

Removal of nitrates and organic compounds from aqueous solutions by zero valent (ZVI) iron reduction coupled with coagulation/precipitation process

Ewa Wiśniowska, Maria Włodarczyk-Makuła*

Częstochowa University of Technology, Poland

*Corresponding author's e-mail: ewisniowska@is.pcz.czyst.pl

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Abstract: The removal of nitrates from aqueous solutions is cumbersome because of their high solubility in water. The use of zero-valent iron (ZVI) for the reduction of nitrates is the chemical process and it is an alternative method to the biological ones. The aim of the present study was to evaluate the effectiveness of nitrates removal from water solution by using the ZVI process. The process was coupled with the removal of COD, phosphates and turbidity by using by-products of nitrates reduction. Batch tests were performed to evaluate the effectiveness of ZVI in the removal of nitrates from aqueous solutions. The effectiveness of nitrates removal was analyzed after 5, 10, 20, 30 and 60 min. and compared to the initial concentration of pollutants. Simultaneously analysis of ammonium nitrogen and nitrites was controlled to identify products of nitrates reduction under various pH. The removal of COD, phosphates and turbidity was also performed in batch tests. The effectiveness of the removal by using three types of chemicals was compared – PIX, FeSO_4 , and waste $\text{Fe}^{2+}/\text{Fe}^{3+}$ from the ZVI process. The results obtained in the study indicate that ZVI can be effectively used in the treatment of water polluted with nitrates and the by-products of the process could be further applied in the removal of COD, phosphates and turbidity. Based on the results the method should be advised as a promising alternative to the technologies used nowadays under technical scale as a technology that fits with a circular economy.

Introduction

Nitrates are increasingly common pollutants in both underground and surface water treated for drinking purposes. Pollution of water with nitrates is mainly caused by use of nitrogen fertilizers (both chemical and natural) in the agriculture (Della Rocca et al. 2007). Because the presence of nitrates in drinking water can pose harmful health effects, such as methemoglobinemia or formation of nitrosamines, WHO and US EPA set a nitrate standard of $50 \text{ mgNO}_3^-/\text{L}$ (Mirvish 1975).

The removal of nitrates in water treatment plants is cumbersome because of their high solubility in water. Under a technical scale the most frequently used methods are the biological ones (heterotrophic or autotrophic denitrification) (Zhou et al. 2011, Zhao et al. 2011). These processes are environmentally friendly because they do not generate toxic by-products. The most frequently used biological systems are the attached growth ones – such as fluidized bed reactors, packed bed reactors or biofilters (Lichtwardt and Hart 2010). In the case of heterotrophic processes an external source of organic carbon is necessary, such as, e.g., methanol, ethanol

or acetic acid, which generates higher costs (Rogalla et al. 1990). Autotrophic bacteria do not need this kind of support, however, the growth rate of these kinds of microorganisms is lower, which could result in a lower rate of nitrates removal compared to heterotrophic processes (Gross et al. 1986).

Also some chemical and physicochemical processes such as ion exchange, reverse osmosis, electro dialysis and adsorption can be used (Dahab 1991). Costs constitute a barrier that makes chemical methods less often used in water technology. Wastes generated during chemical and physicochemical processes pose the problem, e.g. waste brine generation after membrane treatment. Adsorption also generates waste material – waste adsorbent. This generates additional costs for waste material utilization. Generally, the processes mentioned above also show low selectivity of pollutants' removal (Della Rocca 2007, van der Hoek and Klapwijk 1987, Bhatnagar and Sillanpaa 2011).

Use of zero-valent iron (ZVI) for the removal of nitrates as an alternative method to the ones mentioned previously, has been tested in recent years (Park et al. 2008, Fu et al. 2014, Liu et al. 2019, Sun et al. 2016, Makota et al. 2017, Liu et al. 2018, Liu P. 2016). However, most studies have been limited to the

laboratory scale. Zero-valent iron is cheap, easy to produce, easy to use, and requires little maintenance. Moreover, ZVI is non-toxic (Zhu and Getting 2012).

