Colloids and Surfaces A: Physicochem. Eng. Aspects 396 (2012) 224–232

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Controlling aqueous sorption of humic substances on silica gel by directed alkoxysilyl-derivatization of their functionalities

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ARTICLE INFO

Article history:
Received 30 August 2011
Received in revised form
22 December 2011
Accepted 23 December 2011
Available online 5 January 2012

Keywords:
Humic substances
Directed modification
Aqueous sorption
Aminosilanes
Anchoring groups
Immobilization

ABSTRACT

In this study we explored a possibility for enhancing aqueous sorption of humic substances (HS) onto hydroxylated surfaces (e.g., silica gel) by increasing modification rate of their most abundant functional groups – carboxyls with mineral-adhesive alkoxysilyl moieties. The synthesis included treatment of dried humic material with 3-aminopropyl trimethoxy silane (APTS) capable of forming amide bonds with carboxyl groups of HS under anhydrous conditions. The reaction was run at six different HS to APTS ratio for achieving different modification degrees of the carboxyl groups in the humic backbone. The obtained derivatives were characterized using elemental analysis, 13C NMR Spectroscopy, Fourier transform infrared spectroscopy, and size exclusion chromatography that confirmed quantitative incorporation of alkoxysilyl-moieties into HS structure. Aqueous adsorption was investigated in 0.028 M phosphate buffer using silica gel as a surrogate for mineral surface. Both distribution coefficients as well adsorption capacities paralleled the amount of alkoxysilyl-moieties incorporated into backbone of the parental HS. The adsorption capacity reached its maximum value of 210 mg of HS per g of SiO_2 for the APTS derivative synthesized at the equimolar reagent ratio. This value was comparable to the amount of the same HS immobilized onto the APTS-treated silica gel (265 mg of HS per g of SiO_2). Adsorption of alkoxysilyl-derivatives was found to be irreversible under conditions studied. Conclusively, we believe that the directed modification of HS by incorporating alkoxysilyl-moieties is well suited for producing humic derivatives with controllable affinity for aqueous sorption onto hydroxylated surfaces.

1. Introduction

Humic substances (HS) are recalcitrant, highly polydisperse mixtures of natural polyelectrolytes that occur throughout the environment, including aquifers [1]. The basic structure of HS includes a hydrophobic aromatic backbone highly substituted with various functional groups (mostly carboxyls and hydroxyls), aliphatic side chains, and an aliphatic carbohydrate-protein periphery [2].

Due to their ability to chemically bind with metals and organic compounds, HS serve a dual role in terms of regulating the migration of contaminants in the environment. Both roles are considered in our review [3], in which we show humic coatings on mineral surfaces act as highly reactive substrates for contaminant sorption, while dissolved or particulate HS facilitate the solubilization and transport of metals, radionuclides, and organic contaminants. There is ample evidence of humic-facilitated mobilization of radionuclides, both in the field [4–6] and in the laboratory [7–9]. Numerous batch and column studies show humic colloids affecting actinide sorption and transport [10–12]. On the other hand, enhanced sorption of metals and radionuclides on humic-rich solids (silts and bottom sediments) has been reported [13–16]. It was shown that HS can retard trace element migration either by sorption to surfaces or by filtration into the porous medium [17–19].

As such, HS hold a great promise to function as amendments to mitigate the environmental impacts of contaminants and as active agents in remediation. In particular, the capability of immobile HS

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doi:10.1016/j.colsurfa.2011.12.068

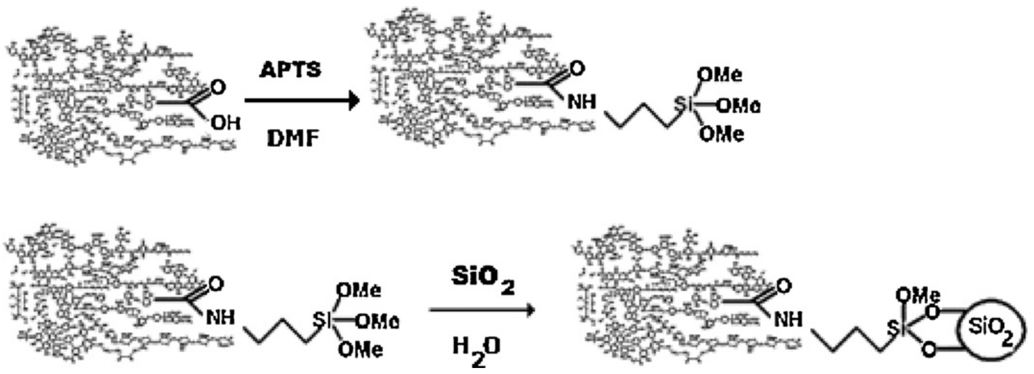

Fig. 1. Schematic reaction pathways for synthesis of alkoxysilyl-humic derivative using 3-aminopropyltrimethoxysilane (APTS) in anhydrous organic solvent (e.g., dimethyl formamide, DMF) and for its consequent immobilization on silica gel surface in aquatic medium.

to retard migration of different chemical compounds (both organic and inorganic) can be used to sequester contaminants from aqueous solutions. The strength of this retention is governed by the properties of humic materials. Hence, a phase-switch from mobile humic colloids to immobile humic coatings can be used to bring about sequestration of dissolved or humic-bound contaminants from the water phase onto a solid support. This phase switch can be achieved with humic materials that possess a high affinity for mineral surfaces.

