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# Pre-treatment of hydrolysable nuclear organic liquids prior to their waste management: Solid impregnation of vegetable oil on surfactant-grafted clay particles

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## Abstract

In the context of advancing nuclear waste management techniques, this study delves into the novel use of surfactant-grafted clay particles for pre-treating hydrolysable nuclear organic liquids. Our research explores the potential of modified clay materials in immobilizing vegetable oil, a surrogate for complex nuclear waste. We systematically investigate the adsorption capabilities of various clays, including metakaolin, diatomaceous earth and sepiolite, when grafted with two surfactants: cetyltrimethylammonium bromide (CTAB) as cationic surfactant and decyl glucoside (DG) as non-ionic surfactant. This study employs comprehensive characterization techniques to assess the physicochemical transformations in clays post surfactant-grafting. Grafting was initially highlighted by TGA, where the breakdown of surfactants can be observed. This is also evidenced by measurements of the  $\zeta$ -potential, which demonstrate a reduction in surface charge upon the addition of the cationic surfactant, excepted for sepiolite for which the surface charge did not change. The increase in  $\zeta$ -potential was about 126% for modified metakaolin. Additionally, Washburn measurements indicate that the grafting process converts hydrophilic particles into hydrophobic ones. The oil absorption tests indicated that the CTAB-grafted sepiolite demonstrated superior characteristics, notably exhibiting no oil rejection. Consequently, this specifically synthesized powder was utilized in a two-step process consisting in pre-impregnation of oil up to 20%v of vegetable oil prior to its immobilization within a geopolymer matrix. Furthermore, the outcomes of the leaching tests revealed that the vegetable oil remained effectively confined within the immobilization matrix, ensuring its retention. The research contributes to the goal of enhancing hydrolysable nuclear waste management practices, ensuring long-term sustainability and environmental safety.

**Keywords** – solid impregnation, surfactant-grafted particles, sepiolite, CTAB, geopolymer.

## 1. Introduction

Nuclear energy plays a significant role in the European Union's power generation, accounting for approximately one-third of its electricity production through more than 141 reactors scattered across the continent in 2020 [1]. This strategic reliance on nuclear power is an undeniable cornerstone of the EU's energy mix and plays a vital role in the efforts to tackle climate change by substantially limiting greenhouse gas emissions. Nevertheless, the handling of radioactive waste continues to loom as one of the foremost challenges associated with nuclear power generation. It becomes increasingly imperative for the nuclear sector to enhance resource efficiency through waste management practices and reduction strategies, ensuring its long-term sustainability and effectiveness. Among the different existing strategies, solid impregnation offers several advantages as an intermediate step in the waste management process, before the immobilization in a cement matrix. The primary advantage of employing this method is that is non-destructive [2], as it allows for the early-stage absorption of the organic liquid onto a solid substrate. This absorbed mixture can then be seamlessly incorporated into the cement slurry in a solid state, simplifying the process in contrast to introducing a liquid phase. This simplification streamlines the overall process and enhances its efficiency. Furthermore, this method is supposed to have a milder impact on the properties of the final composite, especially in terms of mechanical performance, i.e. the preservation of the structural integrity and the mechanical strength of the composite [3].

When considering impregnation techniques, there are two fundamental approaches: (i) the first involves using the precursor materials of the immobilization matrix to trap the organic liquid (ii) the second method involves the use of external filler of charge, to adsorb the liquid before the immobilization. The choice between these two methods is contingent upon a range of factors, including the specific characteristics of the radioactive waste, its chemical properties, and the precise requirements of the waste disposal or containment procedure in question. Almabrok et al. [4] compared these two approaches to immobilize 10 wt.% of mineral oil in a Portland cement. The authors concluded that the addition of kaolinite clay lower the impact of the mechanical properties of the final composite by 2.5, compared with the absorption of oil on cement precursor. Indeed, clays are highly valued in various industrial applications thanks to their remarkable absorption properties [5]. These properties encompass diverse functions, including effective oil absorption [6], the efficient removal of heavy metals [7, 8], or their role as catalysts supports in a multitude of chemical processes [9]. Montmorillonite and sepiolite, two distinct clay minerals, are the most used and exhibit contrasting structures, serving diverse purposes. The selection

between these minerals depends on specific requirements, with sepiolite's fibrous, high-surface-area structure, and montmorillonite's strong cation exchange properties and expansiveness catering to different needs. In this study, a more comprehensive exploration of sepiolite will be undertaken, because this non-swelling clay presents a high absorption capacity, and its fibrous structure and porosity allow it to rapidly adsorb and retain significant amounts of oil [10, 11].

The grafting of surfactants onto the surface of clays is a sophisticated approach to enhance their adsorption efficiency, allowing for the customization of adsorption properties according to specific application requirements while maintaining adequate stability and dispersion. Naturally, sepiolite is hydrophilic and possesses a negative surface charge. However, by grafting quaternary ammonium-type surfactants, it becomes possible to reverse this characteristic. The surface can be modified to become positively charged and hydrophobic, all while preserving the inherent structure of sepiolite [12, 13, 14].

In this research, a comparative analysis will be conducted on three different clays: metakaolin, diatomaceous earth, and sepiolite. Two surfactants, one cationic (CetylTrimethylAmmonium Bromide, CTAB) and one non-ionic (Decyl Glucoside, DG), will be grafted onto these clays to assess their respective effectiveness. The primary objectives of this study encompass (i) examining the extent to which surfactants bond to the clay surfaces, (ii) assessing the impact of grafting on the physicochemical properties of the clays, (iii) analysing their capacity for absorbing vegetable oil, and lastly, (iv) evaluating the absorption efficiency after their incorporation into an immobilization matrix.

## **2. Materials and Methods**

### ***2.1. Materials***

Geopolymers were synthesized using a sodium silicate solution (Woellner, Betol® K 5020 T: 30.0-wt.% SiO<sub>2</sub>, 18.5 wt.% K<sub>2</sub>O and 51.5 wt.% H<sub>2</sub>O, with a molar ratio SiO<sub>2</sub>/K<sub>2</sub>O = 2.54), potassium hydroxide (Verbièse, in the form of pure pellets with an 85 % purity), and metakaolin (Imerys, ARGICAL™ M-1000), which is an aluminosilicate source. Metakaolin powder is characterized by X-Ray Fluorescence as composed of 54.8 wt.% SiO<sub>2</sub>, 39.5wt.% Al<sub>2</sub>O<sub>3</sub>, 1.8wt.% TiO<sub>2</sub>, 1.4wt.% Fe<sub>2</sub>O<sub>3</sub>, 1.0wt.% K<sub>2</sub>O, and other oxides present in less than 1wt.%. For the impregnation, diatomaceous earth (Imerys, Celite ®) and sepiolite (Xatico, ABSONET XTRA 30/60) were used as tested materials. The surfactants used for grafting on particles were hexadecyltrimethylammonium bromide (Sigma-Aldrich, purity ≥ 99.0%) and Oramix NS10 (Seppic, Decyl Glucoside). The vegetable oil chosen as model oil was the sunflower seed from Helianthus seed (Sigma-Aldrich), which was coloured in red using the Sudan III pigment (Sigma-Aldrich, C.I. 26100) for a better visual observation. n-

Heptane (Sigma-Aldrich, purity  $\geq 99\%$ ) was used for Washburn characterization. For measurements with laser granulometer, sodium pyrophosphate (Alfa-Aesar, 98 %) was used at a mass concentration of  $1.5 \text{ g.L}^{-1}$  in order to enhance the dispersion of particles.

## ***2.2.Synthesis and characterization of surfactant-grafted particles***

### ***2.2.1. Synthesis***

The study employs two selected surfactants, cetyltrimethylammonium bromide (CTAB) and decyl glucoside (DG), each with distinct critical micelle concentrations (CMC) of  $1.10 \cdot 10^{-3}$  [15] and  $5.10 \cdot 10^{-3} \text{ mol.L}^{-1}$  [16], respectively, and measured using a Krüss Force Tensiometer - K100. Two separate solutions, each with a volume of 250 mL, comprise 0.90g of CTAB in one and 2.98g of CTAB in the other, are mixed until the surfactants are completely dissolved. Subsequently, 25 g of the chosen powder materials (metakaolin, diatomaceous earth, and sepiolite) are introduced into the solutions, and the mixtures are agitated at 500 rpm for a duration of 4 hours. Following this, the samples undergo centrifugation and are subjected to three consecutive washes with deionized water. After undergoing overnight drying at  $80^\circ\text{C}$ , the grafted powders are obtained (Table 1).

**Table 1. Acronyms for the different synthesized powders, depending on the surfactants used**

<b>Powder</b>	<b>Surfactant</b>	<b>Acronym</b>
Metakaolin	CTAB	Metakaolin-CTAB
	DG	Metakaolin-DG
Diatomaceous earth	CTAB	Diatomaceous Earth-CTAB
	DG	Diatomaceous Earth-DG
Sepiolite	CTAB	Sepiolite-CTAB
	DG	Sepiolite-DG

### ***2.2.2. Characterization methods for powders***

Comprehensive characterization of all powders, both before and after synthesis, includes assessments of their morphology and particle size.

#### ***Size distribution***

The particle sizes are determined using the Mastersizer® 3000 laser granulometer from Malvern Panalytical, using sodium pyrophosphate at a mass concentration of  $1.5 \text{ g.L}^{-1}$  for better particle dispersion.

#### ***Specific surface measurements***

The specific surface area of particles was calculated using the Brunauer–Emmett–Teller (BET) method from the nitrogen adsorption and desorption isotherms at 77 K using a

Micromeritics Tristar 3000 apparatus. Prior to the adsorption measurements, the samples were out gassed for 3 hours at 423 K.

### ***ζ-potential measurements***

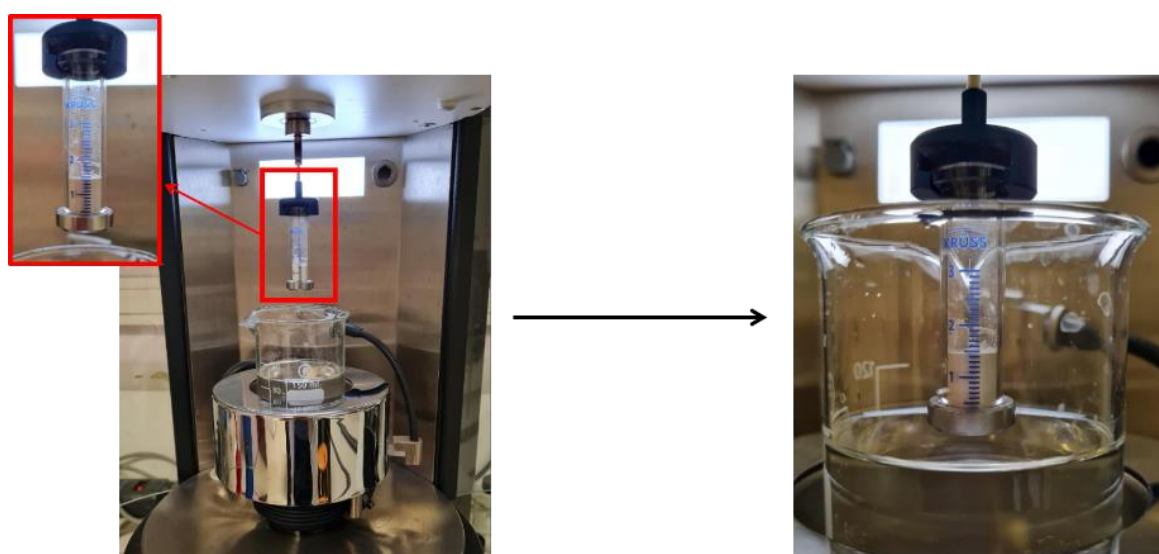
Immediately after dispersing the particles in deionized water (0.01wt.%) using an ultrasonic bath for 5 minutes, 1 mL of dispersion was introduced in a folded capillary zeta cell, and the zeta potential was measured using a ZetaSizer Nano® ZS from Malvern Panalytical.

