Removal of Ammonium Ions and Ammonia from Groundwater by Oxidation Processes

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The process of removal of ammonium ions and ammonia from ground water, which contained these components in quantities exceeding the maximum permissible limit, was studied by the oxidation method. It was shown by the CG-MS method and thin layer chromatography that calcium hypochlorite in certain amounts and at certain pH values oxidizes ammonium ions and ammonia, presumably with the formation of free nitrogen, without forming chloramines, reducing concentration of ammonium ions and ammonia to values below the maximum allowable limit for drinking water.

Keywords: adsorption, oxidation, ammonium ions, ammonia, calcium hypochlorite

In the Republic of Moldova, the content of ammonium ions and ammonia in ground water frequently exceeds the maximum admissible concentration, which creates major health problems for people using it for drinking purposes. Under oxidative conditions, ammonium ions can form toxic nitrite ions at pH values found in ground water. Nitrites lead to oxidation of bivalent iron from hemoglobin to trivalent iron ions, forming methemoglobin, which makes oxygen transport impossible, and therefore causes hypoxia.

Several procedures for removing ammonium ions and ammonia from wastewaters and from gaseous media are known from specialty literature [1-6]. Only a few works are dedicated to physico-chemical processes for removing ammonium ions, ammonia, hydrogen sulfide and other sulfides in mixture from groundwater - waters that will be used later for drinking purposes [7-9].

Thus, a series of paper [10] are known, which, based on the behavior of aqueous ammonia solutions, have allowed the establishment of optimal conditions for the decontamination of groundwater containing free NH_3 and NH_4^+ ions. This process is based on the concurrent action of physical and chemical processes. In general, acid-base, ion exchange and redox chemical processes are used [11-18], for example, surface treatment for potability by ceramics, membranes [19-24] and other osmotic adsorption or ion exchange systems [25-32].

In this paper is presented a process for the removal of ammonia and ammonium ions from groundwater using redox processes with calcium hypochlorite, in order to further use it for drinking purposes.

Experimental part

An inexpensive process would be to create a high pH value (11.5) in the purified water, so that at this pH value all ammonium ions were converted to ammonia, which would then be removed from the system by aeration. Experiments showed that after such a water treatment, ammonia concentration remained virtually the same. This result, in our view, can be explained by the formation of hydrogen bonds that keep ammonia in the solution.

Hydrogen bonds can be broken relatively easily by heating the treated water with subsequent release of ammonia from the system, but such a process cannot be considered for implementation.

Calcium hypochlorite is used as an oxidizing agent when it is expected to remove ammonium ions and ammonia from highly polluted wastewaters. It can also be used for potable ground water, but with great caution, because some toxic compounds may form as a result of the oxidation process.

Calcium hypochlorite in water hydrolyzes with the formation of hypochlorous acid and calcium hydroxide. Formation of hypochlorous acid before the onset of actual oxidation reaction is very important, because this acid partially dissociate, being very weak. Products formed by the interaction of ammonia and hypochlorous acid are monochloramine, dichloramine and trichloramine [5].

At $pH > 7.5$, monochloramine is predominantly formed, at $pH < 7.5$ predominates dichloramine, and at $pH < 7.4$ - trichloramine. Note that in order to reduce significantly the formation of trihalomethanes, it is necessary to remove organic substances from the studied water. Monochloramine, unlike dichloramine and trichloramine, is not toxic. For the formation of monochlorine, it would be ideal to carry out the interaction process of ammonium ions and ammonia with the hypochlorous acid, which is formed by hydrolysis of calcium hypochlorite at $pH = 8.3$ [6].

The pH-profile of the solutions studied was evaluated with the help of a titrator Titro Line 6000 Company SI Analitycs.

For the evaluation of mass spectra measured on the CG-MS spectrometer and thin layer chromatography one was used GC-MS analytical system consisted by an Agilent Technologies 7890A GC coupled with an 5975C Mass-Selecctive Detector (MSD) equipped with split-splitless injector (split, 250°C, split ratio 1:50, 1µL) and HP-5ms capillary calibrated column (30m x0.25mm x 0.25µm; The carrier gaz: helium 1.1 mL/min; oven: 60°C/5min, 15°C/min- 320°C/10min; MSD: ionization energy 70 eV, scan time 1s, acquisition mass range m/z 30-300amu, solvent delay 3 min.

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Results and discussions

Figure 1 shows the dependence of concentration of ammonium ions and ammonia remaining after treatment of demineralized water containing initially 5mg/L ammonium and ammonia ions with 100 mg of Ca(OCl) added to 100 mL solution at different pH values.

