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## SOME OF THE PROBLEMS CONCOMITANT WITH THE REMOVAL OF NITROGEN COMPOUNDS IN POLAND

The sources from which nitrogen compounds enter the watercourses are described and the adverse effect of nitrogen forms on water quality is determined. Nitrogen compounds present in the water taken may be removed by physicochemical and biological methods. Particular attention is given to the significance of ammonia nitrogen and nitrates which occur in groundwater. In Poland, use has been made of dry filtration and filtration through pyrolusite beds for ammonia nitrogen removal and ion exchange for the removal of nitrates. Both the processes are in use on a commercial scale, and pyrolusite beds have found wide acceptance in groundwater treatment.

### 1. INTRODUCTION

The increase in nitrogen compound concentrations has become a recurrent pattern both in surface water and groundwater. The presence of these compounds in natural water is attributable not only to the geochemical changes that occur in the aquifer, but also to some anthropogenic factors [1], particularly in regions of advanced agricultural production and livestock farming. Nitrogen compounds, which originate primarily from the use of fertilizers (readily soluble inorganic nitrogen salts) and pesticides, penetrate into water through different pathways such as surface runoffs (from overfertilized fields and even from short-term storage of fertilizers directly in the fields), landfill leachates, or municipal and industrial wastewaters discharged into the recipient [2].

The nitrogen compounds that are present in natural water generally fall into two classes: those of organic nitrogen and those of inorganic nitrogen. Inorganic nitrogen is the sum of ammonia nitrogen, nitrites and nitrates; organic nitrogen undergoes ammonification, which accounts for its transformation to ammonia nitrogen, both under

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aerobic and anaerobic conditions. Thus, the methods of removing nitrogen compounds that are in use apply principally to the removal of inorganic nitrogen. What is more, nitrites are transition compounds, which undergo either reduction to ammonium nitrogen or oxidation to nitrates. This is why of the inorganic nitrogen forms the following two, ammonia nitrogen and nitrates, are taken into account when considering the removal methods to be used.

The permissible content of nitrogen compounds in water for human consumption has been specified in the Directive of the Health Minister of 29 March 2007 (and of 20 April 2010). Hence, the permissible ammonium ion concentration should not exceed  $0.5 \text{ g NH}_4^+/\text{m}^3$ , whereas those of nitrates and nitrites must not be higher than  $50 \text{ g NO}_3^-/\text{m}^3$  and  $0.5 \text{ g NO}_2^-/\text{m}^3$ , respectively. Although these values are in conformity with the standards established by the EU legislation, it is essential to add that the regulations of the EU, as well as those of the WHO, make a distinction between permissible and recommended concentrations. Yet, there is a divergence as to the ammonium ion concentration in water: the recommended concentration was set at  $0.05 \text{ g}/\text{m}^3$ , and the maximum permissible concentration at  $0.5 \text{ g}/\text{m}^3$ . Regulations of an earlier date imposed a limit also on the concentration of organic nitrogen in water, which was  $1 \text{ g N}/\text{m}^3$ .

The limit for ammonium ion concentration in water results primarily from the necessity of reducing the oxidant doses commonly used for water disinfection [3]; the limit for nitrate concentration in water is attributable to their harmful influence on human organisms. Excessive intake of nitrates is known to cause cyanosis and gastrointestinal disorder. Moreover, nitrates are regarded as precursors of carcinogenesis. It is essential to note, however that water is not the only source of nitrates in humans; some part of them comes from food. The limit for the concentration of nitrites in water should be attributed to the probability that during removal of nitrogen compounds (ammonia nitrogen, nitrates) nitrites will form as an undesired intermediate [4].

## 2. REMOVAL OF NITROGEN COMPOUNDS

In order to remove nitrogen compounds, use is made of biological and physicochemical methods [5–9]. Biological methods include nitrification and denitrification. During nitrification, ammonia nitrogen solely transforms to nitrates *via* nitrites. In some instances, the application of this process may suffice, which, however, it depends on the balance of the nitrogen compounds. Physicochemical methods include the following:

- desorption during aeration on stripping columns; the process requires that the ammonium ion should convert into gaseous ammonia, and this occurs under alkaline conditions ( $\text{pH} > 10.0$ ),

- oxidation with chlorine or ozone, or *via* filtration through a pyrolusite bed,
- selective ion exchange on clinoptylolite (ammonia nitrogen),
- ion exchange on selective anion exchange resins (nitrates).

Denitrification, a biological process used for the removal of nitrates, consists in the biochemical reduction of nitrates to gaseous nitrogen [10, 11], with nitrites as an unwanted by-product when the process is unbalanced. According to the type of denitrification applied, electron donors are organic substances (heterotrophic denitrification) and reduced sulfur compounds or gaseous hydrogen (autotrophic denitrification). In water treatment, preference is given to heterotrophic denitrification, where the content of organic substances is made up with acetic acid. In both heterotrophic and autotrophic denitrification processes oxygen – as an electron acceptor – is a natural competitor for nitrates. This is why, in contrast to the nitrification process, denitrification requires that anaerobic or oxygen-deficient conditions should be provided, and that the carbon source added should be aided by the addition of nutrients, particularly phosphorus compounds.