Previous efforts to immobilize HS on mineral surfaces (e.g., silica gel) required modifications of the mineral support followed by treatment with non-modified humics [20–28]. Koopal et al. [20] described various approaches of modifying silica gel to obtain covalently bound humic coatings. As a rule, carboxyl groups, which are typically abundant within the natural humic materials, were used to creating covalent bonds between humic molecules and inorganic support. For example, Szabo and coworkers [21–25] modified silica gel with 3-aminopropyltrimethoxysilane (APTS) and then treated it with a solution of HS. A similar approach was taken by Prado et al. [26–28] who used epoxy-modified silica surfaces for humic immobilization. These efforts were mostly applied for the preparation of sorbents capable of binding both hydrophobic organic contaminants and metal ions to imitate organic rich natural particles (e.g., those of soils or sediments) [29]. Similar approach was used in [30] to bind HS covalently on the surface of self-assembled monolayers of aminosilanes immobilized onto oxidized Si-wafer for Atomic Force Microscopy (AFM) studies.

Binding humic acids to mineral surfaces with the aid of metal-oxo bridges is another approach used mostly for the in situ installation of humic permeable reactive barriers (PRB) as described in open [31] and patent literature [32]. For both methods, reactive humic barrier installation involves a two-step process: the subsurface injection of alkaline humates followed by injected solutions of acids or di- or trivalent metal salts (M = Ca, Mg, Fe) or the injection of Fe-salts to revert the negative charge of the mineral support followed up by the immobilization of humic polyanions. The success of both methods highly depends on groundwater pH and E_h. For example, a drop in E_h can bring about the reduction of Fe(III) to Fe(II) and in turn produce much lower humic-iron stability constants than with Fe(III) alone [33]. On the other hand, an increase in pH favors the dissolution of precipitated humic acid and not the formation of humic coatings on mineral surfaces.

This work is continuation of our previous studies on in situ binding of humic coatings to hydroxyl-carrying surfaces with a use of humic materials modified with functional organosilanes [34]. The corresponding alkoxysilyl humic derivatives were water soluble, but readily transferred into the solid phase by covalent bonding to the surface of silica gel. Such modified silica gel was capable of sequestering actinides in higher valence state (plutonium (V) and neptunium (V)), which was of particular importance in lieu of new solutions needed for remediation of deep and diluted aquifers contaminated with radionuclides. We suggested that injection of the alkoxysilyl humic derivatives in a form of aqueous solution into aquifer might bring about in situ installation of humic PRB capable of sequestering actinides. The corresponding technology might be particularly favorable and cost-effective for remediation of deep and diluted aquifers, while it would eliminate the need for excavation of the contaminated ground. To explore this concept in further details, we have assumed that the aqueous sorption of the alkoxysilyl derivatives can be effectively controlled by varying modification degree of functional groups within the parental humic materials.

The goal of this research was to study aqueous sorption of the humic derivatives prepared by incorporation of increasing amounts of alkoxysilyl groups into humic backbone by means of the treatment with functional organosilanes. For this purpose, a reaction of coal humic acids with increasing rates of 3-aminopropyltrimethoxy-silane (APTS) was used. The corresponding reaction pathway is shown in Fig. 1.

It is of significance to note that contrary to the previous approaches, humic derivatization is the only reaction that occurs in an organic solvent (e.g., DMF), whereas immobilization of the synthesized derivatives occurs under aquatic conditions upon contacting an appropriate solid support (e.g., silica gel) without consequent heating or drying this support. This is different from direct treatment of silica gel or mineral support with silanes described in [35]. Covalent bonding precludes the facile mobilization of humic film and of any contaminant bound to it. This might be particularly advantageous for sequestering high valence actinides from contaminated groundwater.

2. Materials and methods

2.1. Materials and chemicals

Coal humic acid was prepared by desalination of the commercially available potassium humate from leonardite (Powhumus; Humintech Ltd., Germany). The sample was acidified to pH 1, the formed precipitate of humic acid (HA) was centrifuged, dialysed, rotary-evaporated to dryness, and designated as CHP. All reagents were of analytical grade. KH_2PO_4 and $Na_2HPO_4 \times 12H_2O$ were used for preparation of phosphate buffer; toluene and N,N-dimethylformamide (DMF) were dried and used as solvents in the reactions of chemical modification of CHP. APTS was purchased from Aldrich. Silica gel 60 was purchased from Merck (specific surface area: 540 $m^2\,g^{-1}$) and used as a model of a silica-containing material.

Table 1
Elemental analyses and the content of trimethoxysilyl groups in the CHP-APTS derivatives prepared with increasing rates of APTS in the reaction mixture.

Sample	Content of elements (% mass)[a]					$Si(OCH_3)_{3(exp)}$[c], mmol g^{-1}	$Si(OCH_3)_{3(th)}$, mmol g^{-1}	M[d] (g g^{-1} HA)
	C	H	N	O[b]	Si			
CHP	59.1 ± 0.1[e]	4.31 ± 0.01	1.24 ± 0.05	35.4	2.11 ± 0.01	0	0	0
CHP-APTS-5	55.5 ± 0.1	4.90 ± 0.02	6.44 ± 0.06	30.6	2.58 ± 0.01	0.17	0.15	0.05
CHP-APTS-10	54.7 ± 0.2	5.21 ± 0.03	7.37 ± 0.07	30.0	2.68 ± 0.01	0.2	0.3	0.1
CHP-APTS-20	53.3 ± 0.1	4.97 ± 0.02	5.51 ± 0.05	32	4.22 ± 0.04	0.7	0.6	0.2
CHP-APTS-50	51.5 ± 0.1	5.53 ± 0.03	7.82 ± 0.05	28.7	6.44 ± 0.03	1.5	1.5	0.5
CHP-APTS-100	61.8 ± 0.5	7.40 ± 0.05	6.72 ± 0.08	15.0	8.25 ± 0.05	2.2	2.9	1.0
CHP-APTS-200	43.2 ± 0.1	5.35 ± 0.03	8.76 ± 0.03	31.4	11.3 ± 0.05	3.3	3.5	2.0

[a] The data of elemental analysis are corrected for ash content.

[b] Oxygen was calculated as a difference.

