

Ca²⁺ removal from water by the use of Na-palygorskite for potential water softening

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ABSTRACT

Sodium-treated palygorskite (Na-Pal) sample was investigated for the sorption of Ca²⁺ ions with the aim of treating water hardness. The effective modification of the mineral with Na⁺ was verified by XRD and FT-IR techniques. Batch kinetic experiments in standard solutions were performed proving that 30 g/L of Na-Pal were highly satisfactory as the Ca²⁺ removal reached the 85% for 100 mg/L Ca²⁺ initial concentration, which is very promising for the softening of moderate or hard waters. The Ca²⁺ removal found to be pH and temperature independent, with high removal rates at room temperature and common pH values of water samples (pH 4–12), rendering these circumstances ideal for the low-cost maintenance of the procedure that took place within the first 5 min. The linear form of the Langmuir isotherm model expressed better ($R^2 = 1$) the Ca²⁺ sorption, which means that takes place at specific homogeneous sites of Na-Pal. Thermodynamic analysis proved the non-spontaneous (positive ΔG^0), physical, and exothermic nature ($\Delta H^0 = -10.8197$ kJ/mol) of the reaction, while the kinetic models proved the chemisorption of Ca²⁺ by Na-Pal.

Key words: calcium ions, ion exchange, palygorskite, sodium treatment, water hardness, water softening

HIGHLIGHTS

- Na-Pal is effective for Ca²⁺ removal and water softening.
- 30 g/L Na-Pal reached 85% Ca²⁺ removal in moderate/hard waters.
- Effective Ca²⁺ removal in room temperature pH 4–12 and time 5 min under no special conditions that increase cost.
- Ca²⁺ sorption occurs at specific homogeneous sites of Na-Pal and is characterised as non-spontaneous, physical, exothermic reaction.
- Simultaneous ion exchange and Ca²⁺ adsorption in Na-Pal structure.

INTRODUCTION

Water is one of the most vital necessities. The increased concentrations of several chemical elements in the groundwater can prohibit water's exploitation, leading to less than 1% of the freshwater being available for human consumption (Hailu *et al.* 2019). One major problem for the capable usage of water supplies is the water hardness that is the result of water (in several phases such as moisture or rain) and carbon dioxide reactions with calcium, carbonate, and magnesium ions of the earth surface that subsequently affect the quality of groundwater (Turker *et al.* 2017). When the concentration of such ions is higher than 120 mg/L and 200 mg/L, the water is characterized as hard (Cotruvo 2011) or poor water (Hounslow 2018), respectively. For values higher than 300 mg/L the water is unacceptable for the majority of domestic consumption (Hounslow 2018), while it can cause several health problems, such as dermatitis, kidney stones, chronic inflammatory diseases, pancreatic cancer, etc. (Sengupta 2014).

For the maintenance of magnesium and calcium concentrations in low values, several industrial available procedures have been used, with the most common being the electrolysis (Agostinho *et al.* 2012), microbial (Brastad & He 2013), and electrochemical processes (Gabrielli *et al.* 2006), nanofiltration (Izadpanah & Javidnia 2012), adsorption (Ouar *et al.* 2017), chemical precipitation, ion exchange (Apell & Boyer 2010), etc. Ion exchange is found to be one of the most convenient, effective in use, and regenerated methods (Vaaramaa & Lehto 2003), as a material's structure remains unaffected and can

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be easily returned to its initial form by ion enrichment for further applications. Depending on the nature of the material (synthetic or natural) and the method of modification, such as chemical, thermal, and so on, the cost of the procedure is differentiated (Vaaramaa & Lehto 2003; Kadir *et al.* 2017). Another important physicochemical method for the hardness treatment is adsorption, due to the low initial cost in combination with operational simplicity and lack of formation of harmful substances (Kadir *et al.* 2017).

Zeolites, clays, and clay minerals such as bentonite, kaolinite, and illite, have been used by several researchers as raw or modified natural ion-exchangers for hardness treatment due to their ion-exchange properties (Hailu *et al.* 2019). Moreover, the same materials have been investigated as adsorbents for the reduction of Ca^{2+} and Mg^{2+} ions from water systems, due to their abundant nature, limited cost, and high adsorbance properties (Kadir *et al.* 2017; Gebretsadik & Gebremedhin 2020).

The aim of the present study is the exploitation of modified palygorskite as a low-cost and potentially effective material for the removal of Ca^{2+} in drinking water. Instead of the already tested clay minerals, palygorskite presents an elongated morphology with a high specific surface area and adsorption capacity due to its permanent negative charge and basal channels that are full of exchangeable ions (Galán 1996). For the reinforcement of the hardness treatment, the NaCl modification of the mineral was performed with the aim of the combination of adsorption process with ion-exchange, since the relative affinity of Na^+ and Ca^{2+} that establishes their mutual exchange is already known (Liao *et al.* 2016). Batch kinetic experiments were conducted in order to determine the conditions for sufficient Ca^{2+} ions removal. The raw and modified palygorskite samples were characterized with XRD and FT-IR methods for better understanding of palygorskite's structural and chemical characteristics after the NaCl modification and its influence on ion-exchange and adsorptive properties. The low initial cost of palygorskite in combination with the easy and low-cost modification and the hardness treatment via the economical adsorption and ion-exchange mechanisms can make palygorskite a promising material for such applications.

MATERIALS AND METHODS

Palygorskite treatment and samples' characterization

Raw palygorskite, exploited by Geohellas S.A. in Western Macedonia, Greece, was used after its low-cost sodium-treatment with the purpose of increasing calcium sorption. A supersaturated solution of NaCl with deionized water was prepared. Subsequently, 8 g of a raw palygorskite sample were mixed with 100 mL of the solution under magnetic stirring for 30 min, followed by centrifugation. The supernatant solution was removed and replaced with a fresh 100 mL of NaCl solution. The procedure was repeated twice and the final sediment was washed with deionized water, centrifuged, and dried at 55 °C overnight, in order to remove the ions that did not strongly interact with the palygorskite structure. The sodium-treated palygorskite sample (Na-Pal) was then pulverized and was ready for use.

