

TREATABILITY STUDIES OF GROUNDWATER CONTAINING HIGH AMMONIUM CONCENTRATIONS USING CHLORINE BASED COMPOUNDS

Ion Viorel Patroescu, Cristiana Cosma, Mihaela Alexie, Lucian Constantin, Ionut Cristea

*National Research and Development Institute for Industrial Ecology ECOIND, 71-73 Drumul Podu Dambovitei St., sector 6, Bucharest, Romania
tehnologi@incdecoind.ro*

Abstract

The composition of groundwater is of interest for drinking water service providers due to its implications upon the potabilisation treatment flow. The paper is presenting two case studies from Romania, each groundwater sources containing ammonium and organic load reactive to chlorine. Oxidation tests for NH_4^+ were performed using chlorine and sodium hypochlorite on water samples with the following characteristics: $\text{NH}_4^+ \leq 4.4$ mg/L and $\text{DOC} < 1$ mg/L. Oxidation tests with chlorine at the breakpoint showed that a weight ratios of Cl_2 : $\text{N-NH}_4^+ \geq 10 : 1$ and reaction time of 40 min are needed in order to assure a remanent concentration of NH_4^+ below the admissible value of 0.5 mg/L, residual chlorine concentrations being in the range of 12-20 mg/L, and THM concentration after 24 h in the range of 102-277 $\mu\text{g/L}$. Oxidation tests with NaOCl showed that even at high doses of active chlorine (30 mg/L) and long reaction time of 24h, remanent ammonium concentration is higher than the admissible value of 0.5 mg/L, residual chlorine concentration being of mg/L order. In this case, selection of an alternative raw water source or the replacement of classical oxidation technology using chlorine by biological nitrification is needed.

Keywords: *ammonium, chlorinated by-products, groundwater, natural organic matter*

1. Introduction

The main usage of chlorine in drinking water treatment is for disinfection (pre- and post disinfectant). However, chlorine has also found application for a variety of other water treatment objectives, such as: oxidation of iron, manganese, hydrogen sulfide, ammonia, prevention of algal growth in sedimentation basins and filters, maintenance of biological stability of drinking water by prevention of bacteria regrowth in the distribution system [1].

In Romania, the treatment technologies currently applied for N-NH_4^+ oxidation involve use of chlorine, the only chemical oxidant which can react with NH_4^+ ions at the pH current values of natural drinking water resources, ground water especially.

The use of chlorine in order to reduce NH_4^+ concentration is based on the oxidation reactions to elemental nitrogen, the intermediates compounds being the chloramines (mono-, di-, chloramines and nitrogen trichloride).

The stoichiometric ratio chlorine to nitrogen ammonia ($\text{Cl}_2:\text{N-NH}_4^+ = 7.6:1$) assuring N_2 as major end product is not affected by pH, the ideal operating

values for break point chlorination being situated between pH = 7 and pH = 8. Taking into account the variability of groundwater pollution matrices, the chlorine demand for N-NH₄⁺ break point chlorination is determined by experimental works for each case, the variation domain of Cl₂ : N-NH₄⁺ weight ratio being quite large (Cl₂ : N-NH₄⁺ = 7.6 : 15/1).

Numerous inorganic and organic pollutants/micropollutant can undergo reaction with chlorine, for most of them HOCl being the major reactive chlorine specie. Natural organic matter (NOM) like humic substances present in water resources react with aqueous free chlorine or free bromine, halogenated by-products being formed. Several factors such as: pH, dissolved organic carbon (DOC), bromide concentration, temperature and operational factors like chlorine dose, contact time were reported to affect the formation of halogenated by-products. Aqueous chlorine converts bromide ion to hypobromous acid, which can react with organic matter in the same way as hypochlorous acid to form various bromchlorinated by-products, HOBr being a stronger halogenating agent than HOCl. THM species (CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃) were proven to have adverse effects on human health, especially brominated species being suspected to be much stronger carcinogens and mutagens than non-brominated species.

