

Formation and Stability of mono-, di- and trichloramine in Water Solutions

I. Monochloramine

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Paper objectives were to determine conditions for monochloramine formation in water solutions, its stability against time at pH= 6, 7, and 8, for two series of chlorine : ammonia mass ratios (R), 1:1–8:1 and 2 :2–12:2 (mg/L:mg/L), at 20°C. Maximum monochloramine concentrations were recorded for the ratios 3:1 and 4.18:1 in the first minutes after reagents mixing: 1.8-2.3 mg/L (pH = 6.0), 2.4-3.0 mg/L (pH = 7.0), 2.7-3.7 mg/L (pH = 8.0) mg/L. For the second series the maximum concentration, 5.6 mg/L, was recorded at pH = 7.0 and R= 4.18:1. Due to monochloramine autodecomposition, at 24 hours after reagents mixing for R = 3:1 and 4.18:1, the following percents from initial concentrations were determined: 60.8-72.2% (pH = 6.0), 80.0-83.3 % (pH = 7.0), 96.2 – 97.2 % (pH = 8). These results are useful to natural water treatment for drinking purpose.

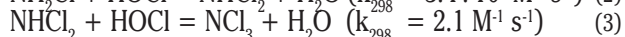
Keywords: monochloramine, dichloramine, mass ratios, pH, stability

The widespread of the concept referring to the using of combined oxidants for water treatment, took place in the last decade. Investigations for the development of new technologies were realized, taking into account oxidation and disinfection processes like, chlorination, chloramination, ozonation and treatment with chlorine dioxide [1-3]. The using of chloramination is justified due to its advantages:

- chloramines are not reactive with organic compounds;
- they remove unpleasant smell and taste;
- residual monochloramine is more stable than free chlorine or chlorine dioxide, thus a better protection against bacterial development in the treatment systems with huge basins and zones with reduced flow of water, is realized;
- chloramines assure decreasing of total number of bacteria and coliforms, and they have strong bactericidal effects;

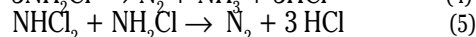
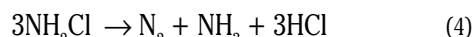
- cheap installations are necessary [4,5].

Inorganic chloramines are disinfectants formed by rapid reactions of free chlorine in waters containing ammonia, when mono-, di- and trichloramine are formed:



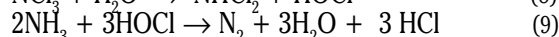
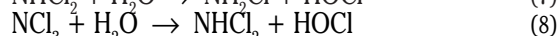
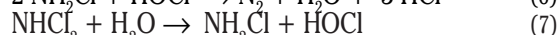
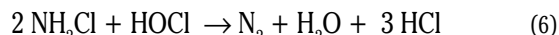
From these, monochloramine is used for natural water treatment to obtain drinking water, and the process is called chloramination [6-8].

Monochloramine is prepared by chlorine introducing in water and then of ammonia, using chlorine:ammonia mass ratios between 2:1-6:1 (mg/L:mg/L). Simultaneously, small dichloramine concentrations are formed. The concentrations of NH_2Cl used in water disinfection are in the range of 1.0-4.0 mg/L [9-11]. Chloramines stability versus time is an actual research field [6,12]. For their autodecomposition, the following reactions were proposed:



When $\text{Cl}_2:\text{NH}_3$ ratios higher than 7.0:1 (mg/L:mg/L) are used for water treatment, all chloramines are formed. But, due to high chlorine concentrations, they are oxidized to nitrogen in few hours, depending on water quality: the chlorine:ammonia mass ratio to which no chloramine and ammonia there are in the water, was called as “breakpoint” [13,14,15]. After this point, the addition of chlorine will produce free chlorine only, in water. So, breakpoint process consists of two successive steps:

- water treatment with chlorine and chloramines, by using of $\text{Cl}_2:\text{NH}_3$ ratios between 7.0 :1–10 :1 (mg/L:mg/L) when chloramines formation takes place, followed by their hydrolysis and oxidation, due to high chlorine doses:



- treatment with free chlorine, dominant species after chloramines oxidation.

