Recovery of Ammonium and Magnesium from Produced Water by Struvite Precipitation

By

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Project title: Recovery of Ammonium and Magnesium from Produced Water by Struvite Precipitation

Description of research problem and research objectives

Problem

The high volumes of fresh water used and consumed during the development of unconventional oil and gas wells has especially garnered public attention. An average of 2.5 million gallons (~10,000 m^3) of water is used to hydraulically fracture a single well (Liden et al., 2018). Produced water, as the largest waste stream generated during unconventional oil and gas production, is often briny, and contaminated with a complex mixture of organics (Riley et al., 2018; Silva et al., 2017). The major hindrance to the wastewater treatment and reuse applications is the high salinity of produced water, measured as total dissolved solids (TDS) including sodium, potassium, bromide, calcium, fluoride, nitrate, phosphate, chloride, sulfate, magnesium, and ammonium (He et al., 2017; Sardari et al., 2018).

Our preliminary analysis of produced water from the Permian Basin has shown that the initial concentration of ammonium, magnesium, and calcium are around 600 mg/L, 700 mg/L, and 4300 mg/L, respectively. Water contaminated with ammonium is harmful both to human health and water body (Huang et al., 2014). Pollution problems related to the ammonium discharge of

produced water commonly include eutrophication and dissolved oxygen depletion in water bodies as well as toxicity to the aquatic life (Muhmood et al., 2018). Excess ammonium intaking can lead to blue baby syndrome, liver damage, and gastric cancer (Liu et al., 2011). Therefore, developing harmless produced water treatment methods is extremely urgent, and removing ammonium from produced water is the key.

Some physical-chemical methods such as ammonia stripping, zeolite adsorption, membrane separation, and microwave radiation have been used to remove high concentration of ammonia from wastewater (Huang et al., 2014; Muhmood et al., 2018). However, Sustainable produced water treatment needs to lower the treatment cost and facilitate the change of treatment technology from removal-centered approaches to recovery-centered processes. In fact, many pollutants in produced water can be reclaimed as reusable resources. For instance, produced water from the Permian Basin is in rich of NH_3-N and Mg, which is an important agricultural nutrient source in the US. Struvite ($MgNH_4PO_4 \cdot 6H_2O$), a valuable slow release fertilizer (Doyle and Parsons, 2002), can be precipitated from produced water to recover ammonium and magnesium simultaneously by adding an external phosphorus source (such as Na_2HPO_4, H_3PO_4, and KH_2PO_4) and/or a magnesium source (such as $MgCl_2$, $MgSO_4$, MgO, $MgCO_3$ and sea salt) (Huang et al., 2017; Muhmood et al., 2019; Wu et al., 2018). The solubility of struvite is 23 mg/100 mL (Doyle and Parsons, 2002), thus, it can naturally crystallize when the combined ion concentration of magnesium, ammonium, and phosphate exceeds its solubility. Struvite forms according to the general reaction shown below:

$$Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow$$
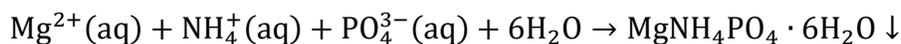
Objectives

The main objective of this project is to simultaneously recover ammonium and magnesium from produced water by struvite precipitation. The optimal conditions of struvite precipitation will be explored while the effects of organic composition, solution pH, Mg/N/P molar ratio, and the competitive cation Ca^{2+} on struvite production will be assessed.

Methodology

Produced water

Produced water samples utilized in this study were collected from the Permian Basin in Jal, New Mexico, USA. Prior to use, produced water was filtered by filter paper in order to minimize the impact of suspended solids. The main characteristics of the filtered produced water are presented in Table 1.

Table 1. The main characteristics of raw produced water.

Parameter	Symbol	Unit	Value
Physiochemical characteristics			
pH	-	-	7.35 ± 0.10
Total organics	TOC	mg L^{-1}	29.3 ± 1.2
Macronutrients			
Ammonium	NH$_3$-N	mg L^{-1}	598.6 ± 10.2
Potassium	K	mg L^{-1}	968.5 ± 30.5
Calcium	Ca	mg L^{-1}	4968.6 ± 105.4
Magnesium	Mg	mg L^{-1}	695.8 ± 25.4
Plant essential metals plant			
Zinc	Zn	mg L^{-1}	2.59 ± 0.08
Copper	Cu	mg L^{-1}	1.67 ± 0.11
Iron	Fe	mg L^{-1}	1.66 ± 0.03
Manganese	Mn	mg L^{-1}	0.66 ± 0.02
Nickel	Ni	mg L^{-1}	0.02 ± 0.004
Plant non-essential metals			
Lead	Pb	mg L^{-1}	0.16 ± 0.01
Arsenic	As	mg L^{-1}	0.87 ± 0.09