Only a small percentage of chlorinated by-products has been quantified/regulated in drinking water: THMs, the MCL total THM being 80 / 100 µg/L (US regulations / EU regulations).

The other by-products reported for treated water using chlorine (oxidation / disinfection reaction) are, as follows: haloacetic acids (HAAS/MCL = 60 µg/L only in US regulations), haloacetonitriles (HANS), haloketones, haloaldehydes chlorinated phenols, chloropicrin, a.s.o. [2÷5]

2. Materials and Methods

The aim of experimental tests was to demonstrate how the chlorination process applied for the treatment of groundwater containing N-NH₄⁺ ions higher than 1 mg/L, and low natural organic matter (TOC < 1 mgC/L) can affect the quality of drinking water.

The following experimental activities were performed:

- Analytical investigation of two groundwater sources (200-340 m depth) in order to evaluate the main quality parameters: pH, turbidity, hardness, conductivity, ammonia, COD-Mn, TOC/DOC, inorganic ions (Fe, Mn), bromide ion;
- Assessment of THM potential formation (THMPF), due to the reactivity of NOM towards chlorine in specific conditions (Cl₂ doses, pH, reaction time, temperature). Periodically, determination of generated THMs along the experimental period (7 days) was done;
- Oxidation of ammonium ion by using chlorine based compounds (Cl₂, NaClO) in specific conditions as follows:
 - **N-NH₄⁺ break-point chlorination**
 - Cl₂:N-NH₄⁺ = 10/15:1 (weight ratio)
 - reaction/contact time = 40 minutes/24 hours

Chlorine water (Cl₂ = 0.9-1 g/L) was used as chlorine source.

Analysed parameters after 40 min/24 hours reaction time were: pH, residual NH_4^+ , residual Cl_2 (total and free), THMs.

- **NH_4^+ oxidation using NaClO**

- Cl^* (active chlorine) doses 10÷ 30 mg Cl^*/L
- reaction/contact time = 40 minutes/24 hours

NaClO solution (1.84 g Cl^*/L) was used as chlorine source.

Analysed parameters after 40 minutes/24 hours reaction time were: pH, residual NH_4^+ , residual Cl_2 (total and free)

Analytical investigations for raw/treated groundwater characterization were performed using standardized methods.

Results and Discussion

Assessment of groundwater quality

The analytical investigations emphasized the main pollutants which are situated above the MCL values (NH_4^+ , turbidity/ Fe_{total}) or can influence the generation of THMs (TOC/DOC, Br⁻). According to the registered data (Table 1), the following remarks are:

- **NH_4^+** concentrations are rather high, around 4 mg/L ($\text{MCL}_{\text{NH}_4^+} = 0.5\text{mg/L}$);
- **Turbidity** values are also higher than $\text{MCL} \leq 5$ NTU, due to the presence of iron hydroxide ($\text{Fe}_{\text{precipitated}} \leq 800 \mu\text{g/L}$);
- Organic load evaluated as total organic/dissolved organic carbon (**TOC/DOC**) is situated below 1 mg C/L (< 0.5 mg/L), majority of NOM being under dissolved form (91-95%);
- **Br⁻** ion, not normed by specific law for drinking water quality, is below the detection limit of method (Br⁻ < 100 $\mu\text{g/L}$).

Table 1. Main physical-chemical characteristics of groundwater located in Targu-Jiu county: P1 and P2 (momentary samples)

Parameter	U.M.	Values	
		P1	P2
pH	-	7.7	8.2
COD-Mn	mgO ₂ /L	2.2	1.5
TOC/DOC	mgC/L	0.41 / 0.39	0.34 / 0.31
Turbidity	NTU	13.5	19
Total hardness	German degree	21	1.3
Conductivity	$\mu\text{S}/\text{cm}$	1005	361
Fe total	$\mu\text{g}/\text{L}$	660	838
Fe dissolved	$\mu\text{g}/\text{L}$	14	< 0.2
Mn total	$\mu\text{g}/\text{L}$	33	24
Mn dissolved	$\mu\text{g}/\text{L}$	28	17
NH_4^+	mg/L	4.2	4.35
Br ⁻	$\mu\text{g}/\text{L}$	< 100	< 100

