

TREATMENT OF GROUND WATER BY USE OF CHLORINE DIOXIDE, CHLORINE AND MONOCHLORAMINE

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ABSTRACT

The use of chlorine dioxide, chlorine and monochloramine for the treatment of ground water containing iron (4 mg/l), manganese (0.49 mg/l) and ammonia (1.14 mg/L), is analyzed in this paper. Manganese was advanced removed, up to 0.01-0.024 mg/l and iron to 0.30-0.46 mg/l, by use of chlorine dioxide. When chlorine dioxide was followed by chlorine, iron and manganese were removed until below admission limits. The maximum yields for monochloramine synthesis by chlorine reaction with ammonia from ground water were determined for chlorine: ammonia mass ratio 3:1; its stability was about 71% after 24 hours. Thus, chlorine dioxide may be used as oxidant and chlorine for conversion of ammonia from ground water into chloramine, as secondary disinfectant.

KEY WORDS:

chlorine dioxide, oxidation, iron, manganese, chlorine, chloramines

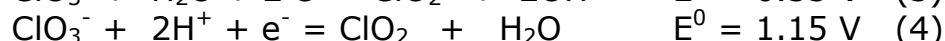
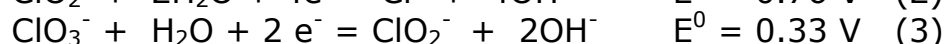
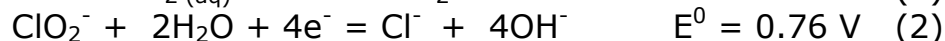
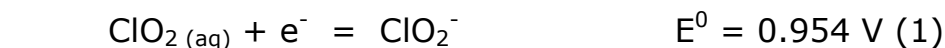
1. INTRODUCTION

Chlorine dioxide is an important compound discovered by Sir Humphrey Davy in 1814. It has been used at a water potable facility at Niagara Falls, N.Y. in 1944, to control taste and odor. In the last fifty years, chlorine dioxide was applied in water treatment as a disinfectant and oxidant in USA, Canada and Europe, both alone and in combination with chlorine, chloramines and ozone, for pre-disinfection, post-disinfection, control of iron and manganese, of hydrogen sulphide and phenolic compounds [1,2,3,4].

Chlorine dioxide is a small, volatile and powerful molecule. Generally, it is not used in gaseous form due to its instability; it may be

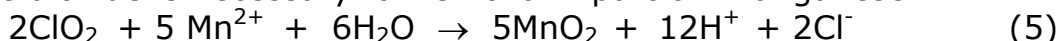
compressed under liquid form, but it can explode if temperature is higher than 40°C and concentration is greater than 10%. One of the most important properties of ClO₂ is its great solubility in water. Chlorine dioxide does not react with water: it is only dissolved in water.

It is a highly selective oxidant due to one electron transfer mechanism, when it is reduced to chlorite (1); other related reactions are (2,3,4):

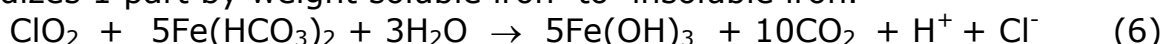


Chlorite is the predominant reaction end-product, with about 50-70% of ClO₂ and chlorate together with chloride, to about 30% of ClO₂. It reacts with naturally organic matter (NOM) from waters by oxidation, but it does not produce chlorinated compounds [5,6,7,8].

Chlorine dioxide reacts more rapidly than chlorine with manganese yielding to manganese dioxide; reaction is rapid and 2.5 parts by weight of chlorine dioxide is necessary for removal 1 part of manganese.



At pH greater than 5, 1.2 parts by weight of chlorine dioxide oxidizes 1 part by weight soluble iron to insoluble iron.



The use of chlorine in water treatment plants, is widely spread out, due to its efficiency and low costs. Advantages of using free chlorine are as follows:

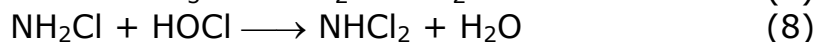
- low cost bacteria control;
- the required equipments are relative simple and cheap;
- easy dosage and control of residual chlorine;
- total oxidation of ammonia to nitrogen, at the break-point dose of chlorine;
- in water, remains a residual chlorine concentration, that assures water disinfection.

