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## Design of organically modified sepiolite and its use as adsorbent for hazardous Malachite Green dye removal from water

Fadwa Largo, Redouane Haounati, Hassan Ouachtak, Naima Hafid, Amane Jada, Abdelaziz Ait Addi

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25 **Abstract**

26 A novel adsorbent design method, based on organic surface modification and carbonization at  
27 350-500°C, of sepiolite, was used to prepare carbon@sepiolite composites which were used  
28 for hazardous malachite green dye removal from water. Prior to their use as adsorbent, the  
29 structure and the morphology of the carbon@sepiolite composites were assessed by various  
30 methods, such as, Fourier Transform Infra-Red (FTIR) spectroscopy, Scanning (SEM) and  
31 Transmission (TEM) Electron Microscopy, Energy Dispersive Analysis of X-rays (EDAX),  
32 and N<sub>2</sub> adsorption/desorption isotherms (BET method). The designed adsorbents showed good  
33 adsorption properties for MG molecules, reaching a maximum dye adsorbed amount of  
34 1198.67 mg/g at 25°C for the carbon@sepiolite composites calcinated at 500°C. Further, the  
35 kinetics and the equilibrium adsorption isotherms of the MG molecules from water onto the  
36 sepiolite-based composites, were well fitted by, respectively, the pseudo-second-order model  
37 ( $R^2 = 0.98$ ) and the Langmuir isotherm ( $R^2 = 0.94$ ) models, indicating that the MG molecules  
38 were homogenously adsorbed and formed a monolayer on the organically modified sepiolite  
39 surface. Moreover, the values of the thermodynamic parameters, such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$   
40 related to the adsorption process, indicated that the adsorption reaction was spontaneous,  
41 feasible and endothermic. In the overall, the present work offers facile ways for the design of  
42 organically modified sepiolite which can be used at large scale as adsorbents for waste  
43 recycling.

44 **Keywords:** Clay; Malachite Green dye; Sepiolite; Adsorption; Waste.

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## 49 **1. Introduction**

50 Organic dyes are extensively worldwide used and mainly in industrial sectors, such as, in the  
51 pulp and paper industry, in the food and paint industries, also in the wool, cotton, leather, silk  
52 and textile industries[1, 2]. All these industries using organic dyes are generating colored  
53 wastewater, leading to a major and a serious environmental problem [3, 4]. Due to their  
54 persistent characteristics, their teratogenicity and carcinogenicity, the organic dyes are toxic to  
55 humans and to the environment [5–9]. Moreover, water polluted by dyes leads to many health  
56 problems such as allergic dermatitis, skin problems, and cancer in humans [10–12]. To treat  
57 the colored water and/or the contaminated water, various chemical, physical and biological  
58 methods, have been developed [13–15]. However, it is essential to develop efficient and  
59 inexpensive methods. Thus, the adsorption is one of the best and most competitive ways to  
60 treat wastewater, due to various advantages, such as, its easy handling, its high efficiency, its  
61 low cost and the wide availability of the adsorbent materials [16, 17]. Further, the adsorption  
62 process does not generate any secondary pollution[18]. On an other hand, when selecting the  
63 adsorbent we have to take into account the fact that the real textile effluents contain mixture  
64 of several dyes [6, 19]. Thus, in order to elucidate the dye adsorption mechanism from water  
65 onto the adsorbent, it is essential to consider initially single-dye systems to reduce the  
66 complexity occurring in the real textile effluent treatment. For this reason, various types of  
67 adsorbents have been extensively used to treat wastewaters, such as activated carbon [20].  
68 However, due to the high costs of these adsorbents, researches have been carried out to find  
69 low-cost adsorbents having high surface areas, high sorption capacities, and having  
70 sustainable and regeneration capabilities. Different types of adsorbents such as sepiolite,  
71 montmorillonite organoclay composites [21], modified sepiolite [22], mesoporous silica [23]  
72 have been used for the removal of dyes from wastewater. It should be noted that sepiolite  
73 (Sep) is a 2:1 type clay mineral, with an excellent adsorption property due its large specific

74 surface area, its high porosity, its ion exchange capacity [3], and its typical structural  
75 properties and its low cost, make it useful in various fields as promising adsorbent for dye  
76 wastewater treatment. As well as, its high surface polarity making the sepiolite surface  
77 negatively charged, which is balanced by inorganic cations (e.g.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ). These inorganic  
78 cations are exchangeable, making Sep efficient adsorbent for various cationic dyes. Proper  
79 disposal of the used Sep is critical to the wide application of Sep in dye wastewater treatment.  
80 However, desorption of cationic dyes from the used Sep can be very difficult, because of the  
81 strong electrostatic interaction between cationic dyes and Sep. As such, traditional  
82 regeneration methods based on desorption are not efficient for recovering the used Sep. Direct  
83 landfill disposal of the used Sep will not only cause serious environmental pollution, but also  
84 be a huge waste of Sep resources. For this reason, it is urgent to find proper methods to  
85 dispose the used Sep.

86 In the present work, MG was selected as a representative of cationic dyes, and after its  
87 adsorption to Sep, the resulting used Sep (MG-Sep) was collected and calcined at different  
88 temperatures, enhancing hence the disaggregation and the performance of the clay. Such  
89 synthesis method producing functional adsorbent is expected to provide a simple way for  
90 treating waste and recycling the organic clay minerals. Further, to improve the adsorptive and  
91 regeneration properties of the sepiolite, the aim of the present work is to decrease, on one  
92 hand, the sepiolite clay mineral surface high polarity, and to increase on the other hand, its  
93 channels and tunnels spacing. Such synthesis method producing functional adsorbent is  
94 expected to provide a simple way for treating waste and recycling the organic clay minerals.

95 The characteristics of the resultant materials (Carbon@Sep) were identified by using  
96 methods such as, FTIR, BET, SEM, TEM and EDS. This study aimed firstly to compare the  
97 differences in properties of the raw sepiolite, calcined sepiolite and the composite-produced  
98 from the carbonization method, and secondly to examine the performance of the

99 carbon@sepiolite in the MG dye removal. Thus, to examine the Carbon@Sep adsorptive  
100 affinity towards the cationic dye removal, experiments were realized by varying  
101 physicochemical conditions (initial pH, adsorbent dosage, MG dye concentration, adsorption  
102 time and temperature). In addition to the experimental adsorption data, theoretical modeling  
103 of the kinetic and the equilibrium dye adsorption on the prepared adsorbent, were also carried  
104 out.

## 105 **2. Experimental**

### 106 **2.1. Materials**

107 The sepiolite (Sep) used in this work was collected from Eskişehir region, in Turkey.  
108 It was crushed and sieved to the desired particle size of less than 50 µm. Malachite Green  
109 (MG, Mw: 364.91, purity ≥99.00%) was obtained from Sigma–Aldrich, and it was used  
110 without any further treatment. The characteristics of MG cationic dye are presented in Table 1  
111 (please see the supplementary file). Aqueous dye solution was prepared by dissolving the  
112 required mass of the dye in bi-distilled water.

### 113 **2.2. Preparation of the organic modified sepiolite**

114 Organic Sep (OSep) was prepared by reconstructing Sep structure in MG solution.  
115 Thus, Sep was first dispersed in MG solution, 1 g of Sep was added into 1 L of 100 mg/L  
116 ( $0.274 \cdot 10^{-3}$  Mole/L) MG solution for 6 h. After MG adsorption from water onto Sep (MG  
117 adsorbed amount of 95.4 mg/g), the resulting used Sep (MG–Sep) was collected and calcined  
118 at different temperatures ranging from 350 to 500 °C for 3 hours, by using a temperature-  
119 controlled furnace. The resulting calcined (MG-Sep) composites were labeled as  
120 (Carbon@Sep).

## 121 **3. Characterization methods**

122 Surface morphologies of the samples were observed by using a Scanning Electron  
123 Microscope (SEM, Supra 40 VP Gemini Zeiss Column), with a maximum voltage of 20 KV.

124 Structural features of the samples were assessed by acquiring images thanks to Transmission  
125 electron microscopy (TEM, Philips, CM 200), operating at an acceleration voltage of 20-200  
126 kV with a magnification ranging from  $\times 10\,000$  to  $\times 200\,000$ .

127 The chemical composition and the elemental distribution of the samples were  
128 determined by Energy Dispersive X-ray Analysis (EDAX). The specific surface areas and the  
129 porosities of the samples were assessed by treating the experimental  $N_2$  adsorption-desorption  
130 data, as performed at 77 K (Micrometrics instrument, ASAP2420), by BET and BJH methods,  
131 respectively.

