waters, such as those from purified oilfield generated waters, municipal or agricultural waste waters, and subsurface brines. [4].

However, to be successful, dissolved silica and calcite forming mineral scale need to be removed. Antiscalant technology is well developed for calcite removal [4]. However, a low energy technol-

ogy is needed for silica removal. The quality of the process affects the reuse and recycle of the reclaimed waters in individual operation. Currently, antiscaling technology enables ~ 10 cycles with calcite removal, however it is reduced down to 1–2 cycles due to silica buildup [4].

Silica solubility depends on many factors such as pH, temperature, pressure and ionic strength. The silica solubility is constant between pH 2 and 8.5, but increases rapidly above pH 9. In the acidic-to-neutral pH range, silica exists as H_4SiO_4 , whereas in basic solutions, it exists as $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ anionic species [5,6]. Silica solubility is highly sensitive to temperature, increasing from 100 – 140 mg/L at ambient temperature, and then up to 300 mg/L at 70 °C [7].

Dissolved silica can be removed by a number of different methods including coagulation, nano-filtration (NF), reverse osmosis (RO), or precipitation [8–10]. Major limitations of NF and RO are fouling and high energy consumption [11]. The drawback of coagulation is that the process occurs at high pH, resulting in increased costs due to pH adjustment [8]. Current technology like alumina precipitation may cause aluminosilicate scaling [11]. Additionally, these are different inorganic ion-exchange materials being used for metal ions separation from water [12–14].

In an effort to develop highly selective silica ion-exchange materials that are robust, and both cost and energy efficient, we are exploring inorganic anion exchangers like hydrotalcites

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(HTC) as silica adsorbents [15]. HTCs are layered double-hydroxides with the general formula $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2]^{x+}[A]_x \cdot mH_2O$ where $M^{(II)} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+},$ and Zn^{2+} ; $M^{(III)} = Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+},$ and Ga^{3+} ; and $A = Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-}, SO_4^{2-},$ silicate-, polyoxometalate-, and/or organic anions [16,17]. HTC is made up of positively charged $[M^{(II)}/M^{(III)}/OH]$ layers, which have a substantial anion exchange capacity of ~ 3 meq/g [15,18]. Our previous work showed the ability of HTC as a highly selective anion exchange material in a low energy, brackish water, desalination process [15].

This work directly relates to needs identified in the Energy-Water Nexus by the US Department of Energy, as an important research area [19]. Herein, the use of HTC ($Mg_6Al_2(OH)_{16}(CO_3)_4 \cdot 4H_2O$) as an ion-exchange material for the selective ion-exchange and capture of silica ions is described in detail. Materials studies of the HTC, the mechanism of silica ion capture, and the efficiency of HTCs for silica removal from simulated industrial waters are explored. Detailed HTC synthesis, structural characterization and silica removal measurements are presented at various pH readings and concentrations levels. Composition studies with Zn-HTC ($Zn_{0.65}Al_{0.35}(OH)_2(CO_3)_{0.167} \cdot (H_2O)_{0.499}$) analog are presented. Furthermore, the adsorption kinetics of the silica removal is determined and discussed.

2. Experimental

Commercial HTC ($Mg_6Al_2(OH)_{16}(CO_3)_4 \cdot 4H_2O$) from Sigma-Aldrich was used in this study. XRD, FTIR, TGA-MS and SEM-EDS were used to confirm the composition of HTC. [15,20]. 15 g batches of HTC were calcined in air at 550 °C for 3 h [20]. Synthetic industrial water (Concentrated Cooling Tower water, CCTW) was made by salt addition to DI water with the following concentrations (mmol/L): 0.41 $MgCl_2$ + 0.05 Na_2SO_4 + 0.62 $NaHCO_3$ + 1.0 $CaCl_2$ + 41.0 $NaCl$ + 0.833 SiO_2 .

For the batch silica removal reactions, typically 25–125 mg of HTC was added to 50 mL of the synthetic CCTW in 50 mL tubes, and the tube placed on a shaker table for 12 h at room temperature. After shaking, the slurry was centrifuged, and the pH and silica concentration of supernatant were determined. The percentage of silica removal was calculated based on the mass of silica removed by HTC to the initial mass of silica in water. The silica adsorption capacity is defined as the mass of silica removed from solution to the mass calcined HTC was used for silica removal.

Silica adsorption by HTC as a function of time was studied. In these experiments, 75 mg of calcined HTC was added to 50 mL of synthetic CCTW in a 50 mL tube; the tube was placed on shaker for a given time, up to 250 min. The resultant slurry was centrifuged, and silica concentration of supernatant was determined by optical spectrophotometry (see below).

