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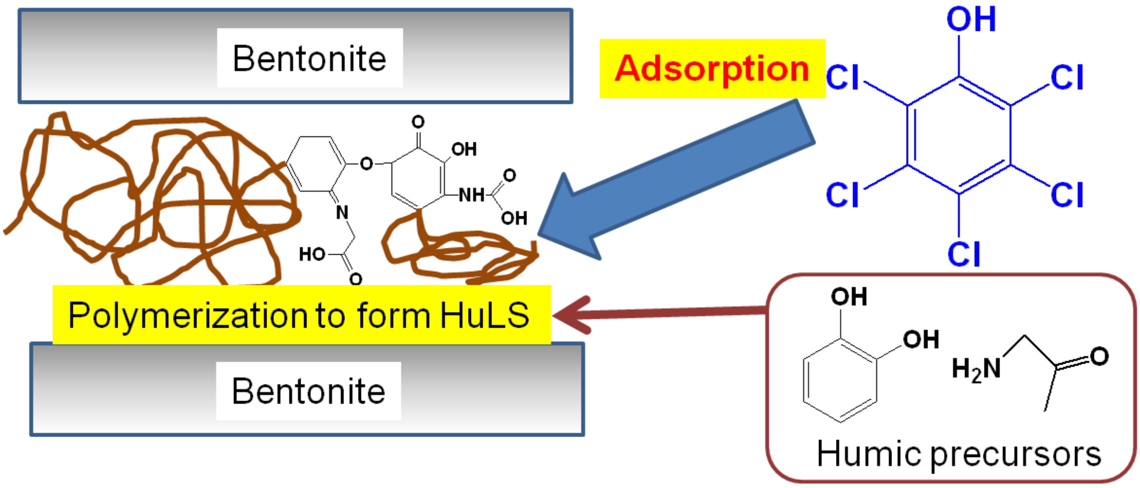
Graphical Abstract

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

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> 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. >

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

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Abstract

Humic substances have natural surfactant characteristics and have a relatively high affinity for pentachlorophenol (PCP). However, humic substances cannot be loaded into bentonite via intercalation because of their larger size. In the present study, a humin-like substance (HuLS) was prepared by polycondensation reactions of humic precursors, such as glycine and catechol, and the product was loaded into bentonite. XRD patterns showed that the basal spacing, calculated from the montmorillonite peak, for the HuLS-bentonite complex was larger than that for bentonite itself, which is indicating that the intercalation of HuLS was successful. The adsorption capabilities of PCP were evaluated from adsorption isotherms at pH 4.0, 5.5 and 6.5. At all pH values, the linear adsorption coefficients of PCP, K_d (L kg^{-1}), for the HuLS-bentonite complex (37 at pH 6.5, 247 at pH 5.5 and 804 at pH 6.5) were significantly larger than those for bentonite itself (not determined at pH 6.5, 40 at pH 5.5 and 94 at pH 4). These results show that the adsorption capabilities of PCP can be enhanced by loading HuLS onto bentonite. In addition, the K_d values for bentonite and the HuLS-bentonite complex were found to be pH-dependent, in that the K_d value decreased with increasing pH. Because of the pK_a for PCP (4.75), more than 90% of the PCP was present as the anionic form at pH 5.5 and 6.5. In addition, the values for the Zeta potentials for bentonite and the HuLS-bentonite complex remained negative at pH 2 – 12 and decreased with increasing pH. It thus appears that electrostatic repulsion between the anionic form of PCP and the adsorbents can affect the adsorption capabilities.