Raw and also sodium-treated palygorskite were characterized via X-ray diffraction and a Bruker D8 Advance (Cu- K_{α} radiation, $\lambda = 1.5418 \text{ \AA}$, nickel filter) with the aim of investigating the structural differences of the samples. The successful treatment of palygorskite was verified by Fourier transform infrared spectroscopy (FT-IR) and especially a Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer from Thermo Scientific™. Measurements were performed in the middle IR region (400–4,000 cm^{-1}) via IR source (Wolfram wire), KBr beam-splitter and a DTGS detector. Moreover, the sodium-treated palygorskite sample was examined in a Scanning Electron Microscope (SEM) JEOL 6300 (JEOL, Tokyo, Japan) operating at 30 kV with an energy dispersive spectrometer (EDS) for the microelemental analysis of the treated sample. The dispersion of sodium onto the clay particles represented by pseudocolorization and point elemental analysis was performed at different parts of the tested sample. The SEM images were obtained from gold-coated fracture surfaces of Na-Pal sample mounted on stubs.

Batch kinetic experiments

A 1,000 mg/L stock calcium standard solution was prepared with the aim of performing batch kinetic experiments. The initial concentrations of 20, 50, 100, 200, and 400 mg/L were created from the dilution of stock solution for the investigation of the removal efficiency of Na-Pal in different initial concentrations of calcium ions. Different Na-Pal dosages were also tested (1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50 and 60 g/L). Further experiments were carried out with a Na-Pal dosage of 30 g/L, due to the efficient decrease of calcium (>85%) and the maintenance of the low cost due to the small quantity of adsorbent dosage. Moreover, the ideal conditions of temperatures (22, 25, 29, 38, 45, $54 \pm 2 \text{ }^{\circ}\text{C}$), pH (2, 2.5, 2.75, 3, 4, 5, 6, 7.2, 8, 9, 10, 11, 12) and optimal contact time (5, 10, 15, 30, 300, 600, 1,800 sec) were investigated for the specification of ideal circumstances of sorption's reaction. The equilibrium time was at 300 sec and room temperature was used for the other measurements. The

EPA 215.2 method (EPA 1983) was applied for the measurement of calcium concentrations carried out via titration with EDTA (Jeong *et al.* 2017). Experiments carried out in triplicates and removal efficiency (% R), with error bars were calculated by the below equation:

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i is the calcium initial concentration and C_e the equilibrium concentration.

Isotherms' study

Langmuir and Freundlich isotherm models were performed with the aim of the investigation of the calcium ions' relationship to the sorbent's surface sites (Chen & Zhang 2014) based on experimental results. The below equations were used for the calculation of the linear form of the Langmuir isotherm model:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \left(\frac{1}{q_{max}} \right) C_e \quad (3)$$

where q_e is the mg of the sorbed calcium per gram of the sorbent (mg/g), C_0 is the initial calcium concentration (mg/L), C_e is the remaining concentration of calcium in the solution (mg/L), V is the solution's volume where the calcium sorption took place (L), and m is the mass of the Na-Pal (g). The q_{max} is the calcium ions' maximum uptake and the K_L is the Langmuir binding constant, calculated from the slope and the intercept of the C_e/q_e against C_e plot, respectively. Subsequently, the constant separation factor R_L was calculated by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Depending on the R_L value, the Langmuir isotherm can be specified as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Azouaou *et al.* 2010).

The Freundlich isotherm's model linear form was calculated by the below equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where q_e is the mg of the sorbed calcium per gram of the Na-Pal (mg/g), and C_e is the remaining calcium concentration in the solution (mg/L). K_F is the capacity of the sorbent, and n is the Freundlich constant, calculated by the intercept and the slope of the $\ln q_e$ against $\ln C_e$ plot, respectively. The heterogeneity of the sorption reaction is characterized by the n value (Aydin Temel & Kuleyin 2016). When the value of $1/n$ is $0 < 1/n < 1$, the reaction is favorable; when $1/n = 1$, the reaction is linear and irreversible; and when $1/n > 1$, the reaction is a chemical process and unfavorable. In the case of $1/n < 1$, the reaction is characterized as physical, whereas it is only slightly suppressed at lower C_e values (Chen & Zhang 2014; Aydin Temel & Kuleyin 2016).

Thermodynamic analysis

Thermodynamic analysis was performed to calculate the Gibbs free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) values for the detailed description of Ca^{2+} sorption's nature. Based on these values, the sorption reaction can be characterized as endothermic or exothermic and spontaneous or non-spontaneous. The Ca^{2+} removal was examined at 22, 25, 29, 38, 45 and 54 °C, and the thermodynamic parameters calculated by the following equations:

$$K_d = \frac{q_e}{C_e} \quad (6)$$

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

where K_d is the distribution coefficient (mL/g), q_e is the mg of the sorbed calcium ion per gram of the Na-Pal (mg/g) and C_e is the remaining Ca^{2+} concentration in the tested solution (mg/L). The $\ln K_d$ plotted against $1/T$ resulted the linear Van't Hoff plot, where the slope and the intercept represent the $\Delta H^\circ/R$ and $\Delta S^\circ/R$ values, respectively. Based on Equation (7), where R is the universal gas constant (8.314 J/K mol) and T is the absolute temperature (K) (Temel & Kuleyin 2016), the standard enthalpy change (ΔH°) was calculated in (kJ/mol) and the standard entropy was calculated in (J/K mol). Equation (8) was used for the measurement of the Gibbs free energy (kJ/mol).

Adsorption kinetic models

The surficial characteristics and adsorption mechanism of Na-Pal was given by the adsorption kinetic models (Karri *et al.* 2017). Pseudo-first and pseudo-second order kinetic models were applied in order to indicate if the adsorbate is adsorbed on a single surface at a time, or on two active sites at time t, and a chemisorption nature, respectively (Genethliou *et al.* 2021). The linearized forms of pseudo-first and pseudo-second order models are expressed in Equations (9) and (10) respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where q_e is the Ca^{2+} removal capacity of the adsorbent (mg/g), q_t the Ca^{2+} removal capacity at time t (mg/g), k_1 (1/min) and k_2 (g/mg min) are the rate constants of calcium adsorption for the pseudo-first and second order kinetic models, respectively. The k_1 and the q_e of the pseudo-first order model can be determined from the slope and the intercept of the linear plot of $\ln(q_e - q_t)$ vs. t respectively, and k_2 and q_e of the pseudo-second order from the intercept and slope of the linear plot of t/q_t vs t respectively.

