Removal of Ammonia from River Water using Breakpoint Chlorination

Muyahavho Enemiah Mugwili, Elvis Fosso-Kankeu, Vhahangwele Masindi, Vhahangwele Akinwekomi, Hein Neomagus and Frans Waanders

Abstract— Herein, we report the use of breakpoint chlorination for the removal of ammonia from river water. Batch experiments were used to fulfil the goals of this study. Evaluated parameters include hydraulic retention time (HRT), and chemical species concentration. Experimental results denoted the feasibility of removing close to 99 % of ammonia from river water using chlorination. The removal efficacy of ammonia was observed to increase with an increase in chlorine concentration until the breakpoint was reached. Optimum conditions, which were suitable for the removal of ammonia were observed to be pH of 6-8 and 30 minutes of HRT. Chlorine-ammonia ratios were observed to be between 7:1 and 8:1 for synthetic water and river water, respectively. This study showed effective attenuation of ammonia with an increase in chlorine concentration. However, there were disinfection by-products (trihalomethanes) which were observed in the product water, albeit their levels being within the South African National Standard (SANS) for drinking water. In light of the above, it can be concluded that breakpoint chlorination could be an alternative treatment option for the removal of ammonia from drinking water.

Keywords— Ammonia, breakpoint chlorination, disinfection by-products, de-ammonification.

I. INTRODUCTION

As a result of rapid population growth, there is large influx of influents into the wastewater treatment plants. This has however resulted to various operational challenges since the plants were designed to handle certain volumes of incoming wastewater, of which in most instances, the inflow exceeds the design capacity by 50% or more. High volumes of influents compromise the performance of the plants in terms of contaminants attenuation. Specifically, influents are generally characterised of organic, inorganic and microbial substances that need to be removed by processes therein. Of prime concern is ammonia, which is supposed to be removed by biological nutrients removal (BNR) system. Ammonia emanates from decomposition of organic wastes and urine. In light of that, the product effluents are rich in ammonia and other nutrients such as phosphate and nitrates. Consequently, this has led to the enrichment of surface water
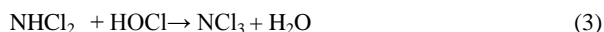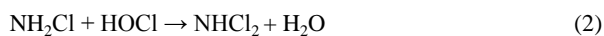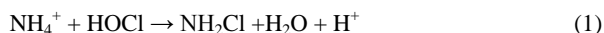
M.E Mugwili, E. Fosso- Kankeu and F Waanders are with Water Pollution Monitoring and Remediation Initiatives Research Group, School of Chemical and Minerals Engineering, North-West University, Potchefstroom, South Africa.
V. Masindi is with department of Environmental Sciences, School of Agriculture and Environmental Sciences, University of South Africa.
M.E Mugwili, V. Masindi and V. Akinwekomi are with Magalies Water, Scientific Services, Research & Development Division, Erf 3475, Stoffberg street, Brits.
H Neomagus is with the Coal Group, School of Chemical and Minerals Engineering at North-west University, Potchefstroom, South Africa

with nutrients leading to a vicious situation of eutrophication and de-oxygenation of water in the catchment after aerobic decomposition of aquatic plants [1, 2]. Although, traces of ammonia remain in the system for long since it is not a primary source of nutrient. Excessive concentration of ammonia can negatively impact the drinking water treatment plants (DWTPs) by reacting with chlorine to form chloramine and this impart objectable taste and smell to water resources [3, 4]. In addition, chloramine reduces the disinfection efficiency of chlorine leading to microbial treatment failures in distribution networks [3] . Furthermore, ammonia in water hinders oxidation of manganese due to competition to available oxidants leading to brownish water emanating from manganese oxidation. This kind of water could taint laundry and textile products after post disinfection of water with elevated levels of manganese [5]. According to WHO and SANS 241 specifications and standards, the maximum allowed limits (MAL) of ammonia in drinking water should be less than 1.5 mg/L. Furthermore, concentration of ammonia exceeding SANS 241:2015 limits does not directly pose a health risk at pH ranges between 6.5 and 8 [3, 6]. Thenceforth, within SANS specification ammonium is regarded as aesthetic determinant which only impacts taste and smell. However, oxidation potential of ammonia leads to formation toxic derivatives such as nitrite. According to WHO, the nitrite levels exceeding 0.9 mg/L N, can lead to oxidation of haemoglobin to methemoglobin, which hampers transportation of oxygen in blood and ultimately lead to the blue baby syndrome. Nitrification normally occurs in drinking water distribution systems posing an immediate health risk to consumers [7, 8]. As such, it is imperative to remove ammonia in drinking water systems. Available technologies that can be incorporated to remove ammonia from surface water include biological aerated filters, ion exchange, electrochemical advanced oxidation, and membrane filtration. However, incorporating the technologies into drinking water treatment system will require structural adjustment, which will increase the operational cost. Furthermore, membrane fouling, cost of regenerating ion exchangers, and energy required for advanced oxidation have limited the technologies to low scale application such as bench scale experiments. Water and wastewater treatment plants incorporate chlorination for disinfection before discharging the water into distribution network or receiving streams and this could potentially play an indispensable role in the removal of ammonia. Chlorine removes ammonia via breakpoint chlorination whereby ammonia is converted to nitrogen gas via oxidation [9]. During breakpoint chlorination, hypochlorous acid initially reacts with ammonium resulting in

