

# Enhanced nitrates-polluted water remediation by polyurethane/sepiolite cellular nanocomposites

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## **Abstract**

Nanocomposite hydrophilic flexible polyurethane foams were prepared by in situ polymerization using an organomodified sepiolite as filler. The sepiolite affinity by nitrates dissolved in water was increased by treating them with quaternary ammonium salts (S-QAS), leading to remarkable nitrates maximum adsorption capacity ( $q_{\max} = 23.30$  mg/g). The Langmuir model well described the adsorption process of the nitrates by the modified sepiolite, and more remarkably, the sepiolite suffers no decrease of their nitrates removal capacity after being imbibed in the flexible polyurethane foam. The proper selection of the polyurethane chemistry allows significant contact between the polluted-water and the sepiolite, even when enclosed inside the cell walls. Accordingly, the as-prepared hydrophilic polyurethane/sepiolite foams provided a facile removal of nitrates-pollution from water, even actual nitrates-polluted water with a competitive adsorption environment, without the need to control or modify the pH and temperature of the polluted water neither to add further filtration steps to collect the active particles from the water.

## **Keywords**

Nitrate removal; Adsorption; Polyurethane; Sepiolite; Wastewater.

## 1-Introduction

Providing access to potable water to the entire population is a global issue of utmost relevance. According to the United Nations (UN), about 11 % of the world's population still does not have access to drinking water, and it is expected that in 2025 half of the entire population is likely to live in water-stressed areas (World Health Organization, 2019).

An important water pollution problem in the entire world is the pollution by nitrogen-containing compounds such as nitrate, nitrite, and ammonium. Specifically, the toxicity of nitrates ( $\text{NO}_3^-$ ) to humans is mainly attributable to a reduction of the oxygen transport to the tissues, called methemoglobinemia, which affects principally to infants under 3 months of age (Guidelines and Quality, 1995). Although the application of the European Union (EU) Nitrates Directive has decreased the nitrates concentrations in both surface and groundwater, nitrates pollution and eutrophication continue to cause problems in many Member States of the EU (**Fig. S.I-1** shows the areas of the EU declared as “Nitrates Vulnerable Zone”) (European Commission, 2018).

Although nitrates are naturally present in open waters, its concentration can rise over the safety thresholds due to human activity. The intensive use of nitrogenate fertilisers (e.g., potassium nitrate or ammonium nitrate), irrigation of crops with domestic residual waters, urban or industrial organic waste, and, above all, the use of manure and slurry derived from livestock activities as fertilizers cause nitrates to release into open waters. Nitrates readily dissolve into the water and reach the human water supply, being difficult to detect due to their odourless and tasteless, but they are potentially toxic (European Commission, 2018). A joint committee of FAO/WHO (JEFCA) established in 2002 that the maximum acceptable daily intake of nitrates is 0.3-0.7 mg/kg (APSSA, 2003). While for human water supply, the

WHO fixed a maximum level of 50 mg/L of nitrates, as well as a quality indicator value of 25 mg/L (APSSA, 2003).

Nevertheless, best available technologies developed for drinking water production to treat nitrate-contaminated water such as reverse osmosis, ion exchange (Matos et al., 2009), nanofiltration (Mahvi et al., 2011; Yousefi et al., 2016), and electrodialysis (Song et al., 2019) cannot be used in-situ to treat polluted water resources due to their technological complexity (Yu et al., 2017). Other alternative processes, such as chemical reduction (Mohanty et al., 2016), adsorption (El Hanache et al., 2019; Rezaei Kalantary et al., 2016), and biological denitrification (Jiang et al., 2018), have been proposed as in-situ remediation techniques (Della Rocca et al., 2007). Among these approaches, adsorption has been explored widely as a nitrate removal technology and offers satisfactory results, especially with mineral-based and/or surface modified adsorbents (Bhatnagar and Sillanpää, 2011). Sepiolite, which is a fibrous magnesium silicate mineral ( $\text{Mg}_4\text{Si}_8\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ ), has been successfully tested as a sustainable adsorbent for the removal of nitrates from water (Nese Öztürk; T. Ennil Köse, 2008). Their wide availability, cost-efficiency, high surface area, and nitrates sorption capability make sepiolite particles a proper candidate for this application (Ugurlu et al., 2011).

Although natural sepiolite can adsorb nitrates from water (Ozcan et al., 2005), their performance can be enhanced by modifying their surface (Öztürk and Bektaş, 2004). For instance, the enhanced mechanism of nitrate adsorption on sepiolite activated by HCl treatment was reported to be ion exchange between the nitrate anions in solution and chloride anions attached to the positively charged surface  $\text{H}^+$  sites produced by the acid treatment. This activation promoted nitrates adsorption from 3.46 to 9.80 mg/g (Öztürk and Bektaş, 2004). Other treatment procedures also proved to enhance the nitrates adsorption performance of the sepiolite. Ozcan et al. (Ozcan et al., 2005) presented sepiolite treated with nonfunctional surfactant dodecylethyldimethylammonium bromide with an increased nitrates adsorption capacity of 453 mmol/kg (equivalent to 28.0 mg/g, while the unmodified sepiolite adsorbed

25 mg/g). For the sake of comparison, these results, as well as other works employing sepiolite as adsorbents of nitrogen-containing pollutants, are summarised in **Table S.1** (see Supplementary Information).

The abovementioned works employed the pristine or treated sepiolite in powder form to be dispersed into the polluted water. This approach takes advantage of the high surface area of the sepiolite in powder form, but at the same time, the use of powder dispersed into the polluted water requires of a complicated additional remediation step, in which the powder should be separated and extracted from the water (Chavan et al., 2016a). A suitable approach to avoid this additional procedure is to anchor the active adsorbent particles to a macroscopic substrate, which could be easily handled and extracted from the water after the nitrates removal. This approach was previously proved in the remediation of heavy metal ions, by incorporating the adsorbents (nanocrystals or coffee waste powder) on the surface of the cell walls of open-cell polymer foams, which high specific surface that allows the interaction between the active particles and the polluted water (Chavan et al., 2016b, 2016a).

The incorporation of fillers as an additive onto polymer foams is well acknowledged and could provide a significant improvement in the physical properties (Mohd Zaini et al., 2017). For instance, sepiolite has often been used as fillers of plastics and polymeric foams. On the one hand, they allow improving various properties, such as mechanical (Janković-Častvan et al., 2016) and thermal properties (Tabatabaei-Yazdi and Mehdipour-Ataei, 2015). On the other hand, they can modify the crystalline structure of polymers (Mejía et al., 2013), acting as nucleants (Cobas et al., 2014), or increase the nucleation of cells during foaming processes (Pardo-Alonso et al., 2012).

