A NEW MULTIFUNCTIONAL SORBENT FOR THE TREATMENT OF COPRODUCED WATERS (CWS) FROM THE ENERGY INDUSTRY

Final report

Maohong Fan and Andrew Thomas Jacobson

Departments of Chemical & Petroleum Engineering
University of Wyoming
Phone: (307) 766 5633   Email: mfan@uwyo.edu

Abstract

Large tracts of Wyoming farmland contain high concentrations of CO_3^{2-} and HCO_3^-. Since these could lead to significant environmental issues such as the reduced availability of micronutrients for plants, coproduced waters (CWs) high in CO_3^{2-} and HCO_3^- cannot be used directly for irrigation in Wyoming. CWs must therefore be treated prior to application, which is a very challenging issue currently facing the fossil fuel production industry. Reducing CO_3^{2-} and HCO_3^-—and thus salinity and alkalinity in CWs—would significantly benefit not only agriculture, but energy development in Wyoming as well.

The proposed project sought to develop a new technology for the on-farm or on-site reduction of salinity and alkalinity to lower carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) from CWs discharged from the energy industry, thus protecting water and soil resources. The purpose and specific goals of the project are to reduce total concentrations of CO_3^{2-} and HCO_3^- in discharged CWs by 90% at a lower cost per metric ton than other commercially available technologies. The project seeks to achieve these goals through the use of recently developed and commercially available $TiO(OH)_2$ to remove carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) in the CWs discharged from oil and gas wells (e.g., wells operated by EOG Resources Inc. and Chesapeake Energy) and oil refining companies (e.g., HollyFrontier, a company currently collaborating with Dr. Fan's group at UW). It should be noted that $TiO(OH)_2$ is different in structure from conventional crystal anatase TiO_2 and $Ti(OH)_2$. The $TiO(OH)_2$ to be used in the proposed project has an amorphous structure, which makes the material highly capable for adsorption. Also, as a high-capacity sorbent, $TiO(OH)_2$ can remove not only CO_3^{2-} and HCO_3^- but other contaminants such as heavy metals [e.g., arsenic (As), selenium (Se), and lead (Pb)] as well.

The project will be realized by demonstrating the proposed CWs remediation technology in pilot-scale applications either at an oil well site of EOG Resources Inc. or a HollyFrontier refinery in Wyoming. Because the high salinity and alkalinity of CWs contaminated with CO_3^{2-} and HCO_3^- degrade water and soil resources needed by farmers for agricultural production, the success of the proposed technology will directly benefit all Wyoming agricultural producers.

1. Objectives

Large tracts of Wyoming farmland contain high concentrations of CO_3^{2-} and HCO_3^-. Since these could lead to significant environmental issues such as the reduced availability of micronutrients for plants, coproduced waters (CWs) high in CO_3^{2-} and HCO_3^- cannot be used directly for irrigation in Wyoming. CWs must therefore be treated prior to application, which is a very challenging issue currently facing the fossil fuel production industry. Reducing CO_3^{2-} and HCO_3^-—and thus salinity and alkalinity in CWs—can significantly benefit not only agriculture, but energy development in Wyoming as well.

The project was designed to develop a new technology for the on-farm or on-site reduction of salinity and alkalinity to lower carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) from CWs discharged from the energy industry, thus protecting water and soil resources. The purpose and specific goals of the project are to reduce total concentrations of CO_3^{2-} and HCO_3^- in discharged CWs by 90% at a lower cost per metric ton than other commercially available technologies. The project seeks to achieve these goals by using recently developed and commercially available $TiO(OH)_2$ to remove carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) in the CWs discharged from oil and gas wells (e.g., wells operated by EOG Resources Inc. and Chesapeake Energy) and oil refining companies (e.g., HollyFrontier, a company currently collaborating with Dr. Fan's group at UW). It should be noted that $TiO(OH)_2$ is different in structure from conventional crystal anatase TiO_2 and $Ti(OH)_2$. The $TiO(OH)_2$ used in the proposed project has an amorphous structure, which makes the material highly capable for adsorption. Also, as a high-capacity sorbent, $TiO(OH)_2$ can remove not only CO_3^{2-} and HCO_3^- but other contaminants such as heavy metals [e.g., arsenic (As), selenium (Se), and lead (Pb)] as well.

2. Significance and Background

2.1 Related Research

Due to the continuous growth of population and industry in Wyoming, developing and securing clean water resources is one of the major challenges we face in the 21st century. Surface water will

still be available to meet various future needs, but rapid economic development in our state may lead to the depletion of these resources. Therefore, other water resources must be developed.

The CWs from various energy production industries (coal, natural or shale gas, and oil) [1, 2] are considered to be important potential new water resources. However, many of these must be treated due to their quality issues, especially high CO_3^{2-} and HCO_3^- levels [2, 3]. Removal of CO_3^{2-} and HCO_3^- from CWs can significantly improve their application in agriculture.

Many methods, including membrane and reverse osmosis [4-6], have been studied either to remove CO_3^{2-} and HCO_3^- or at least lower their concentrations to allowable levels, while adsorption is the most promising method due to its effectiveness and simplicity for point-of-use applications. A search of the literature shows that very little attention has been paid to the adsorption of carbonate and bicarbonate anions by adsorbents. In 1993, L. Zang *et al.* studied the possibility of the adsorption of carbonate and bicarbonate anions on colloidal silver particles [6, 7]. However, using this type of adsorbent for removal of CO_3^{2-} and HCO_3^- is not practical.

Therefore, although their development is challenging, simple and cost-effective methods for removing CO_3^{2-} and HCO_3^- in CWs are worth pursuing. The proposed $TiO(OH)_2$-based method is designed to overcome the shortcomings of the abovementioned methods and to fill a gap in the area of CWs treatment.

2.2 Wyoming Water

It is well known that Wyoming is a semi-arid region in the U.S. Accordingly, Wyoming has limited sustainable surface water resources, and though they occasionally swell to very high levels, rivers and streams in the state have little flow. Moreover, natural disasters such as droughts and tornadoes unpredictably plague regions of Wyoming, undermining agricultural and industrial productivity and adversely affecting the well-being and social fabric of communities. For instance, 2012 was the driest of the last 118 years, which led to the lowest hay crop yield since 2002 [8]. Further, the contamination of waterways from human activity may further weaken Wyoming's ability to meet its water needs. Therefore, Wyoming must be prepared to meet the threat of potential water

shortages. To address this crisis and its associated challenges, Wyoming statute Title 35, Chapter 11, Article 3 (35-11-309) declares that "water is one of Wyoming's most important natural resources, and the protection, development and management of Wyoming's water resources is essential for the long-term public health, safety, general welfare and economic security of Wyoming and its citizens."

