15th International Congress of the Geological Society of Greece
Athens, 22-24 May, 2019 | Harokopio University of Athens, Greece
Bulletin of the Geological Society of Greece, Sp. Pub. **7** Ext. Abs. GSG2019-098

Nitrate Exchange Capacity of Greek Palygorskite and Sepiolite for their Potential Application in Water Treatment

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Introduction

Palygorskite and sepiolite are the only 2:1 clay minerals characterized by fibrous morphology and 2:1 ribbons structure. Both minerals have similar structures, except from palygorskite's shorter b dimension where two Si-O group chains exist, instead of three in case of sepiolite (Moreira et al., 2017). The change in the orientation of the chains is responsible for the interruption of the octahedral layers, and that leads to the existence of empty channels. In order to have charge balance, in the free space can enter variable amounts of either cations or anions which can be exchanged along with zeolitic water (Galan 1996). Their structure, basal spacing as well as crystal morphology and dimensions are the main causes of their high specific surface area and adsorption capacity, which in combination with their abundance and low – cost, enable them as cost-effective adsorbents for a variety of contaminants from water systems.

The aim of this study is the Anion Exchange Capacity (AEC) evaluation of Greek fibrous clay minerals, in order to be exploited for water treatment, as environmental-friendly and low-cost adsorbents. Initial experiments to determine the effect of nitrate initial concentration, adsorbent's dosage and contact time have been carried out. Specifically, palygorskite from Grevena (Western Macedonia, Greece) and sepiolite from Corinth (Peloponnese, Greece) are used for the crucial nitrate removal from water without any modification that increases cost. Nitrate (NO_3^-) presence in groundwater is quite common, especially at the areas with nitrogenous fertilizers oversupply, as almost the 20% of the N-fertilizers leaches into the groundwater, in nitrate form (Lu et al., 2019), making it a widespread water contaminant. Nitrate in high concentration levels consist a threat to the ecosystem, as can contribute to eutrophication and infant's disease methaemoglobovinemia (Capodici et al., 2018), making its remediation with cost-effective and non-toxic methods a significant topic.

Materials and Methods

Palygorskite from Ventzia basin (Grevena/Western Macedonia, Greece) and sepiolite from Solomos village (Corinth/ Peloponnese, Greece) were used for a series of batch experiments. The particular palygorskite deposit is exploited by Geohellas S.A. and was diagenetically formed through the smectite - silica rich solutions interaction (Kastritis et al., 2003) while the sepiolite occurrence was recently discovered by Papoulis et al., (2018) between WNW- and ENE-trending active faults. Samples were fractionated in order to obtain powder sedimentation (< 50μm) and were characterized by XRD, FTIR, SEM and BET that conducted at several laboratories of University of Patras.

Batch kinetic experiments were carried out to examine the adsorption process, for various adsorbent dosage (i.e. 0.4, 0.8, 1.6 and 4 g) in various NO_3^- concentrations (i.e. 15, 30 and 50 mg/L) for both palygorskite and sepiolite. 250 ml conical flasks were employed, filled with 200 ml of the examined NO_3^- concentration and adsorbent dose and were agitated mechanically for 40 min. Samples were taken in various time intervals (i.e. 2.5, 5, 10, 15, 20, 30 and 40 min). The experiments were conducted in room temperature and there was no pH adjustment. Samples were centrifuged at 5.500 rpm for 3 min and filtered through 0.45 μm Whatman filters. For every time interval, and using the proper sample dilution, NO_3^- concentration was measured to a spectrophotometer (Hach-Lange UV-VIS) using a calibration curve at 220 nm according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998). The removal efficiency (%) of each clay mineral was determined based on equation (1).

$$\textit{Removal efficiency} = \frac{c_0 - c_f}{c_0}\ \% \quad (1)$$

Where c_0 is the initial nitrate concentration and c_f is the final nitrate concentration after adsorption process.