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

1. Introduction

Pentachlorophenol (PCP) has been utilized in the past as a biocide in wood preservation industries and other pesticide applications. The disposal of these wastes has resulted in serious soil, leachates, followed by contamination of the groundwater (Laine et al., 1997; Varank et al., 2011). The acute toxicity of PCP to biota constitutes a threat to ecosystems as well as having detrimental health effects in humans (Farah et al., 2004). Thus, adsorbents for preventing PCP leaching from contaminated sites and for removing PCP from contaminated water are urgently needed. Clay minerals are particularly effective adsorbents in barrier materials and can be used to prevent ionic contaminants, which are eluted from landfills to external environments (Gautier et al., 2009; Koutsopoulou et al., 2010; Le Forestier et al., 2011). Clay minerals are, however, ineffective in removing hydrophobic organic contaminants from water. It is possible to modify clay minerals by interaction with surfactants, such as quaternary alkylammonium salts, and this results in the formation of organophilic solid materials (Bergaya and Lagaly, 2001; De Paiva et al., 2008; Kooli et al., 2009). The surfactants were loaded on the bentonite via the intercalation, and the resulting surfactant-intercalated bentonite complex was found to be effective in removing PCP from water (Stapleton et al., 1994; Bouras et al., 2010; Zhang et al., 2012). However, some investigators have suggested that artificially synthesized cationic surfactants like quaternary alkylammonium cations are themselves toxic (Utsunomiya et al., 1997).

On the one hand, humic substances are naturally occurring, surface active materials that have amphiphilic characteristics, thus giving them both hydrophilic and hydrophobic properties. Such functions of humic substances can serve as media for the sorption of hydrophobic organic contaminants, such as polycyclic aromatic hydrocarbons (Fukushima et al., 1997; Wang and Xing, 2005), polychlorinated dibenzo-*p*-dioxins (Yabuta et al., 2004; Tanaka et al., 2005; Fukushima et al., 2006) and chlorophenols (Robinson and Novak, 1994; Paolis and Kukkonen, 1997). In addition, it has been reported that the affinity of hydrophobic organic contaminants for clay minerals can be enhanced by complexation with humic substances (Terashima et al., 2003; He et al., 2006). Thus, humic-clay complexes represent potentially effective and non-toxic adsorbents. The hydrodynamic radii of humic substances have been reported to be in the range of 22 – 71 Å (Kawahigashi et al., 2005). Thus, it would be difficult to intercalate naturally occurring humic substances into the interlayer, because of the smaller spacing of the bentonite (approximately 10 Å) (Grim, 1962). Regarding the abiotic formation of humic substances from their precursors, it is known that minerals such as birnessite, kaolinite, allophane and bentonite can catalyze the formation of dark-colored polymers like humic substances from humic precursors, such as amino acids and phenols (Shindo and Huang, 1984, 1985; Wang and Huang, 1989; Miura et al., 2009; Miura et al., 2011). The formation of humic-like substances via polycondensation reactions of the humic precursors, such as glycine and catechol, by catalytic power of an allophane mineral cannot only produce humic acid-like substance (HaLS) in aqueous phase of the reaction mixtures but also could produce humin-like substances (HuLS) on the allophane surface (Okabe et al., 2011). Such a HuLS-allophane would be expected to have a higher affinity for PCP compared to the allophane mineral alone (Okabe et al., 2011). It has been reported that humic precursors, such as phenols and amino acids, can be intercalated into the interlayers of bentonite (Banat et al., 2000; Kollár et al., 2003). Thus, HuLS can be produced in the interlayer via polycondensation reactions. The resulting HuLS-bentonite complex may serve as an excellent adsorbent for hydrophobic organic contaminants, such as PCP. In the present study, a commercial bentonite was used as a mineral, and the HuLS-bentonite complex was prepared via polycondensation reactions of catechol and glycine as humic precursors in the presence of bentonite. In addition, relations between surface properties and adsorption behaviors of PCP for the prepared HuLS-bentonite complex were compared with those for a non-modified bentonite.