In all cases, a fundamental aspect to achieve these effects is obtaining an excellent dispersion of the sepiolite inside the polymer (Alan and Işçi, 2014; Torró-Palau et al., 1997), being sometimes necessary a chemical modification of the surface of the sepiolite, which improves the compatibility between the sepiolite and the polymer and allows achieving a better dispersion (Chen et al., 2011).

However, none of these sepiolite-polymeric foam composites have previously been used for the treatment of contaminated water. This is because the obtained improvements are achieved by dispersing the sepiolite inside the polymeric matrix, hindering the interaction between the active charges and the contaminated water (i.e., a nanoparticle imbibed inside a polymeric wall with a thickness of tens of microns could not interact with the water in contact with the cell wall of the foam). To use these materials for the treatment of contaminated water, it is necessary that sepiolites are located preferentially in the surface of the cell walls, or that the polymer matrix is permeable to water and allows the interaction between the contaminated water and sepiolite imbibed in the polymer matrix.

The use of polyurethane nanocomposite foams for the in-situ remediation of water polluted with nitrates is proposed. Polyurethane (PU) foams are one of the most versatile foamed materials, with a wide range of applications in industries such as building, sports, furniture, naval, and automotive. These materials can present very low density, high acoustic and thermal insulation, a wide range of mechanical properties, and low cost (Santiago-Calvo et al., 2018). These features make PU foams an excellent choice to develop a porous substrate in which the active particles can be fixed.

Accordingly, natural and modified sepiolites were introduced into open-cell hydrophilic polyurethane foams, which showed the capability to enable the interaction between the polluted water and the sepiolite imbibed in the polyurethane matrix. The optimization of these foams, regarding their porous structure, chemical composition, and the modification and dispersion of the sepiolite allow reaching a high efficiency in the elimination of nitrates, as high as the performance of the modified sepiolite in powder form (about 23 mg of nitrates per g of sepiolite).

## **2-Materials and Methods**

### **2.1-Materials**

A polyurethane prepolymer with a density of 1.20 g/cm<sup>3</sup> and viscosity about 16-18 Pa·s at 25°C was used for the production of the flexible foams. This prepolymer was employed together with distilled water and a surfactant TEGOSTAB B 8522 (polyether-polydimethylsiloxane-copolymer), provided by Evonik Industries, to obtain open cell flexible polyurethane foams.

Sepiolite clays, in particular, hydrated magnesium silicates (formula Mg<sub>4</sub>Si<sub>8</sub>O<sub>15</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O), natural and surface-modified, were provided by TOLSA S.A (Spain) and employed as fillers. These sepiolite particles present a needle-like morphology with an average particle length ranging between 1 and 2 μm, and a thickness about 10-12 nm (García et al., 2011). Natural sepiolite (García et al., 2011) before (Sepiolite\_N) and after treatment with quaternary ammonium salt (Sepiolite\_S-QAS) was studied (García-López et al., 2010). After the treatment, the sepiolite incorporated a 20.54 wt.% of quaternary ammonium salts.

Sodium Nitrate (NaNO<sub>3</sub>, M = 84.99 g/mol, solubility in water at 20°C > 100g/L, melting point: 307°C) was obtained from Quimipur (Spain) and mixed with distilled water to prepare the nitrates solutions.

#### 2.1.1-Preparation of nanocomposite polyurethane foams (SePU).

First, the surfactant was added to the prepolymer (1 wt.%), and the mixture was mixed (EUROSTAR Power control-visc P1, IKA with a 50 mm diameter Lenart disc stirrer) during 2 min at 1,000 rpm and room temperature (RT). Then, the corresponding amount of pristine or treated sepiolite (0, 1, 3, 5, 8, and 10 wt.%, being the nominal sepiolite weight percentage (wt.%) on the final foam related to the prepolymer mass employed to fabricate the foam) was introduced to the blend, and mixed for 2 min at 1000 rpm. Finally, cold distilled water was dropped into the formulation (1:1 wt. with respect to prepolymer) and mixed during 12 seconds at 2,000 rpm to obtain the polyurethane foams. After the mixing, the final formulation was allowed to grow and dry during 24 h in an oven at 70<sup>0</sup> C to complete the foam formation. Bulk cylindrical samples with a height of 6 cm and a radius of 5 cm were obtained.

Cubical samples of  $1 \text{ cm}^3$  were cut from the bulk PU foams and washed before performing further characterization. The washing process consisted of 3 successive washing cycles. In each washing cycle, the samples were immersed in 1,000 mL of the distilled water bath at room temperature and under shaking for 30 min. This procedure was required to remove any unreacted prepolymer or non-attached sepiolite. It was proved by UV-Vis spectroscopy that the samples did not release any compound into the water after the third washing cycle. Once the samples were clean, they were dried overnight in a vacuum oven at  $50 \text{ }^\circ\text{C}$  to remove the absorbed water before further characterization.

## **2.2-Characterization Techniques**

2.2.1-Scanning Electron Microscopy (SEM). The sepiolite (see Supplementary Information, **Fig. S.I-2**) and polyurethane foams morphology were examined by SEM (Hitachi, flexSEM1000). The foams were cut to expose the cellular structure and coated with a thin gold layer (10 nm) using a Sputter Coater (Balzers, scd004) before SEM observation. Cell size has been calculated by averaging the cell size measured in a satisfactory number of cells (about or over 100 cells). Cell density ( $N_v$ , number of cells per  $\text{cm}^3$  of the foam) has been determined with a software based on ImageJ/FIJI (Pinto et al., 2013), which applies the Kumar method (Kumar, 1988).

2.2.2-BET surface area. Surface area of the pristine and modified sepiolite was determined by BET measurements employing a Surface Area and Porosity Analyzed Micromeritics ASAP® 2,420.

2.2.3-Polymer foam features. First, the density of the foams was determined by weighing the samples and measuring their volume ( $\rho_f$ ,  $\text{kg}/\text{m}^3$ ). Then, the cell connectivity of the foams was measured by using a gas pycnometer Accupyc II 1340 from Micromeritics. As the foams were found to be completely open cell, their porosity ( $V_f$ , volume percentage of the gaseous phase) and relative density ( $\rho_r$ , volume percentage of the solid phase) were also calculated from the picnometry and density determination results.

2.2.4-Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra of the sepiolite and nanocomposite foams were collected using a Bruker Tensor 27 spectrometer working in Attenuated Total Reflectance (ATR) method with an MKII Golden-Gate accessory. Each FTIR spectrum was obtained at room temperature after 32 scans, with a resolution of  $4\text{ cm}^{-1}$  in the range  $4,000\text{-}600\text{ cm}^{-1}$ .

