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| Title | Adsorption of pentachlorophenol to a humin-like substance-bentonite complex prepared by polycondensation reactions of humic precursors |
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| Citation | Applied clay science, 87, 136-141 https://doi.org/10.1016/j.clay.2013.10.022 |
| Issue Date | 2014-01 |
| Doc URL | http://hdl.handle.net/2115/54812 |
| Type | article (author version) |
| File Information | CLAY4661R1.pdf |

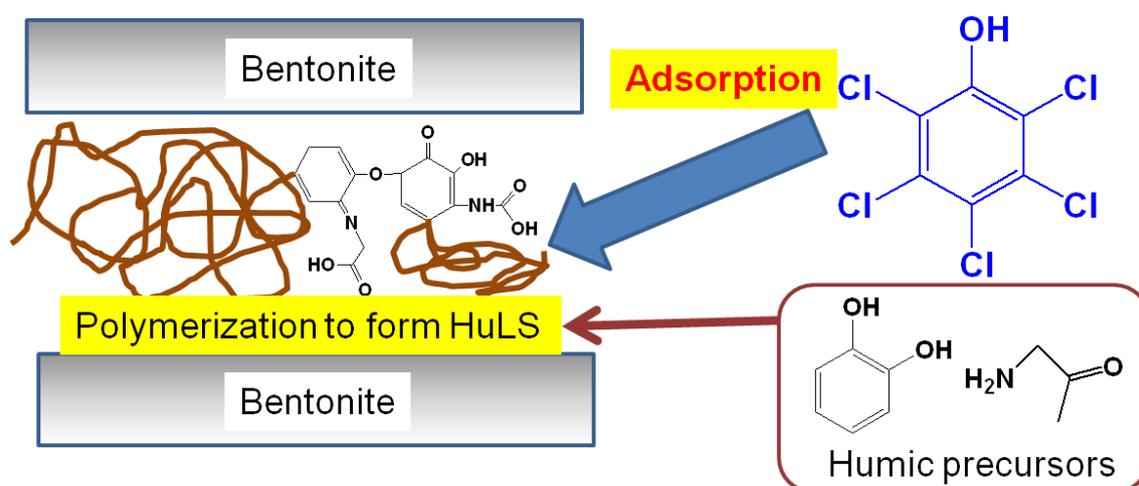


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Graphical Abstract

Adsorption of pentachlorophenol to a humin-like substance-bentonite complex prepared by polycondensation reactions of humic precursors

Masami Fukushima, Ryo Okabe, Ryo Nishimoto, Shigeki Fukuchi, Tsutomu Sato and Motoki Terashima



Highlights

Adsorption of pentachlorophenol to a humin-like substance-bentonite complex prepared by polycondensation reactions of humic precursors

Masami Fukushima, Ryo Okabe, Ryo Nishimoto, Shigeki Fukuchi, Tsutomu Sato and Motoki Terashima

> HuLS-bentonite complex was prepared via polycondensation of humic precursors. > HuLS had more aliphatic character than HaLS that was a water-soluble fraction. > XRD patterns demonstrated the intercalation of HuLS into the bentonite. > The prepared HuLS-bentonite complex had a strong affinity to pentachlorophenol. >

1 **Adsorption of pentachlorophenol to a humin-like substance-bentonite**
2 **complex prepared by polycondensation reactions of humic precursors**

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11

12 **Abstract**

13 Humic substances have natural surfactant characteristics and have a relatively high
14 affinity for pentachlorophenol (PCP). However, humic substances cannot be loaded into
15 bentonite via intercalation because of their larger size. In the present study, a humin-like
16 substance (HuLS) was prepared by polycondensation reactions of humic precursors,
17 such as glycine and catechol, and the product was loaded into bentonite. XRD patterns
18 showed that the basal spacing, calculated from the montmorillonite peak, for the
19 HuLS-bentonite complex was larger than that for bentonite itself, which is indicating
20 that the intercalation of HuLS was successful. The adsorption capabilities of PCP were
21 evaluated from adsorption isotherms at pH 4.0, 5.5 and 6.5. At all pH values, the linear
22 adsorption coefficients of PCP, K_d (L kg⁻¹), for the HuLS-bentonite complex (37 at pH
23 6.5, 247 at pH 5.5 and 804 at pH 6.5) were significantly larger than those for bentonite
24 itself (not determined at pH 6.5, 40 at pH 5.5 and 94 at pH 4). These results show that

25 the adsorption capabilities of PCP can be enhanced by loading HuLS onto bentonite. In
26 addition, the K_d values for bentonite and the HuLS-bentonite complex were found to be
27 pH-dependent, in that the K_d value decreased with increasing pH. Because of the pK_a for
28 PCP (4.75), more than 90% of the PCP was present as the anionic form at pH 5.5 and
29 6.5. In addition, the values for the Zeta potentials for bentonite and the HuLS-bentonite
30 complex remained negative at pH 2 – 12 and decreased with increasing pH. It thus
31 appears that electrostatic repulsion between the anionic form of PCP and the adsorbents
32 can affect the adsorption capabilities.

