# **Crop Fertilizer Recovery from Produced Water**

By

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Project Title: Crop Fertilizer Recovery from Produced Water

## 1. Description of research problem and research objectives

1.1.Research problem.

Produced water (PW) is the largest waste stream resulting from exploration and production of oil and gas. It is estimated that more than 42 billion gallons of PW were generated in New Mexico's Permian Basin in 2018 [1]. Most PW is naturally occurring highly saline water and typically includes specialty chemicals added to enhance oil and gas recovery. In addition, PW may also include valuable nutrients such as potassium, calcium, nitrite, phosphate, magnesium, and ammonium (NH<sub>4</sub><sup>+</sup>) that are specific to the geographical location. It is reported that 40% of the PW generated is discharged directly to the environment posing a severe threat to the ecosystem [2]. Therefore, management of PW is a critical issue for this industry.

Ammonium (NH<sub>4</sub><sup>+</sup>) is a regulated pollutant in the PW due to its high concentrations, averaging at 127 mg/L in the US [3] and 432 mg/L in the Permian Basin [4] which produces more than 50% of all oil and gas in the US [5]. Excess NH<sub>3</sub> can harm the ecosystem by causing eutrophication in receiving waters and reducing dissolved oxygen require for aquatic organisms [6]. Consequently, effective NH<sub>4</sub><sup>+</sup> removal is required before PW is reused or discharged. Thus the U.S. Groundwater Protection Council (GWPC) reports that some National Pollutant Discharge Elimination System (NPDES) permits, issued by the U.S. Environmental Protection Agency (EPA) to regulate PW discharges to surface waters, impose NH<sub>3</sub> concentration limits as low as 1 mg/L [7,8]. Moreover, the EPA's Ambient Water Quality Criteria (AWQC) for NH<sub>3</sub> in freshwater considering aquatic life, underscore its toxicity with acute and chronic limits of 17 mg/L and 1.9 mg/L, respectively at pH 7.0 and 20°C temperature [9].

It has been reported that recovering nitrogen resources in PW as fertilizers can potentially offset approximately 1.5% of the nitrogen fertilizer demand that is currently being served by the energyintensive Haber- Bosch process [3]. This highlights the potential economic and environmental benefits of ammonia recovery compared to conventional ammonia removal methods, which often transfer the pollutant to another waste stream or dissipate to the atmosphere as N<sub>2</sub>. Other motivations behind the N-recovery from PW include the high cost incurred in nutrient removal to meet the discharge standards; potential for eutrophication and NH<sub>3</sub> toxicity that adversely affect aquatic life in the receiving waters; and the high costs associated with the production of virgin crop fertilizer using the traditional Haber-Bosch process. Furthermore, recovering ammonia from PW could be a key strategy in nitrogen management, contributing to the circular economy within the oil and gas industry and advancing progress towards United Nations Sustainable Development Goals (2, 6, and 11) [10].

#### 1.2. Objectives

The objectives of this project are to evaluate the feasibility of recovering  $NH_4^+$ -N from raw PW as a high-purity crop fertilizer in the form of ammonium sulfate,  $(NH_4)_2SO_4$ . It is proposed to demonstrate a novel gas permeable membrane reactor (GPMR) as an efficient process for recovering  $NH_4^+$ -N from PW. Specific goals of this study are to:

- i) Develop a GPM reactor for ammonia recovery from PW.
- ii) Optimize process conditions for ammonia recovery from PW.
- Assess the elemental composition and purity of the recovered (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> against the theoretical compositions of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4.</sub>
- iv) Assess the potential for fouling of GPM when applied to PW.
- v) Compare the N-recoveries from PW using GPM technology against those of conventional technologies reported in the literature.
- vi) Results of this study will also be used to validate a process model developed in our related studies [11] for predicting N-recovery by the GPM.