2.2.5-X-ray Tomography. Sepiolite distribution inside the foams was measured by a lab-designed X-ray Tomography system (focal spot size: 5-20 mm,  $2.5\text{ }\mu\text{m}$  resolution, voltage: 20-100 kV, current: 0-200 mA) with a maximum output power of 20W (Solórzano et al., 2013). Once all the projections were acquired, the reconstruction process of the tomogram was carried out using Octopus, a server/client reconstruction package (Dierick et al., 2004). X-ray absorption difference between the polymer matrix and the sepiolite allowed identifying sepiolite agglomerates with sizes around the resolution of the X-ray system.

2.2.6-Water Absorption Capacity ( $q_w$ ). The obtained PU foams were hydrophilic foams with the ability to absorb water and swell. Three samples of each kind were placed into 6 ml of distilled water until they were completely submerged (usually less than 1 min). The  $q_w$  was calculated as the ratio between the weight of water absorbed and the weight of the foam. To this aim, the weight of the foams before ( $w_i$ ) and after ( $w_f$ ) being in contact with the water were measured, and  $q_w$  was calculated using Equation 1 (Barroso-Solares et al., 2016).

$$q_w = \frac{w_f - w_i}{w_i} \quad (1)$$

2.2.7-Thermogravimetric analysis (TGA). The amount of sepiolite incorporated to the foams (wt.%) was measured by TGA, TGA measurements were performed with a Mettler Toledo TGA/SDTA 851e from 0 to  $950\text{ }^\circ\text{C}$  at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$ , under inert atmosphere ( $\text{N}_2$ ).

2.2.8-UV-Vis spectroscopy (UV-Vis). The nitrates concentration on the polluted water was determined by UV-Vis spectroscopy before and after being in contact with the sepiolite or the



nanocomposite foams. Spectra of 300  $\mu\text{L}$  samples of the polluted water were recorded in the wavelength region from 380 to 190 nm using an Ultra-Violet spectrometer - UV-2,102 PC, Shimadzu. Then, the absorption intensity of the main peaks of the spectra was measured for each sample and related to a calibration line performed with stock nitrates solutions with concentrations from 5 to 200 mg/L to quantify the nitrates concentration on each sample.

2.2.9-pH and Point Zero Charge (PZC) determination. The pH of the nitrate solutions employed in this study was controlled during the process, using a pH bench meter Mettler Toledo FE20 equipped with an electrode LE438. Previous works (see **Table S.1**, Supplementary Information) suggested that by controlling the pH, it is possible to enhance the nitrates adsorption. However, in this work, the pH of the nitrates solution and actual polluted waters was not adjusted, to demonstrate the potential performance of the nanocomposite foams in actual scenarios, in which the pH of the water resources cannot be modified.

Moreover, as nitrate ions are negatively charged, they are expected to be adsorbed by absorbents positively charged. In that kind of absorbents, the point zero charge (i.e., the pH at which the net charge of total particle surface (i.e., absorbent's surface) is equal to zero) will limit the range of application of these materials. The pH corresponding to the PZC ( $\text{pH}_{\text{pzc}}$ ) of the sepiolites modified with quaternary ammonium salts (Sepiolite\_S\_QAS) was determined from acid-base titration (Adam, 2016; Zeng, 2013). With this aim, aliquots with 5 mL of distilled water were placed in different vials. Then, the pH of these vials was adjusted from 2.5 to 11 by addition of 0.01 M solutions of NaOH and HCl at room temperature. Once the initial pH was stabilized ( $\text{pH}_o$ ), 2.5 mg of Sepiolite\_S-QAS were added to the solutions and kept under agitation for three days. The final pH of at least two solutions ( $\text{pH}_f$ ) for each initial pH was measured and their average value plotted with respect to the initial pH to obtain the point zero charge value as the intersection between that curve and the  $\text{pH}_o = \text{pH}_f$  line.

2.2.10- Collection of actual polluted waters. According to the Water Framework Directive of the EU, the Spanish Government sustains a control network of the water resources' quality, which results are available to the public. In particular, in the sedimentary plains of the Duero valley (Castilla y Leon, Spain) one of the main pollutants under surveillance are the nitrates (Government of Spain, 2019). Two nitrates-polluted streams (which from now on will be identified as spot 1 and spot 2) were selected using this public information and water samples were collected from both of them and subsequently tested. Coordinates of both streams, as well as details about the last full chemical composition report of their waters, can be found in the Supplementary Information.

### **2.3-Adsorption Experiments**

First, a stock solution of nitrate ions (200 mg/L) was prepared by mixed distilled water with  $\text{NaNO}_3$  at room temperature during 1 h. Then, 40 mL portions of aqueous solutions with different concentrations of nitrate ions (ranging from 10 to 200 mg/L) were prepared from the stock solution to be used for the nitrates adsorption tests. It was tested the adsorption performance of the pristine and modified sepiolite, the quaternary ammonium salts employed in the treatment of the sepiolite, pristine polyurethane foams, and nanocomposite polyurethane foams. Negligible nitrates adsorption was found for the quaternary ammonium salts and the pristine polyurethane foams. On the one hand, the maximum adsorption capacity of the sepiolite was studied by placing 20 mg of the pristine or treated sepiolite on 40 mL of nitrates solutions with concentrations from 20 to 200 mg/L during 3 hours at RT and under shaking at 300 rpm. After this time, the remaining nitrates concentration in the treated solutions was measured by UV-Vis.

On the other hand, the kinetics of the adsorption process was studied for the modified sepiolite and foams. 20 mg of the treated sepiolite or  $1 \times 1 \times 1 \text{ cm}^3$  samples of the polyurethane and nanocomposite foams (containing about 20 mg of the treated sepiolite) were placed in 40 mL of a 100 mg/L nitrate

solution. Their adsorption capacity was calculated by measuring the remaining nitrates concentration in the treated solutions by UV-Vis after contact times of 15, 30, 60, and 180 minutes at RT and under shaking at 300 rpm. Moreover, the effect of the temperature on the nitrates adsorption was studied for the modified sepiolite following the same procedure for contact times of 180 minutes and temperatures of 15° and 45° C. This study allowed the determination of the thermodynamic parameters of the adsorption procedure, such as Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) (Hu et al., 2015), details about the calculation of these parameters can be found in the Supplementary Information (section S.I-5).