#### 132 **4. Adsorption experiments**

133 Experiments of MG dye removal by Carbon@Sep were conducted by using batch equilibrium  
134 technique. Thus, firstly 1 L of MG stock solution having a dye concentration of 1200 mg/L,  
135 was prepared by dissolving 1200 mg of the dye in 1 L of distilled water, and then other  
136 solutions of desired concentrations were obtained by successive dilution of this stock solution.  
137 Thus, various adsorbate-adsorbent mixture series having initial dye concentration of 100  
138 mg/L were prepared by placing in each 100 ml glass flask, a volume (50 ml) of the diluted  
139 MG solution. Thereafter, various adsorbent amounts (0.2 - 1.5 g) were added to the 100 ml  
140 glass flasks and the mixtures were agitated.

141 In order to investigate the aqueous phase pH, the contact time and the temperature  
142 effects, the pH was varied in the range (2-10); the contact time covered the interval (5– 420  
143 min), whereas the temperature ranged in the interval (298-333 K). Thus, various adsorbate-  
144 adsorbent mixture series having initial dye concentration of 100mg/L were prepared. Further,  
145 the pH values of dye aqueous solutions were adjusted by using 0.1 N hydrochloric acid and  
146 0.1 N sodium hydroxide aqueous solutions. It should be noted that after each dye adsorption  
147 experiment, the resulted dispersion was filtered through 0.2  $\mu\text{m}$  Millipore membrane filter,  
148 and the residual dye concentrations were analyzed at  $\lambda_{\text{max}} = 618$  nm using UV-Visible

149 spectrophotometer (UV-1800, SHIMADZU). The adsorbed amount at the equilibrium ( $q_{ads}$ ,  
150  $mg\ g^{-1}$ ), and the removal percentage (% R), of the MG dye were calculated by using,  
151 respectively, the following equations (1) and (2):

$$152 \quad q_{ads} = \frac{C_0 - C_e}{m} \times V \quad \text{(Eq. 1)}$$

$$153 \quad \%_{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{(Eq. 2)}$$

154 where  $q_{ads}$  is the amount of the adsorbed dye ( $mg/g$ ),  $C_0$  and  $C_e$  are the initial and the  
155 equilibrium concentrations of the dye ( $mg/L$ ),  $V$  (L) is the volume of solution and  $m$  (g) is the  
156 Carbon@Sep mass.

## 157 **5. Results and discussion**

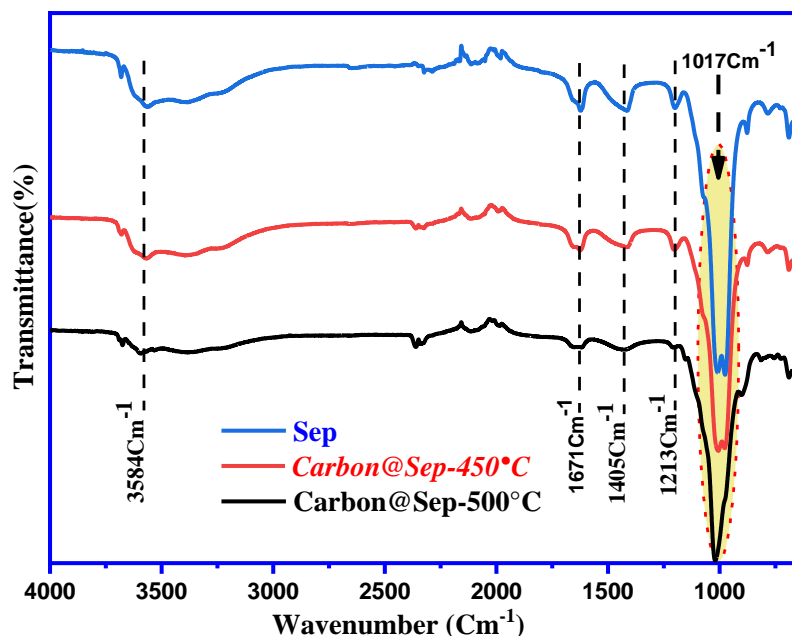
### 158 **5.1. Characterization**

#### 159 **5.1.1. FTIR analysis**

160 The FTIR Spectra of the all prepared samples were recorded from  $400\ cm^{-1}$  to  $4000\ cm^{-1}$  and  
161 they were comparatively investigated. As can be seen in Fig. 1, for the sepiolite, the FTIR  
162 spectrum shows all characteristic peaks of clay mineral. Thus, the  $3584$  and  $1671\ cm^{-1}$  bands  
163 are assigned, respectively, to the OH stretching, representing the zeolitic water in the  
164 channels, and to the bound water coordinated to magnesium in the octahedral sheet. The band  
165 occurring at  $1405\ cm^{-1}$  is due to the hydroxyl bending vibration, reflecting hence, the  
166 presence of bound water. The Si–O coordination bands occurring at  $1213$  and  $1017$   
167  $cm^{-1}$  represent the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet. When  
168 compared to the raw Sepiolite (Sep) spectrum, FTIR spectra of the modified sepiolite  
169 (carbon@Sep  $450^\circ C$  and carbon@Sep  $500^\circ C$ ) show the appearance of all sepiolite bands. In



170 addition, significant decrease in the intensity of all bands were observed, which may be due to  
171 a greater decrease for  $\text{Si}^{4+}$  cations, as compared to  $\text{Mg}^{2+}$  cations caused by high temperature,  
172 changing hence the sepiolite surface structure.



173

174 **Fig. 1. FTIR Spectra of raw Sepiolite, Carbon@Sep-450°C, Carbon@Sep-500°C.**

### 175 **5.1.2. SEM and EDAX analyzes**

176 The surface morphology and the composition of the calcined raw Sep and the  
177 carbon@sepiolite composites, were assessed by using SEM-EDAX instrument in order to get  
178 deeper information on the structural characteristics of the materials, as depicted in Fig. 2. In  
179 addition, the elemental composition data are presented in Table 2. Thus, as can be observed in  
180 Fig. (a) The sepiolite exists in the forms of lamellar particles, as well as, crystal bundles.  
181 When the original sepiolite, the organic and the calcined sepiolite, are compared, it is shown  
182 that the original morphology and the microstructure of the sepiolite crystals are kept intact  
183 after organic and thermal modifications. Further, as shown in Fig.2 c-e, after the organic and

184 the thermal modifications of the sepiolite, the original crystalline structure of the material was  
 185 maintained, and the fiber aggregation phenomenon of the sepiolite decreased more in the  
 186 modified sepiolite in comparison to the pristine one. Moreover, the carbonization process of  
 187 OSep at 500 °C, as depicted in Fig.2 (e), gives material having still large pore diameters and  
 188 more homogeneous surface. On the contrary, the raw sepiolite calcined at 500 °C, Fig. 2 (b),  
 189 shows a lower pore volume in comparison to the Carbon@Sep calcinated at 500 °C.

190 According to the elemental composition results (Table 2), the carbon element is evenly  
 191 distributed along with Silica, Magnesium and Oxygen elements in the Carbon@Sep  
 192 composite produced from the carbonization of the same precursor (Sep/MG) at temperatures  
 193 ranging from 400 °C to 500 °C. Note that during the carbonization process, the resulting  
 194 carbon mass percentage increases from 39 % to 49.7%, by going from 400 °C to 500 °C.  
 195 Further, the EDS data indicate uniform distribution of carbon nanoparticles in the  
 196 Carbon@Sep composites, and confirm the successful modification of sepiolite, by grafting the  
 197 C element in it.

