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RELATIONSHIP OF NITRATES AND NITRITES IN THE WATER ENVIRONMENT WITH HUMANS AND THEIR ACTIVITY

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Nitrates and nitrites in water pose a health and environmental hazards, in particular when exceeding limits defined in the European Union, i.e. max. 50 mg l^{-1} of nitrates. It is not recommended to exceed the limit of 10 mg l^{-1} of nitrates for infants and children. The maximum concentration of nitrites is 0.5 mg l^{-1} for adults and infants less than 0.1 mg l^{-1}. Our work offers a review of the water quality concerning the relationship between nitrates/nitrites and humans. Basic properties and forms of nitrates, their use for human activities, importance and risks to human health and possibilities of their physicochemical determination are summarized. Our study demonstrates also the novel approaches to the nitrates decontamination in a water environment using various nanomaterials. We aimed at a collection of records from the monitoring of nitrates in selected areas in Slovakia to show good quality of water in various water sources, which over time improves due to the increasingly low fertilization intensity and thus of agriculture production, which is gradually being replaced by imports.

KEY WORDS: nitrates/nitrites, importance/risk, determination, decontamination, monitoring

Introduction

A rapidly developed life trend because of its close association with an environment can lead to depreciation of sources, especially water sources. Water as a still extensive part of Earth is irreplaceable for life in any form. Unfortunately, some inadequate human activity can lead to water pollution. Widespread nitrates and nitrites are still considered as prominent sources of water pollution, especially in countries where their use exceeds organizational recommendations for protection against damage of human health. Therefore it is necessary to monitor them continuously. The basic difference between nitrates and nitrites comes from different atoms of oxygen (Fig. 1). They will differ in physicochemical properties, depending on a compounds type they will form.

It is generally known, that nitrates form stable crystalline solids salts of nitric acid. Nitrate anions can be found naturally in every water, atmosphere or on the earth in a form of various mineral as nitratine, nitrocalcite or nitromagnesite (Onac, 2012; Orel and Seinfeld, 1977). Usually, nitrates are prepared in the lab by dissolving metals in nitric acid or by reacting with metal hydroxides, oxides or carbonates. They are soluble in water and stable under aerobic conditions. Nitrites occur in water, where oxygen is absent, as a product of nitrate reduction (denitrification). Nitrite contains nitrogen in a relatively unstable oxidation state. In a natural nitrogen cycle, nitrifying bacteria produce nitrites followed by their oxidation back to nitrates. Nitrites are salts of nitrous acid. They can be prepared by thermal decomposition of alkali metal nitrates or by reduction of their melt e.g. lead. All nitrites are well soluble in water except yellow silver nitrite (Laue et al., 2006). Nitrates and nitrites cause danger in the environment, mainly in groundwater and sources of drinking water, due to an effect of fertilization ("area pollution"), or wastewater leaks ("spot pollution"), which often exceeds maximum concentrations in water sources for a human consumption.

Nitrates dissolve easily in a soil solution, i.e. nitrate salts dissociate in an aqueous medium to very mobile nitrate anions, and due to a low sorptivity on soil particles caused by their negative charge can be washed out of the soil into groundwater that can contaminate or flow into surface sources and rivers. From there it gets into plants and food (Šalgovičová and Krížová, 2006). Nitrates in increased concentrations occur in the soil as a result of agricultural activities (natural and synthetic fertilization), from the animal and industrial waste (from dye productions or engineering plants) (Lenghartová et al., 2015). Nitrate compounds for commercial applications are products of the chemical industry. The most used nitrates are sodium nitrate ($NaNO_3$), ammonium nitrate (NH_4NO_3), silver nitrate ($AgNO_3$) and potassium nitrate (KNO_3). They are widely used as a fertilizer component in agriculture, in glass productions, as an oxidizing agent in pyrotechnics, in a food preserving industry and as a stabilizer of a meat products colour, in medicine (Honikel, 2008; Nakayama et al., 2010; Nujić and Habuda-Stanić, 2017). Nitrites added to meat product causes a red colour, which is a result of many compli-cated reactions related to an oxidation state change of an iron ion in myoglobin localized in muscles. The use of sodium and potassium salts of nitrates and nitrites in the food industry is regulated and limited by laws that take into account their toxicity. The most used food additives are sodium nitrite and potassium nitrite (marked as E250, E249) and sodium nitrate and potassium nitrate (E251, E252). Positive effects of mentioned agents include antioxidant activity, prevention against microbial growth and finally a pleasant flavour of meat (Honikel, 2008).

