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# Preparation of Methoxysilyl Humic Acid Derivatives with the Use of 3-Isocyanatopropyltrimethoxysilane

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**Abstract**—A new method for modifying (methoxysilylating) coal humic acids by reacting them with 3-isocyanatopropyltrimethoxysilane is described. The modification products structurally characterized by FTIR and NMR spectroscopy. The sorption ability of methoxysilated humic acids on silica gel is studied in the batch mode to illustrate their affinity to silicon minerals.

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Humic compounds (HCs) constitute an extensive class of natural compounds, constituents of the organic matter of soils, natural waters, and fuel minerals [1]. Humic compounds consist of a hydrophobic aromatic framework with great percentages of functionalities, dominated by oxygen functionalities, such as carboxy, phenol, hydroxide, carbonyl, and methoxy groups. The specified functionalities are responsible for the complexing properties of HCs and their ability to participate in redox reactions. Studies of metal sorption [2–4] showed that HCs have high ability to sorb heavy metals and radionuclides. Apart from metals, HCs can bind organic compounds [5]. The specified properties of HCs are useful for creating humic sorbents.

A number of processes for preparing humic sorbents have been described. The most widespread approach is to treat a mineral matrix (most frequently, silica gel) with organosilanes and then to anchor an HC film to the surface [6–9]. We should stress that all relevant reactions are carried out in anhydrous organic solvents at elevated temperature (120°C). The products are solid humic sorbents, which are mainly used as model solids for studying the behavior of herbicides on soil particulates [10]. Another approach to preparing humic sorbents is use of sol–gel technologies [11], which produce humic compounds encapsulated in a silica gel matrix. The product of the aforementioned reaction is also used to study the ability of humic compounds to sorb various ecotoxicants.

Noteworthy, all above-described humic sorbents are solid, regardless of their preparation. However, the synthesis of water-soluble humic reagents capable of forming films on mineral substrates is most promising. These reagents provide new ways for developing efficient and economical processes for decontamination of deep aquifers; they can be pumped into a deep aquifer via a set of holes. Humic reagents form films on the surface of a mineral matrix (sand), which performs as a sorbent for dissolved pollutants, which migrate with groundwater flows.

To create such reagents, it is necessary to impart a new property to natural humic compounds, namely, the ability to irreversible sorption on mineral surfaces. This can be done by introducing functionalities having a high affinity to mineral matrices. Alkoxysilyl groups, which are hydrolyzed in aqueous solutions to generate silanol groups, are most promising in this respect. Silanols, in their turn, can form strong Si–O–Si and Si–O–M bonds with hydrosilylated silicon- and metal-bearing surfaces.

In view of the above, in this work we create an efficient method for introducing alkoxysilyl groups into HCs. Previously [12], we used organosilanes with various functionalities (3-aminopropyltrimethoxysilane (APTS) and 3-glycidoxypropyltrimethoxysilane (GPTS)) for derivation of carboxy and phenolic groups. Further studies showed that the alkoxysilylation of HCs with the use of APTS brings about the modification of the carboxy groups of humic acids, decreasing the metal-ion sorption ability of modified HCs. GPTS modified HCs at phenolic groups, but the amount of methoxysilyl groups introduced into the HC structure was not high. Therefore, in this work, we used 3-isocyanatopropyltrimethoxysilane (IPTS) for modifying HCs. The isocyanato group adds to phenolic groups of HCs with high product yields. All humic derivatives were characterized by structural analysis, and their silica gel sorption ability was studied. The sorption ability

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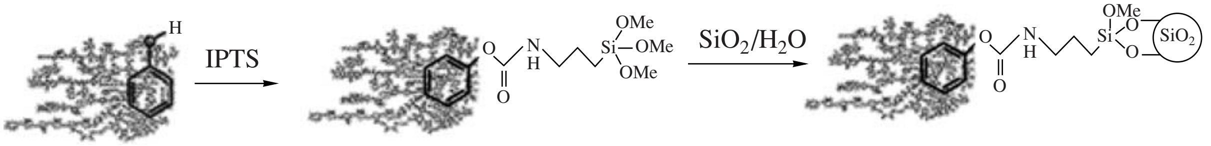

**Scheme 1.** Modification of HCs upon addition of IPTS followed by immobilization on silica gel.

of IPTS-modified humic derivatives is commensurate with the sorption ability of previously prepared APTS- and GPTS-modified humic derivatives.