Struvite recovery without calcium pretreatment

A series of batch experiments were performed without calcium pretreatment to evaluate the influence of Mg:P molar ratio and pH on struvite recovery from produced water. Na$_2$HPO$_4$ was selected as the phosphorus source to adjust Mg:P molar ratio to the desired value (1:1, 1:2, 1:3, 1:5, and 1:7). The solution pH was then adjusted to the desired value (8.0, 8.5, 9.0, 9.5, and 10.0) by using 0.5 M NaOH, which has been suggested as the possible pH condition for struvite recovery from various wastewaters (Wang et al., 2005). The mixed solution was stirred at 200 rpm for 30 min, followed by precipitation for another 30 min. When the reaction was completed, 5 mL supernatant was taken and filtered through a 0.22 μm-pore-size membrane for the composition analysis. Then the obtained precipitates were washed twice with deionized water and dried at room

temperature for 36 h before the subsequent characterizations. All experiments were carried out at room temperature in triplicate according to procedures described above.

Calcium pretreatment

Na_2CO_3 stock solution was added into produced water to precipitate Ca^{2+} as $CaCO_3$. In order to determine the optimal dosage of Na_2CO_3 for Ca^{2+} removal, the molar ratios of $Ca^{2+}:CO_3^{2-}$ were designed as 1:1, 1:1.2, 1:1.4, 1:1.5, 1:1.6, and 1:1.8. When the reaction was completed, 5 mL supernatant was taken and filtered through a 0.22 μm-pore-size membrane to determine the Ca^{2+} removal efficiency and Mg^{2+} loss rate in produced water.

Effect of pH and Mg/N/P molar ratio

To investigate the effect of pH and Mg/N/P molar ratio on struvite precipitation from produced water, two runs of batch experiments were performed by using pretreated produced water. One run of struvite precipitation was conducted with variable initial pH of 8.0, 8.5, 9.0, 9.5 and 10.0. The other one was carried out with varying Mg/N/P molar ratio of 1:1:1, 1.2:1:1.2, 1.5:1:1.5, and 1.8:1:1.8. As shown in Table 1, the NH_3-N molar concentration in produced water was greater than Mg^{2+} molar concentration, making Mg^{2+} become a limited factor for struvite precipitation from produced water. Therefore, $MgCl_2 \cdot 6H_2O$ and Na_2HPO_4 were selected as magnesium and phosphorus sources and added into pretreated produced water to meet the desired Mg/N/P molar ratio values. Each parameter was varied while keeping the other one constant. The mixed solution was then treated following the same procedures as described above.

Analysis

The concentrations of NH_4^+, Mg^{2+}, K^+, Ca^{2+}, Na^+, Cl^-, and SO_4^{2-} in produced water samples were quantified by using an ion chromatograph (IC, ICS-2100, Dionex, Sunnyvale, CA, USA). A pH and conductivity meter (Model 431-61, Cole-Parmer, Vernon Hills, IL, USA) was used to measure electrical conductivity and pH of all liquid samples. Total organic carbon (TOC) in water samples was determined by a carbon analyzer (Shimadzu TOC-L, Kyoto, Japan). An inductively coupled plasma optical emission spectrophotometer (ICP-OES, PerkinElmer, Waltham, MA, USA) was employed to measure the concentrations of heavy metals (Cr, Cd, Cu, As, Fe, Pb, Ni, Mn, and Zn). The morphology of dried precipitates was characterized using a scanning electron microscope-energy dispersive spectrometer (SEM-EDS, S3400N Type II, Hitachi, Pleasanton, CA, USA). The crystalline structure of the obtained precipitates was identified using an X-ray

diffraction analyzer (XRD, MiniFlex II, Rigaku, Japan), which was excited with Cu Kα ($\lambda = 1.5406$ Å) at 45 kV and 40 mA.

