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Abstract

Silica is ubiquitous in produced and industrial waters, and plays a major disruptive role in water recycle. Herein we have investigated the use of mixed oxides for the removal of silica from these waters, and their incorporation into a low cost and low energy water purification process. High selectivity hydrotalcite (HTC, ($Mg_6Al_2(OH)_{16}(CO_3)•4H_2O$)), is combined in series with high surface area active alumina (AA, (Al_2O_3)) as the dissolved silica removal media. Batch test results indicated that combined HTC/AA is a more effective method for removing silica from industrial cooling tower wasters (CTW) than using HTC or AA separately. The silica uptake via ion exchange on the mixed oxides was confirmed by Fourier transform infrared (FTIR), and Energy dispersive spectroscopy (EDS). Furthermore, HTC/AA effectively removes silica from CTW even in the presence of large concentrations of competing anions, such as Cl^-, NO_3^- HCO_3^-, CO_3^{2-} and SO_4^{2-}. Similar to batch tests, Single Path Flow Through (SPFT) tests with sequential HTC/AA column filtration has very high silica removal too. Technoeconomic Analysis (TEA) was simultaneously performed for cost comparisons to existing silica removal technologies.

An Academic Alliance (AA) partnership was established for the second year of this two year LDRD with UNM under the leadership of Prof Kerry Howe. The focus of that part of the study is the scale up of the HTC process.

ACKNOWLEDGMENTS

The work performed here was funded by Sandia National Laboratories' Laboratory Directed Research and Development program (LDRD). Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

TABLE OF CONTENTS

1. INTRODUCTION

Thermoelectric power generation is the largest user of freshwater in the US, at *~500 billion gallons/day which is almost half of all water withdrawn daily*. Replacement of that freshwater with purified oilfield produced waters, municipal or agricultural wastewaters, and subsurface brines is possible only if dissolved silica and calcite are prevented from forming mineral scales during the power generation process. Existing anti-scalant technology can already prevent calcite buildup. However, there is no low energy method for preventing silica scaling, thereby limiting the amount of impaired water recycling that can be achieved. Dissolved silica is ubiquitous in impaired waters, resistant to existing anti-scalants, and difficult to remove from power plant feedwaters. This LDRD is focused on developing silica getter materials that will be tested at the field and pilot scale, and leveraged to commercialization.

Our project is both an innovative approach for developing high silica capacity and selectivity solid sorbent materials, and is cutting edge for collaboratively (1) developing novel materials and their processes for silica removal, with the use of (2) technoeconomic modeling and analysis to aid in real-world implementation. We will build upon our unique experiences in low energy desalination and silica removal screening tests (TRL 1-2) to ensure success in this TRL 3-4 development LDRD.

The project results have been published in a number of sources. Included here are the references and summaries of each.

2. RESULTS AND DISCUSSION

2.1. Exceptional Selectivity for Dissolved Silicas in Industrial Waters using Mixed Oxides

Herein is presented a fast, energy efficient and low cost a application of mixed oxides for removal of silica ions from cooling tower water: combining highly selective hydrotalcite (HTC, ($Mg_6Al_2(OH)_{16}(CO_3)\bullet 4H_2O$)), material with high surface area of activated alumina (AA, (Al_2O_3)). The results indicated that the combined HTC/AA removes >90% silica from batch solutions. SPFT tests point to rapid adsorption of silicate by HTC/AA. Furthermore, the use of this combination of ion exchange materials has added benefits than use of each individually, including: (1) minimized decrease with time of percent silica removed, and (2) combined HTC/AA interactions with the water causes a pH swing back toward neutral at the end of the process.

SEM-EDS and FTIR confirm the presence of silica in the HTC/AA structure. Competing ion adsorption experiments indicate that silica uptake remains high even in the presence of large concentrations of competing anions. Compared to anion-exchange resins, HTC/AA might be applied to brackish, geothermal and cooling tower waters because of its selectivity with respect to silica.

The silica adsorption isotherm was modeled to the Freundlich model and the experimental data fitted well (R^2=0.95), that indicates that there is a direct correlation between the initial silica concentration and the silica captured by combined HTC/AA. Ongoing techno-economic modeling and scale-up analysis will help identify the most appropriate of HTC/AA silica removal research.

This work is presented in full in references 1 and 2:

1) Sasan, K.; Brady, P.V.; Krumhansl, J. L.; Nenoff, T. M. “Removal of Dissolved Silica from Industrial Waters using Inorganic Ion Exchangers”, *Journal of Water Process Engineering*. **2017**, *17*, 117-123.

2) Sasan, K.; Brady, P.V.; Krumhansl, J. L.; Nenoff, T. M. “Exceptional Selectivity for Dissolved Silicas in Industrial Waters using Mixed Oxides” *Journal of Water Process Engineering*. **2017**, submitted.

