

NITRATE ANIONS REMOVAL FROM WATER USING SURFACE MODIFIED CLINOPTILOLITE

S. LAVROVA-POPOVA*, S. STOYANOVA

University of Chemical Technology and Metallurgy, 8 Kliment Ohridski blvd., 1756 Sofia, Bulgaria

*Corresponding Author E-mail: engeco2001@uctm.edu

Received: February 7, 2018, Accepted: February 21, 2018, Online: April 7, 2018

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 influenced 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 Gündüzoğlu, 2010), red mud, sepiolite, etc., (Oztürk and Bektaş, 2004; Cengelloglu 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., 2018; Xi and al., 2010; Liu and al., 2017; Zhan and al., 2011; Allen 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 $((\text{Na,K,Ca})_{2-3}\text{Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36}\cdot 12\text{H}_2\text{O})$, 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 , $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$, $\text{NaOOCCH}_3\cdot 3\text{H}_2\text{O}$, CH_3COOH 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 $\text{g}\cdot\text{dm}^{-3}$ 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 $\text{mg}\cdot\text{dm}^{-3}$ 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 $\text{mg}\cdot\text{dm}^{-3}$) 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 $\text{mg}\cdot\text{dm}^{-3}$ 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).

2.6 Removal efficiency

The efficiency of NO_3^- removal by clinoptilolite was calculated according to the formula:

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

Where C_o is the initial NO_3^- concentration ($\text{mg} \cdot \text{dm}^{-3}$) and the C_t is the concentration at time t ($\text{mg} \cdot \text{dm}^{-3}$).

2.7 Adsorption capacity

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

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

Where C_o and C_e are the initial and equilibrium nitrate ions concentrations ($\text{mg} \cdot \text{dm}^{-3}$), respectively, V is the volume of solution (dm^3) and m (g) is the mass of the clinoptilolite used.

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.

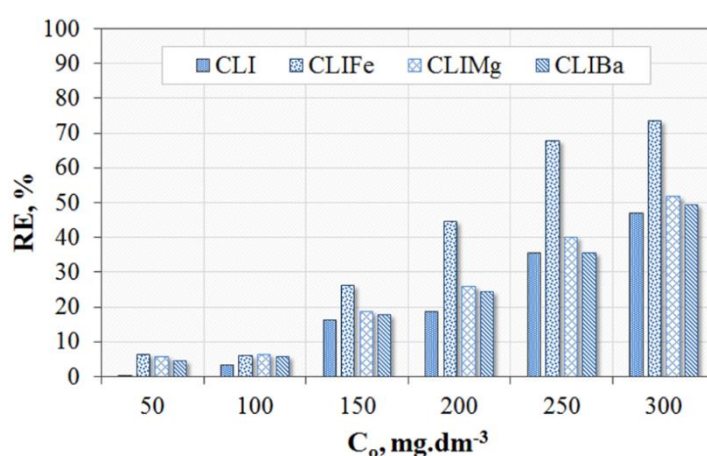


Fig. 1. Removal efficiency of the clinoptilolite.

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 $50.00 \text{ mg} \cdot \text{dm}^{-3}$, whereas that obtained at an initial concentration of $300 \text{ mg} \cdot \text{dm}^{-3}$, 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 $300 \text{ mg} \cdot \text{dm}^{-3}$, respectively, varies from 0.003 to $7.15 \text{ mg} \cdot \text{g}^{-1}$, 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 $300 \text{ mg} \cdot \text{dm}^{-3}$, 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 $11.21 \text{ mg} \cdot \text{g}^{-1}$, while the maximum capacities of CLIMg and CLIBa are 7.91 and $7.54 \text{ mg} \cdot \text{g}^{-1}$, 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

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).

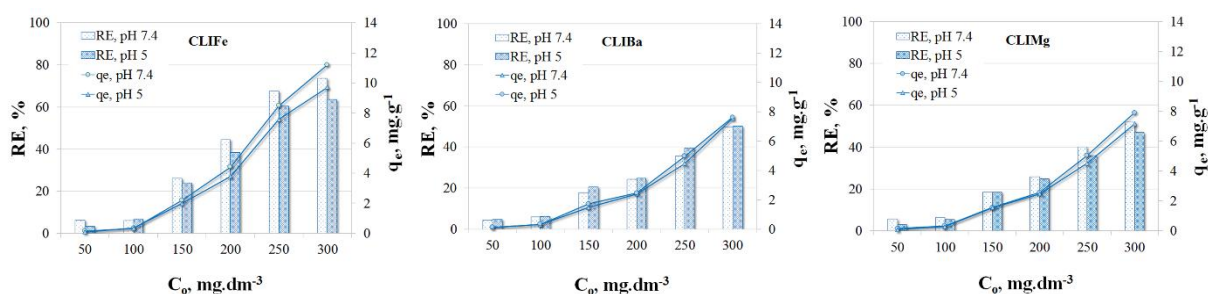


Fig. 2. Removal efficiency and adsorption capacity at different pH.

