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1 **Biocomposites based on bentonite and Lecithin: an experimental approach**

2 **supported by molecular dynamics**

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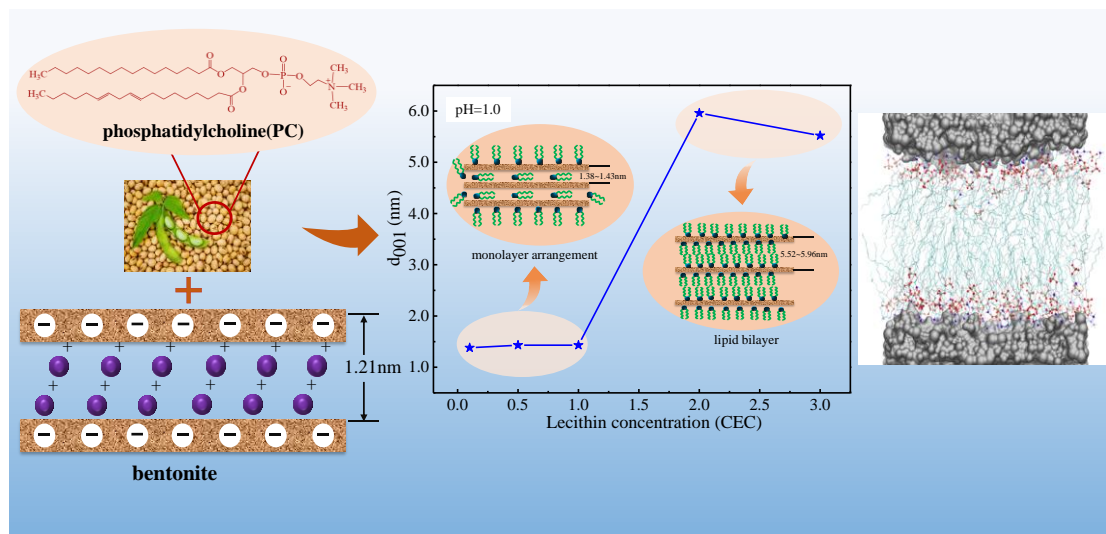
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11 ***Abstract***

12 Natural bio-surfactants have recently attracted much more attention due to their  
13 biodegradability and biocompatibility. They are often associated with clay materials to  
14 synthesize organoclays and can therefore be ideal materials for environmentally  
15 friendly oil-based drilling fluids. In this study, a bio-organoclay was obtained by  
16 modifying bentonite with natural soybean lecithin, and the effects of reaction  
17 temperature, time, pH, and lecithin concentration on the properties of modified  
18 bentonite were analyzed. Structural insights such as clay properties, intercalation  
19 process and lecithin organization were obtained using a large variety of experimental  
20 techniques and molecular dynamics simulations. The results of this study suggest that  
21 some experimental conditions have an important impact on the basal space of the  
22 bentonite. Reaction time and temperature did not have a significant effect on the final

23 properties of the modified bentonite. However, by increasing the pH of the clay  
24 material or with a high concentration of lecithin, the interlayer space fluctuates from  
25 1.21 to 5.96 nm. The lecithin molecules adopt a new spatial conformation in the  
26 interlayer space becoming perpendicular to the clay surface, which largely increase  
27 the interlayer space.

## 28 Graphical abstract



29

30 **Keywords:** organoclay; bentonite; lecithin; bio-surfactant; molecular dynamics

## 31 1. Introduction

32 Clay minerals have been known and applied since antiquity as one of the most  
33 important groups of geomaterials. Clay minerals are generally regarded as a group of  
34 phyllosilicates whose particles are less than 2  $\mu\text{m}$ . The phyllosilicates structures are  
35 based on tetrahedral (T) and octahedral (O) sheet, which can form anisotropic TO or  
36 TOT layer in a 1:1 or 2:1 ratio (Bergaya and Lagaly, 2006). Stacking of these layers  
37 by van der Waals force or weak dipolar interaction lead to the creation of interlayers  
38 space which are occupied by inorganic cations, balancing the charge deficiency  
39 caused by isomorphous substitution of the sheets (Xie et al., 2001). Clay minerals

40 have become essential in modern industry and everyday's life thanks to being  
41 abundant, inexpensive and environmentally friendly. In the past two decades, the  
42 application of clay minerals in rheological control agents, oil-based drilling fluid,  
43 adsorbents of organic pollutants, paints and cosmetics have been widely reported (Li  
44 et al., 2021; Lima et al., 2020; Park et al., 2013; Trigueiro et al., 2018; Zhuang et al.,  
45 2019). Nowadays, modification of clay minerals has attracted more and more  
46 attention (Pereira et al., 2017; Xavier et al., 2016), and the exploration of novel  
47 modification methods on clay minerals has never stopped (Zhu et al., 2017).

48 Bentonite, has gathered considerable research interest due to its availability in  
49 mine deposits and soils, nontoxic nature, and high cation exchange capacity (CEC)  
50 (Churchman et al., 2006). Montmorillonite (Mt), the main ingredient of bentonite,  
51 belongs to the smectite groups where two silica tetrahedral sheets are layered between  
52 an alumina octahedral sheet (TOT) (Cui et al., 2014). The montmorillonite layers are  
53 negatively charged due to isomorphic substitution (Bergaya, 2013). In general, the  
54 aluminum cations in the octahedral sheet is replaced by magnesium ones. Owing to  
55 the special properties of montmorillonite, organic modification by exchange the  
56 interlayer inorganic cations by organic ones is commonly used to develop  
57 organoclays.

58 In previous studies, quaternary ammonium salts were widely applied in  
59 montmorillonite modification and exhibit superior performances in oil-based drilling  
60 fluid (Zhuang et al., 2015);(Zhou et al., 2016);(Zhang et al., 2017);(Makhoukhi et al.,  
61 2013; Makhoukhi et al., 2016; Xie et al., 2002), notably a better dispersibility.

62 Furthermore, the intercalation of oil between the montmorillonite layers induces the  
63 layers to swell and exfoliate while the edges and faces of the dispersed layers form a  
64 “kind of house-of-cards structure” resulting in a gel system (Agwu et al., 2021).  
65 However, the quaternary ammonium salt and quaternary phosphonium salt surfactants  
66 usually induce environmental problems due to their toxicity and poor biocompatibility.  
67 This limitation restricts their potential use in some application fields (Liu et al., 2017).

68 In the last few years, there has been a tremendous amount of interest and various  
69 efforts regarding the preparation of bio-organoclays to solve the main problems listed  
70 above, notably biocompatibility (Biswas et al., 2019). Phospholipids, especially  
71 lecithin, have been reported to be good candidates to synthesize bio-organoclays.  
72 (Merino et al., 2016) investigated the effect of lecithin concentration and reaction time  
73 on modified bentonite and considered that lecithin-bentonites are promising  
74 eco-friendly fillers for bio and nanocomposites. (Nagy et al., 2013) studied the  
75 adsorption characteristics of nanocomposites containing lecithin and bentonite  
76 composite. In addition, the hybrid materials obtained from lecithin-modified clay  
77 minerals have received great attention in the fields of biomedicine and  
78 pharmaceuticals (Denning et al., 2017; Ruiz-Hitzky et al., 2019; Sabzevari et al., 2022).  
79 Phospholipids are a class of lipids constituted of a phosphate polar head-group  
80 attached to non-polar hydrocarbon chains. Lecithin is one of the most common  
81 phospholipids and mainly composed of phosphatidylcholine (PC) (Cui and Decker,  
82 2016). It can be extracted from vegetables and animal sources such as soybeans, rice  
83 beans, sunflower, marine sources, egg yolk, and milk. Lecithin extracted from