formation of chloramine. Continuous addition of chlorine leads to breakpoint and appearance of residual chlorine resulting in complete breakdown of ammonia to nitrogen gas. Reported stoichiometric weight ratio of $Cl_2:NH_3$-N required to breakdown ammonia is 7.6:1 [3, 10]. This ratio is applicable when ammonia is the only chlorine demand in water. Studies have reported higher ratios using breakpoint chlorination on wastewater. Tako [3] reported on a study by laky (2010) which required a $Cl_2:NH_3$-N ratio of 8.6:1, while in Presley [10] studies 8:1 was the required weight ratio. Adam et al.[11] reported that at a $Cl_2:NH_3$-N ratio of 5:1 is when ammonium concentration in aqueous solution starts to decline. The contact time ranging between 10 - 15 minutes is optimal for breakpoint chlorination [3]. However, studies have also reported contact time ranging from 30 minutes to 24 hrs for complete breakpoint [12-14]. Theoretically, breakpoint is a point where free and combined chlorine is non-existent and where chloramine residuals decline to a minimum value after some time of equilibration. Breakpoint chlorination reactions are depicted by the following equations [11]:

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \qquad (1)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \qquad (2)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \qquad (3)$$

Initially, ammonium will react with hypochlorous acid leading to formation of chloramine, water and acidity as shown by equation 1. Continuous addition of chlorine results in formation of dichloramine and finally nitrogen trichloride which is unstable and converts to nitrogen gas leading to decomposition as shown in Equation 4 [3]. Chloramines are made up of the three species of chlorinated ammonia compounds such as monochloramine, dichloramine, and trichloramine (nitrogen trichloride) [15]. The formation of chloramines is pH dependent. Monochloramines are dominant at pH exceeding 8, while dichloramines are primarily dominant at pH lower than 7.5. The unstable Nitrogen trichloride is dominant at pH lower than 7.4 [11] . Based on overall equation, breakpoint chlorination could be summarised as follows:

$$3HOCl + 2NH_3 \rightarrow N_2 + 3H^+ + 3Cl^- + 3H_2O \qquad (4)$$
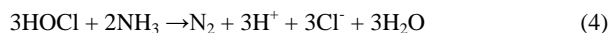
The main challenge associated with the use of chlorine is the production of the disinfection by-products (DBPs).when chlorine is used in water with notable levels of natural and synthetic organic matter (OC). In drinking water plants, trihalomethanes (THMs) such as Bromodichloromethane, Chloroform, Bromoform and Dibromodichloromethane are the main group of DBPs and these products have been reported to be carcinogenic on exposure to living organisms [16, 17]. Thenceforth, this has been confirmed in a number of toxicological and epidemiological reports. Precisely, chlorine dosage, pH, ammonia nitrogen concentration, contact time and bromide ions affect the formation of of DBPs [12]. Activated carbon can be used in conjunction with breakpoint chlorination

to absorb and remove the DBPs that might have formed during the chemical reaction [3]. Furthermore, based on the pH of the solution, between 1 and 15% of ammonium nitrogen is oxidised to nitrate during breakpoint chlorination but the primary product is nitrogen gas [10]. The breakpoint is a readily available technology in water treatment systems and has been used to breakdown ammonia to required levels. However, WTPs have been failing to decompose ammonia to the required levels even with ratios exceeding previously reported levels of ammonia breakdown stoichiometries. To the authors' knowledge, calcium hypochlorite has not been used for breakpoint chlorination and this will be the first study in design and execution to explore the utilization of calcium hypochlorite. The key objectives of this study will be (i) Investigate $Cl_2:NH_3$-N ratios suitable for the decomposition of ammonium in raw water (ii) Investigate the formation of THMs at breakpoint chlorination (iii) Explore the efficiency of calcium hypochlorite for breakpoint chlorination studies.