In this study, the purity of struvite in the obtained precipitates was determined according to the following procedures. First, the dried precipitates were dissolved in 1% HNO_3, and the NH_4^+ concentration was then quantified by an ion chromatograph. Next, the quantity of struvite in the precipitates can be estimated based on the content of NH_4^+ present in the dried precipitates. Finally, the purity of struvite ($P_{struvite}$) was calculated according to Eq. (1) as follows:

$$P_{struvite} = \frac{M_{struvite}}{M_{Total}} \times 100\% \qquad (1)$$

Where, $M_{struvite}$ and M_{Total} represent the masses of struvite and the total mass of the dried precipitates, respectively.

Graphical abstract
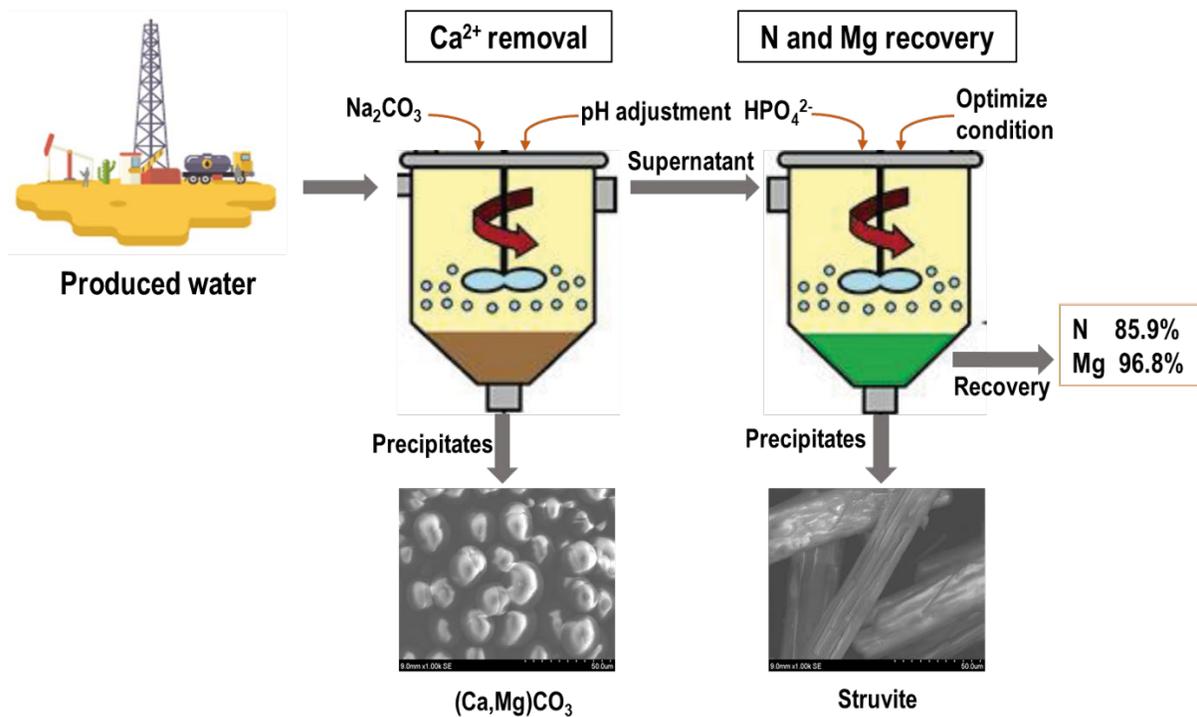
Results, conclusions, and recommendations for further research

Struvite recovery without calcium pretreatment

To investigate the feasibility of direct struvite recovery from produced water without calcium pretreatment, batch experiments were performed at the Mg:P molar ratio of 1:1~1:7 with a pH range of 8~10. As shown in Fig 1a, without calcium pretreatment, the removal efficiency of NH$_3$-N (0.3~6.1%) in produced water were very low even though the phosphorus source was sufficient. In contrast, the removal efficiencies of Ca^{2+} and Mg^{2+} increased significantly with an increase in Mg:P molar ratio (Fig 1b and 1c). The highest Ca^{2+} (98.3%) and Mg^{2+} (77.8%) removal efficiencies occurred at pH 10 and Mg:P molar of 1:7. It was reported that the calcium present in water may affect struvite precipitation (Le Corre et al., 2005), since the calcium can interact effectively with phosphate to form calcium phosphate (Ca$_3$(PO$_4$)$_2$) according to the following equation:

$$3Ca^{2+}(aq) + 2HPO_4^{2-}(aq) \rightarrow Ca_3(PO_4)_2 \downarrow + 2H^+$$
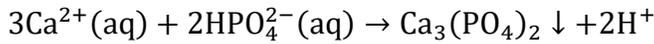
The low removal efficiency of NH$_3$-N can be attributed to the high initial concentration of calcium (4968.6 ± 105.4 mg/L) in raw produced water. Therefore, a pretreatment to effectively remove calcium is urgently required to recover struvite from produced water.
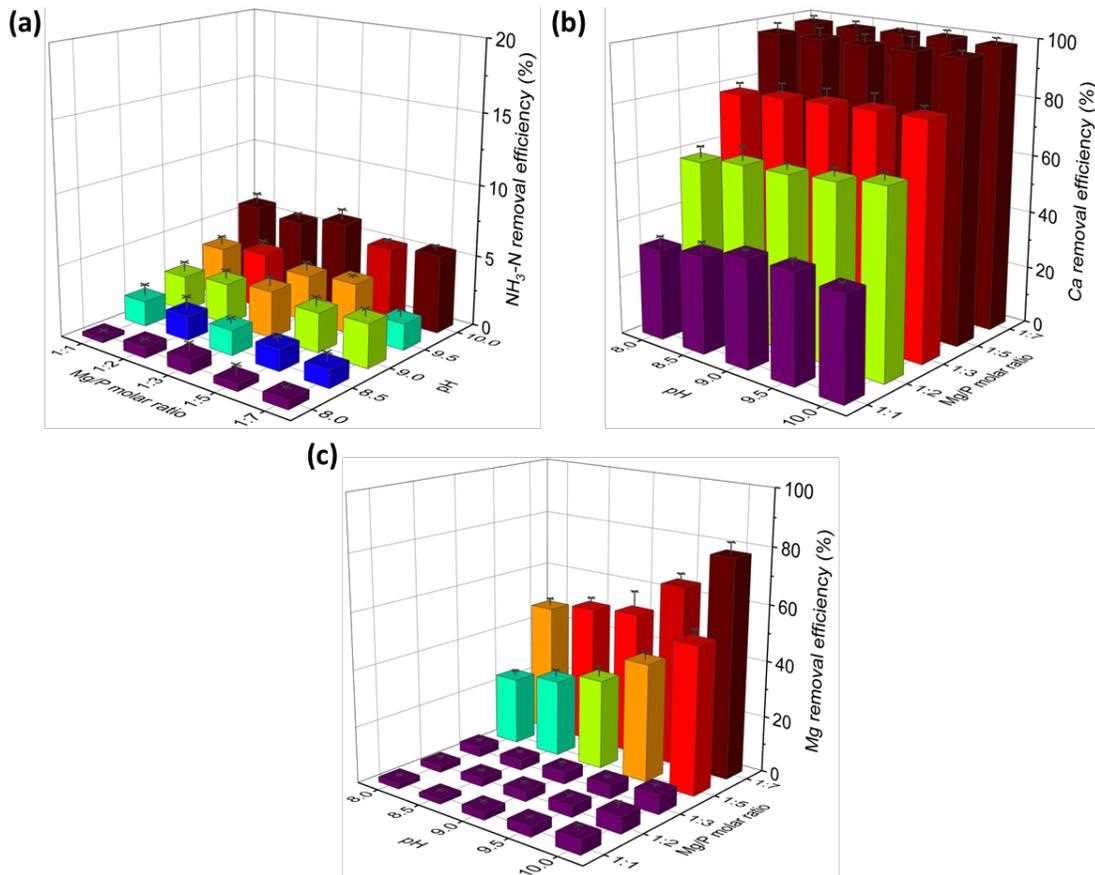

Fig. 1. The removal efficiency of (a) NH$_3$-N, (b) Ca, and (c) Mg during struvite recovery without calcium pretreatment.