## EXPERIMENTAL

### *Isolation of Precursor Humic Compounds*

The precursor humic compounds used were coal humic acids derived from commercial potassium humates: Powhumus (Humintech) and Sakhalin Humate (Biomir 2000). Before use, both samples were protonated as follows: a 50-g aliquot was dissolved in 5 L of water and allowed to stand for 24 h for the mineral component to precipitate. Then, the supernatant was decanted and acidified to pH 1–2 with concentrated HCl. Humic precipitates were separated by centrifugation and washed with distilled water several times. The washed sample was dialyzed through cellulose membranes with a pore diameter of 14 kDa until the washes had a negative $AgNO_3$ test for $Cl^-$. The dialyzed sample was concentrated on a rotary evaporator and stored over $P_2O_5$ inside a desiccator. The HC yield was 67% from Powhumus (CHP) and 54% from Sakhalin Humate (CHS).

### *Modification of HCs by 3-Isocyanatopropyltrimethoxysilane*

**Modification of a CHP sample in acetonitrile.** A 1-g aliquot of the CHP sample was dehydrated by azeotropic distillation with acetonitrile, which was first dried and distilled from $CaH_2$. To CHP, 50 mL of anhydrous acetonitrile was added, after which an equimolar amount (0.41 mL) of 3-isocyanatotrimethoxysilane (IPTS) was added. After 30 min, the reaction mixture was heated to 75°C, and the reaction was carried out under argon for 8 h with continuous stirring. After the reaction was over, the acetonitrile was distilled off in vacuo (2–3 mmHg) into a receiver cooled with liquid nitrogen. The vacuum in the system was compensated with argon. The product was dried in a vacuum drier at 40°C, then several times washed with dry diethyl ether to remove byproducts of the reaction between DMF and IPTS. The purified sample was ground with an agate mortar and pestle and stored in a hermetically stoppered weighing bottle. The product was denoted as CHP-IPTS (Scheme 1). The yield was 78%.

**Modification of a HCS sample in DMF.** A 1-g aliquot of the CHS sample was dehydrated by azeotropic distillation with toluene, which was first distilled from $CaH_2$. To dried HCS, 50 mL of anhydrous dimethylformamide (DMF) was poured, after which an equimolar amount (1.1 mL) of IPTS was added. The reaction mixture was heated to 120°C, and the reaction was carried out for 10 h with continuous stirring. After the reaction was over, the solvent was distilled off in vacuo (2–3 mmHg) into a receiver cooled with liquid nitrogen. The vacuum in the system was compensated with argon. The product was dried in a vacuum drier at 40°C, then several times washed with dry diethyl ether to remove byproducts of the reaction between DMF and IPTS. The purified sample was ground with an agate mortar and pestle and stored in a hermetically stoppered weighing bottle. The product was denoted as CHS-IPTS (Scheme 1). The yield was 87%.

### *Structure of Humic Derivatives*

Precursor and modified HC samples were characterized using elemental analysis and titrimetry. Their elemental compositions were determined on a Carlo Erba Strumentazione CHN analyzer, Model 1106. Silicon was determined spectrophotometrically on a Specord M40 analyzer. The results of elemental analysis are given without corrections for the ash content.

Carboxy and phenolic functionalities were determined by titrimetry using calcium acetate and barite, as described in [13]. With barite, the overall acidity was determined; with calcium acetate, the carboxylic acidity was determined. The phenolic acidity was determined as the difference between the overall and carboxylic acidities. Titration was carried out on a DMS Titrino (Metrohm, Model 716) automated titrimeter equipped with a glass electrode.