### ***Thermogravimetric analysis (TGA)***

Thermogravimetric analysis was performed using a Q500 thermogravimetric analyser (TA Instruments). Each sample was heated from 25 to 900 °C at a rate of 10 °C.min<sup>-1</sup> under nitrogen, with a 5-minute isotherm at 120 °C to ensure complete removal of water.

### ***Washburn characterization***

Washburn tests are conducted utilizing a Krüss Force Tensiometer - K100 in conjunction with the Krüss Windows-based Laboratory Desktop software, specifically in the sorption mode. The procedure involves the placement of 1.0 gram of powder, which can either be in its natural state or hydrophobically modified, into a suitable sample holder. Afterward, the sample is compacted for 30 seconds using a 2 kg weight. Subsequently, the sample is suspended from the balance within the tensiometer. The next step entails raising the liquid until it gently touches the bottom of the porous sample (Figure 1). During this process, data is collected, where squared mass ( $m^2$ ) is measured against time ( $t$ ). This data collection occurs as the liquid progressively permeates into the solid sample, allowing for the investigation of sorption phenomena and the characterization of the material's wettability and sorption properties. All experiments are repeated three times.



**Figure 1.** Illustration of a Washburn test: (i) packing of particles in a capillary tube and (ii) immersion of particles in a given solvent

### 2.3. Study of the absorption of vegetable oil onto particles

#### Determination of the bullet point

The model oil chosen to represent the hydrolysable nuclear organic liquid in this study is the sunflower oil (vegetable oil). The first experiment aimed to determine the amount of vegetable oil that could be absorbed by the various powders. Similar to the oil uptake test (commonly used in paint formulation), oil was added drop by drop onto a constant mass of particles (1g). The measurement is carried out three times by the same operator. After agitation, the mixture's state was observed, leading to the identification of three distinct states: (i) a granular state, where not all powder was utilized to absorb the oil; (ii) a pasty state, where all the particles contributed to oil absorption without any seepage, referred to as the "bullet point" (BP); and (iii) a state where oil seepage was evident (Figure 2). The bullet point *BP*, characterized as a weight percentage, can be mathematically represented by:

$$BP(\text{wt. \%}) = \frac{\text{Mass of oil at the bullet point}}{\text{Total mass of initial powder and oil}} \times 100 \quad (1)$$

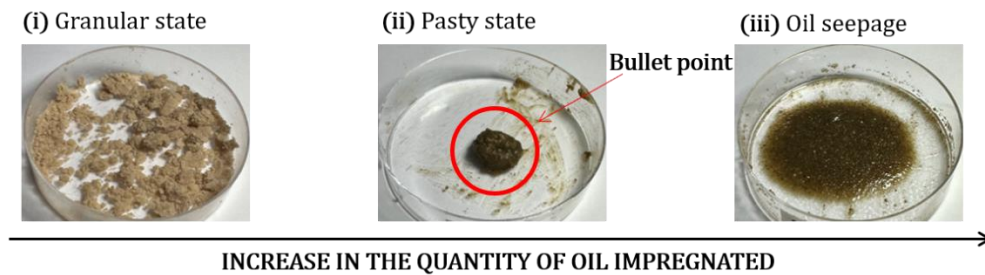


Figure 2. Illustration of the different states obtained during the measurement of the bullet point

#### Impregnation and leaching tests

After establishing the bullet point, impregnation tests are carried out using two distinct weight percentages of oil: at 50wt.% and at BPwt.%. For each test, 1g of powders derived from metakaolin and sepiolite is utilized. As for diatomaceous earth, due to its lower density, a 0.5g sample is taken.

After two days of absorption, the mixture is introduced in a water quantity that is ten times greater in mass than the oil+powder mixture, in order to determine if oil rejection occurs. For this, an optical micrograph with a VHX-900 microscope from Keyence was acquired to visualize or not the oil droplets.

The impregnated powder and the aqueous phase were subsequently isolated, accurately weighed, and subjected to a 15-day incubation in an oven at 40°C. A comprehensive monitoring of the entire water evaporation process was conducted, encompassing both

the powder and the aqueous phase. The objective was to ascertain the mass of oil liberated from the powder and subsequently transferred into the aqueous phase.

### ***2.4. Formulation of geopolymers***

Geopolymers were formulated with a final molar composition  $3.5 SiO_2 \cdot 1Al_2O_3 \cdot 1K_2O \cdot 10H_2O$  (liquid/solid ratio of 1.41) and  $3.5 SiO_2 \cdot 1Al_2O_3 \cdot 1K_2O \cdot 14H_2O$  (liquid/solid ratio of 1.69). Potassium silicate solutions – also called the activating solution – is first prepared by dissolving 11.08g of sodium hydroxide pellets in 72.39g of aqueous silicate (Betol® K 5020 T) with 4.35g deionized water by magnetic stirring at 500 rpm, until the pellets were dissolved. As this dissolution is exothermic, the solution should be brought back to room temperature before use. 62.18g of metakaolin is then added to the activating solution and stirred at 800 rpm with the Heidolph RZR 2051 stirrer for 5 minutes. The blend powder/oil is incorporated in the geopolymer paste for 7 minutes at 1000 rpm, to ensure a good homogeneity. The same apparatus is used to capture the torque in function of time at a selected stirring rate (100 to 1,000 rpm) and recorded via a specific software (Watch/Control 200) provided by Heidolph. The fresh mixture has been shaped using a silicon mould and aged at room temperature with a relative humidity of 100% until the structure is consolidated.

Following the curing period, the finalised materials are immersed in 250mL of deionized water for the purpose of conducting tests on the leaching of vegetable oil. <sup>1</sup>H NMR spectra of the supernatant was recorded at ambient temperature on a Bruker Avance 300 (UltraShield™ magnet) spectrometer operating at a Larmor frequency of 300.130 MHz

## **3. Results and Discussion**

### ***3.1. Influence of the grafting of surfactants on the powders' characteristics***

The primary goal of this study is to investigate the extent to which surfactant grafting on the surface of various powders influences their physicochemical properties. Subsequently, the raw and synthesised powders were analysed through laser granulometry, TGA, as well as measurements of  $\zeta$ -potential and the characterisation of the bullet points.

#### ***3.1.1. Determination of the average size of particles***

Figure 3 displays the size distributions of the different powders: metakaolin, diatomaceous earth and sepiolite before and after grafting by CTAB and DG. The relevant diameters et the *Span* value of all samples are compiled in Table 2. The *Span* value, also referred as granulometric spread, is defined as [17]:

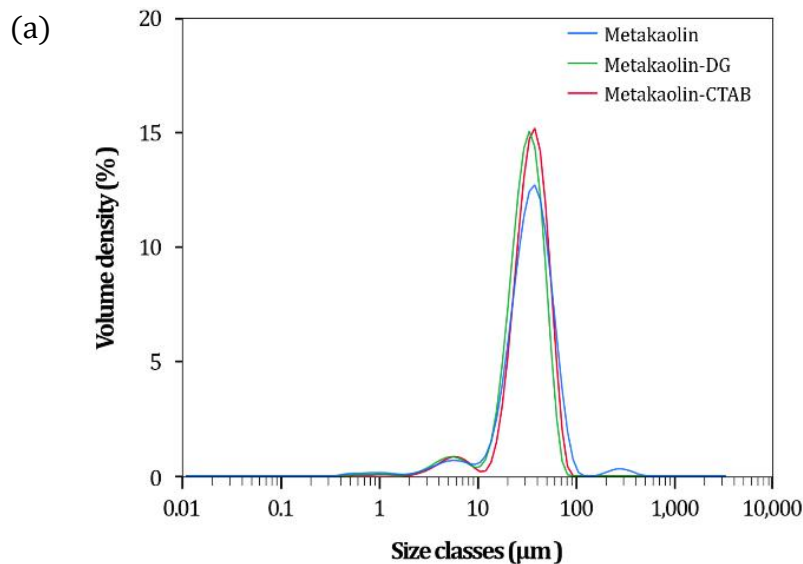


$$Span = \frac{D_v(90) - D_v(10)}{D_v(50)} \times 100 \quad (2)$$

where  $D_v(10)$ ,  $D_v(50)$ , and  $D_v(90)$  represent the sizes below which 10%, 50%, and 90% of the sample particles in volume are located, respectively.

The sepiolite exhibits a high degree of polydispersity, in contrast to metakaolin and diatomaceous earth, which have a Span value close to 1. Prior to grafting, the Span value for sepiolite is approximately 8, reducing to 3.5 after grafting. Surfactant grafting, therefore, does not modify the particle size distribution profiles for metakaolin and diatomaceous earth. In the case of sepiolite, grafting has successfully disrupted aggregates, especially those exceeding 1  $\mu\text{m}$  (Figure 3 (c)).

The distinctions among the average diameters diminish as particle size uniformity increases. Absolute equality in diameters is only achieved in the context of a completely monodisperse distribution [18]. Notably, the ungrafted sepiolite exhibits a  $D_v(90)$  twice as large as the grafted sepiolite. This reduction can be attributed to the fact that, during synthesis, the particles become wet, and in the case of commercial sepiolite aggregation, the wetting disrupts the aggregates, consequently decreasing the mean particle diameters. It can be concluded that the grafting of surfactants has no influence on the shape and the centre of the distribution.