Calcium pretreatment

High calcium concentration in produced water can lead to an unsatisfied struvite recovery efficiency. To solve this problem, calcium pretreatment experiments were conducted by adding Na_2CO_3 into raw produced water. The dosage optimization experiment was performed at the molar ratios of Ca^{2+} : CO_3^{2-} from 1:1 to 1:1.8. When the molar ratio of Ca^{2+} : CO_3^{2-} increased from 1:1 to 1:1.2, 1:1.4, 1:1.5, 1:1.6 and finally 1:1.8, the Ca^{2+} removal efficiency was 89.7 ± 2.4%, 95.9 ± 0.9%, 96.0 ± 1.7%, 96.6 ± 1.2%, 97.4 ± 1.9% and 97.6 ± 1.1%, respectively (Fig. 2). With the addition of carbonate (CO_3^{2-}) in the produced water, some magnesium precipitated as $MgCO_3$ resulting in loss of Mg^{2+} at 8.3 ± 2.5% and 31.3 ± 0.5% when the Ca^{2+} : CO_3^{2-} molar ratio was 1:1 and 1:1.2. The loss rate was significantly increased to 64.9 ± 5.9% when the Ca^{2+} : CO_3^{2-} molar ratio was 1:1.4. Considering both the Mg^{2+} loss rate and Ca^{2+} removal efficiency, the molar ratio of Ca^{2+} : CO_3^{2-} at 1:1.2 was selected to be the optimal condition for calcium pretreatment.
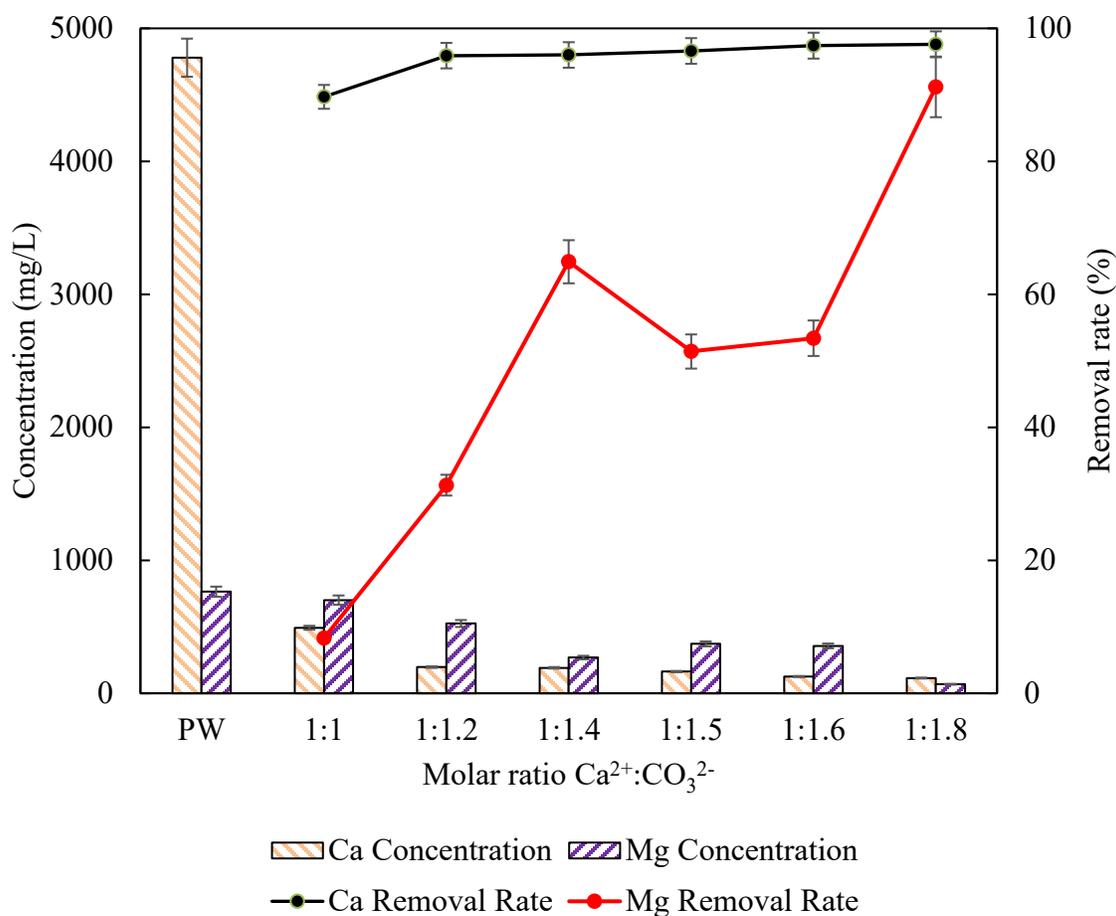

Fig. 2. The removal rates of Ca^{2+} and Mg^{2+} in the supernatant of the pretreated produced water with different molar ratios of Ca^{2+} : CO_3^{2-}.