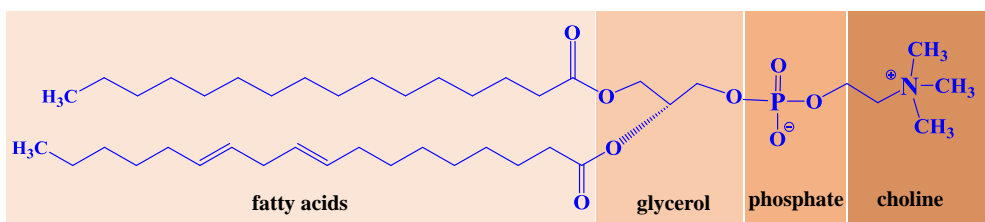
84 soybeans is recognized to be more stable, safer, and affordable from the production  
85 point of view(Le et al., 2019). PC contains a choline part, *i.e.* a positively charge  
86 trimethyl-amino group, in addition to the negative charge on the phosphate group (Bot  
87 et al., 2021). The pKa value of the phosphate group is around 1.5 and it can be  
88 protonated at acidic conditions ( $\text{pH} < \text{pKa}$ ), which means that the lecithin can exchange  
89 interlayer cations in clay minerals.

90 This publication deals with the preparation of new organoclays based on  
91 bentonite and soybean lecithin. The effects of reaction temperature, time, pH, and  
92 lecithin concentration on the properties of modified bentonite were analyzed by a  
93 variety of characterization techniques such as X-ray diffraction (XRD), Fourier  
94 transform infrared (FTIR), Thermogravimetric analyses (TG) and Molecular  
95 Dynamics simulations (MD). The interaction between bentonite and lecithin, the  
96 intercalation behavior, and the configuration of lecithin in the interlayer space are  
97 reported through experiments and molecular dynamics simulations. This study is  
98 expected to provide valuable insights into into the preparation of bioorganoclays from  
99 lecithin. In addition, some conditions can largely impact the physical properties of the  
100 organoclay and help design relevant environmentally-friendly materials.

## 101 ***2 Materials and methods***

### 102 ***2.1 Modified bentonite preparation***

103 Bentonite was first pre-swollen in distilled water and stirred for 16h, while  
104 lecithin was dissolved in ethanol. The 10 ml of 0.01g/ml bentonite dispersion was  
105 added to the 10 ml lecithin solution with different concentrations (0.1~3.0CEC) under  
106 constant stirring for 1.0h of contact time. The molecular structure and functional  
107 groups of PC ( $C_{42}H_{80}NO_8P$ , molecular weight=758.06g/mol) are described in Fig. 1.  
108 To adjust the pH of the mixture between 1.0 and 9.0, a solution of 6.0 mol/L of HCl



**Fig. 1.** The molecular structure and functional groups of phosphatidylcholine (PC)

109 was added dropwise. The solution was then sonicated and heated through an oil bath  
110 at different temperatures (room temperature, 40, 60, 80°C). After this, the mixture was  
111 centrifuged and the resulting precipitate washed several times with a 1:1  
112 ethanol-distilled water solution. The resulting precipitate was dried in an oven at 60°C  
113 for 48h. Finally, the modified bentonite powder was finely ground in an agate mortar.  
114 The schematic representation of experimental workflow followed for preparing  
115 organo-bentonite is provided in Fig. 2.

116 Further description of the materials and characterization technique are available  
117 in supplementary information (SI).