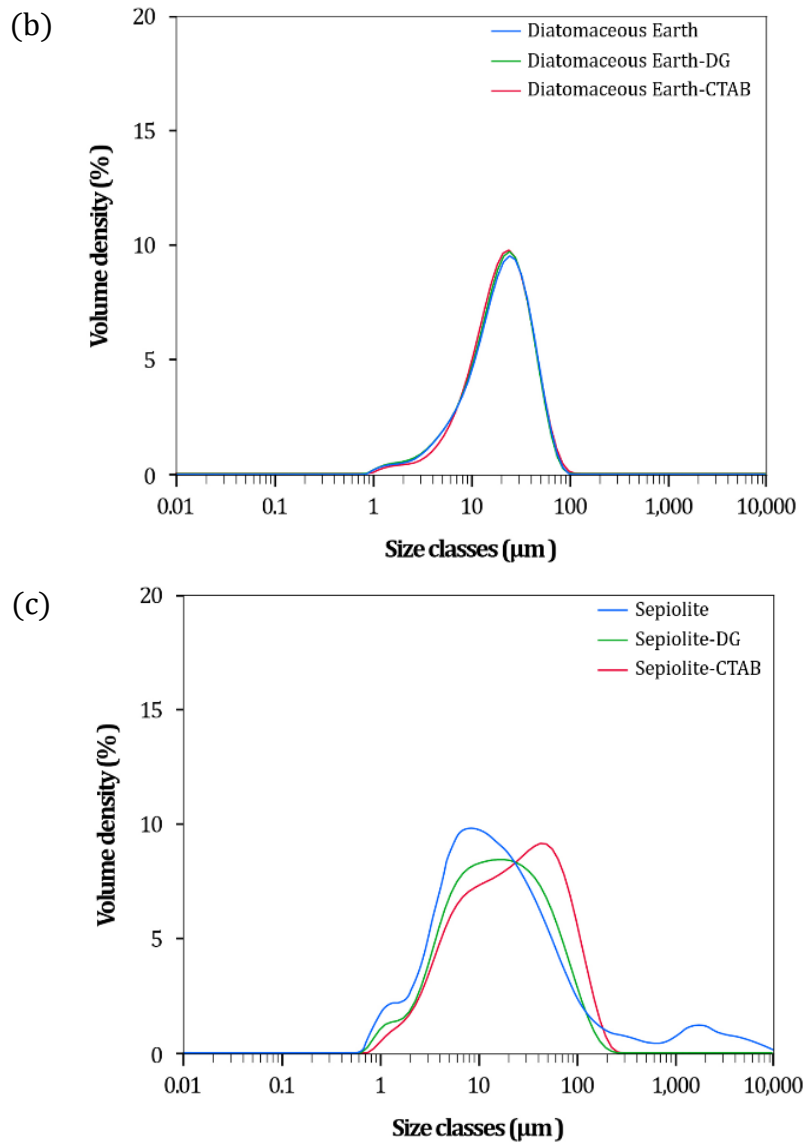


Figure 3. Particle size distribution determined by laser granulometry for the three raw powders ((a) metakaolin, (b) diatomaceous earth, and (c) sepiolite) and surfactant-grafted powders ((a) metakaolin-DG, metakaolin-CTAB, (b) diatomaceous earth-DG, diatomaceous earth-CTAB, (c) sepiolite-DG, and sepiolite-CTAB).

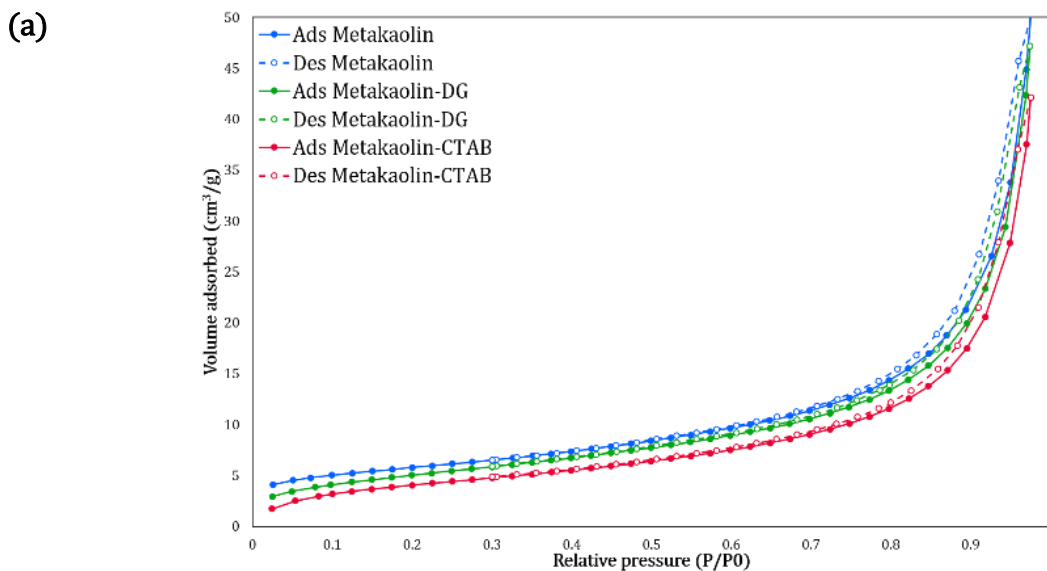
Table 2. Granulometric range (*Span*) and relevant diameters for the various powders investigated (DG = Decyl Glucoside and CTAB = CetylTrimethylAmmonium Bromide).

Powder	Surfactant	<i>Span</i>	$D_v(50)$ ( $\mu\text{m}$ )	$D[4, 3]$ ( $\mu\text{m}$ )	$D[3, 2]$ ( $\mu\text{m}$ )
Metakaolin	<i>Ungrafted</i>	1.313	34.4	39.4	18.7
	<i>DG</i>	1.071	30.9	31.6	20.0
	<i>CTAB</i>	1.040	34.5	35.4	23.3
Diatomaceous Earth	<i>Ungrafted</i>	1.705	11.6	12.9	7.46
	<i>DG</i>	1.686	11.4	12.6	7.40
	<i>CTAB</i>	1.652	11.7	13.2	8.25
Sepiolite	<i>Ungrafted</i>	7.991	7.78	74.8	4.44
	<i>DG</i>	3.504	8.83	13.9	5.06
	<i>CTAB</i>	3.340	12.3	18.4	6.31

### 3.1.2. Determination of the specific surface area

Surface area and pore size represent important parameters that define the quality of adsorbents, playing a direct and significant role in determining their retention capacity. The sorption isotherms for all the particles are displayed in **Erreur ! Source du renvoi introuvable.** Metakaolin, diatomaceous earth, and sepiolite exhibited predominantly mesoporous characteristics, as indicated by their Type IV physisorption isotherm and the presence of an H3 hysteresis loop, according to IUPAC classification [19]. This means that the quantity adsorbed is higher at any specific relative pressure along the *desorption* branch compared to the *adsorption* branch.

For metakaolin, treatments with CTAB and DG do not appear to affect the adsorption capacity, suggesting that these agents may not notably alter the pore structure. In the case of diatomaceous earth and sepiolite, the treatments result in different changes to the materials' adsorption capacities. For diatomaceous earth, DG treatment decreases this capacity the most, while for sepiolite, it is the CTAB treatment. These findings are correlated with the specific surfaces of the materials determined by the BET method, as presented in Table 3. In both cases, surfactant grafting could potentially block pores or chemically modify material surfaces, making them less receptive to adsorption. Sepiolite exhibits the highest specific surface area ( $201.89 \text{ m}^2.\text{g}^{-1}$ ), compared to diatomaceous earth ( $9.65 \text{ m}^2.\text{g}^{-1}$ ) and metakaolin ( $20.60 \text{ m}^2.\text{g}^{-1}$ ). Although surfactant grafting reduces this specific surface area ( $114.89 \text{ m}^2.\text{g}^{-1}$  for sepiolite-CTAB), it can enhance the adsorption quality, particularly for vegetable oil, which is the focus of this study.



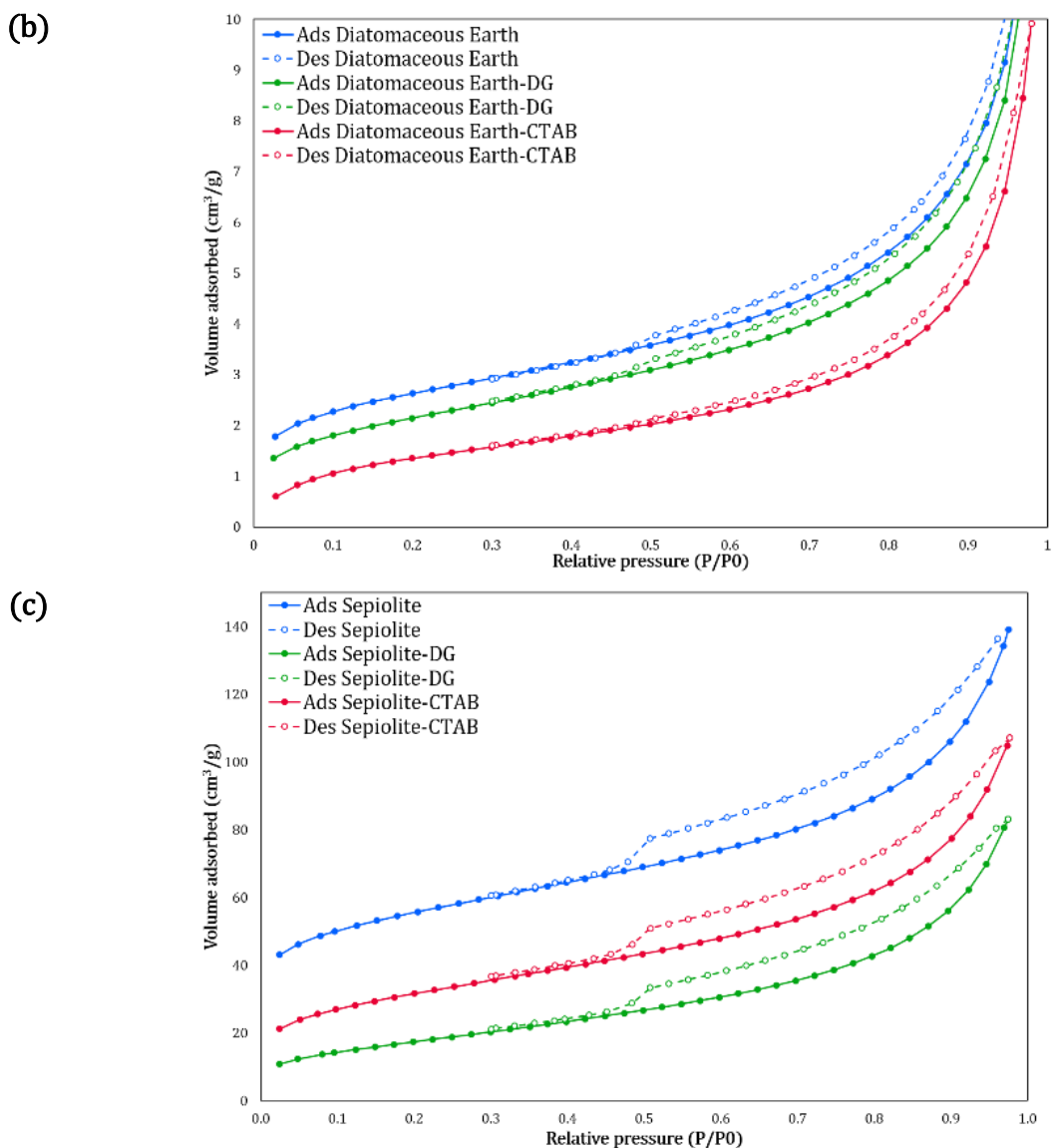


Figure 4. Nitrogen sorption isotherms of raw metakaolin (a), diatomaceous earth (b), and sepiolite (c), with their corresponding surfactant-grafted counterparts (the filled circles represent the adsorption and the open circles the desorption).