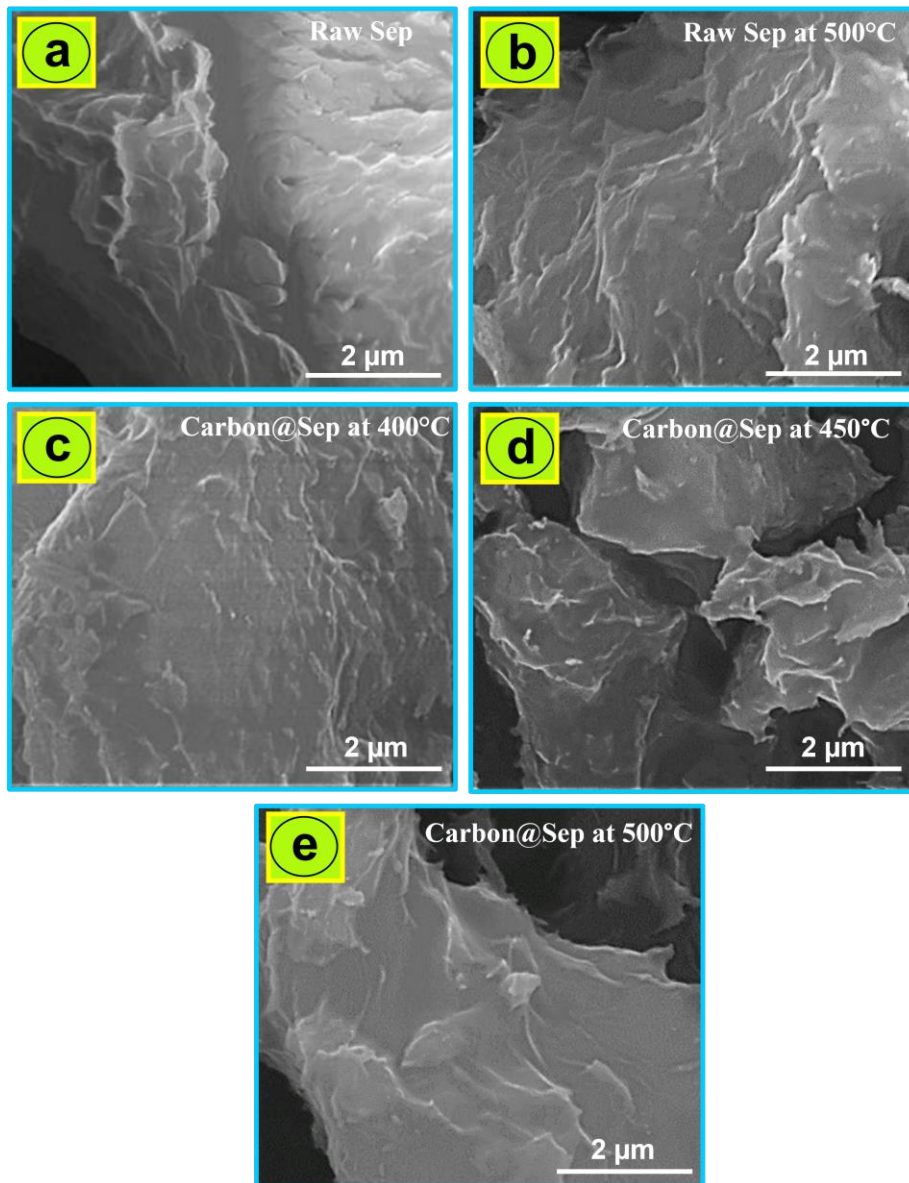
198 **Table 2: Elements mass percentages of the raw Sep, calcined raw sepiolite at 500 °C,**  
 199 **Carbon @Sep(400 °C), Carbon@Sep(450 °C) and Carbon@Sep(500 °C)**

| <b>Sample</b>                      | <b>Si</b>   | <b>Mg</b>   | <b>O</b>    | <b>C</b>    | <b>Ca</b>  |
|------------------------------------|-------------|-------------|-------------|-------------|------------|
| <b>Sepiolite</b>                   | <b>37.8</b> | <b>17.6</b> | <b>44.6</b> | <b>--</b>   | <b>--</b>  |
| <b>Raw Sep. calcined at 500 °C</b> | <b>31.1</b> | <b>16.6</b> | <b>46.5</b> | <b>--</b>   | <b>5.9</b> |
| <b>Carbon@Sep (400 °C)</b>         | <b>12.5</b> | <b>8.5</b>  | <b>39.6</b> | <b>39.2</b> | <b>0.3</b> |
| <b>Carbon@Sep (450 °C)</b>         | <b>10.9</b> | <b>7.3</b>  | <b>36</b>   | <b>45</b>   | <b>0.5</b> |
| <b>Carbon@Sep (500 °C)</b>         | <b>8.8</b>  | <b>6.3</b>  | <b>34.5</b> | <b>49.7</b> | <b>0.3</b> |

200

201 **5.1.3. TEM analysis**

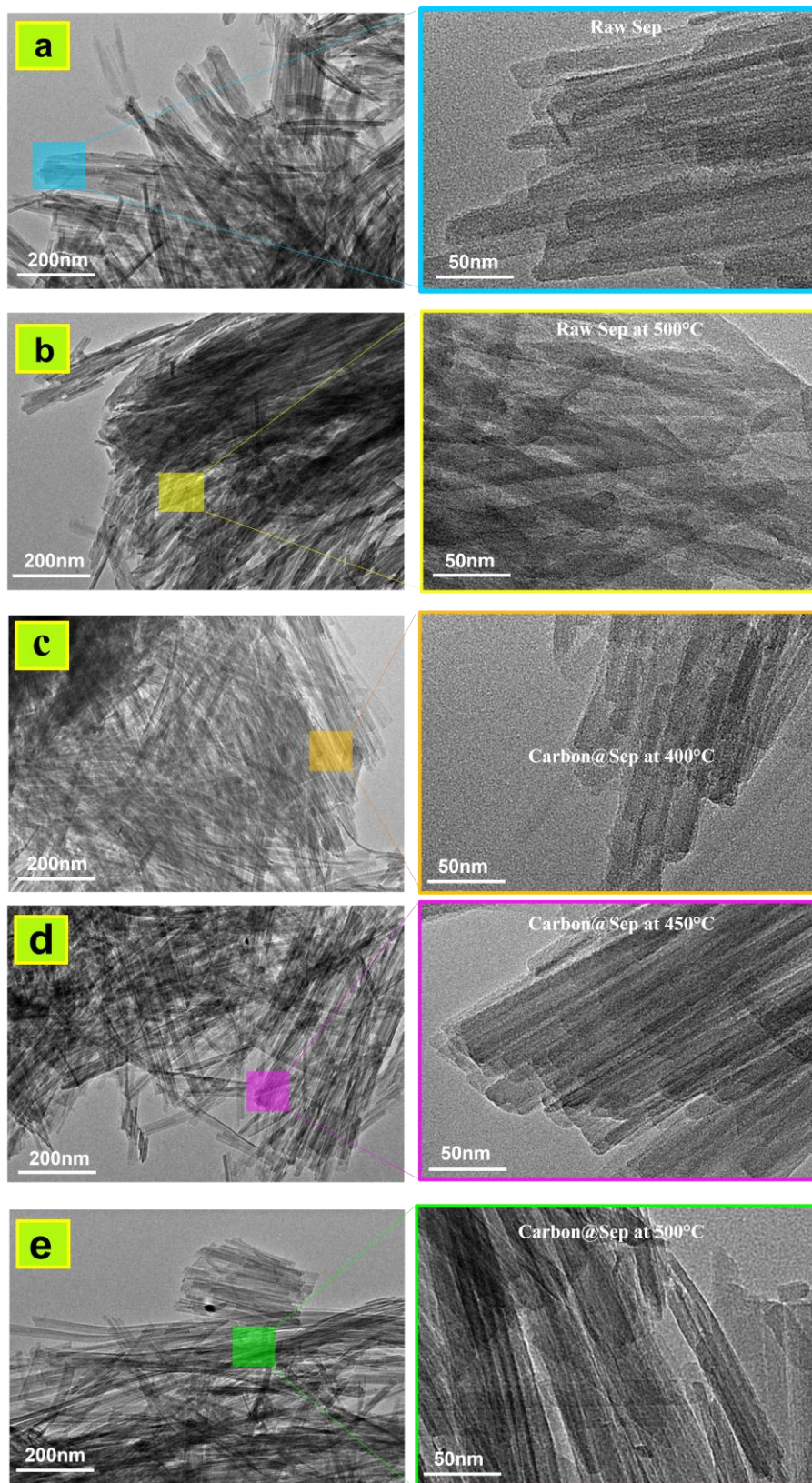
202 The TEM images of the raw Sep, the raw Sep calcined at 500 °C, and Carbon@Sep  
203 composites are shown in Fig.3.



204

205 **Fig.2. SEM micrographs of raw sepiolite (a), raw sepiolite at 500 °C (b), Carbon@Sep at**  
206 **400 °C (c), Carbon@Sep at 450 °C (d), Carbon@Sep at 500 °C (e).**

207 It can be seen in this figure that the raw Sep, and the Carbon@Sep resulted at different  
208 temperature treatments, present all the needle-like fibrous clusters microstructure. space.  
209 Furthermore, in Fig.3 (e), it can be observed larger bundles and disordered fibers structure.