RESULTS AND DISCUSSION

Samples' characterization

XRD analysis verified the sufficient modification of palygorskite with NaCl (Figure 1). The characteristic diffraction peaks at 10.6 Å, 4.47 Å, 3.28 Å, and 2.54 Å of palygorskite are evident in both the samples, representing the crystal structure of the mineral XRD is a primary technique for the examination of critical characteristics, such as crystal structure, its phase

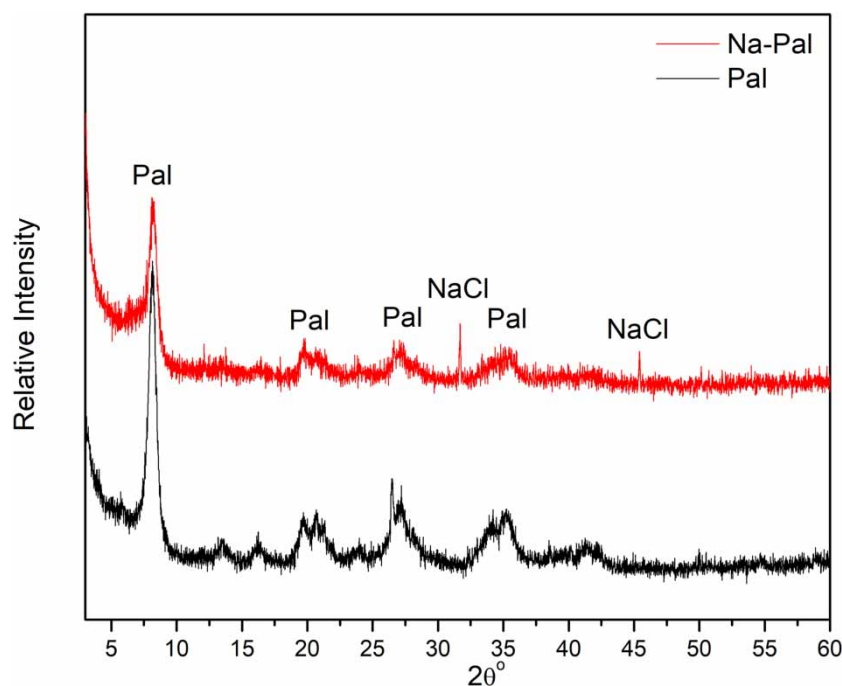


Figure 1 | XRD patterns of raw (Pal) and NaCl-treated palygorskite (Na-Pal) samples.

identification, crystallite size and unit cell dimensions, and so on. Measurements are given in Angstroms (1 Angstrom = 0.1 nm), based on Bragg's Law (Englert 2007; Akbari *et al.* 2011). The above peaks correspond to 8.34° , 19.80° , 27.07° , and 35.27° 2θ . Due to the presence of sodium ions, the peaks of palygorskite are less intense in comparison with the raw palygorskite sample. Moreover, in the Na-treated sample, the presence of sodium chloride particles (NaCl) was found by the characteristic peaks at 2.82 \AA and 1.99 \AA (31.17° and 45.60° 2θ), and confirmed also by the literature (Batdemberel *et al.* 2015).

FT-IR spectra of both palygorskite and Na-treated palygorskite samples (Figure 2) presented the characteristic bands of palygorskite due to the Si-O bond stretching of the mineral at $1,000 \text{ cm}^{-1}$ (Gionis *et al.* 2006). At $1,200 \text{ cm}^{-1}$, the characteristic band of the Si-O-Si bond that is created between the neighbouring ribbons is obvious (Madejová *et al.* 2017). The inner space water's bending modes are presented at $1,650 \text{ cm}^{-1}$ (Mendelovici & Portillo 1976). The characteristic bands in the optical absorption spectrum of the NaCl particles are obvious in smaller wavelengths than 400 nm , where strong near-ultraviolet adsorption is highlighted. In the visible region, the NaCl is transparent and no characteristic bands are observed (Addala *et al.* 2013). For this reason, in the Na-Pal sample, the creation of new bonds was not observed. A small shift between the patterns was detected due to the sodium ions that interacted with the pure palygorskite.

The fiber morphology and efficient sodium-modification of the palygorskite sample was verified also by SEM-EDS analysis. In Figure 3(a), the presence of sodium in the sample of palygorskite is given by pseudocolorization of the sodium-treated sample with red color. The sum spectra, from the point elemental analysis, is given in Figure 3(b), where the peak of sodium is presented. For the sodium modification, a NaCl solution was used and some chlorine ions remained in the sample after the treatment procedure. The presence of non-diluted NaCl particles was verified also by this technique, which is in agreement with XRD analysis. When the point elemental analysis was performed in parts of the sample that included NaCl particles, a higher content of sodium was measured in the samples. In such cases, the red color that corresponds to the pseudocolorization is concentrated in these particles. In contrast with NaCl particles, the dispersion of sodium onto the clays was found to extend in the whole sample, as red points presented all over the tested surface, and this can be described by the efficient maintenance of sodium in the palygorskite structure. In Table 1 the % compound is given, as derived from the point elemental analysis of five different parts of the tested sample. The measurement considers the elements as fully oxidized (Konopka 2013) and for this reason the chloride is not included. The major elements of the tested sample, Mg, Al, Si, Fe and Ca, were determined and agreed with the available literature for the palygorskite deposit

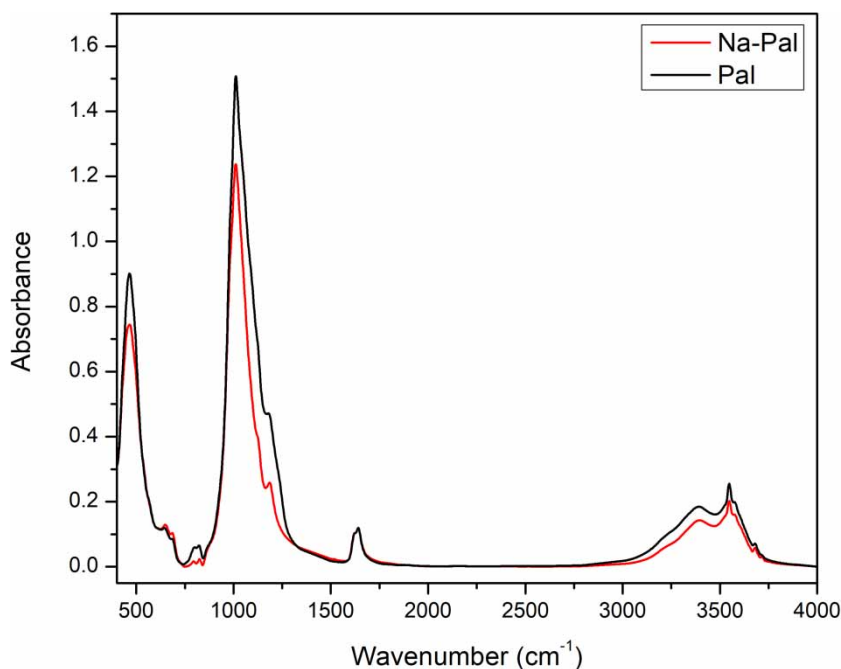


Figure 2 | FT-IR spectra of raw (Pal) and NaCl-treated palygorskite (Na-Pal) samples.