The application of membrane techniques to the removal of both ammonium ion and nitrates is limited by the concurrent demineralization of the water being treated. The inclusion of membrane processes into hybrid systems enabling the desired degree of mineralization to be maintained will contribute to a wider use of this method in removing nitrogen compounds. In Poland, use has been made of the following methods so far [7, 8, 12, 13]:

- dry filtration (nitrification) and filtration through pyrolusite beds (oxidation) for ammonia nitrogen removal,
- ion exchange (in household installations) for the removal of nitrates.

Both the processes are in use on a commercial scale, and pyrolusite beds have found wide acceptance in groundwater treatment.

## 2.1. DRY FILTRATION

Dry filtration involving sand beds has been applied with success in waterworks. In our research onto dry sand filtration, an activated carbon bed was used and its performance was compared with the performance of the sand bed. The process parameters were as follows: sand filter of a grain size  $d_{10} = 0.73$  mm;  $d_{60}/d_{10} = 1.6$ ; activated carbon bed made of Norit type carbon with a grain size ranging from 1 to 3 mm; depth of the filter layer in both the beds amounting to 0.5 m; oxygen supply to water by diffusion from air; during spray irrigation of water oxygen supply above the bed; the height of spray irrigation amounting to 1.0 m for both bed types.

The water subjected to dry filtration showed the ammonia nitrogen concentration approaching  $3 \text{ g N/m}^3$ , an iron concentration of  $1.7\text{--}4.7 \text{ g Fe/m}^3$ , and the manganese

concentration of 0.6 to 0.7 g Mn/m<sup>3</sup>. The removal efficiencies achieved are summarized in Table 1.

Table 1

Removal of pollutants in the course of dry filtration

Parameter	Removal efficiency, %					
	Sand bed			Activated carbon bed		
	1 m/h	2 m/h	3.5 m/h	1 m/h	2 m/h	3.5 m/h
NH <sub>4</sub> <sup>+</sup>	32	8–20	18	90–100	60–73	50–53
Fe	99	96	92	100	92–97	90
Mn	13	12	5–10	38	30–40	20–35

The data in Table 1 make it clear that in comparison with sand filtration, the reduction in ammonia nitrogen and manganese concentrations obtained during dry filtration in an active carbon bed was remarkably higher, and that the efficiency of iron removal was comparable. The effluents from both dry filtration and sand filtration processes contained nitrites whose concentrations ranged between 0.04 and 0.06 g N/m<sup>3</sup>.

The use of aeration on stripping columns for the purpose of oxygen supply abates the quantity of the pollutants removed. The amount of free oxygen required for the oxidation of 1 g N *via* dry filtration (3.56 g O<sub>2</sub>/g N) is lower than the amount required for oxidizing 1 g N by conventional nitrification (4.57 g O<sub>2</sub>/g N) which is attributable to the possibility of utilizing the oxygen that is present in the chemical compounds. However, the demand for free oxygen may increase, when water being treated contains other oxygen-consuming pollutants. The presence of iron and manganese, for example, increases oxygen demand by 0.14 g O<sub>2</sub>/g Fe and 0.29 g O<sub>2</sub>/g Mn, respectively. For this reason, when water to be treated by dry filtration includes ammonia nitrogen, it is recommended that the content of oxygen-consuming pollutants should be largely reduced. In the case of groundwater, it is relatively easy to remove iron compounds (by aeration and sand filtration) but it has to be expected that manganese will persist in the water as long as ammonia nitrogen is present there. Thus, the removal of ammonia nitrogen and manganese during dry filtration will continue to raise problems. The reduction in the concentrations of iron compounds to 1 g Fe/m<sup>3</sup> further upgraded the removal of ammonia nitrogen and manganese.

Oxygenation *via* spray irrigation is concomitant with a reduction of oxygen concentration in water being treated, which has to be attributed to the solubility of oxygen at given temperature. When use is made of mechanical co- or countercurrent oxygenation, the content of oxygen is made up while its depletion in the water proceeds. The application of filter beds of the depth of 0.5 m and the spray irrigation height of 1.0 m required that filtration velocity be limited to 2 m/h. Higher filtration velocities call for filter beds of the depth greater than 0.5 m.

The higher efficiencies of ammonia nitrogen removal obtained with the active carbon bed are attributable to the carbon structure, which enables the grain surface to be colonized by nitrifying bacteria not only in the external but also in the internal pores. That is why the application of active carbon filters did not deteriorate the efficiency of treatment immediately after the backwashing process. These days, dry filters with active carbon beds are being successfully operated in the water treatment plant of the strip mine Konin.