Meanwhile, the mining and energy production industries in Wyoming generate a great amount of coproduced waters (CWs). It is common knowledge that these CWs have high concentrations of CO_3^{2-} and HCO_3^-. Given that many of Wyoming's soil and water resources already contain high concentrations of CO_3^{2-} and HCO_3^-, the disposal of CWs therefore not only further diminishes the quality of these resources, but also wastes highly valuable water resources the state sorely needs. For these reasons, the treatment and recycling of CWs in Wyoming is a win-win strategy for our state. However, conventional treatment methods need either expensive or multi-step methods to remove CO_3^{2-} and HCO_3^- from CWs. The shortcomings of the multi-step methods are obvious, and are not only expensive but can sometimes lead to secondary contamination as well. To overcome these shortcomings, we have made efforts to develop a simple, multifunctional technology for the simultaneous removal of CO_3^{2-} and HCO_3^- to improve the overall quality of CWs, thus providing an inexpensive and reliable water resource for Wyoming.

3. Methodology

3.1. Experimental/Procedure

The $TiO(OH)_2$ powders were synthesized from thermal decomposition of titanium isopropoxide, $Ti(O\text{-}iC_3H_7)_4$, in water, at room temperature as seen in Reaction 1.

$$Ti(O\text{-}iC_3H_7)_4 + 4H_2O \rightleftharpoons TiO(OH)_2 + 4C_3H_7OH + H_2O \qquad R1$$
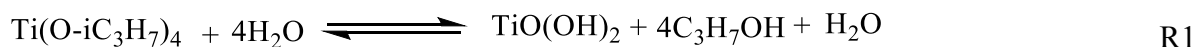
The first step was to add a predetermined amount of $Ti(O\text{-}iC_3H_7)_4$ to DI water with the molar ratio of H_2O: $Ti(O\text{-}iC_3H_7)_4$ being 27.6:1, followed by stirring the resultant mixture for 4 hours. The gel preparation process started when both solutions were mixed together under constant stirring. The

precipitate TiO(OH)$_2$ was then filtered, rinsed two times with DI water and ethanol, then was dried at 100 ^{o}C overnight.

The adsorption experiments were then carried out in three one liter batch reactors, each equipped with a mechanical stirrer. Each reactor had an argon flow connection to clear the reactor head space of CO$_2$, controlled by flow controllers. All experiments completed were run at least three times for statistical analysis. For the experiments, a predetermined amount of NaHCO$_3$ and/or Na$_2$CO$_3$ was added to one liter of DI water in each reactor. This was followed by the addition of a set amount of TiO(OH)$_2$. All reactions were run for 30 hours to guarantee equilibrium was reached. Samples were taken throughout this time for analysis of the bicarbonate and carbonate concentrations left in the water. A picture of the reactor set-ups can be seen in Figure 2.
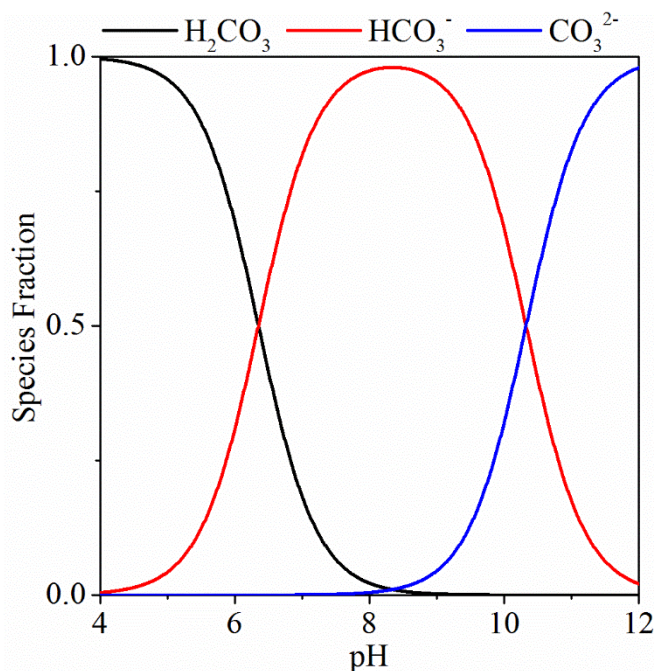

Fig. 1 The speciation fraction dependace of aqueous carbonate with pH

Sets of adsorption experiments (varying initial adsorbate concentrations) completed at one of three pH values. The completed set was at a pH of 8.2 where bicarbonate is the major species present. The set at a pH~10 where the species is a mix of carbonate and bicarbonate, and at a pH of 11 where the main species present is carbonate are to be performed. The speciation with pH can be seen in Figure 1. The first set of experiments (pH=8.2) has had kinetic and isotherm modeling applied.
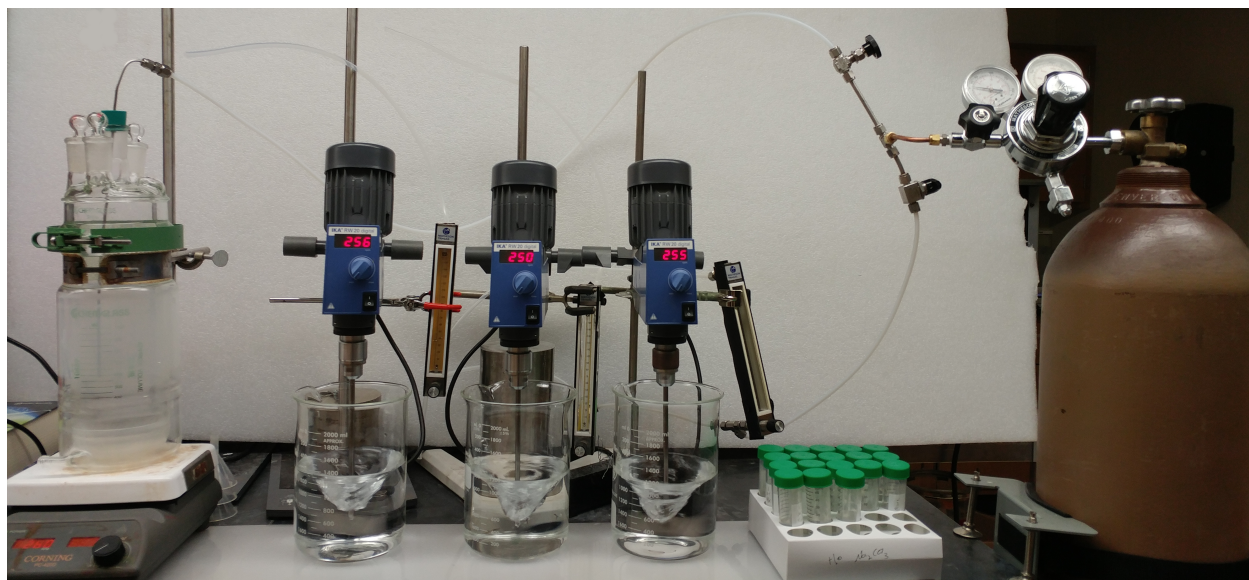
Fig. 2 Experimental set up for carbonate adsorption

