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# Phenolic acids interactions with clay minerals: a spotlight on the adsorption mechanisms of Gallic Acid onto Montmorillonite

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## Abstract

1 For a better understanding of the preservation of organic matter in clay minerals, the  
2 adsorption of a model humic substance, the Gallic Acid (GA), onto a Na-montmorillonite  
3 (Na-Mt) was performed in batch situation for various experimental conditions (pH=2, 5, 7) in  
4 order to mimic the natural context. The adsorption efficiency and change in the clay mineral  
5 were characterized *via* a set of complementary experimental techniques (Fourier transform  
6 infrared spectroscopy, X-ray diffraction, elemental analyses). Adsorption isotherms at the  
7 equilibrium were fitted with the models of Langmuir, Freundlich and Dubinin-Radushkevitch  
8 allowing one to precisely quantify the adsorption through the derived fitting parameters. From  
9 the adsorption data combined with complementary results of the modeled humic-clay  
10 complexes, different types of interactional mechanisms were inferred as a function of  
11 background acidity: (i) at pH=2 while protonated GA was the preponderant form, anionic GA  
12 species can be adsorbed to the Na-Mt surface through electrostatic interaction, leading to the a

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13 slight covering of the clay surface favoring in a second step the GA adsorption by  $\pi$ - $\pi$  and  
14 Van der Waals forces; XRD patterns corroborated via TGA and FT/IR results suggested the  
15 actual intercalation of the phenolic acid within the interlayer space; (ii) At pH = 5, above the  
16 pKa of phenolic acid, only 20% of the protonated form subsisted and these species were  
17 adsorbed via coordinative bonding, without however any perceptible intercalation; (iii) and in  
18 the regime with neutral environment (pH=7), the preponderance of GA anionic species led to  
19 a poor adsorption which appeared to be only located at the external surface of the clay  
20 mineral.

21 **Keywords:** Phenolic acids; Montmorillonite; Adsorption; Organic matter preservation.

22

## 23 1. Introduction

24 Clay minerals were recognized to stabilize soluble organic compounds through the  
25 adsorption of dissolved OM in superficial horizons of soils (Gonzalez, 2002; Kögel-Knabner  
26 et al., 2008; Schmidt et al., 2011; Kaiser et al., 2016). The confinement of organic compounds  
27 within the interlayer space of clay minerals avoids any heterotrophic reactions and leads to  
28 their preservation (Kaiser and Guggenberger, 2007; Wattel-Koekkoek and Buurman, 2004). It  
29 also favors the generation of polymeric macromolecules *via* the condensation of single  
30 monomers (Stevenson, 1982; Wang et al., 1983; Yariv and Cross, 2002). From the numerous  
31 research works on the subject, and more particularly studies focusing on the understanding of  
32 the interaction between clay minerals and humic substances leading to the formation of  
33 humic-clay complexes, it appears that simple blocks of polymeric humic molecules or  
34 elementary monomolecular compounds play a major role in the interaction with the mineral  
35 surface and stabilization of the complexes (Greenland, 1971; Feng et al., 2005; Wang and  
36 Xing, 2005; Chotzen et al., 2016; Chen et al., 2017).

37 The typology of physicochemical mechanisms allowing the establishment of perennial  
38 association between organic compounds and mineral surfaces were extensively studied in  
39 recent years. For example, ligand exchanges and cationic exchanges are reported as  
40 sustainable organo-mineral interaction mechanisms (Keil and Mayer 2014; Lambert, 2018),  
41 while low energy bonding such as van der Waals effects and hydrogen bonding are  
42 acknowledged to establish easily reversible associations (Plante et al., 2005; Lutzow et al.,  
43 2006). Aqueous media chemistry strongly constrains the preponderance of these mechanisms  
44 (Arnarson and Keil, 2000). Background parameters as ionic strength and pH shape clays'  
45 state of charge as well as the degree of protonation of dissolved organic compounds. Hence, it  
46 impacts the type of adsorption driving process. Chen et al., 2017 stressed out higher

47 adsorption performances of humic compounds onto 2: 1 clay minerals at low pH and  
48 suggested the increase of electrostatic phenomena to explain this observation.

49 Besides background properties, organic compounds intrinsic characteristics also  
50 determine the extent of the adsorption and constrain the nature of preponderant bonding  
51 mechanisms (Bu et al., 2017). In the presence of compounds with different spatial structures  
52 and molecular functions, a competition to the occupation of adsorption sites can occur. For  
53 example, the adsorption of amino acids onto montmorillonites is more effective than the  
54 uptake of phenolic acids contained in the same aqueous mixture (Gao et al., 2017).  
55 Understanding these mechanisms is mandatory to assess the potential use of clay minerals in  
56 the adsorption of contaminants of various natures. Clays and clay minerals are investigated  
57 raw, or after chemical modification, as an economically viable removal pathway of petroleum  
58 by-products (Meleshyn and Tunega, 2011; Lamishane et al., 2016) and emerging  
59 pharmaceutical molecules (Li et al., 2011; Thiebault et al., 2015; De Oliveira et al., 2017)  
60 commonly encountered in hydrographic networks. The uptake performance may be boosted  
61 via inorganic pillaring (Liu et al., 2015) or surfactant intercalation (De Oliveira and Guégan  
62 2016).

63 Thus, the study of the fundamental mechanisms of organo-mineral aggregation has  
64 applications in various fields. In this paper, the emphasis is placed on the organo-clay  
65 association, and its further protective role. This role has been assessed in sedimentary  
66 environments through different approaches (Kennedy and Wagner, 2011; Arndt and  
67 Jorgensen, 2013; Mahamat Ahmat et al., 2016, 2017). It appeared that organo-clay  
68 associations involving ionic exchanges and those resulting from interlayer intercalation  
69 allowed efficient isolation against microbial stresses. In pedological context, the mechanism  
70 has mainly been studied from the perspective of complex polymeric humic acids (Chen et al.,  
71 2017; Derakhshani and Naghizadeh, 2018).

72 While the main interaction mechanisms ensuring the stability of the organo-mineral  
73 complexes are rather difficult to determine in the case of humic substances (Tombácz et al.,  
74 2004; Chotzen et al., 2016; Chen et al., 2017), this research work aims at characterizing  
75 precisely the main driving force leading to the aggregation of OM. For this purpose, we focus  
76 on a simple carboxylic acid (gallic acid) as simple blocks or monomeric components in  
77 polymeric humic acids. Gallic Acid (GA) is a phenolic acid found in vascularized plants,  
78 inputted in soil horizons as single molecules or apart of large polyphenolic macromolecules  
79 such as tannins and various ligno-cellulosic by-products. Here, in this research work, we  
80 focus on the sorption mechanisms of GA onto montmorillonite under different experimental  
81 conditions.

## 82 **2. Materials and methods**

### 83 *2.1. Interaction of the carboxylic acids with a clay mineral*

84 A natural Wyoming Na-montmorillonite (Na-Mt) was supplied by the Source Clay  
85 Minerals Repository of the Clay Minerals Society. Its structural formula can be expressed as:  
86  $(\text{Ca}_{0.12}\text{Na}_{0.32}\text{K}_{0.05}) [\text{Al}_{3.01}\text{Fe(III)}_{0.41}\text{Mn}_{0.01}\text{Mg}_{0.54}\text{Ti}_{0.02}] [\text{Si}_{7.98}\text{Al}_{0.02}] \text{O}_{20}(\text{OH})_4$ . Gallic Acid  
87 (GA) was provided from Sigma Aldrich at 97.5 % purity grade and was used without further  
88 treatment. This weak acid can be seen as a phenolic compound owing a carboxylic function  
89 with 2 alcohol groups (Fig. 1). Its physico-chemical parameters (topological surface, pKa) are  
90 summarized in Table 1.