33

34 *Keywords:* Pentachlorophenol; Humin-bentonite complex; Adsorption; Humic
35 precursors; Polycondensation reaction; Intercalation

36

37 **1. Introduction**

38 Pentachlorophenol (PCP) has been utilized in the past as a biocide in wood
39 preservation industries and other pesticide applications. The disposal of these wastes has
40 resulted in serious soil, leachates, followed by contamination of the groundwater (Laine
41 et al., 1997; Varank et al., 2011). The acute toxicity of PCP to biota constitutes a threat
42 to ecosystems as well as having detrimental health effects in humans (Farah et al., 2004).
43 Thus, adsorbents for preventing PCP leaching from contaminated sites and for removing
44 PCP from contaminated water are urgently needed. Clay minerals are particularly
45 effective adsorbents in barrier materials and can be used to prevent ionic contaminants,
46 which are eluted from landfills to external environments (Gautier et al., 2009;
47 Koutsopoulou et al., 2010; Le Forestier et al., 2011). Clay minerals are, however,
48 ineffective in removing hydrophobic organic contaminants from water. It is possible to

49 modify clay minerals by interaction with surfactants, such as quaternary
50 alkylammonium salts, and this results in the formation of organophilic solid materials
51 (Bergaya and Lagaly, 2001; De Paiva et al., 2008; Kooli et al., 2009). The surfactants
52 were loaded on the bentonite via the intercalation, and the resulting
53 surfactant-intercalated bentonite complex was found to be effective in removing PCP
54 from water (Stapleton et al., 1994; Bouras et al., 2010; Zhang et al., 2012). However,
55 some investigators have suggested that artificially synthesized cationic surfactants like
56 quaternary alkylammonium cations are themselves toxic (Utsunomiya et al., 1997).

57 On the one hand, humic substances are naturally occurring, surface active materials
58 that have amphiphilic characteristics, thus giving them both hydrophilic and
59 hydrophobic properties. Such functions of humic substances can serve as media for the
60 sorption of hydrophobic organic contaminants, such as polycyclic aromatic
61 hydrocarbons (Fukushima et al., 1997; Wang and Xing, 2005), polychlorinated
62 dibenzo-*p*-dioxins (Yabuta et al., 2004; Tanaka et al., 2005; Fukushima et al., 2006) and
63 chlorophenols (Robinson and Novak, 1994; Paolis and Kukkonen, 1997). In addition, it
64 has been reported that the affinity of hydrophobic organic contaminants for clay
65 minerals can be enhanced by complexation with humic substances (Terashima et al.,
66 2003; He et al., 2006). Thus, humic-clay complexes represent potentially effective and
67 non-toxic adsorbents. The hydrodynamic radii of humic substances have been reported
68 to be in the range of 22 – 71 Å (Kawahigashi et al., 2005). Thus, it would be difficult to
69 intercalate naturally occurring humic substances into the interlayer, because of the
70 smaller spacing of the bentonite (approximately 10 Å) (Grim, 1962). Regarding the
71 abiotic formation of humic substances from their precursors, it is known that minerals
72 such as birnessite, kaolinite, allophane and bentonite can catalyze the formation of

73 dark-colored polymers like humic substances from humic precursors, such as amino
74 acids and phenols (Shindo and Huang, 1984, 1985; Wang and Huang, 1989; Miura et al.,
75 2009; Miura et al., 2011). The formation of humic-like substances via polycondensation
76 reactions of the humic precursors, such as glycine and catechol, by catalytic power of an
77 allophane mineral cannot only produce humic acid-like substance (HaLS) in aqueous
78 phase of the reaction mixtures but also could produce humin-like substances (HuLS) on
79 the allophane surface (Okabe et al., 2011). Such a HuLS-allophane would be expected
80 to have a higher affinity for PCP compared to the allophane mineral alone (Okabe et al.,
81 2011). It has been reported that humic precursors, such as phenols and amino acids, can
82 be intercalated into the interlayers of bentonite (Banat et al., 2000; Kollár et al., 2003).
83 Thus, HuLS can be produced in the interlayer via polycondensation reactions. The
84 resulting HuLS-bentonite complex may serve as an excellent adsorbent for hydrophobic
85 organic contaminants, such as PCP. In the present study, a commercial bentonite was
86 used as a mineral, and the HuLS-bentonite complex was prepared via polycondensation
87 reactions of catechol and glycine as humic precursors in the presence of bentonite. In
88 addition, relations between surface properties and adsorption behaviors of PCP for the
89 prepared HuLS-bentonite complex were compared with those for a non-modified
90 bentonite.

91

92 **2. Materials and Methods**

93 *2.1. Materials*

94 Catechol (purity >99.0 %) and glycine (purity 99 %) were purchased from Tokyo
95 Chemical Industry (Tokyo, Japan) and Nacalai Tesque (Kyoto, Japan), respectively. PCP
96 (purity 98 %) was purchased from Sigma-Aldrich (St. Louis, MO, USA). A powdered

97 bentonite sample was purchased from Nacalai Tesque. Ultrapure water, prepared using a
98 Millipore ultra-pure water system from distilled water, was used in all experiments.

99

100 2.2. Preparation of HuLS-bentonite complex

101 Two grams of the powdered bentonite were placed in a 300-mL Erlenmeyer flask,
102 and a 150 mL aliquot of an aqueous solution containing catechol and glycine (0.01 M
103 each) was then added. The mixture was shaken at 160 rpm for 2 weeks, and the
104 temperature was maintained at 30 °C. The pH of the solution was adjusted to 7.00 ± 0.50
105 each day using aqueous 0.1 M HCl and 0.1 M NaOH solutions. After a 2-week
106 incubation, the reaction mixture was centrifuged at 10000 rpm for 15 min. The solid
107 was washed with water, and then freeze-dried to give a powdered sample of
108 HuLS-bentonite complex.