ZVI can be used in various forms including granular (with particle diameter larger than 100 nm), nano (having particle sizes of 1 to 100 nm), bimetallic and combined with other amendments. Bimetallic ZVI contains amendment of other zerovalent metal, e.g. nickel or platinum (O'Carroll et al. 2013, Fu et al. 2014, Tratnyek et al. 2014). ZVI reduction of nitrates can be performed in filter beds, batch reactors or reactive barriers (Liu and Wang 2019, O'Carroll et al. 2013, Hu et al. 2019).

Process of chemical removal of nitrates, or more generally nitrogen, from aqueous solutions with iron, involves various oxidation-reduction reactions which requires iron of different valences. Fe^0 and Fe^{2+} reduce NO_3^- and NO_2^- . The products of the process include N_2 , N_2O , NH_4^+ and NO . During the process ferrates could be generated and they can gradually oxidize NO to NO_3^- (Liu et al. 2018). Nitrogen removal from aqueous solutions is connected with electron transfer. In most oxidation/reduction reactions which take place during nitrogen removal iron acts as electron donor, however, it also, under some conditions, could act as electron acceptor (Liu et al. 2018, Ruangchainikom et al. 2006).

In the reduction reaction of nitrates by Fe^0 almost all nitrates are converted to ammonia rather than gaseous N_2 (Liu et al. 2018). According to the literature data, the reduction of nitrates in water by ZVI occurs better under acidic conditions ($\text{pH} < 4$), however, it is possible in pH range 4–7. Ammonia which is generated during the process requires further treatment (Park et al. 2008, Zhu and Getting 2012). It means that the process for individual waters may need the second stage. Summary of nitrate reduction processes by ZVI is presented in Fig. 1.

Rate end efficiency of the method is also connected with the surface area of Fe^0 particles; nanoscale Fe^0 with higher specific surface area is more reactive than larger ZVI particles (Park et al. 2008). The process can be slowed down by the formation of a ferrous deposit (green rust) on the surface of the iron metal. This deactivates oxidation of iron (Zhu and Getting 2012). ZVI reduction of nitrates is also inhibited by specific organic contaminants such as humic acid or calcium ions, which are common pollutants in water prepared for drinking purposes

(Liao et al. 2003). Simultaneously with nitrates reduction the removal of some specific toxic substances occurs. For instance it was stated that arsenic can be in 99% removed from groundwater in the presence of ZVI. The removal capacity of arsenic was up to 2.5 mg per g ZVI (Abedin et al. 2010, Liu and Wang 2019, O'Carroll et al. 2013). Also chlorinated organic compounds, dyes and phenols could be removed by using this process (Fu et al. 2014; Chen et al. 2013). This raises the question of if there is any danger of toxicity of residuals from this process when they are further treated as, e.g. coagulation agents for water or wastewater treatment.

By-products of nitrates' reduction from water by using ZVI should not be toxic because concentrations of toxic elements in water are usually low. The nitrates are most frequently found in groundwater.

Up to now ZVI was successfully used for the reduction of nitrates from drinking water in many studies (Fu et al. 2014, Sun et al. 2016). The first household filter filled with metallic iron was patented in 1856. Similar technology was used between 1881 and 1885 for the water supply of the city of Antwerp (Belgium) (Mwakabona et al. 2017, Hu et al. 2019). In the history of water treatment Fe^0 systems were independently rediscovered several times. At present there is also observed an increasing interest in these types of systems (Hu et al. 2019).