91 The interactions between GA and Na-Mt were conducted in different experimental  
92 conditions under various pH conditions: 2, 5 and 7. Typically, the adsorbent mass was 150 mg  
93 in 50 mL solution spiked with a GA concentration between 10 mg. L<sup>-1</sup> and 2 g. L<sup>-1</sup>. The pH  
94 value was adjusted with both NaOH and HCl solutions (0.1 M). The solutions were stirred at  
95 200 rpm with a magnetic stirrer during 24 hours in order to reach the equilibrium (kinetic data  
96 not shown) at room temperature. The solid fraction (*i.e.* organo-clay complexes) was

97 separated from the liquid one through a centrifugation step (5000 rpm; 10 min) and then  
98 lyophilized before flash pyrolysis analyses.

## 99 *2.2. Experimental Techniques*

100 Adsorbed organic carbon was measured using flash pyrolysis (Thermo Scientific Flash  
101 2000 organic analyzer) performed on organo-clay complexes in powder form.

102 The samples were also characterized *via* Fourier Transform Infrared Spectroscopy  
103 (FT/IR) in the range 650-4000  $\text{cm}^{-1}$ . Measurements were realized using a Thermo Nicolet  
104 6700 FT spectrometer equipped with a Deuterated Triglycine Sulfate (DTGS) detector at  
105 room temperature and for different temperatures controlled by a Linkam thermal device  
106 allowing us to characterize the thermal behavior on a wide range of temperature: 50-550°C.  
107 The analyses were performed in transmission mode and each spectrum corresponded to the  
108 average of 256 scans collected at 2  $\text{cm}^{-1}$  of resolution.

109 The  $d_{001}$  spacing's of the organo-mineral complexes was determined by the first *00l*  
110 reflection from the X-rays patterns which were recorded on a conventional  $\theta$ - $\theta$  Bragg-  
111 Brentano configuration by using a Thermo Electron ARL'XTRA diffractometer equipped with  
112 a Cu anode ( $\text{CuK}_\alpha = 1.5418 \text{ \AA}$ ) coupled with a Si(Li) solid detector. The diffractograms on  
113 dry samples (100°C for 24 h) were performed between 1 and 24° ( $2\theta$ ) with an angular and  
114 time steps of 0.04° and 10 s, respectively.

115 Thermal gravimetric analyses were carried out under atmospheric conditions at the  
116 heating rate of 10  $^\circ\text{C min}^{-1}$  from room temperature (25°C) to 800  $^\circ\text{C}$  using the thermal  
117 gravimetric analyzer (Model: STA PT 1600, manufactured by Linseis Company, Germany).

## 118 *2.3. Sorption Modeling*

119 The fitting of the resulting adsorption isotherms by using Langmuir, Freundlich and Dubinin–  
120 Radushkevich (DR) equation models drive to numerous thermodynamic parameters allowing  
121 to precisely quantify the affinity of GA with the Na-Mt. Briefly, Langmuir model assumes

122 that the whole organic molecules are adsorbed on singularized sites on the accessible surface  
123 of the adsorbent, and each site hosts a unique molecule. This Langmuir model is expressed by  
124 the following equation (LeVan and Vermeulen, 1981):

$$125 \quad q_e = q_{max} K_L / [1 + (K_L C_e)] \quad (1)$$

126 where  $q_e$  is adsorbed amount when equilibrium is reached ( $\text{mol g}^{-1}$ );  $C_e$  is the  
127 remaining concentration in the solution at equilibrium ( $\text{mol L}^{-1}$ );  $q_{max}$  is the maximum  
128 sorption capacity of the Na-Mt, and  $K_L$  is the Langmuir constant ( $\text{L mol}^{-1}$ ) which is related to  
129 Gibbs free energy  $\Delta G^\circ$  ( $\text{kJ mol}^{-1}$ ) through the thermodynamic equation (2):

$$130 \quad \Delta G^\circ = -RT \ln K_L \quad (2)$$

131 where  $R$  represents the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  the temperature  
132 (K).

133 Freundlich and D-R equations takes into account surface heterogeneities on the  
134 adsorption process and deal with the variabilities in the interaction mechanisms leading to the  
135 adsorption of organic compounds that can form or be organized in multi-layers. Freundlich  
136 adsorption model is a linear relation (LeVan and Vermeulen, 1981; Özcan et al., 2005)  
137 expressed through the following equation:

$$138 \quad \ln q_e = \ln K_F + 1/n (\ln C_e) \quad (3)$$

139 Where  $K_F$  ( $\text{g L}^{-1}$ ) and  $n$  are constants and indicate respectively the extent of the  
140 adsorption and the degree of non-linearity between GA and the smectite. Indeed, when the  
141 term  $1/n$  ranges between 0.1 and 1, it suggests that the adsorption mechanism is favorable  
142 (Liu et al., 2011). D-R isotherms allow one to acquire complementary thermodynamic  
143 parameters. Its equation is written as:

$$144 \quad \ln q_e = \ln q_m + \beta^* \varepsilon^2 \quad (4)$$

145 Where  $\varepsilon$  is the Polanyi potential, computed through the relation (5)

$$146 \quad \varepsilon = RT \ln (1+1/Ce) \quad (5)$$

147  $q_m$  is the theoretical potential saturation capacity of the sorbent and  $\beta$  is the constant related to  
148 the activity ( $\text{mol}^2 \text{J}^{-2}$ ) connected to the mean free energy  $E$  of adsorption ( $\text{kJ mol}^{-1}$ ) via the  
149 equation (6):

$$150 \quad E = 1 / \sqrt{2\beta} \quad (6)$$

151 This later parameter gives information whether the adsorption mechanism involves a cation  
152 exchange or physical adsorption. Indeed, if the magnitude of  $E$  is below  $8 \text{ kJ mol}^{-1}$ ,  
153 physisorption is envisaged, while for  $E > 8 \text{ kJ mol}^{-1}$  the adsorption process follows an ion  
154 exchange or a chemisorption mechanism.

155 Moreover, we used an error function ( $F_{error}$ ) in order to evaluate which equation model  
156 was best suited to describe these processes. A lower result from the error function indicated a  
157 smaller difference between adsorption capacity calculated by the model ( $q_{i \text{ cal}}$ ) and the  
158 experimental ( $q_{i \text{ exp}}$ ).  $F_{error}$  can be expressed according to the following Eq. (7)

$$159 \quad F_{error} = \sum (q_{i \text{ cal}} - q_{i \text{ exp}} / q_{i \text{ exp}})^2 \quad (7)$$

160 Where  $q_{i \text{ cal}}$  is a value of  $q$  predicted by the fitted model;  $q_{i \text{ exp}}$  is a value of  $q$  measured  
161 experimentally;  $i$  indicates the values of the initial GA concentration of the experiments; and  
162  $P$  is the number of experiments performed.