109

110 2.3. Separations of HaLS and HuLS

111 The HaLS was separated from the supernatant in the reaction mixture, as described in
112 a previous report (Okabe et al., 2011). The HuLS fraction was separated from the
113 prepared HuLS-bentonite complex according to a previously reported method (Wang
114 and Xing, 2005) with minor modifications. A 1 g portion of the HuLS-bentonite powder,
115 in an acidic solution of ultrapure water, concentrated HF and HCl (5 mL/5 mL/10 mL),
116 was allowed to shake for 8 hours at room temperature. This procedure was repeated 8
117 times with a fresh acid mixture being used each time. After the centrifugation, the
118 precipitate was deionized by dialysis (molecular weight cut-off of 500 Da) and the
119 slurry in the dialysis tube was freeze-dried to give a powdered sample of HuLS.

120

121 *2.4. Analysis of samples*

122 The elemental compositions (C, H, N and ash contents), acidic functional groups,
123 solid-state CP-MAS ¹³C NMR and FT-IR spectra for HuLS and HaLS were determined
124 according to a reported method (Yabuta et al., 2008). X-ray powder diffraction (XRD)
125 patterns of bentonite and HuLS-bentonite were obtained using a Rigaku diffractometer
126 (RINT 1200) using Cu-K α radiation at a scanning speed of 0.02° min⁻¹. The
127 measurements were done under dehydrated conditions using a relative humidity control
128 system for XRD (Watanabe and Sato, 1988). Zeta potentials for the bentonite and
129 HuLS-bentonite complex were measured using a Zetasizer Nano-ZS90 (Malvern
130 Instrument Ltd.) connecting to a MPT-2 automatic titrator. Inorganic elements (Na, Ca,
131 Si, Al, Mg, Fe, K and Ti), pH, specific surface area (SSA) and cation-exchange capacity
132 (CEC) for the bentonite and HuLS-bentonite complex were analyzed, as described in a
133 previous report (Miura et al., 2009).

134

135 *2.5. Assay for PCP adsorption to bentonite and HuLS-bentonite complex*

136 A stock solution of PCP (1 mM) was prepared by dissolving it in aqueous 0.2 M
137 KOH. Aliquots 0.15, 0.45, 0.90, 1.80, 2.70 or 3.60 mL samples of the PCP stock
138 solution were diluted to 20 mL with aqueous 0.1 M KCl, and the pH values of these
139 solutions were adjusted to 4.0, 5.5 or 6.5 with aqueous solutions of KOH and HCl.
140 These solutions were then diluted to 30 g with aqueous 0.1 M KCl the pH of which was
141 adjusted to the desired value with aqueous KOH and HCl (solution A). A 12 mL aliquot
142 of aqueous 0.1 M KCl was added to 160 mg portion of the powdered bentonite or
143 HuLS-bentonite complex. The pH of the dispersion was adjusted to the desired pH by
144 adding aqueous 0.1 M KCl containing 0.01 M HCl using an AUT-501 auto-titration

145 system (DKK-TOA, Tokyo, Japan). After reaching a constant pH of 4.0, 5.5 or 6.5, the
146 dispersion was finally diluted to 20 mL with aqueous 0.1 M KCl the pH of which was
147 adjusted to the desired value (solution B). A 0.4 mL aliquot of solution A, 1.25 mL of
148 solution B and 0.35 mL of the aqueous 0.1 M KCl the pH of which was adjusted to the
149 desired value, were pipetted into a 10-mL glass tube. The glass tube was sealed with
150 parafilm, and allowed to shake 25°C for 24 h. Preliminary experiments confirmed that a
151 shaking period of 24 h was sufficient to achieve equilibrium and the variations of pH
152 values were within ± 0.2 during the period of shaking. After the incubation, the mixture
153 was centrifuged for 10 min at 3000 rpm, and a 1 mL aliquot of the supernatant was then
154 mixed with the 0.5 mL of 2-propanol. PCP in this mixture was analyzed by HPLC,
155 based on the conditions in a previous report (Okabe et al., 2011). The adsorption of PCP
156 can be represented using the following Freundlich-type isotherm equation (Wen et al.,
157 2007).

$$158 \quad q_s = K_f \times C_e^n \quad (1),$$

159 where q_s , K_f , C_e and n denote the concentration of adsorbed PCP to the bentonite or
160 HuLS-bentonite complex ($\mu\text{mol kg}^{-1}$), the Freundlich adsorption coefficient ($\mu\text{mol kg}^{-1}$
161 μM^{-n}), the equilibrium concentration of PCP remained in the aqueous solution and the
162 exponential empirical parameter that accounts for the non-linearity in the adsorption
163 behavior, respectively. In addition, the adsorption data were also analyzed assuming a
164 linear adsorption isotherm:

$$165 \quad q_s = K_d \times C_e \quad (2),$$

166 where K_d is adsorption coefficient (L kg^{-1}), which corresponds to K_f at $n = 1$ in eq 1.