Table 3. Specific surfaces of materials determined using the BET method.

Powder	Surfactant	Specific surface area ( $\text{m}^2.\text{g}^{-1}$ )
Metakaolin	<i>Ungrafted</i>	20.60
	<i>DG</i>	18.54
	<i>CTAB</i>	16.14
Diatomaceous Earth	<i>Ungrafted</i>	9.65
	<i>DG</i>	7.91
	<i>CTAB</i>	5.61
Sepiolite	<i>Ungrafted</i>	201.89
	<i>DG</i>	65.03
	<i>CTAB</i>	114.89

### 3.1.3. TGA measurements

The TGA study was carried out to verify the successful grafting of surfactants onto the surface of the particles.

#### TGA of raw surfactants

Initially, the surfactants were individually analysed to establish their reference points. As DG is not commercially pure but rather diluted in water, a water loss is evident in thermogram from 60 to 120°C (Figure 5). The degradation temperatures for CTAB and DG are 270°C and 330°C, respectively.

#### TGA of raw powders

Concerning the raw powders, metakaolin shows no degradation within the studied temperature range (25-800°C). Sepiolite, being a fibrous mineral with water contained in its crystalline structure, experiences a 10% mass loss, between 50 and 120°C. When subjected to thermogravimetric analysis (TGA), the heat gradually releases the water trapped within its crystalline structure in the form of water vapor [20]. In contrast, diatomaceous earth displays an initial 5% degradation around 250°C, followed by a subsequent 10% degradation at 650°C. The initial loss is attributed to a reaction, or the release of volatile compounds trapped in the diatomaceous earth's structure, while the latter corresponds to the decomposition of more stable compounds or chemical reactions [21].

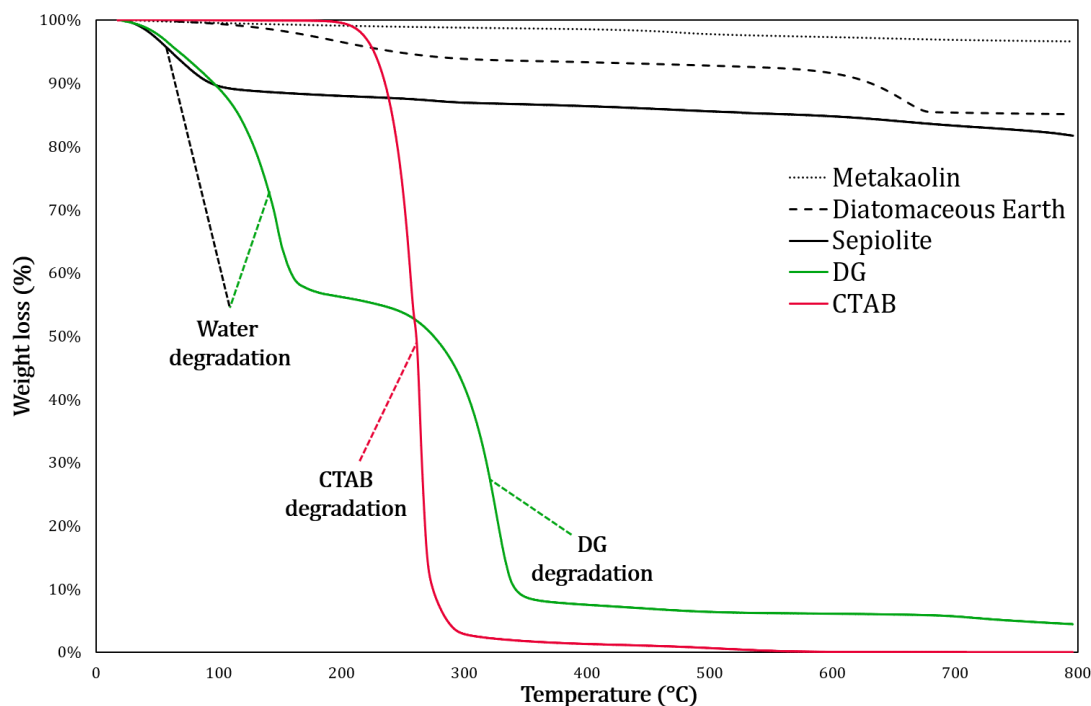


Figure 5. Thermogravimetric curves of references raw materials: surfactants (DG and CTAB) and particles (metakaolin, diatomaceous earth and sepiolite) alone.

## TGA of surfactant-grafted particles

The thermograms of surfactant-grafted particles can be observed in Figure 5. According to the procedure, if the entire quantity of surfactant is adsorbed onto the powder, the maximum yield would be 4%. While challenging to quantify through TGA, this technique allows for the observation of slope changes, revealing how the grafting protocol impacts the particles. Turning attention to the water component initially, a reduction in water content is noticeable in the grafted particles, particularly for sepiolite. The final step of the grafting protocol involves drying the powders at 80°C overnight, leading to the removal of a significant amount of water. Given that sepiolite and diatomaceous earth particles inherently contain water in their structure, it is expected that they, compared to their counterparts, experience the most substantial mass loss at the end of the measurement. Shifting the focus to grafting, distinct slope changes corresponding to the degradation temperatures of surfactants are observed for sepiolite particles. Concerning metakaolin, the evident slope change of CTAB occurs around 250 °C, while the grafting of DG is less discernible. In the case of diatomaceous earth, the slope changes between 200 and 300°C differs between the two grafted particles, possibly indicating the degradation of both surfactants. The mass losses are minimal due to the low surfactant concentration relative to that of the clays. Therefore, particle  $\zeta$ -potential measurements are necessary to determine whether surfactant grafting has modified the surface charge of the particles or not.

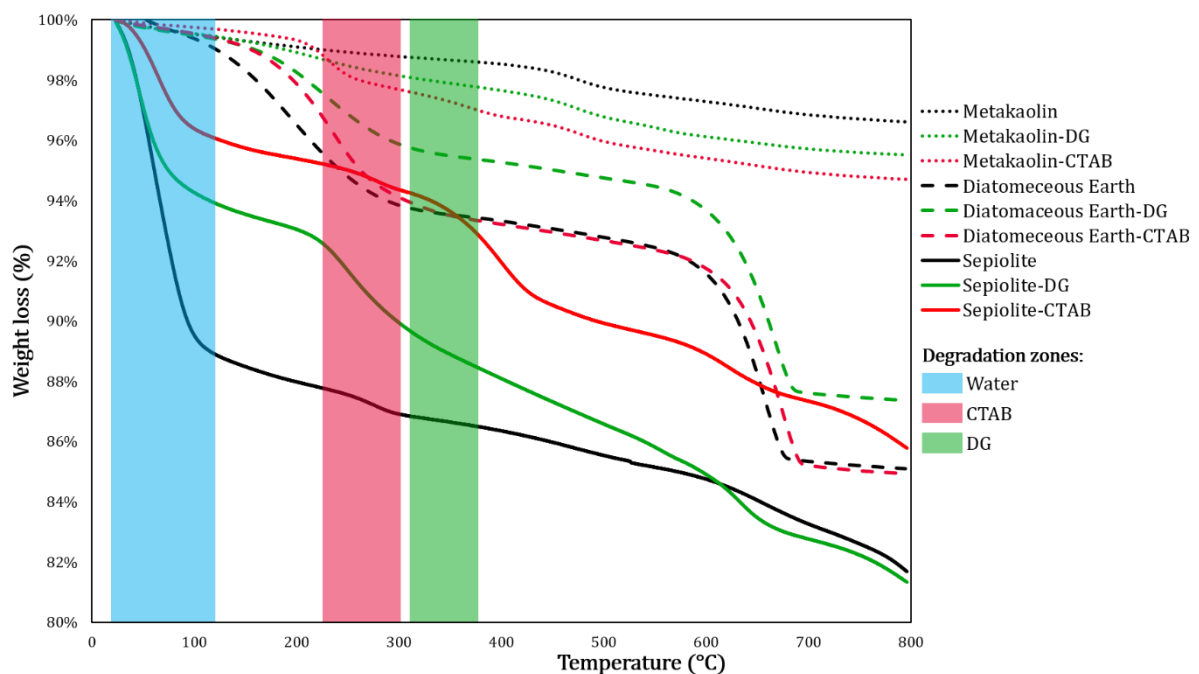


Figure 6. Thermogravimetric curves of the surfactant-grafted powders with Decyl Glucoside and CetylTrimethylAmmonium Bromide.

### 3.1.4. $\zeta$ -potential measurements

When colloidal particles are dispersed in a liquid, they have an interaction with ions of opposing charge in their immediate surroundings. This phenomenon leads to the formation of what is known as a "double electric layer" around these particles. In this electric layer, the area close to the particles becomes enriched with ions carrying opposite charges to the particles themselves, while the farther region contains ions of the opposite charge. The collective charge distribution in this double electric layer creates an intricate electrical structure around the particles. The zeta potential is a crucial parameter that quantifies the difference in electric potential between the particle's surface and a mobile ion layer at a specific distance from the particle [22].

Table 4 illustrates how grafting surfactants onto powders influences their  $\zeta$ -potential. Remarkably, all the powders consistently display a negative zeta potential. In the absence of surfactant grafting, diatomaceous earth exhibits the highest absolute zeta potential value (-29.4 mV), surpassing metakaolin and sepiolite (-26.1 and -18.8 mV, respectively). All measured solutions exhibited a pH ranging from 6 to 7, and it did not change, even for grafted particles. Alkan et al. [23] conducted an analysis on the effect of treating sepiolite with organosilanes on the zeta potential. They revealed that the isoelectric point of natural sepiolite was at a pH of 7.8, and this point was contingent on the treatment applied to the particles. In our study, we did not delve into this alteration as our primary focus in the zeta potential measurements was to ascertain the effective grafting of surfactants.

When non-ionic surfactants are introduced to the particle surfaces, no significant change in  $\zeta$ -potential occurs, as no additional electric charge is introduced. Non-ionic surfactants serve primarily to stabilize suspensions by preventing particle agglomeration through steric repulsion mechanisms.