Effect of pH and Mg/N/P molar ratio

To determine the effects of pH and Mg/N/P molar ratio on struvite precipitation from produced water, the experiments were performed at pH between 8 and 10 with the Mg/N/P molar ratio range of 1:1:1~1.8:1:1.8. It is obvious that the NH_3-N recovery efficiency enhanced with increasing pH value and Mg/N/P molar ratio (Fig. 3a). As shown in Fig. 3a, when the pH value increased from 8 to 9.5 with the Mg/N/P molar ratio of 1.5:1:1.5, the NH_3-N recovery efficiency rapidly increased, reaching a maximum value of 85.9% at pH 9.5. Fig. 3b shows that a significantly higher magnesium recovery efficiency (> 96.8%) was obtained when the Mg/N/P molar ratio escalated from 1:1:1 to 1.5:1:1.5 at pH 9.5~10, indicating that the Mg/N/P molar ratio of 1.5:1:1.5 at pH 9.5 could achieve the highest ammonium recovery efficiency while maximizing magnesium resource recovery in produced water.
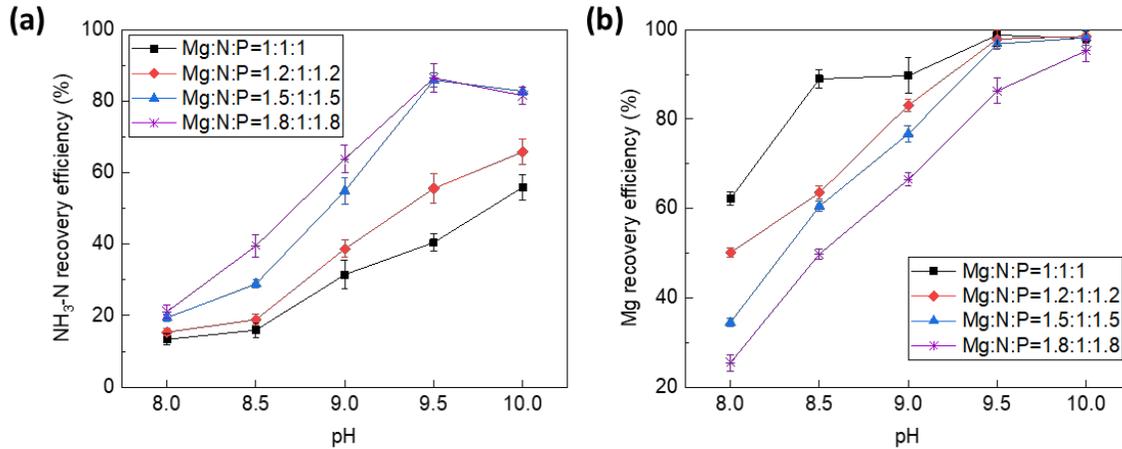

Fig. 3. The variations of (a) NH_3-N and (b) Mg^{2+} recovery efficiency with different solution pH and Mg/N/P molar ratio.

