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# A pilot study on the removal of ammonia from aqueous solution using the integration of struvite synthesis and breakpoint chlorination

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## ABSTRACT

Herein, a pilot study on the removal of ammonia from surface water using the integration of struvite precipitation and breakpoint chlorination is reported. A two staged pilot plant with a capacity of 1000 liters (1 m<sup>3</sup>) per run (LPR) was utilized, of which Stage 1 comprised struvite precipitation and Stage 2 comprised breakpoint chlorination. Optimum conditions (i.e., Stage 1) for struvite precipitation were 110 mg/L of Mg and P dosage (concentration), 150 rpm of mixing speed, 60 minutes of contact time, and lastly, 120 minutes of sedimentation, while optimum condition for the breakpoint chlorination (i.e., Stage 2) were 30 minutes of mixing and an 8:1 Cl<sub>2</sub>-NH<sub>4</sub><sup>+</sup> weight ratio. The synergistic effects of this hybrid system proved to be effective, with Stage 1 increasing the pH from 6.8 to 10.1, reducing Mn (≥97.0%) and Fe (≥99.6%) concentrations steeply, and concomitantly deactivated *E coli* and TPC to ≥ 99% and ≥91%, respectively, while ammonia was reduced from 5.4 mg/L to 2.7 mg/L-N (51.8 %). In Stage 2, i.e., breakpoint chlorination, ammonia was reduced from 2.7 mg/L to 0.02 mg/L-N whilst fully depleting residual microorganisms. Finally, the OPEX amounted to \$ 0.31/m<sup>3</sup>; however, there is a potential for cost savings (≈53.2%) by replacing Kh<sub>2</sub>PO<sub>4</sub> with waste phosphoric

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acid. Lastly, the results from this techno-economic evaluation study showed great potential compared to similar technologies, making this approach a game-changer towards the prudent management of elevated levels of ammonia amongst other problematic contaminants.

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## 1. Introduction

The alarming growth in population has proportionally triggered rapid industrialisation and chemically driven agricultural economic practices. The premier quest is to meet the worrying demands for basic goods and services. As a trade, the quality of surface water is sacrificed through the introduction of toxic and hazardous chemicals from effluents that emanate from myriads of anthropogenic practices. In particular, agricultural practices, industrial processes, and municipal wastewater treatment have been identified as the main culprits impacting surface water quality. Of main concern is the introduction of ammonia; in addition, turbidity, iron (Fe), manganese (Mn), microbial load, i.e., *E. coli*, faecal coliform, and total plate count perpetually increase, hence altering the typical physicochemical and microbial characteristics of raw water [11,25]. Albeit, water treatment entities abstract water from those sources and purify them to the required standard [10]. The ever-growing deterioration of water quality concomitantly increases the treatment requirements and proportionally increases the costs for water treatment [11]. To this end, drinking water treatment systems have shown great success in dealing with water that has high turbidity, microbial load, and metals, amongst other contaminants. However, the presence of ammonia constitutes a different challenge since conventional technologies require an exorbitant amount of chlorine to remove it via breakpoint chlorination and deem the treatment process uneconomical. According to regulatory frameworks, the maximum allowable limit for ammonia in drinking water is  $\leq 1.5$  mg/L-N [28,32] and it is often above the limits, particularly for low- and middle-income countries (LMIC) with no existing or dilapidated, under-designed, and poorly maintained water treatment facilities. The presence of ammonia in drinking water can cause both operational and health challenges on exposure. Specifically, excess ammonia and its nitrate derivative are known to cause blue baby

syndrome and cancer of the stomach, pharynx, and oesophagus [4]. Furthermore, the affinity of ammonia to chlorine also hampers the oxidation of Mn in water, hence affecting the efficacy of the water treatment process [1]. Furthermore, Mn has the potential to affect water aesthetically, i.e., levels that exceed  $\geq 100\mu\text{g/L}$ , tainting laundry and giving water a metallic taste [25,26,32]; levels that exceed  $\geq 400 \mu\text{g/L}$  could potentially lead to neurological disorders and induced mental illnesses [4]. Regarding the environment, excess levels of ammonia have led to the depletion of oxygen in water, eutrophication, and toxicity for fish [3,30]. Taking into consideration both health and environmental effects of ammonia, its recovery and removal are imperative for the sustainability and safety of potable water. Fortunately, numerous technologies have proven effective for ammonia removal, especially in wastewater treatment. Despite its excruciating and indispensable dependence on biological treatment processes, the problem becomes eminent when they underperform and discharge ammonia into the rivers that serve as abstraction points for drinking water. To date, adsorption, precipitations, air stripping, ion exchange, filtration, bio-sorption, bio (phyto)remediation, crystallization, volatilization, and distillation have been employed to remove ammonia from aqueous solution [2,4,8,12,13,21,22,30,34]. These technologies have their advantages and disadvantages, but technological preference is chiefly based on cost-effectiveness, sustainability, efficacy, and waste (sludge) production. So far, biological nutrient removal (BNR) technology is the preferred technology for de-ammonification of water because of its simplicity and effectiveness [1,5]. Specifically, Nikpour et al. [24] evaluated the ammonia removal efficiency of Modified Ludzack-Ettinger (MLE) and modified Ludzack Ettinger process-oxic settling anaerobic (MLE-OSA), achieving  $\geq 97\%$  removal efficacy for ammonia from wastewater. Be that it may, bacterial communities responsible for ammonia removal are

