

# Application of organo-magadiites for the removal of eosin dye from aqueous solutions: thermal treatment and regeneration

**Fethi Kooli<sup>1,\*</sup>, Yan Liu<sup>2</sup>, Mustapha Abouddi<sup>3</sup>, Souad Rakass<sup>3</sup>, Hicham Oudghiri Hassani<sup>3</sup>, Sheikh Muhammad Ibrahim<sup>3</sup>, and Rawan Al-Faze<sup>3</sup>**

- 1 Taibah University-Al-Mahd Branch, Community College, Al-Mahd, 42112, Saudi Arabia.; email: fkooli@taibahu.edu.sa; fethi\_kooli@yahoo.com
  - 2 Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island, Singapore. 627833., email: liu\_yan@ices.a-star.edu.sg
  - 3 Taibah University, Department of Chemistry, POBox 30002, Al-Madinah Al-Munawwarah, 41147 Saudi Arabia.; email: abboudi14@hotmail.com (M.A); oudghiri\_hassani\_hicham@yahoo.com (H.O.H); rakass\_souad@yahoo.fr (S.R.); mdibrahi@gmail.com (S.K.I); rawan.faze@gmail.com (R.A)
- \* corresponding author: fkooli@taibahu.edu.sa; Tel: +966569442963

## Abstract

Na-magadiite exchanged with cetyl-trimethylammonium cations provided organophilic silicate materials that allowed the effective removal of the acidic dye "eosin". The organic cations were intercalated into the interlayer spacing of the layered silicate via an exchange reaction between the organic cations from their bromide salt and the solid Na-magadiite at room temperature. Different techniques were used to characterize the effect of the initial concentration of the surfactant on the structure of the organo-magadiites. The C, H, N analysis indicated that a maximum of

organic cations of 1.03 mmol/g was achieved at initial concentrations higher than 0.25 mmol/g and was accompanied by an expansion of the basal spacing of 3.15 nm, with a tilted angle of 64.5° to the silicate layers. The conformation of the organic surfactants was probed using solid-state  $^{13}\text{C}$ , finding mainly the trans conformation similar to that of the starting cetyl trimethylammonium bromide salt (C16TMABr). Thermal gravimetric analysis was carried out to study the thermal stability of the resulting organo-magadiites. The intercalated surfactants started to decompose at 200 °C, with a mass loss percentage of 8 % to 25 %, depending on the initial loading of the surfactant, and was accompanied by a decrease of the basal spacing from 3.20 nm to 2.51 nm, as deduced from the *in situ* X-ray diffraction studies. At temperatures below 220 °C, an expansion of the basal spacing from 3.15 to 3.35 nm occurred. These materials were used as a removal agent for the anionic dye "eosin". The maximum amount of the dye removed was related to the organic cation content and to the initial concentration of eosin, with an improvement from 2.5 mg/g to 98 mg/g. This value decreased when the organo-magadiite was preheated at temperatures above 200 °C. The regeneration tests indicated that an 85 % removal efficiency was maintained after 6 cycles of use for the organo-magadiites.

**Keywords:** magadiite, organo-layered silicate, removal, eosin, thermal stability, regeneration

## INTRODUCTION

Layered materials have attracted great attention due to their wide application in different fields and to their characteristic cation exchange capacity, acceptance of intercalated guest molecules, exfoliation in different polymer matrixes, and catalytic

properties [1]. The layered silicate, magadiite, is an important member of this family, and it is easily prepared in the laboratory by the hydrothermal treatment of a silica source dissolved in an alkaline solution at a specific temperature of 150 °C for a period of time varying from two to three days [2]. Magadiite consists of multiple negatively charged layers of tetrahedral  $\text{SiO}_4$  with abundant silanol groups on their surfaces. The negative charge is balanced by exchangeable hydrated cations such  $\text{Na}^+$  or protons ( $\text{H}^+$ ) in the interlayer spacing [3]. The magadiite exhibited a theoretical high cation exchange capacity of nearly 200 meq/ 100 gr [4], resulting in good ion exchange properties as a host for many organic and inorganic cations [5,6,7,8, 9 10, 11]. Magadiite was used as a silica precursor to prepare some new microporous zeolite materials with unique structures and properties using small organic templates [12,13]. The acidic properties of the magadiite could be enhanced by the insertion of other cations into the layered silicate, achieved during the synthesis by adding the cations precursors to the mixture of the silica source and NaOH. This adjustment allowed for the diversification of magadiite as a catalyst in special catalytic reactions [14,15,16]. However, using long alkyl ammonium cations, the modified cetyltrimethylammonium-magadiite was used as an intermediate precursor to synthesize mesoporous materials with a controlled distribution of pores sizes [17-18].

In the removal of dyes process, it was underlined that the removal efficiency of organo-clay minerals was affected by the surfactant alkyl chain length. [19] A clay mineral modified with long-chain surfactant exhibited a higher removal capacity than did short-chain surfactant. For this purpose, cetyl trimethyl ammonium ( $\text{C}_{16}\text{TMA}$ ) was the most commonly used cation, obtained from the corresponding salt; the bromide form was used to prepare organo-clays or silicates [20,21]. The effect of the counteranion anion of surfactants was reported in a few studies [22]. In the case of

organo-clays, the highest intercalated amounts were achieved using the bromide form [22], while using acid-activated clays, the C16TMAOH starting solution led to the highest uptake value [23]. In the case of a layered silicate such as magadiite, a previous study reported that the maximum amount of intercalated organic surfactants was achieved using a C16TMAOH solution [24,25]. On the other hand, H-magadiite was difficult to modify either a C16TMABr or C16TMACl solution [25].

In this study, Na-magadiite was modified by different initial C16TMABr solutions at room temperature. The chemical stability of the intercalated surfactants was investigated in HCl and NaOH solutions. An *in situ* XRD technique was used to study the thermal stability of the organo-magadiites. Na-magadiite and its protonated form were used as removal agents for basic dyes, such as methylene blue and other dyes, without modification [26,27,28,29]. However, for acidic dyes, no studies were reported in the literature. In our study, EosinY, a heterocyclic dye containing bromine atoms, was selected as a model dye, as it is used in printing, dyeing, printing ink, and fluorescent pigments as well as in the leather and paint industries [30]. The modified magadiites and the preheat-treated organo-magadiite were applied as a removal agent for the acidic dye "eosin" from artificially polluted water. Different factors were investigated during the removal process of the eosin dye. The regeneration process determines the feasibility of using an applied material in large-scale operations. The resulting spent materials were regenerated by a process friendly to the environment, and their reuse was studied after different consecutive cycles.

## 2. Materials and Characterization

### 2.1 Chemicals

We obtained fumed silica and the salt of cetyl trimethyl ammonium bromide (C16TMABr), which is a cationic surfactant with an average molar mass of 384.44

g.mol from Sigma-Aldrich, USA. The dye eosin was an analytical reagent purchased from across organic. All the reagents were used as received.

## **2.2 Na-magadiite**

Na-magadiite was prepared as reported previously [24]. Fumed silica (16 g) was added to a basic solution formed from 4.8 g of NaOH dissolved in 105 g of water in a SiO<sub>2</sub>/alkali ratio of 4. The mixture was sealed in a Teflon-lined autoclave and left at 150 °C for three days in an dry oven. After cooling, the product was filtered, washed with deionized water and dried overnight in an oven at 40 °C. The Na-magadiite is named Na-mag.