Importance and risks of nitrates and nitrites to human health

The most important reason, why to study and monitor nitrates and nitrites in water sources and food is their effect on human health. Nitrates and nitrites are the normal part of the nitrogen cycle in nature. Living organisms including plants accept them for their needs. They occur in the environment, air, food (especially vegetables and fruits) and in water sources (Nujić and Habuda-Stanić, 2017).

The health benefit of nitrates includes their antibacterial activity in the stomach against microbes as Salmonella or Escherichia coli that cause gastroenteritis. First, nitrates are rapidly reduced by microbes on the tongue in mouth saliva to nitrites, which produce nitrous acid when it reaches a normal human stomach. Nitrates act against dental caries and even on our skin against fungal pathogens. When a human body is exposed to a nitrate-free diet, nitrate can be produced endogenously via nitric oxide synthase that acts on the amino acid L-arginine to produce nitric oxide (NO), from which nitrates are formed under the influence of superoxide or oxidized haemoglobin (Addiscott and Benjamin, 2006). Many studies have shown, that nitrates and nitrites positively affect biological activities of some substances necessary for normal physiological (mainly cardiovascular) functions in the human body (Larsen et al., 2006; Machha and Schechter, 2011; Bondonno et al., 2018). In detail, nitrites and nitrates improve endothelial function, cause vasodilation, inhibit platelet aggregation and play a significant role in NO (nitric oxide) biosynthesis and bioavailability, which improves blood circulation. The nitrite and nitrate application is usually suggested for the treatment and prevention of cardiovascular diseases (Machha and Schechter, 2011).

Despite the many health benefits of nitrates and nitrites it is necessary to take into account that positive biological effects of nitrite and nitrate depend on their systemic concentration from endogenous and exogenous sources (Dejam et al., 2004; Kapil et al., 2010; Lundberg and Weitzberg, 2009). Normal plasma concentrations of nitrites are between 0.01 and 0.6 μM and for nitrates is range 20–40 μM (Machha and Schechter, 2011). As it was in the case of common substances or drugs, also nitrates and nitrites after standard verified concentration limit exceeds will become toxic for humans. This situation may occur most often as a result of incorrect (excessive) fertilization with nitrogen fertilizers, which can get into groundwater through natural transport processes in nature, or excessive consumption of nitrate-containing meat. Contamination can come from food, water sources and wells near the industrial plants or drainage. The main health risk of nitrates comes from their conversion to nitrosamines that belong reportedly to carcinogenic substances acting on nucleic acids causes tumours (Lin, 1990; Gushgari and Halden, 2018). However, despite many epidemiological and experimental studies, there are no direct correlations between cancer development and nitrates and nitrites intake (Knight et al., 1990; Eichholzer and Gutzwiller, 1998). On the other hand, some other works show associations between nitrites and nitrates in meats with an increased risk of cancer formation (Cross et al., 2010; Ferrucci et al., 2010). Intoxication with nitrates and nitrites shows in 3 phases. Nitrate phase starts 3–7 hours after receiving a toxic substance. Symptoms are bloody diarrhoea, colic, cramps, palsy, eventually death. The nitrite phase includes the primary toxic effect of nitrites on the central nervous system and vessels. Tachycardia and hypotension are the main symptoms. This phase of intoxication ends with collapse, eventually death. The last phase is the methemoglobin phase. Haemoglobin is a protein in red blood cells which helps to distribute oxygen in the body. Absorbed nitrates are rapidly reduced to nitrites, which react with haemoglobin followed by the loss of its ability to transport oxygen. Nitrites in the bloodstream cause the oxidation of heamo-