sensitive to cold, i.e., winter conditions, hence hindering their efficacy and performance unless artificial heat is induced. Adsorption has a limitation of quick saturation and poor performance in concentrated solutions, while filtration and ion exchange generate brine and require exorbitant amounts of energy [15,25]. The stripping process, though efficient, is dependent on temperature, air-water ratio, and pH [33,34]. Zanganeh et al. [34] evaluated the effect of temperature on ammonia removal from municipal wastewater and achieved the highest removal (98%) at 45 °C, while the removal efficacy was 6.6% at 34 °C. Furthermore, the stripping process was effective between pH 11 to 12. The high pH, heating (temperatures), and need for air potentially increases operational cost, thus, hindering the application of this technology in drinking water systems. On the other hand, chlorination technology is available in both water and wastewater treatment processes; however, high operational cost and the formation of carcinogenic by-products limits its application [30]. Lastly, struvite precipitation is the most sustainable and stable technology with the least environmental constraints; it produces a valuable by-product that could beneficially be used as slow-release fertiliser [4,14]. Struvite precipitation, even with high ammonia recovery yields, in most cases produces effluent with ammonia concentration higher than those required for drinking water limits, being  $\leq 1.5$  mg/L. Li et al. [9] employed struvite precipitation using spent refractory brick gravel from the steel industry as the magnesium source and recovered >99.6% and >98.2% of phosphate and ammonia, respectively. In their study, the ammonia concentration was lowered from 140 mg/L to 2.5 mg/L-N. As such, to comply with drinking water standards, the effluent will require polishing to reduce the ammonia to the required drinking water quality. Furthermore, researchers are opting to integrate different treatment technologies, and the main quest is to acquire synergetic effects emanating from different techniques assembled together to enhance the efficacy of contaminant removal [18]. However, most of the studies are still in the early stages of development with their efficacies evaluated only at a laboratory scale. In light of

that, the pre-treatment of ammonia rich water via struvite precipitation as the initial stage of the treatment to attenuate the ammonia concentration to lower levels makes it viable to introduce breakpoint chlorination as a polishing step. Recently, Chen et al. [4] employed a combination of hydroxide precipitation, struvite precipitation, breakpoint chlorination, and ferric coagulation for the removal of Mn and ammonia from acidic effluents generated from electrolytic Mn residue. It demonstrated the feasibility and effectiveness of integrating different technologies. Henceforth, our study was designed to demonstrate, for the first time, the integration of chemical precipitation (struvite synthesis) as the pre-treatment and breakpoint chlorination as the polishing stage to treat real surface water enriched with ammonia. Our findings successfully demonstrated the feasibility of integrating struvite precipitation as the pre-treatment step and breakpoint chlorination as the polishing stage. The attained study results were excellent in terms of ammonia removal [23]. Albeit, there was a dire need to upscale the technology and demonstrate it on a pilot scale, hence the current quest to determine the robustness of the technology in real settings. In light of that, this study performed the cost analysis of the removal of ammonia from an aqueous environment using the integration of struvite synthesis and breakpoint chlorination.

## 2. Materials and methods

### 2.1. Sampling

Ammonia-rich raw water was collected from the canal system, which receives water from the Roodeplaas Dam, Gauteng Province, South Africa (25.62083°S 28.37138°E). Specifically, common catchment activities are wastewater treatment facilities and agricultural practices that are located upstream of the catchment. Here, 20 L high density polyethylene (HDPE) containers were used for raw water samples collection. The collected samples were directly used after sampling with no other pre-treatment.

### 2.2. Chemicals

Thermo-chemically activated cryptocrystalline magnesite was procured from the Sterkfontein Carbonates (Pty) Ltd Company. A salt of 500 g of

pure potassium dihydrogen phosphate was procured from Aqualytic™ (Pty) Ltd. Essentially, activated cryptocrystalline magnesite and the sodium dihydrogen phosphate salts were employed as fundamental sources of  $Mg^{2+}$  and  $PO_4^{3-}$ , respectively, for struvite synthesis. The ambient ammonia concentration in real river (canal) water was used as a seeding concentration and the stoichiometry was cognizant of its respective levels. The calcium hypochlorite (High Test Hypochlorite - HTH) grains,  $\pm 70\%$  of available chlorine, were supplied by Protea Chemicals (Pty) Ltd and was effectively employed for the breakpoint chlorination experiments.

