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AMMONIA NITROGEN REMOVAL ON BATTERY-MANGANESE FILTERS

Investigations of the efficiency of ammonia nitrogen removal by filtration through battery-manganese beds showed that the mechanism of removal was still far from being well understood. By analogy with the phenomena occurring in sand filters when covered with manganese oxides it can be anticipated that battery-manganese filters provide favourable conditions for the chemical oxidation of ammonia nitrogen.

1. INTRODUCTION

Ammonia nitrogen not only is a serious hindrance to groundwater treatment, but also requires removal at the concentrations higher than 0.5 g N/m^3 , as postulated by relevant sanitary regulations in Poland. While ammonia nitrogen concentrations measured in groundwaters generally approach 1.0 g N/m^3 , there are certain regions where this value is dramatically exceeded (amounting to approximately 2.0 g N/m^3 in the west Poland and ranging from 6 to 8 g N/m^3 in some groundwater intakes as at the north-west coast) [1], [2].

Nitrogen compounds, which are found in groundwaters, may come from a variety of sources (municipal sewage, industrial effluents, landfill leachates, farming operations, digestion tanks, surface runoff) [3]. The presence of ammonia nitrogen in shallow groundwaters is an indicator of their pollution which does not manifest itself in any other parameter. It should be noted that infiltration water or Quaternary groundwaters are particularly prone to nitrogen pollutants. In infiltration water, there is an increment in ammonia nitrogen concentration at winter temperatures when nitrification process has discontinued. In deep groundwaters, ammonia nitrogen may have its geological background, so the presence of this species not always is an indicator of pollution. In spite of this, excess nitrogen must be removed.

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Water pollution due to nitrogen compounds is also concomitant with some biological processes occurring in the environment. Thus, the ammonification of urea produces nitrogen which, following oxidation by nitrifying bacteria, becomes a nitrate nitrogen source. Under anaerobic conditions, as a result of biological reduction (denitrification), molecular nitrogen and ammonia nitrogen are formed at a final stage of the process. Groundwater ammonia nitrogen may also be formed as a product of nitrate and nitrite reduction in the presence of pyrites, hydrogen sulphide, humic substances or other reducing agents.

To remove ammonia nitrogen from water solutions use is made of physical, biological or chemical methods. Physical methods include desorption and ion exchange. However, desorption fails to be effective when ammonia nitrogen concentrations (temperature and pH being two major limiting factors) are low. Ion exchange involves clinoptylolite which shows a better ion-exchange selectivity with respect to ammonia nitrogen than with respect to other cations. A serious drawback of this method is the poor ion-exchange capacity and the insufficient availability of clinoptylolites. Membrane processes fail to be selective with respect to cation removal from water solutions, and this leads to demineralization.

One of the available biological methods is nitrification in which ammonia nitrogen is converted to nitrate nitrogen. However, the efficiency of nitrification depends strongly on the concentration of nitrate nitrogen in the water to be treated. A satisfying concept involves dry filtration through sand or carbon beds [4], or the French technology known under the name of PICABIOL [5], [9].

The chemical methods, by which ammonia nitrogen is oxidized, include chlorination involving chlorine (predominantly) or ozone. Considering the by-products that are formed in the course of the process, chlorination is not recommendable. As far as ozonation is concerned, the problem of its utility still remains open. Consideration has been given to the ozonation process that runs more effectively under alkaline conditions.

Ammonia nitrogen removal by filtration through a pyrolusite bed has attracted the attention of some investigators, even though the mechanism of removal is still far from being well understood. It may be anticipated that the process of chemical oxidation runs in the presence of MnO_2 . Some authors [6], [7] believe that ammonia nitrogen removal on a pyrolusite bed proceeds *via* nitrification.

This short review of the methods for ammonia nitrogen removal encourages us to further investigation of the problem.

2. METHODS

The experiments were run on a laboratory scale with tap water samples enriched with ammonia nitrogen by addition of ammonium sulphate. The filtration process

involved a battery-manganese bed which had a depth of 0.5 m and a grain size ranging from 0.15 to 0.20 mm. Filtration was carried out at a constant rate (2 to 15 m/h) in 6-hour cycles, irrespective of water quality and head loss increment. Ammonia nitrogen concentrations in raw water samples amounted to 1.0, 2.5 and 5.0 g N/m³. The remaining parameters, i.e., colour, pH, total alkalinity, total hardness, total iron and manganese, ranged from 5 to 15 g Pt/m³, from 7.2 to 7.7, about 100 g CaCO₃/m³, about 270 g CaCO₃/m³, from 0.2 to 0.5 g Fe/m³, and from 0.04 to 0.10 g Mn/m³, respectively [8], [10].