Chlorine reacts with ammonia and organically bound nitrogen, leading to inorganic products named chloramines, whose properties are:

- highly stable products;
- responsible for taste and odour problems;
- bactericide properties, more or less, intensive.

These products are known as bound chlorine or combined chlorine. Among nitrogen compounds, the most important pollutant of water is ammonia. Chlorine, respective HOCl, rapidly reacts with ammonia, resulting chloramines.

Depending on pH, Cl/N mass ratio, contact time and temperature, it is obtained mono- and dichloramine:



The main objectives followed in this paper are:

- comparative determination of iron and manganese removal efficiency from two ground water samples (I, II), both with chlorine and chlorine dioxide;
- investigation of the chlorine dioxide oxidation potential over organic compounds from ground water samples;
- establishment of optimum conditions for monochloramine formation, by chlorine reactions with ammonia in water solutions at pH 6, 7, for chlorine:ammonia mass ratios of 2:1, 3:1;
- conversion of ammonia present in ground water samples, in chloramines over chlorine treatment, and determination of monochloramine stability in time.

2. MATERIALS AND METHODS

For carrying out the above objectives, some ground water samples taken from Drinking Water Treatment Plant no. 1, Timisoara, were treated as follows:

- treatment with chlorine dioxide (1, 2, 3, and 5 mg ClO_2/l), and determination of residual and chlorite ions formed during the oxidation process over time, yield for iron and manganese removal and oxidation of organic compounds;
- combined treatment with chlorine dioxide followed by chlorine addition in the water samples (1, 3, 5 mg ClO_2/l , and 3 mg Cl_2/l). In this case it was determined the yield for iron and manganese removal, residual chlorine and chloramines formed during ammonia conversion, in ground water samples;
- a two-step chlorine addition to the water samples and investigation of the above mentioned parameters.

Chlorine dioxide was obtained during solid-solid reaction between potassium chlorate and oxalic acid. There were obtained chlorine dioxide solutions of 6.5 mg/l. It was analysed using ferrous ammonium sulfate in presence of N,N-diethyl-p-phenyldiamine, DPD-FAS method [9].

Using this method, chlorine, mono-, dichloramines and chlorite, can also be analysed. Chlorine dioxide, present side by side with chlorine, can be differentiated using glycine, that transforms free chlorine in chloroaminoacetic acid, but it doesn't affect the chlorine dioxide. The analyse steps are:

- chlorine dioxide: in 100 ml water sample it is added 2 ml glycine are introduced; in a separate titration flask, 5 ml of buffer reagent and DPD indicator solution, are mixed; glycine treated sample is added and it is titrated with standard FAS until the red color is changed. (reading G, ml);
- free chlorine and chloramines: using a second 100 ml flask with water sample, it is added to the titration flask which contains buffer reagent and indicator solution; first reading, after titration with FAS, free chlorine (A, ml) is determined, and then potassium iodide is introduced: successive readings B and C (ml) represent monochloramine and dichloramine;

- total available chlorine including chlorite: after reading C, 1 ml H₂SO₄ solution is added to the same sample in titration flask, let stand about 2 minutes, and than 5 ml NaHCO₃ solution is introduced; volume of FAS is (D, ml).

The determined species are computed (for 100 ml sample, 1 ml FAS solution = 1 mg available chlorine/l) as follows:

- chlorine dioxide = 5 G (or 1.9 G expressed as ClO₂);
- chlorite = D - (C + 4G);
- free available chlorine = A - G;
- monochloramine = B - A;
- dichloramine = C - B;
- total available chlorine = D; where, A,B,C,D,G = ml FAS.