Results

Palygorskite X-Ray Diffraction pattern showed all its characteristic peaks including at10.4 and 20 Å, meanwhile the 6 Å peak is referred to the smectite mineral saponite which co-exist with palygorskite at Grevena's deposit. Sepiolite presents no impurities at all, or at least bellow detection limits, as it can be seen by its diffraction pattern with its characteristic peak at 7.2 Å. The FT-IR spectra confirmed XRD results. According to SEM observations the clay minerals' fibrous morphology was verified, while according to BET analysis the specific surface area for palygorskite and sepiolite was estimated at 210 m^2/g and 234 m^2/g respectively. Batch kinetic experiments, for both fibrous clay minerals, indicated similar characteristics and behavior for nitrate removal. Specifically, in case of palygorskite the increase of adsorbent's dosage at 4 g, compared to 0.4 and 0.8 g, results to an increased nitrate removal for all the examined concentrations. Specifically for 15 mg/L, minimum and maximum removal reached up 8 and to 20% respectively. Nevertheless the maximum nitrate removal for all dosages is not contact time depended, as in all cases after 15 minutes the adsorbed nitrate concentration almost reaches plateau (Fig. 1a). With initial nitrate concentration increase to 30 and 50 mg/L the nitrate removal capacity of 4 g palygorskite is degrading to 17.6% and 12% respectively, while the other masses' efficiency is even lower. Sepiolite presents similar behavior with palygorskite, as the 4 g dosage is the preferable mass to eliminate all studied nitrate concentrations within 15-20 min. However, sepiolite found to be a better adsorbent for the higher concentration levels of the pollutant, as the 22.6 % and 24.2% of 30 mg/L and 50 mg/L nitrate respectively can be removed, compared to the 15% removal for 15 mg/L nitrate (Fig. 1b).

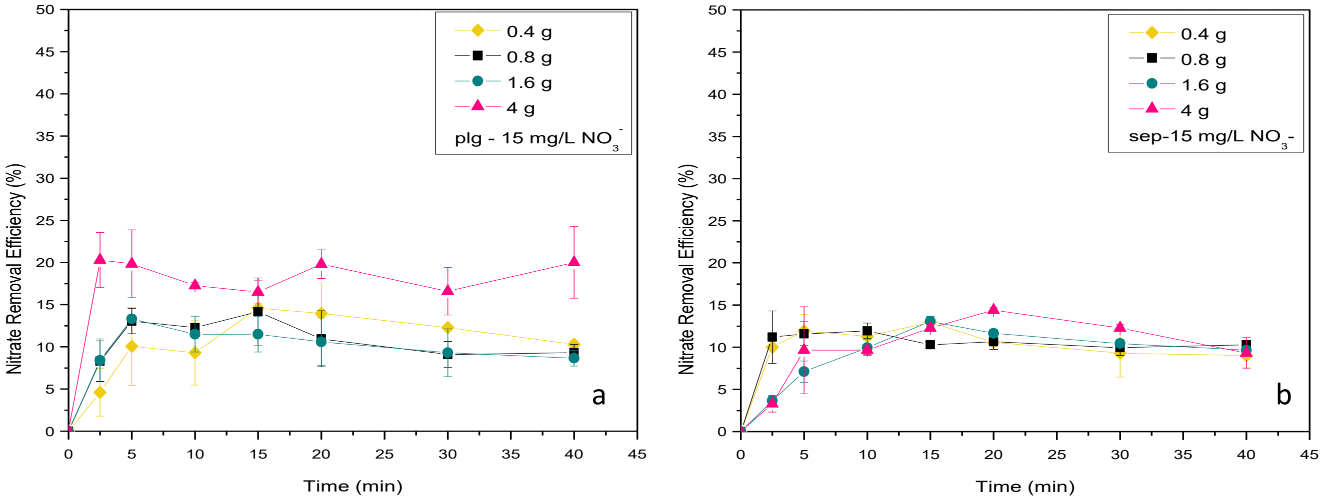

Figure 1. Nitrate removal at 15 mg/L for all dosages for a) palygorskite and b) sepiolite.

Conclusions

Nitrate consist a threatening pollutant for humans health and marine ecosystems, making its removal or degradation from water systems crucial. Palygorskite from Grevena (Greece) and sepiolite from Corinth (Greece) proved to be promising anionic adsorbents depending on the pollutant's initial concentration, the adsorbent dosage and contact time. Palygorskite is more efficient adsorbent at low nitrate concentration levels, in contrast to sepiolite, which nitrate removal efficiency is positively correlated with the initial concentration increase. The adsorbent's mass had impact especially on palygorskite's removal capacity and less on sepiolite's, as the highest examined mass were the most efficient in both cases within 15-20 minutes. However, the maximum removal efficiency through adsorption process for both palygorskite and sepiolite found to be not sufficient for the main nitrate removal mechanism. The possible application of Greek clay occurrences seems promising for pre- or post- water treatment, in combination with more effective but costly technologies, such as biological denitrification or electrochemical methods, in order to gain nitrate remediation via a hybrid and possible more efficient system. Nevertheless, further study needs to be conducted regarding co-existing ions, and clay minerals potential modification or combination with other materials.

Acknowledgements

Special thanks to laboratory of Environmental System's team, at Chemical Engineering Department, University of Patras for their help in batch experiments and the UV-VIS analysis.

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