3. RESULTS

The filtration effects obtained with the battery-manganese bed are plotted in figures 1–4. No technological effects were observed at the beginning of each cycle (and after each rinsing procedure) regardless of the filtration rate applied. The duration of the ripening process depended primarily on the filtration rate. While the initial concentration of ammonia nitrogen contributed slightly to the period of the filtration run which showed no technological effects, this contribution became negligible when filtration rate increased.

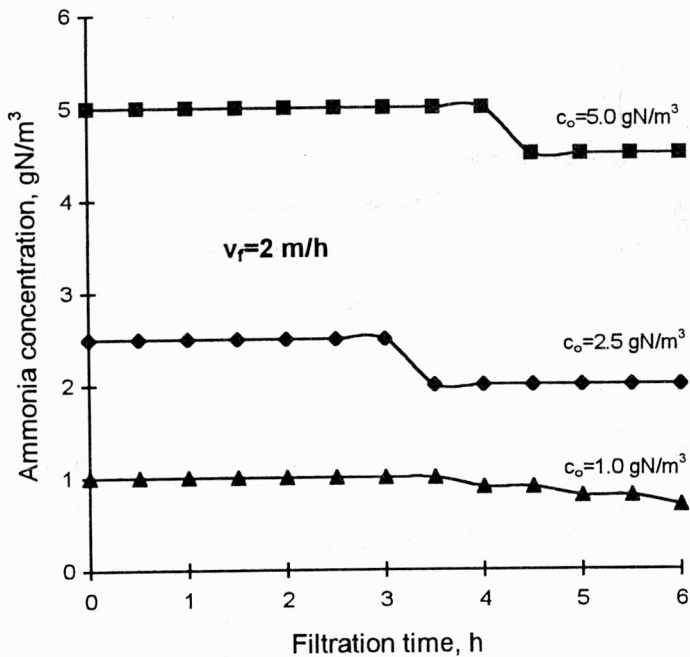


Fig. 1. Ammonia nitrogen removal on a battery-manganese bed ($v_f = 2$ m/h)

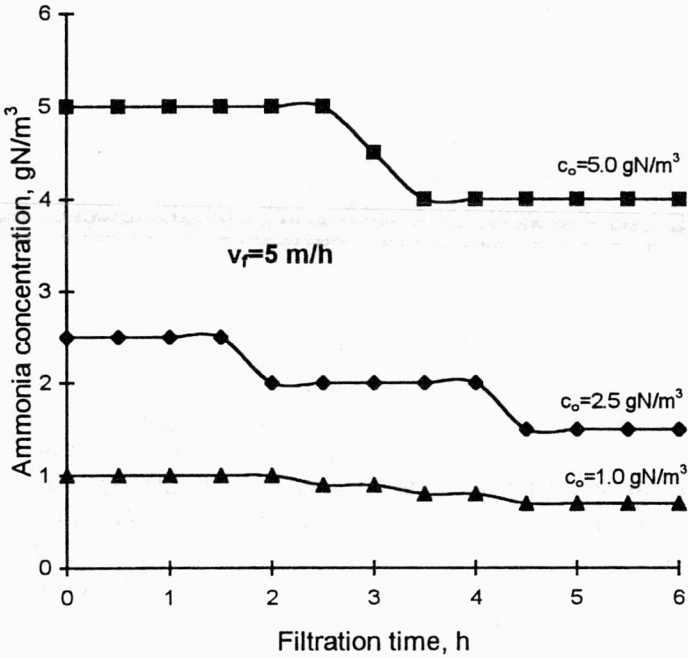


Fig. 2. Ammonia nitrogen removal on a battery-manganese bed ($v_f = 5$ m/h)