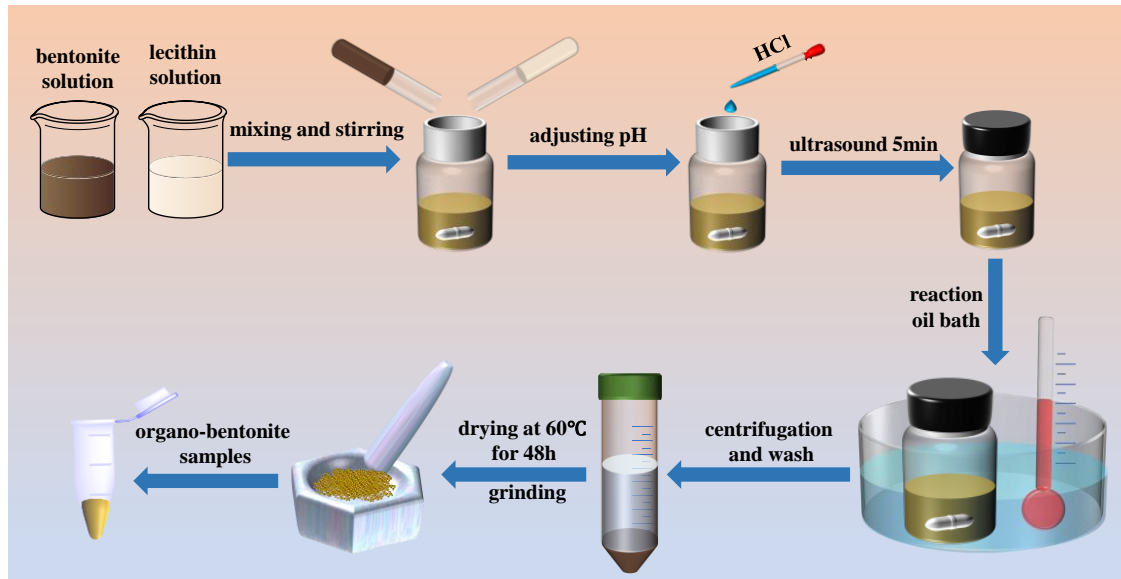


Fig. 2. Schematic representation of the experimental workflow

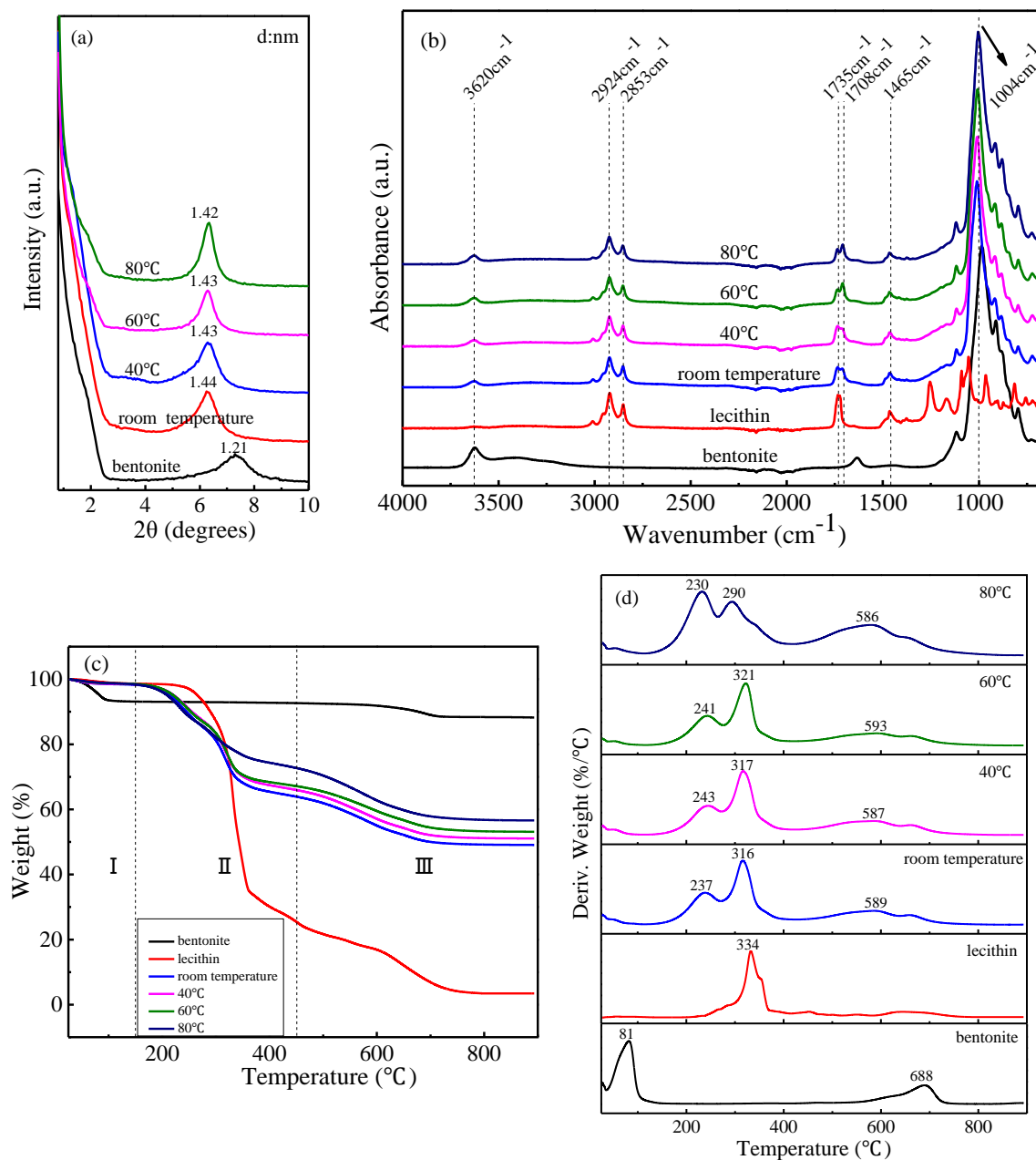
118 **3. Results and discussion**

119 **3.1 Effect of reaction temperature**

120 The effect of reaction temperature on the interlayer space and thermal stability of  
 121 modified bentonite was studied by a series of experiments with pH=1.0 and 1.0CEC.  
 122 The XRD patterns of bentonite and modified bentonite prepared at different  
 123 temperatures were shown in Fig. 3. The bentonite presented a reflection at  $2\theta=7.28^\circ$   
 124 with a basal spacing  $d_{001}$  of 1.21 nm. This reflection shifted to  $2\theta = 6.15^\circ$  in the  
 125 patterns of modified bentonite (room temperature), and the corresponding basal  
 126 spacing is  $d_{001} = 1.44$  nm, indicating that the lecithin molecules were introduced into  
 127 the bentonite interlayer space (Songurtekin et al., 2013). Since the TOT layer  
 128 thickness of montmorillonite is 0.96 nm, the lecithin intercalation increased the  
 129 interlayer space of sample by 0.48 nm. The intercalation behavior is attributed to the  
 130 monolayer arrangement of lecithin molecules in the interlayer space  
 131 (Ouellet-Plamondon et al., 2014). In addition, the XRD results of bentonite modified



132 with lecithin at different temperatures showed that temperature do not have an effect  
 133 on the intercalation behavior of lecithin.



**Fig. 3.** Top: XRD patterns (a) and FTIR spectra (b) of bentonite, lecithin and modified bentonite at different reaction temperature. Bottom: The TG (c) and DTG (d) curves of bentonite, lecithin and modified bentonite at different reaction temperatures.

134 FTIR spectroscopy was applied to investigate and compare the functional groups  
 135 present in raw bentonite, lecithin and modified bentonite. FTIR spectra (Fig. 3) of all

136 modified bentonite samples displayed a band at  $3620\text{ cm}^{-1}$  attributed to the -OH  
137 stretching vibration of the hydroxyl groups of the bentonite structure. The absorption  
138 band centered at around  $1004\text{ cm}^{-1}$  is attributed to the Si-O-Si stretching band of  
139 bentonite (Xue et al., 2007). The bands at  $2924\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  are assigned to  
140 the -CH<sub>2</sub> asymmetric and symmetric stretching vibrations of the lecithin, respectively  
141 (Li et al., 2008; Zhang et al., 2012). An intense band attributed to the C=O group of  
142 lecithin occurred at  $1735\text{ cm}^{-1}$ , and another one centered at  $1465\text{ cm}^{-1}$  belonged to the  
143 deformation vibrations of CH<sub>2</sub>/CH<sub>3</sub> (Liu et al., 2017; Nagy et al., 2013). The presence  
144 of lecithin in the modified bentonite was confirmed by the appearance of the bands  
145 centered at  $2924\text{ cm}^{-1}$ ,  $2853\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$ , respectively. The apparent shift of  
146 the C=O stretching band at  $1735\text{ cm}^{-1}$  in lecithin to  $1708\text{ cm}^{-1}$  in modified bentonites  
147 indicated possible interactions with the clay layers surface (Merino et al., 2016).

148 Various reports in the literature indicated that thermogravimetric analysis is often  
149 used to research the thermal stability of organoclays (Corcione and Frigione, 2012).  
150 The way in which the mass loss steps occur provided information on the structure of  
151 the intercalated molecules (Xi et al., 2005). The decomposition of bentonite modified  
152 with lecithin often occurs in three steps: dehydration of adsorbed water, lecithin  
153 decomposition, and silicate dehydroxylation (Zhu et al., 2011).

154 The thermal gravimetric (TG) and differential thermogravimetry (DTG) results  
155 for bentonite, lecithin and modified bentonite were compared in Fig. 3 and the lecithin  
156 loading amounts were calculated according to the formula in Eq. (1) (Zhu et al., 2017)

157 
$$Q_l = \frac{Q_m}{(1-Q_m) \times CEC \times M} \quad (1)$$

158 where  $Q_l$  is the loading amount of lecithin,  $Q_m$  is the mass loss in the  
159 temperature range of 150~450 °C,  $M$  is the molar mass of lecithin. The mass loss  
160 results of the modified bentonite and loading amount of lecithin are summarized in  
161 Table S1.

162 In the curve for bentonite (Fig. 3), two major peaks were presented. The first  
163 mass loss from the ambient temperature to 150°C and is assigned to dehydration of  
164 physisorbed and represent 6.9%. The other mass loss between 450°C and 900°C is  
165 attributed to the dehydroxylation of the aluminosilicate layer at 688°C (Khalaf et al.,  
166 2017). The mass loss of lecithin mainly occurred between 150 and 450 °C with a mass  
167 loss of 73.5%. The temperature corresponding to the highest rate of mass loss was at  
168 334°C for lecithin. These results were in accordance with previous literature reports  
169 (Wicklein et al., 2010). Three steps of the mass loss were observed for the  
170 organoclays: the first mass loss which is attributed to the dehydration of physisorbed  
171 water varied between 1.5% and 1.8%. The most remarkable difference between the  
172 bentonite and the organic bentonite is in the temperature range 150~450°C. When the  
173 reaction was carried out at room temperature, 40°C, 60°C and 80°C, the second mass  
174 loss in the temperature of 150~450°C was 34.4%, 32.5%, 31.4% and 25.7%,  
175 respectively, which is associated with lecithin decomposition (Ouellet-Plamondon et  
176 al., 2014). It is found that there are two peaks in this range, the peaks at 200~260,  
177 270~340 °C correspond to the decomposition of the adsorbed surfactant and  
178 intercalated surfactant lecithin, respectively. The third mass loss step between 450 to  
179 900 °C is attributed to the dehydroxylation of the structural OH units of the bentonite.