#### 2. Theory

The total ammoniacal nitrogen (TAN) in PW is in the form of ionized ammonia (NH<sub>4</sub><sup>+</sup>) and free ammonia (NH<sub>3</sub>). The NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> are in equilibrium based on the dissociation coefficient of ammonium ions as Eq 3 where  $[NH_3]_{aq}$ ,  $[H^+]_{aq}$  and  $[NH_4^+]_{aq}$  are aqueous phase molar concentrations of NH<sub>3</sub>, H<sup>+</sup> and NH<sub>4</sub><sup>+</sup> respectively and  $K_a$  is the dissociation coefficient of NH<sub>4</sub><sup>+</sup>.

$$[TAN]_{aq} = [NH_4^+]_{aq} + [NH_3]_{aq}$$
Eq 1

$$NH_4^+ \leftrightarrow NH_3 + H^+$$
 Eq 2

$$K_{a} = \frac{[NH_{3}]_{aq}[H^{+}]_{aq}}{[NH_{4}^{+}]_{aq}}$$
Eq 3

Accordingly, when the pH of the PW was increased to above pKa of ammonium ions (9.26 at 25°C), more than 50% of TAN is in the form of NH<sub>3</sub>. Thus, the PW pH is increased above 9.26 at the beginning of each experiment. As the NH<sub>3</sub> molecules reach the membrane, they partition into the air-filled pores of the membrane as gaseous NH<sub>3</sub> according to Henry's law [12]. These gaseous NH<sub>3</sub> molecules diffuse through the pores of the membrane and enter the tube interior where the acid (sulfuric) is recirculated. The acid pH was controlled at a very low value of 2.0 to maintain very low concentrations NH<sub>3</sub> (~0), enabling efficient NH<sub>3</sub> transfer due to the significant concentration gradient across the GPM. As the gaseous NH<sub>3</sub> molecules exit the membrane, they are protonated to form NH<sub>4</sub><sup>+</sup> (Eq 4). These NH<sub>4</sub><sup>+</sup> react with the sulphate ions (SO<sub>4</sub><sup>-2</sup>) to form

 $(NH_4)_2SO_4$  as Eq 5. It's noteworthy that the mass transfer through the GPM results in decreased PW pH due to the continuous forward shift of the equilibrium in Eq 2, releasing protons.

$$NH_3 + H^+ \Leftrightarrow NH_4^+$$
Eq 4  
$$2NH_4^+ + SO_4^{-2} \to (NH_4)_2SO_4$$
Eq 5

#### 3. Research methodology.

1.1. Produced water sampling and characterization.

The raw PW utilized in this study were collected from the Permian Basin in Jal, New Mexico, USA. The total solids (TS) and total dissolved solids (TDS) content were measured following Standard Methods for the Examination of Water and Wastewater, 2540 B and 2540 C, respectively [13]. The PW sample was filtered (1.5 µm Whatman® grade 934-AH filter papers) to remove particulates and analyzed for total organic carbon (TOC); inorganic carbon (IC) and TAN. TOC and IC were analyzed using a TOC-VCPH analyzer (Shimadzu Corp., Kyoto, Japan) following Standard Methods for the Examination of Water and Wastewater, 5310. The TAN concentration was analyzed using HACH® DR6000TM UV/VIS spectrophotometer, following U.S. Environmental Protection Agency (EPA) compliant Salicylate TNT methods 10301 and 10205. The pH and electrical conductivity (EC) were measured using a PC800 benchtop pH/conductivity meter (Apera Instruments, Europe, GmbH). The major elements (Al, B, Ca, Li, Mg, K, Na, Sr, Zn) and heavy metals (Ba, Cd, Co, Cr, Fe, Mn, Mo, Ni, As) were analyzed using Inductively coupled plasma - optical emission spectrometry (ICP-OES) - Perkin Elmer Avio 550 Max. The anions (Br-, Cl-, SO<sub>4</sub><sup>-2</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>) were analyzed using ion chromatography. The phenolphthalein alkalinity and the total alkalinity of the PW were analyzed using Hach Test Kit, Model AL-DT.

1.2. Developing the GPM reactor for ammonia recovery from PW.

The bench-scale non-pressurized GPM reactor used in this study was fabricated out of expanded polytetrafluoroethylene (ePTFE) tube from Zeus Industrial Products Inc., Orangeburg, SC, USA

with an outer diameter of 11.1 mm and thickness of 0.2 mm. The membrane tube was submerged in the raw PW (feed). The headspace in the reactor vessel was minimized to less than 10% of the volume of the feed waste stream to ensure negligible partitioning of ammonia into the headspace during the experiments. Adsorption solution in product side (sulfuric acid, H<sub>2</sub>SO<sub>4</sub>) was circulated through the GPM tube by a peristaltic pump (Masterflex L/S® series pump with Easy-Load® II pumphead). Tygon® E-Lab (E-3603) tubes were used for all the interconnections. The feed was stirred using a variable speed stirrer plate (N-CON Systems Co., Inc.) to reduce mass transfer resistance. The tests were conducted at room temperature. A schematic diagram of the reactor design is shown in Figure 1.



