



## Removal of total organic carbon from olive mill wastewater using palygorskite clay mineral

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Received 9 October 2021; Accepted 20 February 2022

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### ABSTRACT

The production of olive oil is one of the main agricultural activities with a large amount of wastewater. So, the proper treatment of the olive mill wastewater (OMW) is superior for environmental-friendly industries and one of the most efficient and low-cost methods is the sorption of organic compounds. In the present work, palygorskite, a fibrous clay mineral, is proposed for this application as it exhibits high sorption capacity for the organic load (total organic carbon) in olive mill wastewater. The optimum sorption was observed for slightly acidic conditions (pH 4) and reached the sufficient value of 65%. The most efficient mass to volume ratio was 20 g/L and the sorption was completed in 30 min, while it was temperature independent. From this study palygorskite can be considered and further examined as a promising and cost-effective material for the pre-treatment of OMW concerning the removal of the organic compounds.

*Keywords:* Clay minerals; Olive mill wastewater; Palygorskite; Sorption; Total organic carbon

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### 1. Introduction

Olive oil production is a principal agricultural activity in Mediterranean countries where 97% of the total olive oil production is produced, with Greece the third biggest producer of 402.703 t annually [1]. A large amount of wastewater cubic meters results from this extended production, after the wash of olive fruits and olive oil, as well as the centrifugation process [2]. The exact wastewater composition depends on the extraction procedure, the cultivation characteristics and the olive type. Nevertheless, in all cases, it has dark brown to black colour, strong olive smell, pH 3–6,

high values of chemical and biochemical oxygen demand (COD and BOD, respectively) and mainly consists of toxic organic compounds such as polyphenols [3]. The olive mill wastewater (OMW) treatment research is mostly focused on organic pollutants removal, such as phenols [4]. In many studies COD and BOD [5], as well as total organic carbon (TOC) [6], are the measured chemical parameters for the estimation of the successful organic load removal, as it is well known that high levels of COD/BOD and TOC indicate that the OMW is non-biodegradable and toxic to organisms [7]. TOC measures the total organic load which comes mainly from carbohydrates, phenols, protein substances,

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fulvic acids and humic substances [8]. Wastewaters with high levels of organic carbon lead to predominant consumption by microorganism and then to insufficient amounts of dissolved oxygen in marine ecosystems which is a severe threat for aquatic organisms [8].

Accordingly, the OMW effluent treatment for organic substances is essential, therefore a variety of treatment methods has been approached. In particular, OMW effluent treatment has been studied by reverse osmosis [9], advanced oxidation process (AOPs) like photocatalysis or ozonation [10], biological methods [11], coagulation and electrochemical methods [12–14], and sorption [5]. Depending on the initial concentrations of the pollutants the aforementioned procedures can be more or less effective for OMW treatment. As the operational cost for most of the above mentioned techniques is inhibitive, the research for affordable technologies is crucial [1]. The exploitation of natural resources could be a cost-effective and efficient method; however, research is less focused on this domain.

Clay minerals and zeolites have been applied for OMW treatment as catalysts [7,15], as flocculants–coagulants [16], as filter media [3], or as sorbents [5]. The most widely studied clay sorbents are bentonites and Jordanian clay for COD, BOD, and phenols removal, presenting very promising results, however, the efficiency of other types of clay minerals has not been studied.