210

211 **Fig.3. TEM images of the samples; all the samples present short micro-fibrous bundles**

212

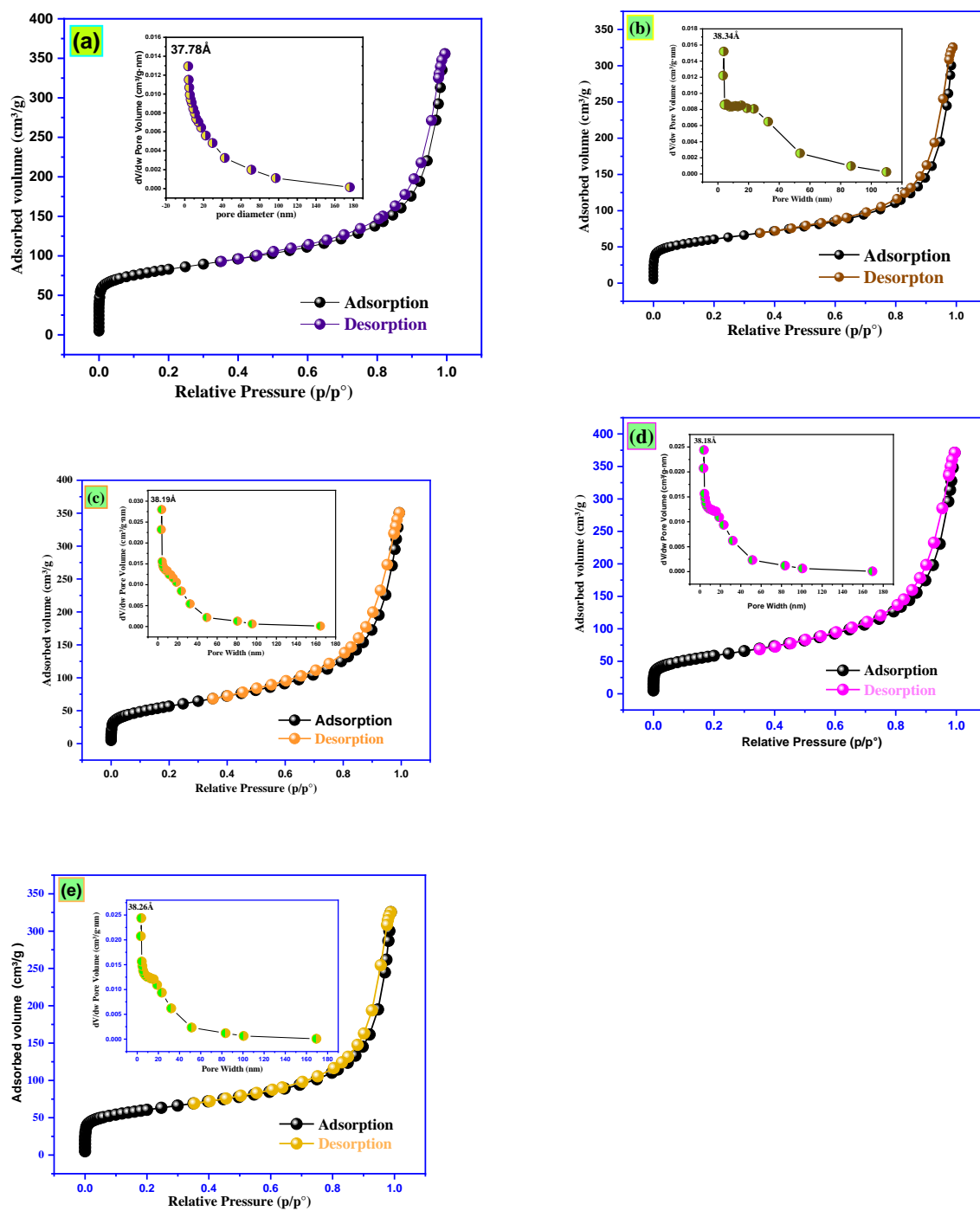
**like morphology**



213 Further, it can be observed in Fig.3 (b) that the calcined raw Sep at 500 °C gives low inter  
214 fibrous bundles distance. On the other hand, Fig.3 (c, d) show a more developed inter-fibrous  
215 bundles

#### 216 **5.1.4. BET surface area assessment**

217 The N<sub>2</sub> adsorption/desorption isotherms and the Barrett-Joyner-Halenda (BJH) pore size  
218 distributions of the five samples are illustrated in Fig.4., the calculated BET surface areas,  
219 pore volumes, and pore sizes, are presented in Table 3. Fig.4 indicates for all samples, that the  
220 N<sub>2</sub> adsorption-desorption isotherms are of type IV with hysteresis loops, mostly attributed to  
221 mesoporous materials, according to IUPAC classification. From these isotherms, the  
222 calculated specific surface area and the pore volume of the Sep were found to be, respectively,  
223 300 m<sup>2</sup>/g and 0.443 cm<sup>3</sup>/g. However, after the successive carbonization of the carbon@Sep  
224 composite in the temperature range 400-500 °C, the specific surface area was found to  
225 decrease from 300.7 m<sup>2</sup>/g for the raw Sepiolite, to 202.4 m<sup>2</sup>/g and 149.48 m<sup>2</sup>/g, for the  
226 Sep/MG composites treated at 400 °C and at 450 °C, respectively. Such decrease in the clay  
227 surface area indicates that N<sub>2</sub> molecules are not easily accessible to the calcined carbon@Sep  
228 sepiolite channels, which is filled by the carbon molecules. On the other hand, the comparison  
229 of the carbon@Sep samples carbonized, at 450 °C and 500°C, show increases in the specific  
230 surface area, and in the pore volume, from 149.8 to 207.5 m<sup>2</sup>/g, and from 0.371 to 0.476  
231 cm<sup>3</sup>/g, respectively. Such results suggest that the carbonized sample (carbon@Sep composite  
232 at 500 °C) has an open structure, which is suitable to promote the penetration of the adsorbed  
233 molecules inside the composite surface. In addition, the average pore diameters of the raw  
234 Sep, the raw Sep calcined at 500 °C, the Carbon@Sep at 400 °C, 450 °C and 500 °C samples  
235 were calculated by using the BJH method, and they were found to be equal to, respectively,  
236 37,78 Å, 38.34Å, 38.19Å, 38.18 Å and 38.26Å. Hence from these data, we can say that the



237 Fig.4.  $N_2$  adsorption-desorption isotherms, and BJH pores, of the raw Sep (a),  
 238 carbon@Sep 400 °C (b), carbon@Sep 450 °C (c), carbon@Sep 500 °C (d) and calcined  
 239 raw Sep. 500 °C (e) adsorbents.

240 thermal treatment and the carbon modification of the sepiolite, significantly affect the specific  
241 surface area.

242 **Table 3. Textural properties of raw Sep, Sep calcined at 500 °C, carbon@Sep 400 °C,**  
243 **carbon@Sep 450 °C and carbon@Sep 500 °C adsorbents.**

| <b>Material</b>            | <b>Surface area<br/>(m<sup>2</sup>/g)</b> | <b>Pore volume (cm<sup>3</sup>/g)</b> | <b>BJH adsorption average<br/>pore diameter (Å)</b> |
|----------------------------|---|---------------------------------------|---|
| <b>Raw Sep</b>             | <b>300.7</b>                              | <b>0.443</b>                          | <b>37.78 Å</b>                                      |
| <b>Raw Sep 500 °C</b>      | <b>216.6433</b>                           | <b>0.446</b>                          | <b>38.34 Å</b>                                      |
| <b>Carbon@Sep (400 °C)</b> | <b>202.442</b>                            | <b>0.503</b>                          | <b>38.19 Å</b>                                      |
| <b>Carbon@Sep (450 °C)</b> | <b>149.4804</b>                           | <b>0.371</b>                          | <b>38.18 Å</b>                                      |
| <b>Carbon@Sep (500 °C)</b> | <b>207.5912</b>                           | <b>0.476</b>                          | <b>38.26 Å</b>                                      |

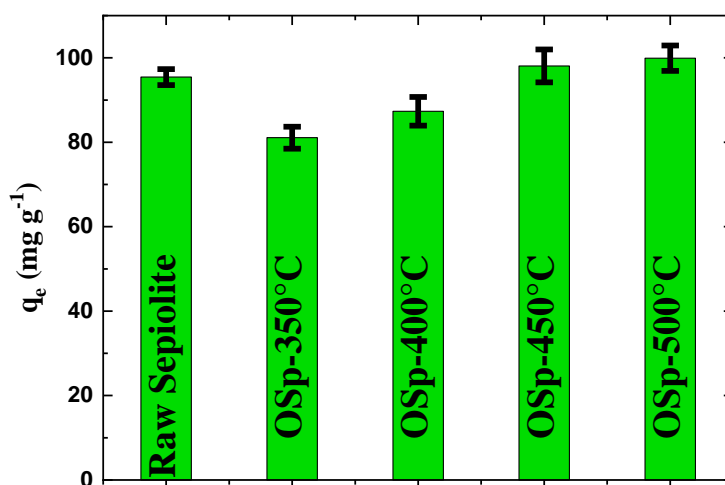
244

## 245 **5.2. Effects of experimental conditions**

### 246 **5.2.1. Effect of the carbonization temperature**

247 The influence of the carbonization temperature on the adsorption efficiency of the MG  
248 dye was studied by using 1g of the raw sepiolite sample which was added into 1 L of 100  
249 mg/L MG solution at initial pH, for a contact time adsorbate-adsorbent of 4 h, resulting in  
250 MG-Sep hybrids (OSep). Thereafter, the MG-Sep powders were calcinated at temperatures  
251 ranging from 350 to 500 °C. Hence, as can be seen in Fig. 5, the MG adsorption on the  
252 calcined organo sepiolite was enhanced upon the organic sepiolite carbonization, and the  
253 adsorbed dye amount increased from 81 mg/g for Sep-350 °C at 99.5 mg/g Sep-500 °C,  
254 **within an experimental error ranging from 2% to 4%.** These results indicate that the  
255 adsorption of MG dye onto Carbon@Sep 500 °C is more efficient, in comparison to the raw  
256 sepiolite, Carbon@Sep 350 °C, Carbon@Sep 400 °C and the Carbon@Sep 450 °C. The