Assessment of THM potential formation (THMPF)

The applied chlorine doses were in accordance with DOC and N-NH₄⁺ concentrations for each source, the work conditions being similar: Cl₂ : DOC ratio = 3 : 1, Cl₂ : N-NH₄⁺ ratio = 8.1 : 1, contact time 1 ÷ 7 days, buffered pH = 7 – 7.2, temperature 20 – 22 °C.

The evolution of THMs concentrations and residual chlorine (total/free) in time is presented in figures 1-2. Also, the speciation of THMs for the first and last day of tested period is presented in the figures 3.1, 3.2.

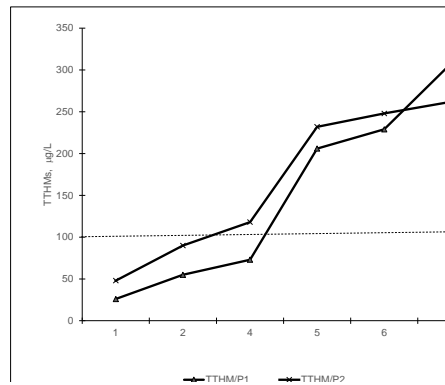


Figure 1. THMPF – Evolution of THMs concentrations vs contact time

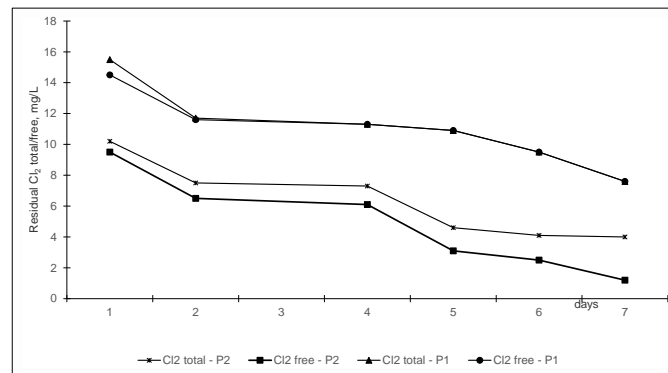


Figure 2. THMPF – Evolution of residual chlorine

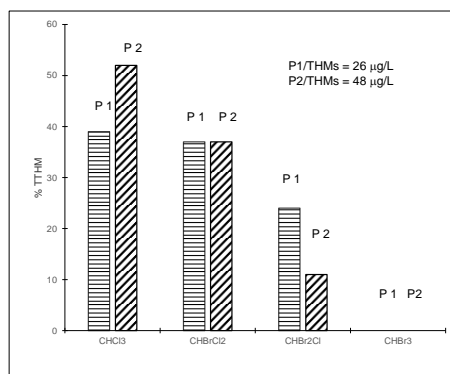


Figure 3.1. THMPF – THMs speciation (day 1)

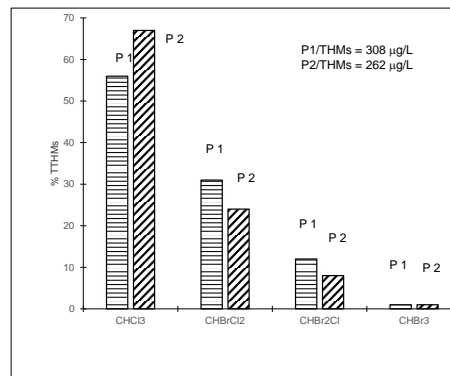


Figure 3.2. THMPF – THMs speciation (day 7)

The following aspects are resulting taking into account the experimental results:

- TTHMs generated in the two groundwater sources (P1, P2) present an increasing evolution in time, proving the reactivity of dissolved organic matter (DOC = 0.31-0.39 mg C/L) toward chlorine and in situ generated bromide. According to the literature data, “high DOC” concentration value, potential to produce THMs higher than MCL (100 µg/L) is situated above 2 mg C/L. But, the presence of high concentrations of associated pollutants such as ammonium ion ($\text{NH}_4^+ \simeq 4 \text{ mg/L}$), which need high doses of chlorine for oxidation the organic/inorganic THMs precursors (DOC/Br) can generate halogenated by-products in watery system.
- Taking into account the low concentration of DOC (< 0.5 mg C/L), the generated THMs are exceeded the MCL value only after 4/5 days (fig. 1). So, TTHMs after 1-2 days are situated below MCL, between 55 µg/L (P1) and 90 µg/L (P2) the generated species being CHCl_3 (54-55%) and brominated derivatives (45-46%), fig. 3.1.
- The final TTHMs concentrations (contact time = 7 days) are two/three times higher than MCL (P1/TTHMs = 308 µg/L; P2/TTHMs = 262 µg/L), the main generated specie being CHCl_3 (P1/ CHCl_3 = 56% TTHMs, P2/ CHCl_3 = 67% TTHMs).

The total brominated derivatives (CHCl_2Br , CHClBr_2 , CHBr_3) are representing 44% (P1) and 33% (P2) of final TTHMs, which confirm the influence of bromide ion even at low concentration ($\text{Br}^- < 100 \text{ µg/L}$) upon THM speciation (fig. 3.2).

- Total residual chlorine concentration is decreasing in time (fig. 2).

Assessment of ammonium ion break point chlorination

The use of chlorine, the only chemical oxidant which can react with N-NH_4^+ , (break point chlorination), generates as reaction products, chloramines as intermediates and elemental nitrogen (N_2).

The experimental results of chlorination testes performed in order to reduce ammonium ion concentrations below MCL (0.5 mg/L) by applying high Cl_2 : N-NH_4^+ ratios (10/15:1) are presented in the table 2.

Table 2. NH₄⁺ break point chlorination. Influence of Cl₂ : N–NH₄⁺ ratio

Cl ₂ :N– NH ₄ ⁺ ratio	Treated water. Residual concentrations					
	NH ₄ ⁺ , mg/L		Free Cl ₂ / Combined Cl ₂ ,mg/L		TTHMs, µg/L	
	P 1	P 2	P 1	P 2	P 1	P 2
10 : 1	0.59	0.48	11 / 1	15 / 2.5	4.3/ 40 min	11.7/ 40 min
					102/ 24 h	250/ 24 h
15 : 1	0.32	0.12	12 / 2.5	19 / 1	4.8/ 40 min	15.5/ 40 min
					220/ 24 h	277/ 24 h
Raw water			Work condition			
P1: pH = 7.54; NH ₄ ⁺ = 4.2 mg/L			Cl ₂ :N-NH ₄ ⁺ = (10÷15) : 1			
P2: pH = 8.2; NH ₄ ⁺ = 4.35 mg/L			τ oxidation = 40 minutes			
			pH = 7 – 7.2			

The following remarks are emphasized:

- NH₄⁺ residual concentration decreasing with applied Cl₂ doses, NH₄⁺ values below MCL for both treated water samples (P1 and P2) being registered for Cl₂:N-NH₄⁺ = 15:1;
- high residual chlorine free and combined concentrations (mg/L) in treated water after 40 minutes of contact/reaction above MCL;
- slow increase of THMs in treated water after 40 minutes of reaction (P1/THMs < 5 µg/L; P2/THMs < 16 µg/L) for both chlorine doses;
- development in time of specific chlorinating reactions (oxidation, substitution) with the increase of THMs above MCL after 24 hours (P1/THMs ≤ 220 µg/L; P2/THMs ≤ 277 µg/L).