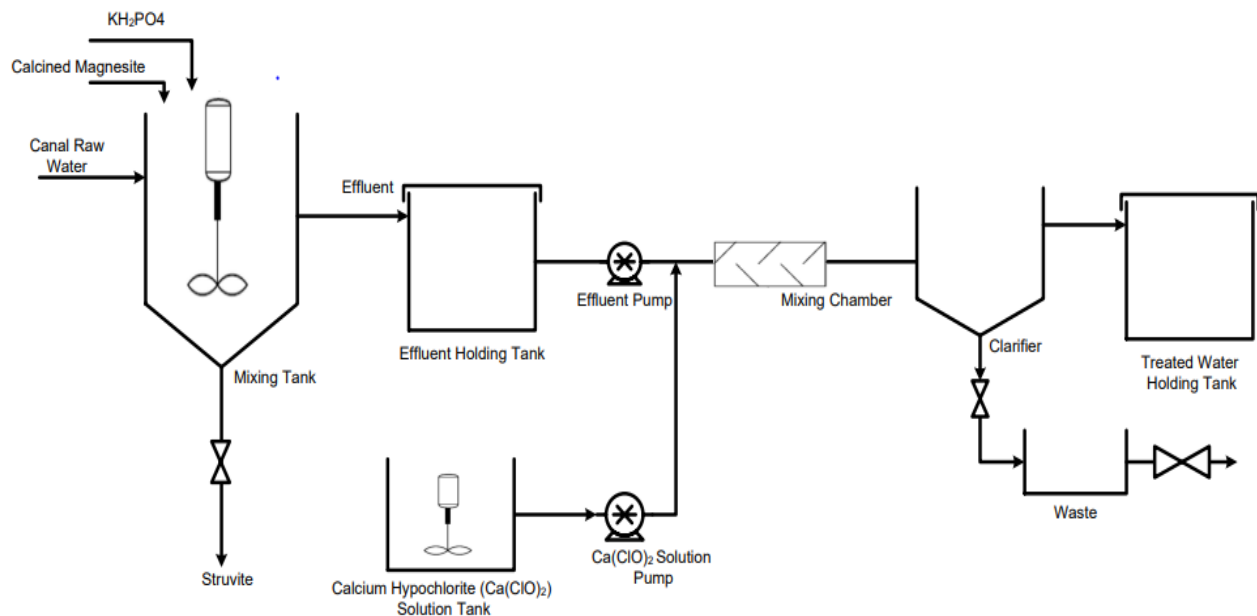
### 2.3. Description of the unit processes

The schematic illustration of the unit processes used for the integrated treatment of real river water for the removal of ammonia is shown in Figure 1. The system comprises of two phases: Phase 1 is struvite synthesis and Phase 2 is breakpoint chlorination.

#### 2.3.1. Struvite synthesis (Stage 1)

In this stage, struvite precipitation was fulfilled as a first step towards attenuating ammonia from the real river water. Specifically, the thermo-mechano-

chemically activated cryptocrystalline magnesite and potassium hydrogen phosphate ( $KH_2PO_4$ ) were seeded to canal water to attain the required stoichiometry and facilitate the chemical reaction. The chief attempt was to remove aqueous ammonia as struvite through the combination of magnesium ammonia phosphate (MAP), popularly known as struvite. The adopted optimum conditions were 110 mg/L of Mg and P dosage, mixing at 150 rpm of mixing speed, 60 minutes of contact time, and 120 minutes of sedimentation [23]. After the experiments, the supernatant was transferred to a 1 m<sup>3</sup> reactor for the breakpoint experiment. In addition, the supernatant was collected from this reactor and analyzed for ammonia, phosphate, calcium, magnesium, pH, manganese, *E. coli*, total coliform, free chlorine, nitrite, nitrate, calcium, and pH. This was done to ascertain the performance of this system on a pilot scale and determine its relativity to the results obtained from the laboratory assays. The experiments were repeated three times, and the results were reported as mean values. This was done to determine the trustworthiness of the results on a pilot scale (1000 L).



**Fig. 1.** The schematic illustration of the unit processes used for the integrated treatment of real river water for the removal of ammonia.

### 2.3.2. Breakpoint chlorination (Stage 2)

In Stage 2 of this study, the 1000 L/hr pilot plant was used for breakpoint chlorination studies. Specifically, the Ebara CDX-90/10, 0.75kW feed pump regulated the flow to 2 L/s in a continuous flow reactor. The Seko TPR603 ORP pump dosed hypochlorite at a chlorine to ammonia ratio of 8:1, which was optimal from the laboratory studies. The treated water (product water) was collected from the product water tank after 30 minutes. Thereafter, the supernatants were characterized for ammonia, phosphate, calcium, magnesium, turbidity, pH, manganese, *E. coli*, total coliform, calcium, and pH. As indicated in section 2.2.1, the experiments were repeated three times, and the results were reported as mean values. This was done to demonstrate the robustness of the system and its ability to give consistent results at various experimental runs.

