1. INTRODUCTION

The protection of the environment, and in particular diminishing water resources, which are most vulnerable to pollution from anthropogenic sources, is and will continue to be one of the major challenges facing the international community. The undertaking of integrated solutions, such as implementation of strict quality standards for discharged industrial wastewater, the creation of special hazard exposure areas by eutrophication or the application of new treatment technologies, resulted in a change in the production technology of many industrial plants, allowing to reduce the amount of generated waste water by about 25% in 2013 (compared to 1980) [1]. Nevertheless, it is still necessary to improve the quality of natural waters, which can only be achieved by reducing the discharge load. However, common wastewater treatment techniques based on physical, chemical or biological processes do not always achieve a sufficiently high level of removal of pollutants, in particular nutrients.

Therefore, it is necessary to search for, study and technically implement new methods of wastewater treatment. New technologies and developments must not only ensure greater efficiency, but also take into account other factors such as energy intensity, the type of chemicals dosed or economic viability. The environmental impact, and in particular the management of by-products, is also a very important issue, which is becoming increasingly problematic especially in the case of sewage sludge. Therefore, new wastewater...
treatment methods should also be characterised by the lowest possible level of production of by-products that are necessary for disposal.

2. NITRATE(V) IN AQUEOUS SOLUTIONS

Nitrates (V) are defined as any inorganic compound (salts) or organic compound (esters) of nitric(V) acid derivatives. In solid form, salts are colourless or white crystalline substances which, during heating above the melting point, decompose with the release of oxygen, thus indicating their oxidative properties [2]. Because of the very good solubility in fluids (according to salts solubility table), in aqueous conditions nitrates(V) are present mainly in dissociated form, i.e. anion NO₃⁻, which is favourable for rapid migration in the environment.

Nitrate ion contains nitrogen at +5 degree of oxidation. In surface water aquifers and surface streams, like other forms of nitrogen, it may originate from natural or anthropogenic sources. Natural sources are [3]:

• Biochemical process of nitrification, i.e. oxidation of ammonium ions and nitrate (III) by microorganisms,
• Atmospheric deposition from the emission of nitrogen oxides.

However, a much higher amount of nitrates(V) in the waters is the result of human interaction through [3]:

• Outflow of inaccurately treated wastewater - mainly industrial wastewater,
• Surface run-off from fertilized fields.

The risk of nitrate(V) overcharging to the aquatic environment is substantial as nitrate(V) ion derivatives and salts have been frequently used as substrates in various industries for many years, including metallurgical, mining and military [4, 5]. Certain nitrates are used in the production of exploding materials or their components (nitrocellulose, nitroglycerine) [2] and in the food industry, as preservatives and agents improving the organoleptic properties of smoked meats [6]. In agriculture, it is used to produce mineral fertilizers and rodenticides, which are chemical preparations for killing rodents [7], in the form of containers placed underground (usually in burrows), where they are detonated and harmful gases are released.

3. METHODS OF NITRATE(V) REMOVAL IN WASTEWATER

Appropriate processes and techniques must be used to remove nitrates(V) from the aquatic environment because of their chemical properties [8]. At present, the following methods are used most frequently:

• Physicochemical separation:
  − Membrane processes
  − Ion exchange
  − Evaporation
• Reduction to gaseous nitrogen:
  − Biological denitrification
  − Chemical reduction
  − Electrochemical reduction
• Oxidation under supercritical conditions.

In the municipal wastewater treatment sector, biological denitrification is used only for the reason of the highest economic profitability and the absence of process inhibitors in wastewater. However, for the industrial wastewater, as well as process waters, which are toxic for the microorganisms of active sludge, it is necessary to apply methods based on physicochemical reactions.

3.1. Physicochemical separation and oxidation

The first subgroup consists of physicochemical methods based on the separation of nitrate(V) ions from wastewater. Depending on the process, there can be used physical barriers – membrane methods, chemical bonding – ion exchange or phase transformations – evaporation. The effectiveness of these operations is significant and can reach even 100%, but the final result is not destruction or transformation of the ions, but only their retention and transfer to another medium. According to the published results [9] for municipal wastewater at an initial nitrate concentration of 40 mg/dm³, the efficiency of the reverse osmosis process (RO) was over 82% (concentration in permeate equal to 7.1 mg/dm³). However, it has to be noted that in each case pre-treatment process was necessary (e.g. ultrafiltration, microfiltration or sand filters filtration). The resulting RO retentate or solution after the regeneration of ion exchange beds contains a significant concentration of nitrates(V), which subsequent utilization is associated with secondary pollutant and significant costs.

