Ammoniacal nitrogen removal from groundwaters using natural and synthetic zeolites

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Abstract* – *in article results of ammoniacal nitrogen occurrence ways into groundwaters analysis was represented. NH_4^+ removing effectivity from simulative solutions by natural (Sokyrnytsia minefield, Ukraine) and synthetic zeolites was compared.

Keywords – groundwaters, drinking water, ammoniacal nitrogen, purification, zeolites.

I. Introduction

Normative meaning of ammoniacal nitrogen concentration in drinking water from water pipeline – not larger than 0,5 $mg \cdot L^{-1}$. In separate occasions, which caused by specific environmental conditions and technology of drinking water preparation, what prevent the proof of drinking water quality to more rigorous normative, water supply enterprises until 1 January 2020 year, have a right enlarge this value to 2,6 $mg \cdot L^{-1}$ [1].

Quality analysis of groundwaters in Lviv region territory, testife about increased content of ammoniacal nitrogen in water of some water-diverting structures, mainly in Chervonograd groundwater minefield. Enlarged content of ammoniacal nitrogen stated: in 2000 year in hole # 49 of Bendiugy's water-diverting structure – 2,03 $mg \cdot L^{-1}$, in hole # 49 of Sosnivskii's water-diverting structure – 4,10 $mg \cdot L^{-1}$; in 2008 year in hole # 1 in Velykomostivskii's water-diverting structure – 1,6 $mg \cdot L^{-1}$, on Zhvyrkivtsi field – 0,6 mg/L^{-1} [2].

Work purpose – analysis of possible occurrence ways of ammoniacal nitrogen into natural, mainly groundwaters; choosing of method and ammoniacal nitrogen removal effectivity compairing from water sulutions by natural and synthetic zeolites.

II. Experimental

Nitrogen formations in view of ammonia salts, nitrites and nitrates have different ways of occurrence in groundwaters:

- Atmospheric precipitations, which owing to soakage through soil layers fall into groundwaters. Immediate factor of precipitations pollution with nitrogen formations is its emission from atmospheric air.
- Inorganic nitric fertilizers. Irrationally using of fertilizers, which are enriched with freely soluble nitrogen formations, in conditions of intensive development of agriculture, often leads to pollution of groundwaters.
- Wastewaters of animal complexes, household and industrial wastewaters (generally chemical and food industries). High content of nitrogen formations found in groundwaters of territories, which do not equipped with water drain systems. It concerned with content and solubility of nitrogen formations in wastewaters, which infiltrate into soils.
- Wastewaters of dumps, which contains nitrogen formation itself. Ammoniacal nitrogen concentration in dumps wastewaters decreasing toward its age.

For ammoniacal nitrogen removing from water currently used next methods:

- ammonia air stripping. The method is based on the inhibition of ammonia hydroxide dissociation in concentrated alkaline media with generation of gaseous ammonia, which can be removed after atomized water splashing.
- Chlorine treatment. The method is based on oxidation reaction of NH_4^+ to N_2 with following its removing.
- Ozone treatment. Under the influence of ozone onto solutions, which contains ammoniacal nitrogen itself, oxidation of the last to nitrates is happening.
- Transferring of ammoniacal nitrogen NH_4^+ to molecular nitrogen by biological method. Ammoniacal nitrogen in this way oxidized to nitrites, and than to nitrates during nitrification process, which provided by aerobic nitrification bacteria.
- Ammoniacal nitrogen removing by ion-exchange method.

From the point of view of economical practicability and depending on local conditions, for water purification can be selected different methods of ammoniacal nitrogen removing. For Central Europe countries (including Ukraine) one of those methods can become cationic-exchange method of natural water purification with natural or synthetic zeolites. Characteristic feature of cationic-exchangers is convertibility, i.e. reaction passage possibility in reverse direction (cationic-exchangers regeneration), which make possible its reusable applying in water purification processes.

In Zakarpattia region is located powerful Sokyrnytsia minefield of natural zeolites. On the Chemical Technology of Silicates Department of Lviv Polytechnic National University was obtained ceramic zeolitecontaining adsorbent in the form of "zeolite NaA-binder" composite.