Until now far less attention has been paid to the final by-products of iron oxidation, which can be both Fe^{2+} or Fe^{3+} compounds depending on the reaction balance and environmental conditions. However, it can be possible to use the final products of nitrates reduction for e.g. coagulation. Mainly research data concerning direct use of ZVI for coagulation, to replace ferric or ferrous salts, are presented in the literature, but no by-products of its oxidation. Lai et al. (Lai et al. 2007) compared the application of ZVI with classical coagulation for coke plant wastewater treatment. They have stated that ZVI process was more effective than classical coagulation, e.g. in the case of COD removal efficiency. The maximal COD removal efficiency from coke plant wastewater by coagulation was 27.5 to 31.8%. COD removal ZVI process was higher and reached 43.6%. Meanwhile both Fe^{2+} and Fe^{3+} can be used for the removal of organic compounds, phosphates and turbidity, but research works concerning use of ferrous and ferric salts present in waste products of ZVI oxidation during nitrates

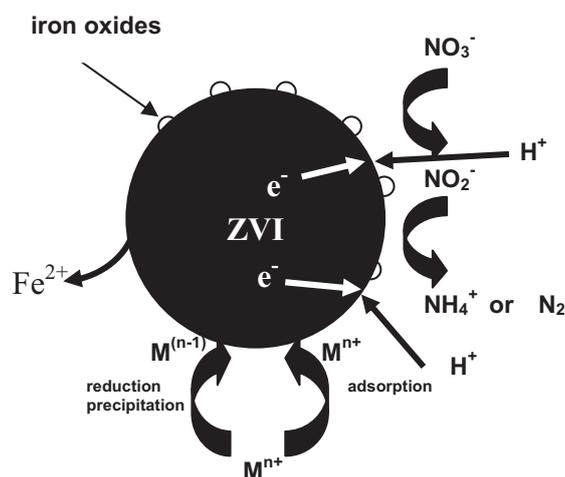


Fig. 1. Mechanism of ZVI based reduction of nitrates (Liu and Wang 2019, Fu et al. 2014)

removal are rarely conducted. Use of them and evaluation of the results are innovative and they are of high interest taking into consideration circular economy.

The aim of the present study was to evaluate the possibilities of use of by-products of nitrates reduction in aqueous solution by using the ZVI for removal turbidity, COD and phosphates. The effectiveness of these products' removal was evaluated.

Materials and methods

Laboratory installation for ZVI reduction of nitrates and removal of organic compounds by waste Fe^{2+}/Fe^{3+}

Batch tests were performed to evaluate the effectiveness of ZVI reduction of nitrates and use waste products of the process for coagulation. The schemes of laboratory installations are presented in Fig. 2. Laboratory installation for ZVI reduction of nitrates consisted of six simultaneously working batch reactors. The volume of each reactor was equal to 2 L (working volume 1 L). The reactors were continuously shaken on a mechanical shaker with horizontal motion (at. 200 rpm). Waste sludge from the ZVI process was collected periodically after the decantation of the treated water solution. The sludge after the ZVI process (containing Fe^{2+}/Fe^{3+}) was then air dried and in the form of waste material used as a coagulation agent.

Coagulation test was performed in laboratory installation in beakers of 2 L volume. They were filled with 1 L of water. Water solutions were mixed by mechanical mixers. After coagulation/ flocculation sedimentation occurred for 2 hour.

Experimental protocol

1 L of solution was used during the tests. For ZVI reduction of nitrates the solution of sodium nitrate was used of initial concentration 100 mg/L. The pH of nitrate solution was adjusted from pH = 2 to pH =7, to evaluate the effect of this

parameter on nitrates removal effectiveness. The effectiveness of nitrates' removal was analyzed after 5, 10, 20, 30 and 60 min. and compared to the initial concentration of pollutants. Simultaneously analysis of ammonium nitrogen and nitrites was controlled to identify products of nitrates reduction under various pH. The ZVI dose used for nitrates reduction was 400 mg/L (it was chosen by previous experiments). ZVI used in the study was commercial powder (granulation < 0.15 mm) obtained from the fireworks factory (B&G, Poland).