Palygorskite, with the trade name attapulgit, belongs to 2:1 fibrous clay minerals. It consists of a ribbon layer with two continuous tetrahedral sheets connected with one discontinuous octahedral sheet extended in one dimension, resulting in a nanorod morphology [17]. Due to this morphology, palygorskite has high porosity, good stability [18], high viscosity in suspensions [19], high specific surface area (more than 200 m<sup>2</sup>/g), and high sorption capacity [20] for a variety of compounds such as heavy metals [18,21], phosphorus [19], and organic pollutants [18]. Palygorskite had been also tested for its sorption efficiency in oils. More specifically, the removal of crude oil hydrocarbons by unmodified palygorskite, in water systems, had been investigated and in the case of total petroleum hydrocarbons (TPH) reached the efficient value of 40% when the clay: oil ratio (w/w) was 5:1 [22]. Also, palygorskite-based membranes with tunicate cellulose nanocrystals have been tested for the separation of soybean oil, pump oil, hexane, and isooctane from water with rejection rate of the oils' microemulsions to reach the 99.87 ± 0.02%, 99.2 ± 0.06%, 99.86 ± 0.01%, and 99.89 ± 0.01%, respectively. The rejection rate of oil was also high in the case of nanoemulsions (>99%), while a synergistic sorption of metals or dyes was held [23]. In another research, palygorskite with peat and scoria in ideal ratios 0.2:0.8:2.0 was used for the purification of an aqueous solution containing petroleum. The mixture was efficient for the removal of total petroleum hydrocarbons, as after 31 d the removal rate reached 96%. Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup> were also decreased [24].

Certain characteristics of palygorskite, that is, its efficiency in adsorption applications, high availability, low cost, and non-toxic effects together with the lack of risk of secondary pollution (e.g., increase of COD in water) [18], make this mineral a promising material for several environmental applications. In this study, palygorskite was studied as

a sorbent material for the removal of organic load, through TOC monitoring, from real OMW.

## 2. Materials and methods

### 2.1. Characterization of palygorskite

A palygorskite sample from the deposit of Ventzia continental basin located in Western Macedonia, Greece, and produced by Geohellas S.A. was used as sorbent material. The structural characterisation of the raw palygorskite sample was performed by X-ray diffraction (Bruker D8 Advance) with Cu-K<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and Nickel filter. Fourier-transform infrared spectroscopy (FT-IR) was used to determine palygorskite and to characterise its chemical properties using an EQUINOX 55 FT-IR spectrometer (BRUKER). Moreover, scanning electron microscopy (SEM) was performed using a SEM LEO SUPRA 35VP for the morphological characterisation of the material. The Specific Surface Area (SSA) was calculated with the BET method using a Micromeritics Tristar 3000 analyser with a SmartPrep degasser. Based on the US-EPA 9081 method, the Cation Exchange Capacity (CEC) was measured using sodium acetate.

### 2.2. <sup>13</sup>C-NMR OMW analysis

A two-phase olive mill wastewater was collected from a small-scale olive mill. The wastewater used for the reduction of total organic compounds without any prior processing. The qualitative analysis and the content determination in the wastewater were performed with nuclear magnetic resonance (NMR) spectroscopy. All the NMR experiments were carried out on a sample containing 11 mg of compound in 0.45 mL of CDCl<sub>3</sub> deuterium solvent. Experiments were carried out at 150-MHz <sup>13</sup>C frequency on a Bruker prodigy AVANCE III-600 spectrometer, equipped with an external 150 W class A/B power amplifier for <sup>13</sup>C. The experiments were carried out in the Instrumental Analysis Laboratory of the University of Patras. The raw wastewater was characterised after the adjustment of the acidic and the alkalic conditions as described below, as well as after the end of the sorption procedure by palygorskite.

### 2.3. Batch experiments

Batch experiments have been conducted to determine the effect of initial TOC concentration and sorbent dosage on TOC removal. Nine OMW samples with different initial TOC concentrations (42.8, 94.9, 123.7, 199.4, 321.8, 365, 522.8, 549.4, 735 mg/L) and six different sorbent dosages (2.5, 5, 10, 20, 40, 60 g/L) were studied. From this study the optimum mass sorbent to OMW volume ratio was determined. This optimal ratio was then used for the study of the effect of pH (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12), and temperature (25°C, 35°C, 45°C, 55°C ± 2°C) on the sorption capacity. All the samples were equilibrated for 30 min, as with initial experiments it was found that beyond this period of time there was no further reduction of the concentration of TOC. TOC analyses were carried out using the combustion-infrared method, Standard Method (SM) 5310B [25] with a

Shimadzu TOC analyser (TOC-VCSH). The analysis of the above-mentioned experiments was carried out in duplicate, and the results are reported as removal efficiency (%R) [Eq. (1)].