Chloramination disadvantages, higher contact times than in the case of chlorine, necessary for bactericidal control, initiation of nitrification process in the distribution systems with high dimensions if ammonia is dosed in excess, are overcome by application of combined treatment processes [16,17]. One of controversial aspects is, if small chlorine:ammonia mass ratios to be used, when residual concentrations of monochloramine with high stability are estimated to be formed or, higher mass ratios to avoid free ammonia in water distribution systems [18, 19].

Stability of monochloramine versus time was investigated for a limited number of chlorine:ammonia mass ratios, e.g., 2:1, 2.5:1, 3.5:1(mg/L:mg/L) [6, 12]. The

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objectives of this paper were to determine conditions in which monochloramine is formed in maximum concentrations, and to evaluate its stability versus time for an extended range of chlorine ammonia ratios at 3 pH values, using reagent concentrations similar with those from water treatment practice.

Experimental part

For investigation of the chloramination process, stock chlorine and ammonia solutions in distilled water were prepared, with the following concentrations: 120 mg/L chlorine and 100 mg/L ammonia. These were used for preparation of two series of chlorine:ammonia mass ratios as follows: R = 1:1, 2:1, 3:1, 4.18:1, 5:1, 6:1, 7:1, 7.6:1 (series A), and R = 2:2, 4:2, 6:2, 8.36:2, 10:2, 12:2 (series B), (mg/L :mg/L), at three pH values, 6,0 ; 7,0; 8,0 and 20°C. pH was kept constant using buffered solutions prepared by mixing monopotassium phosphate (0.1 N) with sodium hydroxide (0.1 N).

The following parameters were investigated: free chlorine, monochloramine, dichloramine, ammonia, versus contact times (2.5 -1440 min) and chlorine: ammonia mass ratios. For the analysis of chlorine, mono- and dichloramine, N,N-diehl-p-phenylenediamine with ferrous ammonium sulphate (DPD-FAS) titrimetric method was used, and ammonia was determined by colorimetric method with phenol and hypochlorite, in the presence of sodium nitroprusside [20]. The following correlation between absorptions measured at 640 nm ($0.011-0.26 \text{ cm}^{-1}$) and ammonia concentrations (0.01 – 0.40 mg/L) was determined: $y = 0.6686x + 0.0039$ with $r^2 = 0.9917$, where y = absorption, x = concentration.

Results and discussion

Chlorine reaction with ammonia was instantaneous, and monochloramine formation took place immediately after reagents mixing.

At pH = 6.0 and R = 1:1, monochloramine concentration at 2.5 min after reagents introduction was 0.80 mg/L. For the following two ratios, 2:1 and 3:1, NH_2Cl formed in the first minutes was 1.4 and 1.8 mg/L, respectively, fig. 1a. From initial concentrations, 72.2-93.7%, were found in solutions after 24 h.

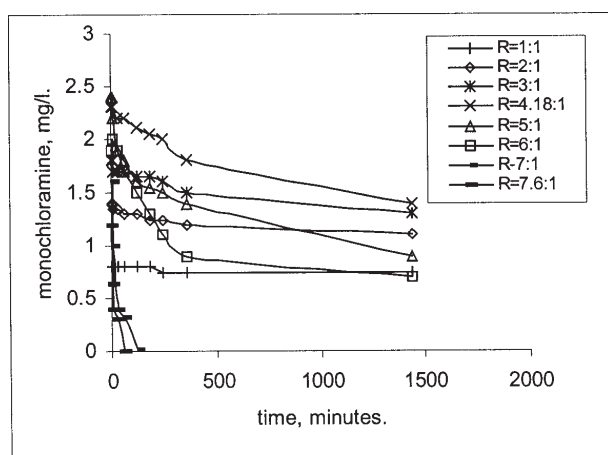
Maximum concentrations of NH_2Cl were obtained for R = 4.18 :1, 5 :1, 2.3 and 2.4 mg/L, respectively. During 24 h these concentrations decreased up to 60.8% and 37.5% respectively, due to monochloramine auto-decomposition (4) and (5). These findings are close to those reported for autodecomposition of 2.5 and 3.5 mg/L mono-chloramine in 24 h, at pH = 6.5 [6,12].