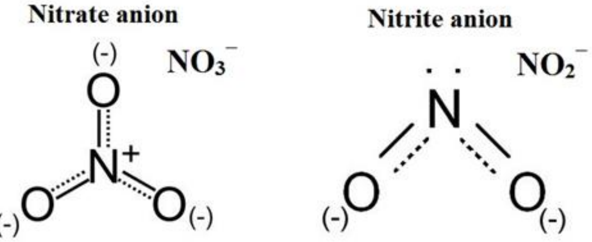

Fig. 1. Structural and chemical formula of nitrate and nitrite anion.

globin to methemoglobin. The Fe^{2+} ion present in the heme group is oxidized to its Fe^{3+} form, and the remaining nitrites bind strongly to heme, which does not allow oxygen transport. Hypoxemia is initialized. The skin turns blue and the blood turns brown. The health condition is called methemoglobinemia and can lead to cyanosis as a result of tissue suffocation. Abortions occur in pregnant women, and this phase can also end in death. In generally, methemoglobinemia represents a different degree of oxygen transport deficiency and poses a great risk especially to infants and children, which have increased oxidability of haemoglobin and relatively low methemoglobin reductase activity. Methylene blue or toluidine blue, ascorbic acid (vitamin C), O_2 treatment, exsanguination transfusion, hemodialysis etc. are usually used to relieve symptoms and treat methemoglobinemia (Ali Mansouri, 1985; Greer and Shannon, 2005; Králinský and Mečiaková, 2014). The most important is early diagnosis of this disorder.

Methods for nitrates and nitrites determination

Nitrates and nitrites monitoring in the human body, food, objects or areas should be performed by use preferred method for their determination. As much as possible it should be the available, inexpensive and time-saving method. Determination of nitrates and nitrites concentration or their presence in an aqueous medium can be performed using various methods, which have been developed over time. Basic principles, detection limits, advantages and disadvantages concerning various methods were processed in some detailed works (Lenghartová et al., 2015; Wang et al., 2017; Singh et al., 2019). Spectroscopic methods, as ultraviolet and visible (UV-VIS), spectrofluorimetric, Raman, infrared, Fourier-transform infrared, atomic absorption, chemiluminescence, mass spectroscopy, electron paramagnetic spectroscopy or nuclear resonance spectroscopy, are the most frequently applied for detection. UV-VIS spectroscopy as basic equipment of each chemical laboratory is usually used. Physical UV-VIS principle allow use catalytic, nitrosation, enzymatic, reduction or Griess assays. Also, nitrates and nitrites can be analyzed by titration methods (acidimetry, manganometry, indirect iodometry, etc.), electrochemical, separation methods (ion chromatography, electrophoresis) (Lenghartová et al., 2015; Wang et al., 2017) or colourimetrically (Woollard and Indyk, 2014). We would like to highlight, the suitability of selected method towards interferences (presence of other ions) and analyte concentration range should be verified before analytic determination (Singh et al., 2019).

Possibilities and new approaches of nitrates decontamination from the water environment

Requirements for high water quality are steadily increasing due to the continued widespread biological and chemical contamination as a result of the population growth over time. Unequal distribution of people in the surrounding environment led to the accumulation of contaminants in endangered areas, where natural flora and fauna have been eliminated in favour of the rapid development of humanity, technology and society.