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

where  $C_i$  is the TOC (mg C/L) initial concentration and  $C_e$  the equilibrium TOC (mg C/L) concentration.

#### 2.4. Isotherms study

The equilibrium concentrations of TOC from the various initial concentrations examined were best fitted with Freundlich isotherm, according to the equations:

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where  $q_e$  is the amount of exchanged C of TOC (mg/g),  $C_e$  is the equilibrium TOC concentrations in solutions (mg/L),  $K_F$  the capacity of the adsorbent, and  $n$  is the Freundlich constant. When the value of  $1/n$  is  $0 < 1/n < 1$ , the adsorption is favorable; when  $1/n = 1$ , the adsorption is linear and irreversible; and when  $1/n > 1$ , the adsorption is a chemical process and unfavorable. The value of  $1/n < 1$  means that the adsorption process is physical, whereas the Freundlich isotherm fit indicates the heterogeneous nature of adsorption [26].

### 3. Results and discussion

#### 3.1. Characterisation of palygorskite

The qualitative X-ray diffraction (XRD) analysis of the palygorskite sample (Fig. 1A) proved the existence of palygorskite as the dominant mineral in the sample with

main peaks at about 10.6 Å, 4.47 Å, 3.28 Å, and 2.54 Å. The peak at 15 Å indicated the presence of saponite as an impurity, which does not reduce the efficiency of the sorbent, since saponite acts synergistically for the sorption of organic molecules [26,27].

The FT-IR spectrum was characteristic of the palygorskite presence (Fig. 1B). The stretching of the Si–O bond of palygorskite indicated by the characteristic band at 1,000  $\text{cm}^{-1}$  [28] and the band at 1,200  $\text{cm}^{-1}$  was a result of the Si–O–Si bond that connects the neighbouring ribbons and it is typical for the fibrous clay minerals [29]. The peak at 1,650  $\text{cm}^{-1}$  corresponds to the bending modes of the inner space water [30]. Moreover, the co-existence of saponite in the sample was indicated by the peak at 650  $\text{cm}^{-1}$ , which corresponds to the Si–O bond deformation that is parallel to the optical axis [31].

The fibrous morphology of palygorskite was verified by SEM, while the crystals' length varied from 400 to 2,000 nm (inset of Fig. 1A). From BET, the pore volume was measured to be 0.810 mL/g and the specific surface area about 297  $\text{m}^2/\text{g}$ . Additionally, cation exchange capacity was measured to be 30 meq/100 g, which is a relatively high value for palygorskite.

#### 3.2. $^{13}\text{C}$ -NMR OMW characterization

The  $^{13}\text{C}$ -NMR characterisation showed that the OMW was mainly composed of aromatic compounds (including phenols) with bands between 110 to 160 ppm and heteroaromatic molecules with characteristic bands between 155 and 170 ppm for all different pH conditions. Depending on the acidity, other compounds such as, ketones (220–300 ppm) in pH 2, alkynes (145 ppm) in pH 3–4, as well as esters, amides, and azomethine (160 ppm) in pH 4 were identified. For alkaline conditions, the main compounds were again the aromatic and heteroaromatic compounds in combination with alkenes (146–157 ppm) and azomethine. After the sorption procedure, the aromatic compounds almost disappeared (no peaks between 137 to 159 ppm), while the number of heteroaromatic components significantly decreased for all pH environments tested. In