## **2.3. Organo-magadiites**

Different quantities of the solid C16TMABr salt were dissolved in 50 mL of deionized water. Then, 2 grams of Na-mag were added to these solutions, which were mixed at room temperature for overnight. The samples were filtrated and washed with water several times (7 to 8 times). The resulting materials were dried at room temperature. The samples are identified as C16Mag-X, where X represents the initial loading of the C16TMA cation in mmoles per 100 grams of Na-magadiite. C16Mag-40 corresponds to an organo-magadiite with a loaded amount of 40 mM C16TMA cations per 100 gr.

## **2.4. Chemical properties**

One selected organo-magadiite (C16Mag-80) was treated with solutions of NaOH, NaCl, and HCl to explore the stability of the intercalated surfactants. For this purpose, one gram of the C16Mag-80 sample was added to 50 mL of a NaOH, HCl or NaCl (0.5 M) solution and left overnight. The sample was filtered and washed extensively with deionised water and dried at room temperature.

## **2.5. Eosin removal**

In the removal experiments, 100 mg of magadiite or organo-derivatives was added to a fixed volume (10 mL) of eosin dye, at different initial concentrations varying from 50 ppm to 1000 ppm, in a sealed tube. Then, the tubes were shaken laterally in a water-bath shaker at a controlled temperature of 25 °C for eighteen hours. After the separation of the two phases (solid and solution) by centrifugation, the change in the eosin concentration solution was determined by a UV Varian spectrophotometer at the maximum wavelength absorption of 610 nm, using a prepared calibration curve. The experiments were carried out using duplicate samples for each experiment.

The removal properties of a selected organo-magadiite (C16Mag-80) preheated at different temperatures were also investigated using the same procedure described above.

## ***2.6. Regeneration studies of spent organo-magadiites***

The following method was applied in previous studies. It is friendly to the environment since small amounts of chemicals and water solutions are used. The spent organo-magadiites were dispersed into a mixture of 10 mL of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and specific amount of oxone. The mixture of solid-solution was stirred for 30 min. The solid was separated by centrifugation, washed six to seven times, and reused for the next run.

## ***Characterization***

The C, H and N contents in the modified magadiites were carried out by an EURO EA elemental analyser. the success of the modification of the organo-magadiites was examined by X-ray powder diffraction was a Bruker Advance 8 diffractometer (Ni-filtered  $\text{Cu-K}\alpha$  radiation with a wavelength of 0.154 nm) was used to obtain the XRD patterns. Scanning electron microscopy (SEM, JEOL model JSM-6700F) technique was

performed to examine the changes in morphology of the synthesized samples. The nitrogen adsorption isotherms were performed to estimate the microtextural properties of the samples. The isotherms were measured on a Micrometrics ASAP 2040. Prior to the adsorption, the samples were evacuated overnight at 373 K. The surface area was estimated using the Brunauer-Emmett-Teller (BET) method, and the pore volume was deduced at a relative adsorption pressure ( $P/P_0$ ) of 0.95. Thermal gravimetry analysis (TGA) were used for the study of the thermal stability of the synthesized samples and to select the temperature values at which the organo-magadiites would be treated prior the removal studies. The analyses were made on a TA Instruments calorimeter, model SDT2960. During the runs, the samples were heated to 800 °C (heating rate: 10 °C/min) in air. Solid-state NMR spectra were measured with a Bruker DSX 400 MHz instrument under MAS conditions in 2.5 mm  $ZrO_2$  rotors with a sample volume of 12  $\mu$ L (rotation frequency: 20 kHz), as reported in previous studies. The  $N_2$  adsorption isotherms were performed using a Micromeritics model ASAP 2040. The specific area was estimated using the BET equation,.

### 3. Results and discussion

#### 3.1. C, H, N Elemental analysis

The carbon, nitrogen and hydrogen analysis was used to quantify the organic contents in organo-clays and other organo-silicates [24, 32,33,34]. The elemental analysis of the organo-magadiites is summarized in Table 1. The data revealed that the contents of carbon and nitrogen increased after modification with the surfactant and then, remained unchanged for initial concentrations greater than 0.80 mmol. The amount of intercalated C16TMA in the magadiite interlayer spaces varied from 0.40 mmol/g to 1.09 mmol/g. The later value was lower than the expected cation exchange capacity, and it indicated that the modification of the Na-magadiite occurred mainly

via a cation exchange process. The EDX data indicated that traces of Na cations occurred with high loadings of organic surfactants. In the case of the similarly layered structure kenyaite, only a partial exchange occurred [33]. This result was not the same for clay minerals, where the uptake amount of C16TMA largely exceeded the CEC values [21]. This variation was related to the different uptake mechanisms for surfactants and layered silicates.

**Table 1.** C, H, N elemental analysis of organo- magadiites prepared with different initial C16TMABr loading solutions.

Samples	C%	H%	N%	Intercalated C16TMA amount (mmoles/g)
C16Mag-20	4.04	1.09	0.06	0.19
C16Mag-40	8.82	2.78	0.21	0.38
C16Mag-80	15.40	3.80	0.73	0.78
C16Mag-120	22.20	4.82	1.11	1.03

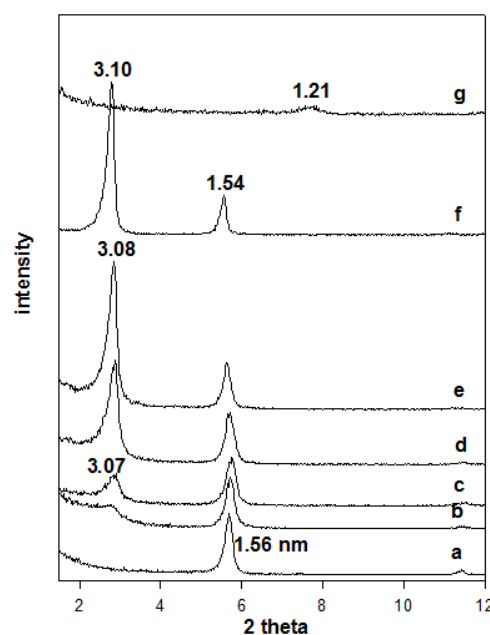
When the C, H, N analysis was performed for the organo-magadiite treated with NaOH or NaCl solutions, the percentages of C and N did not vary, indicating that the organic surfactants were stable and did not exchange with the Na cations from the NaOH solution. However, the percentages of C and N decreased dramatically when the organo-magadiite was treated with the HCl solution, indicating that the organic surfactants were replaced by the protons of the acid solution. Similar data were obtained from organo-clays and organo-silicates. For the sample treated with deionized water, no change occurred.