To evaluate the effectiveness of the coagulation process three types of a coagulating agents were used: PIX 113, $FeSO_4$ and waste Fe^{2+}/Fe^{3+} from the ZVI process. The doses of all reagents were in the range of 0.1–1.0 g/L. PIX 113 was a commercial agent. $FeSO_4$ was dosed in the powder form of $FeSO_4 \cdot 7H_2O$. Waste Fe^{2+}/Fe^{3+} was added as an air dried powder. Before use in the experiment the waste Fe^{2+}/Fe^{3+} was dewatered in laboratory centrifuge and after that the slurry was air-dried. A final product of moisture less than 1% was obtained. No detailed research on the composition of the waste product has been done. The slurry after nitrate reduction in neutral conditions was air-dried and used for further experiments.

After introducing the coagulating agent 5 min. of rapid mixing was performed, followed by 20 min. of slow mixing. After reaction phase 120 min. sedimentation phase took place. The effectiveness of the coagulation process was measured based on three parameters of concentration changes: COD (chemical oxygen demand), turbidity and phosphates. The pH changes were controlled if necessary. The initial concentration of water solution used for coagulation tests was as follows: COD 260 mg/L, phosphates 20 mg/L; turbidity 30.6 NTU. The pH was equal to 7.2. This water solution imitated wastewaters. This was based on the assumption that waste material from the ZVI process will be used for municipal wastewater treatment/ coagulation. The coagulation process was supported by a flocculating agent (Praestol) at a dose of 10 mg/L.

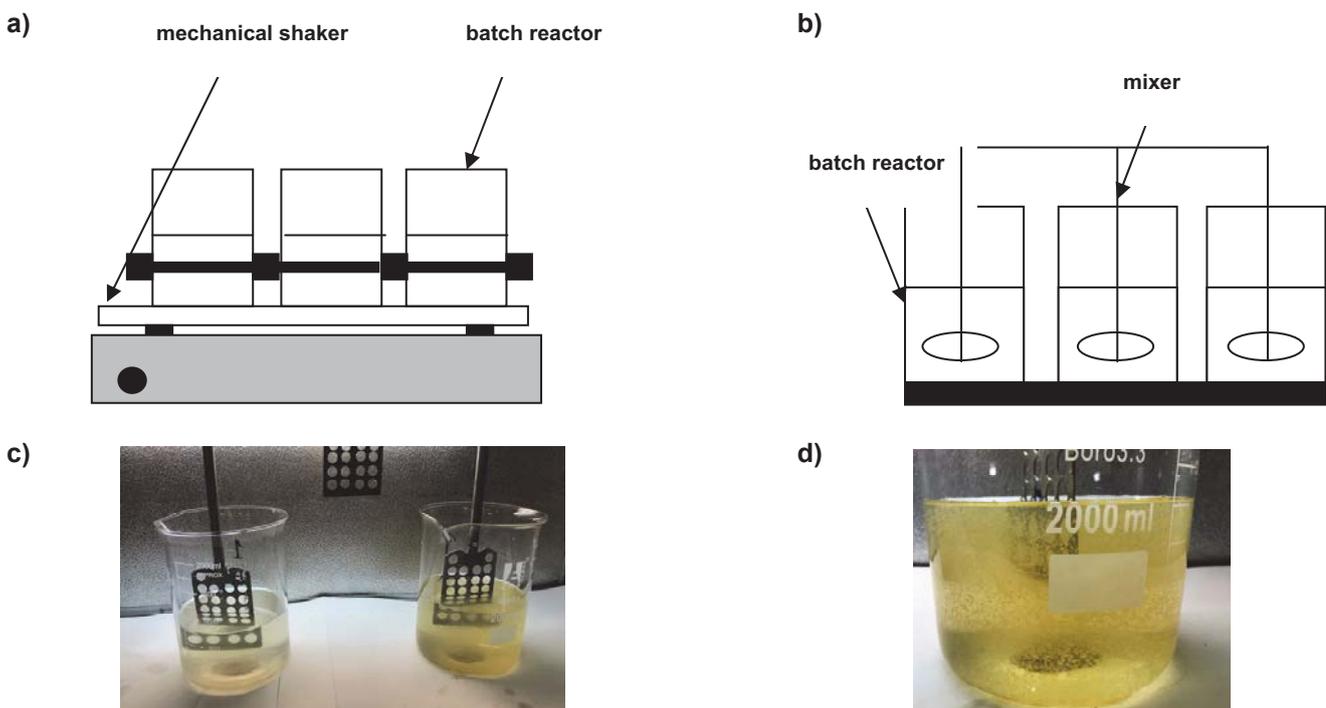


Fig. 12. Laboratory installation for: a) ZVI reduction of nitrates, b), c), d) coagulation by using waste Fe^{2+}/Fe^{3+}