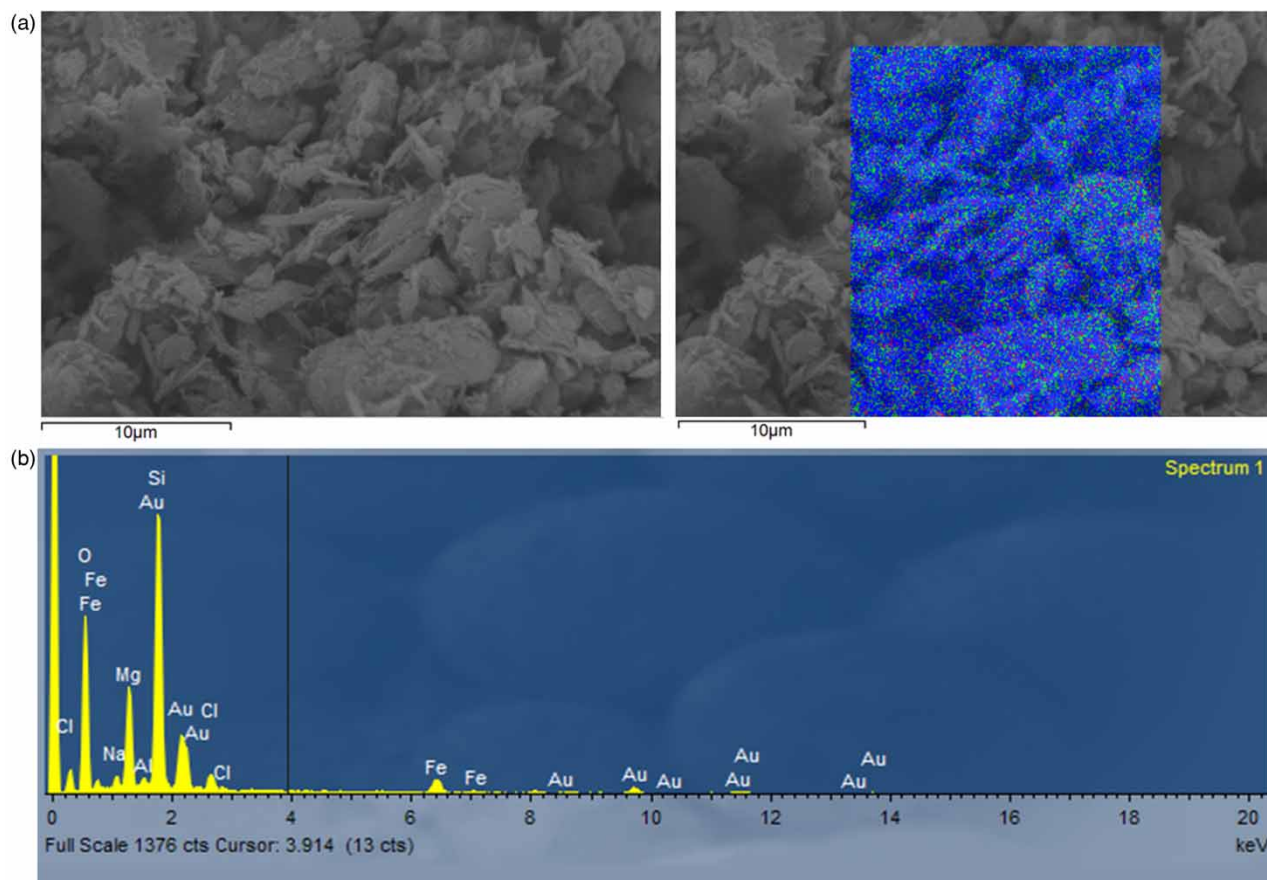


Figure 3 | SEM pictures of Na-Pal sample without and with pseudocolorization (Si, Mg and Na representing with blue, green and red color, respectively) (a) and sum spectra from the point elemental analysis of SEM-EDS (b).

Table 1 | Quantification of elements in the Na-Pal sample by SEM-EDS analysis

Element	Compound %	Error %
Na	4.386	0.408
Mg	16.618	0.426
Al	2.342	0.184
Si	60.318	0.550
Fe	10.426	0.476
Ca	0.326	0.040

of Western Macedonia (Kypritidou *et al.* 2016). The lack of sodium in this deposit was reported by Kypritidou *et al.* 2016, while after the sodium-treatment procedure of the present study, Na reached a value of $4.386 \pm 0.408\%$.

Batch kinetic experiments

Effect of the initial concentration of calcium and the sorbent dosage

Na-Palygorskite was applied in standard solutions for removal of various Ca^{2+} initial concentrations (20, 50, 100, 200, and 400 mg/L). An indicative amount of 1 g sample was added in 50 ml of each solution (20 g/L) in order to examine the potential Ca^{2+} removal capacity of the Na-treated mineral. In Figure 4, it can be observed that Ca^{2+} removal capacity of Na-Pal is negatively correlated with Ca^{2+} concentration increase, since for the minimum examined concentrations (20–50 mg/L) almost