In all the cases, the adsorption capacity ( $q$ ) of the sepiolite, both free and enclosed in the polyurethane matrices, were measured in mg of nitrates adsorbed by gram of sepiolite, and calculated by Equation 2 (Doğan et al., 2008).

$$q = \left[ \frac{(C_0 - C_t)}{w_{sep}} \right] \cdot V \quad (2)$$

where  $C_0$  is the initial concentration of nitrates (in mg/L),  $C_t$  is the remaining concentration of nitrates (in mg/L) at a given time  $t$ ,  $V$  is the volume of the treated solution in litres, and  $W$  is the weight of sepiolite employed as an adsorbent in grams.

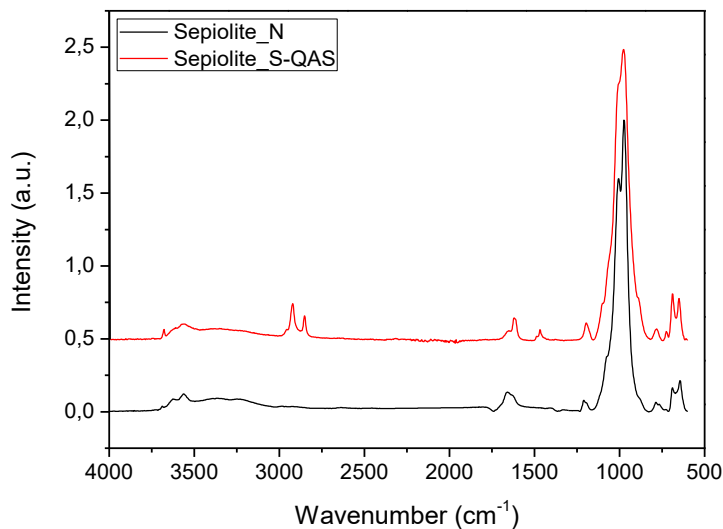
Langmuir (Ouardi et al., 2015; Öztürk and Bektaş, 2004), Freundlich (Ouardi et al., 2015), and Dubinin-Radushkevich (Hu et al., 2015) isotherm adsorption models were employed to fit the experimental data obtained by studying the equilibrium adsorption capacities obtained after 3 hours for different initial nitrates concentrations, details about the models can be found in the Supplementary Information (section S.I-5).

Finally, nitrates adsorption tests from actual polluted waters were carried out using the optimum nanocomposites developed in this work. These tests were carried out following the same procedure abovementioned, at fixed contact times of 180 minutes and RT.

### 3-Results

#### 3.1-Sepiolite characterization

First, it was studied the BET surface area of the pristine (Sepiolite\_N) and treated sepiolite (Sepiolite\_S\_QAS), finding that the treatment with quaternary ammonium salts significantly decreases the surface area of the nanoparticles from 398.0 m<sup>2</sup>/g to 49.1 m<sup>2</sup>/g. This result shows that any potential improvement of the nitrates adsorption provided by the treatment should be mainly related to chemical affinities. Also, it was performed and FTIR analysis of both kinds of sepiolites (**Fig. 1**). The FTIR spectrum of pristine sepiolites (Sepiolite\_N) shows the characteristic bands in the 4,000-3,000 cm<sup>-1</sup> range, corresponding to the vibrations of the Mg-OH group (about 3690 cm<sup>-1</sup>) and coordinated water (about 3,568 cm<sup>-1</sup>). Also, a band about 1670 cm<sup>-1</sup> related to the vibration of zeolitic water and a more complex system of bands characteristic of silicate in the 1,200-600 cm<sup>-1</sup> range. Si-O bonds clearly appear at 1,211, 1,074, and 1,011 cm<sup>-1</sup>; whereas Mg-OH vibrations can be identified at 644 cm<sup>-1</sup> and 688 cm<sup>-1</sup> (Lazarević et al., 2007). After the treatment with quaternary ammonium salts, it is possible to identify most of the aforementioned characteristic peaks and bands of the sepiolites, as well as characteristics peaks of the quaternary ammonium salts. In particular, the C-H stretching bands of alkylammonium cations can be found at 2923 and 2850 cm<sup>-1</sup>, and the bending of CH<sub>3</sub> and CH<sub>2</sub> groups appeared at 1,488 and 1,467 cm<sup>-1</sup> (Kozak and Domka, 2004).



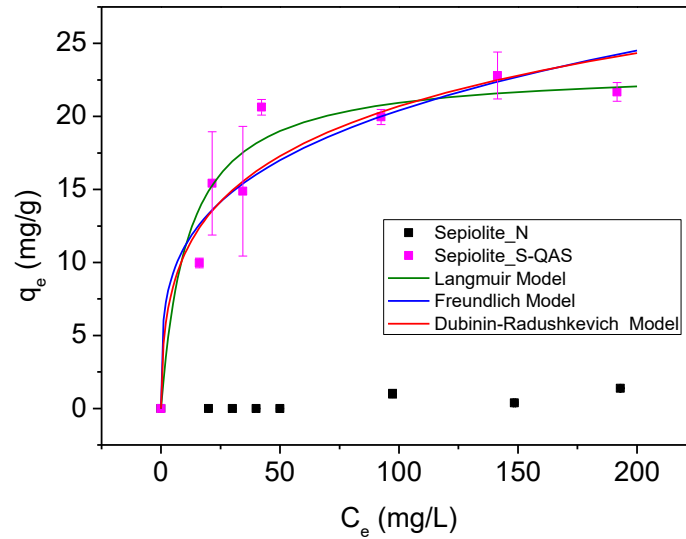
**Figure 1.** FTIR spectra of the Sepiolite\_N (black) and Sepiolite\_S-QAS (red).

### 3.2-Adsorption Isotherms of pristine and treated sepiolite

It was studied the equilibrium nitrates adsorption capacity ( $q_e$ ) of the pristine (Sepiolite\_N) and treated sepiolites (Sepiolite\_S-QAS). 20 mg samples of each kind of particles were deposited in 40 ml of nitrate solutions with concentration ranging from 20 to 200 mg/L, and after 3 hours of interaction between the particles and the solutions, it was measured the remaining equilibrium nitrates concentration ( $C_e$ ). The obtained results are shown in **Fig. 2**. It was found that the pristine sepiolites present negligible adsorption of nitrates from solutions with initial concentrations below 100 mg/L, whereas low adsorption capacities between 0.4 and 1.4 mg/g were found for initial concentrations between 100 and 200 mg/L. On the contrary, the treated sepiolites shown a significant nitrates adsorption even for low initial concentrations (e.g., about 10 mg/g for  $C_0 = 20$  mg/L). Moreover, the treated sepiolites reached their maximum adsorption capacity, slightly over 20 mg/g, when placed in nitrates solutions with concentrations over 50 mg/L (i.e., the safety threshold established by the OMS). In both cases, the pH of the nitrates solutions was about 6.3-6.6, presenting no change during the

adsorption process. According to these results, the pristine sepiolites were discarded for further use, employing only the treated sepiolites in the production of the nanocomposite polyurethane foams.