One way to remove increased amounts of contaminants may be the development of separation technology. As we mentioned above in our paper, nitrites occur in unstable oxidation state and they are transformed back to nitrates in the natural nitrogen cycle, therefore separation technology is aimed at nitrates removal only. Usually, for reducing of nitrates, as durable and soluble ions, separation methods like adsorption, reversal osmosis, ion exchange, electrodialysis and biological, chemical or catalytic denitrification have been used (Kapoor and Viraraghavan, 1997; Soares, 2000; Shrimali and Singh, 2001; Bhatnagar and Sillanpää, 2011; Archna et al., 2012). Currently, the foremost challenge not only for scientists and engineers worldwide is focused on the development of innovative, effective and low-cost water treatments technologies. Highly popular nanotechnological systems could be a promising tool for water treatment and improving the water quality thanks to numerous laboratory studies. Application possibilities of nanotechnology involve membrane filtration, adsorptive elimination of micropollutants, nanocatalysis degradation and microbial decontamination (Li et al., 2008a, b). Madhura in the latest review refers to the interesting physicochemical properties of various nanomaterials characterized by an excellent adsorption capacity, enhanced photocatalysis, and high reactivity useful in separation processes such as reverse osmosis, microfiltration, and nanofiltration (Madhura et al., 2019). The most interesting and intensively studied material – graphene represents a highly promising system for environmental applications in water treatment. Also, low production cost raises the importance of the separation technologies development based on graphene. The one layer of carbon atoms in graphene nanostructure provides extreme thinness, mechanical strength, chemical stability, and inherent impermeability useful as a suitable two-dimensional separation nano-membrane (Celebi et al., 2014). Such application requires functionalization of graphene to achieve permeability, while holes for the transport of small molecules can be created (Hosseini et al., 2018; Shi et al., 2018). Then, nanopores, formed on the functionalized graphene sheet, can be used for nanofiltration of nitrates from contaminated water (Li et al., 2017; Anand et al., 2018). Jahanshahi and co-autors (2018) has used molecular dynamics simulation method to show how water molecules crossed through the fluorinated and hydrogenated graphene pores with different size localized in graphene sheets. Graphene membranes can be applied to nitrate ions elimination from water under various amounts of external pressures. We would like to emphasize that functionalization of graphene nano-membrane by specific chemical substances or groups, molecules or biomacromolecules with enzymatic activity can improve, accelerate, decelerate various ions and acting as a selective, controlled and time-regulated membrane. Also during transport, the chemical composition of holes can change properties of contaminant to more or less toxic. Chemical adjustment of nano-membrane can simply release ions or molecules according to properties of each contaminant, including charge, size and reactivity. The important role in transport processes can play diffusion and electrostatic gradient in the medium. Many researchers of various field of science are intensively engaged to the development of cost-effective synthesis technology for graphene-modified using various elements (e.g. oxygen, hydrogen or metals ions), molecules (e.g. epoxy, hydroxyl, carbonyl, carboxylic groups, or chelates) and magnetic nanoparticles, what continuously increased the popularity for proposing the ability of graphene-based systems to purify water from nitrates contamination by the separation or adsorption methods (Ghadiri et al., 2017; Ma et al., 2018; Jilani et al., 2018). Magnetic nanoparticles (most often of magnetite – Fe_3O_4) size in the range from 1–100 nm provide high surface energy and reactivity, what is the major cause of their different physical properties compared to macroscopic