Analytical methods

The following analytical procedures were used:

- pH was analyzed potentiometrically,
- nitrates by colorimetric method with brucine reagent,
- nitrites by colorimetric method with sulfanilic acid,
- ammonium nitrogen by colorimetric method with Nessler reagent,
- phosphates by colorimetric method with sodium molybdenate,
- chemical oxygen demand (COD) by dichromatic method,
- turbidity with nephelometer.

All analyses were done according to standard methods (Standard methods 2017). Analyses of physicochemical properties were done in triplicates and the results presented are given as an average value.

Results and discussion

The effect of pH on nitrates' concentration at various pH is presented in Fig. 3.

This step of the experimental procedure was mainly connected with the production of waste material containing

$\text{Fe}^{2+}/\text{Fe}^{3+}$ salts or Fe (III) oxides. The literature data (Liu and Wang 2019) on the effect of pH on nitrates removal efficiency were simultaneously confirmed. At pH = 2 the removal of nitrates was performed rapidly and almost 90% of the pollutants was removed during the first 20 min. As pH value increased the nitrate removal efficiency (after 60 min.) decreased. The maximum removal efficiency of nitrates removal at pH = 7 was about 60% of initial concentration.

The results of the experiment on further treatment of wastewater by using waste material from ZVI reduction of nitrates are presented in Fig. 4 and Fig. 5. The effectiveness of waste material containing $\text{Fe}^{2+}/\text{Fe}^{3+}$, was between Fe(II) salt and PIX. Compared to initial COD concentration equal to 260 mgO₂/L the maximum effectiveness of COD removal obtained by using waste material was equal to 38% (Fig. 5). By using Fe(II) salts it was maximally equal to 30%. The best results were, however, obtained by using PIX (44%). The results of coagulation obtained during the study are within the range which is typically obtained during the coagulation of wastewater. According to the literature data (Yargeau 2012) during the coagulation of wastewater by chemical processes the COD removal is within the range of 30–60%.

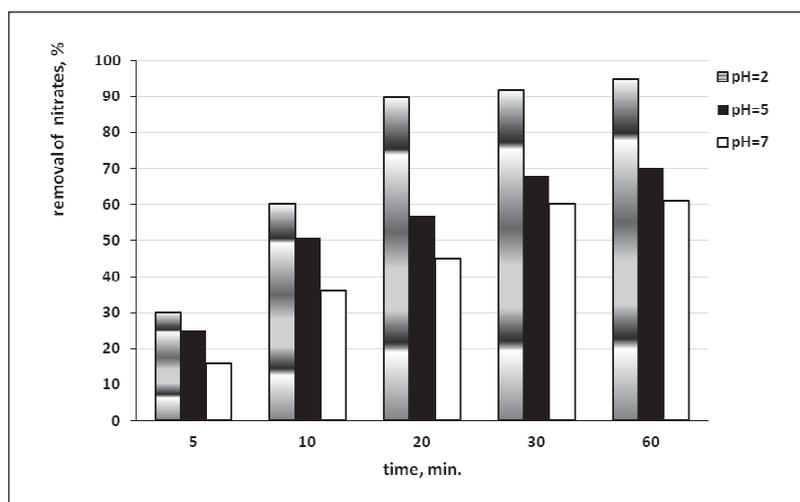


Fig. 3. Effect of pH on percent nitrates removal from water solution at dose of Fe^0 equal to 400 mg/L