Then, to improve the understanding of the nitrates adsorption process, the experimental results were fitted to the Langmuir, Freundlich, and Dubinin-Radushkevich models. **Fig. 2** illustrates the correspondence between the experimental results and the fitted Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherms for the adsorption of nitrate ions onto treated sepiolites. Moreover, the parameters obtained from the fitting for each model (i.e.,  $q_{\max}$  and  $K_L$  for the Langmuir model,  $K_f$  and  $1/n$  for the Freundlich model, and  $q_m$  and  $\beta$  for the Dubinin-Radushkevich model, see Supplementary Information, section S.I-5) can be found in **Table 1**. Although the experimental results present a slight variability for some concentrations, the Langmuir model seems to fit better the nitrates adsorption process, as confirmed by the  $R^2$  values obtained from the fitting (see **Table 1**, the Langmuir model presents a quite proper fitting, with  $R^2 = 0.987$ , while the Freundlich and Dubinin-Radushkevich model fitting are not as good ( $R^2$  takes values of 0.727 and 0.754)). Moreover, the behaviour predicted by the Langmuir model, in which the maximum adsorption capacity ( $q_{\max} = 23.30$  mg/g) is limited by the formation of the monolayer of adsorbate, corresponds to the experimental results, in which a plateau was found once adsorption capacities about 20-23 mg/g are reached.



**Figure 2.** Plots of the adsorption of nitrate ions onto natural (N in black) and treated (S-QAS in magenta) sepiolites. Fitting of the experimental results of the treated sepiolites using the Langmuir (green), Freundlich (blue), and Dubinin-Radushkevich (red) models.

**Table 1.** Langmuir and Freundlich Adsorption Isotherm Parameters

Langmuir parameters			Freundlich parameters			Dubinin-Radushkevich parameters		
$q_{\max}$ (mg/g)	$K_L$ (L/mg)	$R^2$	$K_f$ (mg/g)	$1/n$	$R^2$	$q_m$ (mg/g)	$\beta$ (mol <sup>2</sup> /kJ <sup>2</sup> )	$R^2$
23.30	0.0885	0.987	6.045	0.264	0.727	45.83	$3.13 \times 10^{-3}$	0.754

Moreover, the dimensionless constant separation factor  $R_L$  related to the Langmuir isotherm present values between 0 and 1 for the nitrates adsorption, indicating favourable adsorption (see Supplementary Information, section S.I-5). Also, it is possible to obtain additional information about the adsorption process by calculating the mean free energy  $E$  of the process (see Supplementary Information, section S.I-5) according to the Dubinin-Radushkevich model (as this model does not fit quite well the experimental results this value should be taken just as an estimation). The adsorption process of the

nitrates by the modified sepiolites presents mean free energy about 12.64 kJ/mol, indicating that the adsorption is probably driven by ion-exchange/electrostatic interactions instead of by physical adsorption (Hu et al., 2015).

The obtained results are in good agreement with the literature (**Table S.1**, Supplementary Information). Natural sepiolite presents a poor adsorption capacity for nitrogen-containing compounds, generally less than 4 mg/g (Cobas et al., 2014; Öztürk and Bektaş, 2004; Ugurlu et al., 2011), being possible to improve their capacity by performing different treatments (Öztürk and Bektaş, 2004; Ugurlu et al., 2011). Only Ozcan et al. (Ozcan et al., 2005) reported a higher adsorption capacity of 25 mg/g obtained with an adjusted pH of 2, but they also were able to improve this capacity by modifying the sepiolites (up to 28 mg/g). These adsorption capacity values are also the highest reported in the literature, without any other previous work reporting adsorption capacities over 20 mg/g. Accordingly, the results of the present work confirmed that sepiolites can reach nitrates adsorption capacities over 20 mg/g. Moreover, it is the first time that nitrates adsorption capacities over 20 mg/g are achieved without controlling the pH, which is a relevant advantage that facilitates their use in in-situ remediation approach, in which modifying the pH would be difficult or could damage the environment. Besides, this work demonstrated that a conventional treatment using quaternary ammonium salts, usually performed to improve the affinity between the sepiolite and polymer matrices (Mohd Zaini et al., 2017), can increase the nitrates adsorption of sepiolite up to 20 times (from about 1 mg/g to over 20 mg/g). No other treatment has been reported in the literature with such efficiency to this aim (the best previous result reported only a three times increase of the adsorption capacity, up to about 10 mg/g [9]).

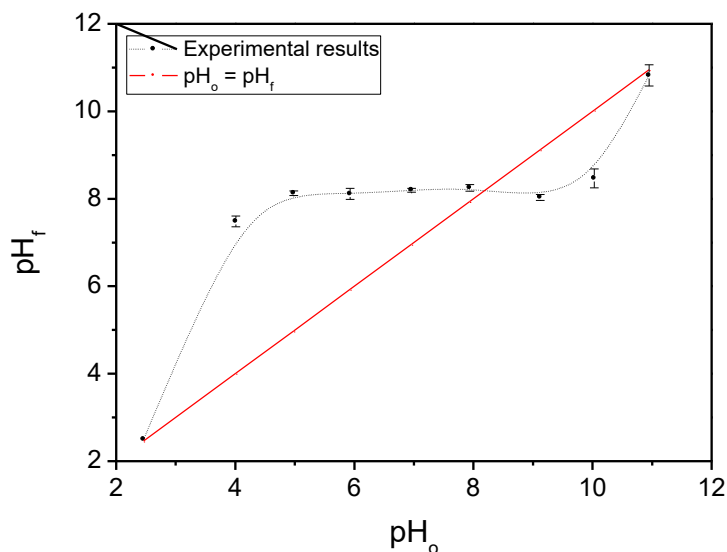
In addition, the characterization of the adsorption capability of the Sepiolite\_S-QAS was completed by the determination of the temperature influence on the adsorption process as well as their point zero charge ( $\text{pH}_{\text{pzc}}$ ). On the one hand, adsorption tests carried out at fixed contact time of 180 minutes and



different temperatures showed that the nitrates adsorption capacity of the modified sepiolites can be promoted up to  $39.9 \pm 0.1$  mg/g by decreasing the water temperature down to 15° C. On the contrary, an increase of the water temperature up to 45° C is enough to decrease the adsorption capacity to  $13.5 \pm 3.2$  mg/g. This result strengthens the potential in-situ application of adsorbent materials based on these sepiolites, as the majority of nitrates polluted waters, at least in the EU, present temperatures clearly below RT during most of the year.