Testing of competitive selectivity of the HTC occurred in three experimental set-ups. (1) **Effect of pH:** 25–125 mg of calcined HTC was added to 50 mL of the synthetic CCTW at pH 4–9 (the initial pH was adjusted by addition of 0.1 mol/L HCl or NaOH). Solution was placed on a shaker table for 12 h at room temperature. Then the slurry was centrifuged and the pH of solution were measured. (2) **Effect of competing anions:** Binary-solute systems of SiO_2/SO_4^{2-} and SiO_2/Cl^- ($NaCl$ and Na_2SO_4 as sulfate and chloride sources), respectively, were mixed with the initial SiO_2 concentration (50 mg/L) and the calcined HTC (125 mg). (3) **Effect of HTC regeneration:** The spent HTC was dried overnight in air at 60 °C, and heated at 550 °C for 2 h. This process allowed for the regeneration of the crystalline HTC after each subsequent calcination for the silica removal process. (4) **Effect of varying HTC composition on silica removal:** Zn-HTC ($Zn_{0.65}Al_{0.35}(OH)_2(CO_3)_{0.167} \cdot (H_2O)_{0.499}$) was synthesized using a method previously reported [21,22]. Typ-

ically, a solution of 0.04 mol $Zn(NO_3)_2$ and 0.02 mol $Al(NO_3)_3$ was mixed in 100 mL of distilled water and added to a second solution containing 0.15 mol of NaOH and 0.03 mol Na_2CO_3 in 100 mL of water at room temperature. The mixture was stirred for 24 h. Then the precipitate product was filtrated, washed few times with distilled water and dried at 80 °C for 24 h. Then, Zn-HTC was calcined in air at 300 °C for 2 h. Silica adsorption by Zn-HTC was also studied. In these experiments, 25–125 mg of calcined Zn-HTC was added to 50 mL of the synthetic CCTW and the solution was placed on a shaker table for 12 h at room temperature. Then the resultant slurry was centrifuged and the silica concentration of the supernatant were determined.

A modified single path flow through (SPFT) measurement was done using synthetic CCTW and calcined HTC [15]. CCTW was pumped through columns containing 100–200 mg of calcined HTC at a flow rate of 0.15 mL min^{-1} . Treated CCTW effluent was periodically collected and the silica concentration and pH determined. The steady state volume of fluid in the reactor was ~ 1 mL, which points to an average fluid residence time of ~ 7 min.

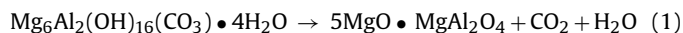
Fourier transform infrared (FTIR) spectroscopy of HTC was collected using a Perkin-Elmer FTIR Spectrometer GX. Spectra were collected in the mid-IR range of 400–4000 cm^{-1} , with a resolution of 2 cm^{-1} . Thermogravimetric-Mass analyses (TGA-MS) were carried out in air using a TA instruments STD 2960 with mass spectrometer GSD 320 from Pfeiffer Vacuum. Heating profile was 5 °C min^{-1} liner ramp from a room temperature to 550 °C. Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Siemens Kristalloflex D500 diffractometer (Cu K α radiation) 40 kv, 30 mA; $2\theta = 5-60^\circ$, 0.05° step size, and 3 s count time. Energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) data were collected on a JEOL JMS-6300 V scanning electron microscope with the LINK GEM light-window energy dispersive spectrometer. A Micromeritics ASAP 2020 instrument was used to collect surface area analysis at -196 °C in N_2 . Prior to analysis, the samples were degassed at 120 °C for 12 h. The surface area was measured by the Brunauer-Emmet-Teller (BET) method, assuming a cross-sectional area of 0.162 nm^2 for the N_2 molecule. The silica concentration was measured by using the optical Hach method 8185 and DR/2400 spectrophotometer. The pH of the solution was measured with a Thermo Scientific pH meter.

3. Results and discussion

3.1. HTC characterizations

The silica removal study was carried out using HTC and simulated CCTW containing ~ 50 mg/L of silica. A variety of materials characterization techniques were used to gain an understanding of both the HTC/silica post adsorption and the mechanism of silica adsorption by HTC.

The surface area of calcined HTC was ~ 138 m^2/g , whereas the uncalcined HTC was ~ 12 m^2/g . (See SI; Fig. S1) The higher surface area for calcined HTC can be a result of the decrease in HTC crystal size caused by thermal treatment as shown in related studies [23,24]. This decrease in crystal size is supported by the broadening of XRD peaks for calcined HTC [24] (Fig. 1). The XRD pattern matches indicates that the HTC structure collapsed and formed mixed oxide during heat treatment [25].



The calcined HTC is reconstructed to its original structure when mixed in water containing anions of the correct size, charge and/or size in the interlayer of the recrystallized HTC [26,27].

TGA analysis of uncalcined HTC shows that thermal decomposition of HTC takes place at two distinct steps (See SI; Fig. S2). In

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