167

168 **3. Results and Discussion**

169 *3.1. Chemical compositions of the HaLS and HuLS*

170 To characterize the dark-colored polymers from reaction mixtures, HaLS and HuLS
171 were separated into aqueous and solid phases, respectively. The HuLS fraction that was
172 separated from the HuLS-bentonite complex was not completely soluble in an aqueous
173 0.1 M NaOH solution, although HaLS was readily soluble in aqueous 0.1 M NaOH. The
174 carboxylic acid and phenolic hydroxyl group contents for HaLS and HuLS are
175 summarized in Table 1. The contents of acidic functional groups for HuLS were smaller
176 than those for HaLS, and the majority of dark-colored polymers were not eluted from
177 the HuLS-bentonite complex by aqueous 0.1 M NaOH. Thus, the dark-colored polymers
178 that were loaded into the bentonite have a character similar to humin.

179 The elemental compositions of the HuLS and HaLS samples are summarized in
180 Table 1. The calculated O/C molar ratio for HuLS (0.86) was larger than that for HaLS
181 (0.60). Because HuLS contains less acidic functional groups than HaLS, the larger O/C
182 ratio for HuLS may be due to oxygen-containing functional groups such as ketones,
183 aldehydes, quinones, ethers and esters. In addition, the H/C molar ratio for HuLS (1.01)
184 was larger than that for HaLS (0.82), suggesting that HuLS has more aliphatic
185 characteristics than HaLS.

186 FT-IR spectra of the HuLS-bentonite complex, bentonite, HuLS and HaLS are shown
187 in Fig. 1. While HuLS contained a relatively higher ash content (12.2% in Table 1), the
188 observed peaks for HuLS were not overlapped with those for bentonite and
189 HuLS-bentonite complex. Thus, it does not appear that ash from the bentonite residues
190 has any significant influence on the FT-IR spectrum of HuLS. As compared to the
191 spectrum of HaLS, the peak at around 2920 cm^{-1} appeared in the case of HuLS (Fig. 1,
192 ▲). This peak corresponds to C-H stretching of methylene groups, and is consistent

193 with the trend for the H/C molar ratio. In addition, the peak at 1154 cm^{-1} , corresponding
194 to C-O-H bending or C-O stretching of aliphatic alcohols and ethers, appeared in the
195 spectrum of HuLS (Fig. 1, ●). The relative compositions of different carbon functional
196 groups were estimated from solid-state CP-MAS ^{13}C NMR spectra (Table 2). The alkyl
197 carbon content for HuLS (30%) was much larger than that for HaLS (13%). These
198 results indicate that HuLS has more aliphatic characteristics than HaLS.

199

200 *3.2. Characterization of bentonite and HuLS-bentonite complex*

201 As shown in Fig. 1, the FT-IR spectrum for bentonite was similar to that for the
202 HuLS-bentonite complex. Thus, FT-IR spectra did not permit the loading of HuLS into
203 the bentonite to be observed. XRD patterns for bentonite and HuLS-bentonite complex
204 are shown in Fig. 2. Montmorillonite (“Mt” in Fig. 2) was the major mineral component
205 in the bentonite, while a few silicate peaks, cristobalite (“C” in Fig. 2) and quartz (“Q”
206 in Fig. 2), were found as concomitants. Because the basal spacing can be increased by
207 the intercalation of water with increasing relative humidity, XRD patterns for the
208 bentonite and HuLS-bentonite complex were recorded by eliminating water using the
209 relative humidity control system for XRD, as reported previously (Watanabe and Sato,
210 1988). In layered minerals, the maximum d-spacing represents the basal spacing of the
211 crystalline structures for the minerals (Grim, 1962). In Fig. 2, the montmorillonite peaks
212 at $2\theta = 7.62^\circ$ for the HuLS-bentonite complex and at $2\theta = 9.04^\circ$ for the bentonite were
213 used to calculate basal spacing values for the interlayer. The estimated values for basal
214 spacing were 9.60 \AA for the bentonite and 11.4 \AA for the HuLS-bentonite complex,
215 indicating that the basal spacing for HuLS-bentonite complex is expanded compared to
216 that for the bentonite. Thus, the expansion of basal spacing in the case of the

217 HuLS-bentonite complex can be attributed to the fact that HuLS is produced in the
218 interlayer via polycondensation reactions of catechol and glycine.

219 The zeta potentials for bentonite and the HuLS-bentonite complex as a function of
220 pH are shown in Fig. 3. In all pH range (2 – 12), the surface potentials for bentonite and
221 HuLS-bentonite complex were negative, while the surface potential was increased when
222 HuLS was loaded at $\text{pH} < 8$. In particular, the zeta potential for the HuLS-bentonite
223 complex decreased with increasing pH. This is due to the dissociation of acidic
224 functional groups, such as carboxylic and phenolic hydroxyl groups, in HuLS with
225 increasing pH. These results indicate that surface potentials for the HuLS-bentonite
226 complex are governed by the acid dissociation of acidic functional groups in the HuLS.
227 The larger values for the negative surface potentials for bentonite can be due to its
228 layered structure that is exchangeable with cations (Grim, 1962). In addition, the pH
229 values for dispersion in H_2O and aqueous 0.1 M KCl for the HuLS-bentonite complex
230 were neutral, and no influence of exchangeable cations in the bentonite layer was
231 observed (Table 3). The cation-exchange capacity and specific surface area were
232 decreased by loading HuLS into the bentonite (Table 3). These results support a
233 scenario in which HuLS is intercalated into the interlayer of the bentonite.