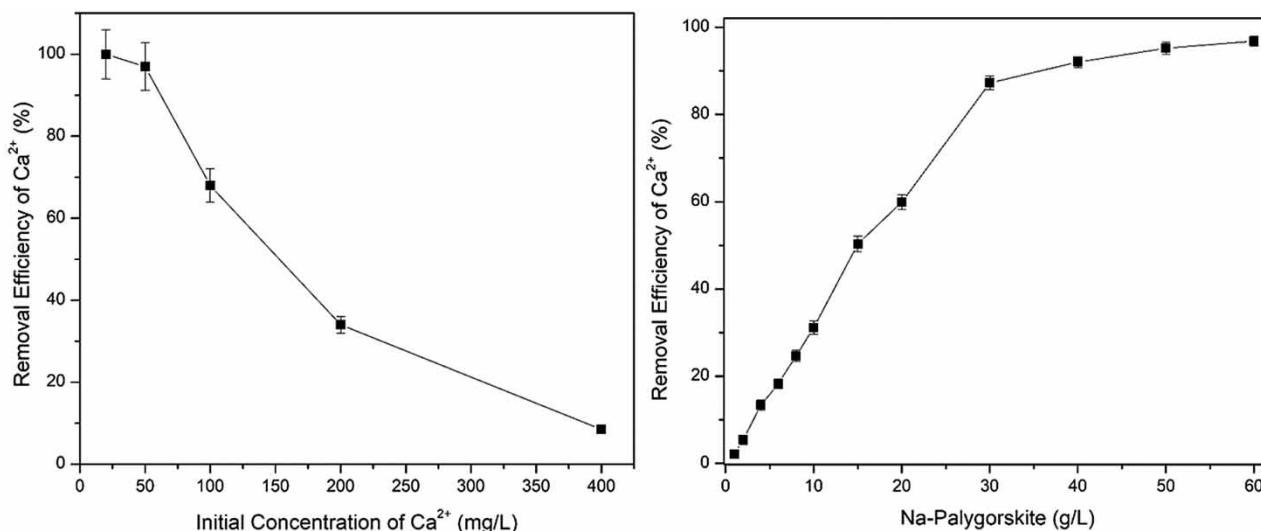


Figure 4 | Effect of initial concentration for Ca²⁺ removal with a dosage of 30 g/L Na-Palygorskite sample, at pH = 7, room temperature and equilibrium contact time 300 sec (left), and effect of Na-Palygorskite sample dosage at initial concentration of 100 mg/L Ca²⁺, pH = 7, room temperature, and equilibrium contact time 300 sec (right).

100% removal was achieved, contrary to the maximum examined ones (i.e. 400 mg/L), which were decreased up to 10%. Moreover, the moderate examined Ca²⁺ concentrations were satisfactorily decreased, as 65 and 40% removal were reached at 100 mg Ca²⁺/L and 200 mg Ca²⁺/L respectively. The examined concentrations were increased in order to be representative of Ca²⁺ concentration in soft, moderate, hard, and very hard waters, respectively. The water hardness is mainly expressed by CaCO₃ concentration; however, the Ca²⁺ is the hardening element that mostly defines the final hardness. Thus, 100 mg/L is close to the upper Ca²⁺ concentration limit in water of 120 mg/L (Kadir *et al.* 2017) and can be representative of the concentration of moderate water, or even hard, if it exists under the CaCO₃ form. This is the reason why the concentration of 100 mg/L Ca²⁺ was chosen as the feed concentration for the following batch tests. According to the above mentioned, Na-Pal can be exploited as a sufficient Ca²⁺ sorbent or ion exchanger, which can also treat moderate or hard water samples. For a more detailed investigation, Na-Pal was also applied in a variety of dosages (1–60 g/L) for the degradation of 100 mg Ca²⁺/L. As is shown in Figure 4, as much the sample's dosage is increasing as higher removal rates are gained. Specifically, when 40–60 g/L are applied, Ca²⁺ is decreased more than 90%, rendering palygorskite capable of softening a moderate or even hard water sample. However, the demanded amount of 60 g/L is not insignificant, leading to increased cost of the procedure; nevertheless, this amount can be mitigated to the half sample amount, at 30 g/L according to Figure 4, where it can be shown that the Ca²⁺ removal exceeded 85%, which is sufficient for water softening and more cost-effective as well. In comparison with a natural kaolinite sample, the Na-Pal had a much enhanced removal capacity for smaller initial concentrations of Ca²⁺ (<100 mg/L), while kaolinite was more effective when the Ca²⁺ concentration increased (>100 mg/L) (Gascó & Méndez 2005). 0.0025 g/L of kaolinite presented a 37.9% removal for 100 mg/L for pH 6.5 and room temperature, while 30 g/L Na-Pal reached a removal of 85% (Gascó & Méndez 2005). Despite that, the sorbents' dosage is not comparable and more experiments in the same scale are needed for the characterization of the most efficient sorbent. Surfactant-modified bentonite was examined in the study of Kadir *et al.* (2017), where the maximum achieved removal of 120 mg/L Ca²⁺ reached 66.67% when 8.75 g/L of 0.75:1 Bentonite:Polyvinyl acetate was used under unknown pH and temperature conditions. Despite the fact that this value was reached for smaller adsorbent dosage than the one proposed in our study, the decrease from such composite was carried out at 60 min (Kadir *et al.* 2017), contrariwise with the simultaneous removal of Ca²⁺ from Na-Pal. It is important to highlight that bentonite is one of the most commercial clay minerals, which was modified for enhanced water softening, with a modification method that demands a high cost, while surfactants may not be so environmentally-friendly. Despite that fact, the Ca²⁺ was not degraded as much as with the Na-modified palygorskite that was used in the present study, which demanded less cost, and also sodium salts are non-toxic either for the environment or for organisms. Based on the literature, the cation exchange capacity (CEC) values of palygorskite mineral aren't so high in comparison with kaolinite or bentonite (Table 2), but palygorskite's specific structure with various functional groups and the high

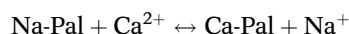
surface area, is capable of adsorption of high quantities of heavy metals from water (Shirvani *et al.* 2006). Moreover, as Tai *et al.* (2016) reported, the sodium modification of palygorskite mineral increased the CEC of the raw palygorskite from 0.278 mmol/g to 0.385 mmol/g, which can increase the calcium adsorption capacity of the Na-Pal sample. To summarize, 30 g/L of Na-Pal were selected as the optimal and cost-effective dosage for 100 mg Ca²⁺/L removal, which are the initializing parameters for the next batch series tests.

Effect of temperature

The sensitivity of the Ca²⁺ removal in temperature fluctuation is demonstrated in Figure 5. Temperatures from 22 to 54 °C were tested and the removal of calcium ions remained almost stable for the temperature range of 22–45 °C. At these values, the removal efficiency was high and remained close to 85%. In higher temperature (54 °C), the removal efficiency of the calcium ions was significantly decreased by up to 10% in comparison to the other tested temperatures, due to the exothermic nature of the sorption (see 3.4). In this case, the reaction slows down or follows the reverse direction if the reaction is in equilibrium. Moreover, the results are in agreement with Aragaw & Ayalew (2019) research, where synthesized zeolite from kaolinite was used for the water hardness treatment and it was supported that low temperature triggers the removal of calcium ions by providing the adsorption/ion exchange of an exothermic reaction. Ultimately, the removal of calcium ions at room temperature (close to 29 °C) can be characterized as efficient, with no need for a temperature-controlling system that could increase the cost. Based on the available literature, room temperature conditions were ideal for the sorption of other ions, such as Mn or Cs, by Na-Pal (Vico & Acebal 2008; Wei *et al.* 2019). Due to this, further batch experiments were carried out in such conditions.

