NITRATE ANIONS REMOVAL FROM WATER USING SURFACE MODIFIED CLINOPTILOLITE

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SUMMARY

Nitrate anions removal from an aqueous medium using unmodified and modified clinoptilolite was carried out. The influence of different physicochemical parameters such as the initial ion concentration in the aqueous solution, pH, the clinoptilolite mass and the contact time, were investigated.

Samples of natural clinoptilolite, taken from Rhodope Mountain in Bulgaria, have been modified with iron, magnesium and barium ions. The removal of nitrate anions efficiency was 73.58 %, 51.87 %, and 49.5 %, respectively. The removal efficiency of 46.93 % was achieved using unmodified clinoptilolite. The acidic pH did not influence the removal efficiency. It was observed only slight decreasing of the modified with iron and magnesium ions clinoptilolite efficiency. The increasing of the removal efficiency (1.07 times) in the case of barium modified clinoptilolite, was negligible. The main nitrates removal was observed at the first minute of the process.

Keywords: Nitrates, Clinoptilolite, Surface modification.

1. INTRODUCTION

The natural waters contain small amounts of nitrate ions, which are nutrients for the phytoplankton. The use of artificial fertilizers and the uncontrolled discharge of polluted water are the main sources of the large amounts of nitrates penetration into the underground water, as well as into surface water. At high concentrations, these ions are dangerous to humans and the environment, and in the watercourses they cause the eutrophication phenomenon. As a result, the quality of water bodies deteriorates drastically, making their water unusable (Savci, 2012). This has led to stricter environmental protection standards, and on the other hand, implies the preliminary wastewater treatment before its discharge into the environment. The most commonly used treatment methods to remove or reduce nitrates are biological, catalytic and chemical denitrification, reverse osmosis and electrodialysis (Bhatnagar and Sillanpää, 2011; Linh, 2013; Parvanova-Mancheva and al., 2015; Darbi and al., 2003; Richards and al., 2010; Abou-Shady and al., 2012). The biological denitrification and ion exchange are determined as nitrate removal methods by World Health Organization, while ion exchange, reverse osmosis, and electrodialysis are approved by US EPA as best available technologies to treat nitrates contaminated water (Canter, 1997; Haugen and al., 2002). The adsorption is also used as a method for nitrates release control. This is because the process is easy and cost-effective and the used adsorbents can be regenerated. A number of experiments were carried out to remove these ions from the wastewater using various adsorbents - powdered activated carbon (Bhatnagar and al., 2008; Mizuta and al., 2004), granular activated carbon (Demiral and Gündüzoglu, 2010), red mud, sepiolite, etc., (Oztürk and Bektaş, 2004; Cengeloglu and al., 2006), charcoals from different agricultural wastes obtained, such as wheat straw (Xue and al., 2016), mustard straw (Mishra and Patel, 2009), etc. The natural minerals like zeolites, were also used as
sorbents for various anions removal from the aqueous media. Due to their structure, the zeolites belong to the cationic exchangers (Margeta and al., 2013). The zeolites have negatively charged surface and that is why they adsorb mainly cations and in small extent anions from the wastewater. For better removal of anions from the aquatic environment this materials have been modified with different organic or inorganic substances (Wang and Peng, 2010; Malekian and al., 2011; Xu and al., 2013; Katal and al., 2012; Lei and al., 2010; Liu and al., 2011; Zhan and al., 2011; Mal and al. 2009; Guan and al., 2010; Bhardwaj and al., 2012; Tao and al., 2015; Ambrozova and al., 2017; Margeta and al., 2013; Latifah and al. 2017).

The aim of this research was to study the possibility of nitrate ions removal from a model aqueous media using surface modified with Fe$^{3+}$, Mg$^{2+}$ and Ba$^{2+}$ natural clinoptilolite.

2. MATERIALS AND METHODS

2.1 Materials

The zeolite used in the experiments was clinoptilolite ((Na,K, Ca)$_2$·3Al$_3$(Al, Si)$_2$Si$_5$O$_{12}$·12H$_2$O), obtained from the eastern part of the Rhodope mountain in Bulgaria. Its particle size was between 0.8 and 2.5 mm. Pure for analysis KNO$_3$, NaCl, FeCl$_3$, MgCl$_2$, H$_2$O, BaCl$_2$, 2H$_2$O, NaOOCCH$_2$·3H$_2$O, CH$_3$COOH and deionized water were used in the experiments.