However, a shift in the  $\zeta$ -potential is observed when cationic surfactants are grafted. This shift is particularly pronounced for metakaolin (from -26.1mV to 5.9mV) and diatomaceous earth (from -29.4mV to -2.2 mV). The substantial increase in zeta potential with cationic surfactant grafting is attributed to the introduction of positive charges from the polar part of CTAB, which enhances electrostatic repulsion between particles, thereby contributing to suspension stability. Conversely, the  $\zeta$ -potential of sepiolite remains largely unaffected by surfactant grafting, regardless of their charge. Similar results [24] have been observed, while grafting TTAB (TetradecylTrimethylAmmonium Bromide) on sepiolite, resulting in a modest decrease in zeta potential from -23.6 to -17.1 mV. This observation may be explained by the fact that sepiolite is a fibrous clay with inherent surface electrical charges due to specific functional groups on its surfaces. If these charges are already relatively high and stable, the addition of surfactants, whether cationic,

anionic, or non-ionic, may not significantly alter the  $\zeta$ -potential. Additionally, sepiolite may possess a unique affinity for surfactants, independent of their charge, allowing for effective adsorption to its surface. Consequently, this adsorption may neutralize the surfactants' impact on the  $\zeta$ -potential, maintaining its stability.

**Table 4. Influence of the surfactant grafting on the  $\zeta$ -potential (mV) of the different powders.**

Powder	Surfactant	$\zeta$ -potential (mV)	Standard deviation (mV)
Metakaolin	<i>Ungrafted</i>	-26.1	0.5
	<i>DG</i>	-22.7	0.6
	<i>CTAB</i>	6.9	1.0
Diatomaceous Earth	<i>Ungrafted</i>	-29.4	1.1
	<i>DG</i>	-26.1	0.9
	<i>CTAB</i>	-2.2	0.3
Sepiolite	<i>Ungrafted</i>	-18.8	0.3
	<i>DG</i>	-17.4	0.2
	<i>CTAB</i>	-16.2	0.2

### 3.1.5. Washburn measurements

Due to the porous nature of the particles, it was not feasible to measure contact angles using the drop deposition method. Even though solid and smooth surfaces were achieved using a uniaxial compression press, the liquids were promptly absorbed into the material upon deposition. Consequently, the Washburn method was employed to investigate the wettability of the powders. For this, a small quantity of the porous material is packed into a capillary tube, which is immersed in a reservoir of a selected liquid

Capillary rise occurs as the liquid is drawn into the porous material due to capillary forces. The rise of the liquid is monitored over time, and the rate of capillary rise varies depending on the characteristics of the powder. The Washburn equation, used to analyse the data and determine relevant parameters, is as follows [25]:

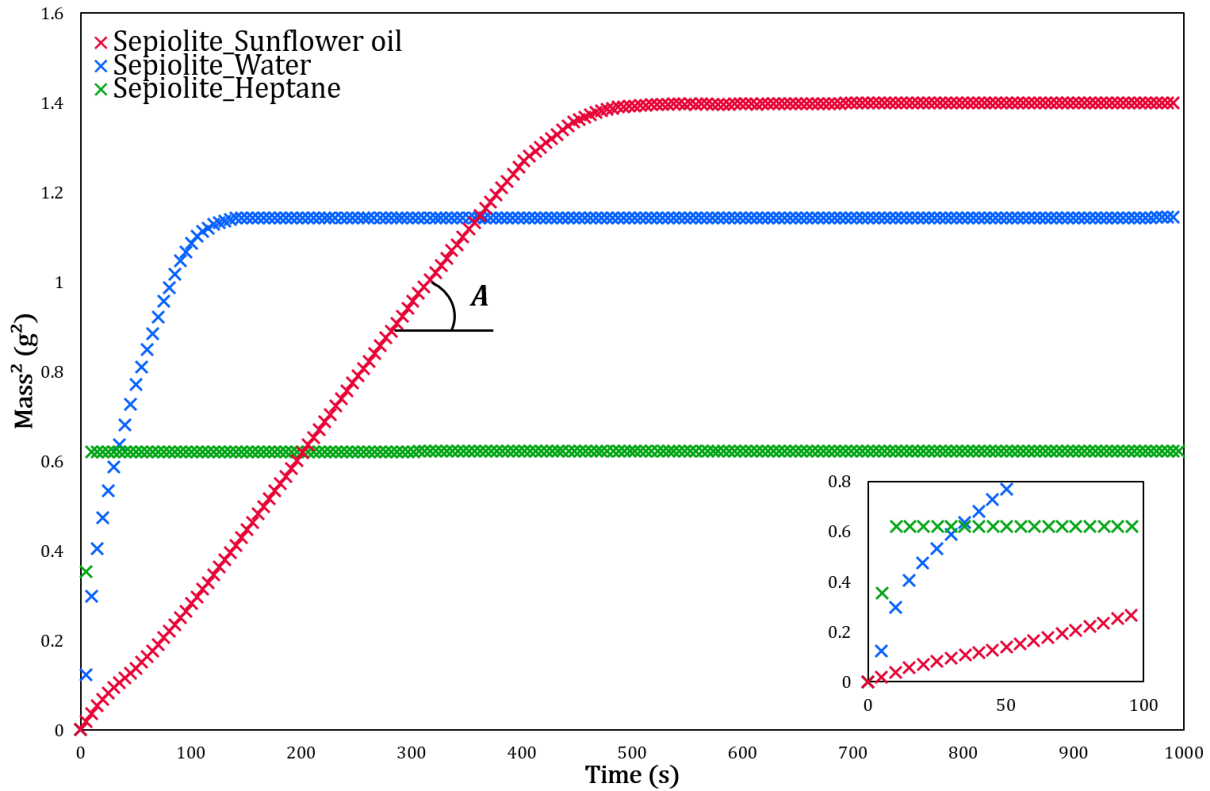
$$m^2 = A \cdot t \text{ and } A = \frac{\rho^2 \cdot \gamma \cdot C \cdot \cos(\theta)}{\eta} \quad (43)$$

where  $m$  (kg) is the mass of liquid adsorbed on solid;  $t$  (s) is the time of contact of the experiment;  $\rho$  ( $\text{kg}\cdot\text{m}^{-3}$ ),  $\gamma$  ( $\text{mN}\cdot\text{m}^{-1}$ ) and  $\eta$  (Pa.s) are the density, the surface tension and the viscosity of the liquid, respectively;  $C$  ( $\text{m}^5$ ) is the capillary constant associated with the material measured; and  $\theta$  ( $^\circ$ ) is the contact angle between the liquid and the solid.



From this plot, it is possible to extract the wettability data, which is the  $C \cdot \cos(\theta)$  part. As there are two unknowns ( $C$  and  $\theta$ ), a preliminary experiment must be carried out to determine the constant  $C$ . For this, *n*-heptane is used (very low surface tension,  $\gamma_{heptane} = 20.5 \text{ mN} \cdot \text{m}^{-1}$  [26]) as the liquid, which perfectly wets the solid, in order to assume a  $\theta$  of  $0^\circ$ . This represents one of the limitations of using the Washburn technique. Indeed,  $C$  represents the packing of particles and reflects the porosity of the powder. Consequently, the manner of packing particles before the experiment must be as constant as possible, with the same weight, time, and operator for the experiment. Any fluctuations can introduce potential inaccuracies when calculating the contact angle, hence, every measurement was conducted twice [27].

For instance, the Figure 7 depicts Washburn curves for sepiolite using three tested solvents: heptane, water, and sunflower oil. For each of the three liquids, the initial variation of  $m^2$  over time forms a straight line, from which the slope  $A$  can be derived. Consequently, by leveraging the known characteristic properties of the fluid (density, surface tension, and viscosity), it becomes feasible to extract the values of  $C \cdot \cos(\theta)$ . The subsequent phase of the curve is distinguished by a plateau, signalling the conclusion of the liquid's capillary ascent. The distinct  $m^2$  values observed at the plateau can be attributed to variations in the density of the three liquids. In the case of heptane, the plateau is quickly reached, signifying rapid wetting of the solid by the liquid. This observation underscores heptane's efficacy as a solvent for determining the capillarity constant. Upon comparing the curves for oil and water, it becomes apparent that water demonstrates a faster wetting of sepiolite compared to oil. This implies that untreated sepiolite exhibits hydrophilic properties.



**Figure 7. Washburn curves for the raw sepiolite with the three tested solvents (sunflower oil, water and heptane)**

With the Washburn measurements, the chosen approach is comparative, and no specific contact angle values will be provided, only the  $C \cdot \cos(\theta)$  term will be discussed afterwards. The objective of this analysis is, indeed, to assess the wettability of powders by making a comparison between natural powders and modified powders. The aim is to understand the influence of introducing a surfactant through grafting on the wettability behavior of particles.

To determine the hydrophilic/hydrophobic properties of the different particles, Table 5 displays the values linked to the slope of the curves  $\Delta m^2 / \Delta t$ , representing the term  $A$  in the Washburn equation, as well as the values of the terms  $C \cdot \cos(\theta)$ . As the slope value increases, particles become more rapidly wetted by the given liquid. This implies that a higher value of  $A$  corresponds to a heightened affinity of particles for the liquid. Conversely, this relationship is inversely proportional for the term  $C \cdot \cos(\theta)$ .

**Table 5. Values of the slopes  $A$  ( $\Delta m^2/\Delta t$ ) corresponding to the curves in the Washburn test for both natural and modified powders, along with the term  $C \cdot \cos(\theta)$ , for heptane, water and vegetable oil.**

		<b>Slope <math>A</math> (<math>\Delta m^2/\Delta t</math>)</b> <b>(<math>10^{-3} \text{ kg}^2 \cdot \text{s}^{-1}</math>)</b>	<b><math>C \cdot \cos(\theta)</math></b> <b>(<math>10^{-16} \text{ m}^5</math>)</b>
<b>Metakaolin</b>	<i>Ungrafted</i>	3.90 <sup>heptane</sup>	1.53 <sup>heptane</sup>
		4.17 <sup>water</sup>	0.58 <sup>water</sup>
		0.21 <sup>oil</sup>	4.75 <sup>oil</sup>
	<i>DG</i>	2.80 <sup>heptane</sup>	1.10 <sup>heptane</sup>
		2.30 <sup>water</sup>	0.32 <sup>water</sup>
		0.16 <sup>oil</sup>	3.62 <sup>oil</sup>
	<i>CTAB</i>	2.60 <sup>heptane</sup>	1.02 <sup>heptane</sup>
		2.13 <sup>water</sup>	0.29 <sup>water</sup>
		0.13 <sup>oil</sup>	2.94 <sup>oil</sup>
<b>Diatomaceous Earth</b>	<i>Ungrafted</i>	8.30 <sup>heptane</sup>	3.25 <sup>heptane</sup>
		26.90 <sup>water</sup>	3.71 <sup>water</sup>
		0.79 <sup>oil</sup>	17.9 <sup>oil</sup>
	<i>DG</i>	10.60 <sup>heptane</sup>	3.91 <sup>heptane</sup>
		14.80 <sup>water</sup>	2.04 <sup>water</sup>
		0.39 <sup>oil</sup>	8.81 <sup>oil</sup>
	<i>CTAB</i>	6.80 <sup>heptane</sup>	2.66 <sup>heptane</sup>
		2.58 <sup>water</sup>	0.36 <sup>water</sup>
		0.95 <sup>oil</sup>	21.5 <sup>oil</sup>
<b>Sepiolite</b>	<i>Ungrafted</i>	60.90 <sup>heptane</sup>	23.84 <sup>heptane</sup>
		9.32 <sup>water</sup>	1.29 <sup>water</sup>
		3.19 <sup>oil</sup>	72.1 <sup>oil</sup>
	<i>DG</i>	8.80 <sup>heptane</sup>	3.44 <sup>heptane</sup>
		5.73 <sup>water</sup>	0.79 <sup>water</sup>
		0.30 <sup>oil</sup>	6.78 <sup>oil</sup>
	<i>CTAB</i>	8.10 <sup>heptane</sup>	2.35 <sup>heptane</sup>
		3.00 <sup>water</sup>	0.41 <sup>water</sup>
		1.07 <sup>oil</sup>	24.9 <sup>oil</sup>

To evaluate the impact of grafting a surfactant onto a powder, there will be a focus specifically on sepiolite. In Figure 8, all the Washburn curves associated with sepiolite, whether grafted or ungrafted, are depicted. When comparing measurements in water, raw sepiolite exhibits higher hydrophilicity than sepiolite-CTAB, and the latter is, in turn,

more hydrophilic than sepiolite-DG. Grafting, therefore, enhances the hydrophobicity of particles, a characteristic observed across all type of powders.