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.

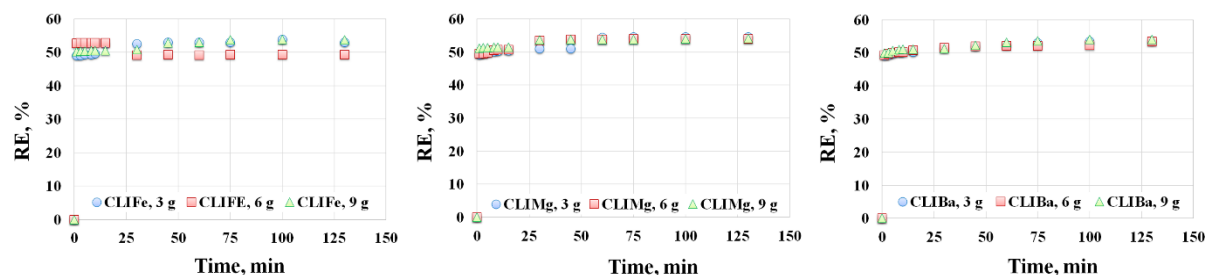


Fig. 3. Effect of the contact time on the removal efficiency.

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

- ABOU-SHADY A., PENG C., BI J., XU H., ALMERIA J. (2012). Recovery of Pb (II) and removal of NO_3^{3-} from aqueous solutions using integrated electrodialysis, electrolysis, and adsorption process. *Desalination*, 286, 304-315.
- ALLEN S., IVANOVA E., KOUMANOVA B. (2009). Adsorption of sulfur dioxide on chemically modified natural clinoptilolite. Acid modification. *Chem. Engin. J.*, 152, 389-395.
- AMBROZOVA P., KYNICKY J., URUBEK T., NGUYEN V.D. (2017). Synthesis and modification of clinoptilolite. *Molecules*, 22, 7, 1107.
- BHARDWAJ D., SHARMA M., SHARMA P., TOMAR R. (2012). Synthesis and surfactant modification of clinoptilolite and montmorillonite for the removal of nitrate and preparation of slow release nitrogen fertilizer. *J. Hazard. Mater.*, 227-228:292-300.
- BHATNAGAR A., JI M., CHOI Y., JUNG W., LEE S., KIM S., LEE G., SUK H., KIM H., MIN B., JEON B., KANG J. (2008). Removal of nitrate from water by adsorption onto zinc chloride treated activated carbon. *Sep. Sci. Technol.*, 43, 886-907.
- BHATNAGAR A., SILLANPÄÄ M. (2011). A review of emerging adsorbents for nitrate removal from water. *Chem. Eng. J.*, 168, 493-504.
- CANTER L. (1997). Nitrates in Groundwater, *CRC Press*, Boca Raton.
- CENGELGLOU Y., TOR A., ERSOZ M., ARSLAN G. (2006). Removal of nitrate from aqueous solution by using red mud. *Sep. Purif. Technol.*, 51, 374-378.
- DARBI A., VIRARAGHAVAN T., BUTLER R., CORKAL D. (2003). Pilot-Scale Evaluation of Select Nitrate Removal Technologies. *J. Environ. Sci. Health., Part A*, 38, 1703-1715.
- DEMIRAL H., GÜNDÜZOĞLU G. (2010). Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresour. Technol.*, 101, 1675-1680.
- GREENBERG A., WASHINGTON D. (1992). Standard methods for the examination of water and wastewater. American Public Health Association (APHA), American Water Works Association (AWWA), and the Water Environment Federation (WEF), 18th edition.
- GUAN H., BESTLAND E., ZHUA C., ZHUA H., ALBERTSDOTTIR D., HUTSON J., SIMMONS C., GINIC-MARKOVIC M., TAOD X., ELLIS A. (2010). Variation in performance of surfactant loading and resulting nitrate removal among four selected natural zeolites. *J. Hazard. Mater.*, 183, 616-621.
- HAUGEN K., SEMMENS M., NOVAK P. (2002). A novel in-situ technology for the treatment of nitrate contaminated groundwater. *Water Res.*, 36, 3497-3506.
- KATAL R., BAEI M., RAHMATI H., ESFANDIAN H. (2012). Kinetic, isotherm and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk. *J. Ind. Eng. Chem.*, 18, 295-302.
- LATIFAH O., AHMED O., MAJID N. (2017). Enhancing nitrogen availability from urea using clinoptilolite zeolite. *Geoderma*, 306, 152-159.
- LEI Z., CAGNETTA G., LI X., QU J., LI Z., ZHANG Q., HUANG J. (2018). Enhanced adsorption of potassium nitrate with potassium cation on H_3PO_4 modified kaolinite and nitrate anion into Mg-Al layered double hydroxide. *Appl. Clay Sci.*, 154, 10-16.
- LINH T. (2013). Removal of nitrate from water and wastewater by ammonium-functionalized SBA-16 mesoporous silica. PhD Thesis. Université Laval, Québec.
- LIU J., CHENG X., ZHANG Y., WANG X., ZOU Q., FU L. (2017). Zeolite modification for adsorptive removal of nitrite from aqueous solutions. *Microporous Mesoporous Mater.*, 252, 179-187.
- MALEKIAN R., ABEDI-KOUPAI J., ESLAMIAN S. (2011). Influences of clinoptilolite and surfactant-modified clinoptilolite zeolite on nitrate leaching and plant growth. *J. Hazard. Mater.*, 185, 970-976.