### 163 **3. Results and discussions**

#### 164 *3.1. pH dependence on the adsorption of GA onto Na-Mt*

165 The adsorption isotherms at the equilibrium stress out the actual affinity of GA with Na-  
166 Mt (Fig. 2). Indeed, adsorption isotherms display a gradual growth of the adsorbed amount

167 when the equilibrium concentration increases. The slope of this growth attenuates at high  
168 starting concentrations emphasizing a saturation state, excepted for the isotherm realized at  
169 pH=5.

170 GA adsorption isotherms are properly fitted by the three equation models used as  $r^2$  values  
171 display values between 0.95 and 0.99 and  $F_{error}$  values are between 0.0010 and 0.130 for GA  
172 (Table 2). Based on  $r^2$  values, experimental data seem to be better adjusted to the Langmuir  
173 model, however its function errors are higher than 0.1 and to those for both Freundlich and  
174 DR equations, which spread out from 0.001 to 0.004. This is a side effect of the logarithmic  
175 scale adopted in Freundlich and DR representations. Although Langmuir equation properly  
176 fitted experimental data, the two latter equations appear to be more suitable for modeling the  
177 adsorption of the phenolic acid onto the clay mineral surface. Indeed, clay mineral shows a  
178 heterogeneous surface leading to a distribution of several adsorption sites that are taken into  
179 account in both Freundlich and DR equation models.

180 Under low pH conditions (*i.e.* below the pKa of GA), the adsorption is particularly enhanced,  
181 with the predominance of the protonated form of GA (*i.e.* acidic form) in solution, due to the  
182 decrease of the repulsion between the neutral GA and Na-Mt. However, the situation may be  
183 rather twisted with antagonist effects. Indeed, under such pH conditions (pH=2), the pH value  
184 is lower than the pH of zero net proton charge (pH<sub>ZNPC</sub>) of Na-Mt, estimated about 4.5  
185 (Tombàcz and Szekeres, 2006). For pH < pH<sub>ZNPC</sub>, the electric charge of the edge-sites of clay  
186 mineral surface changes from anionic to cationic, favoring the adsorption of phenolic acids in  
187 their anionic form, (*i.e.* base) allowing a possible ion exchange process which enhances the  
188 amount of adsorbed organic acids. In contrast, at pH=5 and 7, since both the clay mineral  
189 edge-sites and the equilibrium ratio between the acid/base forms change (Fig. 3), the  
190 adsorption involves additional interactional mechanisms, affecting the lineshape of the

191 adsorption isotherms while reducing the adsorbed amounts. This lowering is due to the  
192 repulsion between anionic charges of both GA and Na-Mt.

193

194 [Fig. 4](#) shows the X-ray diffraction patterns evolution of the GA-clay complexes (dried  
195 for 48 hours at 100°C to prevent any water molecules in the interlayer space that may  
196 interfere in the interpretation and understanding of a possible intercalation of the GA)  
197 following the starting GA concentration. The diffraction patterns display several diffraction  
198 peaks located between 5° and 9° ( $2\theta$ ) related to the  $00l$  reflections. At pH=2, the  $00l$  reflection  
199 shifts to lower angle values, attesting the effective intercalation of the phenolic compound. As  
200 well, it is interesting to remark the narrowing of these reflections suggesting an enhancement  
201 of the organization in the layered material probably due to the increase of the GA density  
202 within the clay-GA complexes. The basal spacing of GA-Mt complexes (*i.e.*  $d_{001}$ ), estimated  
203 with the angular position of the  $00l$  reflection, increases from 9.6 Å for a dehydrated clay  
204 mineral to about 13.3 Å at pH=2. While an intercalation occurs at low pH, this phenomenon is  
205 not observed for the other two pH, where a slight increase of the interlayer space to a value of  
206 11 Å can be noticed ([Fig. 5](#)). This is probably due to both the clay mineral charge density and  
207 the preponderance of the neutral (RCO<sub>2</sub>H) form which play an important role in the  
208 adsorption as well its associated interaction mechanism (*e.g.* coordinative bonding ).

209 The contribution of FT/IR spectroscopy gives important information in the  
210 characterization of GA-clay complexes derived from GA and Mt and confirms its actual  
211 adsorption. Absorption bands observed at 1350, 1384 and 1470 cm<sup>-1</sup> are assigned to stretching  
212 modes of C – O. and bending modes of C-H of O-H respectively ([Fig. 6](#)). The strong vibration  
213 at 1700 cm<sup>-1</sup> was assigned to C=O stretching of GA's carboxylic function. Besides the  
214 existence of a drift or a temperature gradient in temperature during the FT/IR experiments, the  
215 complete degradation of GA is accomplished at relative high temperature in contrast to bulk

216 GA which is decomposed at about 300°C estimated through thermal gravimetric  
217 measurements (Fig. 8). This last observation about the preservation of GA at high temperature  
218 is related to its confinement within the interlayer space of Mt obtained for GA at pH=2.

219 TG analyses allow assessing the loss of weight of the adsorbent during a gradual  
220 heating. Organo-clay minerals display usually three main weight losses during the heating.  
221 The first one is associated to the evaporation of free and adsorbed water, ranging between the  
222 initial temperature and 150°C. The second one is related to the thermal oxidation of adsorbed  
223 organic compounds between 150 and 600°C with a maximal decomposition temperature  
224 related to the characteristics of organic moieties. Finally, for temperatures higher than 600°C,  
225 only the dehydroxylation of clay minerals is expected (Xie et al., 2001). Fig. 8 gathers TG and  
226 DTG curves of GA-Na-Mt composites. Weight losses associated to the dehydration remains  
227 independent from pH values. Corresponding DTG peaks occur between 98 and 105°C. With  
228 growing temperature, the distinction between each sample is more pronounced. Hence,  
229 between 150 and 600°C, no significant weight loss is displayed at pH=7, whereas noteworthy  
230 weight losses are observed at the lower pH values (2 and 5). The first decomposition  
231 temperature is noticed at 247°C and corresponds to the decomposition of acidic group of GA  
232 (Rao et al., 1981; Hussein et al., 2009). In the organic matter combustion range, GA-Na-Mt  
233 complexes aggregated at pH = 5 display one loss of weight (*i.e.* 340°C), while those formed at  
234 pH=2 exhibit two noticeable losses at 310 and 410°C (Fig. 8). This splitting after interaction  
235 at pH=2 might be explained by the distinction between GA adsorbed onto the external surface  
236 of the clay mineral (*i.e.* lower temperature) and intercalated GA (*i.e.* higher temperature) (Zhu  
237 et al., 2017). Hence, this result appears to be consistent with XRD results, in which an  
238 intercalation of GA only occurs after interaction at pH=2.

239 *3.2. Adsorption mechanisms and geochemical model of GA-Mt complexes*

240 The observation that GA adsorption is higher at  $\text{pH} < \text{pKa}$  is in agreement with the  
241 results of [Rabiei et al., 2016](#) which stressed out higher GA adsorptions at  $\text{pH}=3$  (33%)  
242 compared to their experiments performed at  $\text{pH}=7$  (20%). This pH-dependency is related to  
243 the protonation capacity of GA's polar appendage ( $\text{COOH} / \text{COO}^-$ ). It must be noted however,  
244 that the pH control of GA adsorption cannot be generalized to the interaction of other phenol-  
245 based molecules. The study by [Dolaksis et al., 2018](#) for instance, suggested that the  
246 adsorption of phenolic cores devoid of polarizing  $\text{COOH}$  appendix is pH-independent. They  
247 showed that low energy mechanisms (hydrogen bridges) drive the adsorption of  
248 chlorophenols and nitrophenols onto silicate surfaces.