Iron and manganese were determined using atomic absorption spectrometry, with both flame and graphite furnace, using an PERKIN-ELMER equipment "Analyst 100". Organic compounds evolution was determined by chemical oxygen demand (COD), potassium permanganate method. In all cases 500 ml ground water samples, were used. Principal indicators of raw ground water samples I and II, are presented in table 1.

TABLE 1. Values of principal indicators for ground water samples I and II

No.	Indicator	I	II	units
1	pH	6.96	7.2	-
2	Chemical oxygen demand (CCO-Mn)	2.24	2.2	mgO ₂ /l
3	Nitrites	< 0.005	< 0.005	mg/l
4	Nitrates	< 5	< 5	mg/l
5	Ammonium	1.0	1.14	mg/l
6	Turbidity	1.5	1.7	NTU
7	Iron	4.326	3.9	mg/l
8	Manganese	0.496	0.474	mg/l
9	Calcium	60	58	mg/l
10	Hardness	10.2	9.8	°dH
11	Chloride	148	140	mg/l
12	Conductivity	854	865	µS/cm
13	Sodium	110	120	mg/l
14	Magnesium	17.5	20.5	mg/l

3. RESULTS AND DISCUSSION

Results obtained after treatment of ground waters with chlorine dioxide are shown in tables 2 and 3. The evolution of residual chlorine dioxide and of formed chlorite were determined versus time, from the first 10 minutes, until 24 hours.

For a dose of 1 mg ClO₂/l, chlorine dioxide consumption and chlorite obtained are similar for both types of ground water: for the first sample I the oxidant is consumed completely, and for the second sample II in proportion of 90 %, after 24 hours; chlorite obtained is about 87, respectively 85 % from initial 1 mg ClO₂/l.

For higher concentrations of 2, 3, 5 mg ClO₂/l, residual concentrations are different for the two types of water, after the first 10 minutes, and also after 24 hours. After 10 minutes, 35, 33 and 40% of

oxidant reacts with organic and inorganic compounds from water sample I, and 25, 26 and 23% in sample II. After 24 hours, in water sample I, 85, 63 and 56% of chlorine dioxide was consumed, and in sample II was consumed 60, 47 and 34% from chlorine dioxide. For initial doses of 2 – 3 – 5 mg ClO_2/l , the consumptions were of 1.7 – 1.8 – 2.8 mg/l for water I, and 1.2 – 1.4 – 1.7 mg/l, for water II.

Iron and manganese have about the same concentrations in both water samples 4.3 – 3.9 mg Fe/l and 0.49 – 0.47 mg Mn/l. Adding chlorine dioxide in water samples, a brown color appears, caused by rapid precipitation of iron and manganese ions.

Analysing the residual iron and manganese concentration in the settled and filtered water samples, has shown a more efficient removal of manganese than of iron. Manganese residual concentrations were of 0.024 – 0.01 mg/l and iron of 0.46 – 0.3 mg/l, for dose of 5 mg ClO_2/l . A highly removal of iron and manganese is explained also due to an flocculant effect which draw along the metallic ions.

Chlorine dioxide effect onto organic compounds, determined by chemical oxygen demand was not significant; values determined after treatment were greater than those of raw water with 1-2 mg/l. Even the two steps treatment with chlorine dioxide, did not decrease original values, showing intermediate stable oxidized compounds, table 4.

In order to establish optimum conditions for monochloramine formation, reactions of chlorine with ammonia in water solutions at pH=6 and 7, for chlorine: ammonia mass ratios 2:1, 3:1, 4:1 were investigated, fig.1-4.

The obtained results showed that maximum yields for monochloramine formation take place for mass ratios 2:1 and 3:1; for these ratios, the best stability of monochloramine was determined: 83 – 87% of initial concentration were found after 24 hours at pH = 7.

The results of combined treatment, chlorine dioxide for 2 hours (1, 3, and 5 mg ClO_2/l), followed by chlorine addition (3 mg Cl_2/l in water sample I, and 3.5 mg Cl_2/l in sample II), are iron and manganese removal, as well as ammonia conversion to chloramines, monochloramine in principal.