3.2 Instrumentation

For aqueous carbonate/bicarbonate analysis, an SI Analytics Titroline 6000 autotitrator along with a Shimadzu total carbon analyzer was used. C13 nuclear magnetic resonance (NMR) analysis was completed at the University of Colorado in Boulder. Elemental analysis was completed with a PerkinElmer NexION 300S ICP-MS inductively coupled plasma mass spectrometer (ICP-MS). An FEI Quanta FEG 450 field-emission scanning electron microscope (SEM) was used to image $TiO(OH)_2.$ A Nicolet/iS50 Fourier transform infrared (FTIR) spectrometer was used for structure analysis. Thermogravimetric analysis (TGA) of $TiO(OH)_2$ was performed using a TA Instruments SDT Q600 TGA. A Rigaku Smartlab X-ray diffraction system using a Cu Kα1 line (1.5406 Å) operating at 40 kV/40 mA, with 2θ ranging from 10° to 90° was used for the X-ray diffraction (XRD) analysis. The BET (Brunauer-Emmett-Teller) surface area and BJH (Barrett-Joyner-Halenda) pore volume were acquired using a Quantachrome Autosorb IQ automated gas sorption analyser.

3.3 Kinetic Theory

The kinetic models of CO_3^{2-} and HCO_3^- sorption are needed for designing pilot-scale and, eventually, industrial-scale demonstrations of the proposed technology. The kinetic rate equation is expressed as [9, 10]:

$$\frac{dq_t}{dt} = k(q_{eq} - q_t)^2 \tag{E1}$$

where k [g-TiO(OH)$_2$/(mg-HCO$_3^-$.h) or -TiO(OH)$_2$/(mg-HCO$_3^-$.h)] represents the pseudo-second-order rate constant of CO_3^{2-} and HCO_3^- sorption. By integrating E1 with the boundary condition of $q_{t=0} = 0$, the following linear equations can be obtained:

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + kt \tag{E2}$$

or

$$\frac{t}{q_t} = \frac{1}{q_{eq}}t + \frac{1}{V_0} \tag{E3}$$

$$V_0 = kq_{eq}^2 \tag{E4}$$

where V_0 [mg- HCO$_3^-$/(g-TiO(OH)$_2$ h)] is the initial sorption rate. The q_{eq} in E4 can be derived using the slope of t/q$_t$ vs. t, while k in E4 can be determined using the slope of $1/(q_{eq} - q_t) \sim t$.

3.4 Isotherm Theory

The adsorption isotherm for bicarbonate adsorption was characterized using four models; Langmuir, Freundlich, Dubinin-Rasushkevich (D-R), and Redlich-Peterson (R-P) [11]. The Langmuir model can be expressed as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{E5}$$

or in linear form:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad \text{(E6)}$$

where q_e (mg g^{-1}) is the equilibrium adsorbed concentration, C_e (mg L^{-1}) is the adsorbate equilibrium concentration in solution, q_m (mg g^{-1}) is the maximum monolayer coverage capacity, and b (L mg^{-1}) is the equilibrium adsorption constant. The Freundlich isotherm model in its non-linear (E8) and linear (E9) forms are as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad \text{(E8)}$$

$$\ln(q_e) = \ln(K_f) + \frac{1}{n}\ln(C_e) \qquad \text{(E9)}$$

with K_f (mg g^{-1}) being the Freundlich isotherm constant and n the adsorption intensity. Unlike Langmuir, the Fruendlich isotherm is not restricted to the formation of a monolayer. The nonlinear (E10) and linear (E11) forms of the Dubinin-Rasushkevich (D-R) isotherm model are expressed as:

$$q_e = q_s e^{-k_{ad}\varepsilon^2} \qquad \text{(E10)}$$

$$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2 \qquad \text{(E11)}$$

where q_s (mg g^{-1}) is the isotherm saturation capacity, and k_{ad} (mol^2 kJ^{-2}) and ε are the Dubinin-Rasushkevich isotherm constants with ε equal to:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad \text{(E12)}$$

where R is the gas constant and T the absolute temperature (K). Last the Redlich-Peterson (R-P) three parameter isotherm model was applied. The R-P model is a combination of the Langmuir and Fruendlich isotherm models. It is expressed as:

$$q_e = \frac{K_r C_e}{1 + a_r C_e^g} \qquad \text{(E5)}$$

with K_r (L/g) and a_r (mg^{-1}) are the R–P isotherm constants, and g is the R-P isotherm exponent.

4. Principal Findings

4.1 TiO(OH)$_2$ Characterization

Thermogravimetric Analysis (TGA)

For TGA analysis TiO(OH)$_2$ was heated at 20 °C /min up to 1000 °C. Only data up to 600 °C is shown in Figure 3 as there were no changes above this temperature. It was expected to see the evaporation of physically adsorbed water at around 100°C. Thermal decomposition of the TiO(OH)$_2$ started around 300 °C, which is much higher than needed for bicarbonate/carbonate adsorption. The TiO(OH)$_2$ had a total weight loss of about 20 wt.% after decomposition.

Scanning Electron Microscopy

The SEM images in Figure 4 show the porous structure of TiO(OH)$_2$ important for reaction sites in the removal of carbonate and bicarbonate.

Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) spectra collected for TiO(OH)$_2$ can be seen in Figure 5. The FTIR spectrum of fresh TiO(OH)$_2$ shows a characteristic peak in 400-900 cm^{-1} range, which can be attributed Ti–O stretching vibrations. The additional peak at 1000-1700 cm^{-1} range can be attributed to Ti-O-H bonds, while the broad peak in the 2500-3500 cm^{-1} range corresponds to the small amount of water adsorbed on the surface of TiO(OH)$_2$.

