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Removal of Dissolved Silica using Calcinated Hydrotalcite in Real-life Applications

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Abstract

Water shortages are a growing global problem. Reclamation of industrial and municipal wastewater will be necessary in order to mitigate water scarcity. However, many operational challenges, such as silica scaling, prevent large scale water reuse. Previously, our team at Sandia has demonstrated the use of selective ion exchange materials, such as calcinated hydrotalcite (HTC, ($Mg_6Al_2(OH)_{16}(CO_3)\bullet 4H_2O$)), for the low cost removal of silica from synthetic cooling tower water. However, it is not currently know if calcinated HTC has similar capabilities in realistic applications.

The purpose of this study was to investigate the ability of calcinated HTC to remove silica from real cooling tower water. This was investigated under both batch and continuous conditions, and in the presence of competing ions. It was determined that calcinated HTC behaved similarly in real and synthetic cooling tower water; the HTC is highly selective for the silica even in the presence of competing cations. Therefore, the data concludes that calcinated HTC is a viable anti-scaling pretreatment for the reuse of industrial wastewaters.

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NOMENCLATURE

Abbreviation	Definition
FTIR	Fourier transform infrared
HTC	Hydrotalcite
mg	Milligram
min	Minute
mL	Milliliter
ppm	Parts per million

1. INTRODUCTION

Water shortages are a growing global problem. Currently, nearly three billion people are impacted by water scarcity [1]; this number is expected to grow to five billion in the next two decades [2]. One proposed solution to mitigate water scarcity is the treatment and reuse of domestic and industrial wastewaters [3]. While these waters can often be treated to potable standards, there are many operational challenges in these treatment schemes that prevent wide-scale adoption of wastewater recycling or direct potable reuse. One such operational issue is scaling associated with waters high in silica, which is ubiquitous in industrial wastewaters, such as waters recycled from cooling towers in power plants [4]. Low-cost silica removal pretreatments are needed to prevent silica scaling and facilitate water reuse.

Previous studies have demonstrated the efficacy and economy of using various ion exchange materials to remove silica [5-7]. Sasan, et al. [5] studied hydrotalcite (HTC) as a selective and regenerable material for the removal of silica from cooling water. This study demonstrated that calcinated HTC can remove greater than 95% of silica for several regeneration cycles, and that exchange sites responsible for removing silica were not affected by the presence of competing ions, including sulfate and chloride. However, all experiments in this study were performed with synthetic cooling tower water. It is unknown if synthetic cooling tower water behaves comparably to real cooling tower water. As shown in Table 1, the cooling tower water from Center for Integrated Nanotechnologies (CINT) building at Sandia National Laboratories (Albuquerque, NM) used in this study is different from the synthetic cooling tower water used in reference 5. Further studies are needed to investigate if HTC is a viable ion exchange material for removing silica for real wastewaters. The objective of this study is to investigate the ability of calcinated HTC to remove silica from wastewater under real-life applications.

Table 1. Characteristic of synthetic cooling tower water used in reference 5 and the real cooling tower water from Center for Integrated Nanotechnologies (CINT) building at Sandia National Laboratories (Albuquerque, NM) used in this study

Species	Synthetic Cooling Tower Water [5]	Cooling Tower Water (this study)
SiO_2	50 ppm	111 ppm
Cl^-	4700 ppm	80 ppm
SO_4^{2-}	156 ppm	132 ppm

2. METHODS

2.1. Calcination

HTC was calcinated by heating commercial HTC ($Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$, from Sigma Aldrich) at 550 ^oC for two hours [8]. This calcination process increases the surface area for the ion exchange material by causing a collapse in the crystal structure and reducing the crystalite size [9]. This greatly improves the efficacy for removing silica [5].

2.2. Batch Experiments

Batch experiments were conducted by mixing various amounts of calcinated HTC with 50 mL of cooling tower water from Center for Integrated Nanotechnologies (CINT) building at Sandia National Laboratories (Albuquerque, NM). In some experiments, the cooling tower water was spiked with competing ions. Characteristics of the cooling tower water are shown in Table 1.