2. Materials and Methods

2.1. Materials

Catechol (purity >99.0 %) and glycine (purity 99 %) were purchased from Tokyo Chemical Industry (Tokyo, Japan) and Nacalai Tesque (Kyoto, Japan), respectively. PCP (purity 98 %) was purchased from Sigma-Aldrich (St. Louis, MO, USA). A powdered bentonite sample was purchased from Nacalai Tesque. Ultrapure water, prepared using a Millipore ultra-pure water system from distilled water, was used in all experiments.

2.2. Preparation of HuLS-bentonite complex

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

2.3. Separations of HaLS and HuLS

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

2.4. Analysis of samples

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

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

A stock solution of PCP (1 mM) was prepared by dissolving it in aqueous 0.2 M KOH. Aliquots 0.15, 0.45, 0.90, 1.80, 2.70 or 3.60 mL samples of the PCP stock solution were diluted to 20 mL with aqueous 0.1 M KCl, and the pH values of these solutions were adjusted to 4.0, 5.5 or 6.5 with aqueous solutions of KOH and HCl. These solutions were then diluted to 30 g with aqueous 0.1 M KCl the pH of which was adjusted to the desired value with aqueous KOH and HCl (solution A). A 12 mL aliquot of aqueous 0.1 M KCl was added to 160 mg portion of the powdered bentonite or HuLS-bentonite complex. The pH of the dispersion was adjusted to the desired pH by adding aqueous 0.1 M KCl containing 0.01 M HCl using an AUT-501 auto-titration system (DKK-TOA, Tokyo, Japan). After reaching a constant pH of 4.0, 5.5 or 6.5, the dispersion was finally diluted to 20 mL with aqueous 0.1 M KCl the pH of which was adjusted to the desired value (solution B). A 0.4 mL aliquot of solution A, 1.25 mL of solution B and 0.35 mL of the aqueous 0.1 M KCl the pH of which was adjusted to the desired value, were pipetted into a 10-mL glass tube. The glass tube was sealed with parafilm, and allowed to shake 25°C for 24 h. Preliminary experiments confirmed that a shaking period of 24 h was sufficient to achieve equilibrium and the variations of pH values were within ±0.2 during the period of shaking. After the incubation, the mixture was centrifuged for 10 min at 3000 rpm, and a 1 mL aliquot of the supernatant was then mixed with the 0.5 mL of 2-propanol. PCP in this mixture was analyzed by HPLC, based on the conditions in a previous report (Okabe et al., 2011). The adsorption of PCP can be represented using the following Freundlich-type isotherm equation (Wen et al., 2007).

$$q_s = K_f \times C_e^{\ n} \qquad (1),$$

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

$$q_s = K_d \times C_e \qquad (2),$$

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

3. Results and Discussion

3.1. Chemical compositions of the HaLS and HuLS

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

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

FT-IR spectra of the HuLS-bentonite complex, bentonite, HuLS and HaLS are shown in Fig. 1. While HuLS contained a relatively higher ash content (12.2% in Table 1), the observed peaks for HuLS were not overlapped with those for bentonite and HuLS-bentonite complex. Thus, it does not appear that ash from the bentonite residues has any significant influence on the FT-IR spectrum of HuLS. As compared to the spectrum of HaLS, the peak at around 2920 cm^{-1} appeared in the case of HuLS (Fig. 1, ▲). This peak corresponds to C-H stretching of methylene groups, and is consistent with the trend for the H/C molar ratio. In addition, the peak at 1154 cm^{-1}, corresponding to C-O-H bending or C-O stretching of aliphatic alcohols and ethers, appeared in the spectrum of HuLS (Fig. 1, ●). The relative compositions of different carbon functional groups were estimated from solid-state CP-MAS ^{13}C NMR spectra (Table 2). The alkyl carbon content for HuLS (30%) was much larger than that for HaLS (13%). These results indicate that HuLS has more aliphatic characteristics than HaLS.