180 As can be seen from Table S1, with the reaction temperature increase, the mass loss of  
181 loaded lecithin decreases from 0.58CEC (for room temperature) to 0.38CEC (for  
182 80°C). This phenomenon occurs because temperature influences the lecithin molecules  
183 adsorption capacity.

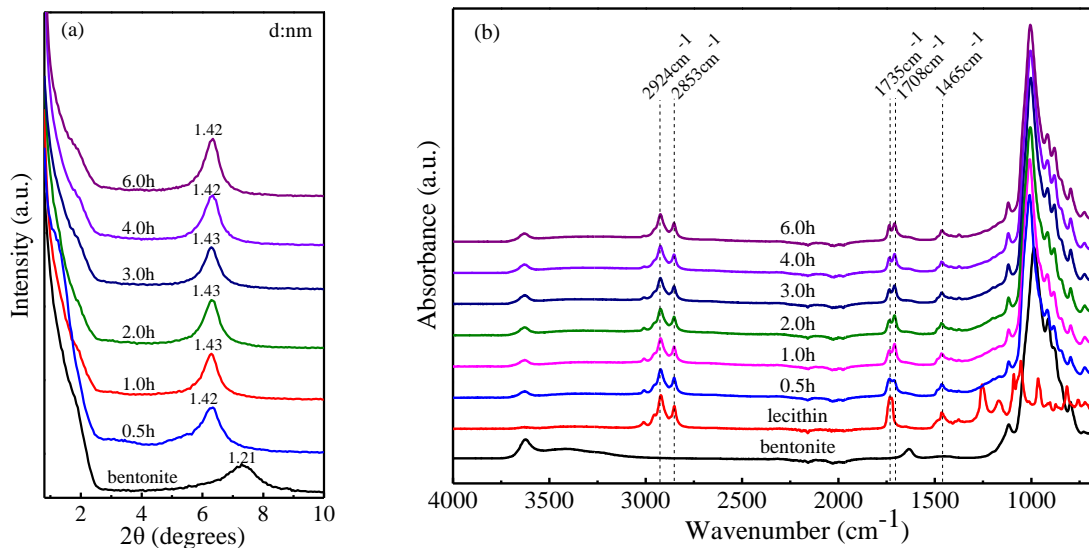
184 The macroscale appearance of the organic bentonite samples obtained at  
185 different reaction temperature are shown in Fig. S1. There was an obvious difference  
186 in appearance characters of organic bentonite samples produced at different  
187 temperatures. The organic bentonite samples presented black flake solid at reaction  
188 temperature below 60°C, while the sample was the yellowish-brown powder when the  
189 temperature was 80°C. The reason for this result may be that temperature affects the  
190 adsorption capacity of lecithin molecules on the surface of bentonite. As the  
191 temperature increased, the adsorption capacity of lecithin on the bentonite surface  
192 decreased, which led to the diminution of the lecithin content in the organic bentonite.  
193 Therefore, the appearance of samples changed from black flake solid to  
194 yellowish-brown powder. This was also consistent with the TG analysis results.

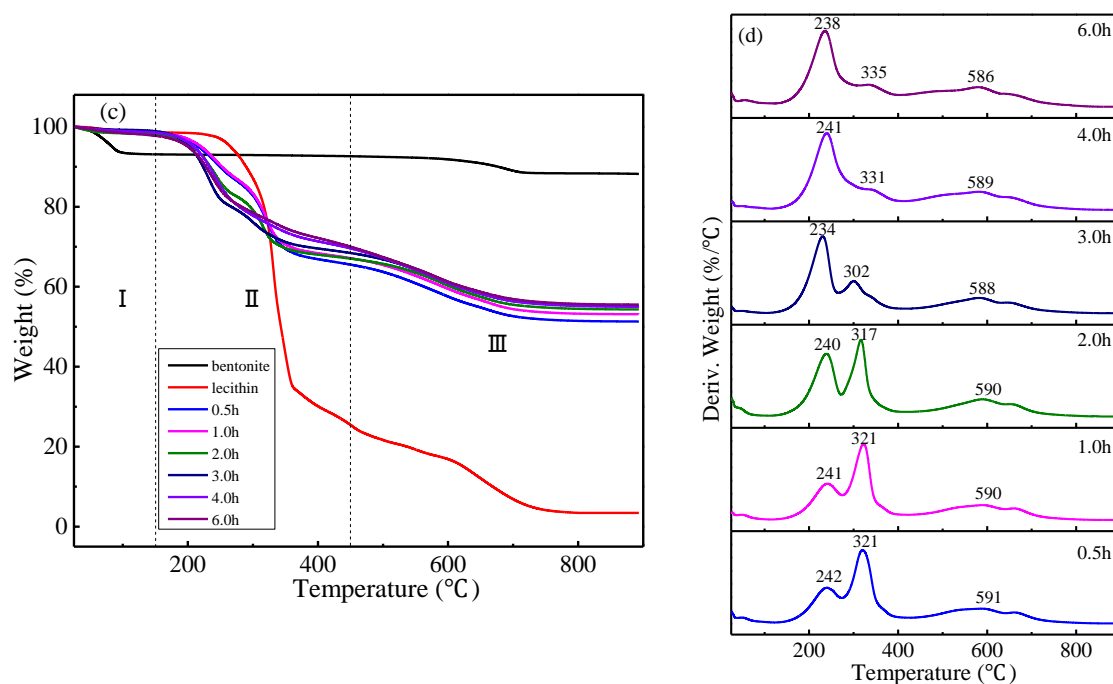
### 195 *3.2 Effect of reaction time*

196 The effect of the length of the reaction time on the properties of modified  
197 bentonite was also studied. The reaction temperature was set to 60°C. Then, the  
198 reaction time was varied from 0.5h to 6.0h.

199 X-ray diffraction patterns of the modified bentonite at different reaction times  
200 were illustrated in Fig. 4. The bentonite showed an interlayer basal spacing of 1.21  
201 nm. After 0.5h of reaction, the X-ray reflection of modified bentonite shifted to a

202 lower angle and the basal spacing increased from 1.21 to 1.42 nm. This indicated that  
203 the intercalation behavior of lecithin molecules was completed at a short time (0.5h).  
204 Additionally, the basal spacing  $d_{001}$  values ( $\sim 1.42$  nm) and reflection intensity did not  
205 change for the organo-bentonite samples at different reaction time, which could be  
206 attributed to the monolayer arrangement of the lecithin molecules in the interlayer  
207 space. This finding indicated that reaction time had no effect on the basal spacing of  
208 the modified bentonite. The result has been found to be in good agreement with the  
209 literature (Merino et al., 2016).





**Fig. 4.** Top: XRD patterns (a) and FTIR spectra (b) of bentonite, lecithin and modified bentonite at different reaction times. Bottom: The TG (c) and DTG (d) curves of modified bentonite at different reaction times.