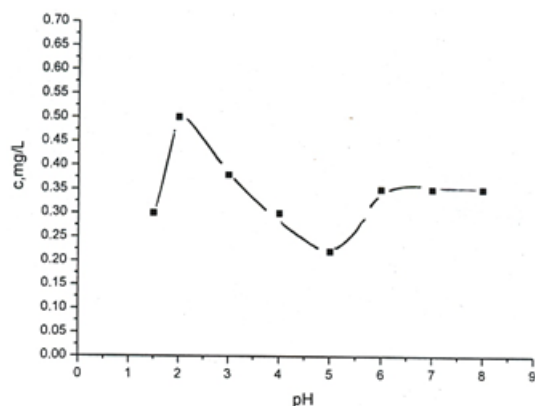Fig.1. Dependence of ammonium ions and ammonia contents remained after oxidation with $Ca(OCl)_2$ on pH. $C_{init} = 5$ mg/L and $C_{Ca(OCl)2} = 100$ mg/100 mL solution

From the data presented in figure 1 can be seen that in the studied pH range, the concentration of ammonium ions and ammonia decreases and is lower than the Maximum Admissible Concentration (MAC) of these compounds according to the norms in force ($MAC_{NH3, NH4}^{+} = 0.5$mg/L). We also note that, at pH values close to 5, the curve has a minimum point where the oxidation process of ammonium ions and ammonia occurs with maximum efficiency. A less efficient, yet significant oxidation process occurs at pH = 2. Ground waters with pH values close to 5 and higher in the Republic of Moldova are attested, although such water sources are very few.

The reduction of calcium hypochlorite amount in the same volume of solution at the same initial concentration of ammonium ions and ammonia (60 mg Ca(OCl) added in 100mL solution at different pH values) also leads to a drastic reduction of these compounds in the studied water (fig. 2).
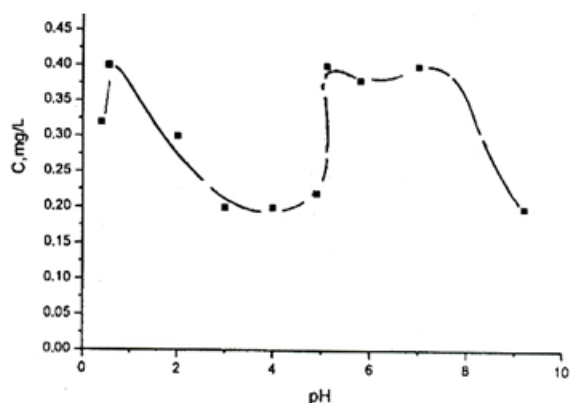

Fig. 2. Dependence of ammonium ions and ammonia content remained after oxidation with $Ca(OCl)_2$ from pH. $C_{init} = 5$ mg/L and $C_{Ca(OCl)2} = 60$ mg/100 mL solution

Figure 2 shows that an efficiency in the process of oxidation of ammonium ions and ammonia is found at pH values close to 5, and a minimum point at pH values somewhat higher than 9.

A further decrease of calcium hypochlorite content to 40 mg added to 100 mL solution also leads to a significant decrease of ammonia concentration and ammonium ions to values below the maximum admissible limit (fig. 3).
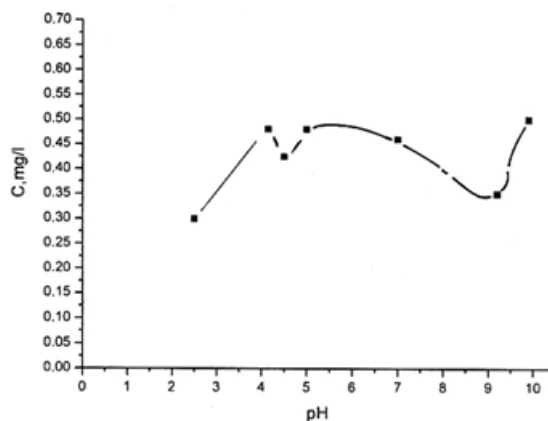

Fig. 3. Dependence of ammonium ions and ammonia contents remained after oxidation with $Ca(OCl)_2$ from pH. $C_{init} = 5$ mg/L and $C_{Ca(OCl)2} = 40$ mg/100mL solution

In figure 3 we find minimum points at the same pH values as in figure 2.

Although the oxidation process occurrs so that the residual concentration of ammonium ions and ammonia is below the maximum allowable limit for drinking water, at values up to pH = 7.4 is possible the formation of dichloramine and trichloramine - toxic products, and therefore only the oxidation process at pH values higher than 7.4 are of interest. At this dose of calcium hypochlorite, the process proceeds more efficiently at pH ~ 9.