Precipitate characterization

The morphology and microstructure of the struvite produced at pH 9.5 with the Mg/N/P molar ratio of 1.5:1:1.5 was characterized. The SEM and EDS results show that the struvite crystals had an orthorhombic structure (Fig. 4a and 4b). The positions and intensities of the peaks on the X-ray diffractogram were similar to that of the reference struvite diffractogram from the International Center for Diffraction Data (MAP, JCPDS 77-2303) (Fig. 4c). It was subsequently found that most of the obtained precipitate was struvite.
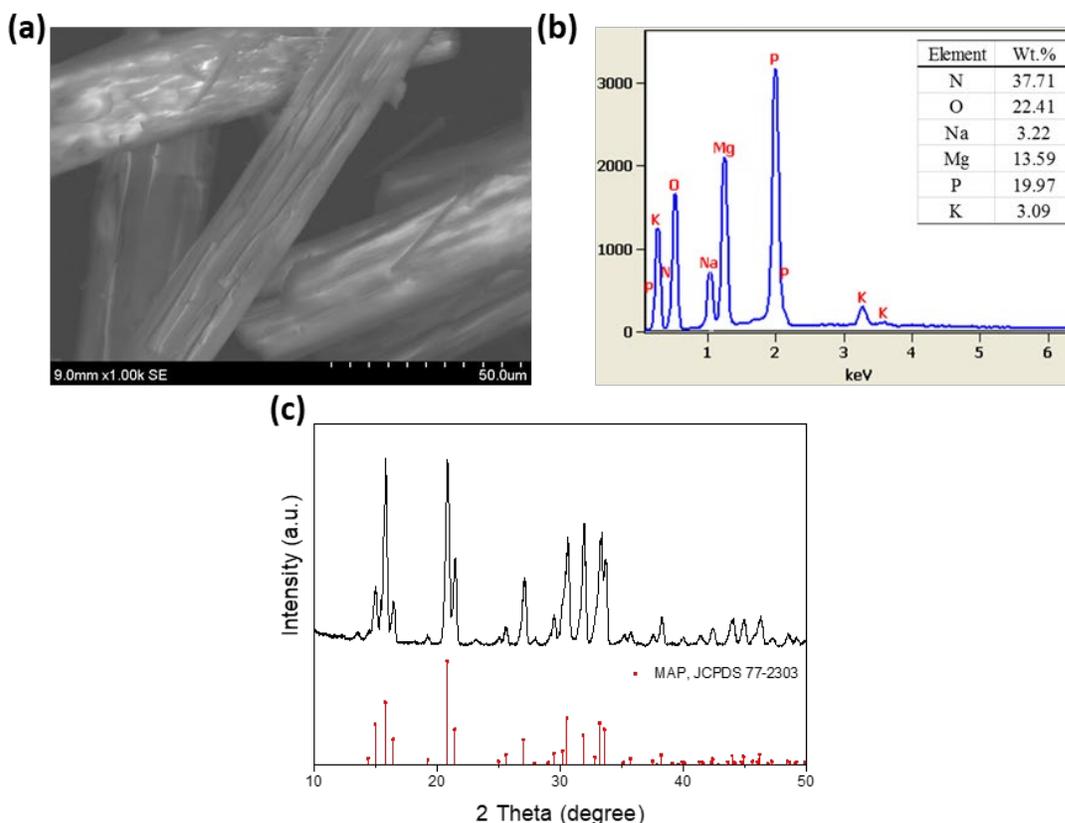
Fig. 4. The (a) SEM photo; (b) EDS peaks; and (c) XRD spectrum of the precipitates obtained at the Mg/N/P molar ratio of 1.5:1:1.5 and pH 9.5 with calcium pretreatment.

Evaluation of the obtained struvite for agricultural use

It has been reported that the presence of heavy metals and organic matters in struvite could limit its use as fertilizers (Muhmood et al., 2019). If high concentrations of heavy metals and organic matters are coprecipitated during this struvite recovery process, it will influence the beneficial agricultural use of struvite. Therefore, changes in heavy metals (Table 2) and total organic matters (TOC, Fig. 5) concentrations before and after struvite precipitation were examined in order to assess the quality of the obtained struvite as a fertilizer. The concentrations of As, Fe, Mn, and Ni in raw produced water before struvite precipitation were 0.8758, 1.66, 0.6583, and 0.0244 mg/L, respectively. These concentrations were reduced to less than the method detection limit (MDL) after calcium pretreatment process, indicating that heavy metals in produced water were removed along with the calcium pretreatment process. Therefore, it can be speculated that the obtained struvite after calcium pretreatment process was free of heavy metals. As shown in Fig. 5, there was almost no difference in the TOC concentration of produced water before and after

struvite precipitation, so it was inferred that organic matters were not accumulated in the obtained struvite during the struvite precipitation process. In addition, it was found that the struvite purity was around 92.8% when the Mg/N/P molar ratio was 1.5:1:1.5 at pH 9.5. Thus, it can be concluded that the quality of struvite obtained from produced water was sufficient for use as a fertilizer on agriculture.

Table 2. Heavy metal contents in produced water before and after struvite precipitation.

| Elem	Raw produced water	Pretreated produced water	Produced water after struvite precipitation	Units	MDL
As	0.8758	ND	ND	mg/L	0.1
Cd	ND	ND	ND	mg/L	0.001
Cr	ND	ND	ND	mg/L	0.003
Fe	1.66	ND	ND	mg/L	0.0287
Mn	0.6583	ND	ND	mg/L	0.0017
Ni	0.0244	ND	ND	mg/L	0.002
Pb	ND	ND	ND	mg/L	0.007
Zn	ND	ND	ND	mg/L	0.0013