## 2.4. Characterization

### 2.4.1. Characterization of aqueous samples

Ammonia was quantified using the Gallery Plus analyser (Anotec) (Discreet Analyser). The pH and electrical conductivity were determined using an HQ40d multimeter probe. The turbidity was ascertained using a HACH 2100 AN turbidity meter. The Hach equipment was procured from the Hach Company (Pty) Ltd (Loveland, Colorado, USA). The metal concentrations of Fe and Mn were evaluated using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Agilent, Santa Clara, CA, USA). The *E. coli* and total coliform were determined using the Colilert method. Specifically, the Colilert method employs a substrate technology wherein the coliforms metabolise nutrient indicators ONPG (detection of  $\beta$ -galactosidase activity), and *E. coli* metabolises the MUG substrate (detection of  $\beta$ -D-glucuronidase activity). Lastly, for levels of plate count (TPC), the pour plate method was employed. Furthermore, standard methods were followed in analysing the samples [27]. In addition, sample analyses were conducted in an ISO 17025 accredited laboratory. The National Institute of Standards and Technology (NIST) standards and inter-laboratory analyses were performed to corroborate the results.

### 2.4.2. Characterisation of feed and product solids

Different analytical and state-of-the-art analytical instruments were used to understand the fate of ammonia in the struvite synthesis reactor. Specifically, the An Auriga Cobra FIB FESEM, Carl Zeiss supplied, Sigma VP FE-SEM, HR-SEM coupled with EDS sputter technology was utilised to ascertain the microstructural properties and elemental composition of the feed and product sludge.

## 2.5. Economic Evaluation

An economic evaluation of the developed process was also performed. Specifically, the developed hybrid technology, i.e., struvite synthesis and breakpoint chlorination, demonstrated good performance in the laboratory scale experiments, and similar results were acquired at a pilot scale. As such, the cost factor was observed to be the fundamental factor influencing the implementation of this technology. This study systematically focused on the comparison of breakpoint chlorination alone and the hybrid system. The quest was to demonstrate the effect of synergy on the costs and efficacy. Prices were acquired from the catalogue of different suppliers that prominently supply different water treatment plants in South Africa to quantify the cost of treating surface water contaminated with ammonia. The techno-economic evaluation meticulously focused on chemicals; however, costs related to civil, equipment, maintenance, electrical, and labor were not included in this assessment. This could be attributed to the fact that there is no intention to change those functionalities except for the chemicals that are used in fully removing and decomposing ammonia from aqueous solution.

## 3. Results and discussion

### 3.1. Water quality results

The current study employed the hybrid approach for effective removal of ammonia from aqueous environments using a combination of struvite precipitation and breakpoint chlorination in a step-wise fashion. Specifically, the first stage, i.e., struvite precipitation, incorporated the use of calcined (activated) magnesite and potassium dihydrogen phosphate as Mg and P sources,

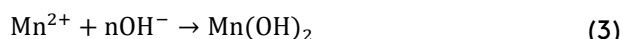
whereas the second stage comprised the polishing of ammonia from the product water (supernatant) emanating from the struvite reactor using breakpoint chlorination. The results depicting the performance of the hybrid approach on the removal of ammonia and other water quality risk parameters at optimum conditions are shown in Table 1.

As shown in Table 1, the obtained results were congruent with the results obtained in our previous study [23]. Specifically, microbial and inorganic contaminants were significantly removed from the aqueous solution. Furthermore, *E. coli*, total coliform, Fe, and Mn were significantly removed in Stage 1 of the chemical reaction. In addition, Table 1 shows a significant reduction in ammonia and TPC in the final water in Stage 1 of the treatment process. However, the effluent concentrations of 2.68 mg/L for ammonia and 2340 MPN/1 mL for TPC were non-compliant as compared to the allowable limits of  $\leq 1.5$  mg/L N for ammonia and  $\leq 500$  CFU/1 mL and  $\leq 1000$  CFU/1 mL for TPC as succinctly summarized in the world health organization (WHO) and SANS 241, respectively. Furthermore, the pH increased significantly in Stage 1 of the treatment process and reached  $\text{pH} \geq 10$ . An increase in pH was primarily due to the dissolution of activated cryptocrystalline magnesite leading to the addition of hydroxyl groups (Eqn. 1 and 2). Furthermore, calcined (activated) magnesite comprised trivial amounts of calcite and brucite (periclase). Their dissolution contributed to the

introduction of Ca and Mg to the waterbodies, which are agents towards an increase in pH [17,27]. Thenceforth, an increase in pH agrees with the results from our laboratory scale studies and other studies reported in the literature [16,19,21]. Furthermore, the dissolution of Mg and Ca from MgO-NPs matrices also contributed to an increase in pH, as illustrated by Equations 1 and 2.



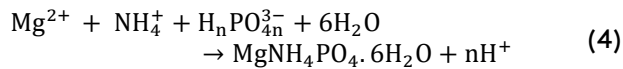
The alkaline conditions with  $\text{pH} \geq 10$ , created after the dissolution of the activated magnesite or MgO-NPs, could possibly hinder the growth of bacteria; thus, leading to their complete deactivation, with *E. coli* and coliform bacteria reaching  $\geq 99.9\%$  reduction, whilst TPC reached  $\geq 91\%$  reduction. In addition, the higher pH, i.e.,  $\text{pH} \geq 9$ , led to the removal of Mn, as illustrated by Equation 3 [25].