The HTC/cooling tower water mixture was shaken overnight to allow for ion exchange. The slurry was centrifuged, and the pH and silica concentration were measured for the treated supernatant and untreated cooling tower water. The remaining HTC was dried and the FTIR and XRD spectrums measured. Characterization methods are described below.

Two classes of batch experiments were conducted. In the first, various masses (25 – 150 mg) of calcinated HTC were mixed with 50 mL of cooling tower water in order to determine the ion exchange capacity in real-life applications. In the second, cooling tower water was spiked with various masses of salts prior to addition of calcinated HTC, so that the concentration of the competing ion varied from 500 to 2000 ppm. The purpose of these experiments was to determine if HTC can selectively remove silica, or if the presence of competing ions interfere with silica removal. Competing ions tested included nitrate (from $NaNO_3$), chloride (from NaCl), and sulfate (from Na_2SO_4).

2.3. Column Experiments

A column experiment was conducted in order to investigate the ability of HTC to remove silica over an extended time scale. 500 mg of calcinated HTC was added to an ion exchange column, as shown in Figure 1. Cooling tower water was pumped through the column at a flow rate of approximately 0.2 mL/min. The column was constructed from a 1 mL pipet tip, so the empty bed residence time was approximately 7 minutes. A filter was added to the column exit in order to separate any HTC exiting with the water. 10 mL samples were collected over the course of one hour for a total of six hours. The pH and silica concentration of each sample were measured.

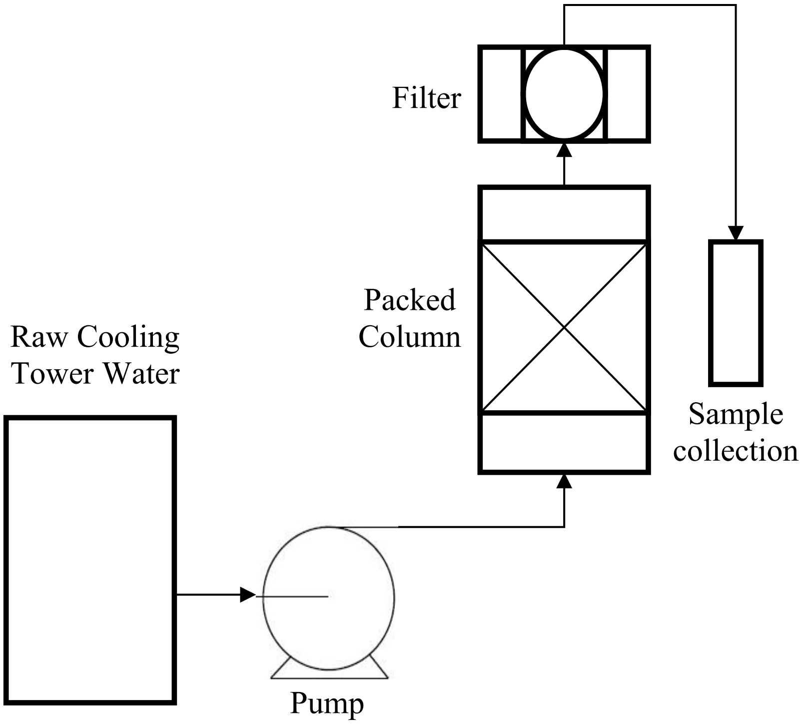

Figure 1. Process flow diagram for column experiments. Raw cooling tower water was pumped through a column packed with calcinated HTC at a rate of 0.2 mL/min. The raw water was filtered at the column exit to remove any HTC. Samples of treated cooling water were collected over the course of one hour.