IR spectra were recorded as KBr disks on a Perkin-Elmer spectrophotometer with resolution of 4 $cm^{-1}$ using 64 scans.

$^{13}C$ NMR spectra of HCs were recorded inside a 5-mm NMR ampoule on Bruker Avance 400 instrument operated at 100 MHz. A test sample (50–70 mg) was dissolved in 0.3 M NaOD (0.7 mL). The spectrum width was 400 ppm; the free induction decay signal time was 0.6 s; the pulse repetition time $T_d$ was 8 s for 90° pulses; the build up time was 72 h. An external standard (MeOH/$D_2O$, $\delta = 49.0$ ppm) was used. Fourier transform was preceded by the exponential weighting of the free induction decay signal with the time constant equivalent to the broadening of 75-Hz lines [14].

**Table 1.** Elemental and functional composition of unmodified and modified HCs

| Sample | Weight percentages of elements | | | | | Atom ratios | | Functional composition (mmol/g) | |
|---|---|---|---|---|---|---|---|---|---|
| | ash content (%) | C | H | N | Si | H/C | C/N | COOH | ArOH |
| CHP | 10.6 | 52.8 | 3.85 | 1.11 | 2.11 | 0.87 | 55.6 | 3.8 | 1.8 |
| CHP–IPTS | 15.2 | 52.9 | 4.37 | 2.32 | 3.97 | 0.99 | 26.3 | 3.6 | 0.8 |
| CHS | 6.3 | 51.4 | 3.42 | 1.94 | 0.89 | 0.80 | 31.3 | 4.1 | 5.2 |
| CHS–IPTS | 24.8 | 49.4 | 4.76 | 7.58 | 7.52 | 1.16 | 7.6 | 3.8 | 0.7 |

### *Immobilization of Modified HCs on Silica Gel*

To characterize the affinity of modified HCs to mineral surfaces, we measured sorption isotherms on silica gel. The equilibration time was determined in an HCs sorption kinetic experiment. For this purpose, aqueous solutions of modified samples were prepared with the concentration 0.1 g/L. Humic derivatives were dissolved by adding several drops of concentrated alkali to weighed aliquots of solid samples with subsequent dilution with a phosphate buffer (0.028 mol/L, pH 6.8) to 10 mL. Silica gel (Merck) having the particle size 0.063–0.100 mm and the surface area 540 m$^2$/g was used. A silica gel sample (0.1 g) was inserted into the solutions of HC derivatives. The onset of the plateau of an equilibrium HC concentration curve was determined spectrophotometrically. The rate curve for the sorption of modified samples on silica gel in aqueous solutions enters the plateau after 3 days. Therefore, 3 days were taken to be the sorption equilibration time for all isotherms.

For measuring sorption isotherms, solutions of humic derivatives were prepared with concentrations in the range from 0.01 to 5.50 g/L. To an 10 mL aliquot of each of the thus-prepared solutions, 0.1 g of silica gel was added. The resulting suspensions were placed into a rotary stirrer for 3 days. After this period, the optical density of the solution was measured at 254 nm. The HC concentration in the solution was calculated using a calibration curve. Absorption spectra were recorded on a Cary 50 (Varian) spectrophotometer equipped with 1-cm quartz cells. The spectrophotometric data were used to plot sorption isotherms for modified samples on silica gel. The weight of sorbed samples were calculated from

$$M_{\mathrm{HC}} = (\Delta C_{\mathrm{HC}} V_{\mathrm{sln}})/M_{\mathrm{SiO_2}}(\mathrm{g}).$$

Here, $M_{\mathrm{HC}}$ is the weight of humic derivatives immobilized on 1 g of silica gel, mg; $\Delta C_{\mathrm{HC}}$ is the change in the equilibrium concentration of humic derivatives in solution in the course of sorption, mg/mL; $V_{\mathrm{sln}}$ is the aliquot volume, mL; and $M_{\mathrm{SiO_2}}$ is the silica gel weight, g.