[c] Trimethoxysilyl ($Si(OCH_3)_3$) group content was calculated from the content of Si given in Table after subtraction of Si content of 2.11% in the parental sample of CHP. Subscript "exp" stands for experimentally determined value, "th" stands for the theoretical value.

[d] M stands for the amounts of APTS (g g^{-1} HA) used for the synthesis of the corresponding humic derivative.

[e] ±stands for standard deviation for three parallel measurements of the element content.

2.2. Preparation of alkoxysilyl-humic derivatives with different reagent ratio

CHP (1 g) was placed into a flask and 60 mL of dry DMF were added. Next, the APTS was added dropwise under continuous stirring. The reaction was carried out for 20 h at 120 °C. The DMF was rotary-evaporated, and the reaction product was dried in a vacuum oven at 40 °C for 4 h. It was then homogenized and stored in a desiccator. The reaction was run at six different APTS-to-humics ratios, nominally: 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 g of APTS per g of CHP. These ratios corresponded to different extents of modification associated with carboxyl groups available within the humic backbone. The content of carboxyl groups in CHP was determined using Ca-acetate method [36] and accounted for (3.8 ± 0.2) mmol g^{-1}. Given that 1 g APTS contains 3.8 mmol of amine-groups, a 1:1 molar ratio of COOH and NH_2 groups was reached by treating 1 g of CHP with 1 g (1 mL) of APTS.

2.3. Structural analyses of the alkoxysilyl-humic derivatives and equipment

CHN analyses were performed on a Carlo Erba Strumentazione automatic analyzer. The Si content was determined using conventional spectrophotometric method which basic principles are described in (e.g., [37]). Ash content was determined as a weight residue after combustion of the humic sample placed in a quartz tube at 750 °C during 40 min.

Fourier transform infrared spectroscopy (FTIR) analyses were performed using a IR-200 spectrometer (ThermoNicolet, USA). Samples were pressed in KBr pellets.

^{13}C NMR spectra were acquired on solutions of humic materials in 0.3 M NaOD at a concentration of 100 g L^{-1} using a 5 mm broadband observe probe head on a Bruker AC 400 (Rheinstetten, Germany) spectrometer operating at 100.62 MHz for ^{13}C, using inverse gate decoupling, a single spin-echo sequence (delay 10 μs) and a interpulse delay of 8 s (acquisition time: 229 ms for HS and 917 ms for selected modified derivatives, respectively; 90-deg (^{13}C): 8.6 s; $T = 303$ K; SW = 71,428 Hz). These conditions have been previously shown to provide quantitative determination of carbon distribution among the main structural fragments of HA [38]. H_3COH/D_2O (80/20 v/v; $\delta = 49.0$ ppm) was used as an external chemical shift reference.

Size Exclusion Chromatography (SEC) analyses were conducted as described in [39]. A liquid chromatography system consisted of a solvent pump (Abimed), a packed column, and a UV–vis detector with variable wavelength. The UV-absorbance was measured at 254 nm. The SEC column was 25 mm × 200 mm packed with Toyopearl HW-55S. Phosphate buffer (0.028 M, pH 6.8) was used as a mobile phase at a flow rate of 1 mL min^{-1}. For SEC analysis, a sample of HS was dissolved in the minimum amount of NaOH and diluted to the concentration of 100 mg L^{-1} with a buffer solution used as a mobile phase; aliquots of this solution (1 mL) were injected for analysis. The SEC column was calibrated using sodium polystyrenesulfonates (PSS), kDa: 14.0; 20.7; 45.1; and 80.84. Standard kits were purchased from the Polymer Standard Service (Mainz). Blue dextran (2000 kDa) served as a void volume probe, and acetone - as a permeation volume probe.

2.4. Sorption experiments

Sorption experiments were conducted at room temperature ($T = 22 \pm 2$ °C) in the presence of air on the day light using silica gel as model support. Solutions of humic derivatives at concentrations of 0.01–5 g L^{-1} were prepared by dissolving corresponding amounts of modified HS in several drops of concentrated NaOH and adjusting volumes to 10 mL with phosphate buffer (0.028 M, pH 6.8). An aliquot (10 mL) of each prepared solution was added to 0.1 g of silica gel. Resulting suspensions were placed into an overhead-shaker for 3 days. To measure dissolved concentration of humic derivatives, the optical density of the solutions was monitored at 254 nm. The calibration curves were plotted for each humic derivative used in this study to account for a substantial decrease in light absorbing capacities of the derivative along with an increase in its modification degree. This was an expected change due to an increase in aliphatic character of the highly modified humic materials (Table 1). A UV–vis spectrometer (Cary 50, Varian Inc., U.S.A.) was used for measuring absorbance of the corresponding solutions. Gathered data were used to calculate the amount of HS sorbed onto silica gel as shown below:

$$\text{Mass of HS (mg) sorbed on 1 g of } SiO_2 = (\Delta C_{HS}(\text{mg mL}^{-1})V_{\text{solution}}(\text{mL}))/\text{m(g)}$$

where ΔC_{HS} is a difference between total (C_0) and equilibrium (C_{eq}) concentrations of HS in the experimental solution, $V_{solution}$ is the volume of HS solution used for sorption experiments, m is the weight of silica gel (SiO_2), g.

2.5. Desorption experiments

Desorption experiments were conducted on the silica gel covered with immobilized HS. Following sorption of humic derivatives to silica gel, 10 ml of 0.028 M phosphate buffer at pH 6.8 were added, shaken on the overhead shaker for 24 h, centrifuged and resuspended with fresh buffer solution for three times. After desorption, the C content (% mass) was determined on the silica gel. This was compared with the carbon content measured before desorption.

2.6. Preparation of aminopropyl silica gel

Surface modification of silica gel particles with APTS was performed as described in [26]. In brief, silica gel was dried by azeotropic distillation with dry toluene. 4 g of dry silica in 15 ml of dry toluene were stirred at room temperature with 3 ml of APTS under atmosphere of argon. Then, the modified silica was centrifuged and transferred to a vacuum box where curing was performed for 20 h under reduced pressure at 150 °C. The resulting substrate was assigned a cipher Si-APTS.