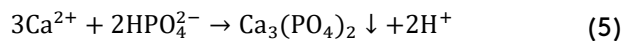
More importantly, the results (Table 1) show a reduction in ammonia and calcium levels in the product water from Stage 1, while both P and Mg levels notably increased. As expected, an increase in Mg resulted from the dissolution of periclase and brucite. However, the  $\text{Mg}^{2+}$  will react with  $\text{PO}_4^{4-}$  and  $\text{NH}_4^+$  in Stage 1 to form a combination of magnesium ammonia phosphate (MAP), popularly known as struvite, which explains the reduction of  $\text{NH}_4^+$  from surface water, as illustrated by Equation 4.

**Table 1.** The microbiological, physical, and chemical properties of feed water before and after the removal of ammonia via struvite precipitation and breakpoint chlorination.

Determinants	Units	WHO	SANS	Feed	Stage 1	Stage 2
<i>E. coli</i>	MPN/100 mL	ND	ND	34	ND	ND
Total coliform	MPN/100 mL	ND	$\leq 11$	2420	ND	ND
Total plate count	CFU/1 mL	$\leq 500$	$\leq 1000$	26000	2340	8
Iron	$\mu\text{g/L}$	$\leq 100$	$\leq 400$	100	0.37	0.37
Manganese	$\mu\text{g/L}$	$\leq 50$	$\leq 100$	113	0.01	0.01
pH @ 25°C	pH units	6.5-8.8	$\leq 5 \leq 9.7$	6.78	10.05	9.11
Ammonia	mg/L N	$\leq 1.5$	$\leq 1.5$	5.42	2.68	0.02
Phosphate	mg/L	-	$\leq 10$	0.66	2.3	6.4
Calcium	mg/L	-	$\leq 300$	25	6, 400	37 000
Magnesium	mg/L	-	$\leq 100$	1.1	39	38

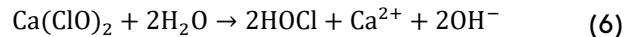


The reduction of the  $\text{Ca}^{2+}$  level from 25 mg/L to 6.4 mg/L could also be attributed to the dissolution of the MgO-NPs. Optimal conditions involved dosages of 110 mg/L for both  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$ ; the residual levels of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  of 38 mg/L and 2.3 mg/L, respectively, confirmed reactions amongst ions in solution during the struvite synthesis (Stage 1). The reduction of  $\text{Ca}^{2+}$  resulted from a reaction with  $\text{PO}_4^{3-}$ , forming calcium phosphate, as presented in Equation 5.

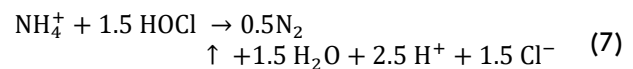


In addition, the reduction of phosphate concentration to 2.3 mg/L in Stage 1 further shows phosphate as the limiting reagent with its high affinity to  $\text{Ca}^{2+}$ , hence limiting the phosphate reaction with  $\text{Mg}^{2+}$ , thus hindering the formation of struvite. The obtained results are similar to those reported in the literature [6,9]. Then, this will require higher dosages of phosphate to overcome its demand and the effect of competing ions. Breakpoint chlorination was employed to further polish the water to the required standard and as stipulated in WHO and SANS-241 standards. Specifically, the product water from Stage 1 was comprised of ammonia and TPC at levels of 2.68 mg/L and 2430 MPN/1 mL, respectively, which exceeded the WHO and SANS 241 maximum allowed limits. However, chlorination technology is primarily employed for deactivating bacteria and viruses [1,29]. In this phase of the study, hypochlorite was added for the removal of residual TPC ( $\approx 8$  MPN/1 mL), which became compliant with the regulated limits of  $\leq 500$  CFU/ 1mL and  $\leq 1000$

CFU/ 1mL in WHO and SANS-241 standards, respectively [28,31]. The interaction of hypochlorite and water is illustrated in Equation 6.



As shown in Equation 6, the addition of high-test hypochlorite (HTH) introduced  $\text{Ca}^{2+}$  into the solution, which further explains an increase in the level of Ca after the treatment of product water with hypochlorite, as shown in Table 1. Furthermore, the formed hypochlorous product was responsible for the deactivation of microorganisms. Its formation led to a reduction of pH from 10.1 to 9.1 in Stage 2. More importantly, the optimal chlorination dosage of 8:1 to weight ratio effluent ammonia was adequate to overcome the demand in the water and eventually led to the reduction of ammonia from 2.7 mg/L to 0.02 mg/L within 30 minutes of contact time, as shown in Equation 7.