257 enhanced adsorption performance obtained by Carbon@Sep 500 can be explained by the high  
258 temperature effect which causes the sepiolite tunnel space increase and then facilitates the  
259 penetration of MG dye molecules inside the tunnels. In addition, the appearance of new  
260 COOH and OH adsorption sites may promote electrostatic interaction between the  
261 Carbon@Sep surface and the MG dye. Thus, all subsequent experiments in this work were  
262 performed using Carbon@Sep 500 °C



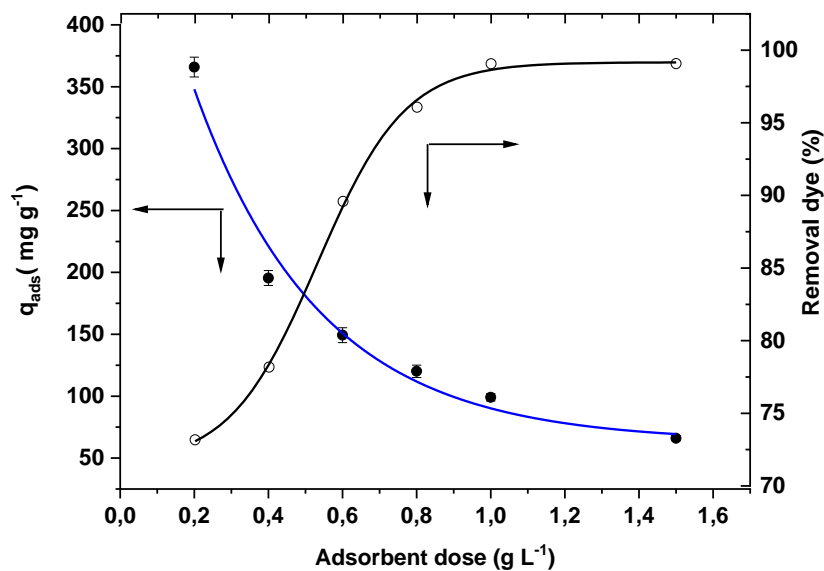
263  
264 **Fig. 5. Effect of carbonization temperature on the adsorption capacity of the raw and**  
265 **the organic sepiolite toward the MG dye (Adsorbent concentration=1 g/L, MG dye**  
266 **concentration=100 mg/L, initial pH, temperature = 25 °C).**

### 267 5.2.2. Effect of the adsorbent dose on the MG dye adsorption

268 The effect of adsorbent dosage on the MG dye removal was investigated, at natural pH, by  
269 varying the Carbon (500°C) dose from 0.2 to 1.5 g. L<sup>-1</sup>, and by fixing, the initial dye  
270 concentration to 100 mg L<sup>-1</sup>, the contact time to 5 hours, and the adsorption temperature to  
271 25°C. **Fig. 6** indicates that the MG removal efficiency is dependent on the Carbon@Sep dose  
272 in the aqueous solution. **Thus, when the Carbon@Sep dose increases from 0.2 to 0.8 g/L, the**



273 adsorbed MG amount,  $q_{ads}$ , decreases from 365 mg/g to 120 mg/g, within an experimental  
 274 error ranging from 2% to 4%. Further, the MG removal increases from 73.2 to 96.1% and  
 275 then reaches an almost constant value. The increase of removal rate can be due to the increase  
 276 of the available active sites of the adsorbent, leading to enhancement in the contact surface  
 277 area between the MG dye molecules and the adsorbent surface. Similar behavior has been  
 278 reported in the literature [8, 11], for the MG removal by using other types of adsorbents.  
 279 In the following, an optimal Carbon@Sep dosage of 0.8 g L<sup>-1</sup> will be used for further  
 280 adsorption experiments.



281

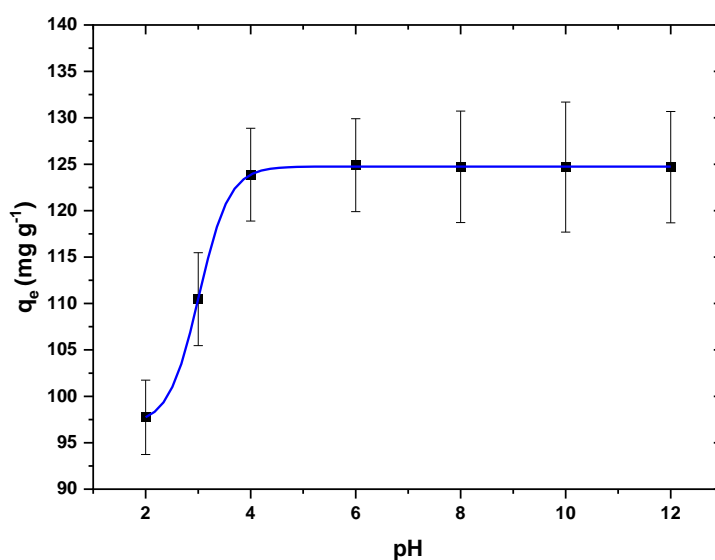
282 **Fig.6. Effect of Carbon@Sep dosage on the MG adsorption (MG concentration=100**  
 283 **mg/L, contact time t=300 min, temperature T= 25 °C, adsorbent dosage = 0.2 g/L to 1.5**  
 284 **g/L, natural pH).**

### 285 5.2.2. Effect of pH

286 The initial solution pH is an important parameter on the adsorption process [20, 21]. Thus, the  
 287 adsorption of MG onto carbon@Sep was studied in the pH range of 2–12, by fixing, the initial  
 288 dye concentration to 100 mg/L, the adsorbent dose to 0.8 g/L, and the contact time to 5h. Fig.

289 7 shows the initial solution pH effect on the MG adsorption from water onto Sep-Carbon  
290 surface. As can be seen in Fig. 7, the removal efficiency and the adsorption capacity, increase  
291 significantly from 97.7 to 124.9 mg/g when the pH increases from 2 to 6, and from 124.9 to  
292 124.68 mg/g when the pH value varies from 6 to 12, **within an experimental error ranging**  
293 **from 4% to 6%**. Thus, in acidic medium (pH<4), the surface of Carbon@Sep was more  
294 protonated due to the presence of protons H<sup>+</sup> in solution, which promotes electrostatic  
295 repulsion between the cationic dye MG and the surface of the adsorbent and consequently the  
296 reduction in the adsorbed amount in an acid medium.

297 At pH > 4, the surface of Carbon@Sep becomes more and more negative by the effect of the  
298 deprotonation of the surface functional groups (Si-OH, Mg-OH, -COOH and -OH) which  
299 leads to an increase in the density of the negatively charged surface groups of the sepiolite  
300 which in turn result in an electrostatic attraction between the adsorbent and the positively  
301 charged molecules of the MG dye.

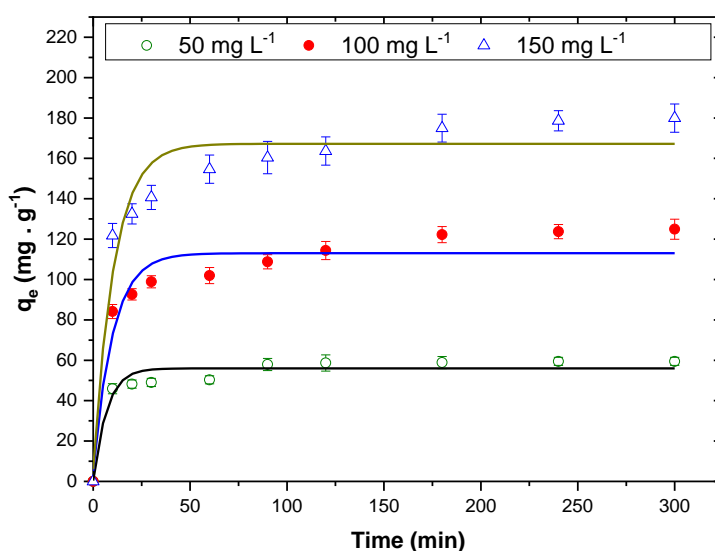


302  
303 **Fig. 7. MG removal effectiveness at different solution pH values using carbon@Sep**  
304 **(C<sub>0</sub>=100 mg L<sup>-1</sup>, adsorption time = 5 h, adsorbent dose = 0.8 g. L<sup>-1</sup> and adsorption**  
305 **temperature, T= 25 °C)**

306 According to these results, the electrostatic interactions between the MG dye and the  
307 Carbon@Sep surface play a predominant role in the adsorption phenomenon. Similar results  
308 were found by Haounati et al. (2020) in their reported work dealing with the adsorption of  
309 MG from water onto SDS/CTAB@Montmorillonite [21]. The optimal pH value of 6 was  
310 selected for next investigation since the maximum removal efficiency was attained at this pH.