Effect of pH

The pH factor was scrutinized as it is a key parameter for the removal of calcium ions (Figure 6). First of all, the removal efficiency was low in acidic conditions (pH values < 3) with reduction less than 75%. As the pH lowers, the H₃O⁺ prevail (Halas *et al.* 2017) and block the ion exchange between the Ca²⁺ ions and sodium places in the palygorskite structure, as H⁺ can substitute the Na⁺ in the palygorskite's active sites. Despite that, in contrast with synthetic zeolite (El-Nahas *et al.* 2020), the adsorption capacity of Na-Pal is still high (75% instead of 65% of the tested zeolite). The removal was drastically increased in pH values higher than 4 (>80%), with an intense adsorption of calcium ions at alkali conditions that reached almost 100% due to the balance between H₃O⁺ and OH⁻, and the adsorption of the positively charged ions in the negative surface of palygorskite's fibers (Potgieter *et al.* 2006). At these circumstances, the calcium removal is favourable, as it is shown in the following equation, where sodium ions can be exchanged by calcium ions (Liao *et al.* 2016), reinforcing both ion exchange and adsorption procedures:



Effect of the contact time

In Figure 7, the effect of contact time for the hardness treatment via Na-Pal is presented. All the tested time periods (5, 10, 15, 30, 300, 600, 1,800 sec) proved efficient Ca²⁺ removal, with values higher than 75%. Nevertheless, the higher removal efficiency was achieved within the 300 sec. The rapid initial stage, supposed to be the result of accessible active sites in the palygorskite structure, in combination with its fine grain, can be a boost for the rapid pace of adsorption (Keyes & Silcox 1994). Clay minerals have the ability to adsorb calcium compounds in the short time of 60 sec (Diamond & Kinter 1966). The removal of calcium ions by the proposed Na-Pal sample, relies in both adsorption and exchange procedures. The

Table 2 | CEC values of kaolinite, bentonite and palygorskite minerals

Material	CEC (meq/100 g)	Reference
Palygorskite (general)	5–30	Singer (1989)
Palygorskite (Western Macedonia deposit)	30	Lazaratou <i>et al.</i> (2020)
Kaolinite	115	Gascó & Méndez (2005)
Bentonite (Guangdong Corporation of Geo-Exploration & Mineral Development)	58.5	Shu <i>et al.</i> (2010)

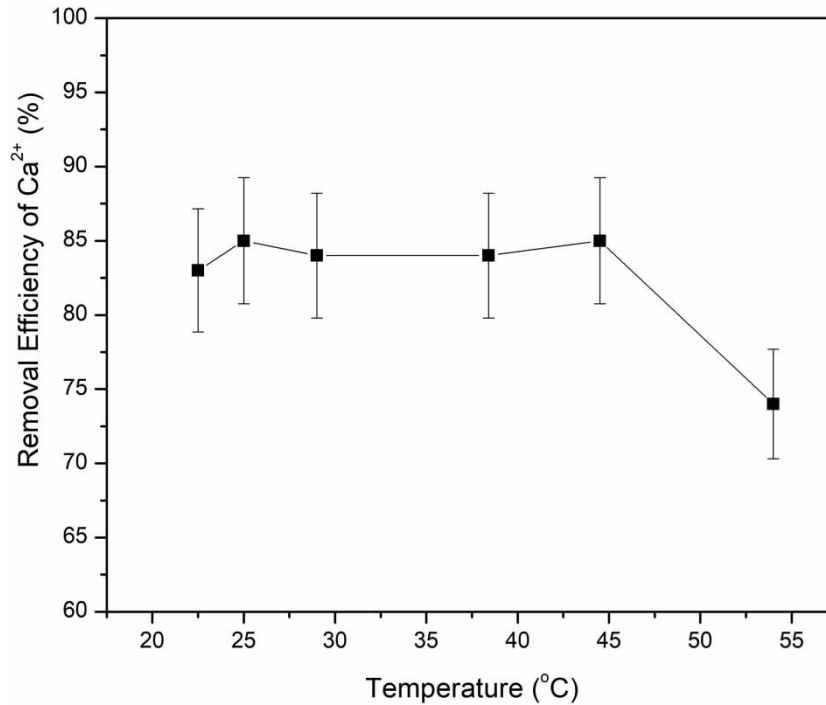


Figure 5 | Effect of temperature for 100 mg/L Ca²⁺ removal by 30 g/L Na-Palygorskite sample at pH = 7, and equilibrium contact time 300 sec.

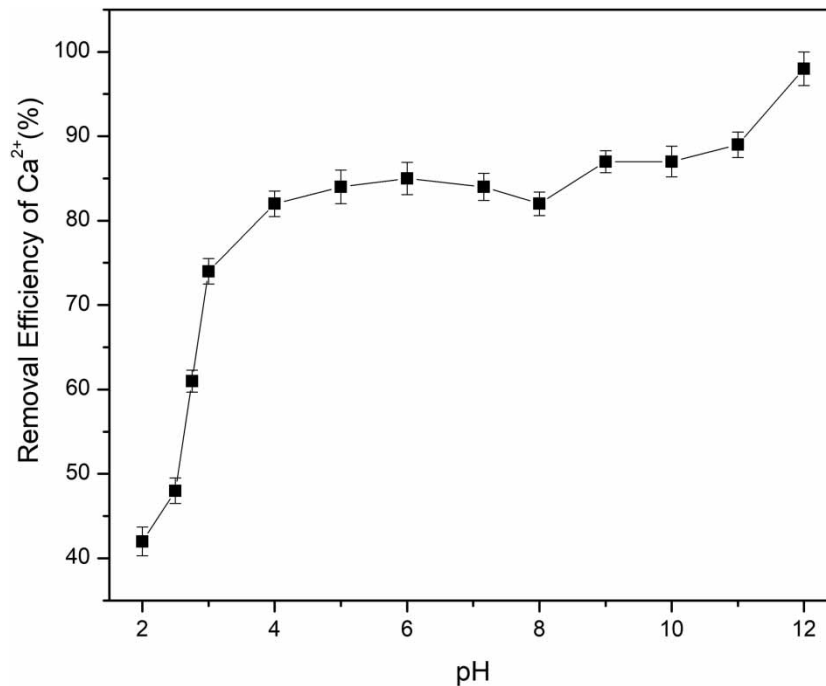


Figure 6 | Effect of pH for 100 mg/L Ca²⁺ removal by 30 g/L Na-Palygorskite sample at room temperature and equilibrium contact time 300 sec.

almost instantaneous reduction of calcium ions by the Na-Pal sample from the 5 first seconds is a result of the ion exchange procedure, which is characterized as an instantaneous mechanism that takes place during the first seconds in general (Farajzadeh *et al.* 2017) and especially for clay minerals (Whittaker *et al.* 2019). After 600 sec, the rhythm of the reaction is slowly