Moreover, it was possible to estimate the thermodynamic parameters of the nitrates adsorption process. It was found that the Gibbs free energy change ( $\Delta G^\circ$ ) varies from -14.9 kJ/mol to -13.1 kJ/mol when the temperature is increased from 15 to 45° C. The negative value of  $\Delta G^\circ$  indicates the thermodynamic feasibility and spontaneous character of the adsorption process. In addition, the higher negative value of  $\Delta G^\circ$  found with the decrease of the temperature demonstrated that the nitrates adsorption is more likely to occur at a lower temperature. The exothermic character of the adsorption process was confirmed by the negative value of the enthalpy change ( $\Delta H^\circ = -30.2$  kJ/mol), whereas also a negative value of the entropy change ( $\Delta S^\circ = -54.6$  J/mol K) was found, corresponding to a decrease of the degree of freedom of the nitrates once they are adsorbent into the sepiolites (Hu et al., 2015).

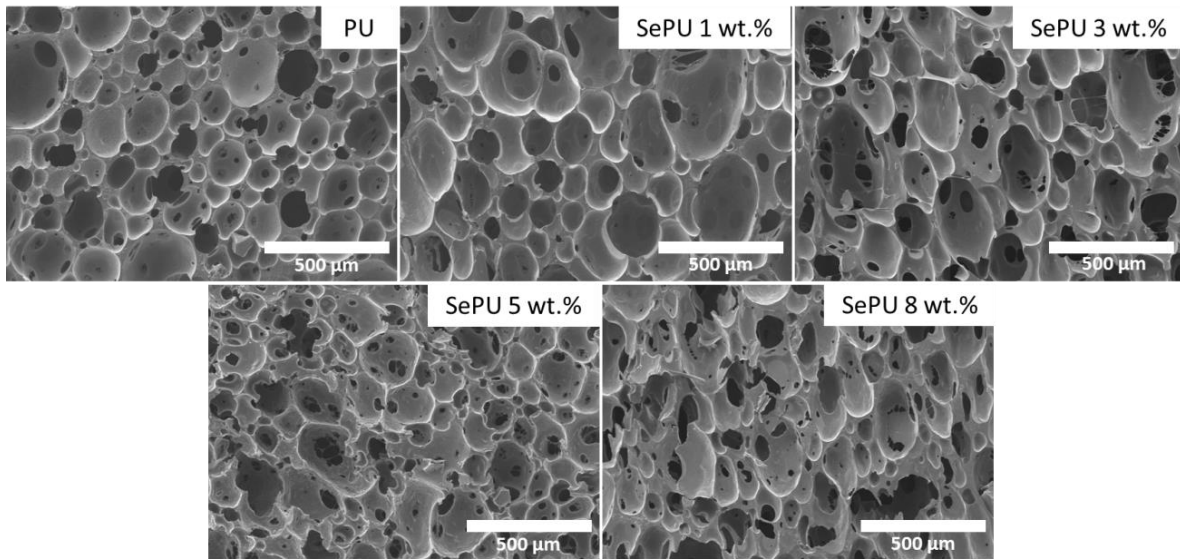
On the other hand, as **Fig. 3** shows, a  $\text{pH}_{\text{pzc}}$  value of 8.18 was found. Moreover, these results proved that in a pH range from about 2.50 to 8.18 the Sepiolite\_S-QAS present a positive charge in their surface (Al-Degs et al., 2000), being appropriate for the nitrates adsorption in that broad pH range.



**Figure 3.** Determination of the point zero charge ( $\text{pH}_{\text{pzc}}$ ) of the Sepiolite\_S-QAS as the intersection point of the experimental  $\text{pH}_f$  values and the line  $\text{pH}_o = \text{pH}_f$ . The dashed line in the figure is a guide to the eye.

### 3.3-Polyurethane foams characterization

Polyurethane foams (PU) and nanocomposite polyurethane (SePU) foams with 1, 3, 5, 8, 10 wt.% of treated sepiolites were fabricated and studied. First, it was analysed the effect of the addition of the treated sepiolite in the cellular structure of the foams. **Fig. 4** shows micrographs of the cellular structure of the fabricated foams, being possible to observe that the addition of the sepiolites has a slight influence on the cellular structure. Foams with sepiolites contents between 1-3 wt.% present similar, or even higher cell sizes, while treated sepiolites between 5-8 wt.% seem to slightly decrease the cell size (see **Table 1**), probably due to their effect a nucleating agent (Bernardo et al., 2017). Higher sepiolites contents (10 wt.%) were found to induce the coalescence and collapse of the cellular structure (see **Fig. S.I-4**, Supplementary Information).



**Figure 4.** SEM micrographs of the Cellular Structure of PU and SePU foams.

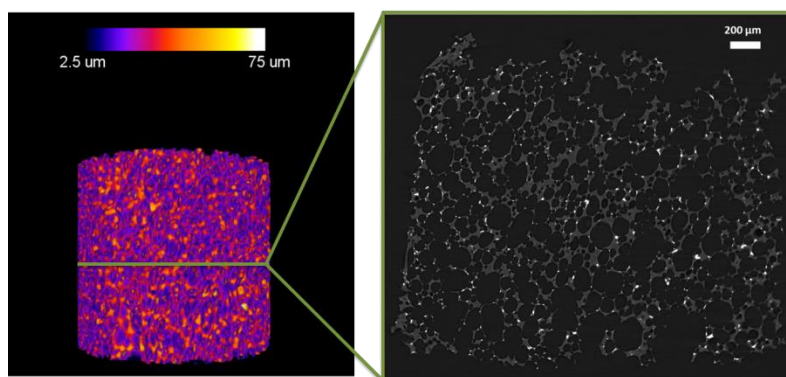
The influence of the treated sepiolite into the SePU foams was further studied by analysing the geometric density, porosity, and open-cell content of the fabricated foams by Gas Pycnometry (**Table 2**). It was found that the introduction of the sepiolite could increase the expansion of the foams, promoting the porosity from 0.86 (pure PU foams) up to 0.90-0.91 (SePU foams with treated sepiolite content over 5 wt.%). Despite the higher porosity, SePU foams with the higher sepiolite content presented slightly higher geometric densities, due to the introduction of the sepiolite. Moreover, the sepiolite does not present any influence on the open-cell content of the foams, presenting all of them a 100 % open-cell content.