249 At a  $\text{pH} < \text{pKa}$ , GA is mainly protonated (neutral) and this form represents about 99.6 % of  
250 the chemical species at  $\text{pH}=2$  ([Fig. 3](#)). However, in acidic condition, the charge density of the  
251 edge-sites of Na-Mt changes and switches below the pH of zero net proton charge estimated  
252 at 4.5 ([Table 1](#)). Here, despite the possibility of an alteration of the structure and probably the  
253 chemical composition of the layered material, the adsorption of GA appears to be enhanced in  
254 acidic conditions. The parameters derived from the fitting procedure, and more particularly  
255 those of the D-R model giving a free energy of adsorption  $E$  slightly above  $8 \text{ kJ mol}^{-1}$ ,  
256 underlining the possibility of chemical process for adsorption or at least strong electrostatic  
257 interactions. Although being less known and implied in the adsorption of anionic compounds  
258 onto Mt, electrostatic interaction was recognized as the main driving force leading to the  
259 intercalation of various kind of anionic compounds: tannic and benzoic acids, anionic  
260 surfactants ([Yan et al., 2007](#); [Zhang et al., 2012](#); [An and Dultz 2007](#)), that may occur  
261 nevertheless, in particular experimental conditions (low pH range) as it is the case here.  
262 Moreover, the increase of the basal spacing of Na-Mt after the interaction with GA at  $\text{pH}=2$   
263 (i.e.  $+ 3.7 \text{ \AA}$ ) is consistent with the molecular size of GA (i.e.  $z=3.7 \text{ \AA}$ , [Figure 1](#)), emphasizing  
264 the possible intercalation of GA through a horizontal monolayer within Na-Mt layers.

265 The adsorption of anionic species, even weak, acts as a coating that may favor further  
266 adsorption of organic molecules as organoclay materials do, nevertheless cannot only explain  
267 the totality of the adsorbed amount reaching about  $1.5 \times 10^{-4} \text{ mol g}^{-1}$ . Indeed, GA is in anionic  
268 form at a low concentration. The amount of anionic species may increase during the sorption  
269 mechanism since the uptake involves the displacement of acid basic equilibrium. This may  
270 allow *in fine* the adsorption of higher amount of anionic species. However, the effect of this  
271 acid basic shift is limited. Protonated species of GA remain preponderant and are likely to be  
272 adsorbed through other bonding mechanisms. Since GA is mainly neutral at  $\text{pH} < \text{pKa}$  as  
273 explained before, its adsorption should be driven through physisorption mechanisms such as  
274 molecular interaction ( $\pi$ -  $\pi$  interaction, van der Waals forces) with the prior adsorbed  
275 molecules and by coordinative bonding through inorganic exchangeable cations located  
276 within the interlayer space and with the carboxylic moieties as both FT / IR and XRD data  
277 highlighted. A recent work stressed out the importance of ion-dipole interaction (a  
278 coordinative bonding mechanism) as the main driving force for the adsorption of nonionic  
279 surfactants (Guégan et al., 2017) onto a Mt surface and can be according to previous studies  
280 in the literature (Sonon and Thompson, 2005; Deng et al., 2006) extended to nonionic  
281 compounds and here GA in its neutral form (Fig. 7).

282 The preponderance and the role of this interaction is confirmed at a pH value of 5 where  
283 the maximum adsorbed amounts at the equilibrium reaches  $1.3 \times 10^{-4} \text{ mol g}^{-1}$ . Based on the  
284 diagram of preponderance of GA species in regards to pH, its neutral form represents about  
285 20% at a  $\text{pH}=5$  (Fig. 3). The experiment with the highest starting concentration of  $2 \text{ g L}^{-1}$   
286 leads to  $5.88 \times 10^{-4} \text{ mol g}^{-1}$  (if one does the hypothesis that such amount is adsorbed – number  
287 of GA moles normalized to the mass of Mt introduced) where 20% are in the  $\text{RCO}_2\text{H}$  form  
288 (neutral one), thus driving to a value of  $1.176 \times 10^{-4} \text{ mol g}^{-1}$ , close to the experimental one  
289 estimated at  $1.3 \times 10^{-4} \text{ mol g}^{-1}$ . At this pH value, the clay mineral displays a cation exchange

290 capacity as well as an anionic charge surface increasing the repulsion between adsorbent and  
291 organic anions. Hence, the protonated form of GA is favored for adsorption, and may interact  
292 to the inorganic exchangeable cations through coordinative bonding forces. However, it is  
293 important to mention that 20% of the inorganic exchangeable cations are located onto the  
294 external surface of the clay mineral (Swartzen-Allen and Matijević, 1975; Shainberg et al.,  
295 1980; Patzko and Decany, 1993; Logdson and Laird, 2004), where they can be easily  
296 mobilized for a cation-exchange or other interactions such as coordinative bonding or other  
297 mechanism such as cationic bridges involving the anionic species and divalent compensating  
298 cations. Here, the adsorption of GA does not lead to any intercalation as the XRD data  
299 displayed and exclusively remains on the external surface. The presence of the inorganic  
300 exchangeable cations at about 20% of the CEC on the external surface can be easily mobilized  
301 through coordinative bonding or via complexation reactions (Fig. 7) with the phenolic acid of  
302 which adsorbed amount match a value lesser than the 20% of the CEC ( $1.6 \times 10^{-4} \text{ mol g}^{-1}$ ).

303 Similar observations are noticed at pH=7, where the adsorbed amount of neutral GA is not  
304 enough to lead to any intercalation as both XRD (Fig. 5) and FT/ IR data showed and restrict  
305 at this pH range principally anionic species in the adsorption. Indeed, in contrast to the  
306 previous pH, where the proportion of neutral species of GA represents about 96 and 20 % at  
307 pH=2 and 5 respectively, at a pH=7, it is insignificant with only 0.25 % (Fig. 3). While, the  
308 anionic form of GA is preponderant, an adsorption is surprisingly observed without however  
309 any intercalation as it was the case for pH=5, leading to an adsorbed amount of about  $1 \times 10^{-4}$   
310  $\text{mol g}^{-1}$  (Fig. 2). Here, the adsorption may involve interaction mechanisms such as cationic  
311 bridges between anionic GA and divalent inorganic cations. Hence, even mostly compensated  
312 with  $\text{Na}^+$ , around 20% of the compensating inorganic cations of Na-Mt are  $\text{Ca}^{2+}$ , that are able  
313 to sorb anionic species through cationic bridges (Errais et al., 2012; Thiebault et al., 2016;  
314 Rabiei et al., 2016). It should be mentioned that this mechanism could also play a key-role at

315 pH = 5, although the distinction between these mechanisms is not possible based on these  
316 experiments (Fig. 7).

### 317 *3.3 Putting into perspective the behavior of GA with other phenolic-based compounds* 318 *and clay minerals*

319 The adsorption of GA is enhanced at low pH, as polyphenolic humic molecules behave  
320 (Feng et al., 2005; Zhang et al., 2012; Chotzen et al., 2016). Polyphenolic molecules as fulvic  
321 and humic acids, exhibit indeed greater adsorption rates with growing acidity (Gouré-Douby  
322 et al., 2018). For instance, the study of Chen et al. (2017) focusing on the adsorption of soil  
323 macromolecular humic acids onto both montmorillonite and kaolinite, pointed out the  
324 enhancement of the adsorption at low pH. GA adopts a similar behavior when background pH  
325 ranges below its pKa and allows a preeminence of its protonated species.