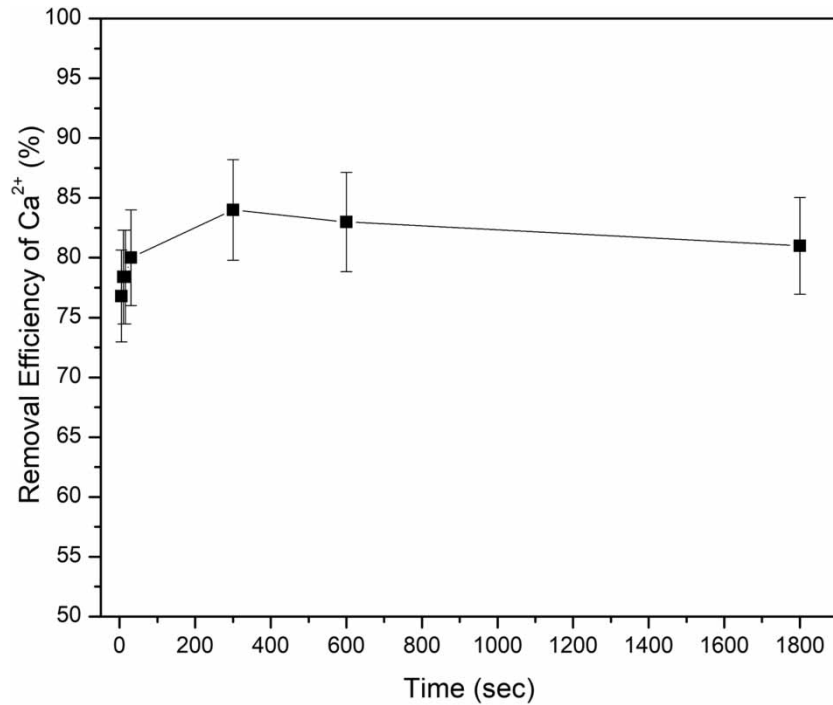


Figure 7 | Effect of time for 100 mg/L Ca²⁺ removal by 30 g/L Na-Palygorskite sample at pH = 7, and room temperature.

decreased due to the fulfilment of palygorskite's potential active sites and the possible start of Ca²⁺ desorption. Despite that, after this critical time the reduction in the calcium ions is almost negligible. After all, as the 300 sec are favourable, they were selected for the performance of batch experiments, while it can be an ideal time for industrial water hardness treatment.

Isotherms models

The nature of the Ca²⁺ adsorption from sodium modified palygorskite was investigated by the application of Langmuir and Freundlich isotherm models (Figure 8) in order to investigate the relationships of the sorbent's active sites and calcium ions (Chen & Zhang 2014). The models were performed for the removal efficiency of 30 g/L for 20, 50, 100, 200 and 400 mg/L

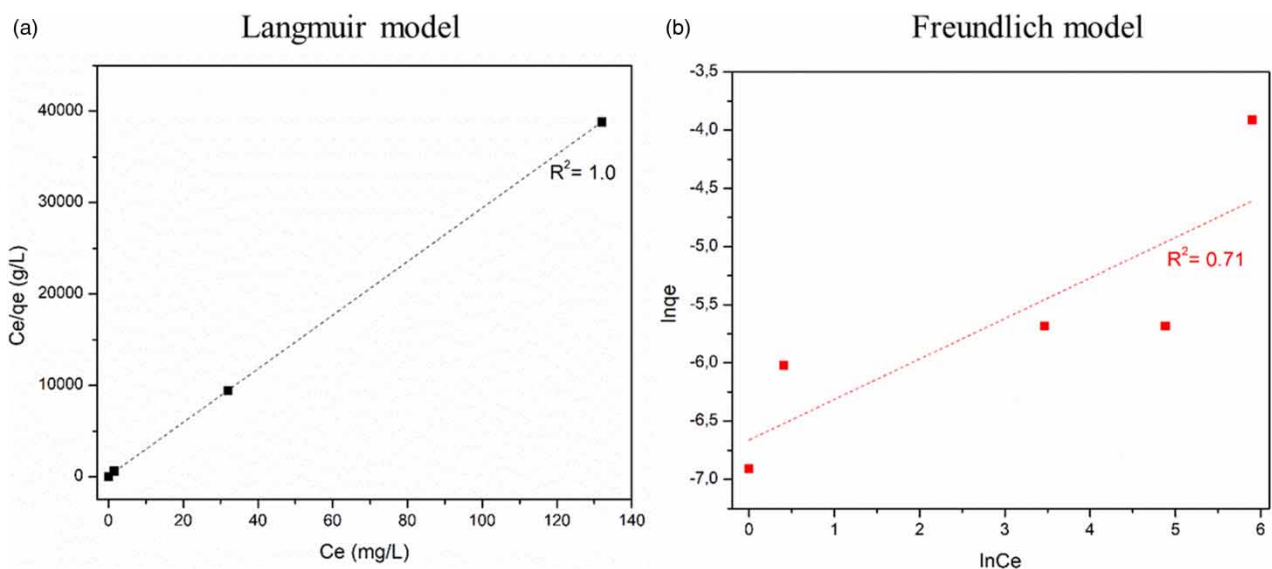


Figure 8 | Linearized (a) Langmuir and (b) Freundlich isotherm models for Ca²⁺ removal by Na-Pal.

Ca²⁺. The parameters for Na-Pal efficiency for both Langmuir and Freundlich isotherm models are given in Table 3. As is shown, the Langmuir isotherm is well fitted in the examined sample with $R^2 = 1$, in contrast with the non-preferred Freundlich isotherm model with $R^2 = 0.71$. According to the R_L value of the Langmuir isotherm model, where $0 < R_L < 1$, the type of isotherm characterized as favorable (Aydin Temel & Kuleyin 2016), which means that the sorption reaction takes place at specific homogeneous sites of Na-Pal. The monolayer nature of the adsorption is in agreement with the literature as calcium-activated palygorskite, which is similar with the sodium-activated palygorskite, or raw palygorskite from the same deposit with the present study reacted by the same process for the sorption of metals (Fe²⁺, Cu²⁺, Ni²⁺) (Bourliva *et al.* 2018; Lazaratou *et al.* 2020).