Figure 1: Schematic diagram of the GPM reactor used for ammonia recovery from raw PW [1-feed (Raw PW); 2- tubular GPM; 3- magnetic stirrer; 4- peristaltic pump; 5- product-side reservoir; 6- temperature probe; 7- pH probe; 8- pH controller; 9- concentrated H<sub>2</sub>SO<sub>4</sub>- dosing solution 1M H<sub>2</sub>SO<sub>4</sub>, 10- concentrated NaOH- dosing solution 10 M NaOH]

The initial adjustment of the feed pH was done with 10M NaOH (Sigma-Aldrich) in the closed reactor. The product side solution initiated with 150 mL of dilute sulfuric acid at pH =2, made from 98% sulfuric acid (Sigma-Aldrich). A pH controller (Bluelab Corporation Limited, New Zealand) was used to maintain the acidic pH of the product side solution at 2.0 throughout the experiment by addition of 1 M sulfuric acid. The pH of the feed was monitored throughout the experiment to evaluate changes in pH due to release and accumulation of protons by dissociation of NH<sub>4</sub><sup>+</sup>. The hourly TAN concentration of the feed was measured using a HACH<sup>®</sup> DR6000<sup>TM</sup> UV/VIS spectrophotometer in duplicates following Salicylate TNTplus<sup>®</sup> method 10205 and 10301. The

volume of the samples collected for TAN measurement (20  $\mu$ L) is considered negligible to cause any difference in the TAN concentration in the reactor. The experiments proceeded until the change in hourly feed TAN concentration was less than 10%. At the end of each experiment, the TAN concentration in the product solution was determined in duplicate using the Salicylate TNTplus<sup>®</sup> method 10205 or 10301 to quantify TAN recovery. Samples of the recovered (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution was oven-dried at 70°C for 24 hr to crystallize (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> [11,14].

#### 3.3. Optimizing process conditions for produced water

The initial experiments were conducted following the optimum conditions reported in Munasinghe -Arachchige et al. [11], using a feed mixing speed of 254 rpm, a product pH of 2.0, a feed pH of 10.0 and an acid circulation rate of 25 mL/min. After achieving 100% TAN removal under these conditions, the initial feed pH was optimized for produced water by comparing removal and recovery efficiencies at pH 10.0 (Experiment E1), 9.8 (Experiment E2), and 9.6 (Experiment E3). This aimed to balance removal and recovery efficiencies against the cost of alkaline agents consumed for pH adjustment.

#### 3.4. Evaluation of ammonium sulphate product purity

Oven-dried (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> crystals (0.1 g) were dissolved in 50 ml of 10% trace pure HNO<sub>3</sub>. The resulting solution was analyzed for the elemental concentrations of As, Cd, Cr, Mo, Ni, Pb, Se, Cu and Zn using inductively coupled plasma optical emission spectrometry (ICP-OES) according to EPA method 200.7 [15]. These concentrations were compared with the guidelines for land application of wastewater-derived biosolids in the US and EU [16].

The  $(NH_4)_2SO_4$  crystals were observed under the scanning electron microscope equipped with energy dispersive X-ray detectors (SEM-EDX) (SU7000 for SEM and Ultima<sup>®</sup> max EDS detectors) and the elemental compositions obtained were compared with the theoretical composition of pure  $(NH_4)_2SO_4$ . 3.5. Characterization of PW and precipitates after the GPM treatment.

The raw PW sample after GPM was characterized for pH, TAN, major elements (Al, B, Ca, Li, Mg, K, Na, Sr, Zn), TOC and IC. The PW after the GPM was filtered using 0.45 µm (Millipore Nylon membrane filter papers) and the precipitates were analyzed using the SEM-EDX analyzer to identify the precipitated compounds.