### 3.2. X-ray Diffraction Data



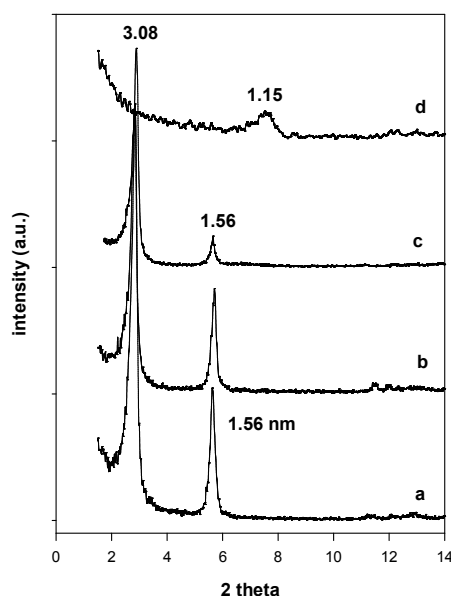
The powder XRD patterns of the Na-magadiite and the organo-derivatives are presented in Figure 1. The Na-magadiite exhibited a basal spacing of 1.54 nm, close to that reported in the literature [2,35,36], when it was reacted with an initial surfactant loading of 0.40 mM and a broad reflection corresponding to 3.10 nm was obtained, indicating a partial exchange of the Na-magadiite occurred. The intensity of the broad reflection at 3.10 nm was improved by increasing the loading concentration of C16TMABr, and the pattern exhibited sharp reflections for a basal spacing of 3.10 nm. This value remained unchanged for initial loading concentrations greater than 0.80 mmol, while an additional reflection at 1.57 nm was detected and could be related to a second-order reflection of the first at 3.10 nm or to an un-reacted Na-magadiite phase. In a previous study, a similar organo-magadiite prepared from protonated magadiite (H-mag) exhibited a first reflection at 3.10 nm and a second one at 1.54 nm. The later value was close to that of Na-magadiite and lower than the reflection of the starting protonated magadiite at 1.21 nm (Figure 1) [6,25]. These data confirmed that the reflection at 1.54 nm was indeed related to the organo-magadiite phase and not to the starting Na-magadiite phase.

The basal spacing of the organo-magadiite of 3.10 nm was higher than the value reported for organo-magadiite prepared with the same C16TMA cations (2.45 nm, [37]), This difference could be related to different arrangement of the C16TMA cations, and to the used solvent during the modification process, N-dimethylacetamide was employed instead of deionized water. The effect of the solvent on the arrangement of C16TMA into the basal spacing of organo-clay minerals was reported using pure ethanol or a mixture of water/ethanol [38].



**Figure 1.** Powder XRD patterns of (a) Na- magadiite treated with different C16TMABr concentrations. (b) 0.20 mM, (c) 0.40 mM, (d) 0.80 mM, and (e) 1.20 mM, (f) corresponds to organo-magadiite prepared from (g) H-magadiite and C16TMAOH solution.

The chemical stability tests indicated that the intercalated surfactants were not readily exchanged with  $\text{Na}^+$  cations using either a NaCl solution or NaOH solution. The powder XRD pattern of the reacted organo-magadiite exhibited a similar pattern with a reflection at  $3.04\text{ nm}$ , close to that of the starting organo-magadiite (Figure 2). However, a different XRD pattern was obtained when the organo-magadiite was reacted with the HCl solution, exhibiting a reflection at  $1.05\text{ nm}$  (Figure 2). This value was close to that reported for H-magadiite in the literature [6,25,39] and indicated that the intercalated C16TMA cations were exchanged with protons from HCl solution.



**Figure 2.** Powder XRD patterns of (a) C16Mag-80 treated with different solutions (b) NaOH, (c) NaCl, and (d) HCl solutions.

The length of C16TMA cations in all *trans* configuration in the range of 2.2 nm to 2.5 nm [25,40]. The basal spacing of Na-magadiite completely dehydrated (similar to H- magadiite) is approximately 1.12 nm [6,25]. The basal spacing is estimated by adding the size of C16TMA cations and the basal spacing of H-magadiite, and to have an average of 3.47 nm, higher than the observed value (3.10 nm). The difference between the observed and calculated values is presumably due to some degree of tilting of the vertically C16TMA<sup>+</sup> cations with the magadiite surface, and the presence of H<sub>2</sub>O in the interlayer spacing [41,42]. This configuration was necessary to balance the charge of the silicate layers. The tilt angle in the organo-magadiite was higher to the tilt angle (57 to 59 °) in the organo-clays with lower charge density [24].

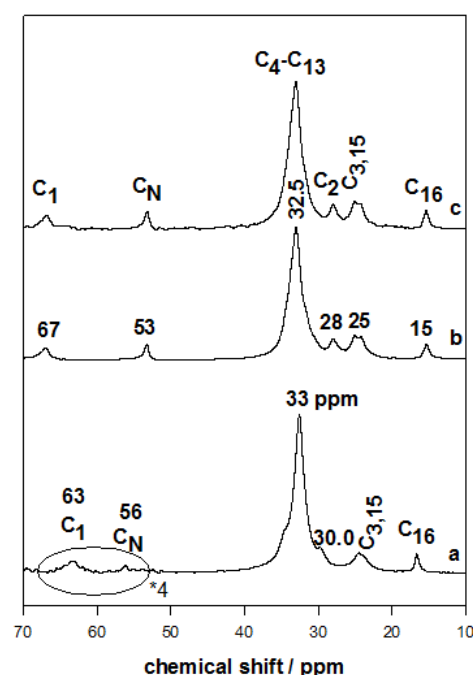
### 3.3. Solid-state NMR studies

The stability of the layered silicate during the exchange process was deduced using Solid-state <sup>29</sup>Si MAS NMR. In fact, the spectrum of the starting Na-magadiite

exhibited one main resonance peak centred at -99 ppm, related to Q<sup>3</sup>-type silicon, and multiple peaks in the range of -110 to -114 ppm, associated with Q<sup>4</sup>-type sites in the basic layered structure of magadiite (Figure S1) [43]. After the reaction with the C16TMABr solution, a similar spectrum was obtained with main resonance peaks at -99 and -110 ppm (Figure 1S). The overall features of the spectrum did not change with different initial loadings of the surfactant solution, indicating that the layered structure of the silicate material was conserved [5,24].

The presence of the C16TMA cations was confirmed by C, H, N and XRD techniques, as mentioned previously. The <sup>13</sup>C CP-NMR technique gives more details about the structure and the conformation of the intercalated cations [44, 45]. The <sup>13</sup>C CP-NMR of the pure C16TMABr solid exhibited an intense resonance peak at 32.7 ppm that was assigned to C<sub>4</sub>-C<sub>13</sub>, corresponding to a dominant *trans* conformation for the CH<sub>2</sub> groups, and an additional shoulder at 30 ppm associated with a minor degree of the *gauche* conformation [23,24,33] (Figure 3). The peaks at 63.7 ppm and 55.5 ppm were related to C<sub>1</sub> and the methyl groups bonded to N (C<sub>N</sub>), respectively [23,24,33]. Full assignments of the other peaks were described in previous works. The intercalated C16-Mag40 and C16Mag-120 exhibited a resonance spectrum similar to that recorded for the C16TMABr solid with an intense peak at -32.5 ppm, resulting from the all-*trans* conformation of the organic cations [46] (Figure 3). The conformation was quite homogeneous, which was not the case of other organo-materials with a certain degree of *cis* conformation (with a peak at 30 ppm). The intensity of the other resonance peaks was enhanced; however, the peaks became broad, and this fact was related to the restricted mobility of the surfactant cations between the silicate layers. In good agreement with the XRD data, the content of the organic cations did not affect the features of the spectra, indicating that the cations

mainly adopted the *trans* conformation (Figure 3). Similar data were reported for organo-kenyaite and organo-clays with closely packed organic contents [23,25,33].