Chlorine compounds distribution versus chlorine dioxide initial concentrations and ammonia concentration from both water samples, are shown in tables 5 and 6. Mass ratio $\text{Cl}_2:\text{NH}_3$ was 3:1, in order to obtain maximum monochloramine quantity.

Distribution of residual chlorine, mono- and dichloramine concentrations versus time, are presented in tables 5 and 6. The results obtained are similar with chloramine preparation from distilled water and buffer phosphate solution, at pH=7, as shown in figure 4. Monochloramine is formed in the first 10 minutes, in proportion of 80 – 90% from maximum concentration, which are obtained after one hour of chlorine addition: 2.12 – 2.24 mg/l for water samples I, and 2.50 – 2.65 mg/l for samples II. Dichloramine is formed in much lower quantities, 0.56 – 0.45 mg/l and 0.50 – 0.65 mg/l respectively. Mass ratio between

monochloramine and dichloramine is about 4.3:1, and is the same as the one obtained in distilled water solutions. Chlorine compounds (chlorine, monochloramine, dichloramine) balance is like the theoretical value, for both water samples. Monochloramine analysed after 24 hours from its formation, shows a good stability in time: average concentration for values from tables 5 and 6, are 71%. These results shows that ammonia present in ground water can be useful by converting it to monochloramine, as a secondary disinfectant.

By using the combined treatment of both chlorine dioxide and chlorine, iron and manganese were removed from water samples until below the admission limits, table 7.

In order to evaluate iron and manganese removal by use of chlorine only, ground water samples were treated in one and two steps, tables 7 and 8. For both ground waters, residual values of iron are closed, about 0.50 mg/l and those of manganese are near to maximum allowable level, 0.05 mg/l. In case of combined treatment, chlorine dioxide (1 and 3 mg/l) and chlorine (3 mg/l), advanced removal of both iron and manganese was succeeded.

Chlorine consumption was different for both water samples: for sample I, was not recorded an initial chlorine consumption, but for water II, 2.5 mg/l chlorine were rapidly consumed; so, chlorine was added in two steps for water II, in order to convert ammonia into chloramines. Monochloramine was stable during 24 hours, like above, in case of combined treatment. The above results may be used for development of a new technology in case of ground water treatment, by use of chlorine dioxide as oxidant and of chlorine for easy conversion of ammonia from water into monochloramine, as a secondary disinfectant.

TABLE 2. Evolution of residual chlorine dioxide and chlorite versus contact time for ground water samples I, treated with 1, 2, 3 and 5 mg ClO_2/l .

no.	time	1 mg ClO_2/l		2 mg ClO_2/l		3 mg ClO_2/l		5 mg ClO_2/l	
		ClO_2 mg/l	ClO_2^- mg/l	ClO_2 mg/l	ClO_2^- mg/l	ClO_2 mg/l	ClO_2^- mg/l	ClO_2 mg/l	ClO_2^- mg/l
1	10	0.5	0.48	1.30	0.70	2.2	0.65	3.04	1.70
2	30	0.20	0.58	0.85	1.0	2.0	0.75	2.8	1.80
3	60	0.17	0.60	0.50	1.30	1.8	0.80	2.6	1.85
4	120	0.1	0.64	0.40	1.40	1.6	1.25	2.4	2.1
5	24 h	-	0.91	0.30	1.50	1.1	1.68	2.2	2.3

TABLE 3. Evolution of residual chlorine dioxide and chlorite versus contact time for ground water samples II, treated with 1, 2, 3 and 5 mg ClO_2/l .

no.	time	1 mg ClO_2/l		2 mg ClO_2/l		3 mg ClO_2/l		5 mg ClO_2/l	
		ClO_2 mg/l	ClO_2^- mg/l	ClO_2 mg/l	ClO_2^- mg/l	ClO_2 mg/l	ClO_2^- mg/l	ClO_2 mg/l	ClO_2^- mg/l
1	10	0.40	0.56	1.45	0.5	2.08	0.60	3.85	1.0
2	30	0.32	0.60	1.2	0.68	1.9	0.80	3.60	1.1
3	60	0.30	0.68	1.1	0.70	1.82	0.90	3.50	1.25
4	120	0.25	0.70	1.0	0.75	1.72	1.0	3.4	1.3
5	24 h	0.10	0.88	0.8	1.0	1.6	1.1	3.3	1.35