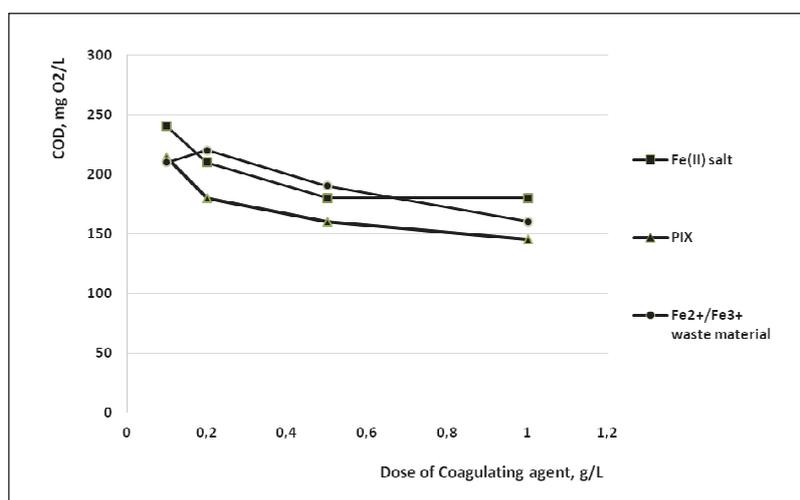


Fig. 4. COD concentration changes by using $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material compared to other coagulating agents

When compared properties of coagulating agents it can be concluded that ferric and ferrous salts coagulation pH range is wide (4.0–9.0) (Ratnayaka 2009). Under technical conditions the effectiveness of $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material could decrease. Under laboratory conditions air-dried solid material was used for the preparation of reagent solution, however, under technical scale probably only press-dewatered material will be used. Doses of it should be chosen experimentally and it is recommended rather to use the waste $\text{Fe}^{2+}/\text{Fe}^{3+}$ material as supporting in a wastewater treatment plant. It will allow to save PIX/PAX reagents. The problem related to the use of waste material with $\text{Fe}^{2+}/\text{Fe}^{3+}$ can be connected with not standardized concentration of inorganic salts in it. It supports the conclusion that this kind of waste material can be used mainly as an additional coagulation agent. However, the probability of toxicity of such waste material is low. Literature data indicate that the removal of potentially toxic compounds, e.g. Zn, by adding ZVI is mainly via reductive precipitation or co-precipitation with iron oxyhydroxides, surface adsorption or complexation. Fe^{2+} and Fe^{3+} which are the products of ZVI oxidation precipitate among others as iron hydroxide and also adsorption and co-precipitation occur on them. These reactions are not easily reversible, and as a result pollutants should not

be leached to the water phase (Cundy et al. 2008; Kishimoto et al. 2011). Moreover, the concentration of toxic compounds in ground water which can be treated by ZVI oxidation with simultaneous nitrates removal is low.

Phosphates removal in the experiment is presented in Fig. 6 and Fig. 7.

Phosphates removal efficiency was the worst when using $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material (compared to Fe(II) salt and PIX), however, the differences were not significant (within the range of 95–96%). It can be, however, stated that all chemicals used during the study were effective in phosphates' removal. Compared to the results which are obtained during the treatment of real wastewater, it means 70–90% (Yargeau 2012), removal efficiencies obtained under laboratory conditions were better. It was probably connected with the fact that under technical conditions phosphorus is present in the solution not only in dissolved form. In the laboratory the solution imitating real wastewater was prepared by using well soluble, inorganic salts which clearly affected the results.

During the experiment also turbidity removal was examined. By using doses of 0.1 to 1 g/L of the waste material no removal of this parameter was obtained (Fig. 8). To remove the turbidity further filtration by the sand filter was necessary (Fig. 9).