The amount of APTS immobilized on the silica surface was calculated from the data of elemental analysis: Si-APTS [C(%): 8.4; N(%): 3.26] and accounted for 1.2 mmol g^{-1}.

2.7. *Immobilization of HS on the aminopropyl silica gel*

The substrate obtained above was used for immobilization of CHP. It was carried out in DMF according to [20]. In brief, 300 mg of CHP were suspended in 30 mL DMF and added with 1.0 g Si-APTS. Another 20 mL DMF were added and the suspension was heated for 20 h at 120 °C under continuous stirring. The product obtained was washed repeatedly with DMF until supernatant became colorless. The obtained product was assigned a cipher CHP-APTS-SiO_2(direct).

3. Results and discussion

3.1. *Structural features of the humic derivatives with incorporated alkoxysilyl-groups*

Modifications of humic acids from leonardite (CHP) with APTS were carried out at six different molar ratios of APTS to CHP aimed at modification of 5, 10, 20, 50, and 100% of carboxyl groups in CHP. One experiment was conducted with APTS in double excess of available carboxyl groups. Its purpose was to evaluate complete modification of carboxyl groups of HS to amide groups upon treatment with APTS. The experiments were conducted in the anhydrous organic solvent to avoid hydrolysis of trimethoxysilyl-groups. Elemental analyses of the humic derivatives including the content of silicon are summarized in Table 1. To follow closer the modification efficiency, the silicon content was used to calculate the amount of trimethoxysilyl-groups incorporated into the humic backbone.

It can be deduced from Table 1 that the amount of incorporated trimethoxysilyl-groups gradually increased with increasing rates of APTS in the reaction mixtures indicating successful modification of HS. However, full modification of carboxyl groups of CHP was achieved only for reaction conditions with APTS present in double excess to the amount of carboxyl groups. It could be connected to non-homogeneous spatial distribution of carboxyl groups within the humic polymers which might impact greatly favorability of the reaction: the surface carboxyl groups would undergo modification much easier as compared to carboxyl groups involved in intra- and inter-molecular binding. In its turn, In its turn, a lack of the distinctive trend in the content of nitrogen along with an increase in the APTS rate (Table 1) might be explained by the presence of residual quantities of the solvent used in this study (DMF) in the reaction products. This is supported by somewhat higher content of nitrogen in the derivatives as compared to the expected one, and by low variation of its value for different reaction conditions.

All derivatives were soluble in aqueous alkali solutions up to concentrations from 5 to 10 g L^{-1}. The solubility was reduced with an increase in modification degree of the carboxyl-groups and was minimal for the derivative with full modification of those (CHP-APTS-200). In general, it can be concluded that the proposed synthetic approach allows for control of the amount of alkoxysilyl units incorporated into the molecular structure of humics leading to derivatives with the desired modification degree.

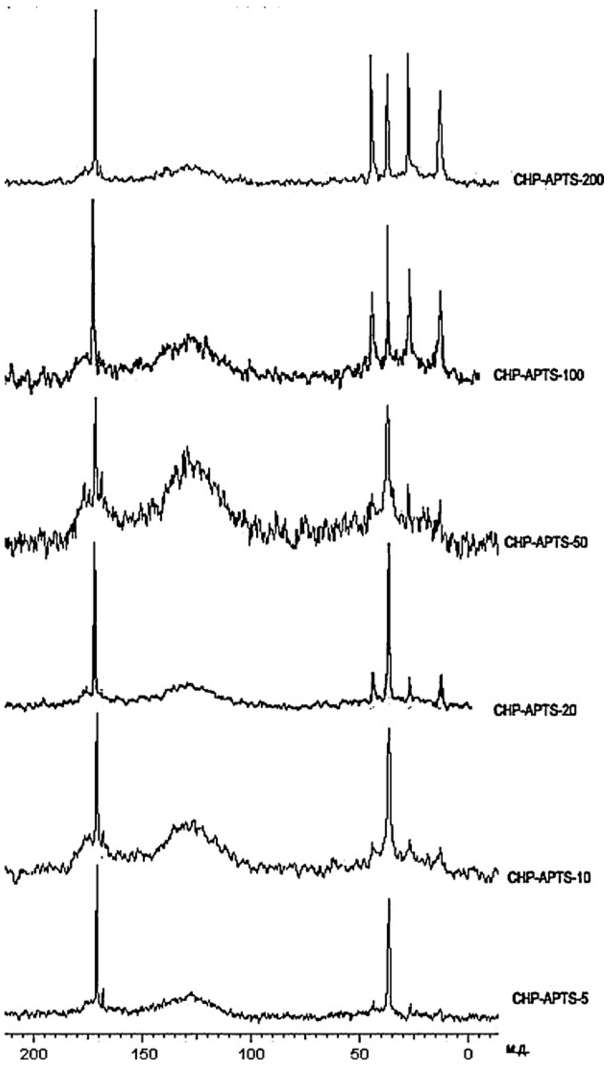

Fig. 2. ^{13}C NMR spectra of the alkoxysilyl-derivatives of coal humic acid (CHP) with different modification degree: CHP-APTS-5, CHP-APTS-10, CHP-APTS-20, CHP-APTS-50, CHP-APTS-100, CHP-APTS-200.

Structures of the alkoxysilyl-HS were investigated by means of NMR and FTIR spectroscopy. ^{13}C NMR spectra of the APTS derivatives of CHP are presented in Fig. 2.