2.2. Removing Dissolved Silica from Waste Water with Catechol and Active Carbon

Our research is focused on low energy, recyclable materials and processes that will effectively remove silica from produced and subsurface waters so that it can be reused in industrial applications. One of the class of materials studied for silica removal was catechol. Reported herein are the details from that study. Utilizing concentrated cooling tower water (CCTW), catechol shows the ability to remove up to 50% of the dissolved silica when utilized at basic pH's between 8 – 10. The assumed mechanism for silica complexation is:

$$R_1\text{-O-H} + \text{H-O-}R_2 \rightarrow H_2O + R_1\text{-O-}R_2.$$

Although this reaction formally shows no pH dependence it is likely that at an intermediate condition where both $H_4SiO_3^-$ and H_4SiO_4 are present in significant proportions is conducive to forming the complexed form of silica rather than only one of the dissolved silica species.

Furthermore, because a recyclable process is desired to reduce secondary environmental waste by the silica removal process (and avoid higher disposal costs to the process), the catechol removal of silica is not preferred. The catechol removal capability is low (maximum 50%). Additionally, it is lower than that for hydrotalcite (HTC) ion exchange materials also utilized in our studies.[1]

The hydrotalcite, which in contrast to the catechol / carbon mix tested here, operates by an anion exchange mechanism. Since silicic acid dissociates to anionic silica ($H_4SiO_3^-$) at pH ~ 9.5, it is not surprising that HTC is most effective in basic solutions, though tests down to 4.5 show a diminished ability to pick up silica at low pH (< 4; Table 2). The HTC process approaches 95% silica removal with recyclability of more than 5 cycles per batch of HTC. This minimizes the secondary waste produced in the process.

In conclusion, we have shown that catechol is a viable silica removal agent when mixed with activated charcoal. While it remains to be an optimized process, it does show that the potential exists for the use of properly hydroxide-functionalized molecules (eg., catechol) for correct recognition and complexation with silica, for silica's removal from waters.

This work is presented in full in reference 3: Sasan, K.; Brady, P.; Krumhansl, J.L.; Nenoff, T.M. “Removing Dissolved Silica from Waste Water with Catechol and Active Carbon”, Sandia National Laboratories, SAND2017-0554, January 2017.

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

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.

This work is presented in full in reference 4: Moore, S. E.; Sasan, K.; Brady, P.V.; Krumhansl, J.L; Nenoff, T.M. “Removal of Dissolved Silica using Calcined Hydrotalcite in Real-Life Applications” SAND2017-9566, September 2017.

2.4. Ongoing Studies

Process modeling outputs included raw material requirements, energy use, and the minimum water treatment price (MWTP). Monte Carlo simulations quantified the impact of uncertainty and variability in process inputs on MWTP. These analyses showed that cost, can be significantly reduced if the HTC materials are optimized. Specifically, R&D improving HTC reusability, silica binding capacity, and raw material price can each reduce MWTP by 40%, 13%, and 20%, respectively. Optimizing geographic deployment further improves cost competitiveness.

This work will be fully presented in reference 5: Heimer, B.W.; Paap, S.M.; Sasan, K.; Brady, P.V.; Nenoff, T. M. “Model Design and Resultant Techno-economic Assessment for Materials to Treat Produced Waters”, *Ind. Eng. Chem. Res.*, **2017**, in preparation.

UNM has constructed a scaled up system and has completed operation of it with current silica removal technologies to establish baseline performance and comparison studies using HTC. Operating parameters were controlled and monitored: (1) for packed columns, the parameters included filtration rate, empty bed contact time, head loss, specific filtration volume (bed volumes) until exhaustion, silica removal efficiency, and other parameters; (2) for suspended-media reactors, the parameters included hydraulic residence time, solids concentration, silica removal efficiency, membrane flux, and fouling rate of microfiltration membrane. Process information has been provided to SNL for technoeconomic analysis (TEA) studies; these results have been provided back to UNM for process economic/cost and energy consumption/savings comparisons.

This work will be fully presented in reference 6: Stomp, J.: Stoll, Z.; Sasan, K.; Nenoff, T.M.; Howe, K. ”Design of System for Use of Hydrotalcites for Silica Removal from Water”, **2017**, in preparation.

3. CONCLUSION

Silica is ubiquitous in produced and industrial waters, and plays a major disruptive role in water recycle. Herein we have investigated the use of mixed oxides for the removal of silica from these waters, and their incorporation into a low cost and low energy water purification process. This two year LDRD was very successful at showing how the hydrotalcite (HTC, ($Mg_6Al_2(OH)_{16}(CO_3)\bullet 4H_2O$)), is a highly selective and recyclable material for the removal of silica from industrial waters. With the addition of high surface area active alumina (AA, (Al_2O_3)), the removal of silica is further improved. Ongoing technoeconomic analysis and UNM scaleup studies are showing the viability of HTC in silica removal.

Successes are being leveraged into follow on funding a leading technology to the upcoming DOE/ AMO water hub, specifically under chemical separations (partnership including UNM). This hub currently has sixteen partners, including three national labs, utilities, industrial partners and universities from around the US.

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1) Sasan, K.; Brady, P.V.; Krumhansl, J. L.; Nenoff, T. M. “Removal of Dissolved Silica from Industrial Waters using Inorganic Ion Exchangers”, *Journal of Water Process Engineering*. **2017**, *17*, 117-123.

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6) Stomp, J.: Stoll, Z.; Sasan, K.; Nenoff, T.M.; Howe, K. ”Design of System for Use of Hydrotalcites for Silica Removal from Water”, **2017**, in preparation.

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