- MARGETA K., LOGAR N.Z., ŠILJEG M., FARKAŠ A. (2013). Natural Zeolites in Water Treatment – How Effective is Their Use. Water Treatment, Dr. Walid Elshorbagy (Ed.), *InTech*, pp. 81-112.
- MISHRA P., PATEL R. (2009). Use of agricultural waste for the removal of nitrate-nitrogen from aqueous medium. *J. Environ. Manage.*, 90, 519-522.
- MIZUTA A., MATSUMOTO T., HATATE Y., NISHIHARA K., NAKANISHI T. (2004). Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. *Bioresour. Technol.*, 95, 255-257.
- OZTÜRK N., BEKTAŞ T.E. (2004). Nitrate removal from aqueous solution by adsorption onto various materials. *J. Hazard. Mater.*, 112, 155-162.
- PARVANOV-MANCHEVA TS., RAZKAZOVA-VELKOVA E., MARTINOV M., STEFANOV S., BESCHKOV V. (2015). Wastewater treatment and energy yield. Part II. Fuel cell based on chemical sulfide oxidation and microbial nitrate reduction. Scientific works of university of food technologies - Plovdiv, Biotechnology and Nanotechnology, 62, 499-504.
- RICHARDS L., VUACHÈRE M., SCHÄFER A. (2010). Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis. *Desalination*, 261, 331-337.
- SAVCI S. (2012). Investigation of effect of chemical fertilizers on environment. *APCBEE Procedia*, 1, 287-292.
- Tao Q., Hu M., Ma X., Xiang M., Zhang T., Li C., Yao J., Liang Y. (2015). Simultaneous removal of ammonium and nitrate by HDTMA-modified zeolite. *Water Sci. Technol.*, 72.11, 1931-1939.
- WANG S., Y. PENG (2010). Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem. Eng. J.*, 156, 2010, 11-24.
- XI Y., MALLAVARAPU M., NAIDU R. (2010). Preparation, characterization of surfactants modified clay minerals and nitrate adsorption. *Appl. Clay Sci.*, 48, 92-96.
- XU X., GAO B., TAN X., ZHANG X., YUE Q., WANG Y., LI Q. (2013). Nitrate adsorption by stratified wheat straw resin in lab-scale columns. *Chem. Eng. J.*, 226, 1-6.
- XUE L., GAO B., WANG Y., FANG J., WANG S., LI Y., MUÑOZ-CARPENA R., YANGA L. (2016). High efficiency and selectivity of MgFe-LDH modified wheat-straw biochar in the removal of nitrate from aqueous solutions. *J. Taiwan Inst. Chem. Eng.*, 63, 312-317.
- ZHAN Y., LIN J., ZHU Z. (2011). Removal of nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent. *J. Hazard. Mater.*, 186, 1972-1978.