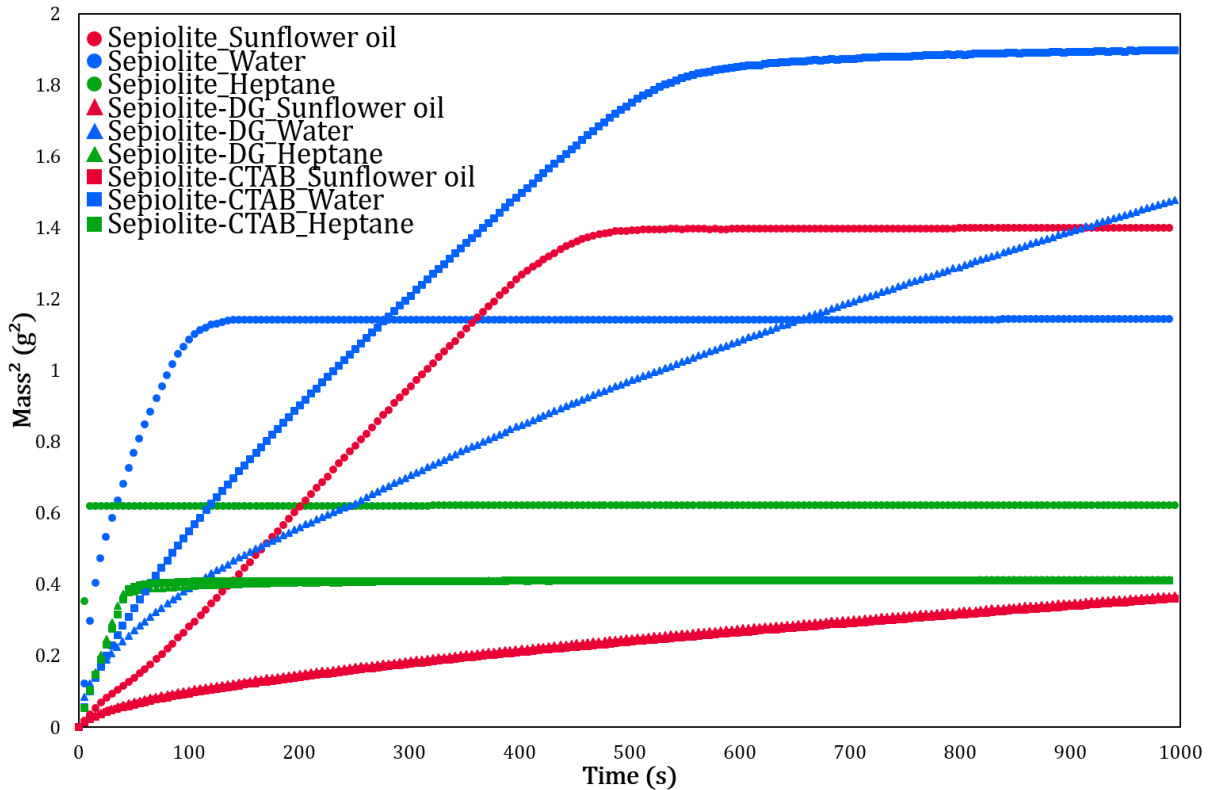


Figure 8. Impact of grafted surfactants (cationic CTAB or non-ionic DG) on the wettability characteristics of particles.

### 3.1.6. Bullet points determination

To assess the impregnation of vegetable oil, the absorption capacity of each powder—whether in its raw or grafted form—was evaluated by measuring the bullet point, using the Equation (1) (Figure 9). The objective was to achieve a well-homogeneous paste incorporating the oil, free from clumps or oil rejection. Diatomaceous earth demonstrates the highest absorption properties, reaching up to 66.4%, compared to metakaolin (41.4%) and sepiolite (33.4%). Grafting a surfactant leads to a reduction in this capacity, with a decrease of 15% for diatomaceous earth-DG and 23% for diatomaceous earth-CTAB. This decrease correlates with the reduction in specific surface area (see 3.1.1). This determination allows us to understand the extent to which a particle can absorb oil before reaching saturation.

Concerning sepiolite and metakaolin, it is evident that surfactant grafting has no influence on the bullet point. As these are all porous particles, and the pores are utilized for oil absorption, it is possible that surfactants do not penetrate the pores for metakaolin and sepiolite but do so for diatomaceous earth. Consequently, even though grafting reduces

the bullet point, it can still enhance vegetable oil absorption, thanks to the apolar, elongated chains of surfactants facilitating additional interaction with the oil.

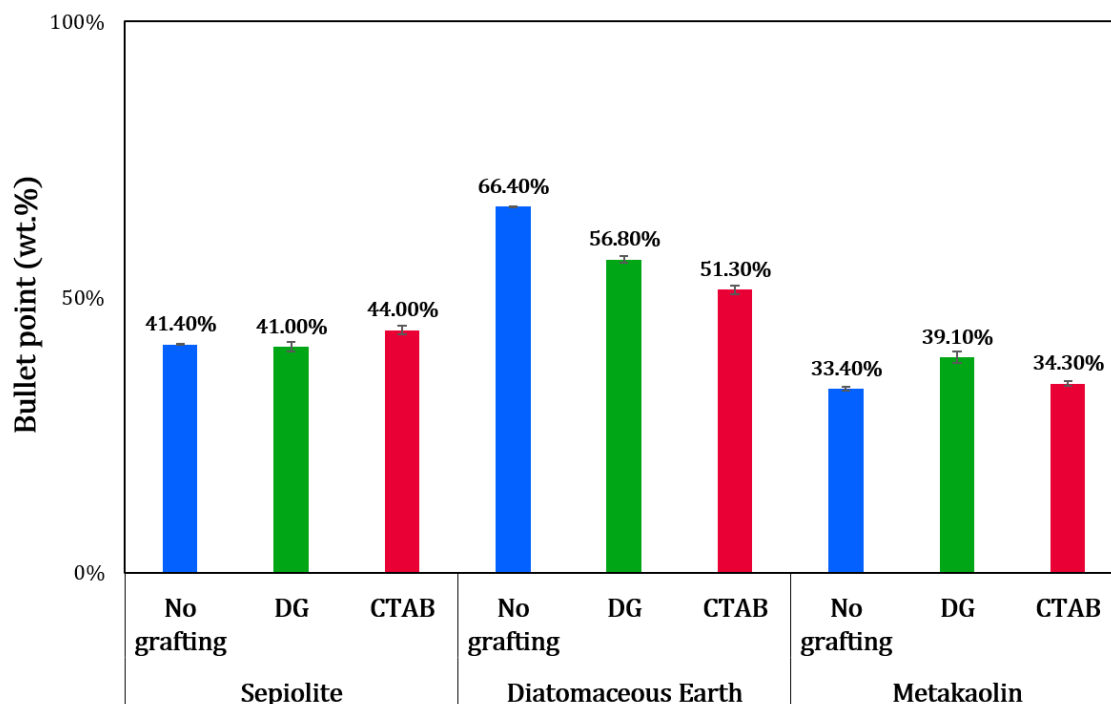




















Figure 9. Determination of the bullet point (wt.%) of metakaolin, diatomaceous earth, and sepiolite, with and without surfactants grafting.

### *3.2. Oil impregnation on the different powders*

The aim of this section is to examine the behaviour of vegetable oil once it permeates various particles. To achieve this, mixtures were prepared with two different weight percentages of oil in powder: 50wt.% and BPwt.% (Table 6). In the case of the first ratio, the diatomaceous earth displays a granular state, as its bullet point significantly surpasses that of metakaolin and sepiolite. As metakaolin and sepiolite, it is noteworthy that a 50wt.% oil results in partial absorption, with observable rejection visible to the naked eye.

**Table 6. Photographs illustrating the vegetable oil:powder blends at varying ratios (either at 50 wt.% or determined by the bullet point measurement), in conjunction with the presence of the grafted surfactant (Decyl Glucoside or CetylTrimethylAmmonium Bromide).**

	No surfactant		Decyl Glucoside		CetylTrimethylAmmonium Bromide	
Metakaolin	 50.0wt.%	 33.4wt.%	 50.0wt.%	 41.0wt.%	 50.0wt.%	 44.0wt.%
Diatomaceous Earth	 50.0wt.%	 66.4wt.%	 50.0wt.%	 56.8wt.%	 50.0wt.%	 51.3wt.%
Sepiolite	 50.0wt.%	 33.4wt.%	 50.0wt.%	 39.1wt.%	 50.0wt.%	 34.3wt.%

Following a two-day resting period for the powder to fully absorb the oil, these mixtures were exposed to demineralized water to investigate any potential oil rejection after this duration. The outcomes, including the final masses and oil rejection, are detailed in Table 7.

Immediately upon contact with water, the untreated diatomaceous earth dispersed, resulting in a substantial oil rejection of approximately 51%, regardless of the ratio. A similar phenomenon was observed for diatomaceous earth grafted with decyl glucoside, with an even higher rejection at the BPwt.%, around 61%. The quick dispersion of diatomaceous earth in water can be attributed to its elevated  $\zeta$ -potential, indicating a pronounced affinity for water. In contrast, both diatomaceous earth and sepiolite, whether grafted or not with cetyltrimethylammonium bromide, exhibited only minimal oil rejection (0.2% for diatomaceous earth and 0 % for sepiolite) and did not disperse in water. The distinctive behaviours can be attributed to the surface modifications induced by the grafting agents. When decyl glucoside is grafted onto diatomaceous earth, it renders the particle surface not enough hydrophobic, leading to the dispersion of the powder in water. Conversely, cetyltrimethylammonium bromide (CTAB), a cationic surfactant, imparts hydrophobicity to the surface of diatomaceous earth and sepiolite, promoting agglomeration rather than dispersion. The cation-anion interactions between the grafted CTAB and the negative charges on the diatomaceous earth's and sepiolite's surfaces contribute to maintaining the aggregated structure. The metakaolin demonstrates consistent oil rejection characteristics, whether it is grafted with a surfactant or not. This can be attributed to its inherently absorbent nature and porous

structure, facilitating interaction with oil, irrespective of the presence or absence of a hydrophobic grafting agent.