3.6. Assessment of the potential for fouling of GPM when applied to PW

A GPMR, fabricated as detailed in Section 3.2, was operated in fed-batch mode under optimized conditions to treat twenty 100 mL batches over a 142.5-hour period. The product side was initiated with a 200 mL sulfuric acid solution (pH 2.0), which was reused for ammonia recovery from all batches. Feed pH was continuously monitored throughout the experiments. Overall flux decline was assessed, and membrane characterization was conducted via SEM-EDX to identify foulant composition. Additionally, changes in membrane hydrophobicity were evaluated by measuring water contact angle before and after operation.

#### 3.7. Validation of GPMR process model for ammonia recovery from PW

A previous study at NMSU had reported on the development of the following semi-empirical process model to predict the temporal decline of the feed-side TAN concentration of the GPMR using an ammonium chloride synthetic solution [11].

$$\ln {\binom{C_{t}}{C_{0}}} = {\binom{-\pi DL}{V}} \times (0.043 - 0.035 \exp^{-0.007\omega}) \times t$$
 Eq 6

where  $C_t$  is the feed TAN mass concentration at time t (g/L);  $C_0$  is the initial feed TAN mass concentration (g/L); D is the membrane diameter (m); L membrane length (m); V is the feed volume (m<sup>3</sup>);  $\omega$  is the feed mixing speed (rpm); and t is the process time (h) [11]. Key assumptions underlying the preliminary model was that the pH of the feed waste stream remained above 9.3 (the pKa of ammonia at 25°C) throughout the process and the product side pH remained constant at 2.0. An objective of this study was to assess the applicability of this semi-empirical model to produced water to assess the model's utility in scaling up the GPM separation process independent of the feedstock used.

## 4. Results and discussion

#### 4.1. Characterization of PW

The characterization of PW used in this study are summarized in Table 1. The ICP-OES analysis results showed high concentrations of Ca, Na, Mg, Sr and K ions (Figure 2). Six of the nine analyzed heavy metals (Ba, Cd, Co, Cr, Fe, Mn, Mo, Ni, As ) were below method detection limits. Barium (Ba), manganese (Mn), and molybdenum (Mo) were detected at concentrations of 2.5 mg/L, 1.7 mg/L, and 0.2 mg/L, respectively.

Parameter	Value		
pН	6.7		
Electrical Conductivity	71.7 mS/cm		
Total Alkalinity (TA)	301 mg/L as CaCO <sub>3</sub>		
Phenolphthalein Alkalinity	0		
TAN	533 mg/L		
Nitrite-N	0.023 mg/L		
Nitrate-N	8.630 mg/L		
Phosphates	0.469 mg/L		
Bromide	1183.9 mg/L		
Chloride	79466.3 mg/L		
Sulphates	1188.8 mg/L		
Total solids	171.7 g/L		
Total dissolved solids	170.6 g/L		
Total organic carbon	16.67 mg/L		
Total inorganic carbon	52.1 mg/L		

Table 1: Characteristics of produced water



Figure 2: ICP-OES analysis results for major metals

4.2. Ammoniacal nitrogen removal, recovery and optimum process conditions

The ammonia removal, recovery, flux and  $(NH_4)_2SO_4$  yield at initial feed pH of 10 (E1), 9.8 (E2) and 9.6 (E3) are compared in the Table 2. The results showed a significant difference between Experiments 2 and 3. This difference can be attributed to the continuous pH drop observed in E3 (from 9.6 to 7.8) compared to the more stable pH range of 9.8 to 9.5 observed in E2 (Figure 3). Higher feed side pH increases conversion of TAN to free ammonia, leading to higher removals [17].

Removal efficiencies and recovery rates of TAN in GPM reactors depend on the feed pH as described by the following equation derived from Equations 1, 2 and 3 discussed in section 2:

$$\frac{[NH_3]}{[TAN]} = \frac{K_a}{K_a + [H^+]} = \frac{10^{-pK_a}}{10^{-pK_a} + 10^{-pH}}$$
Eq 7

When the pH drops below the pKa of ammonium (9.26 at 25°C), the NH<sub>3</sub> concentration in the PW reduces and thus reducing the TAN removal in E3. As predicted by Eq 7, the NH<sub>3</sub> fraction at 25°C and a pH above 9.5 is >63%; at a pH <7.8, this fraction reduces to < 3%. There was no significant difference between the results of E1 and E2 since the pH remained above 9.5 throughout both experiments. Therefore, initial pH of 9.8 was considered optimum to minimize the process related

chemical costs. The temporal variation of pH and TAN concentration of PW is shown in the Figure 3 and Figure 4 respectively.