II. METHODOLOGY

A. Sampling collection and preparation

Raw water was collected from Wallmannsthal WTP canal system. The canal receives water from Roodeplaat dam (25.62083°S and 28.37138° E). The dam is rich in nutrients resulting from wastewater treatment discharge upstream the catchment. High-density polyethylene (HDPE) wide-mouth bottles were used for sample collection. Analytical Grade Ammonium Chloride Crystal AR 500g was procured from Aqualytic (pty) limited and bulk granular calcium hypochlorite (65-70% Cl_2) was procured from Protea Chemicals. .Stock solutions were prepared by diluting appropriate amounts of ammonium chloride and calcium hypochlorite in 1L deionized water and mixing with a magnetic stirrer for 30 minutes. Each solution was kept in 1 L volumetric flasks. The Wallmannsthal Drinking water treatment plant (DWTP) uses conventional treatment method, which includes pre-disinfection/PAC adsorption, Coagulation/Flocculation, Sedimentation, filtration and post disinfection with chlorine. Breakpoint chlorination is the only available technology to deal with high incoming ammonium concentration. As a quality control initiative, the sampling protocols and preparation procedures were duly considered.

B. Analytical techniques

Natural organic matter (NOM) concentration was analysed as total organic carbon total using a Shimadzu TOC-L CPH analyser (Shimadzu Corporation, Japan) for total organic carbon (TOC), and the detection limit was 0.1 mg/L C. Ammonium nitrogen, nitrite and nitrate were measured using a Gallery Plus analyser (Thermo Fischer Scientific Brand, USA). Solution pH and conductivity were measured using an HQ40d multi meter pH meter (Hach Company, Loveland, USA) which was calibrated using standard buffer solutions. Iron and manganese were measured using an Inductively Plasma Optical Emission Spectrometer (ICP-OES), Agilent (Agilent, Santa Clara, CA, USA). Total, free chlorine and monochloramine were analysed using MISP-REM-HAH-DR900 colorimeter

(Hach Company, Loveland, USA). Trihalomethanes were measured using the Gas Chromatography Mass Spectrometry (GC-MS) (Agilent technologies 5975 C, CA, USA) which is connected to a purge and trap (OI Analytical Eclipse 4660 Purge and Trap Sample Concentrator) instrument Standard methods were used to analyze the samples [18].

C. Breakpoint Experiments

Bench scale experiments were conducted for both synthetic water and raw water using a six paddle Phipps and bird jar stirrer. For synthetic water, prepared ammonium stock solution was added into rapidly stirring synthetic water. Ammonium concentration in synthetic water was 2 mg/L. Raw water was analysed for ammonium nitrogen, total organic carbon and pH prior to the experiments. Optimal contact time for breakpoint has been reported to be between 10-15 minutes [3], but for this study, we adopted 30 minutes hydraulic retention time (HRT) used in Charrios studies [14]. Mixing speed adopted was 200 rpm, which represents optimal mixing conditions for the Wallmannsthal water treatment plant. Practically, the plant receive raw water with medium level ammonium concentration (Ranging from 2-8 mg/L). The experiments explored the effect of chlorine concentration on breakpoint chlorination by adding varying concentration of chlorine prepared from calcium hypochlorite into individual 1 L beakers. Required aliquots of the stock standard calcium hypochlorite solutions were added into rapidly mixing raw and synthetic water at chlorine dosages ranging from 2 to 24 mg/ L (0.028-0.336mM). After completion of the experiments, solutions were analysed for total and residual chlorine, ammonium nitrogen, nitrite, nitrate, trihalomethanes (THMs), temperature, pH and conductivity.

D. Analysis of Chlorine byproducts

To ascertain the concentration of disinfection byproducts, the analysis of the four trihalomethanes were conducted using a Gas Chromatograph-Mass Spectrometry (GC-MS) coupled to a Purge and Trap (OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator).). HPLC grade eluent was used as a media for chlorine disinfection by-products. Sample matrix analysis were conducted by transferring 10 ml of the sample into vials. For quality control purposes, the vials were tightly sealed using a new septum each time and this was done to minimise cross-contamination of calibration blanks, control samples and samples to be analysed. The prepared samples were then placed into the OI analytical purge and trap, which trapped water. Thereafter, the sample is purged for approximately 8 minutes with nitrogen gas. Ultimately, the concentrated sample is then transferred to the gas chromatograph using helium gas (7890B, Agilent Technologies, United States). Furthermore, analysis of THMs was done using mass spectrometer (5975C, Agilent Technologies, United States).