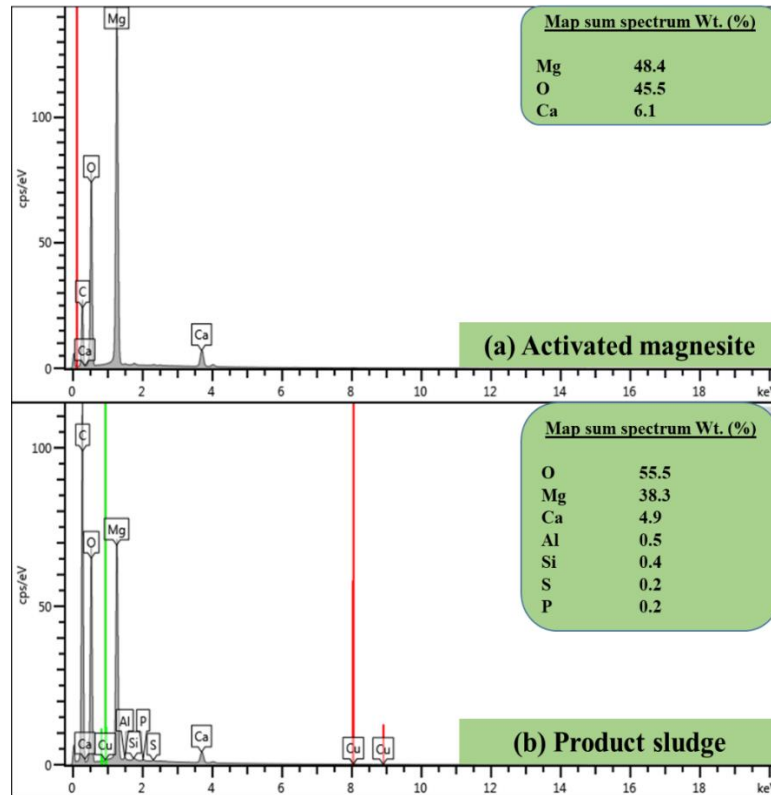
Finally, the combined technology proved to have significant potential in ensuring compliance to potable water standards.

### 3.2. Solids characterization

In this section, insights on the fate of chemical species after the removal of ammonia from aqueous solution as struvite are shown.

#### 3.2.1. Elemental composition from EDX

The elemental composition of feed and product minerals after the removal of ammonia from aqueous solution using MgO-NPs are shown in Figure 2(a-b).



**Fig. 2.** Elemental composition of feed and product minerals after the removal of ammonia from aqueous solution using MgO-NPs.

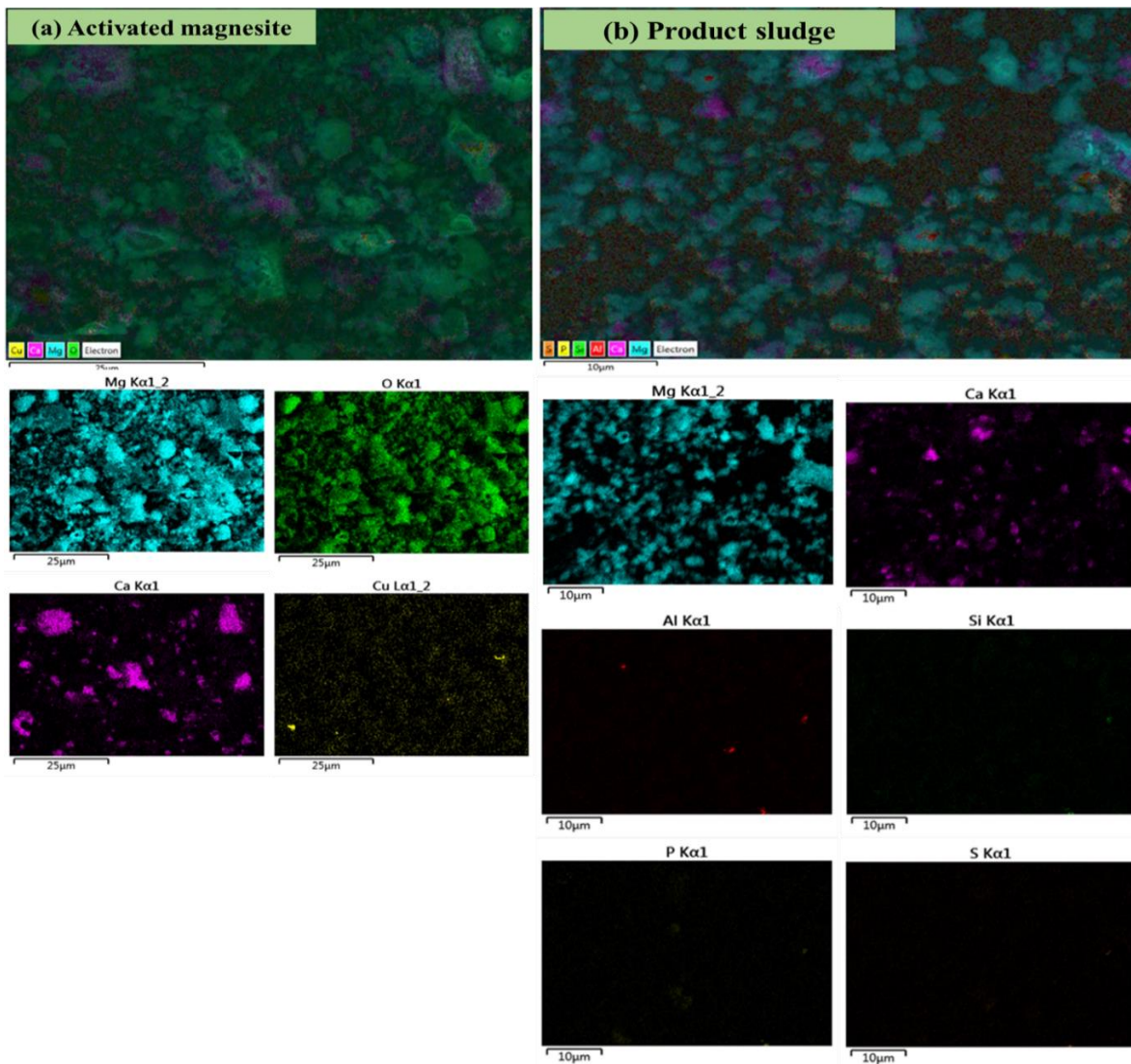
As shown in Figure 2a, calcined magnesite or MgO-NPs was made up of Mg, O, and Ca. The Mg and O were the predominant elements present, hence denoting that the feed mineral was periclase (MgO). The presence of  $Mg^{2+}$  within the feed product was imperative for a reaction with  $NH_3-N$  and  $PO_4^{3-}$ , forming Magnesium Ammonia Phosphate (MAP). Furthermore, Figure 2b shows the elemental composition of the resultant (product) sludge after the removal of ammonia as struvite. As shown in Figure 2b, new elements were observed in the product water after reacting with