234 Phenolic hydroxyl group protons in PCP can dissociate and the $\text{p}K_a$ value for such a
235 compound is known to be 4.75 at 25°C . Based on this, species distribution curves for the
236 phenol (PCP) and phenolate (PCP^-) forms were calculated, and the results are shown in
237 Fig. 3. The pH ranges for landfill leachates from chlorophenol-contaminated wastes are
238 reported to be 4.5 – 7 (Laine et al., 1997; Varank et al., 2011). At this pH, more than
239 50% of the PCP would be present as PCP^- and would be difficult to adsorb to bentonite
240 and HuLS-bentonite complex, both of which have anionic surfaces because of

241 electrostatic repulsion. However, the zeta potentials at pH 4.5 – 7 for the
242 HuLS-bentonite complex were larger than those for the bentonite, as shown in Fig. 3.
243 Thus, a higher adsorption of PCP to the HuLS-bentonite complex would be expected
244 due to the reduction of electrostatic repulsion. In the present study, pH values of 4.0, 5.5
245 and 6.5 were selected for use in the adsorption tests for PCP.

246

247 *3.3. Adsorption characteristics of PCP*

248 The adsorption isotherms of PCP for bentonite and the HuLS-bentonite complex are
249 shown in Fig. 4. Based on the isotherms, the Freundlich parameters (K_f , n and the
250 square of the correlation coefficient, r^2) were estimated by non-linear least square
251 regression analyses of the data set (C_e and q_s) to eq 1 (Table 4). However, the
252 Freundlich adsorption coefficient, K_f , cannot be compared between different isotherms,
253 because this unit is based on the exponent, n , for a given sample. Thus, the linear
254 adsorption coefficients, K_d ($L\ kg^{-1}$), were estimated by assuming a linear adsorption
255 isotherm in eq 2 (Table 4). The K_d values were clearly increased as a result of the
256 loading of HuLS into the bentonite. These results show that the affinity of PCP for
257 bentonite was substantially enhanced as the result of HuLS loading. The level of PCP
258 adsorption to soils is dependent on the hydrophobicity of humic substances on the
259 surface of soil particles (Paolis and Kukkonen, 1997; Li et al., 2009). In addition, the
260 sorption coefficients for 2,4,6-trichlorophenol are correlated with the aliphaticity of soil
261 humic acids (Huang et al., 2008). Thus, the enhanced affinity of PCP for the
262 HuLS-bentonite complex can be attributed to an increase in the hydrophobicity of the
263 adsorbent surface by the loading of HuLS.

264 On the other hand, the K_d values decreased with increasing pH (Table 4), in which the
265 negative charges of the adsorbents and the concentration of PCP^- increased with
266 increasing pH (Fig. 3). In particular, it was not possible to determine the K_d value for
267 bentonite at pH 6.5, because all of the PCP was concentrated in the aqueous solutions
268 (Fig. 4) and were similar to those initially added. The adsorption of PCP to soils is also
269 dependent on the solution pH, in which non-ionized PCP has a higher affinity for soils
270 than at a pH below its pK_a value (4.75), i.e., the anionic species, PCP^- (Paolis and
271 Kukkonen, 1997; Li et al., 2009). As shown in Fig. 3, the majority of PCP is present in
272 an anionic form at a pH above 5. In addition, the bentonite and HuLS-bentonite
273 complex had a negative charge in the pH range of 2 – 12. These results and issues
274 indicate that the electrostatic repulsion between PCP^- and the adsorbents can also affect
275 the adsorption capabilities.

276 The n value can be regarded as an index of site energy distribution on the adsorbent,
277 where the smaller the n , the more heterogeneous are the adsorption sites (Wen et al.,
278 2007). The n values for the bentonite (0.55 – 0.67) were somewhat smaller than those
279 for the HuLS-bentonite complex (0.74 – 0.85), suggesting that the non-linearity of the
280 adsorption of PCP to bentonite is higher than that for the HuLS-bentonite complex.
281 Phenol molecules can form a donor hydrogen bond to bentonite (Lock and Skipper,
282 2007). In addition, a variety of interactions between bentonite and aromatic compounds
283 has been reported, e.g., $n-\pi$ electron-donor-acceptor interaction (Qu et al., 2011) and
284 coordination of the intercalated metal ions with π -electron of benzene ring (Liu et al.,
285 2009). Thus, the intercalation of HuLS can alter the binding sites of PCP to bentonite.
286 These results and related issues support the view that the heterogeneity of the adsorption
287 sites of PCP on bentonite would be expected to be decreased somewhat as the result of

288 the loading of HuLS, which binds to PCP via hydrophobic interactions.

289

290 **4. Conclusions**

291 The adsorption of PCP to bentonite at pH 4 – 6.5 was enhanced by the loading of
292 HuLS to the bentonite, in which the affinity to PCP increased with a decrease in pH. In
293 the HuLS-allophane complex, HuLS, formed via polycondensation reactions between
294 glycine and catechol, was only adsorbed on the surface of allophane via surface
295 complexation, as described in a previous report (Okabe et al., 2011). The K_d value for
296 the adsorption of PCP on the HuLS-allophane complex at pH 5.5 (15) was much smaller
297 than that for the HuLS-bentonite (247). These results support the conclusion that HuLS,
298 when it is intercalated into bentonite layers, has the potential for removing PCP from
299 aqueous solutions in the pH range of 4.5 – 6.5.