Therefore, the CTAB-grafted sepiolite demonstrates outstanding oil absorption characteristics in this context and will be selected for immobilization within a geopolymer matrix.

**Table 7. Experimental data on the initial and final masses of vegetable oil impregnated onto various powders, along with the observed oil rejection, determined through weighing after a 14-day incubation period at 40 °C.**

Powder	Surfactant	Oil wt. %	Initial mass of oil (g)	Final mass of oil (g)	Oil leakage (%)
Metakaolin	<i>Ungrafted</i>	50	0.983	0.034	3.4 %
		BP	0.901	0.003	0.3 %
	<i>DG</i>	50	1.209	0.082	6.7 %
		BP	0.943	0.002	0.2 %
	<i>CTAB</i>	50	1.270	0.103	8.1 %
		BP	0.752	0.005	0.7 %
Diatomaceous Earth	<i>Ungrafted</i>	50	1.015	0.527	51.9 %
		BP	1.067	0.547	51.2 %
	<i>DG</i>	50	0.916	0.404	44.1 %
		BP	1.034	0.627	60.6 %
	<i>CTAB</i>	50	0.918	0.001	0.1 %
		BP	0.952	0.003	0.3 %
Sepiolite	<i>Ungrafted</i>	50	1.548	0.681	44.0 %
		BP	1.016	0.473	46.6 %
	<i>DG</i>	50	1.417	0.656	46.3 %
		BP	1.275	0.475	37.3 %
	<i>CTAB</i>	50	1.428	0.061	4.3 %
		BP	1.443	0.000	0.0 %

### ***3.3. Immobilization of sepiolite-CTAB:vegetable oil blend in geopolymer matrices***

The CTAB-grafted sepiolite demonstrates superior performance in terms of physicochemical properties, particularly in the context of the vegetable oil absorption test where no oil release occurs upon contact with demineralized water. This sepiolite-CTAB was consequently employed to impregnate a specific volumetric percentage of oil into a geopolymer matrix. Notably, 10%v (GP2) (144 g geopolymer paste, 9.2 g vegetable oil and 11.8 g CTAB-sepiolite particles) and 20%v (GP3) (128 g geopolymer paste, 18.4 g

vegetable oil and 23.5 g CTAB-sepiolite particles) were incorporated into a geopolymer characterized by a stoichiometry of  $3.5 \text{SiO}_2 \cdot 1\text{Al}_2\text{O}_3 \cdot 1\text{K}_2\text{O} \cdot 10\text{H}_2\text{O}$ , while 40%v (GP4) (96 g geopolymer paste, 36.8 g vegetable oil and 41.2 g CTAB-sepiolite particles) was integrated into a geopolymer with a stoichiometry of  $3.5 \text{SiO}_2 \cdot 1\text{Al}_2\text{O}_3 \cdot 1\text{K}_2\text{O} \cdot 14\text{H}_2\text{O}$ . 20%v of oil was also incorporated in a reference geopolymer without being absorbed on sepiolite-CTAB. The adjustment of water quantity became imperative, as the augmentation of the incorporated oil necessitated a corresponding increase in the sepiolite-CTAB quantity, and the viscosity was too high to maintain the initial water quantity.

Following a 28-day curing period in an environment maintained at 100% relative humidity, the formulated geopolymers undergo leaching tests. These tests entail immersing the geopolymer in demineralized water to examine any observable oil release. In the instance of GP1, where no grafted particles are present, a distinct expulsion of oil from the geopolymer is noted—a phenomenon consistent with findings from non-published results. This oil release can be attributed (i) to the alkaline nature of geopolymers and, (ii) because of the nature of polar vegetable oil, it can easily flow through the open porous network, facilitating leaching. When vegetable oils are incorporated, they undergo a saponification reaction within this alkaline milieu. This insightful observation sheds light on the intricate interplay between the geopolymer matrix and incorporated oils during leaching tests. [29]. Indeed, this method facilitates the production of macroporous geopolymer, resulting in the formation of porous materials. [26, 27]. In our particular study, the goal is to confine vegetable oil, regarded as a potentially radioactive waste, within the geopolymer matrix. Thus, thanks to these preliminary studies, the phenomenon of vegetable oil expulsion in a geopolymer matrix without the addition of additives is already known, and our results are consistent with this. In Figure 10, both macroscopic and microscopic images of GP2, 3, and 4 are presented. Even to the naked eye, the noticeable red coloration indicates the expulsion of vegetable oil in geopolymer GP4. This serves as clear evidence that incorporating 40%v oil into a geopolymer with this stoichiometry is impractical. On the contrary, regarding geopolymers GP2 and GP3 (with 10%v and 20%v oil, respectively), no macroscopic oil expulsion is observed. At the microscopic level, there are no discernible oil droplets. To corroborate these findings, a  $^1\text{H}$  NMR study of the aqueous phase was conducted (Figure 11), failing to detect any traces (below 0.1mg) of vegetable oil or free glycerol within the detection limit of the spectrometer.



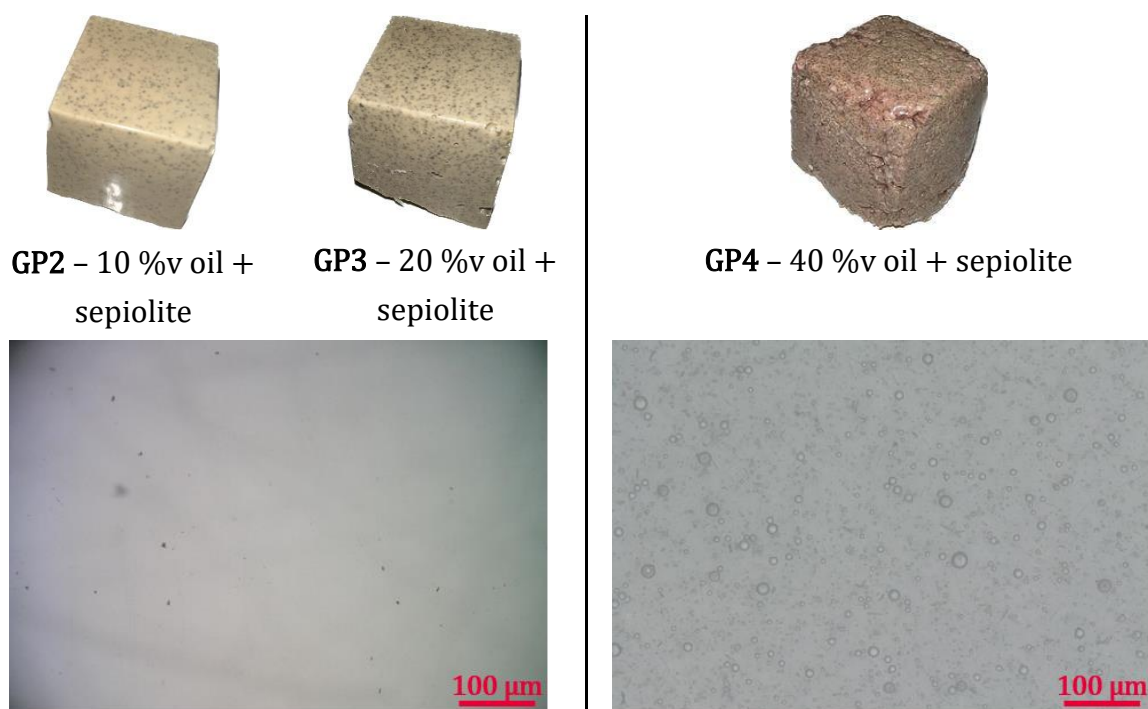


Figure 10. Macroscopic and microscopic photographs of the geopolymers GP1 (10%v oil + sepiolite), GP2 (20%v oil + sepiolite), and GP3 (40%v oil + sepiolite) are provided. Microscopic images were captured at a magnification of x500 under non-polarized light.

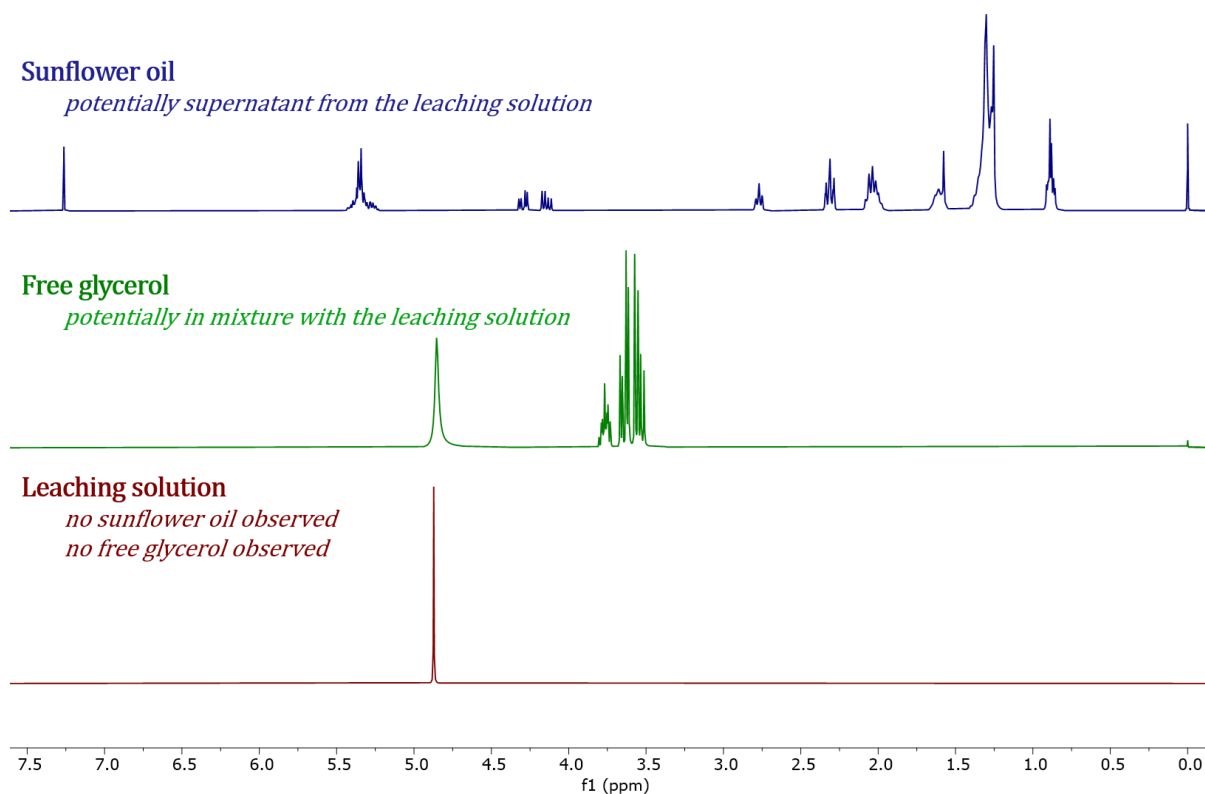


Figure 11.  $^1\text{H}$  NMR spectra of the expected products (sunflower oil,  $\text{CDCl}_3$ , and free glycerol,  $\text{D}_2\text{O}$ ) if leaching had occurred versus the  $^1\text{H}$  NMR spectrum derived from the leaching test sample ( $\text{D}_2\text{O}$ ).