At higher values of R, 7:1, 7.6:1, monochloramine was formed in the first minutes in progressive decreasing concentrations, 1.6 and 1.2 mg/L, respectively. Due to increasing of chlorine concentrations, advanced oxidation of NH_2Cl took place, (6). E.g., monochloramine was not detected in solutions after 2 h and 1 h, at ratios 7:1 and 7.6:1, fig. 1a. The larger $\text{Cl}_2:\text{NH}_3$ ratio, the faster was the oxidation process (6) [12].

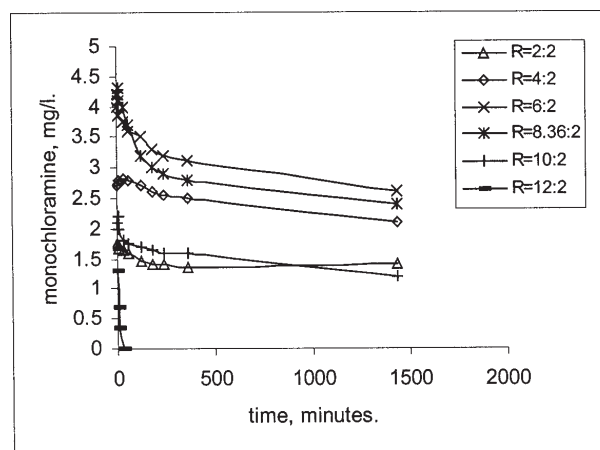
In the case of the second series (B), for R = 2:2-6:2, NH_2Cl was formed in about two times higher concentrations, 1.6-3.6 mg/L at pH =6.0. Its stability was similar with that recorded for series (A): 65.0-84.3% from initial concentrations were determined after 24 h. Complete oxidation of formed NH_2Cl (1.3 mg/L) took place in 30 min at the mass ratio, 12:2, fig.1b.

Table 1
MONOCHLORAMINE EVOLUTION AS PERCENTS FROM INITIAL CONCENTRATIONS AFTER 24 h, VERSUS MASS RATIOS (R) AND pH, SERIES A AND B

time, pH	mass ratios (R), series A					
	1:1	2:1	3:1	4.18:1	5:1	6:1
24h, pH =6.0	93.75	78.5	72.2	60.8	37.5	36.8
24h, pH =7.0	94.1	87.5	83.3	80.0	65.5	34.1
24h, pH =8.0	-	100.0	96.2	97.2	66.6	40.0
time, pH	mass ratios (R), series B					
	2:2	4:2	6:2	8.36:2	10:2	12:2
24 h, pH=6.0	84.3	77.7	65.0	57.1	57.1	-
24 h, pH=7.0	90.9	84.3	95.6	82.1	70.0	-
24 h, pH=8.0	94.1	98.5	96.2	39.2	15.0	-