2.2 Clinoptilolite modification

The clinoptilolite modification was performed by sequential activation with sodium ions and functionalization with iron, magnesium and barium ions, respectively. Prior the modification the natural clinoptilolite was washed with deionized water and dried at room temperature. Its activation was carried out by mixing of 90 g natural clinoptilolite with 900 cm$^3$ of 0.1M NaCl and the resulting suspension was heated at 70 °C using reflux condenser for 3 hours. Then, the procedure was repeated with fresh 900 cm$^3$ of NaCl solution and the suspension was left another 3 hours at the same conditions to complete the cation exchange. Then the phases were separated and the solid fraction was rinsed with deionized water for Cl$^-$ ions removal. The activated clinoptilolite was dried overnight at 60 °C. The sodium-activated clinoptilolite was separated into three portions of 30 g and each of them was put in contact with 300 cm$^3$ MeCl$_{m}$, where Me was either iron (Fe), magnesium (Mg) or barium (Ba). The functionalization was made under reflux condenser at 70 °C for 5 hours. This procedure was repeated with fresh 300 cm$^3$ MeCl$_{m}$ solution. Finally, the phases were separated and the solid one was rinsed with deionized water and dried overnight at 60 °C. The newly obtained materials were named CLIFe, CLIMg, and CLIBa, respectively.

2.3 Preparation of standard solutions of nitrate ions

An initial model solution with concentration 1 g.dm$^{-3}$ of NO$_3^-$ was prepared, by diluting KNO$_3$ with deionized water. Then standard solutions with concentrations of 50.0, 100.0, 150.0, 250.0 and 300.0 mg.dm$^{-3}$ were prepared.

2.4 Removal technique

In order to establish the influence of the initial nitrate ions (NO$_3^-$) concentration and pH of the solution on their removal, 50 cm$^3$ of model solutions with different initial NO$_3^-$ concentration (50 - 300 mg.dm$^{-3}$) were prepared. To each of the samples a certain amount (1 g) of nonmodified natural clinoptilolite (CLI), and modified clinoptilolite (CLIFe, CLIMg, and CLIBa) with a grain size of 0.8 - 2.5 mm, was added, respectively. An acetate buffer was added to each of the samples to adjust pH to 5. The samples were agitated for 48 hours. After that 20 cm$^3$ portions of each sample were taken, filtered through blue ribbon filter paper to remove clinoptilolite particles and were analyzed.

In order to establish the influence of the contact time on the NO$_3^-$ removal as well as the influence of the clinoptilolite dose, 2 dm$^3$ solution with initial nitrate ions concentration of 300 mg.dm$^{-3}$ was prepared. To the aqueous solution was added a weighed amount of clinoptilolite (3, 6 and 9 g). The suspension was agitated for 130 min (Heidolph RZR 2100 electronic) at 200 rpm. Samples were taken after 1, 3, 5, 8, 10, 15, 30, 45, 60, 75, 100, 130 min and filtered through blue ribbon filter paper to remove suspended adsorbent particles. Then they were analyzed.

2.5 Instrument and measurements

The nitrates concentration was determined using standard procedure (Greenberg and Washington, 1992).
Nitrate anions removal from water using surface modified clinoptilolite

2.6 Removal efficiency

The efficiency of NO$_3^-$ removal by clinoptilolite was calculated according to the formula:

$$\text{RE} \% = \left( \frac{C_o - C_t}{C_o} \right) \times 100$$

Where $C_o$ is the initial NO$_3^-$ concentration (mg.dm$^{-3}$) and the $C_t$ is the concentration at time $t$ (mg.dm$^{-3}$).

2.7 Adsorption capacity

The amount of adsorption at equilibrium in (mg.g$^{-1}$) was calculated according to the formula:

$$q_e = \frac{(C_o - C_e) \times V}{m}$$

3. RESULTS AND DISCUSSION

3.1 Effect of the initial NO$_3^-$ concentration and solution pH on the removal efficiency

It was observed that with the initial NO$_3^-$ concentration increasing, the removal efficiency, proportionally increases too (Fig. 1). pH of the initially prepared solution was 7.4.

![Fig. 1. Removal efficiency of the clinoptilolite.](image)

The removal efficiency of 0.11 % was achieved for 48 hours using 1 g of natural unmodified clinoptilolite and an initial NO$_3^-$ concentration of 50.00 mg.dm$^{-3}$, whereas that obtained at an initial concentration of 300 mg.dm$^{-3}$, was 46.9 %. The higher removal efficiency achieved at higher concentrations can be explained by the presence of sufficient vacant sites on the clinoptilolite surface where the NO$_3^-$ contained in the aqueous solution can be captured. The adsorption capacity obtained using 1 g CLI and initial NO$_3^-$ concentrations of 50 to 300 mg.dm$^{-3}$, respectively, varies from 0.003 to 7.15 mg.g$^{-1}$, respectively.