Tuble 2. Initial food pit optimization experimental fostitis						
	E1	E2	E3			
Initial feed pH	10.0	9.8	9.6			
Final feed pH	9.6	9.5	7.8			
TAN removal (%)	99.65±0.07	99.67±0.09	75.61±0.20			
TAN recovery (%)	94.77±1.89	92.58±3.20	$75.02 \pm 2.54$			
TAN flux (g-N/day. m <sup>2</sup> )	63.2±0.04	72.41±4.94	57.55±0.23			
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> yield (g of	2 07+0 11	3 25+0 04	2.10±0.11			
$(NH_4)_2SO_4$ /L of feed)	5.07±0.11	<i>3.23</i> ±0.04				

Table 2: Initial feed pH optimization experimental results



Figure 3: Temporal variation of feed pH



Figure 4: Temporal variation of feed TAN concentration

#### 4.3.Product purity

Figure 5 shows the microscopic image, and the elemental composition of the final product recovered, as determined by the SEM-EDX analysis. The EDX peaks confirmed the abundance of sulfur (S), oxygen (O) and nitrogen (N) in the final product. Their respective compositions were 54%, 28% and 17%, comparable to the theoretical composition of ammonium sulfate (48% O, 24% S, 21% N). These minor deviations could be attributed to the presence of other impurities found in trace amounts of less than 0.5 wt%, including Na, Al, Si, K, Ca, and Mg. Hydrogen (H) in the recovered product has not been detected due to its very low atomic number. These observations support the purity of the obtained ammonium sulfate and confirms the success of the recovery process.



Figure 5: (a) SEM image (b) EDX peaks of the final product recovered from the PW.

The heavy metal concentrations in the recovered product are compared against the ceiling concentration limits in the EPA Part 503 Biosolids rule (EPA/832/R-93/003) [18] in the Table 3. Heavy metal contents in the recovered product were below these limits, supporting their suitability for land application as fertilizers. The heavy metal concentrations in the recovered sample were also within the limits for of the more stringent EPA Exceptional Quality (EQ) and Pollutant Concentration (PC) biosolids regulations, and the regulatory limits for the European Union (Directive 86/278/EEC) [16].

Heavy metal	Concentration in	EPA Ceiling	EPA limit for EQ	EU limits	
	recovered (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	concentration	and PC biosolids	[ma/ka]d	
	[mg/kg] <sup>a</sup>	[mg/kg] <sup>b</sup>	[mg/kg] <sup>c</sup>	[IIIg/ Kg]	
As	<mdl< td=""><td>75</td><td>41</td><td>NA</td></mdl<>	75	41	NA	
Cd	<mdl< td=""><td>85</td><td>39</td><td>40</td></mdl<>	85	39	40	
Cr	<mdl< td=""><td>3,000</td><td>1,200</td><td>NA</td></mdl<>	3,000	1,200	NA	
Mo	<mdl< td=""><td>75</td><td>* *</td><td>NA</td></mdl<>	75	* *	NA	
Ni	0.25	420	420	400	
Pb	<mdl< td=""><td>840</td><td>300</td><td>1200</td></mdl<>	840	300	1200	
Se	1.67	100	36	NA	
Zn	4.22	7500	2800	4000	
Cu	<mdl< td=""><td>4,300</td><td>1,500</td><td>1,750</td></mdl<>	4,300	1,500	1,750	

Table 3: Purity of the recovered (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> product

<sup>a</sup> MDL – method detection limit

<sup>b</sup> EPA/832/R-93/003 - Ceiling Concentration Limits for All Biosolids Applied to Land [18]

<sup>c</sup> EQ – exceptional quality; PC – pollutant concentration (EPA/832/R-93/003) [18]

\*\* As a result of the February 25, 1994, Amendment to the rule, the limits for molybdenum were deleted from the Part 503 rule pending EPA reconsideration.

