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, $(\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O})$), 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 $\sim 1.1\text{g/L}$ 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).

Keywords:

Dissolved silica, industrial waters recycle, ion exchange, hydrotalcite, recycle

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About half of all fresh water withdrawn daily in the US, ~500 billion gal/day, is used by thermoelectric power generation plants.[3] The recovery cost for the impaired waters produced by the inland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 technology 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 recycles 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 $\text{H}_2\text{SiO}_4^{2-}$ 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 (HTC) as silica adsorbents.[15] HTCs are layered double-hydroxides with the general formula $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2]^{x+}[A].mH_2O$ 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 ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$) 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 ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$) 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 hours 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 hours at room temperature. Then the slurry was centrifuged and the pH of solution were measured. (2) **Effect of competing anions:** Binary-solute systems of $\text{SiO}_2/\text{SO}_4^{2-}$ 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 ($\text{Zn}_{0.65}\text{Al}_{0.35}(\text{OH})_2(\text{CO}_3)_{0.167} \cdot (\text{H}_2\text{O})_{0.499}$) was synthesized using a method previously reported.[21, 22] Typically, a solution of 0.04 mol $\text{Zn}(\text{NO}_3)_2$ and 0.02 mol $\text{Al}(\text{NO}_3)_3$ 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 24h. Then, Zn-HTC was calcined in air at 300°C for 2h. 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 hours 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 minutes.

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 to 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 θ = 5-60°, 0.05° step size, and 3s count time. Energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) data were collected on a JEOL JMS-6300V 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 N₂. Prior to analysis, the samples were degassed at 120 °C for 12 hours. The surface area was measured by the Brunauer-Emmet-Teller (BET) method, assuming a cross-sectional area of 0.162 nm² for the N₂ 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 $\sim 138 \text{ m}^2/\text{g}$, whereas the uncalcined HTC was $\sim 12 \text{ m}^2/\text{g}$. (See SI; Figure 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] (Figure 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]

Figure 1. XRD patterns of uncalcined HTC (blue), calcined HTC after heating in air at 550 °C (red) and regenerated HTC after mixing with CCTW (green).

TGA analysis of uncalcined HTC shows that thermal decomposition of HTC takes place at two distinct steps (See SI; Figure S2). In Step I, the initial mass loss begins at room temperature and ends at $\sim 250\text{ }^{\circ}\text{C}$, with $\sim 14\%$ mass lost. This corresponds to the loss of water molecules located between the Mg/Al/OH layers.[28] In Step II, the additional mass loss of $\sim 31\%$ and occurs between $\sim 250\text{ }^{\circ}\text{C}$ and $510\text{ }^{\circ}\text{C}$. Concurrent TGA-MS analysis indicates an initial mass loss of $\sim 7\%$ is associated with carbonate anions, followed by gradual mass loss of $\sim 24\%$ corresponding to loss of interlayer water molecules (condensation of OH groups from the Mg/Al/OH layers).[28] The corresponding XRD shows a broadening of XRD peaks, indicating decrease of the crystal size of HTC. The transition in the structural formulas listed below:

Direct comparison of the FTIR data for uncalcined and calcined HTC clearly shows the decrease in intensity of the infrared peaks from the calcined material, which confirms the decarbonisation and dihydroxylation of the HTC during the calcination process (Figure 2). In the uncalcined HTC data, a peak at 3400 cm^{-1} is attributed to the metal hydroxide and water adsorbed into the Mg/Al/OH layers.[29-31] The peak at 1634 cm^{-1} correspond to water bending mode and the peak at 1434 cm^{-1} is attributed to a carbonate of uncalcined HTC, as previously reported.[29-32] After calcination, the peak at 3400 cm^{-1} and 1634 cm^{-1} have almost disappeared, which is the indicative of dehydration during thermal treatment. Also, the intensity of a carbonate peak at 1434 cm^{-1} has significantly decreased which indicates the carbonate mostly was removed during calcination.

Figure 2. FTIR spectra of uncalcined HTC, calcined HTC and HTC after ion-exchanged (calcined HTC after water treatment). A peak at 3400 cm^{-1} is the absorption spectra of -OH , and peaks at 1634 cm^{-1} and 1434 cm^{-1} correspond to a water bending mode and a carbonate group, respectively.