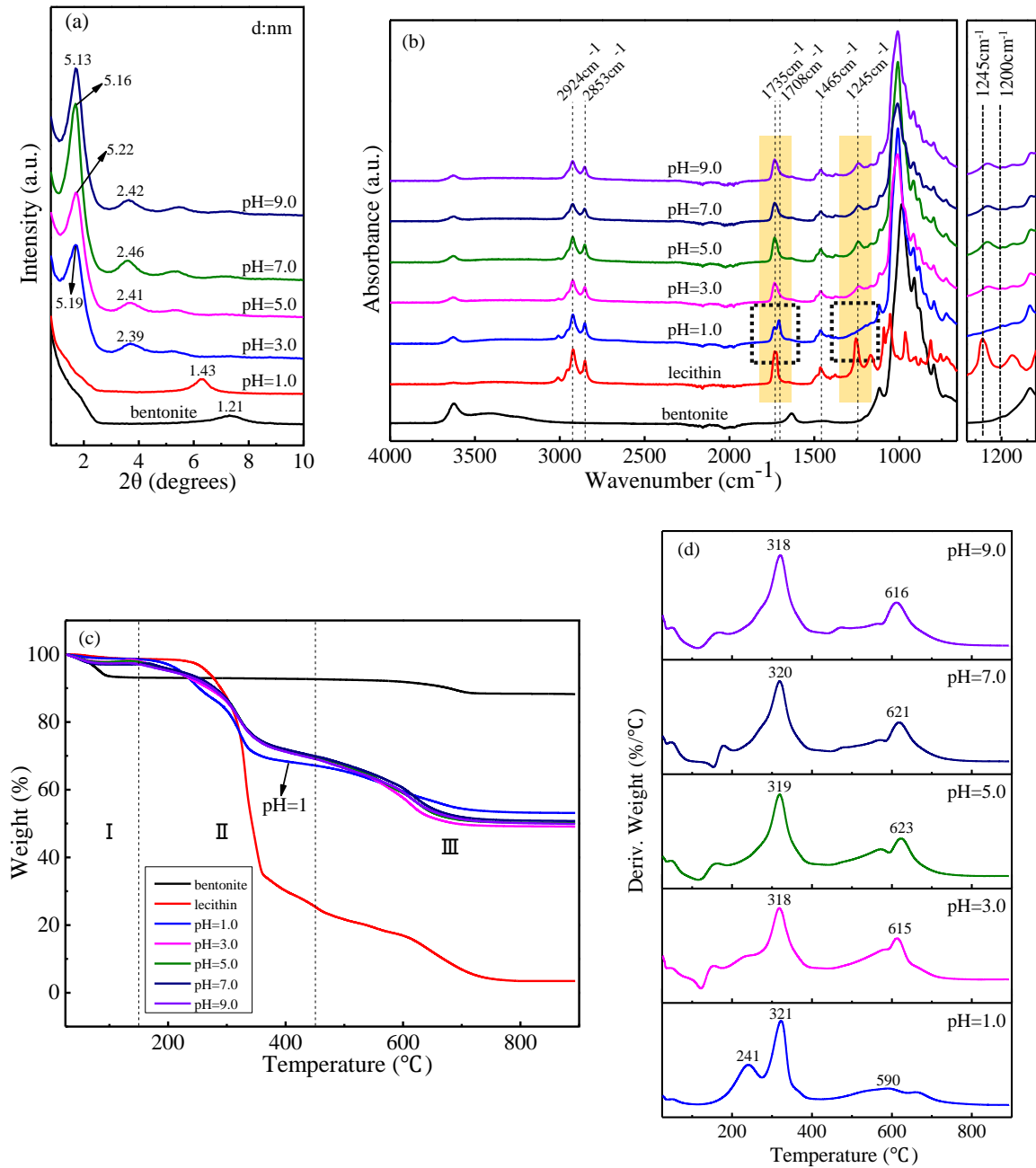
210 The bands in the FTIR spectra were consistent with the ones detailed in the  
 211 previous section (i.e., the effect of reaction temperature). Upon intercalation with  
 212 different reaction times, the FTIR experimental results remained consistent. It showed  
 213 that the reaction time had no influence on the properties of lecithin-modified bentonite,  
 214 which is agreement with the results of XRD.

215 The thermal stability of modified bentonite was evaluated by TG analysis and the  
 216 results of samples were shown in Fig. 4. For modified bentonite, between 150 and  
 217 450°C, the mass loss is mainly caused by the lecithin decomposition. Table S2 listed  
 218 the percentages of mass loss of the different stages and loaded amount of lecithin. The  
 219 maximum mass loss of lecithin, determined from TG curves, was completed at 0.5h

220 (32.6%). When the reaction time increased from 0.5h to 6.0h, the mass loss of lecithin  
221 decreased from 32.6% to 27.7%, which demonstrated that the lecithin molecules  
222 rearrangement were taken place with the increase of reaction time (Merino et al., 2016;  
223 Wicklein et al., 2010). The loaded amount of lecithin molecules slightly decreases  
224 with the increases of time. This was also evidenced from the appearance of the  
225 samples (Fig. S2). The appearance turned from flack solid to powder as the reaction  
226 time increase. The DTG of the modified bentonites showed two peaks between 150  
227 and 450 °C, which are attributed to lecithin decomposition. It can be seen from Fig.4,  
228 the intensity of the first peak increased with reaction time, whereas the second peak  
229 intensity decreased. Changes in the endothermic peak intensity suggested different  
230 conformation states and environments of lecithin in the modified bentonite (Silva et  
231 al., 2014; Wei Xie, 2001). In addition, organo-bentonites began to decompose at  
232 slightly higher temperature with the reaction time increased.

### 233 ***3.3 Effect of pH***

234 The effect of pH on the final performance of modified bentonite was studied.  
235 The reaction temperature was set to 60°C and the reaction time was 1.0h. The pH of  
236 the mixture solution was varied from pH=1.0 to pH=9.0.



**Fig. 5.** Top: XRD patterns (a) and FTIR spectra (b) of bentonite, lecithin and modified bentonite at different pH. Bottom: The TG (c) and DTG (d) curves of modified bentonite at different pH.

237 The XRD patterns of modified bentonites at different pH were presented in Fig.  
 238 5. The typical XRD reflections of bentonite related to the basal spacing appeared at  $2\theta$   
 239  $= 7.28^{\circ}$  ( $d_{001} = 1.21$  nm). This reflection shifted to  $2\theta = 6.16^{\circ}$  in the patterns of  
 240 modified bentonite at pH=1.0, corresponding to a  $d_{001}$ -value of 1.43 nm. This result



241 was already discussed in the previous sections. At pH=3.0, the basal spacing of the  
242 modified bentonite appeared at  $2\theta = 1.70^\circ$ , corresponding to the  $d_{001}$ -value of 5.19 nm.  
243 This showed that when the solution pH reached 3.0, lecithin molecules conformation  
244 has changed and the basal spacing was well expanded, increasing from 1.21 to 5.19  
245 nm. The (001) reflections of samples at pH=5.0, 7.0, 9.0 appeared at  $2\theta = 1.69^\circ$ ,  $1.71^\circ$   
246 and  $1.72^\circ$ , corresponding to  $d_{001}$ -value of 5.22, 5.16 and 5.13 nm, respectively. In  
247 addition, the (002) reflection appears when mixture solution pH exceeds 3.0,  
248 indicating that more surfactants were intercalated into the layer, and multiple  
249 arrangement models of the lecithin molecule were formed (Zhu et al., 2011). It could  
250 be concluded that the pH value of the solution has a great effect on the basal spacing  
251 and the intercalation behavior of lecithin.

252 Fig. 5 exhibited the FTIR spectra of modified bentonite under different reaction  
253 pH. The bands around  $1735\text{ cm}^{-1}$  are attributed to the C=O group of lecithin and the  
254 bands at  $1245\text{ cm}^{-1}$  is assigned to the  $\text{PO}_2$  vibration (Nzai and Proctor, 1998). When  
255 pH=1.0, the band assigned to C=O stretching shifts from  $1735\text{ cm}^{-1}$  to  $1708\text{ cm}^{-1}$ , and  
256 the  $\text{PO}_2$  vibration shifts from  $1245\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  in modified bentonite. However,  
257 when the pH varied from pH=3.0 to pH=9.0, there was no shift of the C=O stretching  
258 band and the  $\text{PO}_2$  vibration. The protonation of the phosphate group on lecithin is the  
259 main reason for this result. The discrepancy reflects the changes of the lecithin  
260 properties at different pH conditions. This change is not only directed by the lecithin  
261 molecule structure and conformation, but also by interaction with mineral surface.