X-ray diffraction (XRD)

X-ray diffraction (XRD) data for pure TiO(OH)$_2$ can be seen in Figure 6. It is clear that the TiO(OH)$_2$ is an amorphous material. The three broad peaks at 30, 45, and 60 2θ can be assigned to small amount of titanium dioxide being present in the material. This TiO$_2$ is likely formed during TiO(OH)$_2$ preparation.

Brunauer-Emmet and Teller (BET) Analysis

Brunauer-Emmet and Teller analysis (BET) was used to study the surface area and pore size/volume of the prepared $TiO(OH)_2$ sample. This data can be seen in Table 1. The high surface area of $TiO(OH)_2$ is beneficial for the adsorption of bicarbonate/carbonate.

Solid Carbon-13 Nuclear Magnetic Resonance (NMR) Analysis

C13 NMR analysis was completed to show the adsorption of carbonate onto $TiO(OH)_2$. This analysis is shown in Figure 7. The samples were analyzed before and after adsorption experiments. The large peak at ~115 ppm is due to the background and Teflon rotor because of single pulse analysis. The small peak at 167 ppm can be seen only in the $TiO(OH)_2$ after adsorption. This peak can be attributed to carbonate adsorbed to the surface.

Table 1 BET data for $TiO(OH)_2$ including surface area, pore volume, and pore size

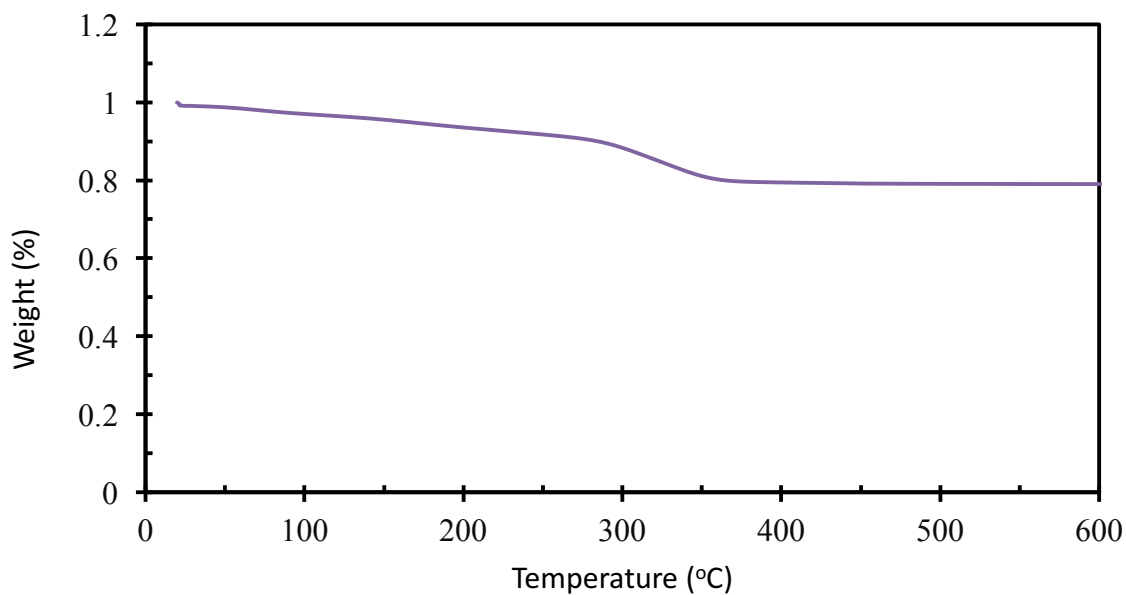| BET data for $TiO(OH)_2$			
Sample	Surface Area (m²/g)	Pore Volume (cm^3/g)	Pore Size (A^{o})
Fresh $TiO(OH)_2$	672.16	0.461	32.97

Fig. 3 TGA of TiO(OH)$_2$ [TGA conditions: heated at 20.00 °C/min to 1000.00 °C, the data above 600°C shows no change, N$_2$ flow = 0.1 L/min
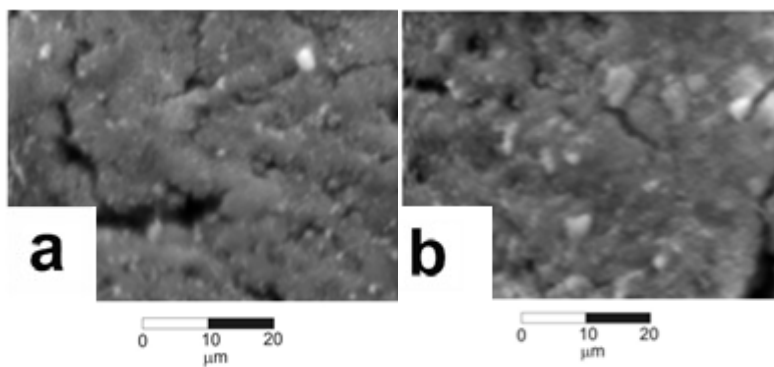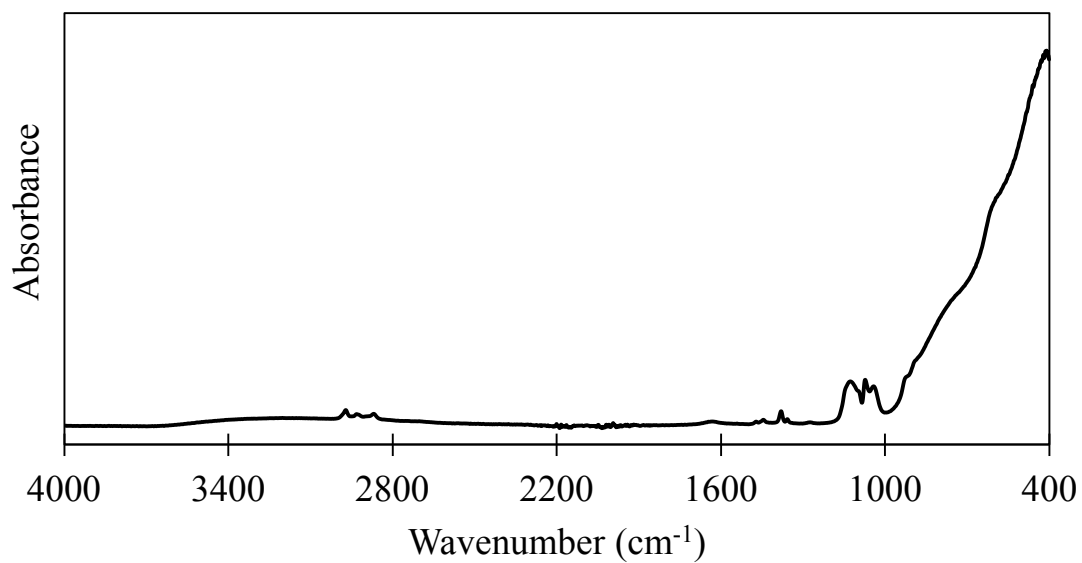