#### 311 5.2.4. Effect of the contact time

312 The contact time effect was examined for the MG adsorption onto Sep-Carbon, at 25°C,  
313 initial pH=6, 0.8 g/L of modified sepiolite dose and three MG concentrations (50, 100 and  
314 150 mg/L). The obtained results are shown in Fig. 8. As seen in the figure, whatever is the  
315 dye concentration, the adsorption capacity of MG increases rapidly within the first 90 min,  
316 and then, slowly, until equilibrium point is reached at 300 min, **within an experimental error**  
317 **ranging from 3% to 7%..** The first MG adsorption step can be explained by the high affinity of  
318 Sep-Carbon towards MG dye molecules.



319  
320 **Fig.8. Effect of contact time and the MG concentration on the adsorption of MG dye**  
321 **onto Carbon@Sep (T= 25 °C, R= 0.8g/L, pH= 6)**

322

323 The following slow step could be due to the penetration-diffusion of MG dye molecules into  
324 the inner surface of the modified sepiolite. Finally, after 300 min of contact time, all the active  
325 sites on the surface of the adsorbent are saturated and the adsorbed amount remains constant.  
326 Hence, the equilibrium time of 5h was fixed for all further adsorption experiments.

### 327 5.2.5. Adsorption kinetics

328 In order to describe the dye adsorption mechanism on the adsorbent surface, we  
329 carried out adsorption kinetics models. In addition, the experimental kinetics data were  
330 compared to the theoretical predictions of the pseudo first-order ( PFO, Eq.3), pseudo second-  
331 order (PSO, Eq.4), and intraparticle diffusion (IPD) models (Eq. 5) [22]. The non-linear forms  
332 of PFO [23], [24], PSO [25-26] and IPD kinetic models are expressed in the following  
333 equations:

$$334 \quad q_t = q_e(1 - e^{-k_1 t}) \quad (\text{Eq. 3})$$

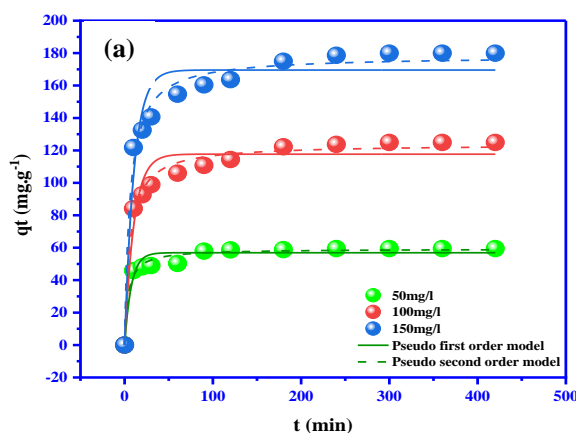
$$335 \quad q_t = (q_e^2 k_1 t) / (1 + k_2 q_e t) \quad (\text{Eq. 4})$$

$$336 \quad q_t = k_{IPD} t^{1/2} + \beta \quad (\text{Eq. 5})$$

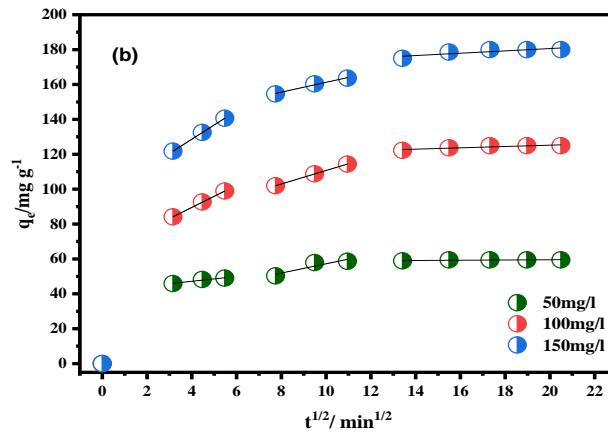
337 where  $q_e$ (mg/g) and  $q_t$ (mg/g) are the amounts of adsorbed dye per weight of adsorbent (mg  
338  $g^{-1}$ ) at equilibrium and at time  $t$ (min), respectively;  $k_1$  ( $\text{min}^{-1}$ ),  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) and  $k_{IPD}$   
339 ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{1/2}$ ) are the rate constant of pseudo-first-order, pseudo-second-order and  
340 intraparticle diffusion adsorption, respectively. The non-linear plots of the pseudo-first-order  
341 and the pseudo-second-order models are presented in Fig. 9 (a). The parameters of kinetic  
342 models are calculated from the experimental data and are summarized, with correlation  
343 coefficients and  $\chi$  values, in Table 4. As can be seen in this Table 4, and based on the higher  
344 correlation coefficient  $R^2$  and lower  $\chi$  values, the MG dye adsorption data were better fitted

345 by the pseudo-second-order (PSO) model for Sep/carbon. Furthermore, by using the PSO  
 346 model, the calculated absorbed amounts  $Q_{e,2}$  were better compared the experimental results  
 347 ( $Q_{e, \text{exp}}$ ), as depicted in Fig.9 (a). Therefore, the PSO model was found to be well suited to  
 348 describe MG dye removal over Sep/carbon.

349 In addition, mass transfer mechanism of the slower adsorption phase between  
 350 adsorbent/adsorbate was studied by using Intra-Particular-Diffusion model. Fig. 9 (b) displays  
 351 the  $Q_t$  vs the time square root ( $t^{1/2}$ ) plots for Sep-Carbon during MG dye adsorption. From Fig.  
 352 9 (b), the MG dye adsorption process presents a multi-linear profile, indicating that the  
 353 adsorption process occurs through three successive steps [27]. The initial step describes the  
 354 mobility of MG ions from liquid phase to the external surface of Sep-Carbon (surface  
 355 diffusion), and the rate of this step is high. The second phase indicates the penetration of MG  
 356 dye molecules into internal surface of modified sepiolite, and the rate of this step is lower than  
 357 the first one and mainly controlled by pore diffusion. The third step is attributed to ultimate  
 358 adsorption equilibrium. As can be seen in Fig. 9 (b), none of the lines passed through the  
 359 origin, indicating that the intra-particle diffusion was not the only rate-controlling step [28-  
 360 30], and others mechanisms such as boundary layer may control the adsorption process to  
 361 some extent [31]. In this part dealing with intraparticle diffusion (IPD), the values of  $k_{IPD}$  and  
 362  $\beta$ , obtained from fitting the initial, second and third linear portions, to equation (5), are listed  
 363 in Table 4. As can be observed in Table 4, increasing the initial MG concentration from 50  
 364 to 100 mg. L<sup>-1</sup>, increases the values of  $\beta$  from 0.57 to 1.70, reflecting thus, the increase in  
 365 the boundary layer thickness [32], and the probable decrease of the external mass transfer.  
 366 Thus, the chance of internal mass transfer was increased [33].



367



368

369 **Fig.9. PFO, PSO (a) and IPD (b) correlation plots for MG dye adsorption onto the Sep-**  
 370 **Carbon adsorbent.**

371 **5.2.6. Adsorption isotherm**

372 The effect of initial MG concentration on its removal by Sep-Carbon was studied at  
 373 different concentrations ranging from 25 to 1400 mg L<sup>-1</sup> at 25°C and pH=6. As shown in Fig.  
 374 10, the adsorbed amounts of MG dye increases gradually with increasing its initial  
 375 concentration. Hence, when the initial MG concentration increases from 10 to 1200 mg/L, the  
 376 adsorbed amount of the dye increases several folds from 12.4 to 1188.82 mg/g. This behavior  
 377 may be explained by the diffusion of the dye molecules from the solution toward the Sep-  
 378 Carbon surface as caused by the increase of the driving force for mass transfer [34-35]. In  
 379 order to elucidate the adsorption mechanism, the adsorption experimental data were compared  
 380 to two theoretical models, the Langmuir model [36] and the Freundlich model [37].