300

301 **Acknowledgment**

302 This work was supported by Grant-in-Aid for Scientific Research from the Japan
303 society for the Promotion of Science (25241017).

304

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415

416 **Figure captions**

417

418 **Fig. 1.** FT-IR spectra of HaLS, HuLS, bentonite and HuLS-bentonite complex.

419

420 **Fig. 2.** XRD patterns for bentonite (a) and HuLS-bentonite complex (b). “Mt”, “C” and
421 “Q” for each peak denote “montmorillonite”, “cristobalite” and “quartz”, respectively.

422

423 **Fig. 3.** Zeta potentials for bentonite (a) and HuLS-bentonite complex (b), and species
424 distribution curves of PCP (solid and dotted lines).

425

426 **Fig. 4.** Adsorption isotherms for bentonite (●) and the HuLS-bentonite complex (■) at
427 pH 4.0, 5.5 and 6.5. Solid lines show the calculated curves, based on the Freundlich
428 adsorption isotherms in eq. (1).

429

Table 1
Elemental compositions and acidic functional group contents for HuLS and HaLS.

| Samples | Elemental composition (%) | | | | | Acidic functional groups (mmol g ⁻¹) | |
|---------|---------------------------|------|------|----------------|-------------------|--|------------------------|
| | C | H | N | O ^a | ash | COOH ^c | Phenol-OH ^d |
| HuLS | 38.4 | 3.25 | 2.17 | 44.0 | 12.2 | 1.2±0.1 | 9.6±0.8 |
| HaLS | 51.5 | 3.53 | 3.77 | 41.2 | N.D. ^b | 2.5±0.4 | 15±3 |

^a %O = 100 - (%C + %H + %N + %Ash). ^b Not detected. ^c Carboxylic acid. ^d Phenolic hydroxyl groups.

Table 2

Relative compositions of different carbon functional groups^a, as estimated from solid-state ¹³C NMR spectra of HuLS and HaLS.

| Chemical shift (ppm) | Assignments | Composition (%) | |
|----------------------|----------------------|-----------------|------|
| | | HuLS | HaLS |
| 0 - 50 | Alkyl-C | 30 | 13 |
| 50 - 110 | <i>N, O</i> -Alkyl-C | 26 | 21 |
| 110 - 140 | Aromatic-(C-H, C-C) | 20 | 35 |
| 140 - 165 | Aromatic-(C-O) | 13 | 20 |
| 165 - 220 | Carbonyl-C | 10 | 11 |

^a Alkyl carbon: Alkyl-C, Alkyl carbon attached to hetero atoms: *N, O*-Alkyl-C, Aromatic carbon attached to hydrogen or carbon: Aromatic-(C-H, C-C), Aromatic carbon attached to oxygen: Aromatic-(C-O), and Carbonyl carbon (carboxyls and ketones): Carbonyl-C.

Table 3

Composition of inorganic elements and surface properties of bentonite and the HuLS-bentonite complex.

| <i>Inorganic elemental compositions (Wt %)^a</i> | | | | | | | | |
|--|------------------|-----------|--|---|------|------|-------------------|------|
| Sample | Na | Ca | Si | Al | Mg | Fe | K | Ti |
| Bentonite | 0.36 | 2.7 | 34.3 | 9.66 | 1.05 | 1.25 | 0.49 | 0.07 |
| HuLS-bentonite | 0.25 | 0.72 | 22.1 | 3.59 | 0.57 | 0.59 | N.D. ^b | 0.02 |
| <i>Surface properties</i> | | | | | | | | |
| Sample | pH ^c | | SSA ^d (m ² g ⁻¹) | CEC ^d (cmol kg ⁻¹) | | | | |
| | H ₂ O | 1 M KCl | | | | | | |
| Bentonite | 10.05±0.10 | 8.50±0.13 | 63±1 | 53±3 | | | | |
| HuLS-bentonite | 6.48±0.03 | 6.12±0.04 | 56±1 | 44±1 | | | | |

^aOrganic carbon contents: bentonite, not detected; HuLS-bentonite complex, 1.1%. ^b Not detected.

^cBentonite : liquid = 1:15. ^dSpecific surface area. ^e Cation-exchange capacity.

Table 4

Freundlich adsorption parameters and linear adsorption parameters.

| Sample | pH | Freundlich adsorption parameters | | | Linear adsorption parameters | |
|----------------|-----|----------------------------------|-------------------|-------------------|------------------------------|-------------------|
| | | K_f^a | n | r^{2b} | K_d^c | r^{2b} |
| Bentonite | 4 | 383±10 | 0.55±0.03 | 0.988±0.006 | 94±11 | 0.948±0.016 |
| | 5.5 | 124±24 | 0.67±0.07 | 0.991±0.006 | 40±2 | 0.975±0.004 |
| | 6.5 | N.D. ^d | N.D. ^d | N.D. ^d | N.D. ^d | N.D. ^d |
| HuLS-bentonite | 4 | 1220±120 | 0.79±0.07 | 0.988±0.004 | 804±43 | 0.963±0.008 |
| | 5.5 | 403±53 | 0.85±0.07 | 0.985±0.012 | 247±1 | 0.985±0.001 |
| | 6.5 | 83±1 | 0.74±0.02 | 0.981±0.007 | 37±4 | 0.991±0.008 |

^amol kg⁻¹ M⁻ⁿ. ^bSquare of correlation coefficients for the curve-fitting. ^cL kg⁻¹. ^dNot determined.