TABLE 4. Chemical oxygen demand evolution for ground water samples II, treated with chlorine dioxide in two steps: 1 and 2 mg/l for two hours, followed by 1, 2 and 3 mg/l, respectively.

time	(1+1) mgClO ₂ /l			(1+2) mgClO ₂ /l			(2+3) mgClO ₂ /l		
	ClO ₂ mg/l	ClO ₂ ⁻ mg/l	CCO-Mn (mgO ₂ /l)	ClO ₂ mg/l	ClO ₂ ⁻ mg/l	CCO-Mn (mgO ₂ /l)	ClO ₂ mg/l	ClO ₂ ⁻ mg/l	CCO-Mn (mgO ₂ /l)
24h	-	1.72	3.17	0.48	2.52	3.01	1.04	4.28	2.36

TABLE 5. Chlorine, monochloramine and dichloramine distribution versus contact time for ground water samples I, treated with chlorine dioxide (1, 2 and 3 mg/l) for 2 hours and then with chlorine (3 mg/l).

no.	time	1 mgClO ₂ /l + 3 mg Cl ₂ /l			3 mgClO ₂ /l + 3 mgCl ₂ /l			5 mgClO ₂ /l + 3 mgCl ₂ /l		
		Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l	Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l	Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l
1	10	0.40	2.0	0.42	0.40	2.10	0.35	0.4	2.12	0.35
2	30	0.20	2.20	0.50	0.18	2.24	0.45	0.28	2.64	0.40
3	60	0.15	2.24	0.56	0.15	2.28	0.55	0.20	2.12	0.76
4	24 h	0.10	1.42	0.64	0.28	1.32	0.60	0.18	1.96	0.76

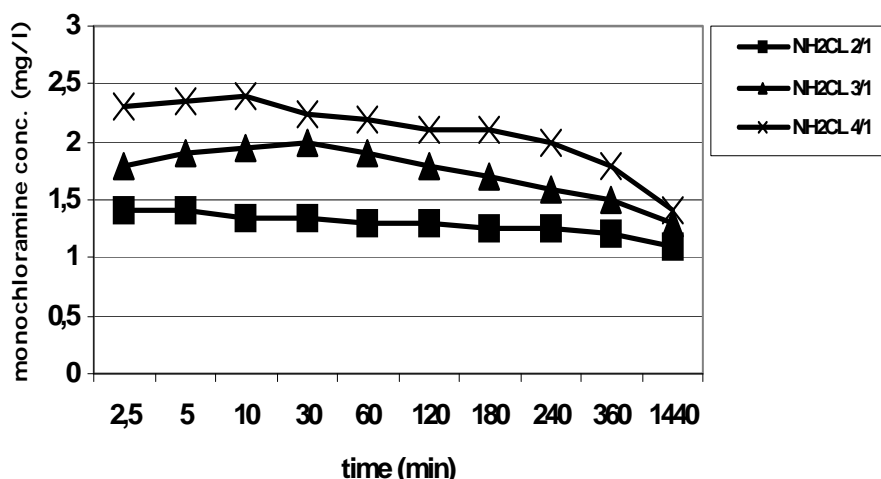


FIG.1 MONOCHLORAMINE FORMATION VERSUS TIME AND MASS RATIO Cl/N at pH=6.