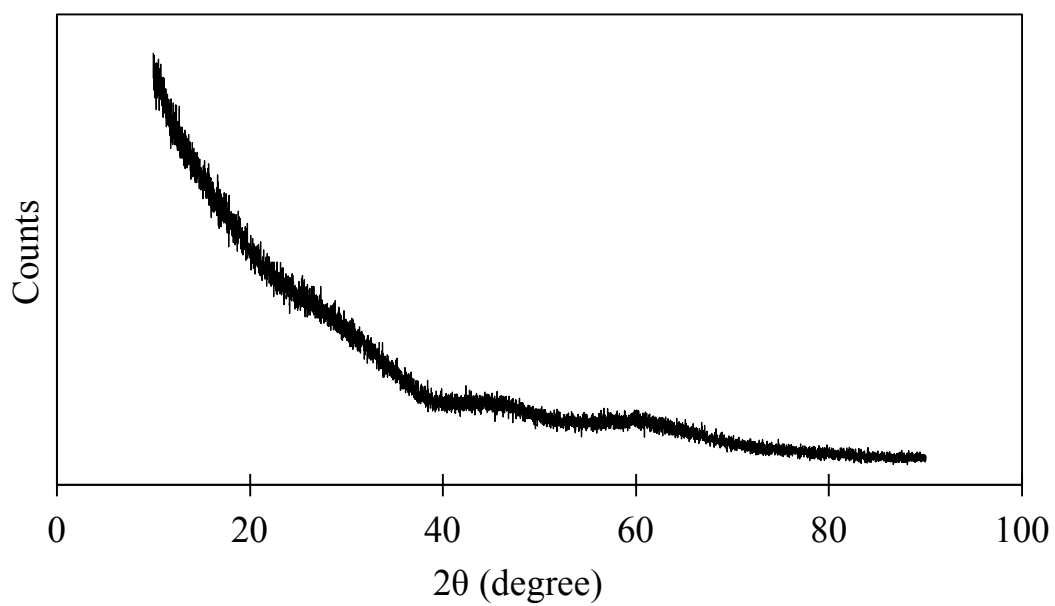**Fig. 4** SEM images of TiO(OH)$_2$

Fig. 5 FT-IR spectra of TiO(OH)$_2$

Fig. 6 XRD data for TiO(OH)$_2$

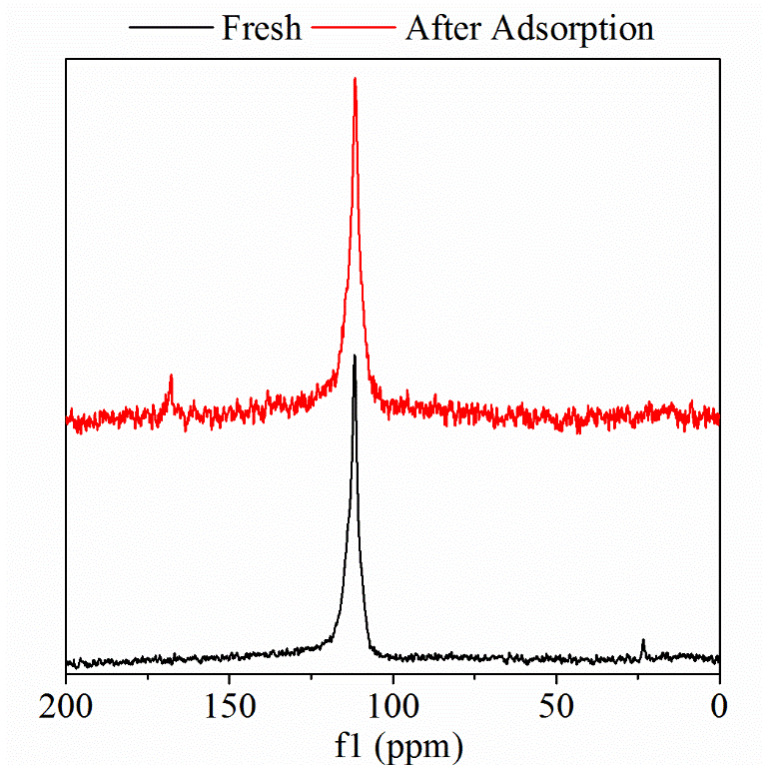**Fig. 7** C13 NMR of TiO(OH)$_2$ before and after the adsorption of carbonate

4.2 Adsorption Experiments

Variation of TiO(OH)$_2$ dosage in HCO$_3^-$ adsorption

Experiments have been completed on variation of the TiO(OH)$_2$ dosage for bicarbonate removal. These results can be seen in Figure 8. The figure includes the linearly regressed pseudo second order kinetic model described previous overlaid the experimental data. The kinetic data derived from the linear regression can be seen in Table 2. The regression coefficients (r^2) were all above 0.9995, indicating the pseudo second order kinetic model chosen is an acceptable model. As anticipated, sorption of HCO$_3^-$ increases with an increase in TiO(OH)$_2$ dosage. A final dosage of 4 g/L was chosen for all successive experiments.
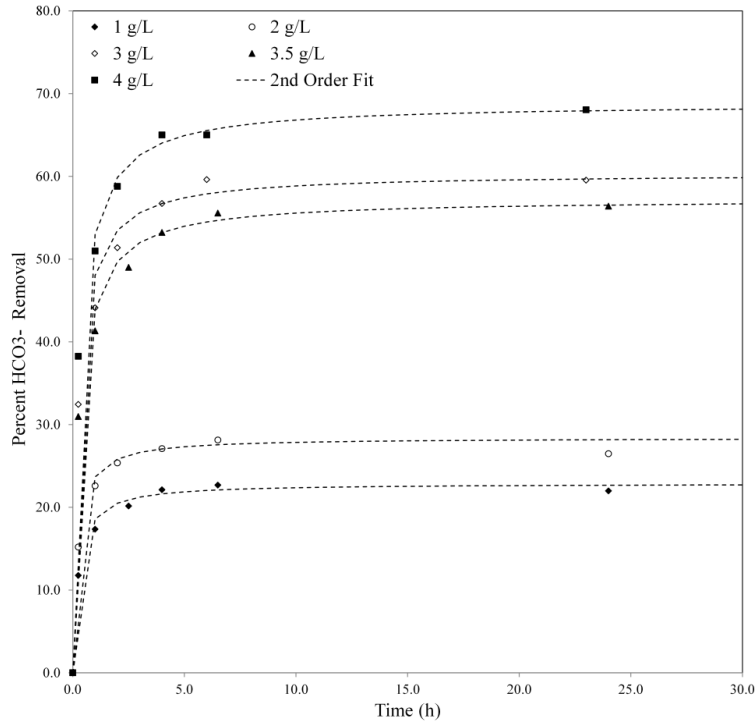
Fig. 8 HCO_3^- adsoprtion as a function of $TiO(OH)_2$ dosage. The pseudo-second order kinetic linear regression (dotted lines) are overlaid. Initial HCO_3 concetration was 4.8 mmol/L in a total volume of 1 L at a pH of 8.2.