systems with the same chemical composition. Thanks to the unique properties and availability, their application possibilities constantly expand from the medical science, technology and industry to the environmental scope. Magnetic nanoparticles are commonly used to remove hazardous contaminants from wastewaters. Nanomagnetite thanks to the high specific surface area can be used as a nano-adsorbent. Superparamagnetic properties allow magnetic separation under external magnetic fields and after the treatment process, magnetic nanoparticles can be effortlessly retained and reused (Mayo et al., 2007). Similarly, magnetite nanoparticles, modified by 3- aminopropyl-triethoxysilane, were used to enhance the removal of nitrate ions from contaminated groundwater. The proposed system with good adsorption selectivity for nitrate ions can provide fast and efficient decontamination and rapid separation by using just an external magnetic field (Poursaberi et al., 2013). Another experiment has shown, that Fe_3O_4-based magnetic nanoparticles coated on powder activated carbon can be applied for the spontaneous and endothermic adsorption of nitrate from aqueous solutions (Rezaei Kalantary et al., 2014). Besides the absorption capacity of magnetic nanoparticles, their next advantage is catalytic activity allowing oxidative or reductive degradation of pollutants. Many studies on magnetic nanoparticles of magnetite coated by various surfactants have shown degradation activity of such durable materials as lysozyme amyloid fibrils (Bellova et al., 2010; Kopcansky et al., 2015). Despite that the precise mechanism of magnetic nanoparticles effects on various objects is still not fully understood, the catalytic effect is highly expected also in interaction with nitrates in the water environment. We assume, that the effectiveness of the remediation process of nitrates will dependent on the reaction time, the concentration of the catalytic agent (magnetic nanoparticles), the properties and composition of the surfactant (surface charge – zeta potential) and surrounding medium (pH). Interesting material for NO_3^- degradation seems to be intensively studied magnetoferritin, a semi-biological nanomaterial consisting of apoferritin cage with the size of 10–12 nm, which surrounds magnetic nanoparticles. The study of application possibilities of magnetoferritin was focused especially on the medical field of science. Magnetoferritin can be used as standard in diagnosis of various diseases, contrast agent in MRI, drug delivery system for targeted anti-cancer therapy, catalytic agent (peroxidase-like activity: protective agent against oxidative stress, destruction activity on fibrils responsible for amyloid disorders), etc. (Koralewski et al., 2012; Melnikova et al., 2014; Kopcansky et al., 2015; Strbak et al., 2017; Xue et al., 2019). According to the fact that magnetoferritin is expensive material related to the apoferritin origin, which is isolated from the biological organism (horse spleen), its use is limited to a large extent against surface water, groundwater and wastewater treatment. Application of magnetoferritin with catalytic activity is again directed to medical use, where exsanguination transfusion or hemodialysis for NO_3^- removal could be equipped e.g. by modified graphene nanostructured membrane functionnalized by magnetoferritin nanoparticles, which could serve as nano-adsorbent for NO_3^- anions. Magnetoferritin due to the catalytic activity under specific conditions of medium can provide chemical adsorption, while NO_3^- could be catalytically destructed. Next benefit of magnetoferrritin comes from its biogenic form, which was confirmed in various works. "Biogenic" magnetoferritin occurs in patients with neurodegenerative or cancer diseases (Kirschvink et al., 1992; Kobayashi et al., 1997; Dobson, 2001; Brem et al., 2006) and there are indications that it could be the part of healthy organisms similarly. In that case, magnetoferritin could play thanks to its catalytic activity a protective role against intoxication by nitrates. However, further experimental evidence is needed for these hypotheses.