3.2 Mechanism of silica removal

Two different adsorption mechanisms can be used to describe the silica removal by HTC. The first process is direct ion-exchange with the interlayer anions of uncalcined HTC.[23] The second process involves the silica removal by calcined HTC, in which the collapsed material is dispersed into an aqueous solution containing silicate ions, and the HTC structure recrystallizes around the silicate ion.[23, 33, 34]

To understand which ion-exchange mechanism favors silica removal, both uncalcined HTC and calcined HTC were individually treated with CCTW (see Figure 3). Using either 75 or 125 mg of calcined HTC resulted in more than 90% silica removal. By contrast, using 125 mg of crystalline HTC resulted in only 10% silica removal. This demonstrates that the calcined HTC is a more effective silica removal material than uncalcined HTC. The silica adsorption capacity of calcined HTC is approximated to be $45\text{ mg SiO}_2/\text{g HTC}$ (see Figure 3) In the process of HTC calcination, higher surface area is generated available for ion-exchange which results in higher silica removal on calcined HTC ($\sim 138\text{ m}^2/\text{g}$) compared to uncalcined ($\sim 12\text{ m}^2/\text{g}$).

Figure 3. Silica removal from CCTW by uncalcined HTC and calcined HTC (pH = 7.0, 25 °C, 50 mg/L SiO₂).

Figure 4 shows data from time-dependent silica removal studies. Silica removal starts at a rapid rate in the first 25 minutes. However, the adsorption rate slows and reaches equilibrium early (~50 mins) and is completed by ~200 minutes.

Figure 4. Time-dependent silica removal during ion-exchange by calcined HTC (75 mg HTC, pH = 7.5, 50 mg/L SiO_2).

3.3. Single Path Flow Through (SPFT) measurement

The SPFT test was used to measure HTC uptake of silica under more rapid flow-through conditions and to provide a measure of uptake capacity.[15] Recall that the fluid residence time in the SPFT is ~ 7 minutes; batch reaction times were carried out to 25 hours. Greater than >90% silica removal occurs rapidly and persists until ~4 hours, at which point the rate of silica removal declines (see Figure 5). The SPFT results point to a silica adsorption capacity for calcined HTC of ~ 45 mg SiO_2 /g HTC which match well with adsorption capacity measurement from the batch testing (see Figure 3).

Figure 5. SPFT: Silica removal from CCTW (pH = 7.0, 25 °C, 50 mg/L SiO₂), 200 mg calcined HTC with a flow rate of 0.15 mL min⁻¹. Arrows included to clarify axes.

3.4 Effect of pH on silica removal by calcined HTC

Changing the initial pH from 4 to 9 results in no significant effect on the silica removal performance by calcined HTC. Silica exists in the neutral form (H₄SiO₄) in the initial pH range (4 - 9), and is not available for ion-exchange.[35] As the pH of the solution rapidly increase to ≥ 9.8 after the addition calcined HTC to the CCTW solution; this is concurrent with the formation of H₃SiO₄⁻ silica ions in solution.

Figure 6. The pH of CCTW solutions after treatment with calcined HTC. At pH >9.5 the silica exists as a H_3SiO_4^- anion.

Changing the solution pH and adsorption silica ions by calcined HTC occurs as follows:

(1) OH^- ions are generated during reconstruction of HTC from magnesium and aluminum mixed oxides to the original crystalline structure (Eq.2). Concurrently, all available ions (Cl^- , HCO_3^- , CO_3^{2-} , etc.) are adsorbed into the HTC interlayer (see Eq.2). [36]

(2) As the pH rises to greater than 9.5, most of the silica is in the form of H_3SiO_4^- ions, (Figure 6) and thus is available for ion-exchange by the HTC.[6, 35] Remaining oxides crystallize to HTC with the adsorbed silicate anions in the interlayers (see Eq. 3).

XRD and FTIR analyses (Figures 1 and 2) confirm the recrystallization of HTC after exposure to CCTW. SEM-EDS spectroscopy confirms the presence of both silica and chlorine in the regenerated HTC phase (Figure 7).