**Figure 3.**  $^{13}\text{C}$  CP MAS of (a) pure C16TMABr salt, and organo-magadiites exchanged with C16TMABr solution at different concentrations. (b) 0.20 mM, (c) 0.40 mM, and (d) 0.80 mM

### 3.4. Microtextural studies and Specific surface areas

The  $\text{N}_2$  adsorption studies were performed to study the changes in the textural properties of Na-magadiite. The starting Na-magadiite exhibited an adsorption isotherm of type IV, related to a non-porous material, with the condensation of nitrogen molecules occurring at higher relative pressure values and within the voids of the magadiite particles (Figure S2). The organo-magadiites showed the same feature of the  $\text{N}_2$  isotherms with a decrease of the  $\text{N}_2$  uptake at relatively low-pressure values. This decrease continued to when the magadiites were fully exchanged with C16TMA cations. The decrease in the  $\text{N}_2$ -adsorbed volume indicated that the  $\text{N}_2$  molecules accessed the interlayer space; however, the intercalated C16TMA molecules occupied

the active sites, which left the least-active sites for N<sub>2</sub> adsorption. In addition, the BET surface was related to the active sites on the surface, and since the C16TMA intercalation proceeded through cation exchange, the surface adsorption of the intercalated molecules would be accounted for in the  $S_{\text{BET}}$  surface diminution [33].

**Table 2.** Microtextural properties of Na- magadiite and its organo-derivatives prepared with different initial C16TMABr loading solutions.

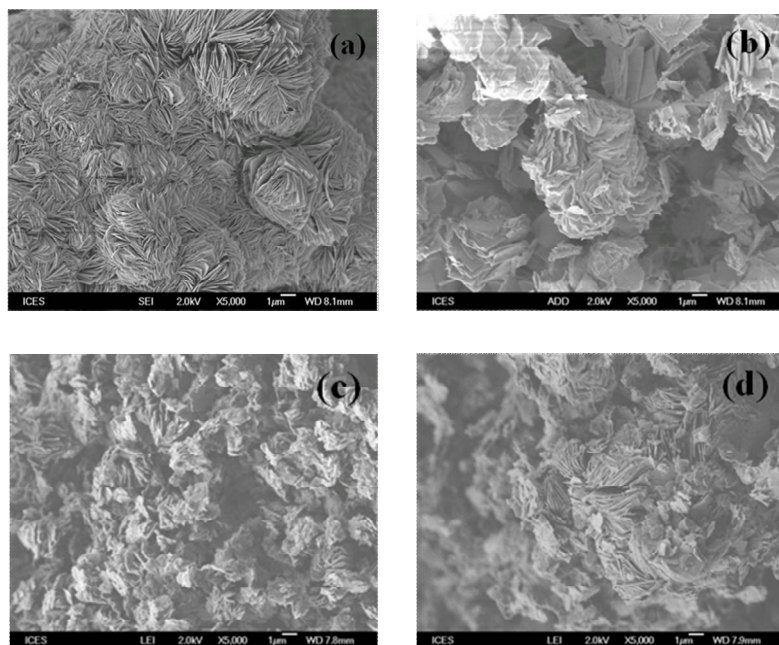
Samples	$S_{\text{BET}}$ (m <sup>2</sup> /g)	T.P.V* (cc/g)	A.P.D <sup>+</sup> (nm)
Na-mag	34.7	0.082	10.25
C16Mag-20	23.2	0.068	11.8
C16Mag-40	20.7	0.062	12.1
C16MAg-80	15.40	0.054	13.09
C16Mag-120	13.33	0.042	12.58

\*(T.P.V.) total pore volume, <sup>+</sup>(A.P.D.) average pore diameter

The BET surface areas ( $S_{\text{BET}}$ ), total pore volume (T.P.V.) and average pore diameter (A.P.D.) are summarized in Table 2. The Na-magadiite exhibited a  $S_{\text{BET}}$  value of 35 m<sup>2</sup>/g, close to that reported for similar materials and other layered silicates such as kanemite and kenyaite [33,36,47]. The modification with C16TMA cations led to a decrease of the  $S_{\text{BET}}$  value from 25 m<sup>2</sup>/g for the partially exchanged magadiite (C16Mag-20) to 13 m<sup>2</sup>/g for the fully exchanged magadiite (C16-Mag80). These values were similar to those of other organo-silicates and organo-clay minerals [33, 48, 49]. The average pore volume deduced from the N<sub>2</sub> isotherms was mainly related to the voids between the particles of the organo-magadiites. In the case of organo-clays, Bhatt et al. have attributed the reduction in the average pore volume to the formation of closely packed aggregates due to interparticle hydrophobic interactions

and to the shape of the voids [49]. The A.P.D. size increased as the content of C16TMA<sup>+</sup> cations.

### 3.5. SEM micrographs



**Figure 5.** SEM micrographs of (a) Na- magadiite treated with different C16TMABr solutions. (b) 0.20 mM, (c) 0.40 mM, (d) 0.80 mM.

The SEM micrographs of the starting magadiite and the resulting organo-magadiites are presented in Figure 5. Na-magadiite exhibited silicate layers intergrown to form spherical rosettes [35]. When reacted with organic surfactants at initial concentrations of less than 0.8 mM (C16Mag-80), the resulting magadiites exhibited similar morphologies due to the partial exchange. However, for the fully exchanged magadiite, the rosette structure vanished, and the layers of silicates were clearly separated (C16 Mag-120). <sup>29</sup>Si MAS NMR indicated that the layered structure was

not altered during the exchange reaction, however, a morphological change occurred.

Similar data were reported for Na-kenyaite and Na-magadiite modified by similar cations from a hydroxide solution [23,33].

### **3.5. Thermal Stability**

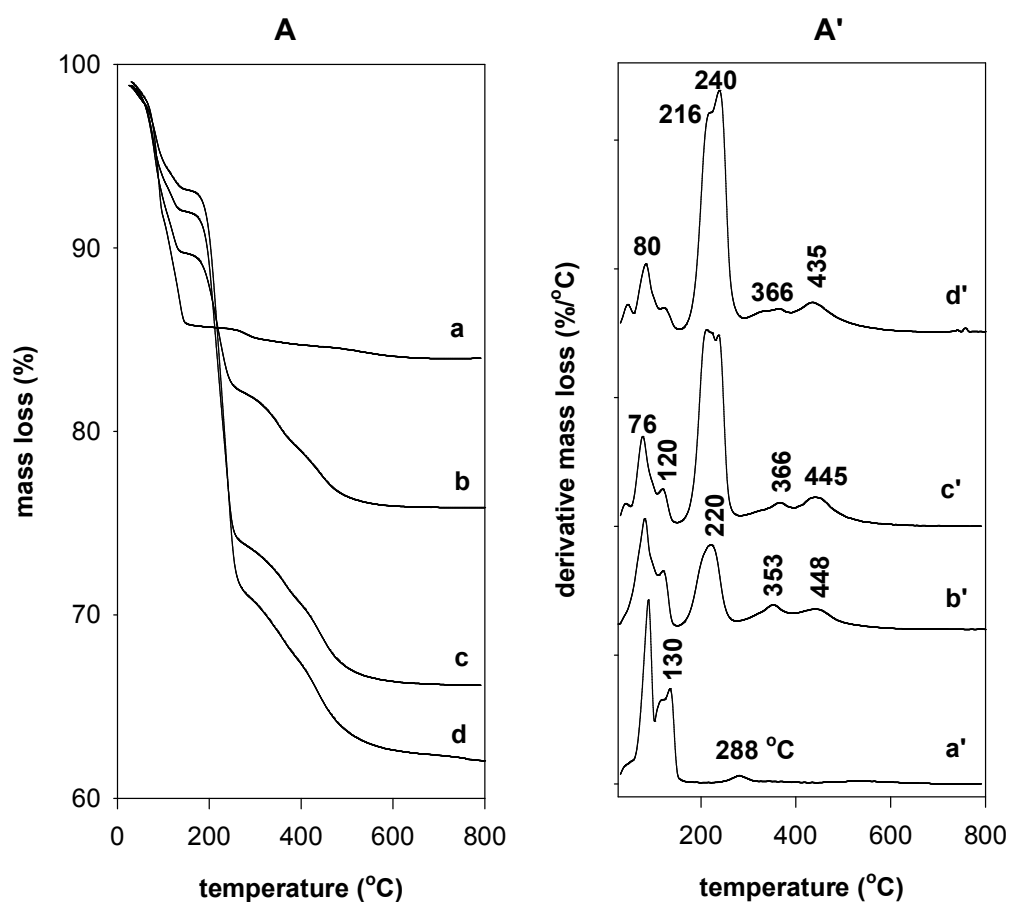
#### **3.5.1. Thermal Gravimetric Analysis (TGA)**