3.2. Characterization of bentonite and HuLS-bentonite complex

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

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

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

Phenolic hydroxyl group protons in PCP can dissociate and the pK_a value for such a compound is known to be 4.75 at 25°C. Based on this, species distribution curves for the phenol (PCP) and phenolate (PCP^-) forms were calculated, and the results are shown in Fig. 3. The pH ranges for landfill leachates from chlorophenol-contaminated wastes are reported to be 4.5 – 7 (Laine et al., 1997; Varank et al., 2011). At this pH, more than 50% of the PCP would be present as PCP^- and would be difficult to adsorb to bentonite and HuLS-bentonite complex, both of which have anionic surfaces because of electrostatic repulsion. However, the zeta potentials at pH 4.5 – 7 for the HuLS-bentonite complex were larger than those for the bentonite, as shown in Fig. 3. Thus, a higher adsorption of PCP to the HuLS-bentonite complex would be expected due to the reduction of electrostatic repulsion. In the present study, pH values of 4.0, 5.5 and 6.5 were selected for use in the adsorption tests for PCP.

3.3. Adsorption characteristics of PCP

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

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

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

4. Conclusions

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

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Figure captions

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

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

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

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

Table
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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 ^{13}C NMR spectra of HuLS and HaLS.

Chemical shift (ppm)	Assignments	Composition (%)	
		HuLS	HaLS
0 - 50	Alkyl-C	30	13
50 - 110	*N*, *O*-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.

Inorganic elemental compositions (Wt %)[a]

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

Surface properties

Sample	pH[c]		SSA[d] (m^2 g^{-1})	CEC[d] (cmol kg^{-1})
	H_2O	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

[a] Organic carbon contents: bentonite, not detected; HuLS-bentonite complex, 1.1%. [b] Not detected.
[c] Bentonite : liquid = 1:15. [d] Specific 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^2[b]	K_d[c]	r^2[b]
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

[a] mol kg^{-1} M^{-n}. [b] Square of correlation coefficients for the curve-fitting. [c] L kg^{-1}. [d] Not determined.

Figure
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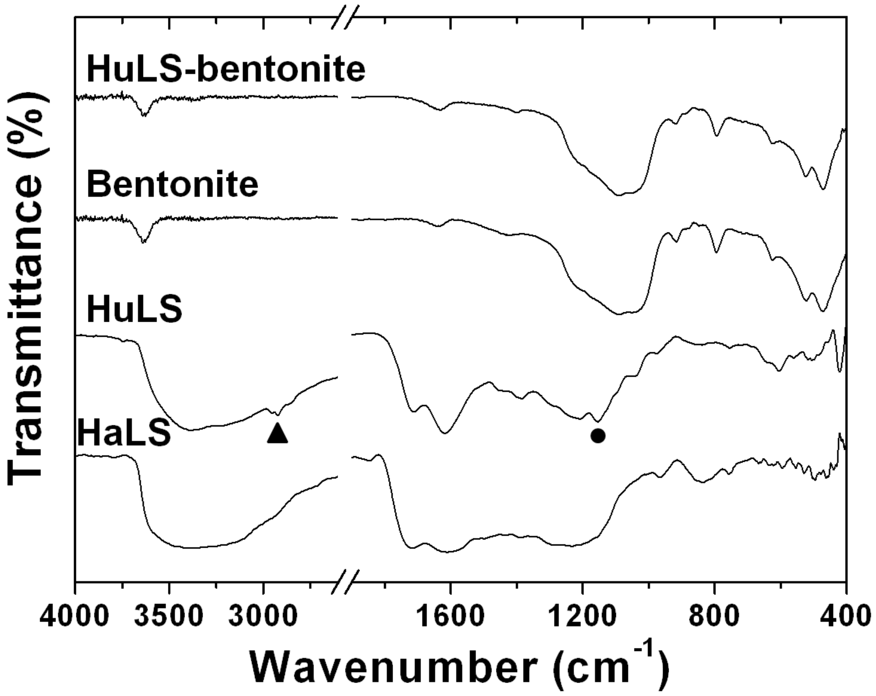
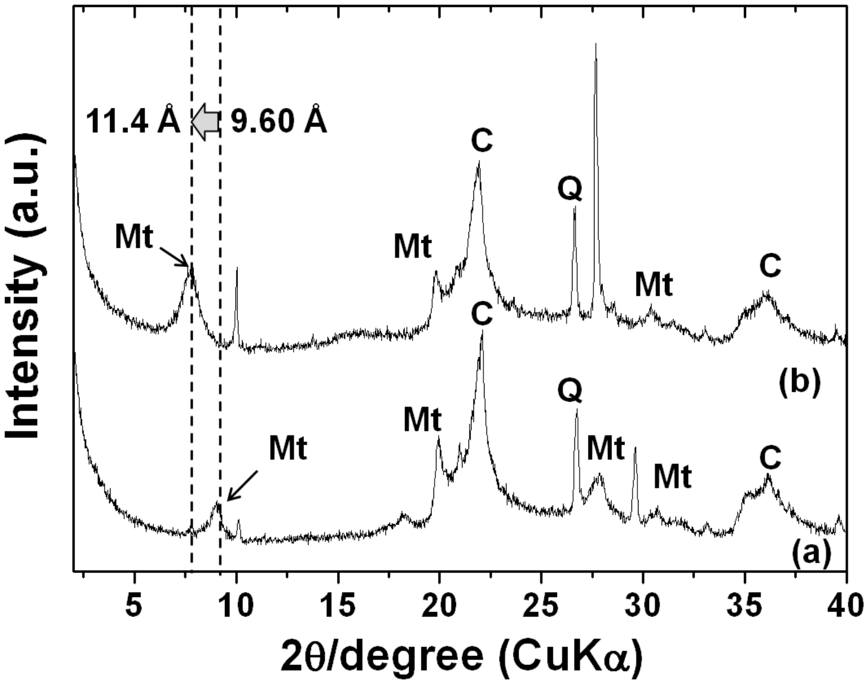