Separation technologies also do not have any selective properties. In the process of electrodialysis and
reverse osmosis, almost all cations and anions in wastewater are stopped on the membrane. Although this is advantageous for the treatment efficiency, it results in significant operating costs associated with fouling process and frequent membrane cleaning procedures, as well as shortening the lifetime of membranes [9]. The method based on the process of evaporation of water from the solution, similarly, does not allow selective removal of the contamination, but only enables higher concentration of the contamination. At the same time, it is highly demanded for electricity.

The ion exchange process in theory provides a certain selectivity of the reaction due to the possibility of modifying the chemical properties of the anionites. For instance a strong-base ion exchange resin IONAC SR-7 is characterized by a selectivity with respect to nitrates which is three times as high as the selectivity of any of the anion exchangers available on the market [10]. For this type of ion exchange bed, the nitrate removal efficiency was at least 99% [10] and did not significantly change depending on the filtration velocity (10-25 m/h) or the initial nitrate concentration (15-30 gN/m^3). However, the reactivity series of anions indicates that in the absence of nitrate ions, sulphate(VI), chloride or bicarbonate ions may also be removed, which results in ionite exploitation, shortened working time period of the bed and the necessity of regeneration process.

Supercritical water oxidation and wet air oxidation are methods which are performed only on an experimental scale. Hydrothermal oxidation is made by using oxygen dissolved in heated water, which makes the pollutants oxidize with the release of carbon dioxide and water, inorganic salts and acids [2]. Despite the high effectiveness – complete destruction of nitrates(V) and other substances – and non-toxic final products of the reaction, this technology has several significant disadvantages, mainly [11]:

- Production of supercritical water, which can only be obtained at a temperature of 374°C and a pressure of 218 atmospheres. Expensive and energy consuming equipment is needed to create such a reaction environment.
- Lack of continuity of the flux and concentration of contaminants in the purified water solution.
- Generation (under certain conditions) of by-products containing undesirable nitrogen oxides – NOx.

### 3.2. Electrochemical reduction

Electrochemical reduction is based on electrolysis, that is chemical transformation of electrolyte components (sometimes also electrode material), which takes place on electrodes under the impact of electric power flow. Nitrate ions(V) also underwent such transformation in the aqueous solution. Theoretically, during cathodic reactions, nitrates are mainly reduced to nitrites, ammonium ions and molecular nitrogen, which is electrochemically inactive [12]. Nitrites and ammonium ions, which are indirect products, are oxidized directly to gaseous nitrogen during anode reactions. However, theoretical process flows are not always achievable under all conditions, so it is necessary to adjust them so that the two reactions: reduction on the cathode and oxidation on the anode are properly occurring. The choice of materials which are used for electrodes production is also an important issue, as it affects the efficiency of the process and nitrate(V) selectivity. The electrodes used in the process are as follows: [4, 5, 12]:

- **Monometallic:** Pb, Ni, Zn, Rh, Ru, Ir, Pd, Cu, Ag, Au, Fe, Ti
- **Bimetallic:** Pd/Cu, Ti/Pt, Ti/RuO₂, Ti/IrO₂, Ti/IrO₂-Pt, Ti/RuO₂-Pt.

According to the publication of many studies, copper is the best electrode material for electrochemical nitrate reduction, however, the final product of the reaction is ammonium ion, especially in alkaline solutions with a potential similar to the hydrogen evolution reaction (HER) [4]. However, in neutral solutions, better results can be achieved with the use of an iron cathode.

For bimetallic electrodes high efficiency and selectivity are achieved with connections of:

- **Palladium with copper** – Pd/Cu – as a cathode, operating with a platinum anode [4].
- **Metal oxides** (e.g. ruthenium, iridium) with titanium and platinum – Ti/IrO₂-Pt, Ti/RuO₂-Pt – as anodes, working with copper-zinc platinum cathode (Cu/Zn) [12].

Another important factor affecting the electrochemical reduction process of nitrates(V) is the presence of other substances in the solution. The research shows, that chlorides (Cl⁻) change the reaction. Without chlorides, the oxidation of ammonia to gaseous nitrogen results from direct oxidation by successive dehydrogenation and from indirect oxidation by the hydroxyl radicals. In the presence of chlorides, oxidation efficiency increases significantly, mainly due to indirect oxidation of ammonium and nitrate(III) ions.
by ClO\(^-\) anions formed on the anode. In a study [12] it was found that the presence of sodium chloride solution can result in a reduction of nitrates(V) to molecular nitrogen with high effectiveness, using the anode made of Ti/IrO\(_2\)-Pt. The detailed results are presented in Table 1.