After the natural clinoptilolite modification, the removal efficiency increases, especially in the case of iron-modified material usage. The results obtained at pH 7.4 show that the CLIFe usage leads to the best results. The removal efficiency achieved with this modification is on average 1.9 times higher than that achieved using nonmodified clinoptilolite.

The CLIMg also gives good results compared to the unmodified natural clinoptilolite. At initial nitrate concentration of 300 mg.dm$^{-3}$, CLIFe, CLIMg, and CLIBa have removal efficiencies of 73.58 %, 51.87 %, and 49.5 %, respectively, which means that the CLIFe is better at nitrate removal by 1.4 and 1.5 times in comparison with CLIMg and CLIBa. The barium-modified clinoptilolite leads to least removal efficiency. The same trend was observed in the adsorption capacities of the above-mentioned modifications. Thus, the adsorption capacity of CLIFe was 11.21 mg.g$^{-1}$, while the maximum capacities of CLIMg and CLIBa are 7.91 and 7.54 mg.g$^{-1}$, respectively. It is noteworthy, that the surface modification of the clinoptilolite with barium chloride leads to a decrease in its sorptive ability with respect to nitrate ions.

Comparative experiments were made in an acidic environment.
aqueous media at the same initial concentrations and using of 1 g of the three different modifications of clinoptilolite - CLIFe, CLIMg, and CLIBa (Fig. 2).

An acetate buffer was added to the samples to adjust pH 5. The results show that at this pH a less treatment efficiency was achieved using CLIFe and CLIMg. For both modifications, the removal efficiency decreased on average by 1.2 times. The same tendency was observed in the adsorption capacity of this clinoptilolite modifications. Unlike CLIFe and CLIMg, CLIBa changes, albeit to a negligible extent (average 1.07 times), its removal efficiency. Overall, there was no significant difference in the efficiency of the materials used at pH 5 and 7.

3.2 Effect of contact time and clinoptilolite dosage on the removal efficiency

From the analysis of the data obtained, it is seen that the binding of the NO₃⁻ takes place in the first minute from the beginning using various modifications of the natural clinoptilolite (Fig. 3). After that, there was not observed any change.

This means that the adsorbents used were saturated. Removal efficiencies of 49.06 %, 49.22 %, and 49.24 % were achieved at the first minute, using 3 g of CLIFe, CLIMg, and CLIBa, respectively. The maximum effects achieved at the 130th minute from the process beginning, with the same amount of the modified clinoptilolite, were 53 %, 54.51 %, and 53.6 %, respectively. This means that there was a slight increase in the removal (1.08, 1.1 and 1.09 times, respectively).

The same tendency was observed using larger amounts of CLIFe, CLIMg, and CLIBa. The usage of double and triple greater doses of the corresponding modifications of the natural clinoptilolite results in almost identical removal efficiencies. The best removal at the 1st minute was achieved with 6 g CLIFe (52.74 %) and up to the 130th minute - with 3 g of CLIMg (54.51 %). In general, the removal of nitrate ions from the aqueous medium using 3, 6 and 9 g of the different zeolite modifications was about 50 %. It can be concluded that the use of larger doses of CLIFe, CLIMg, and CLIBa did not improve significantly the results.

4. CONCLUSION

In the experiments with unmodified and modified clinoptilolite, with the initial nitrate concentration increase, the proportional removal efficiency increase was observed too. The unmodified clinoptilolite shows lower removal efficiency in comparison with modified forms. As a result of the natural clinoptilolite modifications
applied, its ability to remove the anions contained in the aqueous medium increased. As a whole, the largest nitrate anions removal efficiency was observed with CLiFe usage. It was found that the acidic pH of the aqueous medium did not increase the efficiency. Only when using CLiBa, the removal efficiency increased insignificantly (1.07 times) while the usage of the other two modifications of clinoptilolite - CLiFe, CLiMg, led to lower removal efficiency. The binding of the nitrate anions contained in the aqueous medium with the natural unmodified and modified clinoptilolite occurs in the first minute of the interaction, after which there was almost no change. The amount of the adsorbents used has negligible influence.

REFERENCES