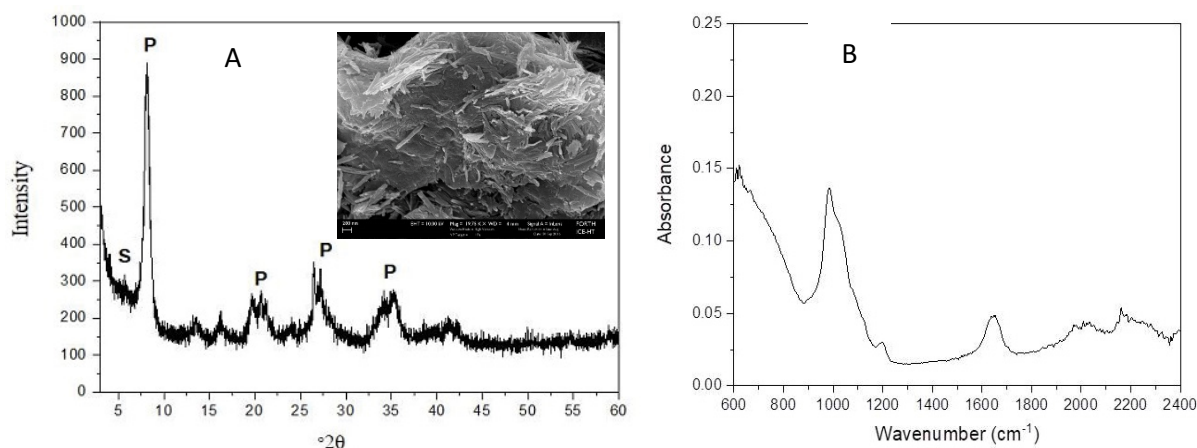


Fig. 1. (A) XRD pattern of palygorskite (inset scanning electron microscopy picture of palygorskite) and (B) FT-IR spectrum of palygorskite.

extremely acidic conditions (pH 2), no ketones were determined in the treated olive mill wastewater as opposed to amides.

In Fig. 2A the characteristic  $^{13}\text{C}$ -NMR spectrum (before sorption) for pH = 4 is presented, while in Fig. 2B it is after the end of the sorption process.

### 3.3. Batch experiments

#### 3.3.1. Effect of sorbent dosage

Various dosages of raw palygorskite sample (2.5, 5, 10, 20, 40 and 60 g/L) were applied for the TOC removal of real OMW with an initial TOC concentration of 735 mg C/L. Fig. 3 shows that TOC removal for all palygorskite dosages is almost constant at 50% except for the dosage of 2.5 g/L. Moreover, the dosage of 20 g/L was found to be slightly more effective than the others examined (53%). As this result is in agreement with our previous studies [21,32] it was selected as the optimal sorbent dosage to be used for the further experimental studies.

These results indicate a 50% sorption capacity concerning the organic load, which is in good agreement with other studies for OMW as it is presented in Table 1.

#### 3.3.2. Effect of initial concentration

In Fig. 4 it can be seen that the TOC removal with 20 g/L palygorskite is positively correlated with the increase of TOC initial concentration. In particular, when the TOC concentration increased, that is, from 43 mg/L to

520–550 mg/L; palygorskite's removal capacity was doubled, that is, from 30% to 60%. Palygorskite powder presented similar results as in the study of Al. Haddabi et al. [33] for the Dissolved Organic Carbon (DOC) sorption behaviour where the removal capacity increased when the DOC initial concentrations increased. When the TOC sorption on palygorskite reaches its maximum, no further organic compounds can be sorbed. As it is shown in Fig. 4, for higher concentrations its removal efficiency decreases (53% from 61%), and partially TOC concentration is desorbed from palygorskite sorption sites, probably because of the existence of other competitive substances in wastewater [5].

#### 3.3.3. Effect of pH

The OMW pH plays a key role in TOC sorption on palygorskite. As it can be seen in Fig. 5 the sorption is favourable under acidic conditions (pH < 5) and especially at pH 4 (65%). As the pH increases, the removal efficiency decreases, reaching the value of 30% at pH 12. According to Huang et al. [34], who studied tannin removal from flavonoids (phenolic group) by modified palygorskite, in acidic pH values, the hydrogen bonding may easily be formed compared to more basic ones. Moreover, at pH > 9 palygorskite fibres repel each other because of the high magnitude of negative charge, resulting in the independent particle movement with low viscosity through suspension [35]. The effect of the pH was in agreement with the NMR analysis after the sorption of TOC from OMW,