Variation of Initial HCO_3^- Concentration

Initial bicarbonate concentrations are an important component in the science of their removal for both the kinetic and isotherm modeling. Therefore, experiments have been done in the variation of HCO_3^- initial concentrations. The data acquired can be seen in Figures 9-12. Figure 9 shows the lower concentrations common of alkaline waters. This data is also shown in Figure 10 as percent removal. All of initial concentrations in Figure 9 and 10 are within the slight to moderate hazard range of irrigation water (Table 2). The percentage removal in Figure 10 shows that many of the initial concentrations studied were brought down to no or slight irrigation hazard. The dotted lines of Figure 9 and 11 are the pseudo-second order kinetic applied. The values regressed from this kinetic analysis can be seen in Table 3. All the regression coefficients are over 0.999, signifying a suitable model. The kinetic constants decrease with an increasing initial concentration due to the slower kinetics adsorbing more bicarbonate. Figure 11 also show the TC analysis is very close to the autotirator analysis. This confirms the reliability, consistency, and accuracy of the titration

analysis. Figure 12 shows the four isotherm models that were applied to the bicarbonate adsorption experiments. The R-P model resulted in the best fit, which indicates the adsorption mechanism is a mix of chemisorption and physisorption. The values regressed from these models are displayed in Table 4.

Table 2 Bicarboante/carbonate hazard of irrigation water

	Bicarbonate (HCO_3) hazard of irrigation water (meq/L) [2]		
	None	Slight to Moderate	Severe
(meq/L)	<1.5	1.5-7.5	>7.5

Table 3 Kinetic data of varying initial HCO_3^- concentrations derived from the pseudo second order kinetic model

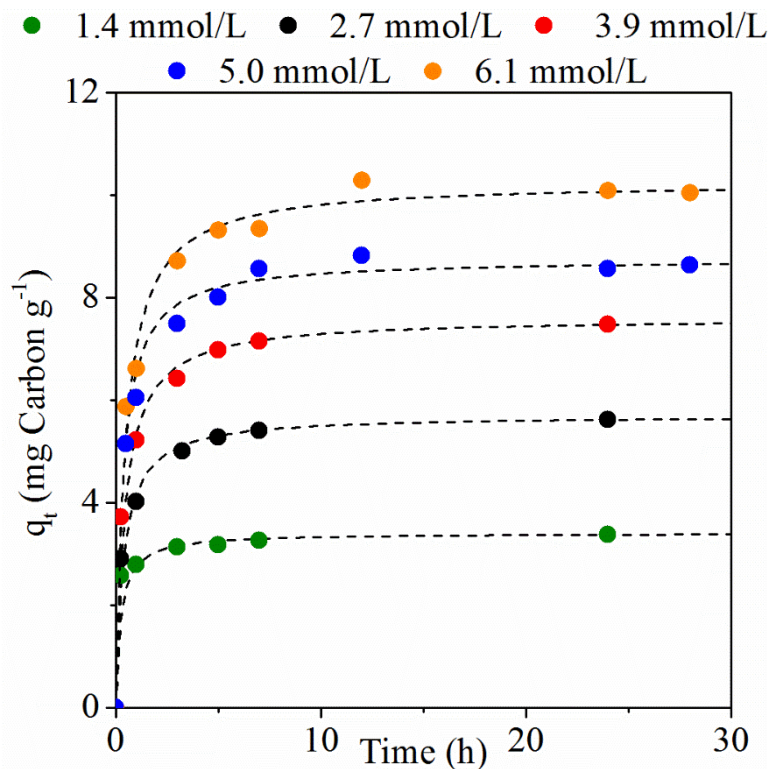| Variation of Initial HCO_3^- Concentration Kinetic Data			
Initial HCO_3^- (mmol/L)	k (g/(mg hr)	q_e (mg C /g)	r^2
1.4	1.2323	3.405	0.9999
2.7	0.4683	5.701	0.9999
3.9	0.3087	7.599	0.9998
5.0	0.3385	8.749	0.9993
6.1	0.2117	10.256	0.9996
12	0.2027	13.093	0.9995
24	0.1818	17.970	0.9998
48	0.0915	25.689	0.9990
72	0.0311	34.670	0.9991

Fig. 9 Adsoprtion as a function of HCO_3^- initial concetration. Linearly regressed kinetic fit overlaid. Initial $TiO(OH)_2$ concetration was 4 g/L in a total volume of 1 L at a pH of 8.2.
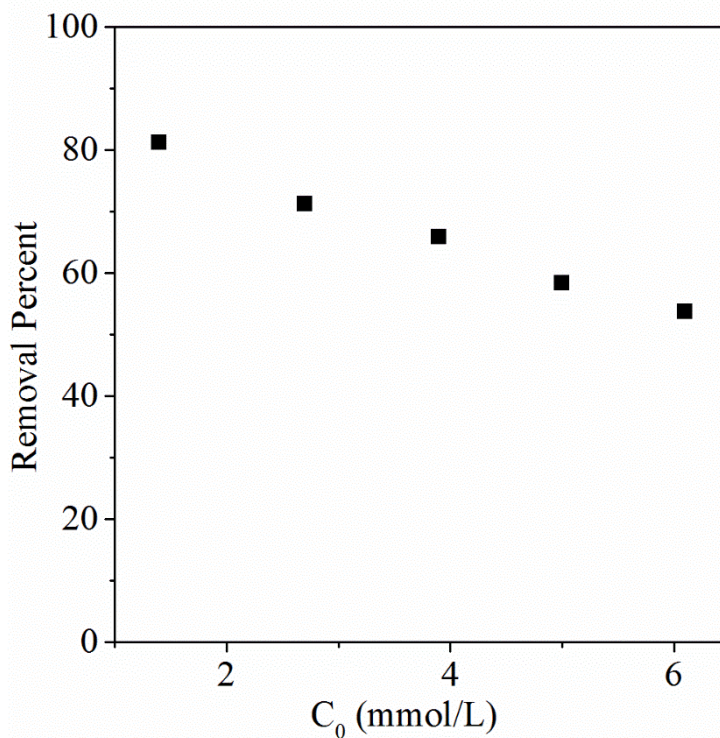

Fig. 10 Removal percentage of HCO_3^- as a function of HCO_3^- initial concetrations. Initial $TiO(OH)_2$ concetration was 4 g/L in a total volume of 1 L at a pH of 8.2.