Figure 7. SEM-EDS pattern of calcined HTC after silica adsorption from CCTW. It confirms the presence of silica and chlorine.

3.5 Effect of competing ions on silica removal by calcined HTC

Cooling tower water contains ions such as sulfate and chloride which might compete with silica for HTC adsorption sites.[37] This study focuses on the ability of HTC to adsorb silica in the presence of competing anions. Binary solute systems of $\text{SiO}_2/\text{SO}_4^{2-}$ and SiO_2/Cl^- , respectively, were measured with calcined HTC. Table 1. shows that at silicate/chloride = 1/20, ~98% of dissolved silica was removed suggesting a strong preference of HTC for silicate over chloride. Similarly, at silicate/sulfate = 1/20, ~95% of the silicate was removed. The slightly lower silica removal in the presence of sulfate may be a due to the higher charge of SO_4^{2-} over Cl^- . [15] Overall, the competing ions studies

indicate that silica adsorption by calcined HTC is selective in the presence of competing ions such as Cl^- and SO_4^{2-} .

Table 1. Percent silica removal by HTC in presence of varying concentration of chloride and sulfate ions (initial silica concentration 50 mg/L, 50 mL, 125 mg HTC).

Sample ratio Silica: Chloride	Removed silica (%)	Sample ratio Silica: Sulfate	Removed Silica (%)
1:1	99.0%	1:1	99.0%
1:5	98.8%	1:5	97.0%
1:10	98.5%	1:10	95.8%
1:15	97.9%	1:15	95.2%
1:20	97.6%	1:20	94.8%

3.6 Regeneration of HTC

Thermal regeneration of spent HTC was performed at 550 °C. The HTC after each subsequent calcination was used again for the removal of silicate anion from CCTW. The XRD patterns from four subsequent regeneration cycles show that the HTC peak intensities decreased after each calcination and reconstruction cycle (see Figure 8).

Figure 8. XRD patterns of HTC during regeneration cycles with CCTW. A1 is the original HTC sample. Cycle 1 (A2/A3) is regeneration calcination and recrystallization of the HTC. Cycles 2 (A4/A5), 3 (A6/A7), and 4 (A8) are subsequent regeneration cycles.

The repeating cycles of calcination/reconstruction processes gradually reduced the adsorption capacity of the HTC. The regeneration studies (see Table 2) show that the sorption capacity decreased by ~30% after the three cycles; a decrease in capacity is seen in subsequent cycles though the HTC continues to adsorb silica. The change in the sorption capacity was influenced by the ability of calcined HTC to regenerate the layered crystal structure during the ion-exchange process.[38] XRD of HTC after each regeneration (Figure 8) shows a decreased in HTC crystallinity (peak intensities). [38] The decreased ability of calcined HTC to recrystallize to the original HTC structure after each regeneration cycle was commensurate with the decrease in silica adsorption capacity.

Table 2. Percent silica removal from CCTW (pH = 7.5, 25 °C, 50 mg/L SiO₂), 125 mg calcined HTC during the regeneration process.

HTC Samples	Removed Silica (%)
Calcined HTC for first time (A2)	97.5%
Calcined HTC for 2 nd times (A4)	96.4%
Calcined HTC for 3 rd times (A6)	95.3%
Calcined HTC for 4 th times (A8)	65.4%

The structural affects of HTC regeneration can also be seen by FTIR. The peak at ~1050 cm⁻¹ (Figure 9) increases, which is attributed to an increase in the stretching mode of Si-O.[6] The intensity of this absorption peak gradually increased after each calcination and reconstruction cycle. The combination of the FTIR data with the XRD data (showing a decrease in crystallinity with regeneration) suggests that with regeneration the 2D layers of the HTC are broken apart, and bound interlayer Si-O are allowed to stretch which is normally restricted in the interlayers of crystalline HTC.

Figure 9. FTIR spectra of HTCs (after silica removal process) during multiple regeneration cycles.