Fig. 1. (CLAY4661)



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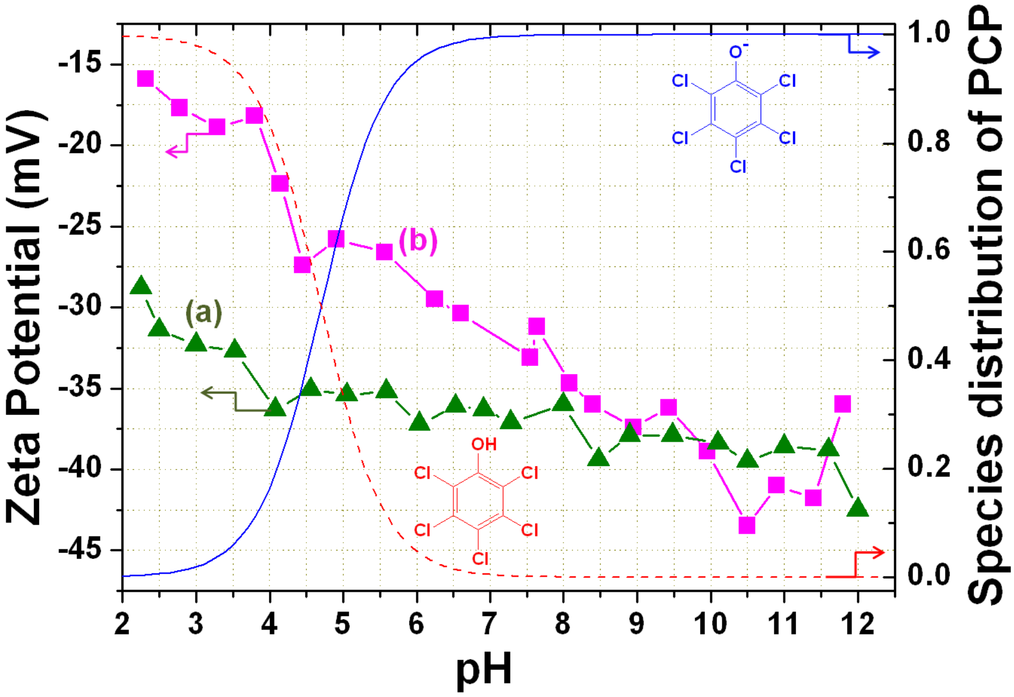