**Table 2.** Polyurethane (PU) and nanocomposite polyurethane (SePU) foams features.

Sample	Geometric Density (kg/m <sup>3</sup> )	Porosity	Relative Density	Cell size (μm)	Nv (x10 <sup>5</sup> cell s/cm <sup>3</sup> )	q <sub>w</sub> (g/g)
PU	163±23	0.86±0.02	0.14±0.02	146±93	1.7±0.4	14.6±0.5
SePU 1 wt.%	136±10	0.89±0.01	0.11±0.01	181±92	0.9±0.2	12.9±1.6

SePU 3 wt.%	153±23	0.89±0.02	0.11±0.02	150±85	2.9±1.3	10.7±1.7
SePU 5 wt.%	139±13	0.91±0.01	0.09±0.01	131±68	2.7±0.7	11.0± 1.3
SePU 8 wt.%	185±18	0.90±0.01	0.10±0.01	132±77	1.9±0.7	9.9±0.4
SePU 10 wt.%	174±9	0.91±0.00	0.09±0.00	-	-	6.3 ± 0.5

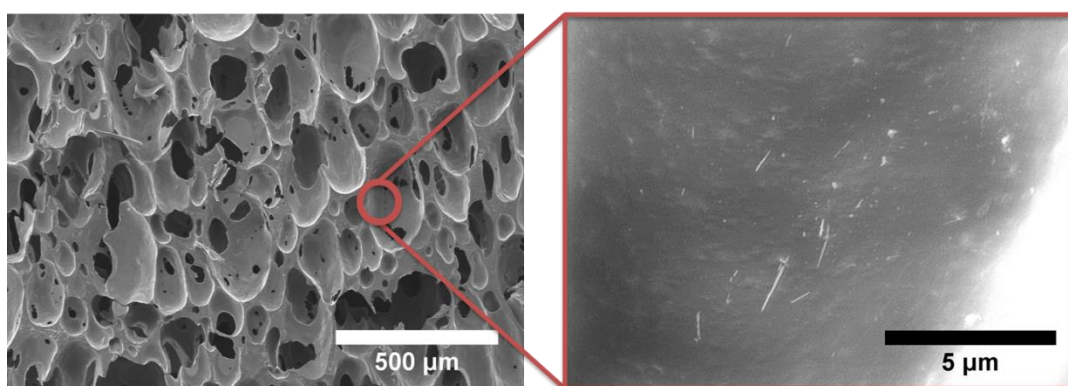
Also, all the studied foams present a quite high water absorption capacity ( $q_w$ ), being reduced by the addition of the sepiolite from 14.5 g/g of the pure PU foams to 6.3 g/g of the SePU with 10 wt.% of treated sepiolite. Nevertheless, all the samples present an appreciable swelling due to the introduction of the water between the polymer chains of the matrix of the foams. This behaviour, combined with the very high open cell content, which was also confirmed by X-Ray Tomography (**Fig. 5**), guarantees that the sepiolite dispersed on the foams will be able to interact with the polluted water independently of their location (e.g., in the surface or inside of the cell walls or struts).



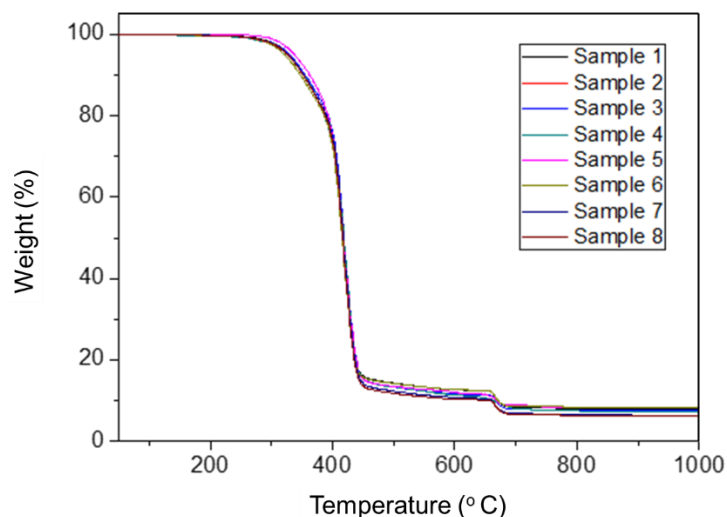
**Figure 5.** X-ray Tomography 3D reconstruction and cross-section reflecting the high connectivity between the cells, as well as some agglomerates of sepiolite nanoparticles (with spots) are appreciated on the cell walls.

Although some sepiolite agglomerates were found by X-ray Tomography (**Fig. 5**), it was proved by SEM that individual sepiolites were dispersed throughout the polyurethane foam (**Fig. 6**). According to

the results described in this section, the nanocomposite polyurethane foam (SePU) with 8 wt.% of treated sepiolite (Sepiolite\_S-QAS) was selected as the most promising candidate for the nitrates removal application, as presented the higher amount of the active particles (i.e., the treated sepiolite) without compromising the integrity of the foam (see **Fig. 4** and Supplementary Information, section S.I-7). Further tests were carried out to ensure the homogeneous distribution of the sepiolite in the bulk foams. In particular, TGA measurements from eight different areas and samples of the bulk SePU 8 wt.% confirmed that the composition of the nanocomposite foams was homogeneous and that the solid final residue, corresponding mainly to the sepiolite, confirmed the presence of 8 wt.% of sepiolite in these foams (**Fig. 7**).



**Figure 6.** SEM micrographs of the cellular structure of SePU 8 wt.% (left) and a close-up of the individual sepiolites dispersed in the cell walls (right).



**Figure 7.** TGA analysis of eight samples from different areas and samples of SePU 8 wt.% foams.

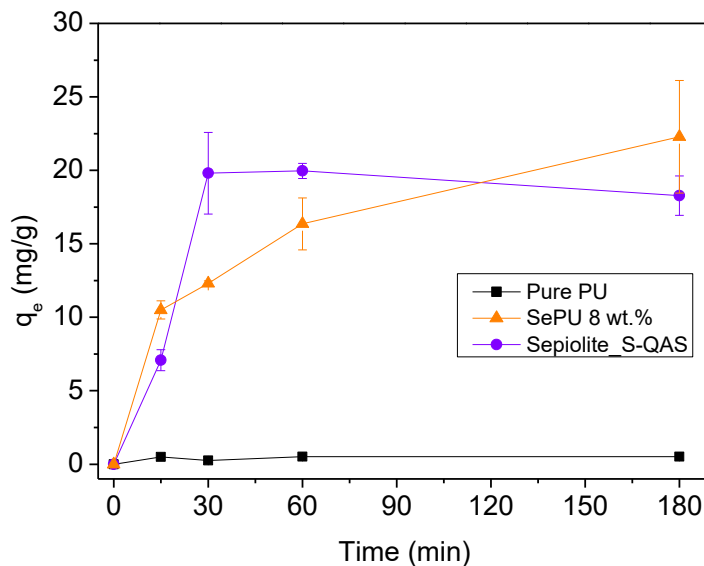
In addition, it was found by FTIR spectroscopy that the addition of the sepiolite did not modify the polymerization of the polyurethane matrix (**Fig. S.I-5**, Supplementary Information).