## 2.2. FILTRATION IN THE PYROLUSITE BED

The mechanism governing ammonia nitrogen removal by filtration in a pyrolusite bed entails oxidation of ammonia nitrogen to nitrates. The oxidation proceeds *via* a chemical route with  $\text{MnO}_2$  as an oxidant and *via* a biological route with nitrification. The mechanism of nitrification is still far from being fully understood, since not all of the nitrification conditions are fulfilled in this case. What leaves room for doubt is the oxygen balance. The mechanism of chemical oxidation seems to dominate, although a substantial utilization of  $\text{MnO}_2$  has not been observed so far. Regardless of the mechanism considered above, the fact is that owing to the treatment efficiency achieved with this method of filtration, pyrolusite beds have been used with success in the past two decades for groundwater treatment even if ammonia nitrogen was absent.

Water subjected to filtration contained ammonia nitrogen, iron and manganese compounds at the concentrations of 1–5 g N/m<sup>3</sup>, 0.2–0.5 g Fe/m<sup>3</sup>, and 0.04–0.1 g Mn/m<sup>3</sup>, respectively. The process was conducted using a pyrolusite bed 0.5 m deep and of the grain size from 0.15 to 0.20 mm. Filtration velocity ranged between 2 and 15 m/h. The results are shown in Table 2.

Table 2

Removal efficiency of ammonia nitrogen  
in the pyrolusite bed [%]

Initial $\text{NH}_4^+$ concentration [g N/m <sup>3</sup> ]	Filtration velocity [m/h]			
	2	5	10	15
1.0	8	14	23	32
2.5	10	18	28	45
5.0	2	12	15	22

These data make it clear that for the pyrolusite bed of the depth of 0.5 m removal of ammonia nitrogen was the highest when its initial concentration was 2.5 g N/m<sup>3</sup>, and when filtration velocity amounted to 15 m/h. With such water parameters however, it is necessary to increase the bed depth to 1.5 m in order to achieve the treatment

effect desired. And it is the influence of the filtration velocity on the efficiency of ammonia nitrogen removal that raises doubts about the mechanism involved. The increase in filtration velocity is generally blamed for the deterioration of water quality but in our case an upgrade in water quality was observed. Neither our own observations nor those made by other investigators have led to an unequivocal definition of the mechanism governing the process. Nevertheless, pyrolusite filters are being implemented in water treatment plants not only owing to the satisfying efficiency of iron and manganese removal or the reduction in ammonia nitrogen concentration (which ranges between 1 and 2 g N/m<sup>3</sup>), but also to the possibility of applying higher filtration velocities, which makes it possible to reduce the number of filters that are in use.

### 2.3. ION EXCHANGE

The removal of nitrates using selective anion exchange resins proceeded according to the principles of ion exchange. Tap water to be tested was enriched with nitrates ranging in concentration from 15 to 30 g N/m<sup>3</sup>, which were removed using the anion exchange resin IONAC SR-7 with the efficiency of approximately 99%. The breakthrough point occurred at the bed volume ratio higher than 400 when the concentration of nitrates totalled 15 g N/m<sup>3</sup>, and at the bed volume ratio higher than 200, when the concentration of nitrates amounted to 30 g N/m<sup>3</sup>. The twofold increase in the concentration of nitrates caused the bed volume ratio to decrease twofold, without changing the quantity of the pollutants retained in the bed.

The effect of filtration velocity (which ranged between 10 and 25 m/h) on the efficiency of nitrate removal was negligibly small. The calculated exchange capacity of the ion exchange resin varied from 0.3 to 0.5 val/dm<sup>3</sup> and was lower than the one included in the manufacturer's specification, which is 0.65 val/dm<sup>3</sup>, and depended on the initial concentration of nitrates. Seemingly, this difference is to be attributed to the fact that exchange capacity was calculated for nitrates alone, while other anions were neglected. Similar observations were reported for the selective anion exchange resin IMAC HP-555.

It is essential to note that a radical sulfates breakthrough was observed when the value of the bed volume ratio was half the value of nitrates breakthrough. After the exchange capacity with respect to nitrates had been exhausted, sulfates were removed with no breakthrough of nitrates. This finding is of particular significance, as this means that selective anion exchange resins can be used to remove nitrates from water in the presence of sulfates.

### 3. CONCLUSIONS

- Presence of nitrogen compounds in water compels, on the one hand, their removal and, on the other hand, reduction of the pollution source. Any elimination of the

pollution sources will make it possible to abandon some of the sophisticated technologies that are used for the removal of nitrogen compounds.

- The methods of removing nitrogen include ammonia nitrogen and nitrate nitrogen removal. In the water treatment plants operated in Poland, the problem of removing nitrogen compounds is primarily focused on the elimination of ammonia nitrogen.

- Ammonia nitrogen is generally removed by filtration in pyrolusite beds. Nitrification in dry filters or BAFs is well understood in technological terms and therefore ready for implementation.

- Understanding of the operating parameters of denitrification is rather poor, and that is why it has failed to find acceptance in Poland for the time being.

- Implementation of a well known ion exchange method requires that the retention tanks equalizing the physicochemical composition of water in the technological train should be modernized. An unsolved problem that has taken on a sense of significance is the neutralization of wastewater and post-regeneration sludge.

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