At a calcium hypochlorite dose of 40 mg per 100 mL solution (fig. 3), we fond a very efficient oxidation process of ammonium ions and ammonia throughout the studied pH range. Practically, the residual concentration of ammonium ions and ammonia after treatment is lower than the maximum admissible concentration according to current regulations.

The products obtained during the oxidation process present interest. Considering that the model water subjected to study contained only ammonia and ammonium ions was, we assume that after the treatment with calcium hypochlorite containing 31% of active substance, would form chloramines - monochloramine, dichloramine and trichloramine. Hydrazine probably would not form because the treatment process was not carried out at high (boiling) temperatures, but at room temperature.

In order to elucidate the nature of products that can be obtained from the oxidation process of ammonium ions and ammonia with calcium hypochlorite, in the model solution containing 5 mg/L ammonium ions and ammonia, 40 mg of Ca(OCl) in 100 mL demineralized water. After 30 min of mixing, the pH value was measured, it was 10.35. The concentration of ammonium ions and ammonia became equal to 0.45 mg/L, and thus lower than the MAC. To the so treated water n-heptane (4.0 mL) was added to extract obtained products for mass spectrum (CG-MS) measurement. Mass spectrometry analysis revealed the lack of chloramines. The obtained spectrum resembles that of bromobenzene (figs. 4 and 5).

In order to confirm chlorine deficiency in the water treated with calcium hypochlorite, the following experiments were carried out.

To 90 mL of treated water 2 mL of n-heptane were added. Content was stirred for 3 min after which organic solvent was separated using a small decantation funnel. Then 2 mL of n-heptane were added to the solution again and it was stirred for 3 min. The organic solvent was separated and combined with the first extract. To ~ 4 mL of n-heptane was added 0.1 g of anhydrous Na_2SO_4 to
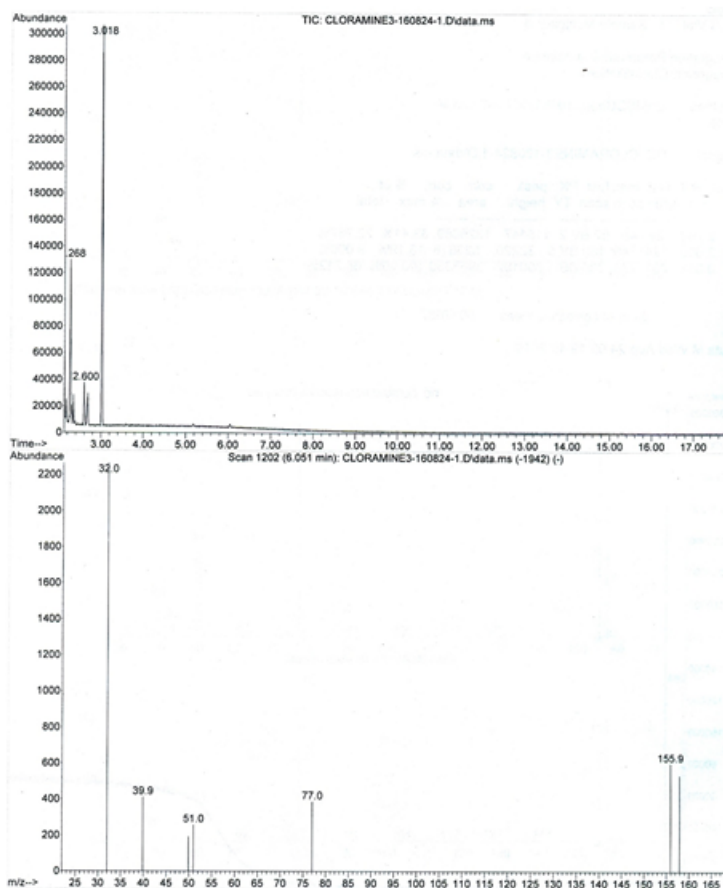
Fig. 4. CG-MS spectrum of ammonium ions and ammonia oxidation products extracted in n-heptane

Fig. 5. Mass spectrum of bromobenzene

remove water traces from the extract. The extract was further subjected to chromatographic investigations. Analysis of mass spectra measured on CG-MS spectrometer and thin layer chromatography showed the lack of chloramines in the n-heptane extract.

Figure 6 shows mass spectra of mono-, di- and trichloramine previously presented in [4].