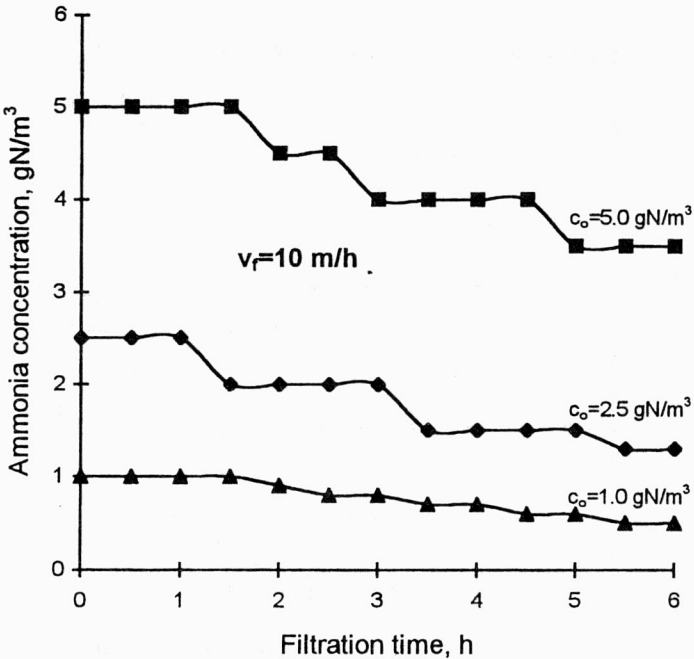


Fig. 3. Ammonia nitrogen removal on a battery-manganese bed ($v_f = 10$ m/h)

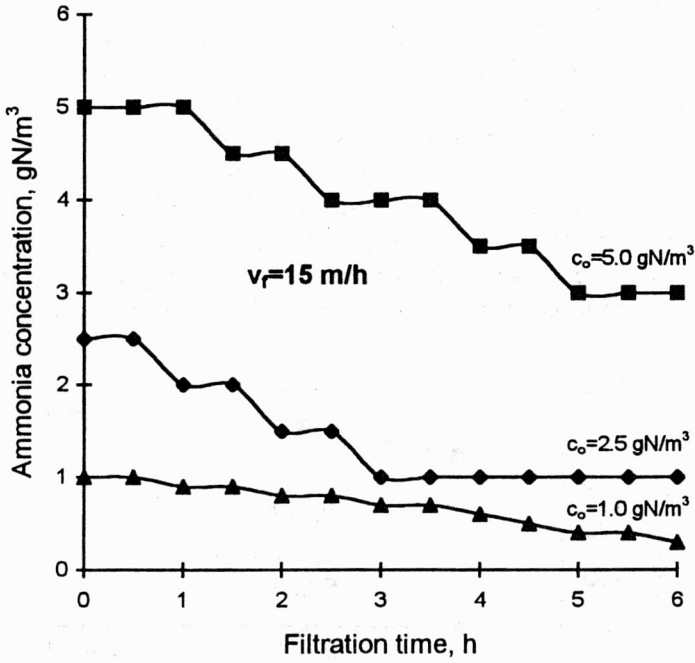


Fig. 4. Ammonia nitrogen removal on a battery-manganese bed ($v_f = 15 \text{ m/h}$)

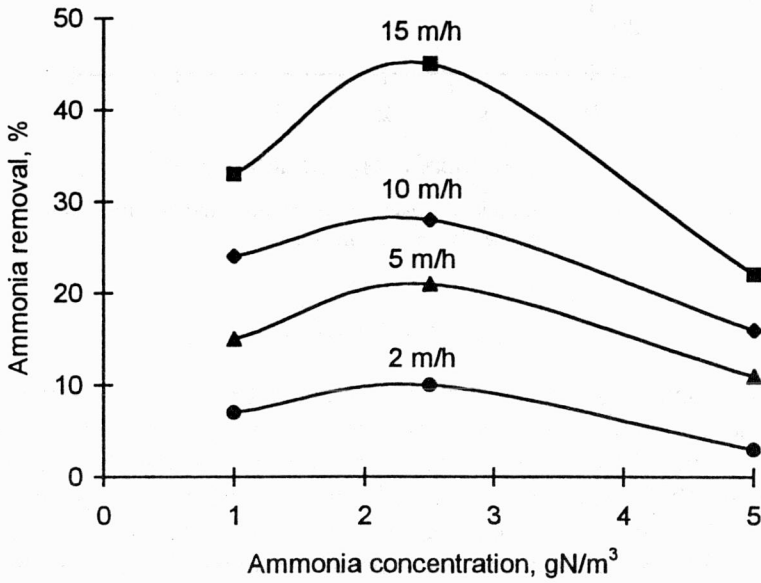


Fig. 5. Effect of ammonia nitrogen concentration and filtration rate on average removal efficiency in the filter run