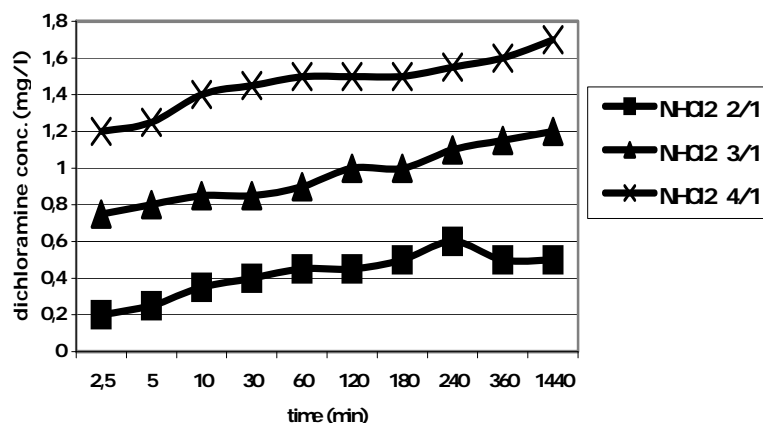


FIG.2 DICHLORAMINE FORMATION VERSUS TIME AND MASS RATIO Cl/N at pH=6.

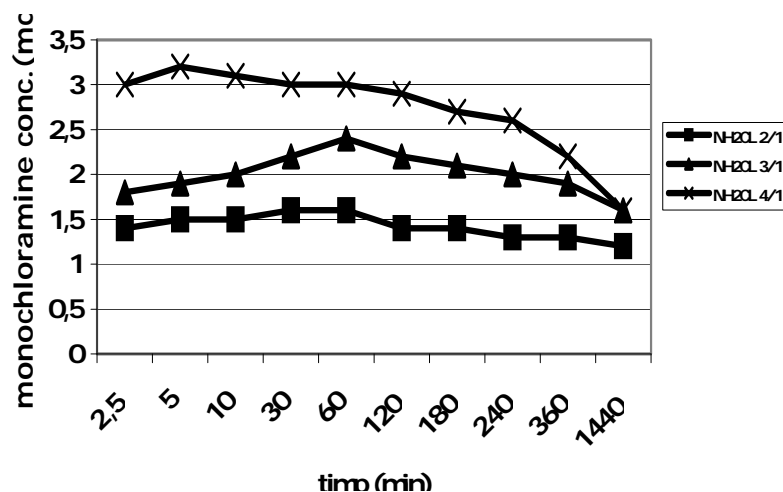


FIG.3 MONOCHLORAMINE FORMATION VERSUS TIME AND MASS RATIO Cl/N at pH=7.

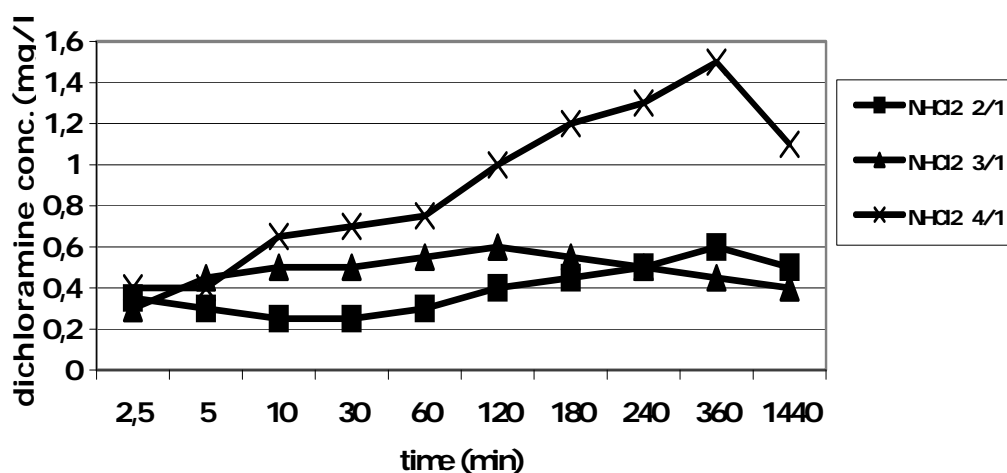


FIG.4 DICHLORAMINE FORMATION VERSUS TIME AND MASS RATIO Cl/N at pH=7.