381 The nonlinear equations of Langmuir (Eq.6) and Freundlich (Eq.7) models are given below:

382 
$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad \text{(Eq. 6)}$$

383 
$$Q_e = K_F C_e^{1/n} \quad \text{(Eq. 7)}$$

384 where  $Q_e$  (mg/g) is the equilibrium adsorbed amount,  $C_e$  (mg/L) is the equilibrium  
 385 concentration,  $Q_m$  (mg/g) is the maximum adsorbed amount,  $K_L$ (L/mg) and  $K_F$   
 386 (mg/g)/(mg/L)<sup>1/n</sup> are the Langmuir and Freundlich adsorption constants, respectively, n is the  
 387 Freundlich isotherm exponent that determines the isotherm non-linearity. Hence, the  
 388 adsorption is favorable for  $n>1$  and unfavorable when  $0<n<1$ .

389 **Table 4. Kinetic parameters for the adsorption of MG onto Sep-Carbon.**

| <b>Pseudo-first-order (PFO)</b> |                       |                      |                      |       | <b>Pseudo-second-order (PSO)</b> |                       |   |       |        |
|---------------------------------|-----------------------|----------------------|----------------------|-------|----------------------------------|-----------------------|---|-------|--------|
| $C_0$                           | $Q_{e, exp}$          | $Q_{e,1}$            | $k_1$                | $R^2$ | $\chi$                           | $Q_{e,2}$             | $k_2$                                   | $R^2$ | $\chi$ |
| (mg/l)                          | (mg g <sup>-1</sup> ) | (mg.g <sup>1</sup> ) | (min <sup>-1</sup> ) |       |                                  | (mg g <sup>-1</sup> ) | (mg g <sup>-1</sup> min <sup>-1</sup> ) |       |        |
| 50                              | 59.4                  | 56.9                 | 0.133                | 0.95  | 4.03                             | 59.29                 | 0.0043                                  | 0.98  | 2.44   |
| 100                             | 124.9                 | 117.7                | 0.095                | 0.94  | 9.42                             | 123.79                | 0.0013                                  | 0.98  | 5.37   |
| 150                             | 179.9                 | 169.6                | 0.094                | 0.94  | 12.56                            | 178.30                | 0.0009                                  | 0.98  | 6.49   |

390

391 **Intraparticle diffusion (IPD)**

**Initial linear portion                      Second linear portion                      Third linear portion**

| $C_0$ | $k_{IPD}$ | $\beta$ | $R^2$ | $\chi$ | $k_{IPD}$ | $\beta$ | $R^2$ | $\chi$ | $k_{IPD}$ | $\beta$ | $R^2$ | $\chi$ |
|-------|-----------|---------|-------|--------|-----------|---------|-------|--------|-----------|---------|-------|--------|
| 50    | 54.2      | 0.57    | 0.99  | 0.15   | 99.5      | 7.33    | 0.89  | 2.19   | 61.8      | 0.66    | 0.84  | 0.19   |
| 100   | 128.9     | 1.70    | 0.99  | 0.97   | 161.5     | 4.50    | 0.99  | 0.49   | 134.0     | 1.39    | 0.99  | 0.07   |
| 150   | 176.9     | 1.45    | 0.98  | 1.42   | 190.5     | 1.79    | 0.99  | 0.18   | 200.1     | 1.90    | 0.97  | 0.58   |

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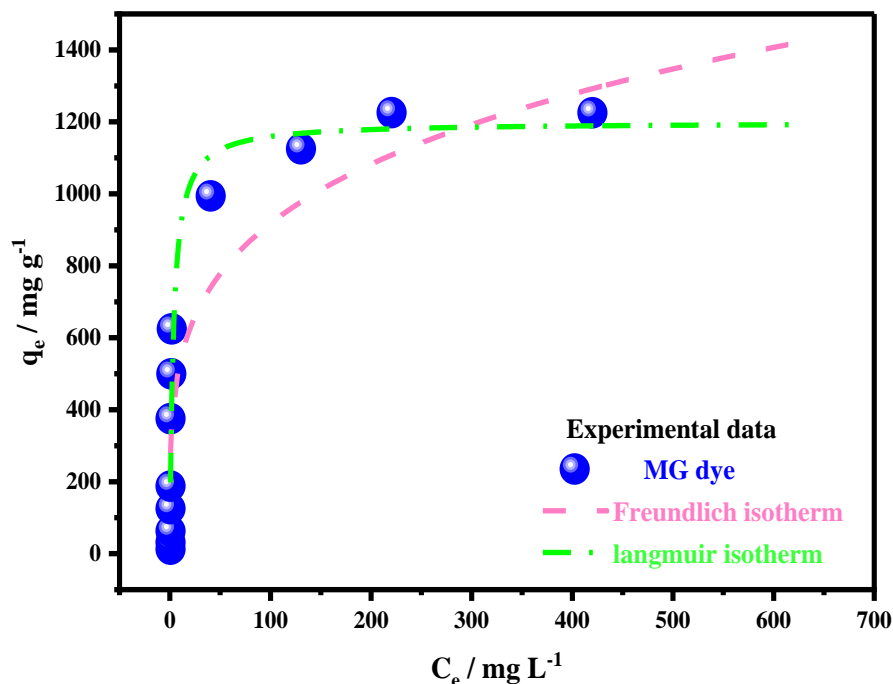
393

394 Further, to assess the goodness of the fits, the correlation coefficients  $R^2$ , and the  $\chi$  values  
395 were determined and they are presented in Table 5. Recall that the Langmuir model considers  
396 that the adsorption takes place on a homogeneous surface leading to the formation of a  
397 monolayer of the adsorbate on the adsorbent surface. On the other hand, the Freundlich model  
398 assumes that the adsorption process takes place in more than one surface layer (multilayer)  
399 and that the adsorbent surface is heterogeneous, with a non-uniform distribution of heat of  
400 adsorption.

401 When the organic sepiolite was used as adsorbent, the fitting of the adsorption experimental  
402 data to the Langmuir model yielded higher  $R^2$  coefficient ( $R^2=0.94$ ) and lowest  $\chi$  ( $\chi=77.02$ )  
403 values, in comparison to the Freundlich model. This finding suggests that the MG dye  
404 adsorption forms a monolayer pattern on a homogeneous adsorbent surface, and a saturated  
405 adsorption capacity is expected due to limited adsorptive sites on the surface. The maximum  
406 dye adsorption capacity was determined to be  $1198.67 \text{ mg g}^{-1}$  on the organic sepiolite. Such  
407 high dye adsorbed amount value indicates that the organic sepiolite material can be used as  
408 potential adsorbent to efficiently clean-up the industrial effluent containing dyes.

409





410  
 411 **Fig. 10. Experimental adsorption isotherms of MG onto Sep-Carbon, compared to the**  
 412 **nonlinear Langmuir and Freundlich theoretical models.**

413  
 414 **Table 5. Isotherms parameters for the MG adsorption from water onto the modified**  
 415 **Sepiolite surface.**

| Dye | Langmuir     |              |       |        | Freundlich   |      |       |        |
|-----|--------------|--------------|-------|--------|--------------|------|-------|--------|
|     | $Q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $\chi$ | $K_f$ (mg/g) | $n$  | $R^2$ | $\chi$ |
| MG  | 1198.67      | 0.2941       | 0.94  | 77.02  | 305.9        | 4.19 | 0.848 | 95.85  |

416  
 417 The comparison of the adsorption capacity of the sepiolite-carbon, used in the present work,  
 418 with others adsorbents, as reported in the literature, for MG dye, is presented in Table 6.  
 419 Clearly, our prepared adsorbent, as compared to different adsorbents reported in the literature,  
 420 showed the highest MG adsorption capacity. This could be explained by the presence on the  
 421 adsorbent surface of mineral functions such as Si-OH, Mg-OH and organic functions

422 carboxylic groups –COOH and hydroxyl groups -OH that are able to interact with the cationic  
 423 MG dye through electrostatic interactions and hydrogen bonding, improving hence the MG  
 424 removal from water.

