

Synthesis and Study of a Sorbent Based on Silica Gel Modified with Hyperbranched Poly(dichloromethylsilylpropyl)carbosilane with Molecular Imprints of 2,4-Dichlorophenoxyacetic Acid

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Abstract—A new sorbent for selective sorption of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solutions—silica gel modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane with molecular imprints of 2,4-D (SG-MI)—has been synthesized, and its specific surface area has been estimated. Sorption of 2,4-D has been studied under static conditions. Analysis of sorption isotherms shows that SG-MI is capable molecular recognition of 2,4-D. The selectivity of the sorbent synthesized was estimated for structurally related compounds.

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Molecularly imprinted polymers (MIPs) are finding increasing use for selective sorption of organic compounds [1–8]. Molecular imprinting is a technique to obtain organic or inorganic materials capable of recognizing the template molecules. Molecular recognition is possible since such matrices contain regions (so-called molecular imprints) that have the capability to specifically (complementarily) interact with template molecules or structurally related compounds [9, 10].

Most works in the field of molecular imprinting have dealt with polymers, which is explained by relatively simple synthesis of such materials, a wide set of monomers and crosslinking agents, and a high stability of MIPs to chemical and physical treatments.

The methods of obtaining MIPs have been fairly well developed. The synthesis consists of several stages: formation of an intermolecular prepolymer complex between monomer and template molecules; polymerization of the prepolymer complex in the presence of large amounts of a crosslinking agent, which leads to a polymer with a rigid structure; grinding and screening of the polymer to the required particle size; repeated washing with organic solvents to remove the template [8–11]. In addition, polymer layers capable of molecular recognition can be applied to a substrate, such as an inorganic oxide carrier, silica gels being the most widely used. Uniform arrangement of hydroxyl groups on the silica gel surface makes it possible to obtain ordered structures on this surface. As a rule, a

polymer coating is applied to the activated silica gel surface, then a template molecule is introduced into the spatial network of the polymer, and finally the polymer network is formed and the template molecule is removed from it by washing with organic solvents [9, 12]. The simplest method of preparation of chemically modified oxide capable of molecular recognition is based on the polycondensation of alkoxysilanes in the pores or at the surface of silica gel in the presence of a template molecule [9, 12]. However, works dealing with the synthesis of inorganic matrices with molecular imprints are few in number [9, 12–15].

In the present work, hyperbranched carbosilane polymers were used as a functional layer capable of forming molecular imprints at the silica gel surface. The synthesis of such polymers, including their chlorosilyl derivatives, has been fairly well developed [16, 17]. Hyperbranched polymers are globular molecules with a molecular weight of 5000–20000 amu. An important feature of these polymers is a combination of reactive functional groups and a rather inert carbosilane skeleton. Taking into account the high content of functional groups in macromolecules, this feature allows one to treat hyperbranched polycarbosilanes as rather promising polymer matrices capable of chemical transformations, in particular, capable of forming a selective template shell on the surface of the pristine silica gel.

The aim of this work is to synthesize a new sorbent based on silica gel modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane with molecular imprints of 2,4-dichlorophenoxyacetic acid (2,4-D) and study its sorption properties. The choice of the template molecule is determined by the fact that 2,4-D is a

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widely used pesticide, so that the search for sorbents for selective extraction of this compound from water, soil, and foodstuffs is an important task.

EXPERIMENTAL

Reagents and instrumentation. The objects of investigation were 2,4-dichlorophenoxyacetic, 3,4-dichlorophenoxyacetic, and 4-hydroxybenzoic acids; and phenol, 2-chlorophenol, 3-chlorophenol, and 2,4-dichlorophenol. Initial solutions (0.01–0.001 mol/L) of these compounds (chemically pure grade) were prepared by dissolving exact weighed portions in distilled water. Working solutions of the compounds were prepared by dilution of the initial solutions immediately before use.