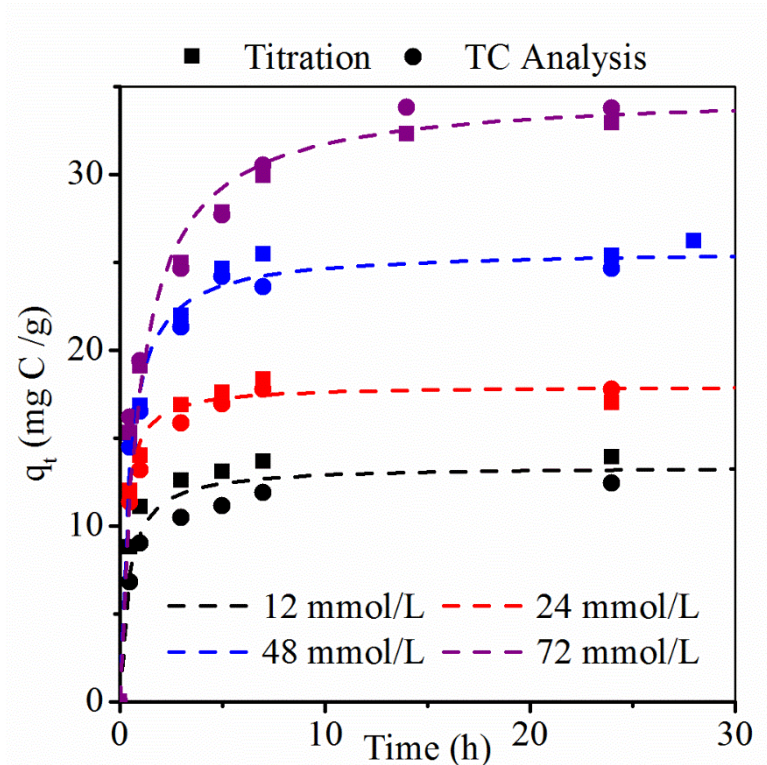**Fig. 11** HCO_3^- adsoprtion as a function of HCO_3^- initial concetration. Psuedo-second order kinetic fit overlaid. Initial $TiO(OH)_2$ concetration of 4 g/L in a total volume of 1 L at a pH of 8.2.
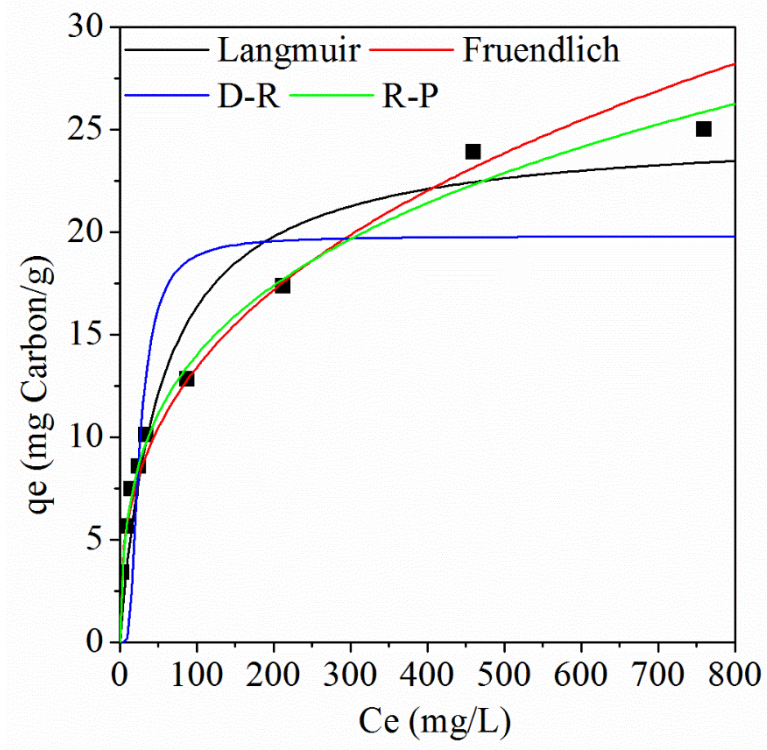

Fig. 12 HCO_3^- adsoprtion isotherms fits. Initial $TiO(OH)_2$ suspension was 4 g/L in a total volume of 1 L at a pH of 8.2.

Table 4 Isotherm parameters derived from non-linear regressions of adsorption data

Model	Parameters	
	q_m (mg/g)	25.024
Langmuir	b	0.019
	R^2	0.9358
	K_f (mg/g)	2.577
Freundlich	n	2.793
	R^2	0.9911
	q_s (mg/g)	19.795
Dubinin-Rasushkevich	k (kJ/mol)	83.715
	R^2	0.6080
	K_r (L/g)	2.696
Redlich-Peterson	a_r (mg^{-1})	0.669
	g	0.718
	R^2	0.9990