Under these conditions, the process of oxidation of ammonium ions and ammonia is likely to result in free nitrogen formation. The following reaction takes place:

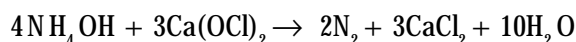$$4\,N\,H_4\,OH + 3Ca(OCl)_2 \rightarrow 2N_2 + 3CaCl_2 + 10H_2O$$

Table 1 below shows the results of model-water treatment (residual concentration of ammonium ions and ammonia), initially containing 5mg/L ammonium ions and ammonia with different amounts of calcium hypochlorite at different pH values. The pH values were adjusted.

From data presented in Table 1 we find that at 25 mg of calcium hypochlorite added to 100 mL solution, and to adjusted pH values (pH = 9), residual concentration of NH_4^+, NH_3 does not exceed the maximum admissible concentration.

Further was studied the real water from artesian well in Budesti village.

5L of water from Budesti well was collected, containing: Ca^{2+} - 14.08 mg/L, Mg^{2+} - 17.9 mg/L, SO_4^{2-} - 93.5 mg/L, Cl^- - 14.3 mg/L, NH_4^+ - 2.49 mg/L, H_2S - 1.19 mg/L. Further, 1 g of $Ca(OCl)_2$ was added, mixed for 30 min at high stirring speeds (150 p/min). The pH was 8.2. 0.5 mL of concentrated HCl was added to adjust the pH. The clear water thus treated was pumped through a AG-3 active carbon column of small size (450x20 mm). Filtration rate was 45 mL/min.
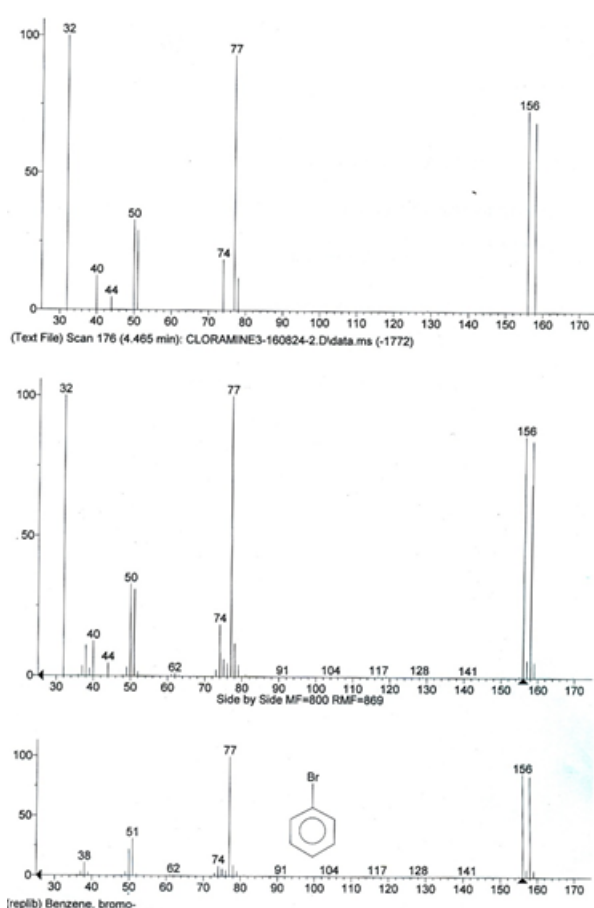
Analysis of the water thus treated showed an increase in the concentration of ions of Cl^- - 100.7 mg/L (MAC chlorides - 250 mg/L), and the concentration of ammonium ions and hydrogen sulfide became equal to zero.

Next, 1.0 g of $Ca(OCl)_2$ was added to 5L of Budesti water, the content was mixed, and samples were taken every 10 min and pH values were measured. Data are shown in figure 7.

Figure 7 shows a significant decrease in pH over 30 min. This result can be explained by the fact that $Ca(OCl)_2$ in water hydrolyzes with the formation of calcium hydroxide, which is poorly soluble in water, and which interacts with carbon dioxide during mixing, to form finely dispersed calcium carbonate. After 30 min of mixing and 30 min of decantation, we found a relatively low sedimentation rate of obtained calcium carbonate. Next, to those 5L of treated water, 0.5 mL of concentrated hydrochloric acid was added to dissolve the obtained calcium carbonate, but also to correct the pH value of the treated water. As a result, only a part of the precipitate dissolved. The volume of hydrochloric acid wasn't increased in order to dissolve all the precipitate quantity was not carried out, because that would have led to a pH lower than 6 of the treated water, which cannot be allowed in some cases.

The process of purification of ground water from ammonium ions, ammonia and hydrogen sulfide was patented [7].

Figure 8 presents the technological scheme of purification of ground water from Budesti.