the real canal water. Specifically, Al, Si, S, and P were identified as additional elements in the product sludge. The presence of new elements in the product sludge was the confirmation of a reaction of chemical species in water and MgO-NPs. The identified elements were similar to the ones of struvite, as reported by Masindi et al. [12].

### 3.2.2. Elemental mapping from EDX

The elemental mapping of MgO-NPs and the resultant sludge during the removal of ammonia from aqueous solution are shown in Figure 3(a-b).





**Fig. 3(a-b).** The elemental mapping of MgO-NPs and the resultant sludge during the removal of ammonia from aqueous solution.

As shown in Figure 3a, the elemental analysis showed that the feed material was concentrated with Mg, O, and some Ca. The results agreed with the map spectrum results from the preceding section. Elevated levels of Mg and O denoted that the material was periclase (MgO-NPs). Finally, the results for the elemental composition of the resultant sludge, as shown in Figure 3b, were comprised of Mg, Ca, Al, S, Si, and P. More importantly, the observed concentration of  $\text{PO}_4^{3-}$  and  $\text{Mg}^{2+}$  within the resultant sludge, coupled with the reduction of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  in surface water, confirmed that precipitation of struvite was more probable.

#### 4. Economics analysis

In this section, the process of removing ammonia from the aqueous solution was examined from an economic point of view. The economic evaluation was estimated based on the current chemical costs from recent marketing catalogues. Specifically, the primary consideration for economic evaluation strictly focused on chemical reagents. Other possible costs, such as manpower, design, and electricity, were not considered in this instance. Results for the techno-economic evaluation of the removal of ammonia using breakpoint chlorination and a combination of breakpoint chlorination and struvite synthesis are shown in Table 2.

**Table 2.** Results for techno-economic evaluation of the removal of ammonia using breakpoint chlorination and a combination of breakpoint chlorination and struvite synthesis.

Hybrid Technology			
Chemicals	Chemical cost (\$/m <sup>3</sup> )	Dosage (g)	Treatment Cost (\$)
Calcined Magnesite or Activated MgO	0.159	70	0.0111
Potassium dihydrogen Phosphate	0.649	20	0.0130
Calcium hypochlorite	2.197	3.06	0.0067
Lime	0.254		
Coagulant	0.923		
Cost @/100L			0.03083
Cost (\$/m <sup>3</sup> )			0.3083
Breakpoint Chlorination			
Chemicals	Chemical cost (\$/m <sup>3</sup> )	Dosage (g)	Treatment Cost (\$)
Calcined Magnesite			
Potassium dihydrogen Phosphate			
Calcium hypochlorite	2.197	22	0.0483
Lime	0.254	1.9	0.0005
Coagulant	0.923	0.8	0.0007
Cost @/100L			0.0496
Cost (\$/m <sup>3</sup> )			0.49560