III. RESULTS AND DISCUSSION

A. Effects of Cl_2/NH_3-H ratio for ammonia removal

The concentrations of NH_3-N of the effluents for both synthetic and raw water experiments were measured before and after the reactions. Raw and synthetic water concentrations prior the experiments were 2.5 mg/L and 1.7 mg/L respectively. On both experiments, increasing the chlorine dosage resulted in decrease in the ammonium concentration with 99.09 % de-ammonification efficacies achieved at Cl_2/N ratio of 8:1 for raw water (Figure 1) and 98.64 % de-ammonification of synthetic water at Cl_2/N ratio of 7.05:1 (Figure 1). Effluent ammonium concentrations after breakpoint are lower than SANS 241:2015 limits (NH_3-H $\leq$ 1.5 mg/L N). Figures 1 and 2 shows the breakpoint for both synthetic and raw water experiments.
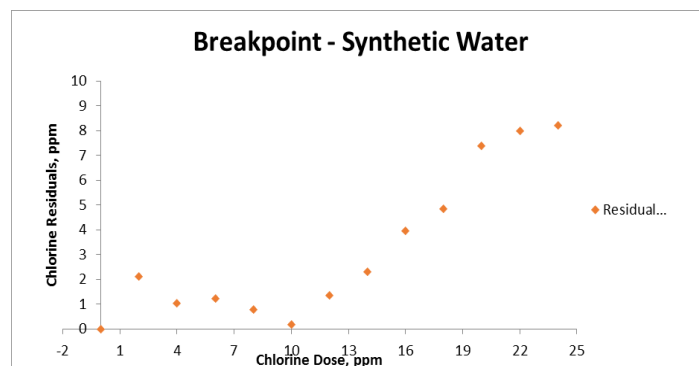

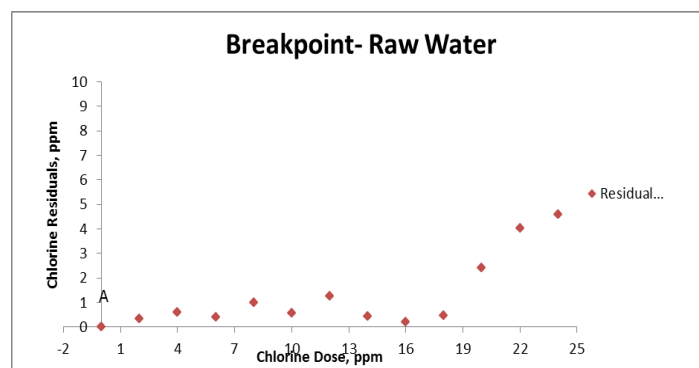Fig. 1: Breakpoint Curve for synthetic Water

Fig. 2: Breakpoint Curve for Raw Water

The obtained results corroborate what has been reported in literature [3, 10]. Quick breakpoint could be explained by the fact that synthetic water had only ammonium as a chlorine demand, thus ruling out potential competition for chlorine. The ratio (7.05:1) to decompose the ammonia was lower than the stoichiometric ratio of 7.6:1 reported in previous studies [15]. Experiments carried out on the raw water with initial concentration of 2.5 mg/L and organic carbon resulted in breakpoint achieved at Cl_2/N ration of 8:1 and this was notably high in relation to synthetic water. Researchers have reported varying breakpoint mass ratios and concluded that the ratio is dependent on the chlorine demand of the water being treated. Presley[10] and Tako [10] studies have reported ratios of 8:1 and 8.6:1 respectively when using breakpoint in wastewater which has high chlorine demand [3, 10]. The ratio from this study is lower due to the lower demand expected from the surface water compared to wastewater. The relationship between ammonia and chlorine dosage (mg/L) is illustrated in
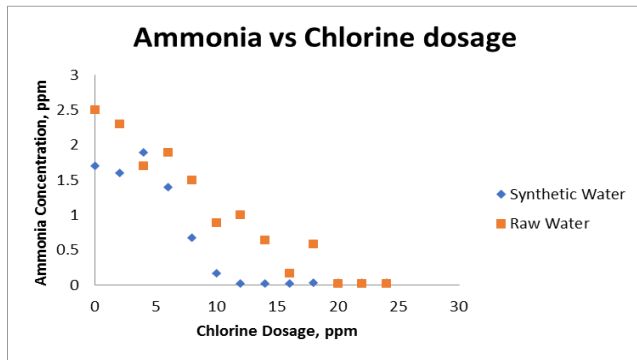
Figure 3 and 4.