Conclusions

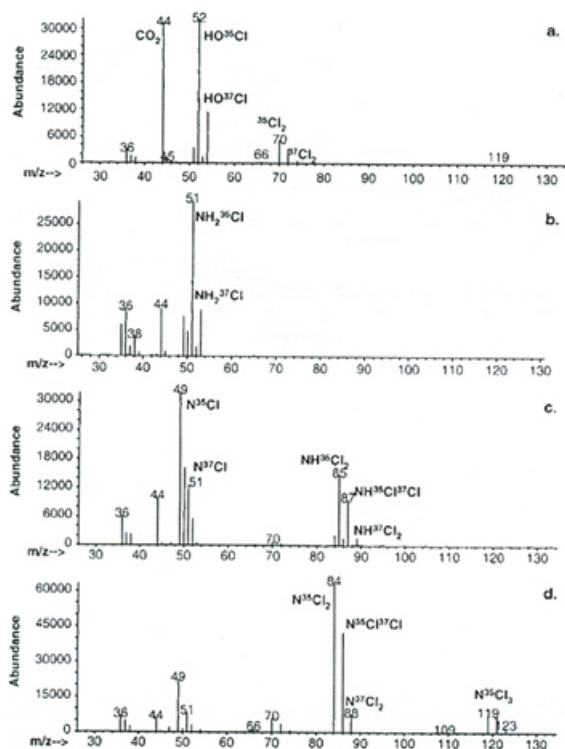Based on experimental data, the following conclusions are drawn:

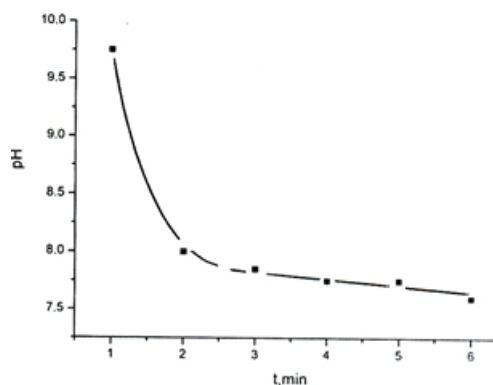Fig. 6. Mass spectra of mono- (b), di- (c) and trichloramine (d) [4]

Fig. 7. pH value variation over time at a dose of
calcium hypochlorite 0.2 g/L

Nr.	Dose de Ca(OCl)₂ mg/100mL solution	pH	Residual concentration of NH₄⁺, NH₃, mg/L	MAC, NH₄⁺, NH₃, mg/L
1.	20	2.5	3.1	0.5
2.	20	3.2	2.2	-//-
5.	25	4.2	0	-//-
6.	25	9.0	0.48	-//-
7.	30	1.85	1.35	-//-
8.	30	3.6	0.7	-//-
9.	30	4.8	0.6	-//-
10.	30	9.2	0.5	-//-
11.	35	9.4	0.4	-//-

Table 1
DOSE OF Ca(OCl)₂, pH AND RESIDUAL
CONCENTRATION OF NH₄⁺, NH₃
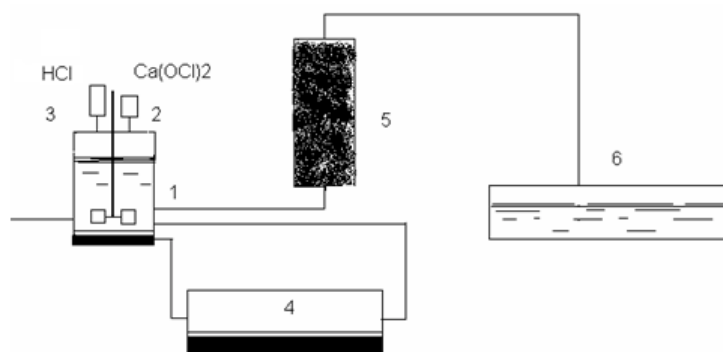AFTER TREATING THE MODEL WATER

Fig. 8. Technological scheme for drinking water potability
from artesian wells in Budesti:
1 - reactor with mixer, 2 - calcium hypochlorite doser (salt),
3 - HCl doser, 4 - decanter, 5 - AG-3 activated carbon
adsorption column, 6 - clean water reservoir

- the study of oxidation process of ammonium ions ammonia from ground water that are to be used for drinking purposes using calcium hypochlorite as an oxidant demonstrated the possibility of removing ammonium ions and ammonia to values below the maximum permissible limit.

- the CG-MS method and thin layer chromatography proved the lack of cloramine in the oxidation products after ammonium ions and ammonia oxidation.

- a technological scheme is proposed for the potabilization of ground water in Budesti, which contains ammonium ions and ammonia much above the maximum admissible limit.

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