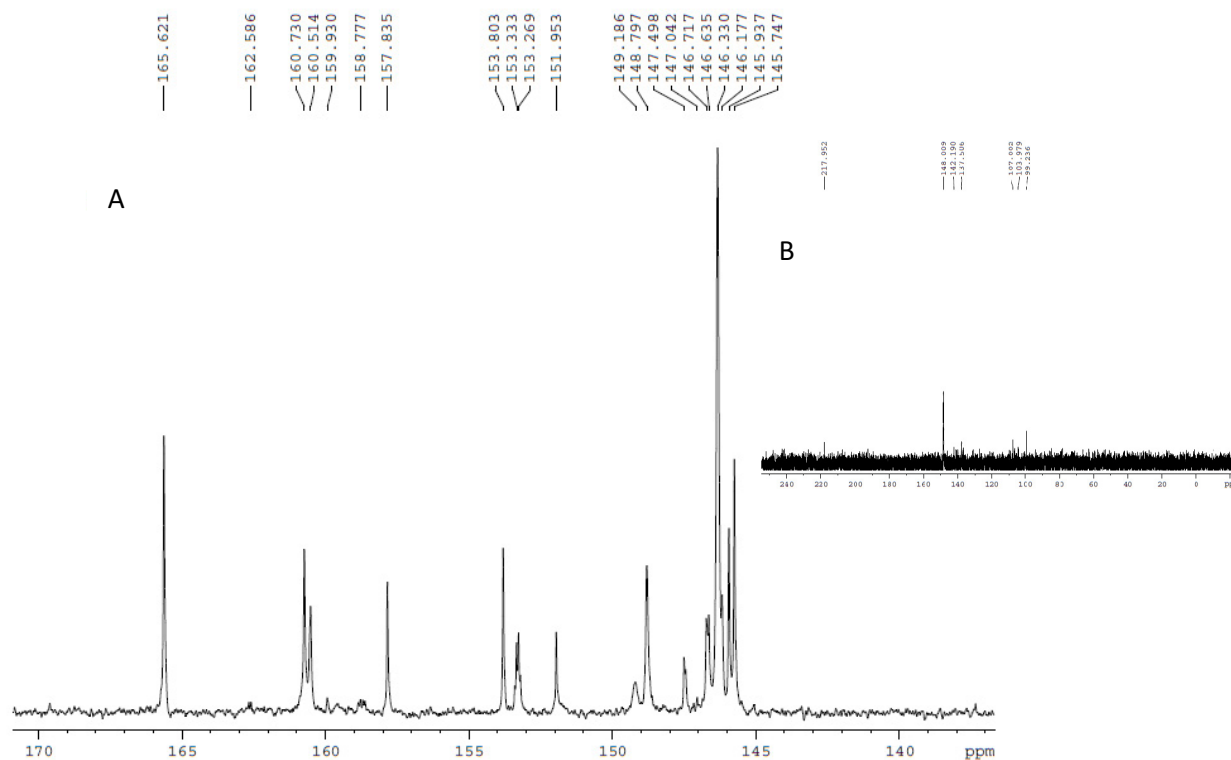


Fig. 2. (A) OMW  $^{13}\text{C}$ -NMR spectrum (before sorption) and (B) after the end of the sorption process for pH = 4.

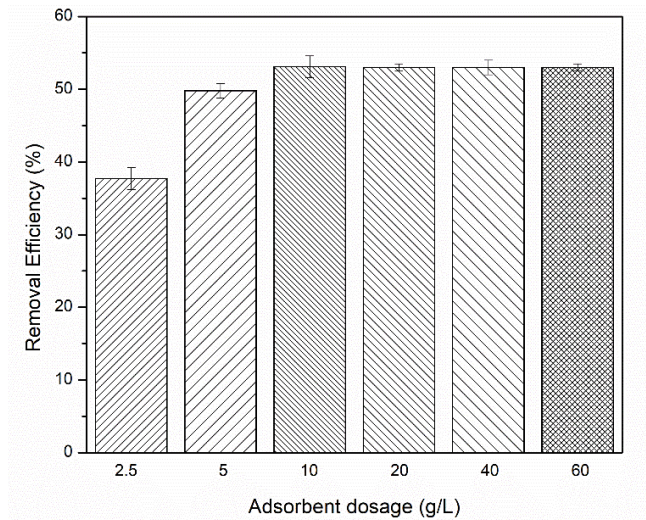


Fig. 3. Effect of raw palygorskite dosage on TOC removal from OMW.

as in acidic conditions the ketones, and aromatic/heteroaromatic compounds were effectively decreased while amides remained in the waste.