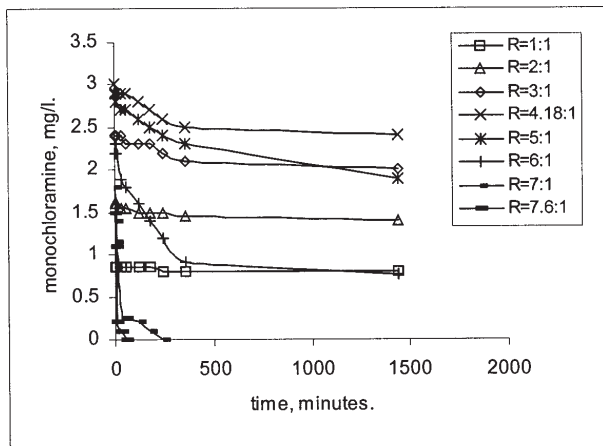


1a- series A

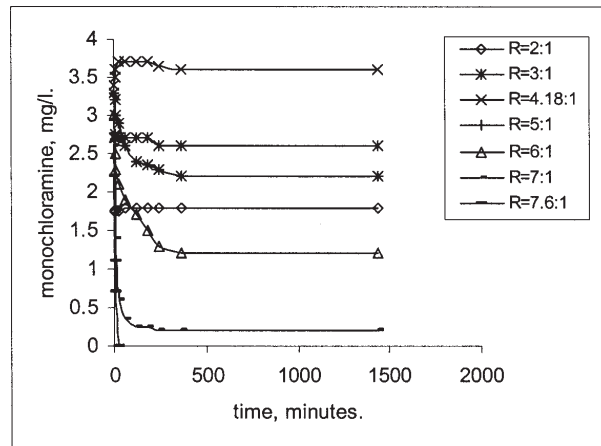


1b- series B

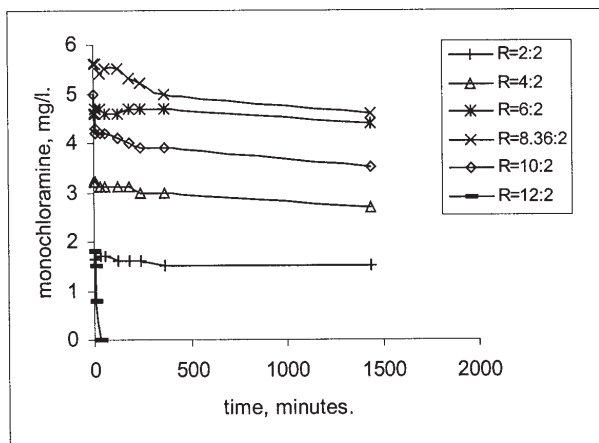
Fig. 1 Variation of monochloramine concentrations versus time and chlorine: ammonia mass ratios (R, mg/L:mg/L) at pH=6.0: 1a- series A; 1b - series B



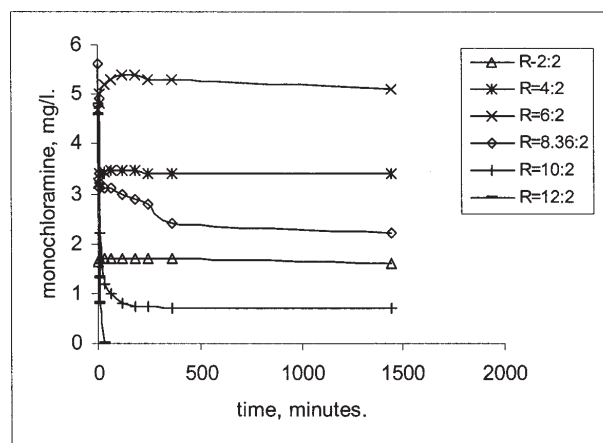
2a - series A



3a - series A



2b - series B



3b - series B

Fig. 2 Variation of monochloramine concentrations versus time and chlorine:ammonia mass ratios (R, mg/L:mg/L) at pH=7.0: 2a - series A; 2b - series B

Fig. 3 Variation of monochloramine concentrations versus time and chlorine:ammonia mass ratios (R, mg/L:mg/L) at pH=8.0: 3a - series A; 3b - series B

At $pH = 7.0$ and $R = 2:1-5:1$, NH_2Cl concentrations determined in the first minutes were higher than those from $pH = 6.0$, as follows: 1.6 mg/L (12.5%), 2.4 mg/L (25.0%), 3.0 mg/L (23.3 %) and 2.9 mg/L (17.2 %), fig. 2a. After 24 h, 80.0–94.1% from these concentrations were determined.

For higher chlorine concentrations, NH_2Cl formed at $R = 7:1, 7.6:1$ (1.8 and 1.5 mg/L) was oxidized in 4 h and 1 h, respectively.

In the case of the second series (B), the process followed the same trend as above: for $Cl_2:NH_3$ ratios 2:2-10:2, 1.65-5.6 mg/L monochloramine were formed in the first

time, pH	mass ratios (R), series A					
	1:1	2:1	3:1	4.18:1	5:1	6:1
1h, pH=6.0	0.15	0.4	0.9	1.45	2.3	2.9
1h, pH=7.0	0.15	0.3	0.5	0.75	1.4	1.7
1h, pH=8.0	-	0.08	0.085	0.10	0.45	0.4
time, pH	mass ratios (R), series B					
	2:2	4:2	6:2	8.36:2	10:2	12:2
1h, pH=6.0	0.30	0.90	2.05	3.4	5.4	0.9
1h, pH=7.0	0.15	0.50	0.50	1.60	2.50	1.40
1h, pH=8.0	0.025	0.05	0.50	0.50	0.45	0.45