#### 4. Conclusion

In conclusion, this study offers significant insights into the pre-treatment of hydrolysable nuclear organic liquids through the solid impregnation of vegetable oil on surfactant-grafted clay particles. The findings underscore the efficacy of this two-step process (impregnation and conditioning into mineral binders such as geopolymers), particularly highlighting the superior performance of sepiolite-CTAB in oil absorption, with the ability to immobilize 20% v/v of vegetable oil in a geopolymer matrix without oil detected after 90 days. The successful grafting of surfactants onto clay surfaces, as evidenced through various characterization methods, notably enhances the adsorption efficiency and alters physicochemical properties of the clays, making them more suitable for nuclear waste management applications.

The study's comparative analysis of different clays and surfactants demonstrates the nuanced interplay between the type of clay, the choice of surfactant, and the resulting oil absorption and immobilization capabilities. The clear distinction in performance between different surfactant-clay combinations indicates the potential for tailored solutions based on specific waste management requirements.

Ultimately, this research contributes to the broader goal of enhancing nuclear waste management practices, ensuring long-term sustainability and environmental safety. The method's potential for scalability and application in real-world scenarios makes it a promising avenue for further exploration and development in the field of nuclear waste management.

#### CrediT authorship contribution statement

**Jordan Bassetti:** investigation – writing – original draft. **Yann Boland:** investigation. **Jean-François Dechezelles:** resources, supervision. **Christel Pierlot:** resources, supervision, review & editing, funding acquisition. **Arnaud Poulesquen:** resources, supervision, review & editing, founding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Bibliography

- [1] SRIA SNEPT, "SNEPT Strategic Research And Innovation Agenda," Brussels, Belgium, Jul. 2021. Accessed: Sep. 28, 2023. [Online]. Available: <https://snetp.eu/wp-content/uploads/2021/09/SRIA-SNETP-1.pdf>
- [2] International Atomic Energy Agency (IAEA), "Predisposal Management of Organic Radioactive Waste," Vienna, Technical Report N°427, 2004.
- [3] C. Reeb, C. Pierlot, C. Davy, and D. Lambertin, "Incorporation of organic liquids into geopolymer materials - A review of processing, properties and applications," *Ceram. Int.*, vol. 47, no. 6, pp. 7369–7385, Mar. 2021, doi: 10.1016/j.ceramint.2020.11.239.
- [4] M. H. Almabrok, R. McLaughlan, and K. Vessalas, "Investigation of oil solidification using direct immobilization method," presented at the Environmental Research Event, Sydney, Australia, 2011.
- [5] H. H. Murray, "Overview - clay mineral applications," *Applied Clay Science*, vol. 5, no. 5–6, pp. 379–395, 1991, doi: [https://doi.org/10.1016/0169-1317\(91\)90014-Z](https://doi.org/10.1016/0169-1317(91)90014-Z).
- [6] M. O. Adebajo, R. L. Frost, J. T. Kloprogge, O. Carmody, and S. Kokot, "Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties," *J. Porous Mater.*, vol. 10, no. 3, pp. 159–170, 2003, doi: 10.1023/A:1027484117065.
- [7] M. K. Uddin, "A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade," *Chem. Eng. J.*, vol. 308, pp. 438–462, 2017, doi: <http://dx.doi.org/10.1016/j.cej.2016.09.029>.
- [8] C. Teerawattanasuk, "Improved heavy metal immobilization of compacted clay by cement treatment," *Heliyon*, vol. 7, no. 4, p. e06917, 2021, doi: <https://doi.org/10.1016/j.heliyon.2021.e06917>.
- [9] J. M. Adams and R. W. McCabe, "Clay Minerals As Catalysts," in *Handbook of Clay Science*, vol. 1, 2006, pp. 541–581.
- [10] E. Galan, "Properties and applications of palygorskite-sepiolite clays," *Clay Minerals*, vol. 31, no. 4, pp. 443–453, 1996.
- [11] A. Alvarez, J. Santarén, A. Esteban-Cubillo, and P. Aparicio, "Current Industrial Applications of Palygorskite and Sepiolite," in *Developments in Palygorskite-Sepiolite Research*, vol. 3, pp. 281–298.
- [12] J. Weng, Z. Gong, L. Liao, G. Lv, and J. Tan, "Comparison of organo-sepiolite modified by different surfactants and their rheological behavior in oil-based drilling fluids," *Appl. Clay Sci.*, vol. 159, pp. 94–101, 2018.
- [13] Y. Zheng *et al.*, "Study of STAB- and DDAB-modified sepiolite structures and their adsorption performance for emulsified oil in produced water," *Colloids Interface Sci. Commun.*, vol. 34, no. 100231, 2020, doi: 10.1016/j.colcom.2019.100231.
- [14] Y. Li, M. Wang, D. Sun, Y. Li, and T. Wu, "Effective removal of emulsified oil from oily wastewater using surfactant-modified sepiolite," *Appl. Clay Sci.*, vol. 157, pp. 227–236, 2018, doi: 10.1016/j.clay.2018.02.014.
- [15] S. K. Shah and A. Bhattarai, "Interfacial and Micellization Behavior of Cetyltrimethylammonium Bromide (CTAB) in Water and Methanol-Water Mixture at 298.15 to 323.15 K," *J. Chem.*, p. 13p, 2020, doi: 10.1155/2020/4653092.

- [16] K. Shinoda, T. Yamaguchi, and R. Hori, "The Surface Tension and the Critical Micelle Concentration in Aqueous Solution of  $\beta$ -D-Alkyl Glucosides and their Mixtures," *Bull. Chem. Soc. Jpn.*, vol. 34, no. 2, pp. 237–241, Feb. 1961, doi: 10.1246/bcsj.34.237.
- [17] R. Xu, *Light Scattering Methods*, Springer. in Particle Technology Series. Dordrecht, The Netherlands, 2000.
- [18] M. Alderliesten, "Mean Particle Diameters. Part I: Evaluation of Definition Systems," *Part. Part. Sys. Charact.*, vol. 7, no. 1–4, pp. 233–241, 1990, doi: 10.1002/ppsc.19900070138.
- [19] S. J. Gregg and K. S. W. Sing, *Adsorption, surface area, and porosity*, 2nd ed. London: Academic Press, 1982. Accessed: Jan. 06, 2024. [Online]. Available: <http://www.gbv.de/dms/bowker/toc/9780123009562.pdf>
- [20] G. Tartaglione, D. Tabuani, and G. Camino, "Thermal and morphological characterisation of organically modified sepiolite," *Microporous Mesoporous Mater.*, vol. 107, no. 1–2, pp. 161–168, 2008, doi: 10.1016/j.micromeso.2007.04.020.
- [21] S. Benayache, S. Alleg, A. Mebrek, and J. J. Suñol, "Thermal and microstructural properties of paraffin/diatomite composite," *Vacuum*, vol. 157, pp. 136–144, 2018, doi: 10.1016/j.vacuum.2018.08.044.
- [22] I. D. Morrison and S. Ross, *Colloidal dispersions: suspensions, emulsions, and foams*. New York: Wiley-Interscience, 2002.
- [23] M. Alkan, G. Tekin, and H. Namli, "FTIR and zeta potential measurements of sepiolite treated with some organosilanes," *Microporous Mesoporous Mater.*, vol. 84, pp. 75–83, 2005, doi: 10.1016/j.micromeso.2005.05.016.
- [24] L. B. Fitaroni, T. Venâncio, F. H. Tanaka, J. C. F. Gimenez, J. A. S. Costa, and S. A. Cruz, "Organically modified sepiolite: Thermal treatment and chemical and morphological properties," *Appl. Clay Sci.*, vol. 179, no. 105149, 2019, doi: 10.1016/j.clay.2019.105149.
- [25] M. Thakker, V. Karde, D. O Shah, P. Shukla, and C. Ghoroi, "Wettability measurement apparatus for porous material using the modified Washburn method," *Meas. Sci. Technol.*, vol. 24, no. 125902, p. 8pp, 2013, doi: 10.1088/0957-0233/24/12/125902.
- [26] L. I. Rolo, A. I. Caço, A. J. Queimada, I. M. Marrucho, and J. A. P. Coutinho, "Surface Tension of Heptane, Decane, Hexadecane, Eicosane, and Some of Their Binary Mixtures," *J. Chem. Eng. Data*, vol. 47, pp. 1442–1445, 2002, doi: 10.1021/je025536+.
- [27] L. Susana, F. Campaci, and A. C. Santomaso, "Wettability of mineral and metallic powders: Applicability and limitations of sessile drop method and Washburn's technique," *Powder Technology*, vol. 226, pp. 68–77, 2012, doi: 10.1016/j.powtec.2012.04.016.
- [28] C. Pierlot *et al.*, "Selection of suitable surfactants for the incorporation of organic liquids into fresh geopolymer pastes," *Chem. Eng. Sci.*, vol. 255, p. 117635, Jun. 2022, doi: 10.1016/j.ces.2022.117635.
- [29] J. Bassetti, C. Pierlot, C. Davy, D. Lambertin, and A. Poulesquen, "Characterization of hydrolysable organic nuclear waste prior to their immobilization in geopolymers by quantitative  $^1\text{H}$  NMR," *Sci. Talks*, p. 100205, Mar. 2023, doi: 10.1016/j.sctalk.2023.100205.
- [30] C. Bai, G. Franchin, H. Elsayed, A. Conte, and P. Colombo, "High strength metakaolin-based geopolymer foams with variable macroporous structure," *J. Eur. Ceram. Soc.*, vol. 36, no. 16, pp. 4243–4249, Dec. 2016, doi: 10.1016/j.jeurceramsoc.2016.06.045.
- [31] M. S. Cilla, M. D. de Mello Innocentini, M. R. Morelli, and P. Colombo, "Geopolymer foams obtained by the saponification/peroxide/gelcasting combined route using

different soap foam precursors," *J. Am. Ceram. Soc.*, vol. 100, no. 8, pp. 3440–3450, Aug. 2017, doi: 10.1111/jace.14902.