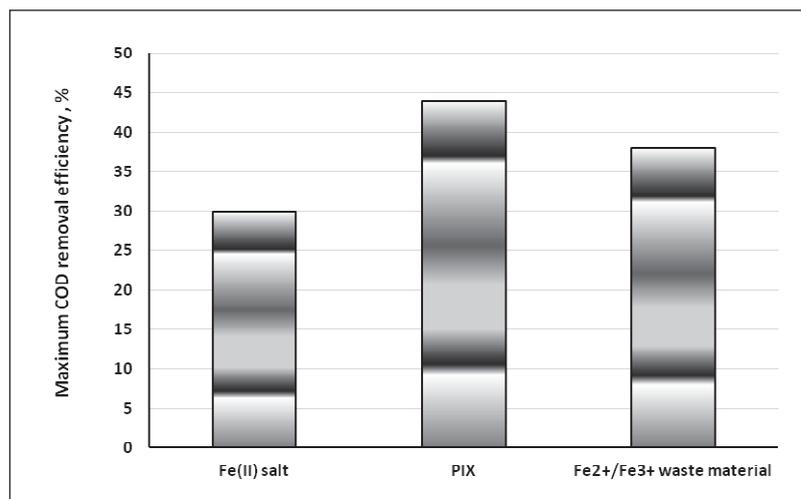


Fig. 5. COD removal efficiency by using Fe(II) salt, PIX and $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material (at optimal doses equal to 0.5 g/L Fe(II) salt; 1 g/L PIX and 1 g/L $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material)

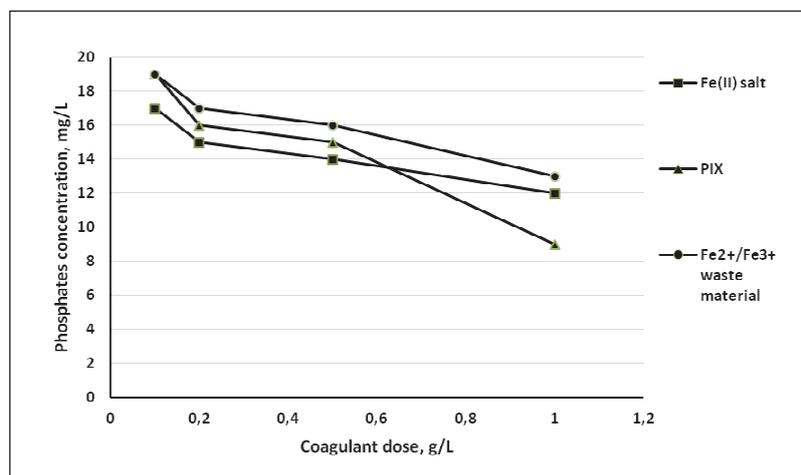


Fig. 6. Phosphates concentration changes by using $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material compared to other coagulating agents

Classical coagulants removed these parameters by 30–50% compared to initial turbidity value (30.6 NTU). An increase in wastewater turbidity by adding $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material as a coagulating agent was connected with the consistency. It was powder which, by adding water, generated suspension of $\text{Fe}^{2+}/\text{Fe}^{3+}$

salts and probably Fe^{3+} oxides. This suspension had high turbidity and by adding to prepared wastewater solutions also increased this parameter value in wastewater. This phenomenon confirms that the use of waste material from ZVI reduction of nitrates should be rather a supporting method than the basic one in WWTPs.

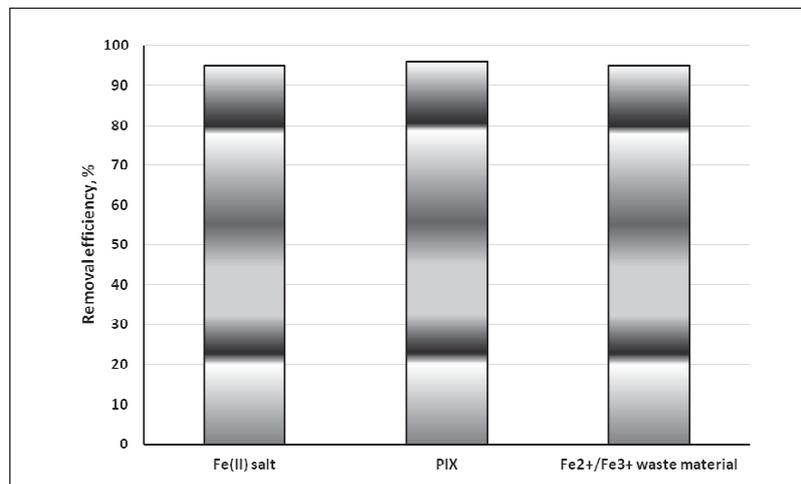


Fig. 7. Phosphates removal efficiency by using Fe(II) salt, PIX and $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material (at optimal doses equal to 1 g/L of each coagulating agent)