<sup>d</sup> EU Directive (86/278/EEC) [16]

#### 4.4. PW contaminant removal during GPM treatment

The characterization of PW after the ammonia recovery showed a 3% reduction in TOC and an 88% reduction in IC. The IC reduction is likely due to the conversion of bicarbonates in the PW to carbonates during the pH adjustment (Eq 8), followed by the precipitation of these carbonates with Ca and Mg ions in the PW (Eq 9).

$$HCO_{3}^{-} + OH^{-} \leftrightarrow CO_{3}^{-2} + H_{2}O$$

$$Eq 8$$

$$CO_{3}^{-2} + Ca^{+2} \leftrightarrow CaCO_{3}$$

$$Eq 9$$

ICP-OES analysis revealed a 9% decrease in B and a 30% decrease in Mg concentrations in the PW following GPM treatment. The observed Mg reduction might be attributed to the formation of magnesium hydroxide precipitate during pH adjustment, as described by the Eq 10.

$$Mg^{+2} + 2OH^{-} \leftrightarrow Mg(OH)_2$$
 Eq 10

To understand the fate of precipitates formed during pH adjustment, SEM-EDX analysis was conducted. The EDX peaks (Figure 6) revealed dominant presence of O, C, Cl, Mg, Na and Ca. This suggests that while some Mg (OH)<sub>2</sub> and CaCO<sub>3</sub> dissolved due to protonation during the GPM process, a significant portion remained in the reactor. Notably, NaCl formation was observed, likely due to supersaturation of Na ions during pH adjustment. The SEM elemental mapping images (Figure 7) confirmed the availability of Mg (OH)<sub>2</sub>, NaCl and CaCO<sub>3</sub>.



Figure 6: Elemental composition and EDX peaks of the precipitate formed in PW during GPM ammonia recovery.



Figure 7: SEM elemental mapping images of the precipitates

## 4.5. Evaluation of membrane fouling potential

The trans-membrane flux of TAN in the twenty treated batched in fed-batch mode were calculated using Equation 11, where  $C_0$  is the initial TAN concentration (g/L);  $C_t$  is the final TAN concentration (g/L); V is the feed volume (m<sup>3</sup>), A is the effective area of the membrane (m<sup>2</sup>), and t is the process time (day). The trans-membrane flux and the final feed pH variation in these batches are shown in Figure 8.

Transmembrane flux = 
$$\frac{(C_0 - C_t) \times 10^3 \times V}{t \times A}$$
 Eq 11



Figure 8: Variation of trans-membrane TAN flux and final feed pH of membrane fouling evaluation experiments

The trans-membrane flux was influenced by feed pH, particularly after the treatment of the first five batches. A lower feed pH reduces TAN conversion to free ammonia, leading to decreased removal rates and consequently lower trans-membrane fluxes. However, the initial flux decline from 69 to 54 g TAN/m<sup>2</sup>/day appears attributable to inorganic fouling by Mg (OH)<sub>2</sub>, NaCl, and CaCO<sub>3</sub> precipitates, as the final pH of the first five batches was approximately 9.4.

4.6. Validation of the GPMR process model for ammonia recovery from PW

One of the goals of the current study was to assess the applicability of the preliminary process model (Eq 6) developed by Munasinghe-Arachchige et al. [11] to the PW. During this study, it was noted that the feed-side pH of the E3 had dropped significantly below pKa of 9.3, defying the key assumption underlying the preliminary model. This pH drop was likely due to the continuous removal of NH<sub>3</sub> which promotes dissociation of NH<sub>4</sub><sup>+</sup> in the feed waste stream, leading to increased release and accumulation of protons (H<sup>+</sup>) in the feed. As such, the model validation was performed for E1 and E2 where the feed pH remained >9.3 during the tests. Figure 9 demonstrates

a strong correlation between measured and predicted TAN concentrations, with an  $R^2$  value of 0.989. All data points fall within ±1 log unit of the parity line.



Figure 9: Measured vs. predicted TAN concentrations in the PW

#### 4.7. Comparison with conventional ammonia recovery processes

Various physical, chemical, and biological methods have been investigated for ammonia removal from wastewater. While many of these processes transform ammonia into different nitrogenous compounds, some directly convert it to nitrogen gas and dissipates to the atmosphere. Biological treatments, such as activated sludge utilize nitrifying bacteria to oxidize ammonia to nitrates and nitrites [19]. During algal treatment, microalgae assimilate organics and nutrients in PW [20] Electrochemical treatment, employing metallic electrodes like Al and Fe, provides a direct route for ammonia oxidation to nitrogen gas [21]. Precipitation of struvite is considered as an effective and economical approach for simultaneous recovery of ammonium, potassium and magnesium from PW [22]. A comparative analysis of these approaches and proposed method in this study is presented in Table 4.