The TGA curve of the as-synthesized Na-Mag showed two general mass losses within the temperature ranges of the respective DTG peak limits. The first mass-loss step of 7.5 %, in the range of 26 to 100 °C, corresponded to the loss of the surface-adsorbed water molecules and was associated with a maximum temperature peak at 90 °C. The second mass loss of 7.5 %, between 100 to 150 °C, followed the loss of water molecules more strongly bound to Na<sup>+</sup> cations and was associated with the DTG peak at a maximum temperature of 140 °C. A weak third mass step of 1.2 %, at temperatures above 200 °C, was assigned to the dehydroxylation of the silicate layers that occurred at a maximum temperature of 280 °C (Figure 5(A)). This feature was similar to that reported for the magadiite materials [4,3,36].

After the reaction with the C16TMABr solution with an initial loading of 0.40 mM, the TGA curve exhibited an additional mass-loss step, in the range of 200 °C to 400 °C, that started at 180 °C and was due to the pyrolysis followed the combustion of the organic materials (Figure 5(A)). This loss was approximately 8 % and was accompanied by a maximum loss temperature peak at 220 °C [23]. A continuous mass loss occurred in the temperature range of 290 to 450 °C and was associated with the burnout of the residual carbonaceous material of the decomposed surfactants with two DTG temperatures peaks at 353 and 430 °C [24] (Figure 5(A')). As the content of the surfactants increased in the organo-magadiites, the features of the TGA and DTG did



not change (Figures 5(A) and (A')), however, the intensity (or the area) of the DTG peak related to the mass loss of the surfactants increased and reached a maximum for organo-magadiite prepared using an initial loading concentration of 2.8 mmol. A mass loss of 28 % was achieved in the range of 200 to 350 °C. At the same time, the percentage related to the loss of water molecules decreased, indicating the exchange of Na cations by the organic surfactants and the hydrophobic character of the organo-magadiites and was associated with a decrease in the intensity of the DTG peaks in the temperature range of 25 to 120 °C (Figure 5A') [33]. Compared to the pure C16TMABr salt (Figure 4S), the decomposition of the intercalated surfactants occurred at low temperatures and with different steps, which were associated with the presence of silicate layers that acted as a retardant.



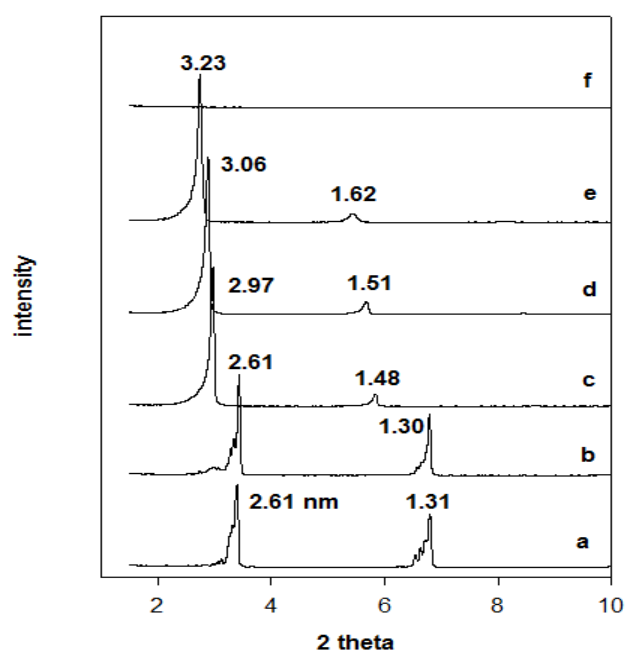
**Figure 5.** TGA (A) and DTG (A') features of (a,a') Na-magadiite treated with different concentrations (b, b') 0.40 mM, (c, c') 0.80 mM, and (d, d') 1.20 mM of C16TMABr

### 3.5.2. *in situ* Powder XRD studies

The thermal stability of the organo-magadiites was followed by *in situ* studies, meaning the real temperature values were obtained when collecting the powder XRD patterns and without cooling down the samples. To better understand the thermal

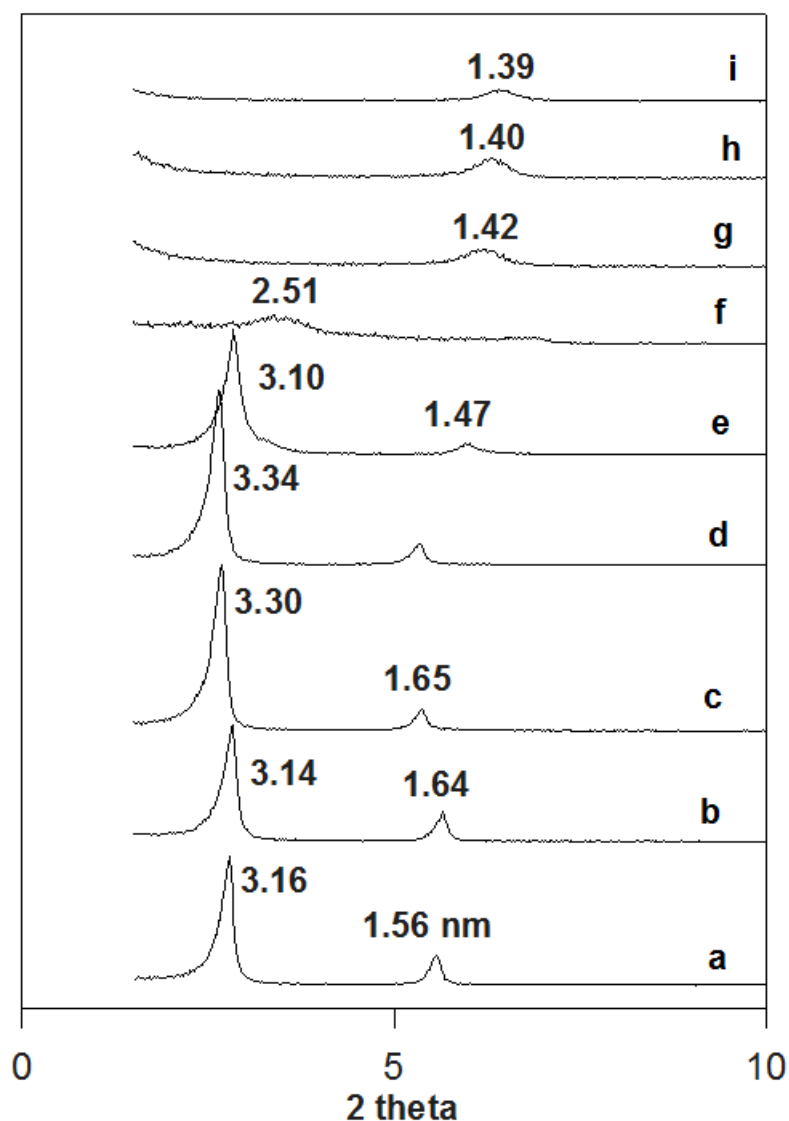
stability of the organo-magadiites, the thermal stability of the starting magadiite and the C16TMABr salt was studied.