262 Phosphatidylcholine (PC), which is the main component of lecithin, contains a

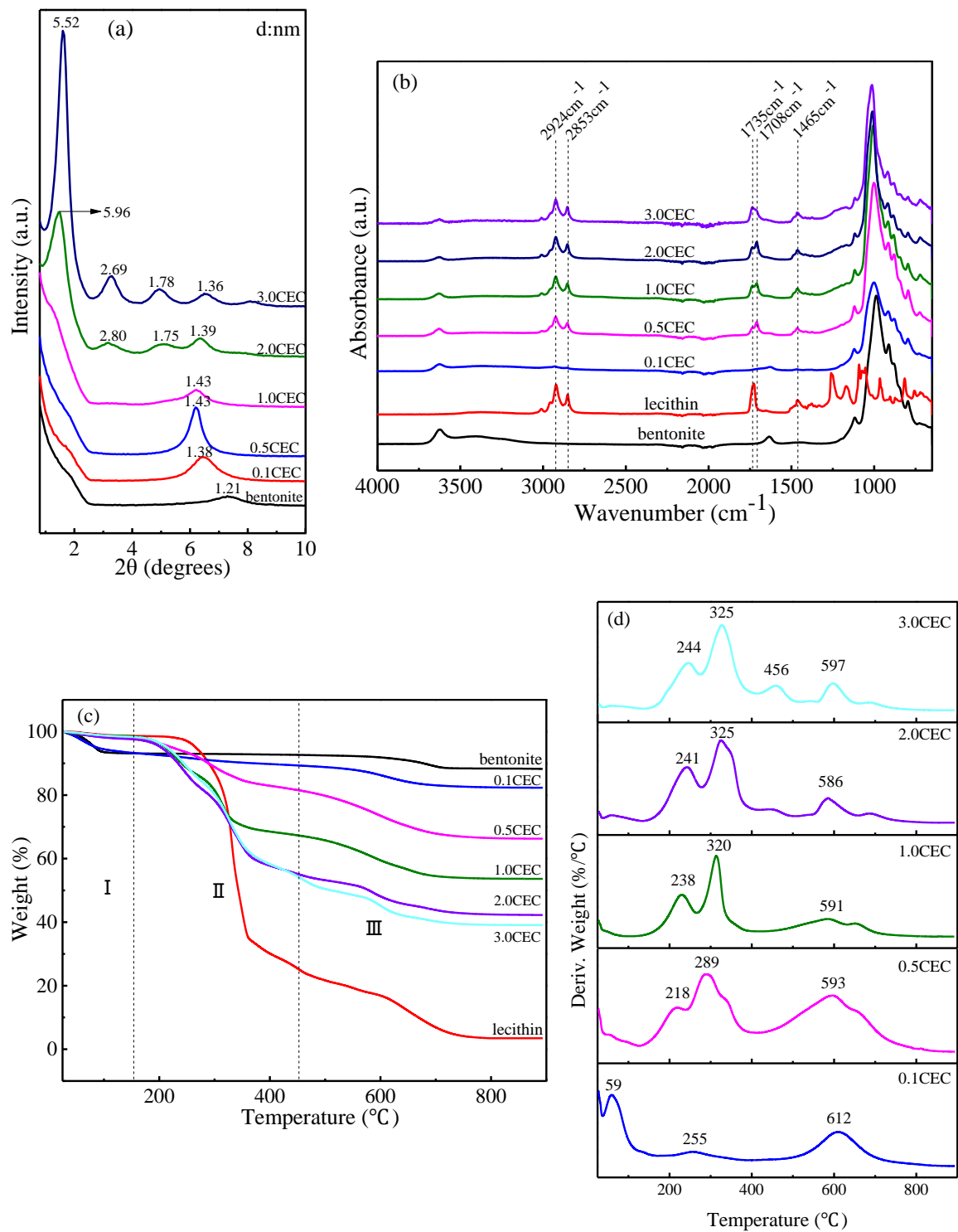
263 choline part that has a negative charge on the phosphate group and a positive charge  
264 on the trimethyl-amino group (Fig. 1) (Bot et al., 2021). The pKa value of the  
265 phosphate groups PC is around 1.5 (Ogawa et al., 2004). A.J. De Koning and K.B.  
266 McMullan(De Koning and McMullan, 1965), who investigated the acid hydrolysis of  
267 phospholipids, have shown that the oxygen atom in the phosphate group is available  
268 for protonation. In a strongly acidic medium( $\text{pH} < \text{pKa}$ ), the phosphate group is  
269 protonated, resulting in a positively charged molecule. This change in properties  
270 causes different lecithin molecule arrangement, resulting in obvious increase in the  
271 interlayer space. The appearance characteristics of the organic bentonite samples  
272 indicated that the samples were homogeneous powder when the pH exceeds 3.0  
273 (Fig.S3). The appearance of the samples also reveals the effect of pH on the  
274 intercalation behavior of lecithin.

275 The TG and DTG results for modified bentonite samples at different pH were  
276 shown in Fig. 5 and Table S3. When the pH of the solution is 1.0, the maximum mass  
277 loss is between 150 and 450°C (31.4%). However, it can be found that, when the pH  
278 is higher than 1.0, all the TG curves exhibited similar variation tendencies from room  
279 temperature to 900°C, and the amount of lecithin decomposition was around 28.0%  
280 and the loaded amount of lecithin was around 0.43CEC between 150 and 450 °C. The  
281 corresponding DTG curves in Fig. 5 showed that when  $\text{pH} \geq 3.0$ , there were two peaks.  
282 The center of the peak was 318°C, corresponding to lecithin decomposition and the  
283 center of the peak was 615°C, corresponding to the dehydroxylation of the  
284 aluminosilicate layer, respectively. However, when  $\text{pH}=1.0$ , there was three peaks.

285 The centers of the peaks were 241,321 and 590°C, respectively. Lecithin molecules  
286 can exhibit cationic properties due to the protonated choline groups in the highly acid  
287 condition (pH=1.0), while display zwitterionic nature when pH≥3.0 (Liu et al., 2017;  
288 Ouellet-Plamondon et al., 2014). We have also observed that at pH = 1.0 there are  
289 more lecithin molecules absorbed than at pH= 3.0 (Table S3) despite having a smaller  
290  $d_{001}$ , i.e. 1.43 vs 5.19 nm. The main reason for this result is the interaction of  
291 protonated lecithin with the negatively charged clay surface at pH=1.0. Some  
292 surfactant molecules attach to the bentonite surface increased the amount of lecithin,  
293 which can be confirmed by a new peak at 241°C for DTG curves.