TABLE 6. Chlorine, monochloramine and dichloramine distribution versus contact time for ground water samples II, treated with chlorine dioxide (1, 2 and 3 mg/l) for 2 hours and then with chlorine (3 mg/l).

no.	time	1 mgClO ₂ /l + 3.5 mg Cl ₂ /l			3 mgClO ₂ /l + 3.5 mgCl ₂ /l			5 mgClO ₂ /l + 3.5 mgCl ₂ /l		
		Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l	Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l	Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l
1	10	0.30	2.40	0.25	0.35	2.45	0.20	0.25	2.45	0.25
2	30	0.28	2.56	0.32	0.28	2.68	0.52	0.20	2.40	0.45
3	60	0.28	2.64	0.32	0.28	2.68	0.56	0.15	2.20	0.70
4	24 h	0.16	1.64	0.28	0.16	2.28	0.48	0.10	2.18	0.70

TABLE 7. Iron and manganese removal from raw ground water samples, by treatment with chlorine, chlorine dioxide and by chlorine dioxide followed of chlorine.

raw ground water samples I	Fe (mg/l)	Mn (mg/l)	raw ground water samples II	Fe (mg/l)	Mn (mg/l)
3 mg Cl ₂ /l	0.75	0.059	3 mg Cl ₂ /l	0.80	0.07
4 mg Cl ₂ /l	0.60	0.059	4 mg Cl ₂ /l	0.75	0.06
5 mg Cl ₂ /l	0.50	0.059	5 mg Cl ₂ /l	0.60	0.055
1 mg ClO ₂ /l	1.50	0.157	1 mg ClO ₂ /l	1.40	0.12
2 mg ClO ₂ /l	1.10	0.10	2 mg ClO ₂ /l	0.95	0.06
3 mg ClO ₂ /l	0.60	0.047	3 mg ClO ₂ /l	0.40	0.018
5 mg ClO ₂ /l	0.46	0.024	5 mg ClO ₂ /l	0.30	0.010
1 mg ClO ₂ /l + 3 mg Cl ₂ /l	0.07	0.03	1 mg ClO ₂ /l + 3 mg Cl ₂ /l	0.08	0.04
3 mg ClO ₂ /l + 3 mg Cl ₂ /l	0.02	0.009	3 mg ClO ₂ /l + 3 mg Cl ₂ /l	0.02	0.01

TABLE 8. Chlorine compounds distribution in ground water samples I and II, treated with chlorine in one and two steps: 2.5 mg/l for two hours, followed by 2.5 and 5.0 mg/l, respectively.

no.	Time (min)	I + 3 mg Cl ₂ /l			II + (2.5+2.5) mg Cl ₂ /l			II + (2.5+5) mg Cl ₂ /l		
		Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l	Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l	Cl ₂ mg/l	NH ₂ Cl mg/l	NHCl ₂ mg/l
1	10	0.24	1.8	0.5	0.16	1.12	0.30	0.4	1.84	1.76
2	30	0.25	1.9	0.65	0.28	1.40	0.32	0.4	1.8	1.6
3	60	0.15	2.1	0.7	0.28	1.64	0.68	0.28	1.92	1.52
4	24 h	0.01	1.6	0.55	0.20	1.44	0.80	0.28	1.2	0.52

4. CONCLUSION

Manganese from ground water samples treated with chlorine dioxide was advanced removed (0.01 – 0.024 mg/l), but in case of residual iron, values were 0.30 – 0.46 mg/l. A removal degree greater than stoichiometry ratio may be explained also due to an flocculant effect which draw along the metallic ions.

Using the combined treatment of chlorine dioxide followed by chlorine, iron and manganese were removed from water, until below the admission limits.

The maximum yields for monochloramine synthesis by chlorine reaction with ammonia in distilled water solutions, were determined in case of mass ratios 2:1 and 3:1. By treatment of ground water samples with chlorine, ammonia content was converted into monochloramine; its stability was about 71% after 24 hours.

These results may be used for development of a new technology in case of ground water treatment, by use of chlorine dioxide as oxidant and of chlorine for easy conversion of ammonia from water into monochloramine, as secondary disinfectant.

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