Structural alterations in APTS-modified HS as observed by carbon NMR (Fig. 2) included the appearance of narrow NMR resonances indicative of HS modification with rather mobile side chains and the appearance of a narrow peak in the carbonyl derivative section (XC = O; X = OH, NH, OR) with a concomitant decrease of the carboxylic envelope intensity, suggesting conversion of some HS derived carboxylic acids into amides. The gross carbon NMR assignments of aminopropyl side chains were as follows ($\delta(^{13}C)$, ppm): 36–CH_3OSi; 11, 24 and 42–methylene groups of the APTS propyl chain; 49–CH_3OH resulting from the partial hydrolysis of the methoxysilyl groups in the presence of NaOD; 169–amide bonds formed as a result of the reaction between COOH groups of humic materials and the NH_2 group of APTS, 175–residual COO^- groups.

FTIR spectra of all APTS-derivatives of CHP are shown in Fig. 3. The spectra were normalized to the intensity of C–H stretching vibrations (2920 cm^{-1}) to provide a better comparison between derivatives representing different degrees of modification.

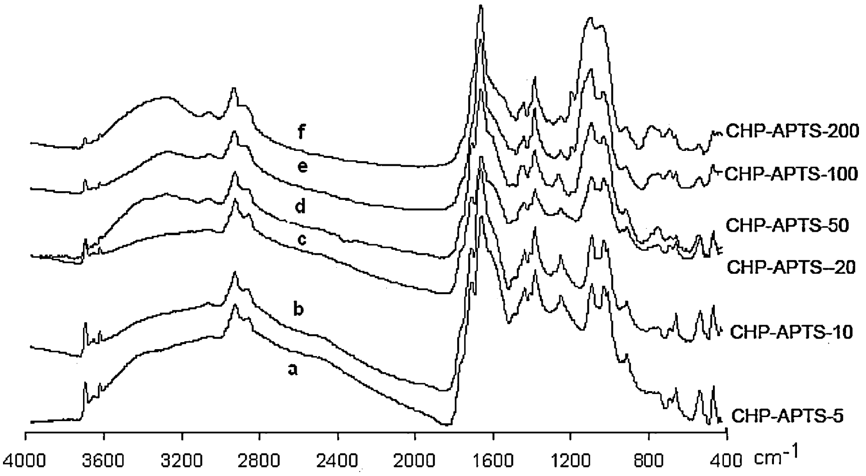

Fig. 3. FTIR spectra of the alkoxysilyl-humic derivatives with different modification degree: (a) CHP-APTS-5, (b) CHP-APTS-10, (c) CHP-APTS-20, (d) CHP-APTS-50, (e) CHP-APTS-100, (f) CHP-APTS-200.

The spectra of all derivatives show the presence of absorption frequencies characteristic of APTS, nominally: 900–750 cm^{-1} (Si–O), 1110–1000 cm^{-1} ($Si–OCH_3$), 1250 cm^{-1} ($Si–CH_2$), 1470–1350 cm^{-1} (CH_2, bending), 2950–2800 cm^{-1} ($–CH_2$, stretching). This can be interpreted as an evidence of successful modification. Of particular importance is that along with increasing modification, an associated decrease in the intensity of COOH-peaks (1720 cm^{-1}) and an increase in the intensity of amide bonds (1690 cm^{-1}) were observed. These findings again supported the claim that the synthesis described herein produces humic derivatives with controllable amounts of the alkoxysilyl groups. FTIR data were in good agreement with results of the elemental analysis which showed substantial increase in the content of silicon and nitrogen along with an increase in modification degree of the derivatives.

Molecular weights of humic derivatives were estimated by SEC. For all alkoxysilyl-derivatives, SEC elution curves were characterized with very wide monomodal distributions (Fig. 4). Corresponding molecular weight characteristics including number- and weight-averaged molecular weights (M_N and M_W, respectively) and polydispersity (a ratio of M_W to M_N values) are summarized in Table 2.

Table 2
Number- and weight averaged molecular weights (M_n and M_w, respectively) and polydispersity (M_w/M_n) of the humic materials studied.

Sample	M_n (kDa)	M_w (kDa)	M_w/M_n
CHP	1.8 ± 0.2[a]	6.0 ± 0.4	3.3
CHP-APTS-5	1.1 ± 0.2	8.7 ± 0.6	7.9
CHP-APTS-10	1.4 ± 0.2	8.8 ± 0.3	6.2
CHP-APTS-20	1.7 ± 0.2	8.6 ± 0.3	5.0
CHP-APTS-50	2.1 ± 0.4	11.6 ± 0.4	5.5
CHP-APTS-100	2.6 ± 0.4	12.7 ± 0.3	4.9
CHP-APTS-200	2.2 ± 0.3	15.7 ± 0.5	7.1

[a] ±stands for standard deviation for three parallel measurements.

A significant increase in weight-averaged molecular weight was observed with an increase in the amount of alkoxysilyl-groups incorporated into the humic backbone. The highest molecular weight of 15.7 kDa (as compared to 6.0 kDa for the parental humic material) was found for CHP-APTS-200. The same derivative was