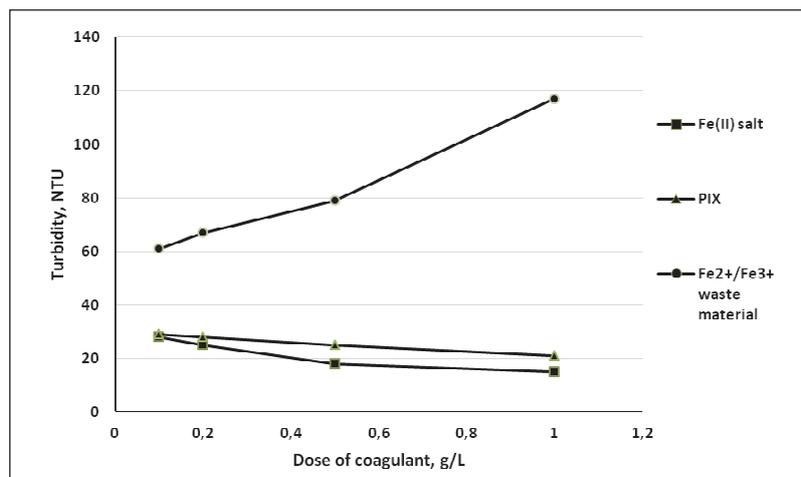


Fig. 8. Turbidity changes in wastewater by coagulation process with various coagulating agents used in the study

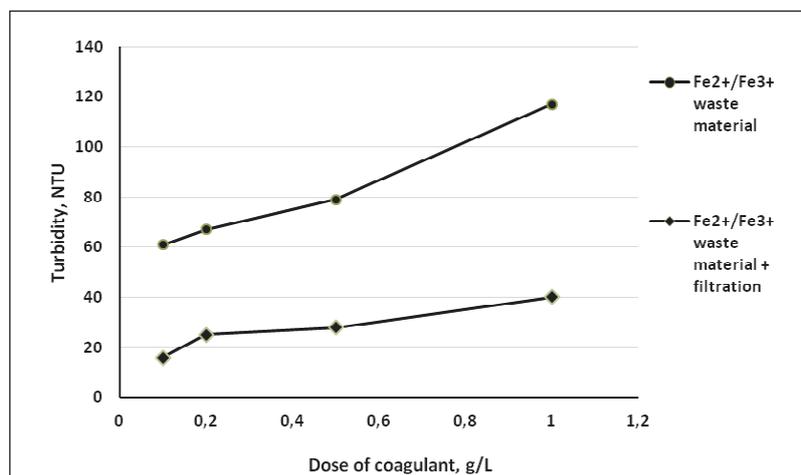


Fig. 9. Turbidity changes by using $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material and filtration through the sand filter

Conclusions

The conclusions are as follows:

1. The results obtained in the study indicate that ZVI can be effectively used in the treatment of water containing nitrates and the by-products of the process could be further applied in wastewater treatment.
2. The maximum removal efficiency of phosphates by using $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material was 95%, and was comparable with the one obtained by using PIX and Fe(II) salt.
3. The removal of COD was up to 38%, and it was higher than in the case of Fe(II) salt. By using Fe(II) salt it was 30%, whereas by using PIX 44%.
4. The use of $\text{Fe}^{2+}/\text{Fe}^{3+}$ waste material is recommended mainly as a supporting method to the classical coagulation. It allows for the removal of both organic compounds and phosphates. The removal of turbidity by using this method needs to use sand filtration as an additional step.

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