In the first stage, the powder XRD pattern of the C16TMABr solid corresponded to a layered structure consisting of a series of (00l) reflections with high rationality order at 2.6 nm, 1.32 nm and 0.86 nm (Figure 6) [24,33]. Indeed, the structure of the C16TMABr salt was described as nonpolar bilayers located between polar layers. The (001) reflection was detected at 2.6 nm, and this value was slightly higher than the length of the C16TMA cations, reported to be close to 2.5 nm [24]. When the C16TMABr salt was preheated at different temperatures, the layered structure was preserved until 215 °C. Then, further expansion of the basal spacing followed, as mainly deduced from the variation of the (001) reflection from 2.6 nm to 3.23 nm. Finally, the C16TMABr melted, and no reflections were detected (Figure 6). The increase in the basal spacing was related to a solid-solid transition phase at 103 °C, as deduced from the DSC study [50].



**Figure 6.** *in-situ* powder XRD patterns of (a) C16TMABr solid salt preheated at different temperatures. (b) 100 °C, (c) 150 °C, (d) 200 °C, (e) 210 °C, (f) 250 °C,

For the case of the fully exchanged organo-magadiite (C16Mag-80) was selected as model sample), the *in situ* PXRD patterns are depicted in Figure 7. The intercalated C16TMA cations behaved in the same manner as the solid C16TMABr salt. Indeed, the basal spacing of the organo-magadiite increased from 3.16 nm to 3.34 nm when preheated in the temperature range from 50 °C to 150 °C. The reflection at 1.56 nm followed the same behaviour, confirming that it was a second-order reflection of the first one. Upon heating at 200 °C, the basal spacing started to shrink to 3.10 nm, and then it collapsed to 2.51 nm at 215 °C. The presence of the silicate layers caused the expansion of the intercalated cations in a short temperature range compared to that of the pure C16TMABr salt. At temperatures higher than 215 °C, further collapse was recorded at 1.42 nm, and the spacing was retained close to this value at higher temperatures, with a slight decrease from 1.42 nm to 1.39 nm. [24]. Loss of crystallinity was observed with a decrease of intensity and general broadening of the XRD reflections.



**Figure 7.** *in-situ* powder XRD patterns of (a) C16Mag-80 preheated at different temperatures. (b) 50 °C, (c) 100 °C, (d) 150 °C, (e) 200 °C, (f) 215 °C, (g) 250 °C, (h) 300 °C, and (i) 400 °C

These obtained values (1.40 nm) were higher than the basal spacings of the pristine Na-magadiite preheated at the same temperature values, as presented in Figure S3. The Na-mag exhibited a basal spacing of 1.15 nm at 200 °C [24]. This fact was related to the presence of residual carbonaceous materials between the silicate layers regenerated during the heating. The loss of water molecules in the interlayer spacing occurred at a temperature of 100 °C, accompanied by a decrease in the basal spacing

from 1.54 nm to 1.38 nm and that of water molecules bound to Na cations occurred at a higher temperature of 150 °C, resulting in a further shrinkage of the basal spacing from 1.38 nm to 1.15 nm (Figure S3). These data were in good agreement with the TGA results [36].

### **3.6. Removal of Eosin studies**

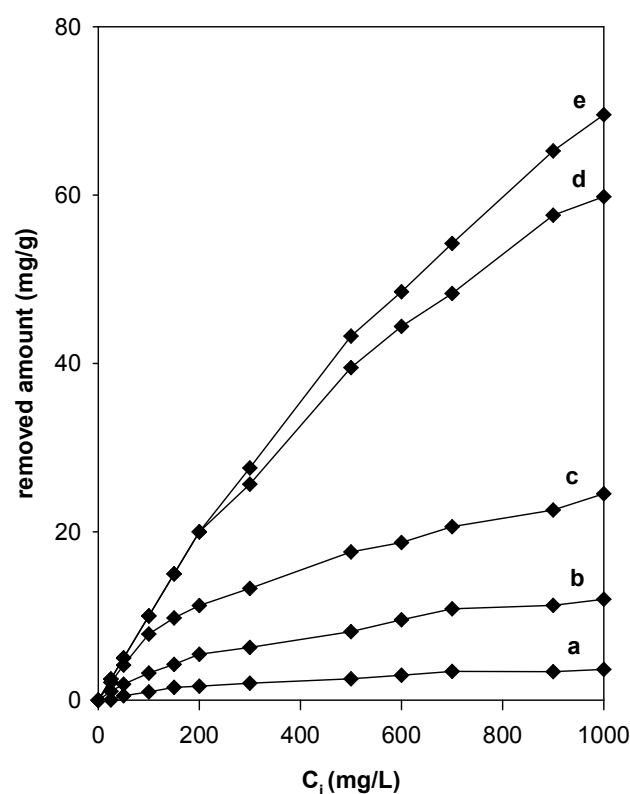
#### **3.6.1. Effect of initial concentrations ( $C_i$ )**

The organo-magadiites were applied as a removal agent for the Eosin dye. C16-Mag80 was used as a model sample in this paragraph. A given amount of organo-magadiite can only remove a fixed amount of dye, hence, the initial dye concentration is an important factor to study. Figure S4 shows the variation in the amount removed (milligram of eosin per gram of used material, mg/g) with the initial concentration ( $C_i$ ), which varied from 25 ppm to 900 ppm, at an equilibrium time of 18 hours and using 0.1 g of material. The increment of initial eosin concentration enhanced the amount of the removed eosin from 2.5 mg/g to 86 mg/g, as the driving force of mass transfer became large [51,52]. In the meantime, the removal percentage was noticed to decrease from 100 % at lower  $C_i$  values (less than 200 ppm) to 57 % at values greater than 700 ppm (Figure 4S). This fact was related to the available surface sites on the organo-magadiite. At lower  $C_i$  values, sufficient adsorption sites were available for the removal of a smaller number of dye molecules. However, at higher  $C_i$  values, the number of eosin dye molecules was high compared to the available sites, causing a decrease in the removal efficiency [33]. These data indicated that the organo-magadiite exhibited a performance with potential to remove eosin from polluted water.

#### **3.6.2. Effect of organic content**

The removal of eosin was investigated using the organo-magadiites with different organic (surfactant) contents, prepared previously. We previously reported that the organic contents improved the removal capacity of acidic dyes [33; 53]. We used magadiite in this fashion due to its higher cation exchange capacity (200 meq/g), thus, a higher organic content on the same order of magnitude as that in organo-clay minerals could be achieved.