The sorbent was synthesized in an inert atmosphere and dry solvents. Organic solvents (hexane, toluene, tetrahydrofuran (THF), methanol) were additionally dried and distilled over CaH_2 . Diallylmethyl-, dichloromethyl-, and chlorotrimethylsilanes were distilled immediately before use. Hydrosilylation was carried out in the presence of a platinum catalyst (PC 072, Aldrich), the complex of zerovalent platinum with 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (a 2.1–2.4% Pt solution in xylene).

Silica gel 60 (SG, Meck Kieselgel 60) with a grain size of 0.063–0.100 mm for column chromatography was used.

^1H NMR spectra were recorded on a Bruker WP-250 SY (250.13 MHz) radiospectrometer. The internal reference was tetramethylsilane. Absorption spectra and optical densities of solutions were recorded on an Akvilon SF-103 spectrophotometer, and pH values were monitored with an Ekspert 001 ionometer.

Synthesis of hyperbranched poly(diallylmethylsilylpropyl)carbosilane was carried out as described in [16]. In a sealed one-neck flask preliminarily purged with argon, a solution of 1.7 g of diallylmethylsilane in 2 mL of hexane and 4 μL of a PC-072 platinum catalyst were stirred with a magnetic stirrer for 24 h. The reaction mixture was evacuated at 1 mmHg for 30 min, which gave a colorless viscous polymer in 100% yield. ^1H NMR (CDCl_3 , δ , ppm): -0.03 (t, 3H, SiCH_3), 0.5 (m, 4H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 1.3 (m, 2H, CH_2), 1.52 (m, 2H, $\text{SiCH}_2\text{CH}=\text{CH}_2$), 4.82 (m, 2H, $\text{CH}_2=$), 5.85 (m, 1H, $\text{CH}=\text{}$).

Synthesis of hyperbranched poly(dichloromethylsilylpropyl)carbosilane (I). In a sealed one-neck flask preliminarily purged with argon, a solution of 1.07 g of hyperbranched poly(diallylmethylsilylpropyl)carbosilane and 1.32 mL of dichloromethylsilane in 2 mL of hexane and 10 μL of a PC-072 platinum catalyst were stirred with a magnetic stirrer for 48 h. The end of the reaction was monitored by observing the disappearance of the signals of the protons at the double bond in the ^1H NMR spectra of reaction mixture sam-

ples. The reaction mixture was evacuated at 1 mmHg for 30 min to remove a chlorodimethylsilane excess. The polymer was dissolved in 10 mL of toluene in an argon atmosphere, and the resulting solution was used in further reactions.

Chemical activation of the silica gel surface. Sodium hydroxide (0.188 g) in 9 mL of methanol was added to 3.36 g of dry silica gel, and the mixture was kept for 5 h with intermittent stirring and then was evacuated with an oil pump and dried in a vacuum oven at $145 \pm 20^\circ\text{C}$ and 6 mmHg to constant weight.

Modification of silica gel with hyperbranched poly(dichloromethylsilylpropyl)carbosilane (II). Chemically activated silica gel (3.41 g, 0.0045 mol), 20 mL of THF, and 5.4 mL of a toluene solution containing 1.09 g (0.0045 mol) of hyperbranched poly(dichloromethylsilylpropyl)carbosilane (I) were placed in a two-neck flask with a reflux condenser and an argon flow. The mixture in the flask was periodically shaken over four days at 50°C . Then, 10 mL of toluene was added, and the reaction mixture was filtered in an argon flow through a Schott filter. The modified silica gel were separated from the unreacted polymer by washing successively with 50 mL of toluene and 100 mL of THF and dried for 10 min. The resulting modified silica gel was divided into two portions and used in further transformations. After evaporation of the mother liquor containing unreacted polymer I, we obtained 0.47 g of the polymer; i.e., 0.62 g of poly(dichloromethylsilylpropyl)carbosilane was involved in the modification reaction.