326 In the case of natural polyphenolic molecules (humic substances), it has been repeatedly  
327 observed that in addition to background acidity, the nature of the adsorbent has a predominant  
328 role. Clay minerals of the 1:1 group such as kaolinite appear more conducive to the adsorption  
329 of humic -type of polyphenols. This is promoted by edges electrostatic phenomena. The  
330 extent of the adsorption through edge electrostatic interaction principally depends on the  
331 physico-chemical properties and mineralogy of a clay mineral, and more particularly its pH of  
332 zero net proton charge (pH<sub>ZNPC</sub>) which is estimated to 4.5 for Na-Mt (Tombàcz and Szekeres,  
333 2006), lower than other soil clayey components such as kaolinite (Williams and Williams,  
334 1978; Gupta and Miller, 2010). With its particular properties: a pH<sub>ZNPC</sub> and background  
335 protonation leading to a proper dispersion of clay mineral particles, kaolinite favors the  
336 adsorption of macromolecular humic acids at large content in contrast to Na-Mt besides its  
337 large CEC and specific surface area values (Chotzen et al., 2016). With similar background  
338 chemistry, GA is likely to mimic the behavior of such soil poly-phenolic compounds. Since  
339 sorbent's charge distribution varies according to clayey groups; mineralogical typology must

340 be added to the key criteria ruling GA's adsorption. However, care should be taken in  
341 comparing the uptake of these phenolic-based compounds as differences in molecular masses,  
342 spatial arrangements and number of charges may induce differences in sorptive behaviors.

343 Although being poorer from quantitative perspective, the interaction of GA with Na-Mt  
344 remains interesting from a protective point of view since its neutral form may intercalate (Fig.  
345 2; Fig. 7) under specific acidic conditions ( $\text{pH} < \text{pK}_a$ ). Interlayers isolations are reported to  
346 reduce bioavailability (Theng et al., 2001) and help to prevent biotic redox transformations.

347 In our case, the pH dependence of the adsorption appears to be consistent with the  
348 trends shown by other phenolic and polyphenolic molecules. However, the nature of the  
349 interactional mechanisms varies according to the molecules and does not display any  
350 systematic pattern. Although our results suggest intercalation and surface complexations via  
351 weak mechanisms (coordinative bonding), ligand exchanges are often involved in the  
352 interaction of long phenolic chains.

353 This encourages to complexify our view of the aggregation modalities of clays and  
354 phenol-like molecules and the possibility of organic matter stabilization process that it  
355 inducts. Na-Mt interactional mechanisms seems to differ whether the involved organic  
356 molecule are heavy macromolecular acids or singularized phenolic compounds. Thus, in a  
357 pedological environment where micro-fauna regime induces high rates of polymeric lyses and  
358 solubilizes a high quantity of phenolic acids, the stabilization process follows a different  
359 pathway from the configuration where polymeric humic acids are weakly degraded. In the  
360 first case, our data suggest that intercalation should prevail during the adsorption of poly-  
361 phenolic acids by-products in acidic pH conditions, while several studies point out adsorption  
362 on the edge and ligand exchanges in the ecological context where polymeric forms are  
363 preserved (Feng et al., 2005; Zang et al., 2012; Chotzen et al., 2016; Chen et al., 2017).

#### 364 **4. Conclusions**

365 The series of organo-clay interactions performed here under evolutionary batch  
366 equilibrium conditions allowed to characterize the adsorption mechanisms of GA, a common  
367 phenolic acid in natural pedological media, onto Na-Mt. The parameters derived from fitting  
368 of GA data with a reasonable agreement (high  $r^2$  values) to the adsorption models used:  
369 Langmuir, Freundlich and D-R equations, gave pertinent insights for a proper description of  
370 the phenomena under different approaches which pointed out the good affinity of the phenolic  
371 acid to Na-Mt. Additional experimental results obtained by FT/IR, TGA and XRD  
372 corroborated the actual adsorption of GA onto Na-Mt.

373 From the set of data, it appears that this monomolecular acid is mainly adsorbed  
374 through coordinative bonding interaction in contrast to macromolecular humic acids at low  
375 pH range, where ligand exchanges or complexation reaction occur according to the literature.  
376 Here, GA, a singularized element of large pedological compounds, interacts with the clayey  
377 mineral mainly via both surface and interlayer processes at low pH, leading to its confinement  
378 within the interlayer space which may allow a sustainable preservation of the organic matter  
379 in that way.

#### 380 **Acknowledgement**

381 This study was supported by the project MONITOPOL funded by the French region  
382 Centre Val de Loire (grant number 00117247). The authors are grateful to Marielle Hatton for  
383 her analytical contribution.

#### 384 **Figures Captions**

385 Fig. 1: Chemical structure of Gallic Acid (GA).

386 Fig. 2: Adsorption isotherms of Gallic Acid. Beige squares represent the data obtained at pH  
387 2, green ones are for the data measured at pH 5 and the red triangles represent those collected  
388 at pH 5. The continuous line represents Langmuir model fit.

389 Fig. 3: GA speciation following pH conditions.

390 Fig. 4: Graph of the 3D evolution of XRD diffraction patterns of dehydrated Gallic Acid (GA)  
391 and Na-Mt composite samples as a function of the starting GA concentrations in solution for  
392 pH=2. Only the results going up to  $0.1 \text{ g L}^{-1}$  are presented here, since no particular evolution  
393 of  $(001)$  planes was observed beyond this concentration.

394 Fig. 5: Evolution of the  $d_{001}$  basal spacing determined by the 00l reflection of Na-Mt layers  
395 obtained for GA / Na-Mt humic-clay like samples.

396 Fig. 6: FT/IR spectra of GA/Na-Mt composite samples (pH=2): thermic evolution.

397 Fig.7: Schematic representation of the possible adsorption mechanisms leading to the  
398 intercalation of GA within the interlayer of a Na-Mt at pH=2, and adsorption for the pH=5  
399 and 7.

400 Fig. 8: TG (solid lines) and DTG (dashed lines) curves of GA/Na-Mt ( $C_{GA} = 0.1 \text{ g L}^{-1}$ )  
401 composite samples after interaction at pH=2 (dark gray lines); pH=5 (dark lines) and pH=7  
402 (light gray lines).

### 403 **Tables Captions**

404 Table 1: Physico-chemical properties of implemented clay mineral (Na-Mt) and GA.

405 Table 2: Adsorption isotherm constants determined with Langmuir, Freundlich, and Dubinin-  
406 Radushkevich model fit for the adsorption of GA onto Na-Mt for different pH.

### 407 **Supplementary data**

408 Appendix 1: Spectroscopic observations (FT/IR) of GA-Na-Mt complexes aggregated at  
409 different levels of GA starting concentrations.