Table 2
DICHLORAMINE CONCENTRATIONS (MG/L) VERSUS CHLORINE:AMMONIA MASS RATIOS (mg/L:mg/L) AND pH, 1 h AFTER REAGENTS MIXING, AT 20° C

time, pH	mass ratios (R), series A					
	1:1	2:1	3:1	4.18:1	5:1	6:1
1h, pH=6.0	0.0	0.05	0.05	0.05	0.15	0.10
1h, pH=7.0	0.0	0.0	0.025	0.025	0.05	0.025
1h, pH=8.0	0.0	0.012	0.012	0.025	0.012	0.0
time, pH	mass ratios (R), series B					
	2:2	4:2	6:2	8.36:2	10:2	12:2
1h, pH=6.0	0.075	0.10	0.15	0.20	0.25	0.0
1h, pH=7.0	0.025	0.05	0.05	0.10	0.15	0.0
1h, pH=8.0	0.012	0.010	0.012	0.012	0.010	0.0

Table 3
CONCENTRATIONS OF AMMONIA (mg/L) AFTER 24 h IN MONOCHLORAMINE SOLUTIONS, VERSUS MASS RATIOS (R) AND pH

minutes. Due to the increasing of reagent concentrations, complete oxidation of NH_2Cl took place at $R = 12:2$ in 30 min (fig.2b).

The higher concentrations of NH_2Cl were formed at $\text{pH} = 8.0$, as follows: 1.7 mg/L (2:1); 2.7 mg/L (3:1); 3.7 mg/L (4.18:1), fig. 3a. After 24 h, 96.2–100.0 % of these concentrations were determined. The obtained results are similar with those reported for monochloramine evolution during 24 h, at $\text{pH} 8.3$ [6,12]. For $R = 7.6:1$, formed monochloramine was oxidized during 30 min.

Again, the complete oxidation of monochloramine took place at smaller ratio than for series A, 12:2 (4.6 mg/L), 30 minutes after reagents introduction in solutions.

Dichloramine was formed simultaneously with monochloramine. Minimum concentrations were obtained for $R = 1:1$ -4.18:1 at $\text{pH} = 7.0$ and 8.0, 0.015-0.75 mg/L and 0.08-0.10 mg/L respectively, one hour after reagents mixing, table 2. Similar results were determined for the second series. Concentrations of free ammonia were very small, e.g., for 2:1-6:1 and 24 h, 0.012-0.15 mg/L ammonia were determined and for higher ratios ammonia was absent, table 3.

Conclusions

Monochloramine formation depends on initial concentrations of chlorine and ammonia, their mass ratio, and pH. Investigation of monochloramine formation for two mass ratios (R) series, 1:1-7.6:1 (A) and 2:2-12:2 (B) (mg/L:mg/L), at $\text{pH} = 6.0; 7.0; 8.0$ in distilled water solutions, showed its formation in maximum concentrations for $R = 3:1$ and 4.18:1, as follows:

1.8-2.3 mg/L ($\text{pH} = 6.0$), 2.4-3.0 mg/L ($\text{pH} = 7.0$), 2.7-3.7 mg/L ($\text{pH} = 8.0$) series A, in the first min after reagents mixing; in case of series B, maximum concentration 5,6 mg/L, was recorded at $\text{pH} = 7.0$ and 4.18:1 mass ratio.

Monochloramine stability versus time depends on its formation conditions:

- at 24 h after reagents mixing and $R = 1:1$ -4.18:1, the following percents from initial concentrations were determined: 60.8 -93.7 % ($\text{pH} = 6.0$), 80.0-94.1 % ($\text{pH} = 7.0$), 96.2 - 100.0 % ($\text{pH} = 8$); similar results were recorded for $R = 2:2 - 8.36:2$;

- stability decreased gradually for higher ratios and at $R \geq 7.6:1$, monochloramine was not found in solutions after contact time of 60 min. at $\text{pH} = 6.0$ and 7.0, and 30 min at $\text{pH} = 8.0$, series A; NH_2Cl oxidation was finished in 30 min at $R = 12:2$ and 3 pH values, series B.

Maximum monochloramine concentrations with high stability in water solutions, and minimum values for

dichloramine were observed for chlorine:ammonia mass ratios 3:1, 4.18:1, at $\text{pH} = 7.0$ and 8.0. These results are useful in water treatment technology, when chloramination process is applied.

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