Suspensions containing the maximal concentration of modified HCs (5.5 g/L) were centrifuged, and precipitates were repeatedly washed with a phosphate buffer. The resulting silica gels with immobilized HCs were dried in a vacuum drier. Depending on the type of derivative, the samples were denoted as CHP-IPTS-Si or CHS-IPTS-Si (Scheme).

## RESULTS AND DISCUSSION

Methoxysilyl groups react with the hydroxide groups of silica gel in aqueous solutions to produce strong siloxane bonds [15]. Therefore, to prepare HC-based samples that would be capable of sorbing on silica gel, Perminova et al. [12] proposed to introduce methoxysilyl groups into the humic framework. Modification by silylating agents should be carried out in anhydrous media, because even trace water can initiate the polycondensation of methoxysilyl groups with polysiloxane formation. For this reason, all solvents and precursor humic acids were carefully dried.

Both samples were first synthesized in acetonitrile. CHP modification occurred with high yield, whereas for CHS the reaction practically did not occur. A probable reason for this was the lower solubility of the CHS sample in acetonitrile, caused by its high phenolic acidity, which is three times the value for CHP (Table 1). Further experiments on CHS modification were carried out in DMF, where alkoxysilylation of HCs was previously carried out with addition of 3-aminopropyltrimethoxysilane [12].

The reaction ratios were calculated from the functional composition of HC, namely, the percentage of phenolic groups, which are the first to be modify in the reaction with 3-isocyanatopropyltrimethoxysilane. Thus, 1 mol of 3-isocyanatopropyltrimethoxysilane was reacted with 1 mol phenolic groups of HC, which were determined as the difference between the overall and carboxy acidities.

The CHP and CHS samples were modified with 3-isocyanatopropyltrimethoxysilane to produce methoxylated humic acids: CHP-IPTS and CHS-IPTS.

These derivatives were characterized by elemental analysis and titrimetry. The results are displayed in Table 1.

The low atom ratio H/C found for precursor HCs indicates the high percentage of aromatic structures in these samples, which is characteristic of coal humic