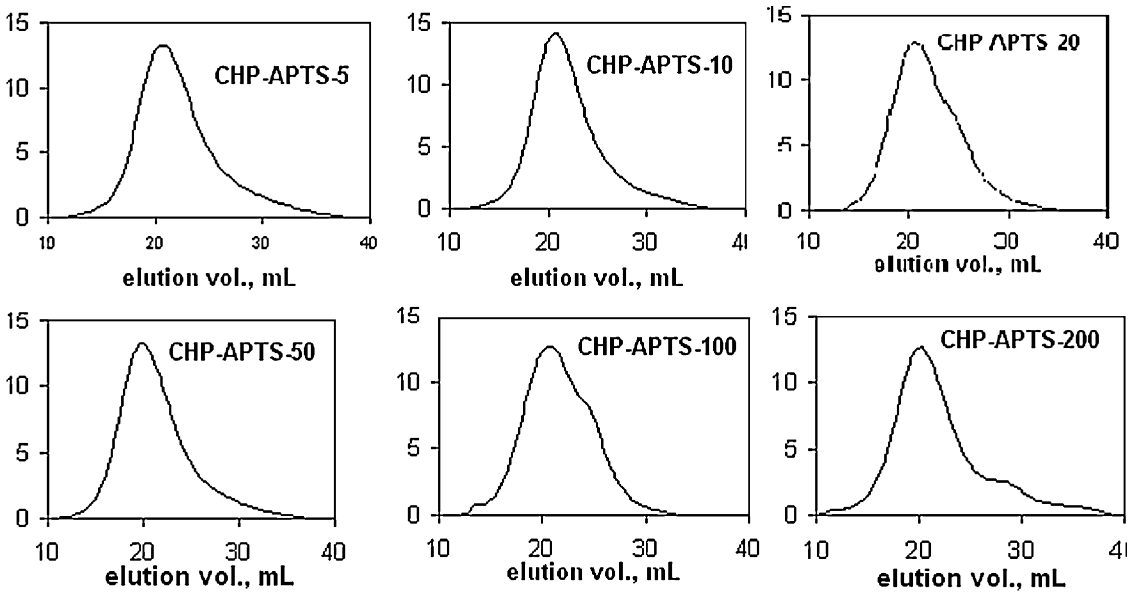

Fig. 4. SEC-chromatograms of alkoxysilyl-derivatives of CHP (coal humic acid) with different modification degree.

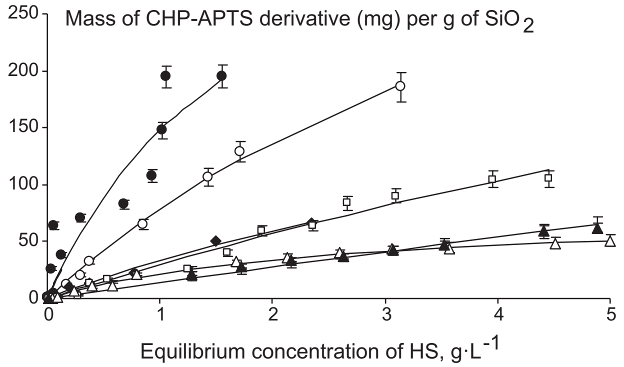

Fig. 5. Adsorption isotherms of the alkoxysilyl-derivatives of CHP with different modification degree: ▲, CHP-APTS-5; △, CHP-APTS-10; □, CHP-APTS-20; ♦, CHP-APTS-50; ○, CHP-APTS-100; ●, CHP-APTS-200.

characterized with very high polydispersity reaching a value of 7. Of importance is that an increase in molecular weight was consistent with the degree of modification.

3.2. Aqueous sorption–desorption of alkoxysilyl-humic derivatives onto silica gel

The aqueous solubility of trimethoxysilyl-humic derivatives may present opportunities of using these materials to create humic coatings on hydroxyl-carrying surfaces of minerals in situ under aquatic conditions. To demonstrate this concept, aqueous sorption of the derivatives was examined in 0.028 M phosphate buffer at pH 6.8 using silica gel as a model support. The given conditions were used in our studies as environmentally relevant providing close to neutral pH and ionic strength of $4.4\,10^{-2}$ mol L^{-1} which can be met in many natural aquifers [40]. Sorption isotherms for the alkoxysilyl-derivatives of CHP with different modification degree are shown in Fig. 5.

It can be deduced from Fig. 5 that all alkoxysilyl-derivatives possessed much higher adsorption affinity for silica gel as compared to the parental humic material (CHP) which did not exhibit adsorption to appreciable amount under conditions used. All adsorption isotherms appeared linear below the solubility limit of each derivative (i.e., not Langmuir) which motivated the calculation of distribution coefficients K_d (L kg^{-1}) as the slope of a fitted linear model. Adsorption capacity (Q_{max}) was estimated by the content of organic carbon in the silica gel contacted with the solution of the highest concentration (5.5 g L^{-1}) of CHP-APTS derivatives (except for CHP-APTS-200 where the precipitate was formed with concentrations exceeding 4 g L^{-1}). The corresponding results are summarized in Table 3.

Results showed unmodified HS exhibited a very low adsorption capacity for silica gel (Q_{exp} values from 1 to 10 g kg^{-1} SiO_2). This is because at the conditions studied (pH 6.8) they experienced strong repulsive interactions with the negatively charged surface of silica gel. The contribution of repulsive interactions decreased along with an increase in modification degree of the derivatives while it was accompanied with a substantial drop in the surface charge of humic associates due to conversion of carboxyl to amide groups. In addition, the incorporated alkoxysilyl groups served as a function of anchoring moieties due to rapid hydrolysis to silanol groups in aqueous medium. The latter are capable of forming siloxane bonds with the surface of silica gel which drives formation of humic adlayer. This explains why alkoxysilyl-derivatives demonstrated much higher sorption capacities reaching a maximum Q_{max} value of 210 mg g^{-1} SiO_2 for the derivative with 100% modification of carboxyl groups.

The assessment of a layer thickness (h) from the Q_{max} values given in Table 3 leads to a rough estimate below 1 nm ($h = Q_{max}/540\rho$, where 540 is the surface square of silica gel in $m^2\,g^{-1}$, ρ is density of HS which we take as 1 g cm^{-3}). This suggests that the film thickness does not exceed a monolayer. The obtained estimate is in general agreement with the linear type of the adsorption isotherms (Fig. 5) corresponding to the initial part of isotherm when the saturation stage of active sites on the silica gel surface has not been reached yet. This is because of the limited solubility of the alkoxysilyl derivatives in water. As a result, the deposited amount is self-limited to a monolayer.

For the purposes of this study, particularly important is that adsorption affinities paralleled the extent of modification of the parental humic material. From degrees of modification in excess of 20%, maximum sorption was observed for CHP-APTS-200. CHP-APTS-5 and CHP-APTS-10 did not show appreciably larger sorption capacities in comparison with the parent coal HA-CHP. From the point of view of retaining desirable properties of the original HA, such as ion exchange, the optimum extent of modification appears to be 20%. The CHP-APTS-20 derivative shows substantial sorption affinity and possesses 80% of the initially available COOH-groups. This provides for ion-exchange in this derivative; but, otherwise a property suppressed as the degrees of modification increases.