Zeolites of Sokyrnytsia's minefield – it's rocks with light-green colour, which characterized by next oxide composition, mass %: SiO_2 – 69,43; Al_2O_3 – 13,04; Fe_2O_3 – 1,05; TiO_2 – 0,18; CaO – 2,10; MgO – 0,17; K_2O – 2,64; Na_2O – 2,06; P_2O_5 – 0,03. Loss on ignition equal to 9,30 %. Main rock-forming mineral of natural zeolite – clinoptilolite belongs to acid zeolite group.

Synthetic zeolite NaA (LTA) represents the main work phase in the composite material makeup. Technological sequence of its synthesis from thermoactivated kaoline is

presented in the work [5]. This zeolite, oxide formula of which $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4{,}5\ H_2O$, characterized with ratios Si/Al and Na/Al equal to 1. For this reasons can be hypothesized that it can show better cationic-exchange properties in comparison to natural clinoptilolite.

Ceramic zeolitecontaining adsorbent production was performed by classic ceramic technology, using the way of liquid-phase homogenization of cryptocrystalline zeolite NaA powder with modified clay binder, further dehydration of suspension to plastic mixture consistency, semi-finished good intermediate drying and its firing at 700 ^oC [6]. As result composite was characterized with high porosity and technologically acceptable mechanical resistance.

Water purification process using natural and synthetic zeolites was studied in dynamic conditions with motionless material layer.

Zeolite materials before the investigation was crushed in ball mill, sieved on standart sieves, washed with distilled water and dried to fixed mass. Selected fractional composition of materials (0,5–1,02 mm) hitting to granulations spectrum, which are widely used in practice.

Natural zeolite was treated in static conditions by 0,9 N solution of sodium chloride NaCl for its transferring to Na-exchange form. After this material was washed with distilled water up to decreasing chloride-ions concentration to 10 $mg \cdot L^{-1}$ and dried to fixed mass in drying camera at 100 ^oC. Chloride-ions content in filtrate was determined following to technique of titration with silver nitrate $AgNO_3$ under standardized method [4].

Synthetic zeolitecontaining material wasn't modified before investigation.

Laboratory-scale plant consisted of glass column what was fixed on metallic holder. Column edges was connected with capacity for simulative solution and with capacity for filtrate collection (purified water). All joints of column with capacities was made of silicone hose.

Movement direction of simulative solution during natural zeolites investigation was ancestry, synthetic zeolites - degressive.

Volume of loaded into column natural zeolites was V_z=0,7 L. Filtrate consumpsion q = 8 L^3/hour.

Volume of loaded into column synthetic zeolites was $V_ц$ = 0,1 L. Filtrate consumpsion q = 3 L^3/hour.

Initial solution of ammonia chloride NH_4Cl with volume 1 cm^3 contained 1 mg NH_4^+ itself. Simulative solution of ammonia chloride NH_4Cl was prepared before determination passage by the way of addition of some quantity of original solution into distilled water for reaching the concentration of ammoniacal nitrogen equal to 6 mg $NH_4^+ \cdot L^{-1}$.

During the investigation filtrate samples was picked out at regular intervals and than, using method of direct nesslerization, quantity of residual ammonia cations were determined [3].

During the investigation of synthetic zeolites, vibration of filtrate consumption meanings was found.

Ammonia cations concentration 0,5 $mg \cdot L^{-1}$ have been observed in filtrate at values V/V_z = 1303 for natural zeolites and V/V_z = 1730 for synthetic speciments (V-filtrate volume). So, synthetic zeolites in compairing to natural characterized with larger on over 30 % ammoniacal nitrogen removal effectivity from water solutions.

But, determining of work and full exchange capacities of materials, origins of decreasing water filtration speed through layer of material in time, influence of modification on cathartic properties of synthetic zeolites and other questions demands realization of further researches.

Conclusion

Water from some water-diverting structures of Lviv region is characterized with enlarged containing of ammoniacal nitrogen, concentration of which is strictly regulated. One of the methods of improving the quality of natural water can be its cationic-exchange purification using natural and synthetic zeolites. Results of realized investigations testify that synthetic zeolites in compairing to natural is characterized with larger on over 30 % ammoniacal nitrogen removal effectivity from water solutions. Determination of basic quantitive characteristics for zeolites as purifiers of natural waters demands realizations of further researches.

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