As shown in Table 2, the overall cost to break down ammonia from aqueous solution amounted to \$ 0.31/m<sup>3</sup> for the hybrid process. The hybrid process was conducted using pure chemicals, i.e., potassium dihydrogen phosphate and HTH, and it contributed to 61.6% of the overall cost. In Table 3, the overall treatment cost, after the potential replacement of potassium dihydrogen phosphate with the readily available waste phosphoric acid as a phosphate source, could culminate in better and cheaper technology, with an estimated cost of \$ 0.051/m<sup>3</sup>, coupled with the replacement of highest hypochlorite with liquid chlorine, with the current cost of \$ 0.758/m<sup>3</sup>. Replacement of the chemicals has the potential to reduce the overall operational cost to \$ 0.145/m<sup>3</sup> (Table 3), which

explicitly equates to a 53.2% savings in costs. A study by Huang et al. [7] achieved a savings of 68% when they replaced pure chemicals with calcined magnesite and phosphoric acid. More importantly, even with the potential to save costs when replacing pure chemicals, this technology emerges above the rest when compared to technologies being piloted to treat different water sources to potable water standards. In general, breakpoint chlorination was expensive compared to the integration of struvite synthesis and breakpoint chlorination. Hence, the synergy between the two technologies offered the cheapest, most effective, and ecologically friendly technology that can be employed by water treatment entities.

**Table 3.** Estimated operational costs of hybrid technology with liquid chlorine and waste phosphoric acid as the main reagents.

Hybrid Technology with Ferric and Liquid chlorine			
Chemicals	Chemical cost (\$/m <sup>3</sup> )	Dosage (g)	Treatment Cost (\$)
Calcined Magnesite	0.159	70	0.011123
Waste Phosphoric	0.051	20	0.001016
Liquid Chlorine	0.758	3.06	0.002318807
Lime			
Coagulant			
Cost @/100L			0.014457
Cost (\$/m <sup>3</sup> )			0.144622

Numerous processes have been employed for the removal of ammonia from aqueous solutions. In particular, Mavhungu [20] employed the synthesis of struvite and drinking water reclamation from wastewater using reverse osmosis. The cost of their technology amounted to \$ 0.8/m<sup>3</sup>, which was equivalent to R 12.584/kl (\$0.8/m<sup>3</sup>), considering the current exchange rate for the US dollar to Rand of R 15.73. Masindi et al. [18] valorized acid mine drainage for drinking water reclamation using a battery of technologies, which was comprised of metals precipitation, gypsum synthesis, and reverse osmosis (RO). In their study, the overall treatment cost amounted to \$ 3.59/m<sup>3</sup>. Furthermore, as presented in Table 2, chlorine technology requires additional steps, such as stabilization with calcium hydroxide and coagulation with a polymer, which eventually increases the chemical cost to \$ 0.50/m<sup>3</sup>. The potential to reduce the operational cost of the hybrid approach, struvite synthesis, and chlorination to \$ 0.145/m<sup>3</sup> when replacing pure chemicals substantiates the feasibility and economic sustainability of the hybrid process. In addition, the potential for benefiting from the formed struvite as slow-release fertilizer will be a magnificent trade-off since it has the retail price of \$ 274.7/ton as reported in Mavhungu et al. [19]. The ecological and economic trade-off will also contribute to reducing costs, but more importantly, a reduced environmental impact of the produced sludge, which becomes a resource compared to current classification systems for generated waste.

## 5. Conclusions

The cost analysis of the removal of ammonia from an aqueous environment using the integration of struvite synthesis and breakpoint chlorination was successfully evaluated at the pilot scale. A 1000 litres (1 m<sup>3</sup>) per run (LPR) pilot plant was utilised to fulfil the goals of this study. Specifically, this novel techno-economic study adopted optimum conditions from the laboratory assays comprised of 110 mg/L of Mg and P dosage (concentration), 150 rpm of mixing speed, 60 minutes of contact time, and 120 minutes of sedimentation (Stage 1); the optimum conditions for the breakpoint chlorination were 30 minutes of mixing and 8:1 Cl<sub>2</sub>-

NH<sub>4</sub><sup>+</sup> weight ratio (Stage 2) and duly verified them. The results of this study demonstrated the techno-viable synergistic and complementary effects, with Stage 1 having an increase in pH from 6.8 to 10.1 and a steep reduction in Mn (≥97.0%) and Fe (≥99.6%) concentrations. The deactivation of *E. coli* and TPC led to ≥ 99% and ≥ 91% reduction, respectively, while the attenuation of ammonia ranged from 5.4 mg/L to 2.7 mg/L-N (51.8 % removal efficacy). In the Stage 2 breakpoint chlorination, the ammonia was reduced from 2.7 mg/L to 0.02 mg/L-N after the interaction of water with chlorine, whilst the micro-organisms were completely removed. Last but not least, the techno-economic evaluation established chemical costs of \$ 0.31/m<sup>3</sup>; however, there is a massive potential for cost savings (53.2%) by replacing Kh<sub>2</sub>PO<sub>4</sub> with waste phosphoric acid. Finally, the results from the cost analysis evaluation study showed great potential when compared to similar studies. It will be a game-changer and will play a notable role in managing elevated levels of ammonia and other contaminants, specifically for low- and middle-income countries (LMIC) and further afield.

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