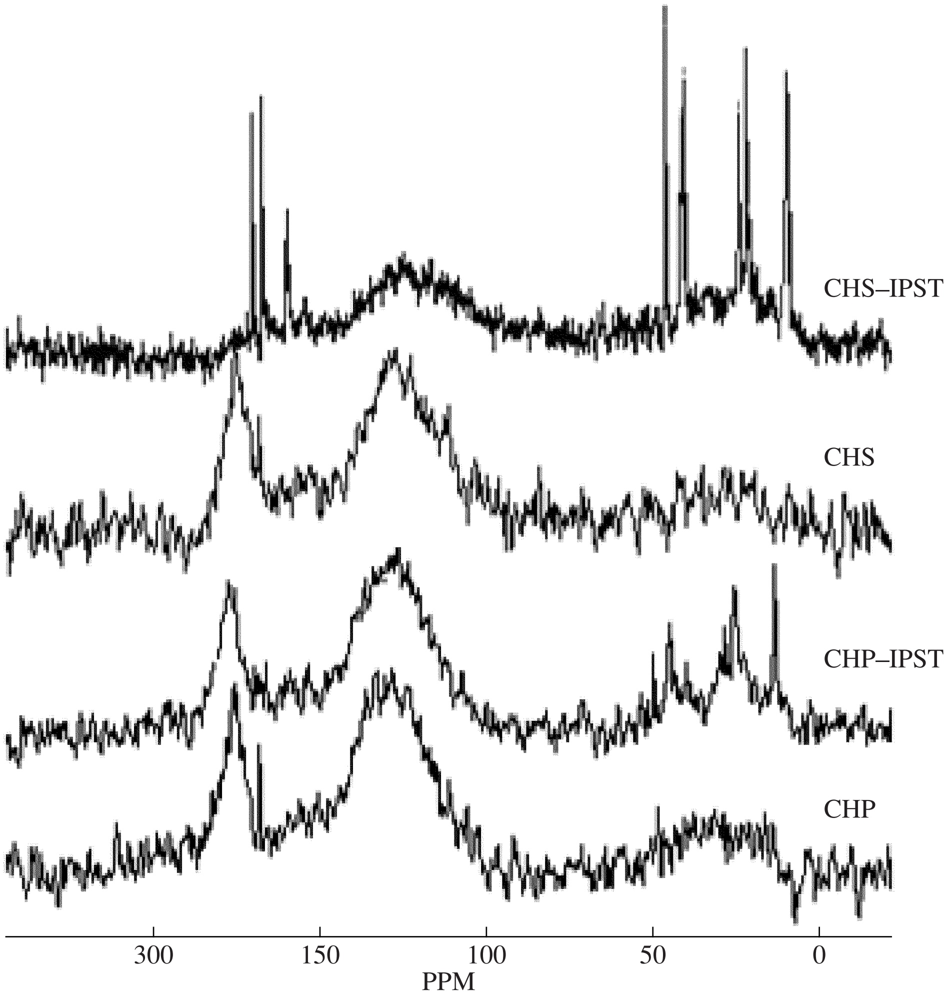

**Fig. 1.** $^{13}$C NMR spectra of unmodified and modified HCs.

acids [16]. The increased H/C ratio for modified samples is evidence of the appearance of IPTS aliphatic moieties in the structure. The decreased C/N proportion in the IPTS-modified sample verifies the incorporation of the nitrogen-containing groups of IPTS into the HC framework. Another piece of evidence is the increased silica percentage in modified samples compared to unmodified HCs.

We should emphasize that the precursor humic acids considerably differed from one another in the number of carboxy and phenolic groups. For example, the number of Ar–OH groups in CHS considerably exceeded the number of these groups in CHP. Logically, the higher the phenolic acidity of the initial sample, the greater the amount of reacting IPTS. The results agree with this suggestion; a greater IPTS amount (1.0 g) reacted with the CHS sample than with the CHP sample (0.21 g). Therefore, both the silicon percentage and the number of methoxysilyl groups are higher in CHS-IPTS.

The proportion of phenolic groups is an important characteristic of IPST-modified samples, because it enables the determination of the degree of the reaction. From titrimetric data, the percentage of phenolic groups in IPTS-modified HC samples is considerably lower than in the unmodified samples. From this, we can infer that most phenolic groups of HCs have reacted with the isocyanato group of the modifier. The resulting compounds were structurally characterized using IR and $^{13}$C NMR spectroscopy. The general pattern of $^{13}$C NMR spectra for precursor HCs corresponds to those reported in [14] (Fig. 1). The spectra of the CHP and CHS samples have similar sets of peaks; prevailing are overlapping signals in the range of aromatic carbon atoms (100–150 ppm) and carbon atoms of carboxy groups COOH (160–180 ppm).

The spectra of modified samples are characterized by similar sets of peaks.