MDL: Method Detection Limit; ND: Non-Detect.
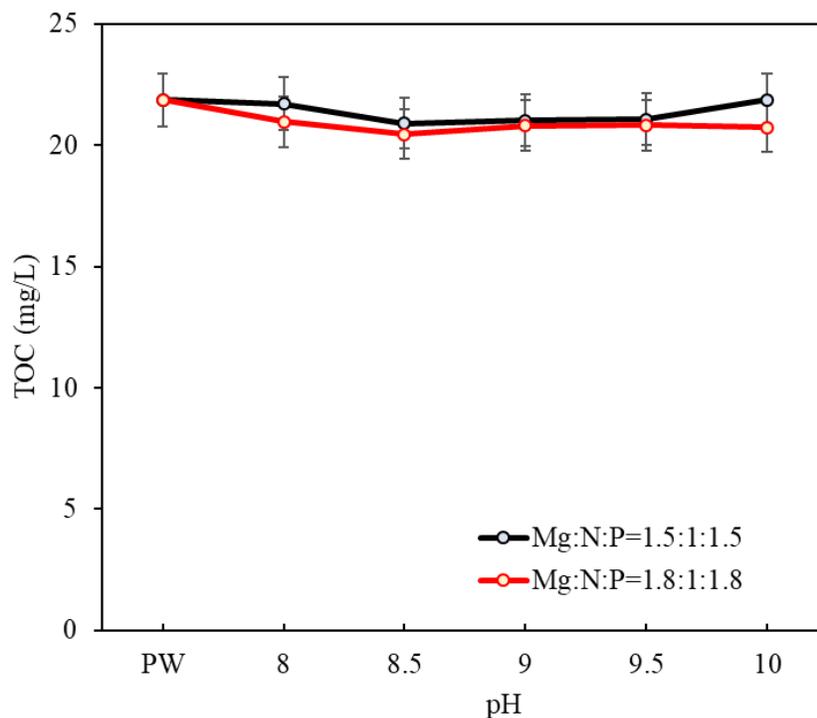
Fig. 5. The concentration of TOC in raw produced water, and produced water after struvite precipitation with different solution pH (Mg:N:P = 1.5:1:1.5 and 1.8:1:1.8).

This work has demonstrated the successful recovery of ammonium and magnesium as high-quality struvite from produced water with a NH_3-N recovery efficiency of 85.9% and a Mg^{2+}

recovery efficiency of 96.8%, which will encourage further efforts to develop new methods for resource recovery from produced water.

Beneficiaries of research

The proposed processes in this research could remove toxic ammonium in produced water and recover the beneficial minerals as resource. The precipitated struvite can be potentially used as a slow release fertilizer and it has been suggested to display excellent fertilizer qualities under specific conditions when compared with standard fertilizers. In addition to the removal of ammonium and magnesium in produced water, the calcium in produced water could also be removed through the calcium pretreatment process. Therefore, the proposed process is also a promising pretreatment process to minimize the scale formation in membrane-based desalination for the treatment of produced water. Considering the low cost and relatively simple technology, struvite precipitation process has the potential to simultaneously recover ammonium and magnesium from produced water in a large-scale application. Thus, the oil & gas company and farmers will benefit from my research results.

Budget

By May 15th, 2019, $1483.44 has been used for the purchase of chemicals and supplies, $214.25 has been used for the lab analysis, $4516.56 has been used for RA salary. The remaining balance is zero.

Presentations

➢ **Hu, L.**, Yu, J., Luo, H., Xu, P., Zhang Y. (2019) Recovery of ammonium, potassium and magnesium from produced water by struvite precipitation. The 2019 AEESP Research and Education Conference, May 14-16, **2019**, Phoenix, AZ

➢ **Hu, L.** and Zhang, Y. (2019) Recovery of ammonium, potassium and magnesium from produced water by struvite precipitation. Two Nations One Water Summit, April 23-25, **2019**, Las Cruces, NM.

➢ **Hu, L.** and Zhang, Y. Recovery of ammonium, potassium and magnesium from produced

water by struvite precipitation as a slow release fertilizer. New Mexico Produced Water Conference, November 15-16, **2018**, Santa Fe, NM.

➢ **Hu, L.** and Zhang, Y. Recovery of ammonium, potassium and magnesium from produced water by struvite precipitation. 63rd Annual New Mexico Water Conference, October 17-18, **2018**, Las Cruces, NM.

Other students or faculty members who assisted on

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Acknowledgments

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