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572

573

## Highlights

- Gallic acid (GA) adsorption onto Na-Mt was performed in batch conditions;
- Data were fitted to Dubinin-Radushkevitch, Langmuir and Freundlich equations;
- Following the acidity, both edge and interlayer interactions modes were observed;
- GA intercalates under its neutral form;

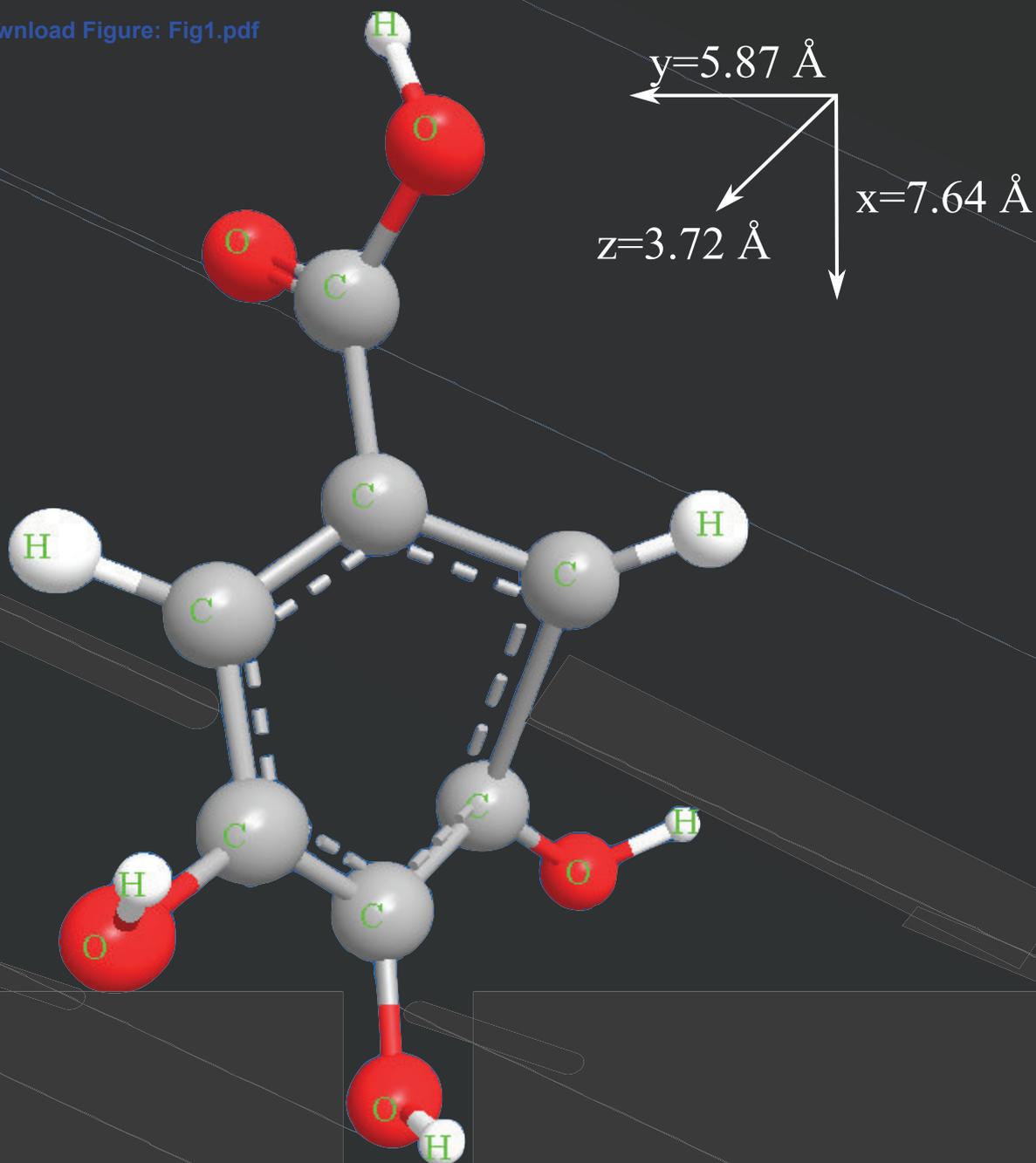
**Table 1**[Click here to download Table: Table 1.docx](#)

	Properties	Values
<b>Na-MMt</b>	C.E.C (mol.g <sup>-1</sup> )	8.10 <sup>-4</sup>
	p <sub>znc</sub>	4.5
<b>GA</b>	COOH pKa	4.4
	Surface area (Å <sup>2</sup> )	98

	Langmuir					Freundlich					Dubinin-Radushkevich				
	$q_{\max}$ (mol.g <sup>-1</sup> )	$K_L$ (L.mol)	$\Delta G$ (kJ.mol)	$r^2$	$F_{\text{error}}$	$K_F$ (L.g <sup>-1</sup> )	$n$	$r^2$	$F_{\text{error}}$	$q_{\max}$ (mol.g <sup>-1</sup> )	$E$ (kJ.mol <sup>-1</sup> )	$r^2$	$F_{\text{error}}$		
pH 2	$2.12 \times 10^{-4}$	$1.2 \times 10^3$	-17.40	0.961	0.176	$1.02 \times 10^{-3}$	3.08	0.960	$3 \times 10^{-3}$	$3.64 \times 10^{-4}$	11.04	0.964	$4 \times 10^{-3}$		
pH 5	$1.19 \times 10^{-4}$	$1.4 \times 10^3$	-18.00	0.977	0.199	$4.87 \times 10^{-4}$	3.50	0.976	$7 \times 10^{-4}$	$2.51 \times 10^{-4}$	7.88	0.963	$2.0 \times 10^{-3}$		
pH 7	$1.52 \times 10^{-4}$	$5.8 \times 10^2$	-15.77	0.977	0.034	$1.33 \times 10^{-3}$	1.78	0.981	$1 \times 10^{-4}$	$3.51 \times 10^{-4}$	7.76	0.988	$1.5 \times 10^{-3}$		

Figure 1

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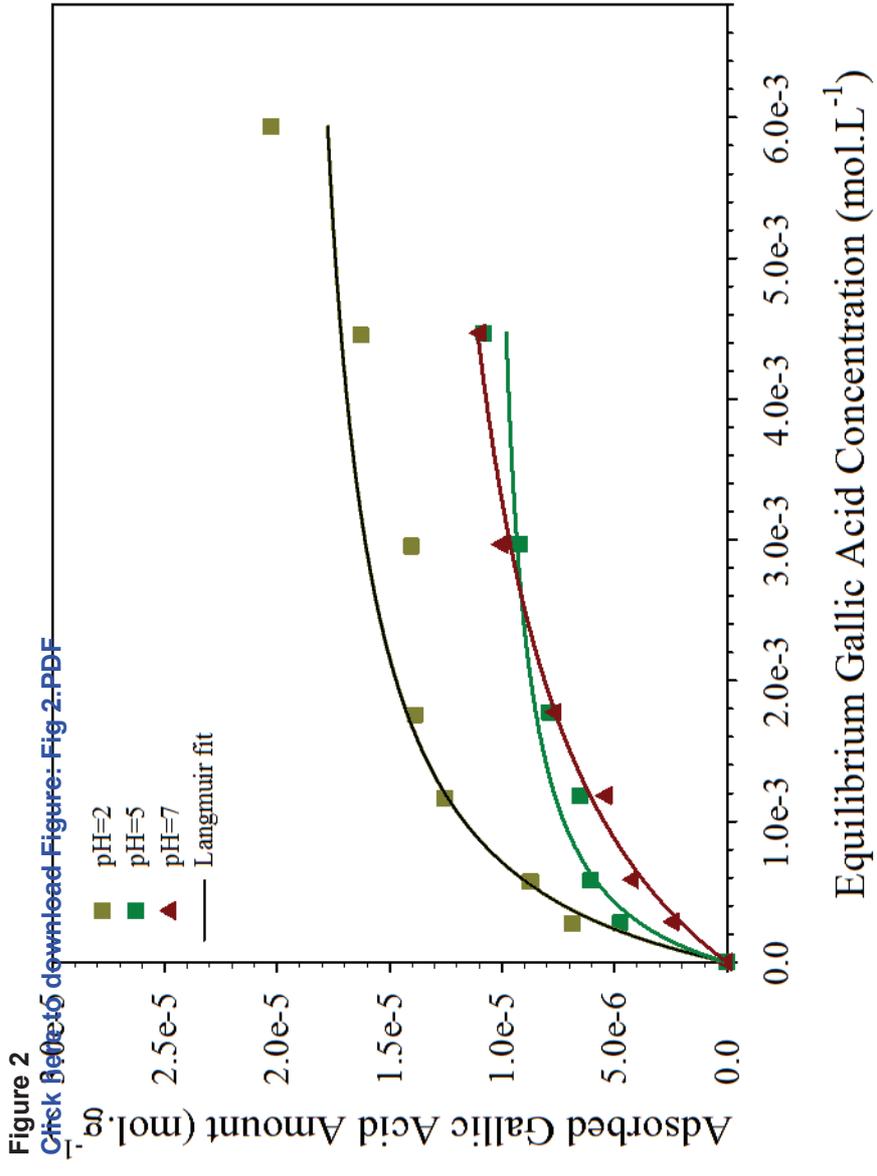