Thermodynamic analysis

The thermodynamic analysis is applied for investigation of the nature of the adsorption and its description as an endo- or exothermic reaction, as well as the randomness of the Ca²⁺ removal by Na-Pal that is derived from the Gibbs free energy (ΔG^0) equation (Equation (8)). As is given in Table 4, the ΔG^0 values are positive for every case, proving the non-spontaneous nature of the Ca²⁺ adsorption on Na-Pal. Moreover, when the temperature was increased, an increase in ΔG^0 values was demonstrated that indicates the reaction's preference in higher temperatures (Sari *et al.* 2007), which is in agreement with the batch experiments up to the temperature of 45 °C. The standard enthalpy change (ΔH^0) was negative (−10.8197 kJ/mol), indicating the physical (<20 kJ/mol) and exothermic nature of the Ca²⁺ adsorption reaction. The value of entropy change (ΔS^0) was negative, with values less than −10 J/mol, which is the critical value for the characterization of the reaction's mechanism as associative or dissociative (Atwood 1997), leading to the conclusion that Ca²⁺ sorption on the Na-Pal surfaces is an associative mechanism. In this way, the free energies of activation are considered as the difference between the free energy of the system (Na-Pal and Ca²⁺) and the free energy of the initial materials from which it was formed (Laidler 1965).

Adsorption kinetic models

The linear forms of pseudo-first and pseudo-second order kinetic models were applied in order to investigate the Ca²⁺ adsorption mechanism on Na-Pal. Table 5 presents the relative kinetic parameters, proving that the linear form of the pseudo-first order model does not fit on the Na-Pal adsorbent due to the correlation coefficient $R^2 < 0.0003$. Moreover, q_e , which is a critical parameter for the adsorption mechanism, is not efficiently calculated from the pseudo-first order plot (q_{ecal}), since it is much smaller than the q_e that resulted from the batch tests (q_{eexp}). Quite the opposite, the pseudo-second order kinetic model has a better fit on Na-Pal, since the R^2 value is 0.9996. In addition, the q_{ecal} form pseudo-second order plot is correlated with q_{eexp} , with values of 2.996 and 3.000, respectively, expressing adequately the Ca²⁺ removal capacity by Na-Pal. The results of the present study agree with other studies focused on the metals' removal capacity of palygorskite. When

Table 3 | Langmuir and Freundlich isotherm models constants for Ca²⁺ removal

	Langmuir constants				Freundlich constants		
	q_m	K_L	R_L	R^2	K_F	$1/n$	R^2
Na-Pal	3.41	4.2191	0.0012–0.0117	1	1.279	0.3479	0.712

Table 4 | Thermodynamic parameters for Ca²⁺ removal by Na-Pal

T (K)	K_d	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol·K)
295	0.244	3.0612	−10.8197	−46.9503
298	0.283	3.1786		
302	0.263	3.3664		
311	0.263	3.8077		
318	0.283	4.0941		
327	0.142	4.5401		

Table 5 | Kinetic parameters of pseudo-first and pseudo-second order kinetic models for Na-Pal

	Pseudo-first order				Pseudo-second order		
	q_{exp} (mg/g)	q_{ecal} (mg/g)	k_1 (1/min)	R^2	q_{ecal} (mg/g)	k_2 (1/min)	R^2
Na-Pal	3.000	0.248	0.0027	0.0003	2.996	-0.5606	0.9996

palygorskite was investigated for the removal of Pb^{2+} , Co^{2+} , Ca^{2+} , Mg^{2+} , K^+ and Na^+ , the pseudo-second order kinetics expressed better the adsorption procedure, rendering a chemisorption (Chen & Wang 2007; He *et al.* 2011; Nel *et al.* 2014). The rate constant k_2 has negative value, which indicates a desorption process (Tan 2018) and this is in agreement with the contact time batch experiment, where partial desorption takes place in the system after 300 sec, due to the rapid Ca^{2+} adsorption on Na-Pal active sites in combination with the instantaneous ion exchange of Na^+ and Ca^{2+} .

Based on the abovementioned, Na-Pal can be efficiently used as a powder for the treatment of moderate to even hard waters (100 mg/L to 200 mg/L Ca^{2+}) or the pre-treatment of very hard waters followed by supplementary procedures. The ideal amount of the adsorbent for the maintenance of low cost in combination with the enhanced Ca^{2+} removal is 30 g/L. The Na-Pal powder was found to react sufficiently in all the tested temperatures (22–54 °C) and in pH values from 4–12, which means that the specification of such conditions is not needed. Due to this, no extra equipment is required for the maintenance of pH or temperature. The reduction of calcium ions was a rapid procedure that completed during the first 5 min, due to the nature of the reaction, which is based in both adsorption and instantaneous ion exchange mechanisms. The use of Na-Pal material in other forms, such as granola filters, column-adsorption systems, and so on, is interesting for future researches.

The sustainable management of the tested sample after the enrichment with calcium is mandatory. After the water hardness treatment, the sample can be characterized as Ca-Palygorskite, which can be used as powder for other applications that are already known based on the literature. More specifically, Ca-Palygorskite samples have been efficiently used for the adsorption of heavy metals, and especially Ni (Sheikhhosseini *et al.* 2013), Fe^{2+} (Lazaratou *et al.* 2020), Cd and Pb (Shirvani *et al.* 2015). Summarizing, the procedure can be characterized as waste free, taking into consideration the subsequent usage of Ca-Palygorskite in adsorbent applications.

CONCLUSIONS

Natural palygorskite underwent Na- treatment in order to be examined for Ca^{2+} removal and potential water softening. The modification effect was determined via XRD and FT-IR characterization methods. A series of batch kinetic experiments indicated that Na-palygorskite can efficiently degrade Ca^{2+} by more than 85% for a range of 20 mg/L to 200 mg/L with 30 g of sample addition, rendering palygorskite as well as Na-modification significant factors for sufficient Ca^{2+} removal, and moderate or hard water softening. The exchange of Na^+ with Ca^{2+} was found not to be pH or temperature dependent, while high removal rates were achieved for pH values 4–12, which are the most common for water samples, as well as at all the examined temperatures. Na-palygorskite can be a cost effective and environmentally friendly solution for water softening that takes place rapidly, within 5 min. The probably simultaneous, Ca^{2+} adsorption on palygorskite surface and exchange with Na^+ led to high removal rates, in which the procedure is physical and takes place in one homogeneous layer, as was expressed by thermodynamic analysis and the Langmuir isotherm model, respectively. The linear form of the Langmuir isotherm ideally expresses the reaction, since the isotherm is linear according to the correlation coefficient $R^2 = 1$, while based on the ΔG^0 , ΔH^0 , and ΔS^0 values from thermodynamic analysis, the Ca^{2+} removal by Na-palygorskite is a physical, exothermic and associative procedure, respectively. The Ca^{2+} adsorption was chemisorption as it was well fitted to the pseudo-second kinetic model.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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