**CHP-IPTS (ppm).** 168.35 (COOH), 156.02 (OCO–NH), 110–148 (Ar), 48.57 ($CH_3O$), 43.30

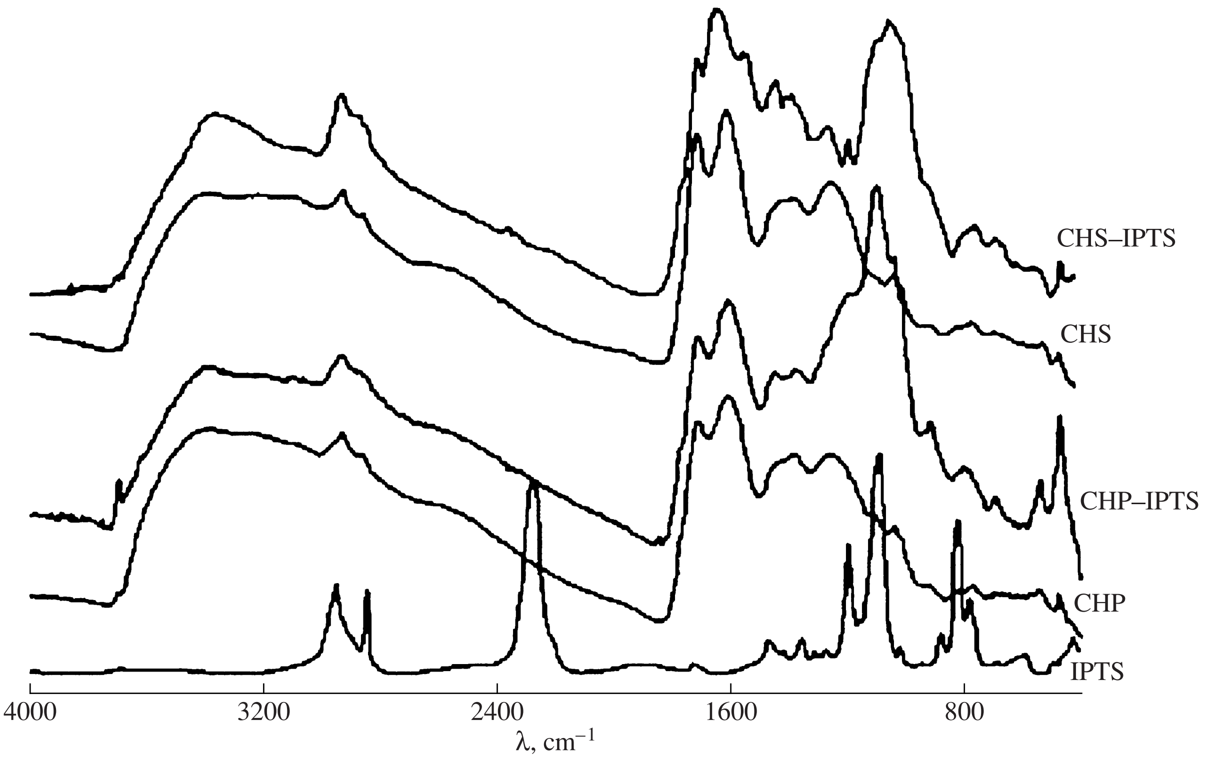

**Fig. 2.** IR spectra of unmodified HCs, modified samples, and IPTS.

$(\underline{CH_2}–CH_2-CH_2–Si)$, 24.43 $(CH_2–\underline{CH_2}–CH_2–Si)$, 12.32 $(CH_2–CH_2–\underline{CH_2}–Si)$.

**CHS-IPTS (ppm).** 168.36 (COOH), 155.71 (OCO–NH), 110–150 (Ar), 48.61 $(CH_3O)$, 43.63 $(\underline{CH_2}–CH_2–CH_2–Si)$, 24.51 $(CH_2–\underline{CH_2}–CH_2–Si)$, 12.60 $(CH_2–CH_2–\underline{CH_2}–Si)$.

The spectra of modified samples contain peaks characteristic of both precursor HCs and IPTS. The peak at 156 ppm indicates the generation of a new chemical bond (OCO–NH) between the phenolic groups of HCs and the isocyanato group of the modifier. The high-field peaks are due to the aliphatic carbon atoms of immobilized IPTS and to $CH_3O$ groups.

The peaks at 26.91 and 160.87 ppm in the spectrum of the CHS-IPTS sample show that DMF remained in the sample after the reaction. The 171 ppm peak is due to the by-product of the reaction between DMF and IPTS.

Thus, NMR spectroscopy showed that the addition of 3-isocyanatopropyltrimethoxysilane to the humic framework generated a chemical bond through the urethane group. Different HCs yield similar sets of reaction products.

The structure of modified HCs inferred from $^{13}C$ NMR spectra was confirmed by IR spectroscopy.

Figure 2 shows IR spectra for humic derivatives. Assignment was done with reference to related literature [17].

The IR spectrum of IPTS contains a strong band at 2250 cm$^{-1}$, which is characteristic of the isocyanato group (N=C=O). Bands at 2940–2845 cm$^{-1}$ are due to the vibrations of $CH_2$ groups. The range 1090–1020 cm$^{-1}$ is characteristic of alkoxysilanes (Si–O–C).