425 **Table 6. Comparison of the adsorption capacity of the modified sepiolite with other**  
 426 **adsorbents reported in the literature, for the MG dye removal from water**

| Adsorbent   | pH  | t <sub>c</sub><br>(min) | R<br>(g/l) | T<br>(°C) | Q <sub>m</sub><br>(mg.g <sup>-1</sup> ) | References |
|---|-----|-------------------------|------------|-----------|---|------------|
| Pine wood decayed by fungi <i>Poria</i><br>cocos  | 4   | 1140<br>(24h)           | 2          | 40        | 42.63                                   | [38]       |
| Magnetic Nickel Oxide Nanoparticles               | 7   | 40                      | -          | 25        | 87.72                                   | [39]       |
| Rice husk   | 6   | 60                      | -          | 40        | 7.40                                    | [40]       |
| acid treated coffee husk                          | 6.8 | 120                     | 0.2        | 60        | 263                                     | [41]       |
| SDS/CTAB@Montmorillonite<br>organoclay composites | 6   | 140                     | 1          | 25        | 1021.45                                 | [25]       |
| almond gum  | 7   | 120                     | 5          | 30        | 172.41                                  | [42]       |
| diatomite   | 7   | 90                      | -          | 25        | 23.64                                   | [28]       |
| Chitosan/ sepiolite clay/ algae<br>bio composite  | 8   | 17,5                    | 0,1        | 30        | 515,7                                   | [43]       |
| Carbon@Sep  | 6   | 240                     | 0,8        | 25        | 1198.67                                 | This study |

427  
 428 **Thermodynamic analysis**  
 429 To better understand the adsorption process, the determination of the MG dye adsorption  
 430 thermodynamic parameters is important. Accordingly, the MG adsorption from aqueous  
 431 solution onto organic Sep adsorbent was carried out in the temperature range varying from  
 432 298 to 338 K. The thermodynamic parameters such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were then  
 433 calculated according to the following equations:

434 
$$\Delta G^\circ = -RT \ln K_e^\circ \quad (\text{Eq. 8})$$

435 
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (\text{Eq. 9})$$

436 
$$\ln K_e^{\circ} = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (\text{Eq. 10})$$

437 
$$K_e^{\circ} = \frac{(1000 \times K \times \text{molecular weight of adsorbate}) \times [\text{adsorbate}]^{\circ}}{\gamma}$$

438 Where: R is the universal gas constant (8.314 J K<sup>-1</sup>mol<sup>-1</sup>),

439 T is the absolute temperature (K),

440  $K_e^{\circ}$  is the thermodynamic equilibrium constant,

441  $\gamma$  is the coefficient of activity (dimensionless),

442  $[\text{adsorbate}]^{\circ}$  is the standard concentration of the adsorbate (mol L<sup>-1</sup>),

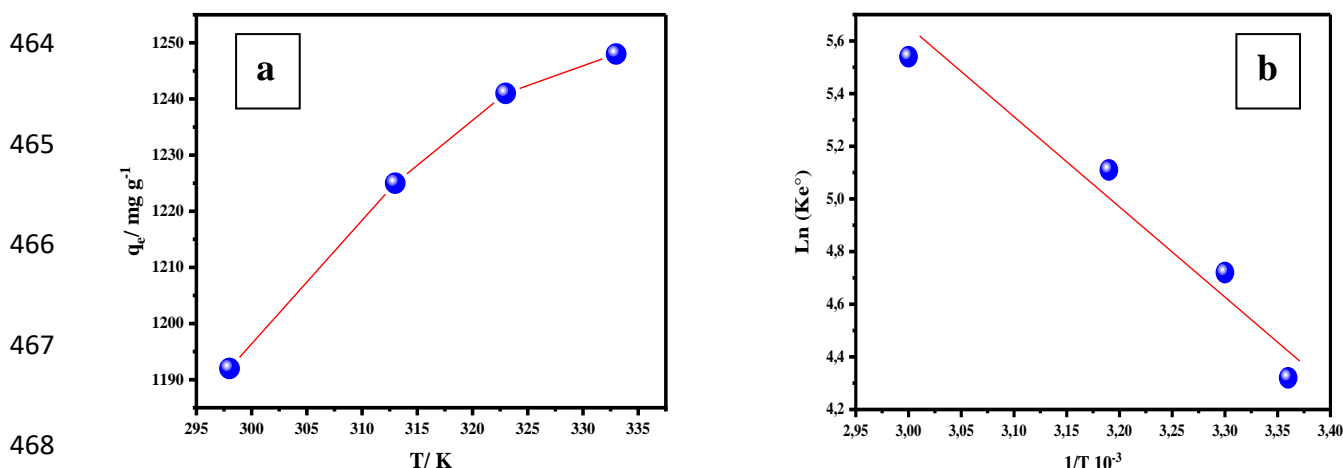
443  $K_L$  (L/mg) is the Langmuir equilibrium constant.

444 Thus, as can be seen in Fig. 11 (a), the adsorption capacity of MG dye increases as the  
 445 temperature value increases in the range of 298-338 °K. Thus, at higher temperature the  
 446 maximum adsorbed amount of the MG dye is reached. Further, the plot of  $\ln K_e^{\circ}$  versus 1/T  
 447 is shown in Fig. 11 (b). The changes in entropy  $\Delta S^{\circ}$  and in enthalpy  $\Delta H^{\circ}$  were determined,  
 448 respectively, from the intercept and the slope [44- 45] of the  $\ln K_e^{\circ}$  versus 1/T curves. The  
 449 obtained values of the thermodynamic parameters, of the MG dye adsorption on the  
 450 Carbon@Sep, are presented in Table 7. The negative values of  $\Delta G^{\circ}$  indicate that the dye  
 451 adsorption process over the temperature range of T=298-338K is spontaneous and feasible. It  
 452 can also be observed that the  $\Delta G^{\circ}$  magnitude values increase from -27.82 to -34.46 KJ.mol<sup>-1</sup>,  
 453 with increasing temperature, indicating that the adsorption process was more favorable at  
 454 higher temperatures in the studied range. In addition, the obtained positive value of  $\Delta H^{\circ}$  (26.8  
 455 kJ. mol<sup>-1</sup>) indicates that the dye adsorption process is endothermic. Furthermore, when  
 456 comparing the positive value of  $\Delta H^{\circ}$ , which is lower than 40 kJ mol<sup>-1</sup>, to the  $\Delta G^{\circ}$  value  
 457 which is approximately equal to -20kJ/mol, it is likely that the adsorbate-adsorbent interaction  
 458 has a physisorption character [44]. Finally, the positive value of  $\Delta S^{\circ}$  indicates an increase in  
 459 the system's randomness at the solid-solution interface during the adsorption of MG dye  
 460 adsorption on the Carbon@Sep composite.

461 **Table 7. Thermodynamic parameters for adsorption of MG dye onto Sep-Carbon**  
 462 **composite.**

| <b>T</b>   | <b>q<sub>ads</sub></b> | <b>K<sub>L</sub></b> | <b>Ke°</b>             | <b>ΔG°</b>                   | <b>ΔH°</b>                   | <b>ΔS°</b>                                  |
|------------|------------------------|----------------------|------------------------|------------------------------|------------------------------|---|
| <b>(K)</b> | <b>(mg/g)</b>          | <b>(L/mg)</b>        | <b>*10<sup>3</sup></b> | <b>(KJ.mol<sup>-1</sup>)</b> | <b>(KJ.mol<sup>-1</sup>)</b> | <b>(KJ.mol<sup>-1</sup>.K<sup>-1</sup>)</b> |
| <b>298</b> | <b>1198.67</b>         | <b>0.294</b>         | <b>75.19</b>           | <b>-27.82313</b>             | <b>26.8</b>                  | <b>0.127</b>                                |
| <b>313</b> | <b>1225.5</b>          | <b>0.307</b>         | <b>112.17</b>          | <b>-32.55455</b>             |                              |   |
| <b>323</b> | <b>1241</b>            | <b>0.454</b>         | <b>165.67</b>          | <b>-34.0727</b>              |                              |   |
| <b>333</b> | <b>1248.3</b>          | <b>0.698</b>         | <b>254.68</b>          | <b>-34.4686</b>              |                              |   |

463



464  
 465  
 466  
 467  
 468 **Fig. 11. (a) Effects of temperature on the adsorption of MG onto Sep-Carbon; (b) Van't Hoff plot of MG removal by Sep-Carbon composite.**

## 471 **6. Conclusions**

472 In summary, Sepiolite-carbon composite adsorbents were prepared by adsorbing maximum  
 473 amount of Malachite Green (MG) dye on the pristine sepiolite, followed by drying, and  
 474 calcinating the resulting mixture at temperatures ranging from 350 to 500 °C for 3 h. The  
 475 Sepiolite-carbon composite sample heated at 500°C (carbon@sepiolite, 500°C) was found to  
 476 have the highest specific surface area (207,59 m<sup>2</sup>/g), and showed the highest MG adsorption

477 capacity of 1198.67 mg/g at 25°C, when it was compared to others adsorbents cited the  
478 literature. Further, at the equilibrium, a good agreement was found between the experimental  
479 adsorption data and the theoretical Langmuir isotherm, whereas the kinetic adsorption  
480 isotherms were found to follow the pseudo-second-order model. The temperature effect on the  
481 MG removal from water onto carbon@sepiolite, 500°C, revealed that the adsorption process  
482 was spontaneous, endothermic and led to an increase in the randomness at the solid-solution  
483 interface. The overall data indicate that suitable adsorbents for the treatment of effluents  
484 containing cationic dyes can be designed by organically modified sepiolite. Carboxylic and  
485 hydroxylic functional groups, formed on the organically modified clay mineral surface, were  
486 found to be responsible for the efficient dye removal from water and the strengthen  
487 interaction occurring between the dye molecules and the adsorbent surface.

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493 **Data Availability.** All data are included within the text.

494 **Conflict of Interest.** The authors declare no competing interests.

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