### 3.3.4. Effect of temperature

TOC removal using palygorskite was examined under different temperature conditions. In Fig. 6 it can be observed that TOC sorption on palygorskite is largely independent of the temperature values since its removal is almost stable in the temperature range of 24°C–53°C. Usually, the temperature-independent sorption reflects on high fractional surface coverage, while sorbent's surficial dehydration does not occur [36]. Moreover, the effective TOC removal in room temperatures can maintain the procedure's cost low.

### 3.3.5. Isotherms study

In order to determine the nature of TOC from OMW adsorption on raw palygorskite, the isotherm models of Langmuir and Freundlich were applied. It was found that the results were obeyed with good correlation to Freundlich model ( $R^2 > 0.97$ ), indicating the heterogeneous nature of adsorption, while the Langmuir model cannot be applied. For Freundlich model the  $\ln q_e$  vs.  $\ln C_e$  (Fig. 7) was plotted;

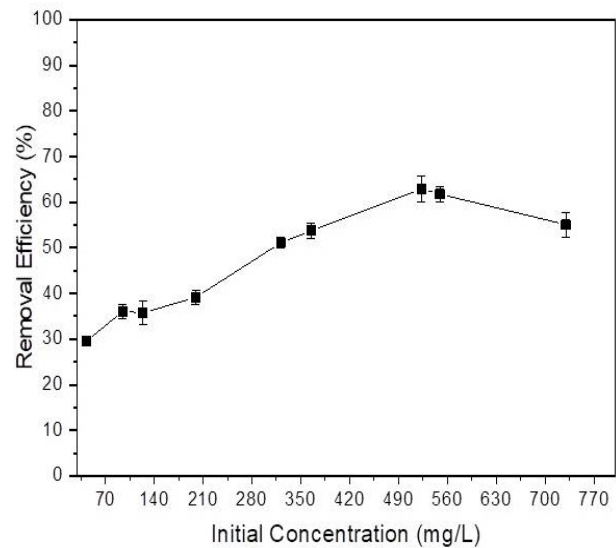


Fig. 4. Effect of initial concentration on TOC removal from OMW with palygorskite.

and the slope and intercept of the plot were calculated that represent the  $1/n$  and  $K_f$ , respectively. The calculated values are presented in Table 2, indicating a chemical sorption procedure.

## 4. Conclusions

Raw palygorskite from Ventzia Basin (Grevena, Greece) supplied by Geohellas S.A. was applied in two-step olive mill wastewater (OMW) as organic load sorbent. The OMW was analysed with the  $^{13}\text{C}$  NMR method and was found rich in aromatic and heteroaromatic compounds, making its organic load removal essential. Palygorskite was firstly characterised by XRD, SEM, FT-IR, BET, and CEC methods and then used in batch kinetic series experiments to determine the optimal conditions for organic load removal, by monitoring TOC. According to the results from the batch experiments, 20 g/L palygorskite was effective for TOC sorption as satisfactorily reduced 61% of the initial concentration of 549.4 mg C/L within 30 min. The sorption procedure was found to be favourable in acidic conditions (pH 2–5) based on NMR and batch experiments, while the removal efficiency was decreasing with pH increase, and it proved temperature independent for a range from 24°C–51°C.