It was of interest to examine quantitative relationships between the found aqueous adsorption parameters of the alkoxysilyl-derivatives and the amount of alkoxysilyl-groups incorporated into the structure of the parental humic substances. The graphs of the corresponding relationships are given in Fig. 6.

The given relationships reflect very close correlations between adsorption parameters of the alkoxysilyl-humic derivatives and the amount of alkoxysilyl-groups incorporated into the humic backbone. This shows that the aqueous sorption of the derivatives is governed by the alkoxysilyl-moieties. Hence, the proposed modification approach can be efficiently used for gaining control over adsorption properties of natural humic substances.

To assess sorption reversibility, desorption experiments were carried out with silica gels treated with solutions of each humic

Table 3

Distribution coefficients (K_d) of the APTS-derivatives in the water–silica gel system, adsorption capacity (Q_{max}) of the modified humic materials, and content of carbon in humic-treated silica gel before and after desorption with 0.028 M phosphate buffer.

Sample	K_d (L kg^{-1})	Q_{max} (g HS kg^{-1} SiO_2)[a]	C, % mass before desorption	C, % mass after desorption
CHP	8.7 ± 0.8[b]	10 ± 1	n.d.[c]	n.d.
CHP-APTS-5	12.9 ± 1.0	60 ± 5	1.0 ± 0.05	1.0 ± 0.05
CHP-APTS-10	10.5 ± 0.9	50 ± 1	1.1 ± 0.09	1.1 ± 0.09
CHP-APTS-20	26.4 ± 0.9	104 ± 8	2.3 ± 0.09	2.2 ± 0.09
CHP-APTS-50	44.8 ± 0.9	155 ± 10	4.9 ± 0.1	4.7 ± 0.08
CHP-APTS-100	69.9 ± 0.8	210 ± 12	9.2 ± 0.5	9.2 ± 0.3
CHP-APTS-200	110.0 ± 0.9	194 ± 10	11.2 ± 0.7	11.0 ± 0.7

[a] Q_{max} stands for adsorption capacity estimated by the content of HS in the silica gel contacted with the solution at concentration of 5 g L^{-1} of CHP-APTS derivatives (except for CHP-APTS-200 measured at 4 g L^{-1}.

[b] ±stands for standard deviation for three parallel measurements.

[c] n.d., "not determined".

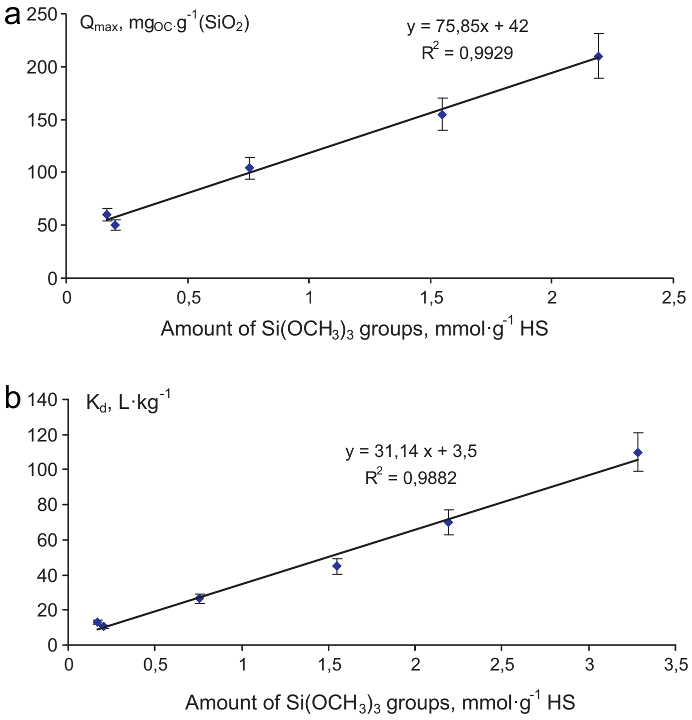

Fig. 6. Relationships of alkoxysilyl-group content within the modified humic material (CHP-APTS) versus its adsorption capacity (a) and distribution coefficient (b) with respect to silica gel in 0.028 M phosphate buffer at pH 6.8.

derivatives (5 g L^{-1}). Reacted samples of silica gel were repeatedly desorbed with 0.028 M phosphate buffer and analyzed for organic carbon content. The latter refers to the maximum sorption capacity of silica gel with respect to the trimethoxysilyl-derivatives. Results as given in Table 3 demonstrate unaltered organic carbon content, indicative of irreversible sorption of trimethoxysilyl-derivatives onto silica gel under conditions studied (pH 6.8). However, an increase in pH above 9 caused substantial desorption of the adsorbed humic layer due to instability of siloxane bonds in the range of alkaline pH.

3.3. *Comparison with the immobilization of humic substances onto modified silica gel*

The obtained values for adsorption capacities were compared with those published for the immobilization of purified Aldrich humic acid on aminopropyl silica and glutaraldehyde-activated aminopropyl silica using traditional approach [20], in which non-modified humic materials are attached onto APTS-modified silica gels. The corresponding values accounted for 124 and 60 mg HS g^{-1}, respectively, which is lower than the approach proposed here.To confirm the obtained results, the “direct” method of HS immobilization onto silica gel, shown in Fig. 7, was reproduced in this work using CHP as a humic material. The amount of CHP immobilized on the aminopropyl silica gel was 269 mg HS g^{-1} SiO_2 which is much higher than the above values [20] and comparable to the “reverse” approach proposed in this work (210 mg HS g^{-1} SiO_2) (Table 3).