The general pattern of IR spectra for CHP and CHS agrees with the spectra reported in the literature [1]. The appearance of the strong band of the C=C stretching vibrations in the aromatic ring (near 1610 cm$^{-1}$) signifies the existence of an aromatic framework in HCs. The band about 1710 cm$^{-1}$ is associated with the C=O stretching vibrations (carboxy and carbonyl groups); the band at 1250 cm$^{-1}$ is due to the C–O stretching vibrations in phenolic and carboxy groups; and the bands in the region 1050–1150 cm$^{-1}$ correspond to the C–O stretching vibrations in alcoholic groups. The appearance of these bands is indicative of the existence of various oxygenated functionalities in HCs.

The spectra of modified samples contain bands characteristic of both HCs and alkoxysilanes. For example, the appearance of bands in the region 1090–1020 cm$^{-1}$, which are associated with the Si–O–C stretching vibrations, signifies the existence of methoxysilyl groups. The spectra of modified HCs do not contain peaks of isocyanato groups, which can be regarded as evidence of occurrence of the reaction between HCs and IPTS. The increased intensities of the bands in modified samples in the range 2940–2845 cm$^{-1}$, which are responsible for the vibrations of $CH_2$ groups, verify

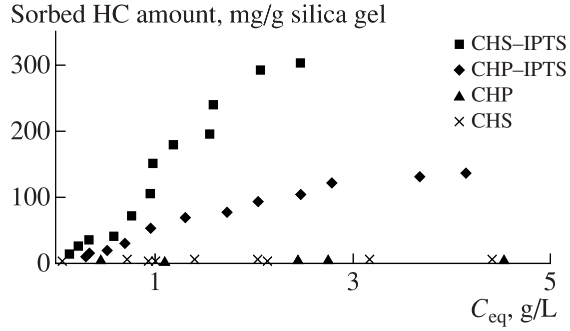

**Fig. 3.** Sorption isotherms for unmodified and modified HCs on silica gel (pH 6.8).

the incorporation of aliphatic fragments into the structure of modified HCs. In addition, the band at 1250 cm$^{-1}$, associated with the C–O stretching vibrations inside phenolic and carboxy group, had lower intensities in modified samples. This confirms the entrance of phenolic groups of HCs into the reaction with IPTS.

The appearance of a band at 1580 cm$^{-1}$ (O–C(O)–NH) in modified samples indicates the generation of new bonds between the isocyanato group IPTS and the Ar–OH groups of HCs. These bands are not characteristic of precursor HCs and IPTS.

The spectra of both modified and initial samples contain broad bands at 3500–3300 cm$^{-1}$ due to HC-bound water.

The sorption ability of humic derivatives was studied using isotherms.

Figure 3 displays sorption isotherms for precursor HC samples and modified HC samples.

Unmodified HCs are not sorbed on silica gel, whereas modified samples have high sorption abilities.

The experimental data were used to calculate the maximal HC amount that can be immobilized on silica gel from aqueous solutions (Table 2). These values are commensurate with previous results from modification by other functional organosilanes. The maximal sorption ability of HCs modified with 3-aminopropyltrimethoxysilane was 220 mg per gram of silica gel against 51 mg for the same HC modified with 3-glycidoxytrimethoxysilane [12]. Aminosilane modifies carboxy groups, whereas glycidoxysilane modifies phenol groups of HCs.

**Table 2.** Sorption ability characteristics of methoxysilylated coal humic derivatives for silica gel

| Sample | $Q$*, mg | $C$**, % |
|---|---|---|
| CHP–IPTS–Si | 135 | 6.22 |
| CHS–IPTS–Si | 298 | 9.25 |
| CHP–APTS–Si*** | 220 | 9.20 |
| CHP–GPTS–Si*** | 51 | 3.56 |

*The maximal amount of HCs immobilized on 1 g silica gel.