Assessment of ammonium ion oxidation using NaClO

In Romania a large number of DTWPs for small communities (raw water-groundwater) is using sodium hypochlorite (NaClO) for water disinfection and also for specific pollutants oxidation (NH₄⁺±NO₂⁻±S²⁻±Mn²⁺).

The reaction between NaClO (solution, typically with 12.5% available chlorine) and water: NaClO + H₂O → HClO + Na⁺ + HO⁻ releases hydroxyl ions that will increase the pH of water.

The aim of experimental tests was to evaluate the reactivity of NaClO towards NH₄⁺ ions, the applied doses being between 10 and 30 mg Cl^{*}/L, at contact/reaction time of 40 minutes and 24 hours.

The influence of applied doses at contact/reaction time of 40 minutes is presented in the figure 4, also the influence of contact time was evaluated (Table 3)

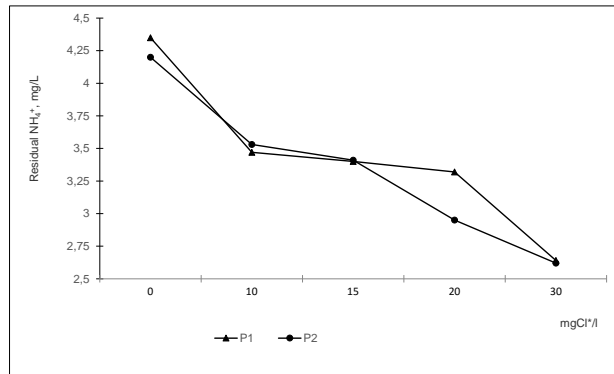


Figure 4. NH₄⁺ oxidation using NaClO. Influence of oxidant dose (contact time = 40 minutes)

Table 3. NH₄⁺ oxidation using NaClO. Influent of contact / reaction time

Parameter	20 mg Cl [*] /L				30 mg Cl [*] /L			
	τ = 40 min		τ = 24 h		τ = 40 min		τ = 24 h	
	P 1	P 2	P 1	P 2	P 1	P 2	P 1	P 2
pH	8.14	8.3	8.12	8.1	8.15	8.35	8.14	8.20
NH ₄ ⁺ ,mg/l	3.36	2.95	2.02	1.5	2.64	2.62	1.33	1.2
Total residual Cl ₂ / Free Cl ₂	8.4/0.1	9.1/0.1	3/0.1	2.7/0.1	10/0.1	10.1/0.1	3.4/0.1	3.2/0.1
Raw water								
P1 : pH = 7.54; NH ₄ ⁺ = 4.2 mg/L								
P2: pH = 8.2; NH ₄ ⁺ = 4.35 mg/L								

According to experimental results the following aspects are emphasized:

- Oxidation yields of NH₄⁺ are depending on oxidant applied dose, a slow increasing being registered (P1 = 17-37%; P2 = 14-36%).
- The increasing of contact/reaction time at 24 hours leads to the improvement of oxidation efficiencies ($\eta_{\text{NH}_4^+} \leq 71\%$), but the NH₄⁺ residual concentrations are situated above MCL (P1/NH₄⁺ = 1.33 mg/L; P2/NH₄⁺ = 1.2 mg/L).
- The residual chlorine (mg/L) is majority under combined forme.

Conclusion

In Romania, the treatment technologies currently applied for ammonium ions oxidation involve use of chlorine based compounds (Cl₂/NaClO). The experimental tests performed in order to verify the process applicability for the treatment of groundwater containing NH₄⁺ > 1 mg/L and organic natural matter (DOC < 0.5 mg/L) leads to the following conclusion:

- high doses of chlorine required by N-NH₄⁺ break point chlorination (Cl₂:N-NH₄ ≥ 10:1) are able to affect the quality of treated water;
- the noncompliance aspects related to the treated water intended to human consumption (THMs concentration, residual chlorine free and combined chlorine ratio a.s.o.) impose the replacement of classic process based on chemical oxidation with other process (biological nitrification).

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