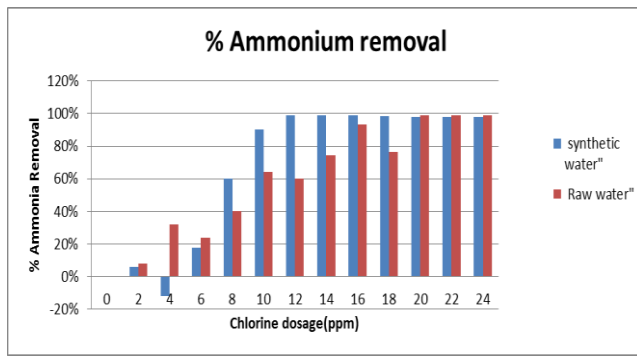Fig. 3: Ammonia removal against chlorine dosage

Fig. 4: Percentage ammonium removal

As shown in Figures 3 and 4, there was an increase in breakdown of ammonia with an increase in chlorine dosage. At breakpoint, 98.64 % and 99.09 % de-ammonification was achieved for synthetic and real water, respectively. This could be attributed to the reaction of chlorine to ammonia leading to its decomposition to nitrogen gas as shown in Equation 4. This is consistent to what has been reported by other authors [3, 9, 15]. The quality of the synthetic and raw water are summarised in table I and II below.

TABLE I: RAW AND SYNTHETIC WATER CHARACTERISTICS

Determinant	Unit	Synthetic	Raw
Nitrate	mg/L	4.8	2.7
nitrite	mg/L	0.010	0.010
TOC	mg/L	1.82	8.39
pH	mg/L	7.83	7.16

TABLE II: TREATED SYNTHETIC AND RAW WATER RESULTS.

Determinant	SANS 241	Treated Synthetic	Treated raw water
Nitrate	$\leq$ 11 mg/L	2.1-4.8	0.22-3.8
Nitrite	$\leq$ 0.9 mg/L	0.010	0.010-0.41
TOC	$\leq$ 10 mg/L	2.7-4.63	8.83-12.2
pH	7.6-8.6	6.79-8.21	7.25-8.13

The effluent nitrite and nitrate from the breakpoint experiments were within SANS 241 drinking water limits; and pH varied from 6.79 to 8.21 based on the concentration of chlorine added. Increased in chlorine dosage decreased the pH in both experiments.

B. *Effects of Cl_2/NH_3-H ratio on THMs.*

Breakpoint chlorination was evaluated on both river and synthetic water in an effort to evaluate the influence of Cl_2:NH_3-H ratios on THMs formation in water that is concentrated with ammonium.. Raw water has natural organic matter, which was expected to react with chlorine resulting in formation of disinfection by-products during breakpoint chlorination. THMs in drinking water were first identified in 1972 leading to compliance regulation on the discharge to avoid acute health risk to end users. South African drinking water standards have set discharge limits for each THMs to avoid health risk. Table III shows the THMs results for both raw and synthetic water during the experiments.

TABLE III: THMs RESULTS FOR TREATED SYNTHETIC RESULTS.

Determinant	Unit	SANS	Synthetic	Raw
Bromodichlomethane	µg/L	$\leq$100	0.24-30	0-25
Bromoform	µg/L	$\leq$100	0-26	0-15
Chloroform	µg/L	$\leq$300	2.6-47	2.4-120
Dibromochlomethane	µg/L	$\leq$60	0-28	0-0.64

From the experimental results, Chloroform peaked at 120 µg/l for raw water and 47 µg/l for synthetic water and Cl_2:NH_3-N ratio of 9.6:1 and 14:1 respectively. Bromoform peaked at 2.4 µg/l for raw water and 26 µg/l for synthetic water. The bromodichloromethane highest values were 25 µg/l and 30 µg/l while the dibromodichloromethane highest values were 0.64µg/L and 28µg/L for raw and synthetic water respectively. Impact on formation of THMs was minimal from the breakpoint experiments using calcium hypochlorite even on ratios higher than breakpoint. Results of THMs were all significantly lower than the SANS 241.

IV. CONCLUSION AND RECOMMENDATION

This study successfully demonstrated that ammonia can be removed from aqueous solution using breakpoint chlorination. Findings from this study revealed that:
- Close to 99.09 % of ammonia was removed from raw water at 8:1 ratio whereas 98.64 % of ammonia was removed from synthetic water at 7.05:1ratio.
- The required hydraulic retention time (HRT) of 30 minutes is adequate to fulfil the goals of this study.
- The DBPs (THMs) resulting from breakpoint chlorination were lower than the South African drinking water standards even at higher chlorine dosages.
- Calcium hypochlorite provides an alternative chlorine source that is suitable for ammonium decomposition by breakpoint chlorination.

Future research should focus on techno-economic evaluation and feasibility assessment. Furthermore, upscaling of the developed technology in a real water treatment plant should be explored.

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