3.7 Effect of varying HTC composition on silica removal

The effect of HTC composition on silica removal from CCTW was investigated. Zn-HTC was calcined in the air at 300 °C for 2h, as previously reported.[22] As shown in figure 10, using 125 mg of Zn-HTC resulted in only 84% silica removal, while using either 75 or 125 mg of calcined HTC resulted in more than 95% silica removal. (see figure 10). Also, the average silica removal of Zn-HTC is 41.3% after 4 regeneration cycles (see SI; Table 1). By contrast, the average silica removal for 4 regeneration cycles of HTC is 88.6% (see Table 2). Upon calcination of Zn-HTC a stable phase of spinel ZnAl_2O_4 is formed (see SI Figure 4). [22] This spinel is a dense phase and probably influence with silica adsorption. Overall, these results indicate that original HTC is a better silica removal material than Zn-HTC.

Figure 10. Silica removal from CCTW by calcined HTC (Mg-HTC) and Zn-HTC (pH = 7.0, 25 °C, 50 mg/L SiO_2).

3.8 Kinetics of silica removal by calcined HTC

In order to further investigate the kinetics of the HTC as an ion-exchange material for silica removal, four different rate equation models were used to fit the experimental results; first order, second order, pseudo-first order and pseudo-second order models.

The silica adsorption kinetics were best represented by a Pseudo-second order equation, $[t/q_t = 1/k_2^1 q_e^2 + t/q_e]$, where K_2^1 (g/mg/min) is the Pseudo-second order rate constant.[39-41] The values of t/q_t were plotted against given time (t) as shown in Figure 11, the rate constant and regression coefficient (R^2) are given in Table 3. The regression coefficient value (R^2) of 0.99 indicated that this model provides an excellent fit to the experimental data of all four models for removing silica.

Figure 11. Silica removal by calcined HTC; pseudo-second order equation plot, R^2 value = 0.99.

Fitting this model implies that the rate of silica adsorption on the calcined HTC ion-exchanged sites is proportional to the square of the number of unoccupied active sites.[39] Since

the ion-exchange kinetics is largely controlled by the active sites of calcined HTC available for sorption, the initial fast rate of ion-exchange (Figure 4) is attribute to the availability of adsorption free sites especially on the surface of the calcined HTC.

Table 3. Kinetic rate parameters for silica removal by calcined HTC

First Order		Second Order	
K_1	R^2	K_2	R^2
0.0058	0.85	0.0006	0.97
Pseudo-first Order		Pseudo-second Order	
K_1^1	R^2	K_2^1	R^2
0.0126	0.96	0.006	0.99

4. Conclusions

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 is presented a fast, energy efficient and low cost material for the removal of silica ions from industrial waters: the high selectivity anion-exchanger hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$, HTC) material. The results indicated that the calcined HTC removes >90% silica from batch solutions as compared to uncalcined HTC. SPFT tests point to rapid adsorption of silicate and an overall uptake capacity of ~ 45 mg SiO_2 /g HTC. Structure study indicates that the silica ions are exposed to a larger number of ion exchange sites on the calcined HTC. Composition studies with zinc analog HTC show decrease silica adsorption properties.

Materials characterization studies indicate that in the calcined HTC the silica anions have easy access to the oxide exchange sites. XRD and FTIR confirm both the recrystallization of the HTC when mixed with silica containing waters; SEM-EDS confirms the conclusion of the silica in the HTC. By utilizing the solubility of silica in water at varying pHs, and the selectivity of the HTC ion-exchange material, >90% silicate anion removal is obtained from waters such as simulated CCTW and waters with

competing ions such as SO_4^{2-} and Cl^- . Early stage research on regeneration shows that the HTC can be regenerated and reused multiple times.

The kinetics data demonstrate that the silica removal rate by calcined HTC is independent of starting pH of the waters. The pseudo-second order model high R^2 value (0.99) fit indicates that the silica removal rate is proportional to square number of unoccupied sites on the calcined HTC. This kinetic model indicates that fast initial rate of silica removal is due to the availability of free adsorption sites on the calcined HTC.

Overall, this study proves that using the HTC as an ion-exchange material is an effective method for removal of silica from CCTW. Ongoing studies into technoeconomic modeling and scale-up analysis will help direct this research toward real world implementation.

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Graphical Abstract

Use of hydrotalcite (HTC) as an ion exchange material is an effective method for removing dissolved silica from industrial and utility water supplies.