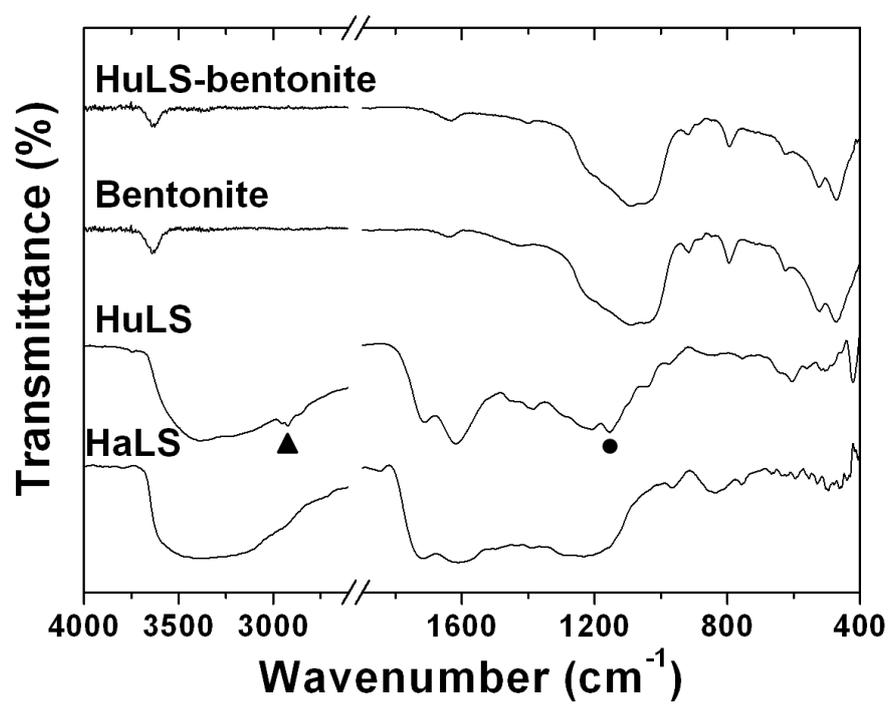


Fig. 1. (CLAY4661)

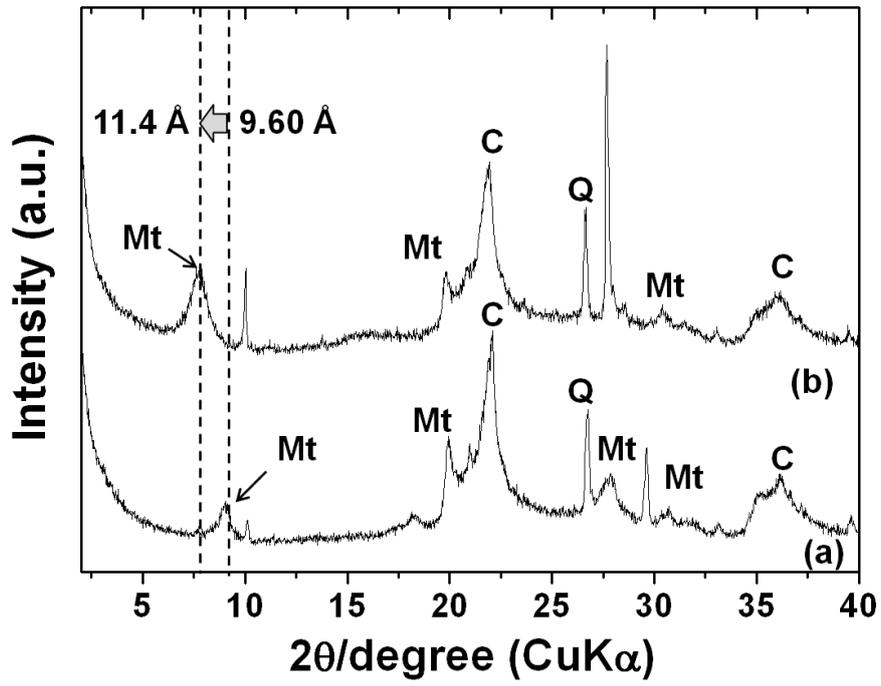


Fig. 2. (CLAY4661)