**Carbon percentage in silica gel after HC immobilization.

***Previous results published in [12].

To characterize HCs immobilized on silica gel, we determined their organic carbon percentages (Table 2).

The data displayed in Table 2 make it clear that the CHS-IPTS sample has a greater sorption ability than the CHP-IPTS sample. The apparent reason for this is the greater content of phenolic groups in the initial CHS sample compared to the CHP sample. As a result, the modified CHS-IPTS sample was characterized by a high content of methoxysilyl groups, which endowed it with the high sorption ability.

This inference agrees with the organic carbon percentages in immobilized HCs (Table 2): the CHS-IPTS sample contained a greater organic carbon percentage than the CHP-IPTS-Si sample.

Comparing the characteristics of modified samples with previous data (Table 2), we can infer that IPTS modification provides for samples with the sorption ability commensurate with that of APTS-modified samples and exceeding that of GPTS-modified samples. However, unlike APTS-modified samples, IPTS modification leaves carboxy groups free, conserving their high ability to complex with metal ions and determining their potential for use in the purification of groundwater from heavy metals.

Thus, our complex studies demonstrated the potential of targeted chemical modification for preparing humic derivatives with desired properties. Both processes ensure the complete modification of HCs with 3-isocyanatopropyltrimethylsilane.

When these derivatives are employed for the decontamination of groundwater, however, the reaction in acetonitrile is preferred to the reaction in DMF because of the low toxicity of acetonitrile and the smaller number of side reactions. The resulting methoxy derivatives are water soluble and stable at neutral pHs. They have far higher sorption ability compared to the precursor HCs and can be immobilized on mineral surfaces from aqueous solutions. These reagents provide new possibilities for developing efficient and economical processes for the decontamination of deep aquifers.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Orlov, D.S., *Gumusovye kisloty pochv i obshchaya teoriya gumifikatsii* (Humic Acids and the General Humification Theory), Moscow, 1990.
2. Cherwinski, K.R., Buckau, S., Scherbaum, F., and Kim, J.I., *Radiochim. Acta*, 1994, vol. 65, p. 111.
3. Kim, J.I., Wimmi, H., and Klenze, R., *Radiochim. Acta*, 1991, vol. 54, p. 35.

4. Artinger, R., Marquardt, C.M., and Kim, J.L., *Radiochim. Acta*, 2000, vol. 88, p. 609.
5. Kopinke, F.D., *Environ. Sci. Technol.*, 1995, vol. 29, p. 941.
6. Prado, A.G.S., *Surf. Sci.*, 2003, vol. 542, p. 276.
7. Prado, A.G.S., *Colloids Surf.*, 2004, vol. 242, p. 137.
8. Klavins, M. and Eglite, L., *Colloids Surf.*, 2002, vol. 203, p. 47.
9. Koopal, L.K., Yang, Y., Minnaard, A.J., and Theunissen, P.L.M., *Colloids Surf.*, 1998, vol. 14, p. 385.
10. Szabo, G. and Bulman, R.A., *Humic Substances in Aquatic Environment*, New York: Wiley, 1991.
11. Laor, Y. and Zolkov, Ch., *Environ. Sci. Technol.*, 2002, vol. 36, p. 1054.
12. Perminova, I.V., Ponomarenko, S.A., Karpiouk, L.A., and Hatfield, K., *Patent pending, PCT application No. RU2006/000102*.
13. Swift, R.S., *Organic Matter Characterization*, New York, 1996.
14. Kovalevskii, D.V., Permin, A.B., Perminova, I.V., and Petrosyan, V.S., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2000, vol. 41, p. 39.
15. Andrianov, K.A., *Kremniiorganicheskie soedineniya* (Organosilicon Compounds), Moscow, 1955.
16. Lawson, G.J. and Stewart, D., *Coal Humic Acids: Search of Structure*, New York, 1989.
17. L. Bellamy, *The Infrared Spectra of Complex Molecules*, New York: Wiley, 1958. Translated under the title *IK-spektry slozhnykh molekul*, Inostrannaya Literatura, Moscow, 1963).