Assessment of water quality from nitrates monitoring in various water sources in Slovakia

The concentration of nitrates in selected areas in Slovakia depends on anthropogenic, agricultural, industrial, urban activities and complex of meteorological (seasonal changes), hydrological, hydropedological and soil-chemical processes (e.g. precipitation and its transport together with fertilizers over and through the surface soil to streamflows). Nitrates can contaminate surface water, groundwater and rainwater. The greatest danger is the pollution of drinking water sources. The requirement for the drinking water quality and its control is defined by the law of the Ministry of Health in Slovakia, monitoring microbiological, biological, physical, chemical and radiological indicators. Drinking water treatment technologies are different. Various filtering equipment is used to remove nitrates and nitrites. Water quality control in surface and underground sources is provided by water companies or municipalities. The public health authority and regional public health authorities monitor the quality of drinking water within the framework of monitoring. Monitoring is carried out continuously and permanently, and sampling points are collected in premises or buildings where water flows out of taps normally used for human consumption. Determination of nitrates in various water sources (in surface, subsurface and rainwater) is carried out in Slovakia in the framework of the national monitoring program by the Slovak Hydrometeorological Institute or by scientific institutes to determine the suitability of studied water as a drinking water source. Pekárová and Miklánek evaluated nitrate concentration trends in five sub-basins of the Ondava River between 1968–93 taking into account the hydrometeorological elements (discharge, temperature, precipitation). A rapid decrease of nitrate concentration after 1989 was observed, most probably caused by a lower intensity of agricultural production and fertilization in Slovakia as a result of economic changes. Daily sampling in 1989 was compared also to those derived by Slovak Hydrometeorological Institute. The 25-years time series of monthly nitrate concentrations of the Ondava river area in 1968/69–1989/90 was analyzed. The mean annual concentrations increased from 2.9 mg l^{-1} in 1968/69 to 12.8 mg l^{-1} in 1988/89. After 1988/89 the mean annual nitrate concentration decreased to 5.3 mg l^{-1} in 1992/93 (Pekárová and Miklánek, 1993). Decreasing of nitrate concentration in surface water since 1989 was mentioned also in the next study (Pekárová and Pekár, 1996), where the environmental impact of forestry, agriculture and urban activities on the quality of water over short and long time-scaled was analyzed. The annual nitrate specific load varied from 5.90 to 110 kg $ha^{-1}.year^{-1}$, while the highest average annual nitrate concentration (47.4 mg l^{-1}) was determined in micro basin Rybárik and the lowest in the mountainous catchments Jalovecký Potok (2.02 mg l^{-1}), Bystrá (2.37 mg l^{-1}), forested micro basins Manelo (1.76 mg l^{-1}) and Lesný (2.78 mg l^{-1}) (Pekárová and Pekár, 1996). Another study was aimed at assessment of monthly time series of nitrate-nitrogen concentration monitoring in Ondava River by Slovak Hydrometeorological Institute (period 1987–1991) compared with daily time series of nitrate-nitrogen concentration monitoring by the Institute of Hydrology Slovak Academy of Sciences. The long-term development of nitrates content in Ondava River for the period 1967–2002 and trend analysis shows decreasing of nitrates amount and a further decline is expected (Pekárová et al., 2006). A long-term hydrological and water chemistry research was performed in three experimental micro basins: Rybarik, Lesny, and Cingelova within the larger Mostenik basin, differing in land cover. Nitrate concentration was investigated for a period of 3 years (1991–1993). Comparison of the net imported/ exported loads has shown that the nitrate content leached from the agricultural micro basin is ~3.7 times higher than that from the trees covered micro basin. These analyses justify that land cover land-use practices (fertilization in agriculture) may actively affect the retention and export of nitrates from the micro basins, and have a pronounce impact on the quality of stream-water. Agriculture and the use of natural or synthetic nitrogen fertilizers are the main anthropogenic source of nitrates. The number of nitrogen fertilizers applied in Slovakia between 1950 and 2005 has shown a decreased trend (Onderka et al., 2010). The continuous decrease in fertilization is caused by reduction of agricultural activity, increased fertilizer prices and lower number of farm animals. The evaluation of the content of nitrate-nitrogen ($N\text{-}NO_3^-$) in the surface waters and the monitoring of the qualitative characteristics of drainage canals in the East Slovakian lowlands was carried out at the Institute of Hydrology of the Slovak Academy of Sciences in 1999 and 2000 (Ivančo and Pavelková, 1999; Pavelková and Ivančo, 1999; Pavelková, 2000). Pavelková and Petrík in 2011 realized the analysis of nitrate content in water from house wells in 1997–2010 in districts Michalovce and Sobrance (Pavelková and Petrík, 2011). The recent study of Pavelková and Petrík was aimed at the monitoring of nitrate levels in house wells in the villages of Michalovce and Sobrance district (Pavelková and Petrík, 2016). Qualitatively and quantitatively determination of specific parameters in water environment can help better assesses the suitability of surface or subsurface water for human consumption in specific localities. Also, the scientific organization can prove the negative effects of specific contaminants in water and study various interaction processes and numerical modelling of dynamic processes of pollutants flow in water supplies. Due to the decreasing fertilization and agricultural activity in Slovakia, lower limits of nitrates in the last decades was observed. Slovakia still belongs to the states with a good quality of water. Nevertheless, there are endangered areas in Slovakia with over-limit concentrations of nitrates, therefore it is necessary to deal with monitoring and possibilities of their elimination.

Conclusion

This review aimed to summarize information about the relationship between nitrates and nitrites in the water environment with humans and their activity. Our assessment rises from the terms of environmentalism, biology, chemistry and nanotechnology. Unfortunately, higher nitrate levels in the soil and water worldwide are the result of the human inadequate activity. It is necessary to constantly monitor these pollutants, particularly in areas with increasing populations. Just as tons of waste is produced by humans, including agriculture, urbanism and industry, in the same way, humans can eliminate the number of contaminants from the environment with the help of nature or using synthetic nanomaterials as still popular graphene or magnetic nanoparticles. We would like to highlight that the improved situation was observed in Slovakia from hydrological monitoring after reducing agricultural activity. Finally, we would like to emphasize that it is necessary still to develop greenways to produce new separation materials for various pollutant reduction and removal following environmentally friendly approaches and technologies, that ensure good efficiency, rapidity and low cost.

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