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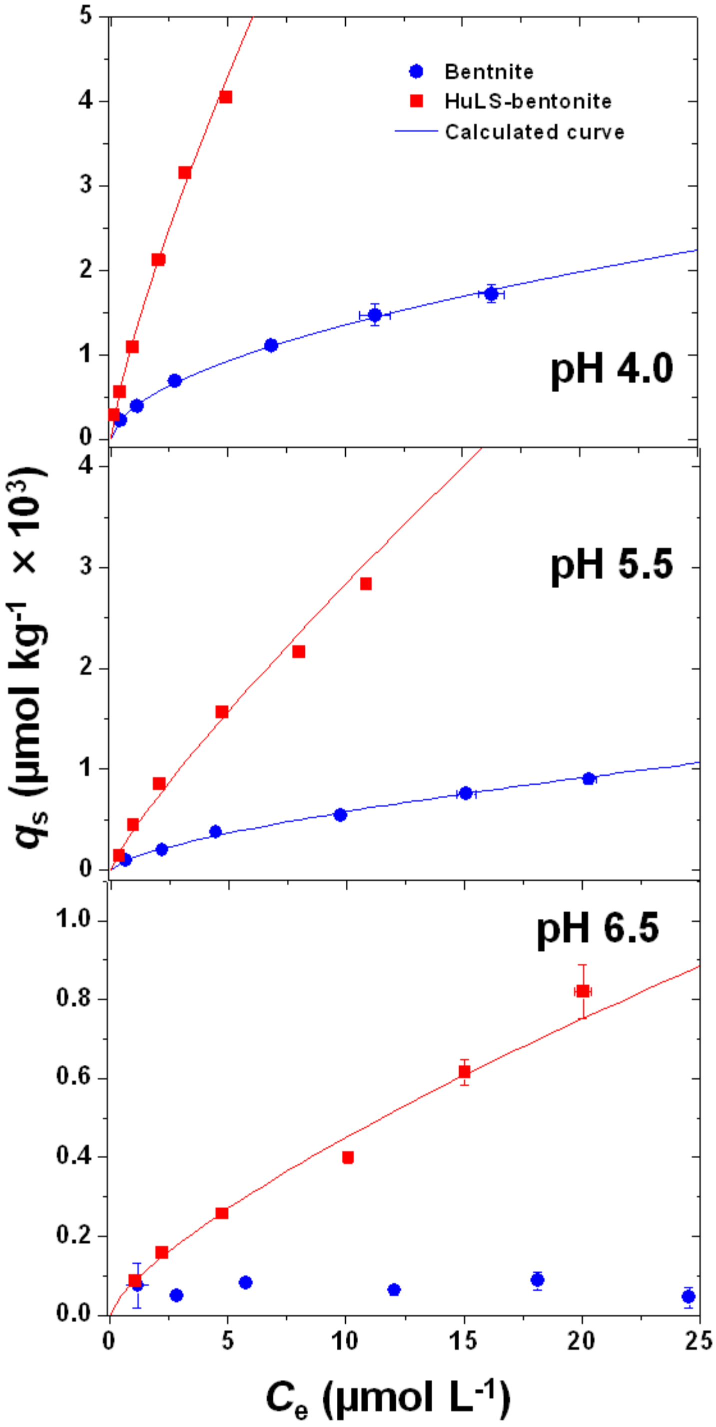

Fig. 4. (CLAY4661)