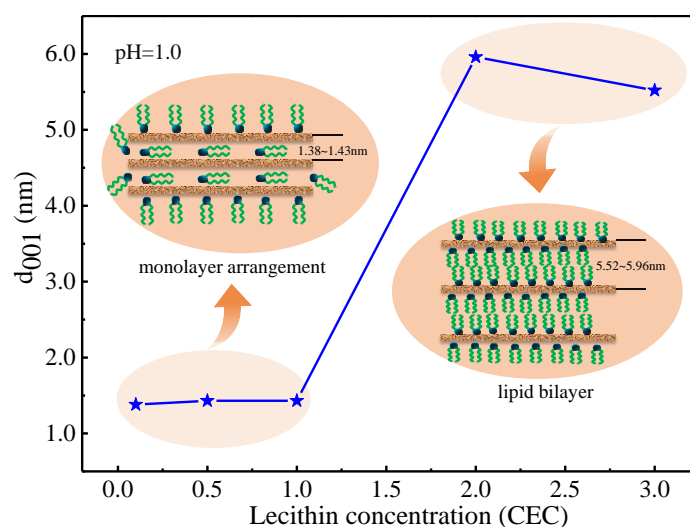
#### 294 ***3.4 Effect of lecithin concentration***

295 The effect of lecithin concentration on the interlayer space and thermal stability  
296 of modified bentonite was studied. The amounts of lecithin selected for the  
297 experiment were equivalent to 0.1, 0.5, 1.0, 2.0, and 3.0 times of the bentonite CEC.  
298 The pH of the mixture solution was adjusted to pH=1.0, the temperature was set to 60°C  
299 and the reaction time was 1.0h.



**Fig. 6.** Top: XRD patterns (a) and FTIR spectra (b) of bentonite, lecithin and modified bentonite at different lecithin concentration. Bottom: The TG (c) and DTG (d) curves of modified bentonite at different lecithin concentration.

301 illustrated in Fig. 6. The basal spacing  $d_{001}$  of bentonite (1.21nm) shifted to 1.38, 1.43,  
 302 1.43, 5.96 and 5.52nm after modification with 0.1, 0.5, 1.0, 2.0 and 3.0CEC,  
 303 respectively. When the lecithin concentration was between 0.1 and 1.0 CEC, the  $d_{001}$   
 304 reflection increased slightly from 1.38 to 1.43 nm, which is correspond to lateral  
 305 monolayer arrangement of the lecithin molecule. From 2.0 to 3.0 CEC, lecithin  
 306 expanded the bentonite basal spacing  $d_{001}$  up to nearly 5.52nm, which hold an  
 307 interlayer space of 4.56nm (after subtraction of the TOT layer thickness value of  
 308 0.96 nm). These results indicated that the lipid bilayer adopt a different conformation  
 309 in the interlayer space (Fig. 7). In regards to the length of one PC molecule (about  
 310 3nm) we can imagine that PC molecules are now perpendicular to the clay surface in  
 311 an upright position. In addition, when the lecithin concentration is increased from 2.0  
 312 to 3.0 CEC, the 001 reflections turn to be much shaper and intensity become much  
 313 higher, which suggested that the lecithin molecules arrangement in the clay layers  
 314 were more ordered.



**Fig. 7.** Schematic diagram of the lecithin arrangement in the interlayer space at different

concentration.

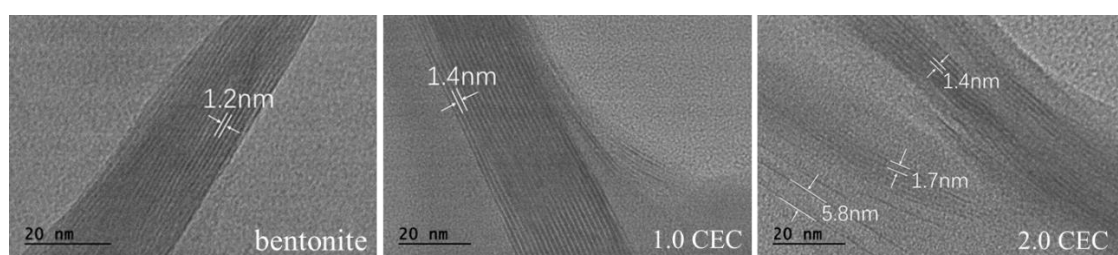
315 For organic bentonite modified with 0.5, 1.0, 2.0CEC, the elemental composition  
316 of the samples were determined by XRF analysis, obtaining data in Table 1. The raw  
317 bentonite had alumina and silica as the major species, at 22.9% and 65.1% by weight,  
318 respectively.  $\text{Na}^+$  and  $\text{Ca}^{2+}$  are the main exchangeable cation of bentonite. It was  
319 found that  $\text{P}_2\text{O}_5$  were present in organic bentonite at 3.59%(0.5CEC), 6.17%(1.0CEC)  
320 and 11.4%(2.0CEC), respectively. This implies that the intercalation of lecithin  
321 molecules was successful by ion exchange. In addition, the experimental results  
322 suggest obvious decreases in the cations of the interlayer ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ), which confirms  
323 that cation exchange and replacement are the mechanisms of action in the  
324 modification process.

325 **Table 1.** Chemical composition of raw bentonite and organic bentonite measured by XRF.

lecithin concentration /CEC	chemical composition (mass%)								
	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{CaO}$	$\text{K}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{P}_2\text{O}_5$	other
0 (raw bentonite)	2.56	2.84	1.23	0.32	22.9	65.1	4.22	0.06	0.77
0.5	0.31	2.32	0.42	0.30	23.1	64.9	4.74	3.59	0.24
1.0	0.21	2.51	0.29	0.24	22.7	63.6	4.04	6.17	0.26
2.0	0.15	2.30	0.32	0.24	21.3	60.1	3.97	11.4	0.24

326 For a better understanding of the morphology of organoclays, TEM micrographs  
327 of raw bentonite and the obtained organoclays are presented in Fig. 8. The micrograph  
328 of raw bentonite (left picture) suggested that the untreated bentonite is mainly  
329 composed of a layered structure with a  $d_{(001)}$  measured = 1.2 nm, in good agreement  
330 with the value obtained by XRD analysis. The second micrograph of organoclay  
331 modified with 1.0CEC lecithin (middle picture) clearly displayed an increase in the

332 interlayer spacing compared to raw bentonite. Finally, for organic bentonite modified  
333 with 2.0CEC lecithin (right picture), multiple interlayer spacings are observed at 5.8,  
334 1.7, and 1.4 nm, slightly smaller than the XRD measured  $d_{001}$ -value of 5.96 nm.  
335 Indeed, XRD results corresponds to an average value while TEM measurements are  
336 based on individual layers.



337

338 Fig. 8. TEM micrographs of raw bentonite and organoclays modified with lecithin at different  
339 lecithin concentration.

340 The peaks that appeared in the FTIR spectra were consistent with the ones  
341 detailed in the previous section (i.e., the effect of reaction temperature). The  
342 absorption peak intensity of samples increased as a function of the lecithin  
343 concentration, indicating that more lecithin was adsorbed onto the clay surface and  
344 intercalated into the interlayer of bentonite. It can be seen from Fig. S4 that the  
345 sample color was getting darker and gradually changing from powder to flake solid.  
346 This was mainly caused by the excessive loading of lecithin on the bentonite.