### 3.4 Nitrates removal using SePU foams.

The nitrates adsorption capacity of pure PU and SePU 8 wt.% foams was studied after different contact times (between 15 and 180 minutes) using 40 mL of a 100 mg/L nitrates solution (**Fig. 8**); with the aim to test their capability to remove nitrates from polluted waters with nitrates concentration over the safety threshold. Moreover, their performance was compared with those of the treated sepiolite (Sepiolite\_S\_QAS) in powder form, to demonstrate if the adsorption capacity of sepiolite imbibed in the foams were affected by the polyurethane matrix.

**Fig. 8** shows that pure PU foams were not able to interact with nitrates, showing a negligible nitrates adsorption capacity. Any nitrates adsorption found in the SePU foams should be related to the presence of the Sepiolite\_S-QAS. Accordingly, the sepiolite of the SePU 8 wt.% foams showed a noticeable nitrates adsorption capacity, reaching values as high as those obtained when the treated sepiolites were

employed in powder form (**Fig. 8**). These results prove that the sepiolites imbibed in the polyurethane matrix are free to interact with the polluted water, due to the swelling capability of the chosen polyurethane.



**Figure 8.** Effect of the contact time on the adsorption of nitrate into (■) Pure PU foams, (●) Sepiolite\_S-QAS and (▲) SePU 8 wt.% foams.

The main difference found between the treated sepiolite used in powder form or imbibed into the polyurethane foam is that the required time to reach adsorption capacities over 20 mg/g is higher for the imbibed sepiolite (about 2 hours instead of about 30 minutes). This behaviour is consistent with the fact that the Sepiolite\_S-QAS imbibed in the polymeric matrix do not interact directly with the nitrates solution, but the polluted water must first impregnate the polymer and cause the swelling before interacting with the sepiolite. However, the appropriate selection of the hydrophilic polymer matrix has allowed these circumstances to occur, also avoiding possible negative interactions between the Sepiolite\_S-QAS and the PU, which could affect their capacity to absorb nitrates. An appropriate synergy was obtained between the treated sepiolite and the PU foams, by providing a porous substrate

that facilitates the handling of the active sepiolite without affecting the nature of their interaction with the nitrates or their adsorption capacity (i.e., reaching values comparable to those achieved by the sepiolite in the powder form as well as predicted by the Langmuir model (23.30 mg/g)).

Moreover, the safety of the handling of the SePU foams after the nitrated adsorption was addressed. It was proved that, once the nitrates were adsorbed, they cannot be accidentally released again to the water. With this aim, SePU 8 wt.% already employed for nitrates removal from polluted water were placed in clean water and kept under shaking at 300 rpm for 24 hours. Then, this water was collected and analysed by UV-Vis, finding no nitrates, neither other compounds, released to the water.

Finally, the nitrates adsorption performance of the SePU foams was tested on actual polluted water collected from nearby streams. The water collected in the first spot presented an initial nitrates concentration of 46.5 mg/L and a pH of 7.93, whereas the second spot showed a higher nitrates concentration of 86.2 mg/L and a pH of 7.99. Although the pH of these polluted water was close to the  $\text{pH}_{\text{pzc}}$  of the modified sepiolite (8.18), in both cases the SePU foams were able to remove nitrates, reaching adsorption capacities of  $11.2 \pm 0.5$  and  $7.8 \pm 0.6$  mg/g. The decrease of the nitrates adsorption capacity on actual polluted waters is mainly related to the presence of other ions which can interact with the adsorbent. In fact, it is known that the adsorption of sulfates and bicarbonates by positively charged adsorbents is more favourable than the adsorption of nitrates (Gouran-Orimi et al., 2018; Mehdinejadani et al., 2019). However, even in the competitive adsorption environment of actual nitrates-polluted water the nanocomposites developed in this work were able to reach a noticeable nitrates adsorption capacity without requiring any additional treatment of the polluted water (such as modifying the pH, see Table S.1 in the Supplementary Information for comparison with published works under laboratory conditions).

The obtained SePU foams demonstrated to be a safe and suitable approach for the in-situ remediation of nitrates-polluted water resources. On the one hand, the proposed treated sepiolite presented one of



the highest nitrates adsorption capacities ever reported for this kind of particles, without requiring a pH or temperature control, which would be unsuitable for in-situ applications. On the other hand, the chemistry of the polyurethane foam in which the sepiolites were imbibed proved to be appropriate to allow the interaction between the polluted water and the sepiolites without negative effects on their nitrates adsorption capability. These unique features, and the non-expensive nature of the materials and production routes employed make the proposed SePU foams a promising candidate for the in-situ remediation of nitrates-polluted water resources.

#### **4-Conclusions**

This work proposes the conventional functionalization of sepiolite with quaternary ammonium salts as a facile route to achieve a high nitrates adsorption capacity (about 23 mg/g), without controlling the pH or temperature such as it was required in previous works. The interaction between the treated sepiolite and the nitrates was studied using isotherm models, finding that the Langmuir model explains this interaction. Moreover, the use of polyurethane foams as a porous substrate to improve the handling of the sepiolite in the in-situ remediation approaches is proposed, avoiding additional separation steps to remove the sepiolite in powder form from the treated water. The optimal amount of treated sepiolite included into the polyurethane foams was found to be 8 wt.%, as, although the sepiolite demonstrated to enhance the cell nucleation, they also induce the collapse of the foams at higher contents. It was proved that the open cell structure of the foams, and the proper chemistry of the polyurethane, which swells with water, allow the polluted water to interact with the sepiolite imbibed in the foams just as they interact in powder form. Consequently, the imbibed sepiolite on the nanocomposite foams (SePU) was able to reach their maximum adsorption capacity (23 mg/g), without any later accidental release of nitrates nor sepiolite. Moreover, these nanocomposite foams were tested in actual nitrates-polluted water, being able to reach noticeable nitrates adsorption capacities (up to 11 mg/g) even in that

competitive adsorption conditions. The proposed SePU foams prove to be a low-cost, safe, and easy-handling adsorbent for the in-situ removal of nitrates-polluted water resources.

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