2.4. Characterization

The experiments described above were characterized by measuring the pH and silica concentration in treated waters, Powder X-ray diffraction (XRD) and the Fourier-transform infrared (FTIR) spectrums of the HTC. The pH was measured using a Thermo Scientific Orion 4Star pH meter and the FTIR spectrum was measured using a Thermo Scientific NiColet iS10 infrared spectrophotometer. XRD patterns were recorded at room temperature on a Siemens Kirstalloflex D500 diffractometer (Cu Kα radiation) 40 kv, 30 mA; $2\theta= 5\text{-}60^{o}$, 0.05^{o} step size, and 3 s count time. The silica concentration was measured following the Hach silicomolybdate method for measurement of high range silica using a Hack DR1900 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Material Characterization

Commercial HTC was calcinated; the FTIR spectrum of HTC was measured before and after calcination. As shown in Figure 2, the calcination process greatly reduces the intensity of peaks associated with carbonate and hydroxyl groups. This is indication of the dehydration and removal of carbonate that occurs during the calciation process, as previously reported [5].

The FTIR spectrum of dried HTC was also measured after batch experiments, reported below. During the ion exchange process, the calcinated HTC returns to its original structure, as evidenced by the recurrence of the carbonate and hydroxyl peaks, as previously reported [10].

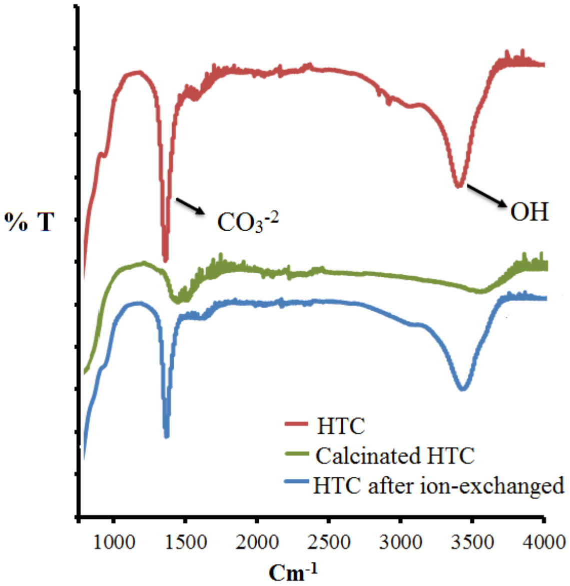

Figure 2. FTIR spectra for commercial HTC, calcinated HTC, and dried HTC after ion exchange experiments were conducted. Note the disappearance of the carbonate and hydroxyl peaks after calcination, and their reappearance after ion exchange.

The activation (or amorphization) of HTC is initiated by a calcination process. The XRD patterns (See Figure 3) indicates that the HTC structure collapsed resulting in no long range crystallinity and therefore no XRD peaks. During this process it formed mixed oxide phases (calcinted HTC) during heat treatment, as previously reported [5]. The calcinated HTC is reconstruct (recrystallized) to its original structure when exposed to water and silica anions (See Figure 3).

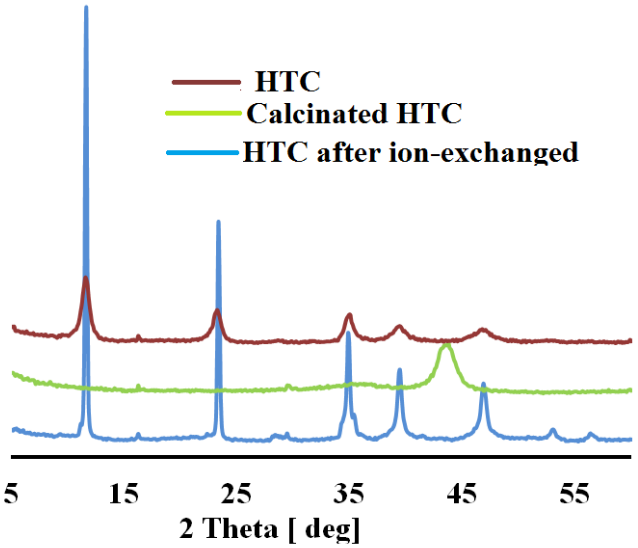

Figure 3. XRD spectra for commercial HTC (blue), calcinated HTC (green), and dried HTC after ion exchange experiments (red) were conducted.