The advantages of the electrochemical nitrate reduction process are [12]:
- High purification efficiency,
- No sludge production,
- Small space occupied by equipment,
- Relatively low capital costs.

However, the main disadvantage is the necessity to supply electricity in order to carry out the reaction. In addition, wastewater properties and the presence of specific substances can interfere with the process and damage the electrodes, causing the necessity to be replaced.

### 3.3. Chemical reduction

Studies on the chemical reduction of nitrates(V) were initiated in 1964 [5], however the intensive development of research was resumed in the last two decades. This method is considered to be a very beneficial alternative to the current used processes, as it is characterized by high speed, no generation of hazardous indirect products and easy control. The different substances shown in Table 2 may be used for the chemical reduction of nitrates(V). Gaseous hydrogen is the primary reducer, which reacts as follows [3]:

\[
2\text{NO}_3\text{(aq)} + 5 \text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{OH}^-\text{aq} + 4\text{H}_2\text{O}_\text{aq} \quad (1)
\]

Although the process is thermodynamically favourable, its speed can be increased by using metallic catalysts, including a combination of palladium and copper [13]. Nevertheless, the process has not been used on a technical scale, as the significant costs of generating gaseous hydrogen make the technology currently unprofitable.
Another reducing agent is active metals (iron, zinc, aluminium) [3]. For economic reasons, iron is most often used in various forms – nanoparticles and micro-particles of zero-valent iron or metallic iron in the form of shavings. Iron in the form of nanoparticles, due to its largest specific surface area, is characterised by the best efficiency in the reduction process, which can be as high as nearly 95% (Figure 1).

Nowadays it is assumed that electrons necessary for reduction must be directly or indirectly generated from corrosion products – iron(II) ions and hydrogen [14]. Since both the reactions of oxidation of metallic iron to iron(II) ions and reduction of nitrate(V) ions to gaseous nitrogen are thermodynamically favourable, the reduction of nitrate(V) using Fe⁰ is also thermodynamically advantageous.

The effectiveness of the chemical process of nitrate(V) denitrification using metallic iron depends on several factors, including mainly [5, 14, 15]:
- Properly selected dose of metallic iron.
- Forms of dosed metallic iron.
- Mixing speed in a batch system or number of wastewater recirculation stages in the column reaction.
- Reaction time and initial concentration of nitrate in solution.
• Chemical reaction environmental reaction.
• Presence of reaction catalysts.

The exemplary effectiveness of the chemical reaction of nitrate(V) reduction using Fe\(^0\) in the form of iron powder (160–200 mesh) for different reaction conditions (various initial NO\(_3\)–N concentration and pH value) are shown in Figure 2 and Figure 3.

The studies also reveal the possibility of simultaneous application of two reducing agents in the form of metallic iron and organic substance – urea. An essential advantage of the presence of two reducing substances is that, different form of iron can be used, for example: a steel swarf (a waste product from machining process) and moreover, both a steel swarf and urea are cheap and commercially available products [16]. In order to extend the contact time of wastewater with iron and increase the efficiency of the process, it is possible to use a flow system with steel swarf as a bed in the filtration column. In this type of system, the nitrate reduction efficiency was mainly determined by the recirculation rate, initial heating of the wastewater and adjustment of the pH value of the reaction solution. For a two-stage system with six time recirculation, the maximum efficiency of over 92\% was achieved (initial concentration 5156 mg/dm\(^3\), final concentration 400 mg/dm\(^3\)) [16].

4. SUMMARY

The removal of nitrate(V) ions from the wastewater can be made using many different technological methods. For economic reasons, the most cost-effective process is biological denitrification, making it the most widely used and optimised method [1].

The physicochemical methods discussed in this review are highly effective (up to about 100\%) and less sensitive to pollutants (such as toxic substances) that determine the inapplicability of processes based on activated sludge. As a result, they can be applied practically in all process environments. The present trends in water and wastewater technology are directed towards membrane techniques and, in a lesser part, ion exchange, due to the good knowledge and appropriate level of development of these technologies. However, the most important disadvantages are non-selectivity and no degradation of contaminants, but only their concentration in the form of effluent, which must be utilized.

Methods based on the chemical and electrochemical reduction are characterized by a better possibility of modification and thus higher selectivity. Appropriate selection of reagents and process conditions are the main factors that influence the chemical reaction and the final product. As a result, direct reduction of nitrates(V) to neutral molecular nitrogen is possible. The disadvantage of this method is first of all the lack of operating installations on a technical scale and the absence of ready-made solutions offered by manufacturers on the market. Additionally, in comparison to biological methods, both reduction processes (chemical and electrochemical) require higher operating costs related to the need to supply electricity, heat or chemical substances.

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REFERENCES