The non-modified "Na-magadiite" removed an amount of eosin, approximately 4 mg/g (Figure 8), that was lower than those reported for other silicate materials such kenyaite or clay minerals [33,53]. These materials have a consistent negative charge and a poor affinity for negatively charged anionic dyes [54]. Therefore, Na-magadiite had to be modified with suitable quaternary amine cations to enhance its capacity and gain a net positive charge on its surface [55,56]. Figure 8 shows the effect of the modification of Na-magadiite by C16TMA cations on the removal capacity of the eosin dye. For all the tested organo-magadiites, the amount removed was enhanced when the initial concentration ( $C_i$ ) was increased from 25 ppm to 900 ppm, and it was highly dependent on the C16TMA content at high initial eosin concentration values above 500 ppm. The maximum amount of eosin removed was 64 mg/g for C16-Mag120.



**Figure 8.** Evolution of the removed amount of eosin with the content of C16TMA<sup>+</sup> cations in organo-magadiites. (a) 0, (b) 0.20 mM, (c) 0.40 mM, (d) 1.03 mM and (e) 1.09 mmol

In general, the modification of Na-magadiite with organic surfactants improved the removal properties of eosin compared to that of Na-magadiite, and the organo-magadiites removed a high amount compared to that of the Na-magadiite. Similar results were observed in the case of organo-kenyaite and organo-clays for the removal of eosin or acidic dyes [33, 53, 55]

The modification of the silicate surface by organic cations and mainly long ones, such as C16TMAs, rendered the magadiite an organophilic material similar to organo-clays [57]. The negatively charged surface of the silicate may adsorb the C16TMA<sup>+</sup> cations via an ion exchange mechanism, where a monolayer of cationic surfactants on the surface of the clay was formed. The positively charged ends of the



cationic surfactants were exchanged with the exchangeable interlayer cations of the magadiite ( $\text{Na}^+$ ), and the hydrophobic head of the cationic surfactants was arranged outward [56]. The  $\text{C16TMA}^+$  cations generated an organophilic phase partition in the interlayer spacing, and the partition occurred through the interaction of the dye with the cationic  $\text{C16TMA}^+$  cations [58, 59,60].

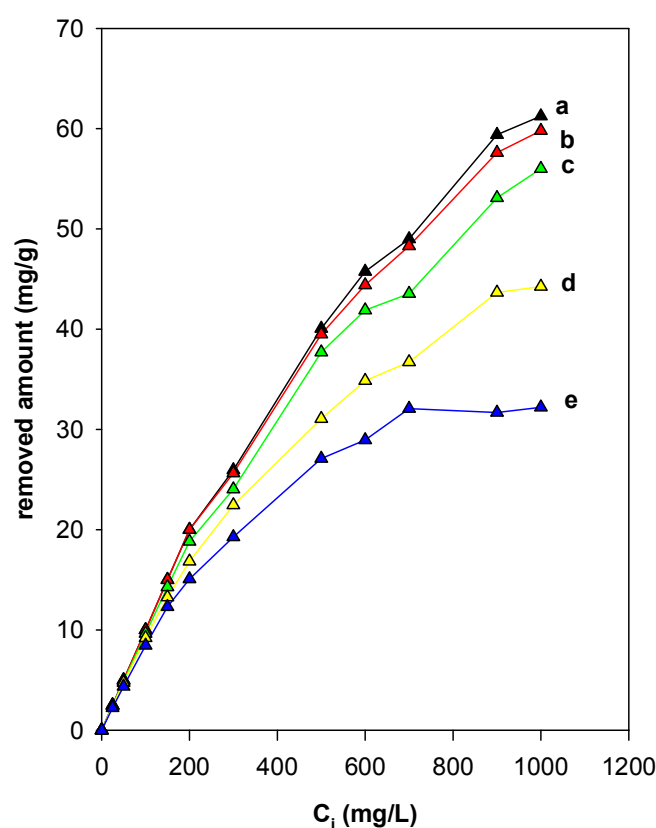
### ***3.6.3. Effect of removal temperature***

The removal of eosin was performed at different initial concentrations ( $C_i$ ) for a representative sample (C16-Mag80) and at different temperatures. The maximum temperature for the removal properties was selected as 50 °C because no change in the XRD pattern of organo-magadiite was observed (see above paragraph). The data indicated that the removal efficiency at lower initial concentrations was not affected by the temperature change since 100 % removal occurred at room temperature (RT) for values from 25 ppm to 200 ppm. This fact was due to nearly all the initial eosin being fixed by the available active sites on the adsorbent in accordance with a process that was not temperature dependent. However, at higher initial concentrations above 500 ppm, the removal percentage and the amount removed depended on the temperature value. At 50 °C, the removal was enhanced to 85 % and a maximum of amount removed of 90 mg/g was achieved for a  $C_i$  of 900 ppm. These results were due to a higher partitioning rate of dye molecules in organophilic silicates, similar to that of organoclays and organo-kenyaite [33,48], or to the temperature activation of other sites (a function of the intercalated C16TMA) that started to fix eosin molecules and led to the increase of the amount removed. This fact indicated that the removal of eosin was an endothermic process [61].

### ***3.6.4. Effect of preheated temperature of organo-magadiite***

The thermal treatment at a fixed temperature above 200 °C of organo-silicates such as organo-clays was used as a method to regenerate spent absorbents for further reuse. In this study, we reported in detail the effect of the preheat treatment of C16-Mag80 on its removal properties. Figure 9 depicts the variation in the amount of removed eosin as a function of the preheated temperature of the organo-magadiite for an initial concentration of 25 to 900 ppm. The amount removed was not affected by preheated temperatures less than or equal to 150 °C for  $C_i$  values less greater than 200 ppm. A reduction in the amount of eosin removed was noted for organo-magadiite preheated at temperatures higher than 200 °C, and this fact was related to the start of the breakdown of the intercalated C16TMA cations, as indicated by the TGA data and the *in situ* studies. A noticeable decrease in the eosin amount removed occurred at temperatures greater than 230 °C due to the complete disintegration of the intercalated C16TMA cations (as indicated by the *in situ* XRD studies), and thus, a loss of the active sites necessary for the removal of eosin.

In comparison to pristine Na-mag, the amount removed was still high, and it could be associated with the presence of the remaining active sites necessary for the removal of the eosin dye, that could be originated from the residual carbonaceous materials. This suggestion would not be useful, as the improvement in the removal capacity was associated with the intercalated C16TMA cations. Nevertheless, the heat treatment may help to find the optimal temperature at which the modified magadiite could be used. Similar data were noticed for an organo-kenyaite preheated at different temperatures for the removal of eosin and for organo-clays for the removal of nitrobenzene [33, 62].



**Figure 9.** Effect of preheated temperatures of C16Mag80 on the efficiency of eosin removal. (a) RT, (b) 100 °C, (c) 200 °C, (d) 215 °C and (e) 250 °C

### 3.6.7 Maximum amount of eosin removed

To determine the maximum amount of eosin removed using different organo-magadiites under different conditions (before or after the preheat treatment), the Langmuir model was used. This model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface.[63]. The linearized Langmuir isotherm allows for the calculation of the adsorption capacity ( $q_{\max}$ ) and the Langmuir constant ( $K_L$ ) that are equated by the

following equation:  $\frac{C_e}{q_e} = \frac{1}{q_{\max} \cdot K_L} + \frac{C_e}{q_{\max}}$ , where  $C_e$  and  $q_e$  are the concentration at equilibrium (mg/g) and the amount adsorbed at equilibrium (mg/g), respectively.,

$q_{\max}$  is the maximum adsorption capacity (mg/g), and  $K_L$  is the Langmuir constant (L/mg). These constants can be estimated from the intercept and slope of the linear plot of the experimental data of  $C_e/q_e$  versus  $C_e$ .