Process	Status	Process	NH <sub>3</sub>	NH <sub>3</sub>	Recovered	Ref.
		influent*	removal	recovery**	product	
Constructed	Pilot	PW RO effluent	98%	NA	NA	[23]
wetlands	Laboratory	Raw PW	72%	NA	NA	[24]
Struvite	Laboratory	Filtered Raw	86%	86%	Struvite	[22]
Precipitation		PW				
Polysulfone	Laboratory	PW after	92%	NA	NA	[25]
membranes		coagulation and				
		sedimentation				
Activated	Full scale	PW DAF	~100%	NA	NA	[19]
sludge		effluent				
	Full scale	Raw PW	>90%	NA	NA	[26]
Electrochemical	Laboratory	PW	100%	NA	NA	[27]
treatment		Clarification				
		effluent				
	Laboratory	PW Filtration	92%	NA	NA	[21]
		effluent				
Algal treatment	Laboratory	Raw PW	100%	NA	NA	[20]
	Laboratory	Raw PW	99.6%	NA	NA	[28]
	Laboratory	Raw PW	100%	NA	NA	[29]
Gas Permeable	Laboratory	Raw PW	99.7%	95%	Ammonium	This
Membrane					sulphate	study

Table 4: Comparison of ammonia removal and/or recovery with literature

\*PW- produced water; RO - reverse osmosis; DAF - dissolved air floatation

\*\*NA – not applicable

## 5. Conclusions

This study assessed the feasibility of gas permeable membrane (GPM) technology for recovering ammonia directly from raw produced water (PW). The GPM reactor developed in this study

successfully removed and recovered nearly 95% of the ammonia in PW in a single step. Optimal conditions for nitrogen recovery in the GPM reactor were identified as an initial feed pH of 9.8, a product pH of 2, and moderate mixing of the feed at room temperature. The purity of ammonium sulphate fertilizer recovered from the PW complied with US EPA and EU guidelines for land application as crop fertilizers as confirmed by the scanning electron microscopic and energy dispersive X-ray (SEM-EDX) and the Inductively coupled plasma - optical emission spectrometry (ICP-OES) analyses. A preliminary process model developed using test data on a synthetic waste stream was shown to be adequate in predicting the fate of TAN concentrations in PW with a r<sup>2</sup> of 0.989.

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## 7. Budget

By August 29<sup>th</sup>, 2024, \$6184.86 has been used for the purchase of chemicals and lab supplies for experiments, \$810 has been used for the lab analysis, \$50 has been used for purchasing software, \$439.15 has been used for travelling and poster printing for 68<sup>th</sup> annual New Mexico Water Conference and State of Science Event 2024. The remaining balance is approximately \$100.

## 8. Presentations

- W.M.L.K. Abeyratne, Y. Zhang, N. Nirmalakhandan, Crop Fertilizer Recovery from Produced Water, 68th Annual New Mexico Water Conference, November 8-9, 2023, Albuquerque, NM.
- W.M.L.K. Abeyratne, Y. Zhang, N. Nirmalakhandan, Nitrogen Crop Fertilizer Recovery from Produced Water, 20th Annual RMSAWWA/RMWEA Student Conference, May 17, 2024, Las Cruces, NM.
- W.M.L.K. Abeyratne, Y. Zhang, N. Nirmalakhandan, Crop Fertilizer Recovery from Produced Water, NM Alternative Water Supply: State of the Science to Advance Diversified Water Treatment and Reuse, June 27, 2024, Las Cruces, NM.

## 9. Publications

W.M.L.K. Abeyratne, S.P. Munasinghe-Arachchige, H. Bayat, Y. Zhang, C.E. Brewer, N. Nirmalakhandan, Gas Permeable Membrane Technology for Nitrogen Fertilizer Recovery from Nitrogen-rich Waste Streams, Journal of Resources Conservation and Recycling (2024) – Under review

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