Table 1  
Comparison of other methods used for OMW treatment or olive processing wastewaters

Method	Efficiency
Zeolite based method [3]	Decreased concentrations of $\text{NO}_3^-$ , B, K, P, and total fat in OMW by mean percentages of 78.0%, 92.4%, 66.6%, 48.3%, and 93.3%, respectively
Electrocoagulation [12]	50% COD removal and 100% color removal
Coagulation and advanced oxidation processes [13]	54% COD removal
Copper-exchanged aluminum-pillared montmorillonite [15]	45% TOC removal



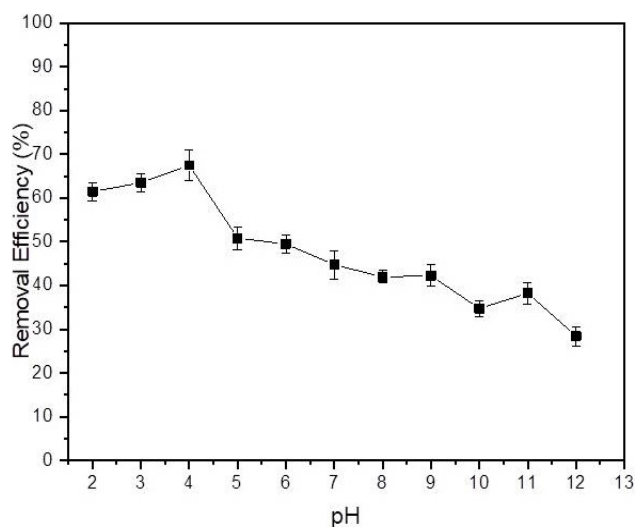


Fig. 5. Effect of OMW pH on TOC removal with palygorskite.

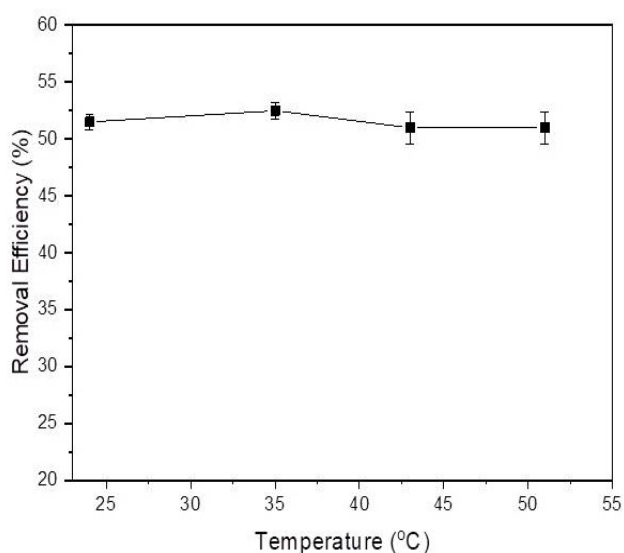


Fig. 6. Effect of temperature on TOC removal from OMW with palygorskite.

Table 2  
Freundlich isotherm model parameters

Freundlich		
$1/n$	$K_F$	$R^2$
1.64	0.002	0.979

The above results indicate that this material is a promising efficient sorbent for the pre-treatment of OMW.

#### Acknowledgements

The authors want to thank Dimitris Vachliotis of the Instrumental Analysis Laboratory, University of Patras for

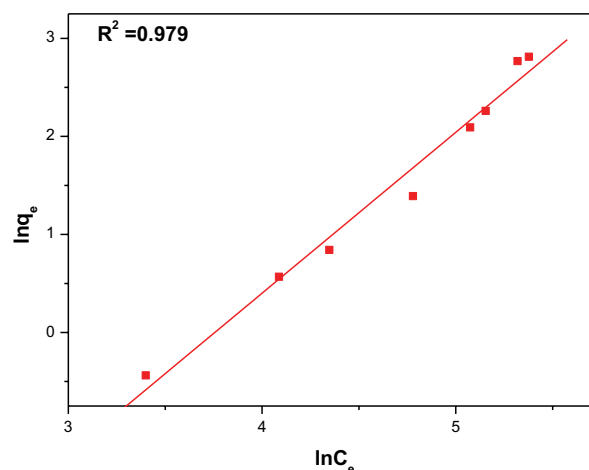


Fig. 7. Freundlich isotherm.

his help with the NMR spectra and Vassilios Dracopoulos for the SEM images.

#### Conflict of interest

The authors have declared no conflict of interest.

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