CO_3^{2-} and HCO_3^{2-}/CO_3^{2-} Adsorption Experiments

Studies of carbonate (pH~11) and bicarbonate/carbonate (pH~10) removal are still in the preliminary phase, with more experiments currently being completed. Experimental data completed thus far can be seen in Figure 12. Experiments have shown that the introduction of $TiO(OH)_2$ into a carbonate system causes the equilibrium to shift and transforms the carbonate ion into bicarbonate. This is a promising find as previous experiments have shown the adsorption of bicarbonate onto $TiO(OH)_2$ is spontaneous therefore CO_3^{2-} removal can be achieved by first its transforming into HCO_3^- and then its adsorption onto $TiO(OH)_2$.
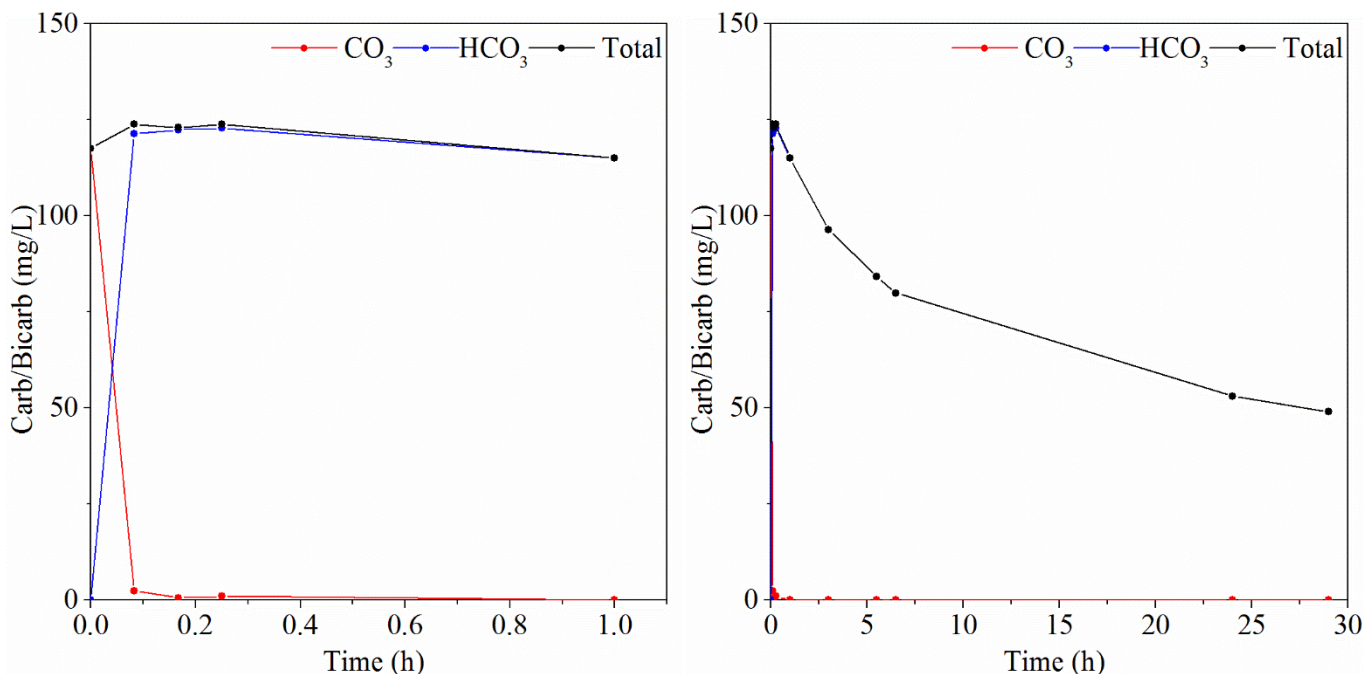
Fig. 13 CO_3^{2-} removal with an initial concetration of 125 mg/L. $TiO(OH)_2$ dose was 4 g/L in a total volume of 1 L.

5. Parties Involved, Publications, Presentations, etc.

5.1 Student Involvement and Citations

The completion of this project has been assumed by the following:

Andrew Thomas Jacobson is a PhD candidate in chemical engineering at the University of Wyoming. Andrew was the leading researcher of the project and was tasked with experimental design, experimental execution, sample analysis, and data analysis.

Maryam Irani is a PhD candidate in chemical engineering with a final examination date of May, 10 2018. Maryam was the assistant researcher to the project and helped with performing experiments.

Mohammad Ali Assiri earned his PhD in 2016 in chemistry at the University of Wyoming. He helped with the sorbent characterization experiments.

5.2 Involved Student Publications during Project Period

The following research has been published by the students involved during the project time period:

- Andrew T. Jacobson and Maohong Fan, *Evaluation of natural goethite on the removal of arsenate and selenite from water Journal of Environmental Sciences,* In Press, Available online 30 April 2018

- Maryam Irani, Andrew T. Jacobson, Khaled A.M. Gasem, Maohong Fan, *Modified carbon nanotubes/tetraethylenepentamine for CO_2 capture*, Fuel 206 (2017) 10–18.

- Maryam Irani, Khaled A.M. Gasem, Bryce Dutcher, Maohong Fan, *CO_2 capture using nanoporous TiO(OH)$_2$/tetraethylenepentamine*, Fuel 183 (2016) 601–608.

5.3 Presentations

- Andrew T. Jacobson (2017, August) *A New Multifunctional Sorbent for the Treatment of Coproduced Waters (CWs) from the Energy Industry.* Presented at Wyoming Water Development Commission Office, Cheyenne, WY.

- Andrew T. Jacobson (2018, May) *Evaluation and Development of Solid Adsorbents for Water Remediation.* Presented at PhD Preliminary Examination, Laramie, WY.

5.4 Notable Awards and Achievements

- Andrew T. Jacobson was a NSF EE Nanotechnology Fellow at UW.
- Mohammad Ali Assiri received his PhD in chemistry during the project period.
- Maryam Irani received her MS in chemical engineering during the project period.

6. References

1. Alapi, T., Gajda-Schrantz, K., Ilisz, I., Mogyorosi, K., Sipos, P., Dombi, A., Journal of Advanced Oxidation Technologies (2008), 11(3), 519-528

2. http://www.lenntech.com/applications/irrigation/bicarbonate/bicarbonate-hazard-of-irrigation-water.htm

3. Dallbauman, L., Sirivedhin, T., *Separation Science Technology* (2005) 40, 185-200.

4. Pahmer, A., Coal-Bed Methane Produce Water Treatment, US DOE Report (DE-FG01-05EW07033), 2008, 1-26.

5. Badawy, M. I., Gohary, F. El., Ghaly, M. Y., Ali, M. E. M. Journal of Hazardous Materials (2009), 169(1-3), 673-679.

6. Zang, L., Liu, C. Y., Ren, X. M., Journal of Photochemistry and Photobiology A: Chemistry (1993), 74, 267-271.

7. Patrito, E. M., Olivera, P. P., Electrochimica Acta (1998), 44, 1237-1245.

8. http://trib.com/news/state-and-regional/another-dry-year-wyoming-ranchers-prepare-for-potential-drought/article_0d9922c2-d72d-53b2-8ae0-bb701319c98f.html

9. Chan, Y. T., Kuan, W. H., Chen, T. Y., and Wang, M. K., *Water Research* (2009), 43, 4412-4420.

10. Jang, M., Shin, E. W., Park, J. K., Choi, S. I., *Environmental Science & Technology* (2003), 37, 5062-5070.

11. Foo, K.Y. & Hameed, B.H. (2010) Insights into the modeling of adsorption isotherm systems. Chem. Eng. J., 156, 2-10.