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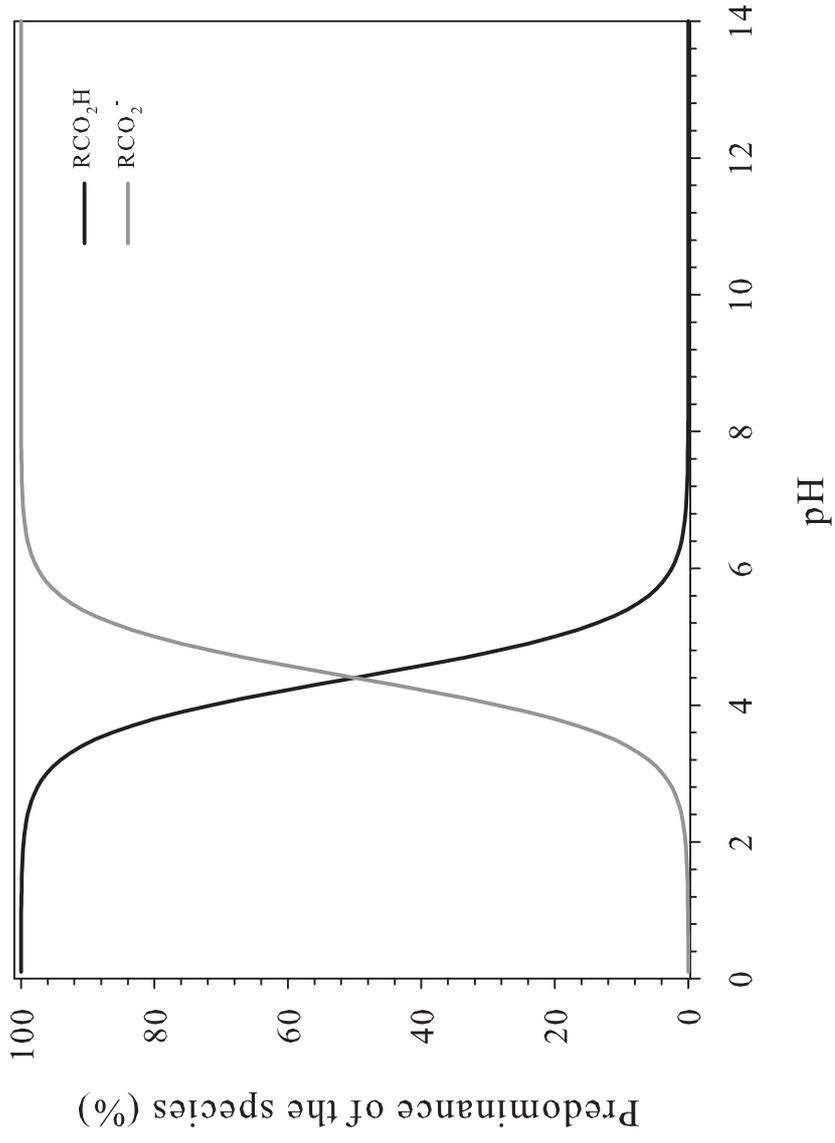


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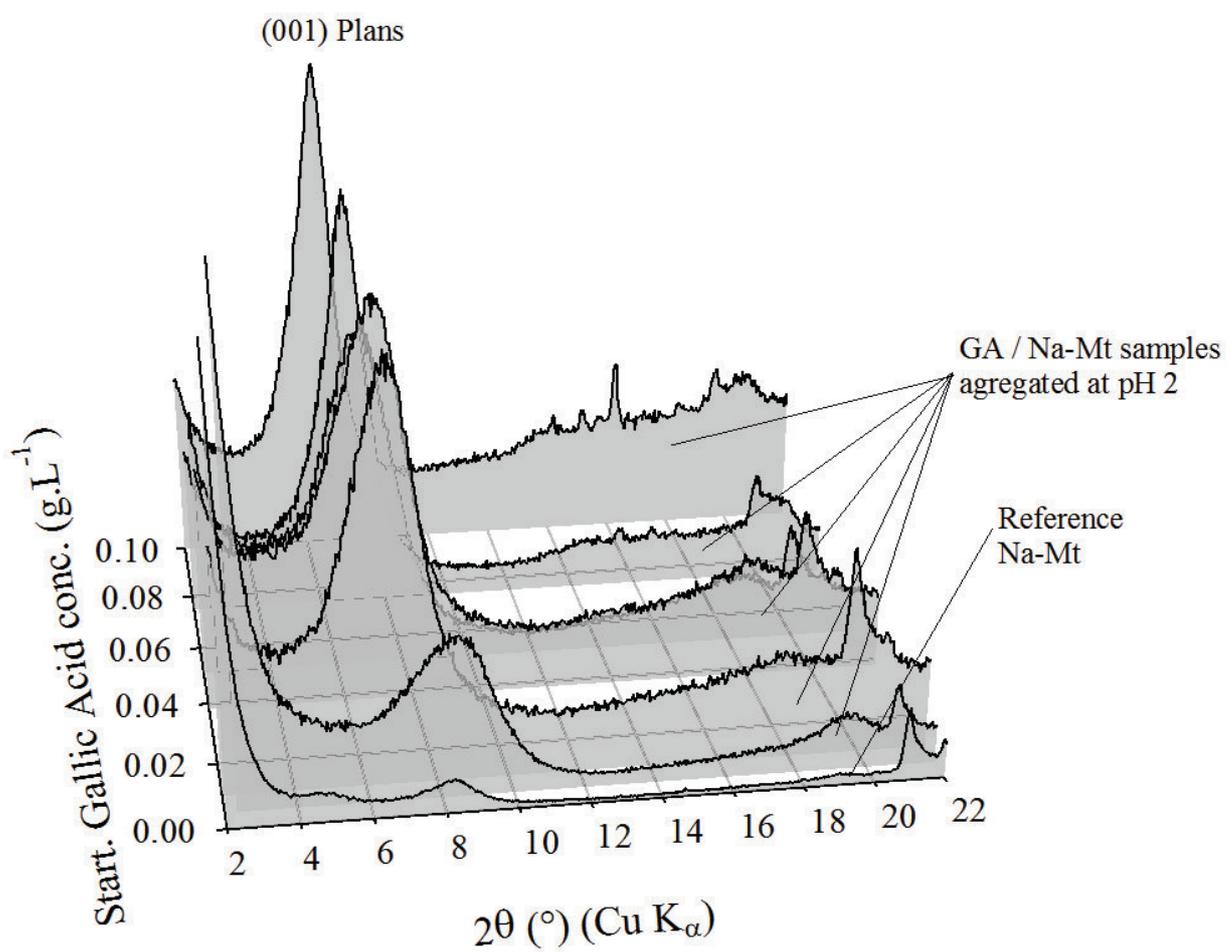