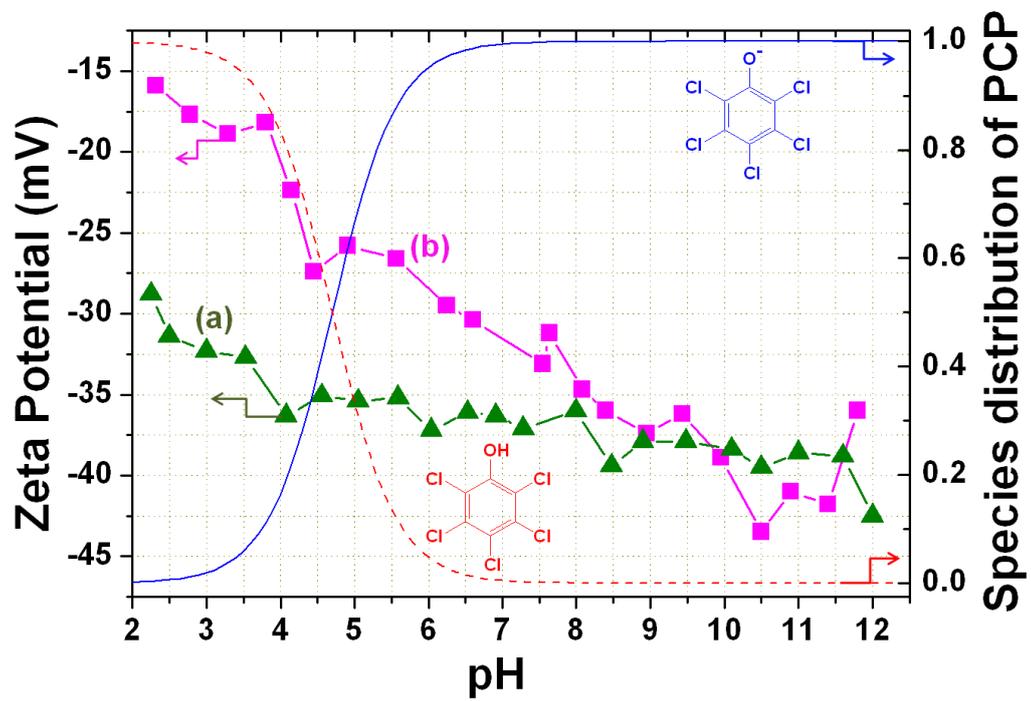


Fig. 3. (CLAY4661)

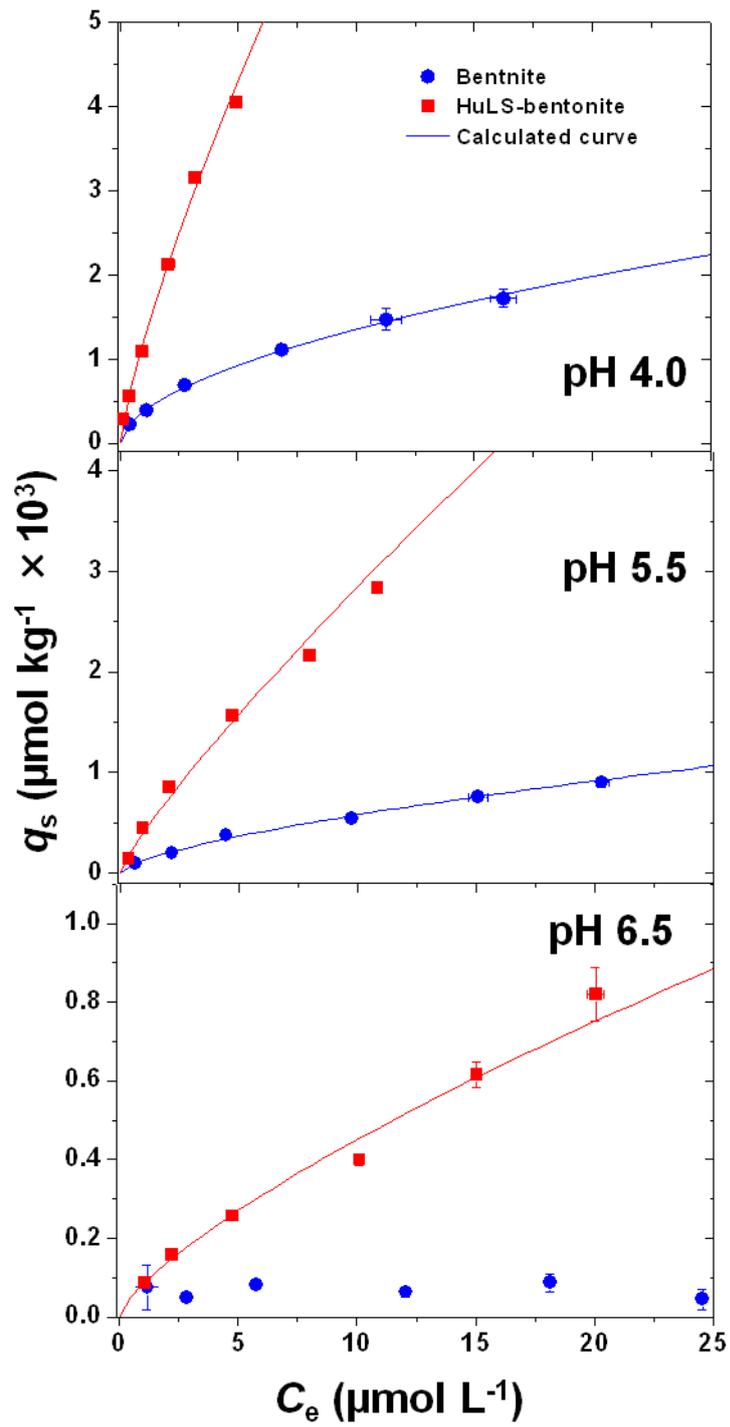


Fig. 4. (CLAY4661)