3.2. Batch Experiments

First, a batch experiment was performed in order to investigate the effect of HTC concentration on the removal of silica from cooling tower water. The silica concentration and pH of the resultant supernatant were measured and are shown in Figure 4.

Figure 4. Percent silica removal (a) as a function of pH, and (b) for several masses of calcinated HTC (50 mL, pH:9.1, reaction time 15 h, SiO_2:111ppm).

As expected, the silica concentration increased with the mass of HTC added until most of this silica was removed. This occurred around 100 mg of HTC (See Figure 4a). The pH also increased with the addition of HTC (See Figure 4b) .

3.3. Effect of competing anions on silica removal

Additionally, batch experiments were conducted in order to evaluate the selectivity of HTC for silica removal by adding various concentrations of several competing ions, shown in Figure 5. As the concentration of the competing ion increases, the percent removal modestly decreases; independent of competing cation the percent removal of silica always remains above 90%. This demonstrates that competing ions have a small effect on silica removal by HTC, but only for concentration an order of magnitude higher than silica concentrations (See Figure 5a). This also indicates that HTC can selectively remove silica from cooling tower water. The pH was also measured during the competing ion experiments (See Figure 5b). As expected, the presence of competing ions had a negligible effect on the pH of the solution. The pH increase observed in Figure 4b is attributed to the ion exchange process during the silica removal [5] ; therefore, no pH change is expected, because the presence of competing ions has no effect on silica removal process (See Figure 5a).

Figure 5. Percent silica removal (a) and pH (b) for several concentrations of competing ions, including nitrate, chloride, and sulfate (calcinated HTC:100 mg, 50 mL, pH:9.1, reaction time 15 h, SiO_2:111ppm).

3.4. Column Experiment

A column experiment was performed in order to investigate the ability of HTC to remove silica under continuous operation. Recall that the fluid residence time in the column test was ~ 7 minutes; batch reaction times were carried out to 6 hours. Results are shown in figure 5. The HTC in the column experiments was able to remove greater than 96% of silica for a period of six hours (See Figure 5a). This results confirmed to rapid uptake of silica during column filtration.

Figure 6. Percent removal of silica (a) and outlet pH (b) as a function of time in a continuous packed bed reactor (calcinated HTC:500 mg, 50 mL, pH:9.1, SiO_2:111ppm).

3.5. Comparison to Synthetic Cooling Tower Water

The data from experiments conducted with real cooling tower water, presented here, compare well to those conducted with synthetic cooling tower water, presented in reference 5. Qualitatively, the trends were the same. Silica removal increased with increasing masses of calcinated HTC until approximately 96% of the silica was removed. Sasan, et al. also reported similar trends for silica removal in the presence of competing ions. [5] They reported that silica removal decreased slightly in the presence of chloride ions, and slightly more in the presence of sulfate ions; the same trends are observed here.

Quantitative comparison between the data presented here and in reference 5 is challenging because the silica concentration in cooling tower water is more than twice that used in the synthetic cooling tower water. However, a comparison may be made by calculating the silica adsorption capacity. The silica adsorption capacity is defined as the mass of silica removed from solution to the mass of calcinated HTC used for silica removal. The silica adsorption capacity was calculated for each data point in Figure 2 and for the comparable data presented in [5]. The average silica adsorption capacities for removing silica from real cooling tower water and synthetic cooling tower water were 0.0739 and 0.0633, respectively. These figures are 14.3% different, so it can be concluded that the synthetic cooling tower water used in reference 5 is a good approximation of real cooling tower water for studying silica removal.

4. CONCLUSION

The efficacy of calcined hydrotalcite for removing silica from cooling tower water was investigated and compared to similar experiments conducted with synthetic cooling tower water. It was found that calcinated HTC behaves similarly in synthetic and real wastewaters in its ability to remove silica. Therefore, it can be concluded that calcinated HTC is a viable low cost technology for removing silica from wastewater in real-life applications. Such technology is necessary to prevent processing issues associated with reuse of industrial wastewater in order to facilitate development of a sustainable water source.

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