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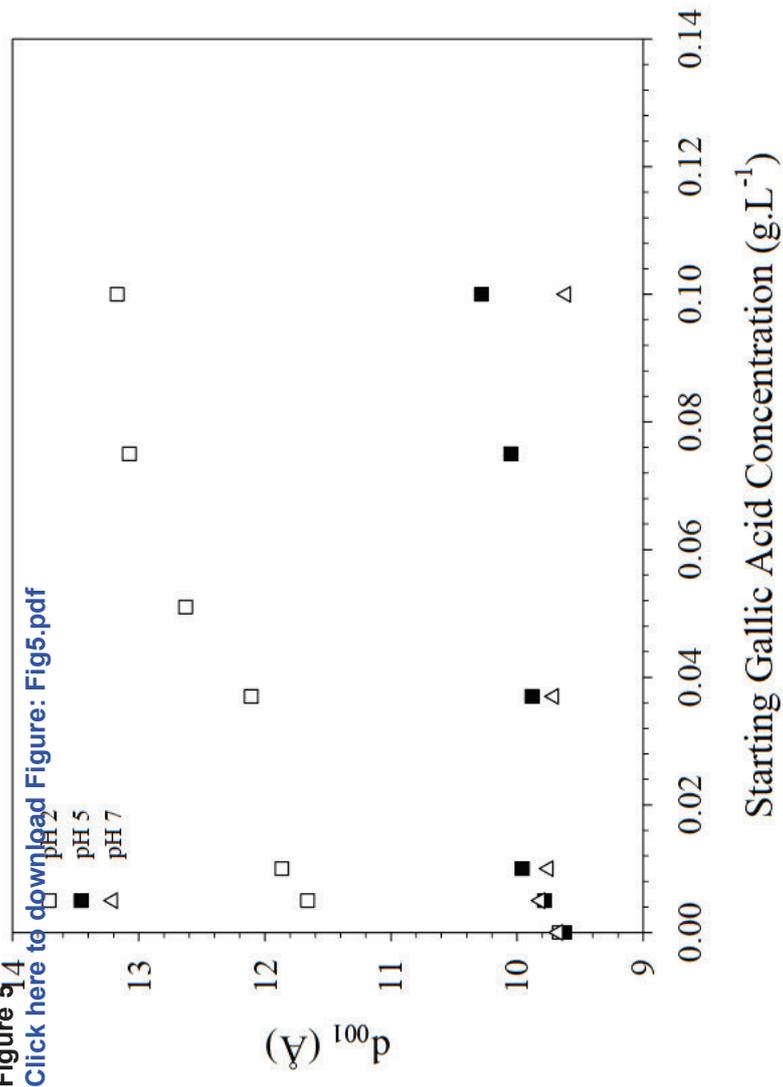


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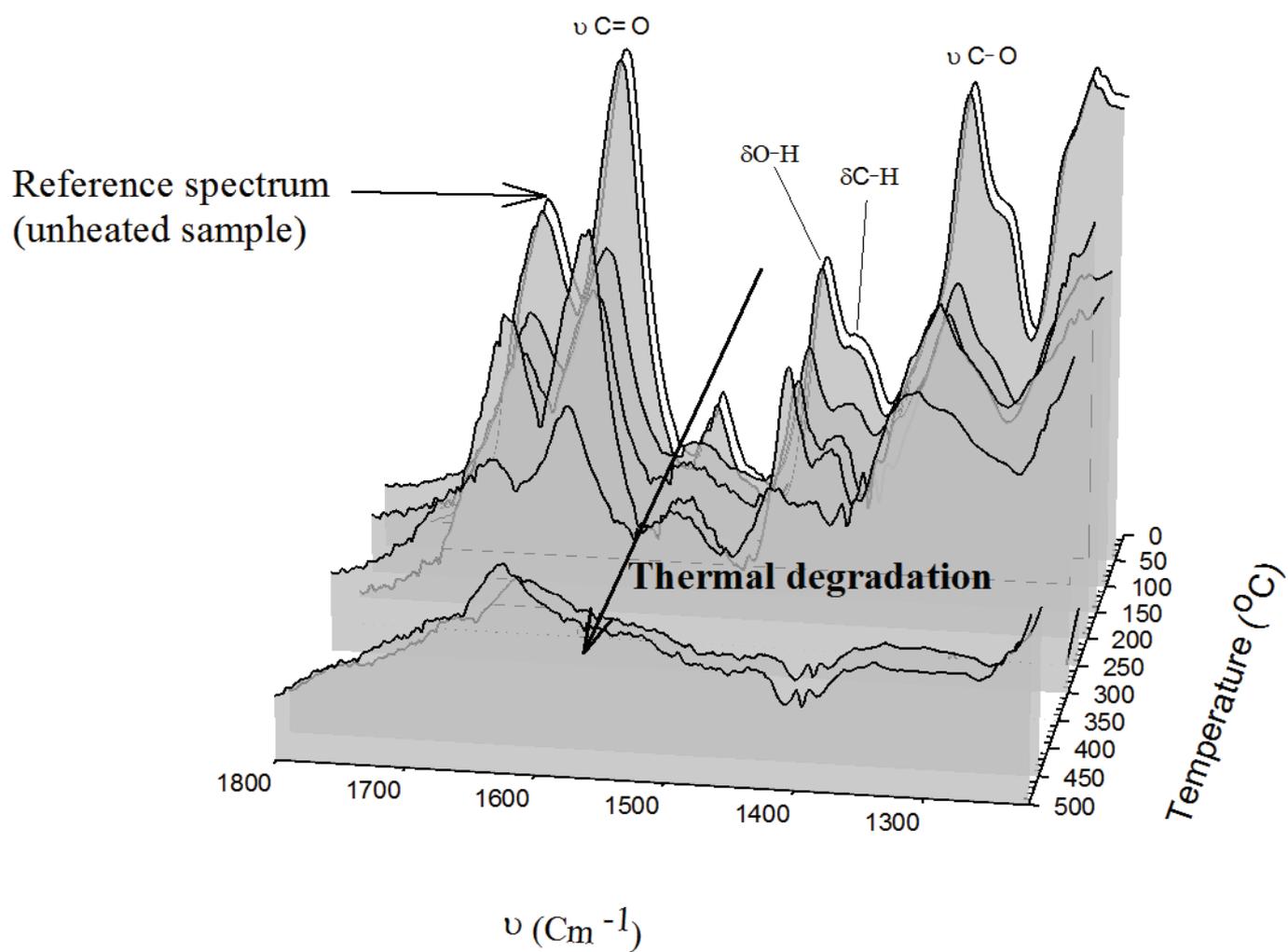


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