The average efficiency of ammonia nitrogen removal obtained in the 6-hour cycle is shown in figure 5. According to the plots presented, there was a strong relationship between removal efficiency, initial ammonia nitrogen concentration and filtration rate. Thus, removal efficiency increased with the increasing filtration rate and decreasing initial concentration. The highest removal effect was achieved when the initial concentration of ammonia nitrogen amounted to 2.5 g N/m^3 . The small increment in head loss after 6 hours of filtration (figure 6) indicates that the actual filtration run will be much longer. And this means that we can also expect a higher efficiency of ammonia nitrogen removal, because the proportion of the filter run period with no technological effects will be smaller in the whole extended cycle.

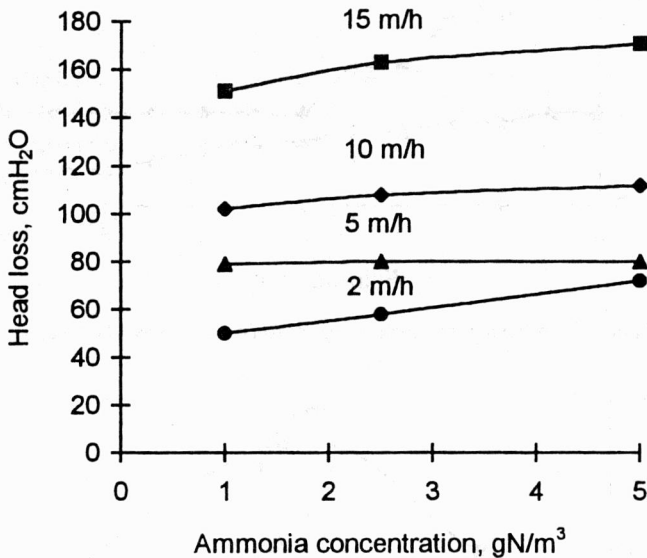


Fig. 6. Effect of ammonia nitrogen concentration and filtration rate on heads loss in the filter run

4. DISCUSSION

This study confirmed what had been commonly known so far – the mechanism governing the removal of ammonia nitrogen in the course of filtration through a battery-manganese bed is still far from being well understood. Taking into account the phenomena that occur in a sand bed covered with manganese oxides (i.e., in a rippened bed), it can be anticipated that battery-manganese filter beds provide favourable conditions for chemical oxidation of ammonia nitrogen. In this study, no increment of nitrite nitrogen or nitrate nitrogen concentrations was observed [8], which indicates that no chemical oxidation occurred in the course of the filtration process. Those who argue in support of biological oxidation (nitrification on the filter

bed) [7] claim to have identified nitrifying bacteria growth on the filter bed. Yet, the oxygen balance makes them uncertain about the course of the nitrification process. In our opinion, biological oxidation cannot be the most important phenomenon involved in the removal of ammonia nitrogen, the more so as better treatment effects have been obtained by increasing the filtration rate.

The study indicated that the mechanism governing ammonia nitrogen removal on a battery-manganese bed was quite different from that on sand bed. However, it can be concluded that (1) this mechanism is highly sophisticated, and (2) flocculation might have influenced the final effect of ammonia nitrogen removal.

In conclusion, it can be stated that the efficiency of ammonia nitrogen removal on a battery-manganese bed depended on the initial concentration of this species and on the filtration rate; the increase of the filtration rate in the investigated range improved the removal effect. The removal efficiency is much better than that on sand filters.

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USUWANIE AMONIAKU NA ZŁOŻACH PIROLUZYTOWYCH

Wykazano, że efektywność usuwania azotu amonowego podczas filtracji wody przez złoża piroluzytowe zależy od jego początkowego stężenia i prędkości filtracji. W badanym zakresie prędkości filtracji (2–15 m/h) wzrost prędkości wpływał na zwiększenie stopnia usuwania azotu amonowego. Stwierdzono, że mechanizm usuwania azotu amonowego na złożach piroluzytowych nie jest jednoznaczny, gdyż nie można go wyjaśnić chemicznym ani też biologicznym utlenianiem azotu.