Silica gels with immobilized humic materials prepared using the proposed (“reverse”) and direct approaches (CHP-APTS-100-$SiO_{2(rev)}$ and CHP-APTS-$SiO_{2(direct)}$, respectively) were analyzed using FTIR-spectroscopy (Fig. 8).

Both spectra exhibited similar peaks. The presence of the peaks characteristic of HS is evidence of a successful HS immobilization. Functional groups from HS, silica gel, APTS and the chemical bonds formed in the immobilization process contribute together to the FTIR spectra of the immobilized humic acids: the broad band at 3450 cm^{-1} and the band at 1640 cm^{-1} were assigned to amide bonds; 2920 cm^{-1} was assigned to the asymmetric stretch vibrations of CH, CH_2 and CH_3; peaks in the range of 1600–1500 cm^{-1} were assigned to C=C aromatic groups, the range 1250–1000 cm^{-1} was assigned to Si–O–Si bonds, and a peak at 800 cm^{-1} was assigned to Si–OH. These data confirm modified HS were indeed chemically bonded to the silica gel.

The experiment here demonstrates that both approaches for immobilization of humic substances on silica gel gave substrates with similar properties with respect to the bound organic compartment. This indicates feasibility of controllable adsorption of alkoxysilyl-derivatives on surface of natural mineral supports which might be used for in situ immobilization of humic coatings in the contaminated aquifers. The immobilized humic coating may

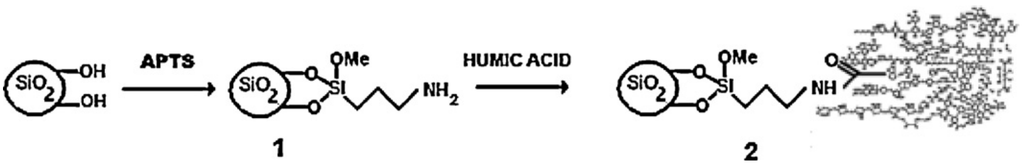

Fig. 7. Schematic reaction pathways for modification of silica surface with APTS followed by immobilization of humic substances from coal (CHP) on the aminated surface.

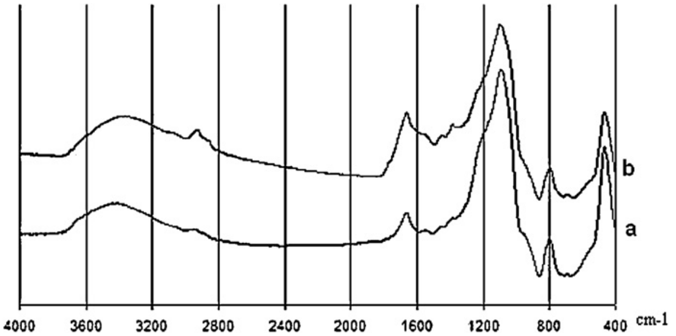

Fig. 8. FTIR spectra of silica gels coated with humic substances from coal using different immobilization approaches: (a) the humic coating was prepared using “reverse approach” proposed in this paper implying immobilization of alkoxysilyl humic derivatives on non-modified silica gel (CHP-APTS-100-$SiO_{2(rev)}$), and (b) the humic coating was prepared using “direct approach” by immobilizing non-modified humic materials onto aminated silica gel (CHP-APTS-$SiO_{2(direct)}$).

facilitate retention and sequestration of waterborne contaminants, e.g., of actinides in higher valence state, as it was shown in our previous publication [34]. With this regard, the results of this study may have important implications for an inexpensive alternative to installing PRBs by excavation. The humic PRB may be installed by injecting solutions of humic reagents into contaminated aquifer using a well transect. This method of installation may be particularly advantageous in the remediation of deep diluted plumes.

The important step forward to developing this environmental technology is exploring alternatives to DMF – organic solvent used in this study at the step of modification of HS which is our immediate goal. In case of success, the proposed method can lay the grounds for broad environmental applications based on a use of reactive properties of humic coatings.

4. Conclusions

Our data demonstrate successful directed modification of humic acid from coal using 3-aminopropyltrimethoxysilane leading to alkoxysilyl-derivatives with predictable aqueous sorption parameters. The obtained derivatives possessed the unique property to bind covalently to OH-carrying surfaces of silica gel under aqueous conditions at neutral pHs. Sorption of a novel suite of alkoxysilyl-humic derivatives with different modification degree onto silica gel under aqueous conditions revealed close correlation of sorption parameters to the amount of alkoxysilyl-units incorporated into the structure of parental HS. The binding to silica gel proved feasible because the acquired methoxysilyl-humic derivatives were water soluble, possessed reduced surface charge and were capable of forming siloxane bonds to silica due to rapid hydrolysis of alkoxysilyl to silanol groups. The proposed method of controlling aqueous sorption of HS on solid surfaces is comparable with the widely accepted method of immobilization of non-modified humic materials onto aminopropyl-silica [20]. The humic coatings bound to mineral surfaces under aqueous conditions might serve as promising sorbents for intercepting both hydrophobic organic substances and metal ions from contaminated aquatic environments. We base this assumption on our previous work [34] where we have shown for Pu(V) and Np(V) that alkoxysilylated humic derivatives covalently bound to silica gel exhibited a higher sorption capacity for these actinides than pure silica gel. To make the proposed approach compliant with environmental requirements we are exploring possibilities of using more environmentally friendly solvents than DMF. In case of success, these derivatives can serve as agents of new remediation technology aimed at in situ installation of humic permeable reactive barriers.

Acknowledgements

We wish to thank Dr. B.N. Tarasevich (Department of Chemistry, MSU) for invaluable help in acquiring and interpretation of FTIR-spectra. This research was supported by RFBR (grants 10-03-00803, 11-03-12177), US DOE (project RUC2-20006) and NATO-CLG (grant ESP.EAP.CLG 983197).

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