The isotherms of interest fitted well with this model with a linear square regression correlation coefficient of  $R^2$  greater than 0.995. The parameters of the Langmuir model are presented in Table 3.

**Table 3;** Langmuir parameters for the removal of eosin by different organo-magadiites.

Samples	$q_m$ (mg.g <sup>-1</sup> )	$K_L$ (L.g <sup>-1</sup> )	$R^2$
Na-Mag	3.47	0.006	0.931
C16Mag-20	25.06	0.116	0.9943
C16Mag-40	42.54	0.093	0.99610
C16Mag-80	63.06	0.0562	0.9943
C16Mag-120	69.54	0.0712	0.9965
C16Mag-80 (100)*	62.12	0.0562	0.9913
C16Mag-80 (150)*	59.23	0.0551	0.9856
C16Mag-80 (200)*	54.00	0.0284	0.9946
C16Mag-80 (215)*	44.62	0.0216	0.9875
C16Mag-80 (250)*	33.43	0.0207	0.9665

\* corresponds to heating temperature value (in °C) of the organo-magadiites

The maximum amount of eosin removed ( $q_{\max}$ ) was enhanced as the content of C16TMA cations increased in the organo-magadiites and reached a maximum of 100 mg/g for eosin using the C16-Mag120 sample. Similar data were obtained for organo-

kenyaite and clay minerals. However, this value depended on the preheated temperature for a fixed content of C16TMA cations, and a slight variation of the removed capacity was maintained when the sample was preheated at temperatures below 200 °C (before its usage), due to the stability of organo-magadiite in this temperature range (as indicated by the *in situ* XRD study). However, at temperatures higher than 200 °C, a reduction began, and it continued to increase with the preheat temperature to a value of 60 mg/g. This fact was due to the initial loss of C16TMA intercalated cations. The increase of  $K_L$  during the removal of eosin by organo-magadiites could be related to the strong interaction with the silicate surface, however, the role of the C16TMA should also be taken into account, given that the increase was significant in comparison to the  $K_L$  value for pure Na-magadiite and that for C16-Mag120 preheated at temperatures higher than 215 °C.

The amount of eosin removed by organo-magadiites was higher than that of organo-kenyaite, local organo-clay minerals and other materials (Table 4). This difference was due to the high organic content on the organophilic magadiite derivatives, which was enhanced by its high cation exchange capacity compared to kenyaite and local clay minerals.

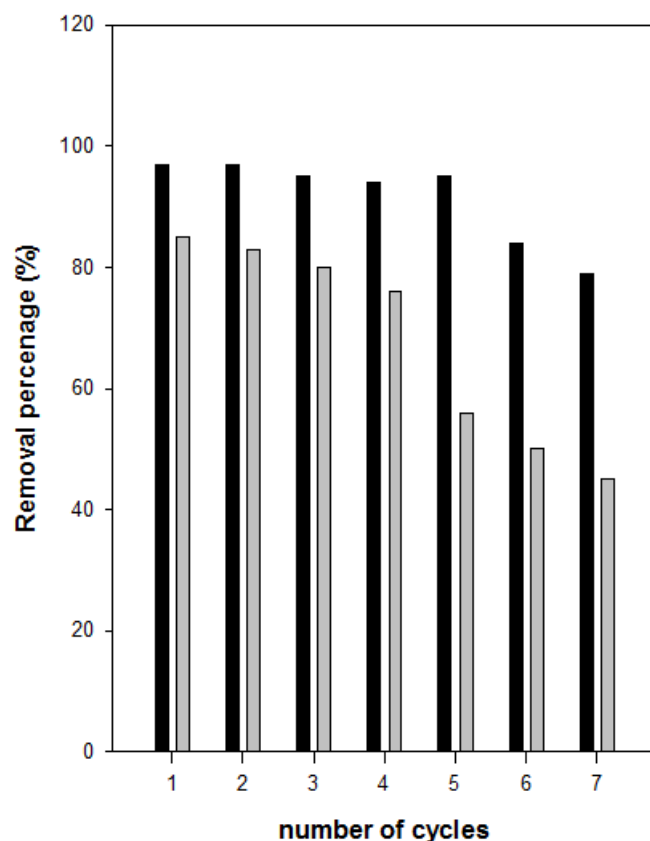
**Table 4.** Removal capacities of various adsorbents for eosin dye

Samples	$q_m$ (mg/g)	references
Organo-kenyaite	48.01	[33]
Organo-magadiite	69.54	[This study]
Raw fly ash	43.48	[64]
Alumina nanoparticles	47.78	[65]
Organo-clays	48.66	[53]

### 3.7. Removal/Regeneration tests

The removal of dyes from wastewater by solid adsorbents is a transfer process of pollutants from the liquid to the solid phase, thus, it brings another type of pollution for the spent adsorbents because of its disposal in landfills. The regeneration process is of great interest to reuse these spent materials and to reduce further contamination of landfills and its environmental impact. Different methods of regeneration were investigated including biological, Fenton oxidation, wet air oxidation, microwave, ultrasound, electrochemical, and thermal treatments [66]; each method has its drawbacks, as reported in the literature, mainly involving time consumption and energy use [66].

In this study, a simple method that did not require many chemicals or a large volume of water was adopted and used in our previous studies [33,31]. C16-Mag120 was used as the model sample with a  $C_i$  of 500 ppm. As shown in Figure 10, the removal efficiency of organo-magadiite was unchanged over 3 removal/regeneration cycles, and it varied slightly from 86 % to 80 %. Then, it dropped to 50 % after 7 cycles. The decrease in the removal efficiency could indicate that some eosin molecules were strongly adhered to the removal sites, making it difficult to remove them. However, using a low  $C_i$  value of 200 ppm, the removal efficiency was not altered and remained unchanged for 5 removal/regeneration cycles, dropping to 80 % after the 6 cycles. These data indicated that organo-magadiite could be used as a potential removal agent for eosin dye.



**Figure 10.** Regeneration/removal cycles of C16Mag-80 using Ci of 200 mg/L (dark bars) and 500 mg/L (grey bars), respectively.

#### 4. Conclusion

The modification of Na-magadiite with C16TMA cations was successfully achieved, and the content of the surfactants could be tuned by using different initial loading concentrations; a maximum C16TMA concentration of 1.02 mmol/g was achieved. The expansion of the basal spacing at 3.10 nm was independent of the intercalated surfactant. The  $^{13}\text{C}$  CP NMR study indicated that the intercalated cations exhibited a homogeneous *trans* conformation similar to the C16TMABr solid. The *in situ* PXRD results indicated an increase in the basal spacing in the temperature range of 50 to 200 °C, due to the expansion of the intercalated surfactants. Above this

temperature, a decrease in the basal spacing to 2.15 nm occurred and was related to the decomposition of the surfactant cations.

The removal of negatively charged dye molecules is weak at the Na-magadiite surface, however, the modification with C16TMA exhibited considerable improvement in the removal efficiency and capacity; a maximum of 100 mg/g was achieved. This capacity depended on the initial concentration, the operating temperature and the preheat treatment of C16-Mag120 prior to the removal process. The intercalated cations played an important role in the eosin removal, and their decomposition reduced and affected this property. These results showed that modified magadiite could be used as a potential candidate for the removal of eosin, and its reuse was maintained after 6 cycles of regeneration.

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