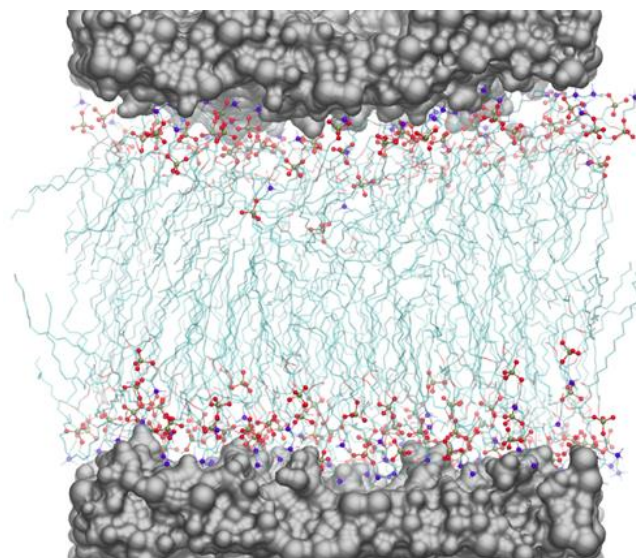
347 TG and DTG results also hint at a larger number of intercalated at higher lecithin  
348 concentrations (Table S4). The mass loss between 150°C and 450°C goes from 4.0%  
349 to 43.5% when the lecithin concentration is between 0.1 and 3.0CEC. For bentonite  
350 modified with 0.1CEC, the first degradation peak was observed at around 59°C, with  
351 a 6.7% mass loss assigned to the evaporation of the adsorbed water. When the

352 temperature was between 150 and 450 °C, the sample exhibited only one degradation  
353 peaks at 255 °C, which can be attributed to the decomposition of intercalated lecithin  
354 molecules. The thermal decomposition stages for the 0.5CEC sample are similar to  
355 those for the 1.0CEC and 2.0CEC sample with DTG peaks (Fig. 6). But when the  
356 temperature varied between 150 and 450°C, the degradation temperature of samples  
357 shifted to a higher temperature with the lecithin concentration increased, which  
358 displays a further enhancement in the thermal stability. With the increase in surfactant  
359 concentration, a new endothermic peak appeared at ~456 °C for 3.0CEC. This step  
360 could be ascribed to the presence of triglycerides and other impurity, which is  
361 consistent with the already published literature(Ouellet-Plamondon et al., 2014).

362 In order to have a deeper understanding of the physiochemical processes of  
363 organic matter and clay minerals at the microscopic level, classical molecular  
364 dynamic (MD) simulations have been proven to be an effective method to obtain  
365 structural information among the constituents (Kovar et al., 2010). We have modelled  
366 the system at pH=1.0, 60°C and when a PC concentration regarding the CEC of 2.0  
367 was added. The calculation details are available in supplementary information(SI).

368 Five molecular dynamics simulations (MD) of 10 ns were performed on a small  
369 slab of montmorillonite, composed of  $9 \times 9 \times 2$  (x,y,z) unit cells. At first all PC  
370 molecules are added directly inside the interlayer space of the clay randomly, the  
371 exact number is related to the experimental loading amount measured.





**Fig. 9.** Snapshot of the last step of the MD3. The N and PO<sub>4</sub> group of the PC molecules are highlighted using ball representation. The montmorillonite surface is represented by a gray surface with a probe radius of 1 Å. The color code used is the following: blue N, red O, gold P, green C.

372 **Table 2.** Computed  $d_{001}$  at the last step of the related MD and percentage of N (from amine) or OH  
 373 (from phosphate) of the PC molecules in interaction with the surface at a distance of 0.68 nm.

MD number	1	2	3	4	5
Computed $d_{001}$ (in nm)	6.214	6.14	6.029	6.02	6.33
%N (amine) in interaction with the surface	94%	91%	91%	92%	92%
%OH (phosphate) in interaction with the surface	69%	63%	66%	62%	66%

374 From these dynamics results, we can draw some conclusions (Fig. 9). First we  
 375 will discuss about the PC absorption. We have observed that the PC auto-organized  
 376 themselves quickly, even before the MD production. The amine head points in the  
 377 direction of the T layer of the montmorillonite. However, it is often not directly in  
 378 interaction with this one, but in most cases, involved in a hydrogen bond network with  
 379 a water molecule in between the clay structure and the PC. The second type of  
 380 interaction comes from the OH group of the phosphate which is protonated at pH=1.0.  
 381 It is either directly bonded to the oxygen atom of the T sheet of the Mt or through a

382 water molecule. In Table 2, we have printed the percentage of nitrogen (from the  
383 amine group) or O (from the OH group of the phosphate) in interaction with the  
384 surface *i.e.* below 0.68 nm. This distance corresponds to the sum of the Van der Waals  
385 radius of either the amine group, a water molecule and an oxygen of the silicate or the  
386 OH group of the phosphate, a water molecule and an oxygen of the silicate. For all  
387 MDs more than 90% of the lecithin molecules are in interaction with the surface.  
388 However some of them do not interact at all and instead in interaction with other PC.  
389 Finally, once the PC is in interaction with the montmorillonite, no major  
390 displacements are observed during the MD. This tends to validate the experimental  
391 observations where the PC is strongly absorbed in the interlayer space at 60°C.

392 Let's now focus in the orientation of the PC tails in the interlayer space. The PC  
393 molecule optimized in vacuo using DFT calculations has a length of 3 nm (from a  
394 carbon of the amine group to the last carbon of the tail). In comparison to the  
395 maximum interlayer space measured (4.56 nm when removing the TOT distance), 2  
396 PC molecules cannot fit inside the interlayer space without some bending. In the Fig.  
397 S5, we have represented several possible organizations of the PC molecules. They can  
398 adopt a lot of different conformation, some are nearly linear while others are heavily  
399 bended. On top of this, several PC (green, orange in Fig. S5) interact with the surface  
400 with both amine and phosphate groups but also with the oxygen atoms of the linear  
401 chains. In the end, the disposition of PC molecules is relatively random, maybe due to  
402 the short time of the simulation.

403 Finally we also analyzed the distance of the interlayer space during the MD. As

404 written before the PC tends to self-organized very quickly, and after 4 ns the stable  
405 regime is observed regarding the total energy of the system. For each MD, the relative  
406 distance of the interlayer space is reported in Table 2 and taken from the last step of  
407 the simulation. It is difficult to give a precise number as the TOT layers of the  
408 montmorillonite are slightly altered by the MD due to not being constrained. In any  
409 case, for the 5 MDs the computed  $d_{001}$  distance reproduced accurately the measured  
410 one with a maximum deviation of 6 %. One of the reasons could be that we have  
411 added too many PC molecules in the interlayer space. As written before 5 to 10 % of  
412 PC molecules are not in interaction with the clay, and instead are freely moving in the  
413 interlayer space, disrupting the local order.

#### 414 *Conclusions*

415 In this study, a series of organo-bentonites were synthesized by using natural  
416 soybean lecithin at different experimental conditions. The effects of reaction  
417 temperature, time, pH, and lecithin concentration on the properties of modified  
418 bentonite were analyzed. The results of FTIR, XRD, TG and molecular dynamic  
419 simulations support the intercalation of lecithin in the interlayer space of  
420 montmorillonite. The characterization results demonstrate that the intercalation  
421 behavior of lecithin can be completed in a short time (0.5h). Lecithin concentration  
422 and pH greatly influence the structural characteristic of modified bentonite. In general,  
423 the basal spacing of the organo-bentonite has a positive correlation with lecithin  
424 concentration and pH. In the case of pH=1.0, the interlayer spacing of modified  
425 bentonite increases with the lecithin concentration and the surfactants exhibit different

426 arrangements among the bentonite layers. Lecithin adopts a lateral monolayer  
427 arrangement at low concentrations (0.1~1.0CEC) in contrary to a lipid bilayer at high  
428 concentrations (2.0~3.0CEC), this last one being perpendicular to the surface.  
429 Regarding the effect of the pH , the  $d_{001}$  of the bentonite layer was significant higher  
430 for the samples prepared at  $\text{pH} \geq 3.0$  due to the properties change of both the surface  
431 and the lecithin. For example, when the pH shifts from 1.0 to 3.0, the interlayer  
432 spacing of organoclay was increased from 1.43 to 5.19 nm, which is of great  
433 significance for the preparation of low-cost organobentonite for industrial applications.  
434 These results demonstrate that the modified bentonite with lecithin have quite  
435 different structural properties, and they may have special applications in the industrial  
436 fields.

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