Preparation of silica gel modified with hyperbranched poly(dichloromethylsilylpropyl) carbosilane with molecular imprints of 2,4-D (IV, SG-MI). To 3.19 g of silica gel modified with hyperbranched dichlorocarbosilane polymer (portion 1), 10 mL of THF, 0.34 g of 2,4-D, and 0.2 mL of pyridine as an acceptor were added, and the mixture was heated at 50°C for 60 h. The precipitate (product III) was filtered off in an argon flow, washed with 50 mL of THF, and placed in a two-neck flask, which was purged with dry ammonia for 7 h (with periodic shaking). Then, 20 mL of a THF–water (1 : 1) mixture was added, and the mixture was allowed to stand for two days (with periodic shaking). Modified silica gel (IV, SG-MI) was filtered off, washed with 50 mL of THF, and dried in a vacuum oven at $145 \pm 20^\circ\text{C}$ and 6 mmHg to constant weight.

Preparation of silica gel modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane (reference, SG-M). To obtain a reference sample, 2.17 g of modified silica gel II (portion 2) in 7 mL of THF and 1 mL of water were heated in a one-neck flask with a reflux condenser at 50°C for 60 h. The precipitate was filtered off in an argon flow, washed with 50 mL of THF, and dried in a vacuum oven at $145 \pm 20^\circ\text{C}$ and 6 mmHg to constant weight.

Sorption procedure. Sorption was carried under static conditions. A weighed portion of the sorbent (0.040 ± 0.001 g) was introduced into a flask with a sealing plug containing the analyte solution (5 mL), and the mixture was shaken until sorption equilibrium was achieved. Then, the sorbent was separated from the solution by filtration through a folded filter, and the analyte concentration in the equilibrium aqueous phase was determined spectrophotometrically.

Recovery levels (R , %) were calculated by the equation

$$R, \% = \frac{C_0 - C}{C_0} \times 100\%, \quad (1)$$

where C_0 is the analyte concentration in an aqueous solution before sorption, and C is the analyte concentration in the solution after sorption.

The distribution coefficients (D) were calculated by the equation

$$D = \frac{R, \%}{(100 - R\%)} \frac{V}{m}, \quad (2)$$

where V is the volume of an analyte solution (mL), and m is the sorbent weight (g).

The capability of the sorbent with 2,4-D molecular imprints to recognize the template molecule was estimated using the imprinting factor

$$IF = \frac{D_{SG-MI}}{D_{SG-M}}, \quad (3)$$

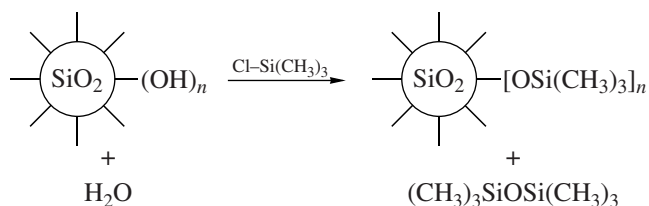
where D_{SG-MI} is the distribution coefficient of 2,4-D on the sorbent with 2,4-D molecular imprints, and D_{SG-M} is the distribution coefficient of the substance on the reference sorbent.

RESULTS AND DISCUSSION

Preparation of a Sorbent Based on Silica Gel Modified with Hyperbranched Poly(dichloromethylsilylpropyl)carbosilane with 2,4-D Molecular Imprints

Important steps of the preparation of silica gel for modification are removal of water traces and chemical activation of its surface. Different method of water removal from silica gel have been studied: simple drying in a vacuum oven at $147 \pm 20^\circ\text{C}$ and 6 mmHg to constant weight (method 1); drying with preliminary azeotropic distillation: treatment with THF followed by drying on an oil pump for 1.5 h and then in a vacuum oven at $147 \pm 20^\circ\text{C}$ and 6 mmHg to constant weight (method 2); heating under reflux for 4 h with toluene in a flask with a Dean–Stark trap followed by drying in a vacuum oven at $147 \pm 20^\circ\text{C}$ and 6 mmHg to constant weight (method 3).

Residual water in silica gel was quantified by studying the ^1H NMR spectra of the products of the heterofunctional condensation of silica gel with chlorotrimethylsilane (Scheme 1).



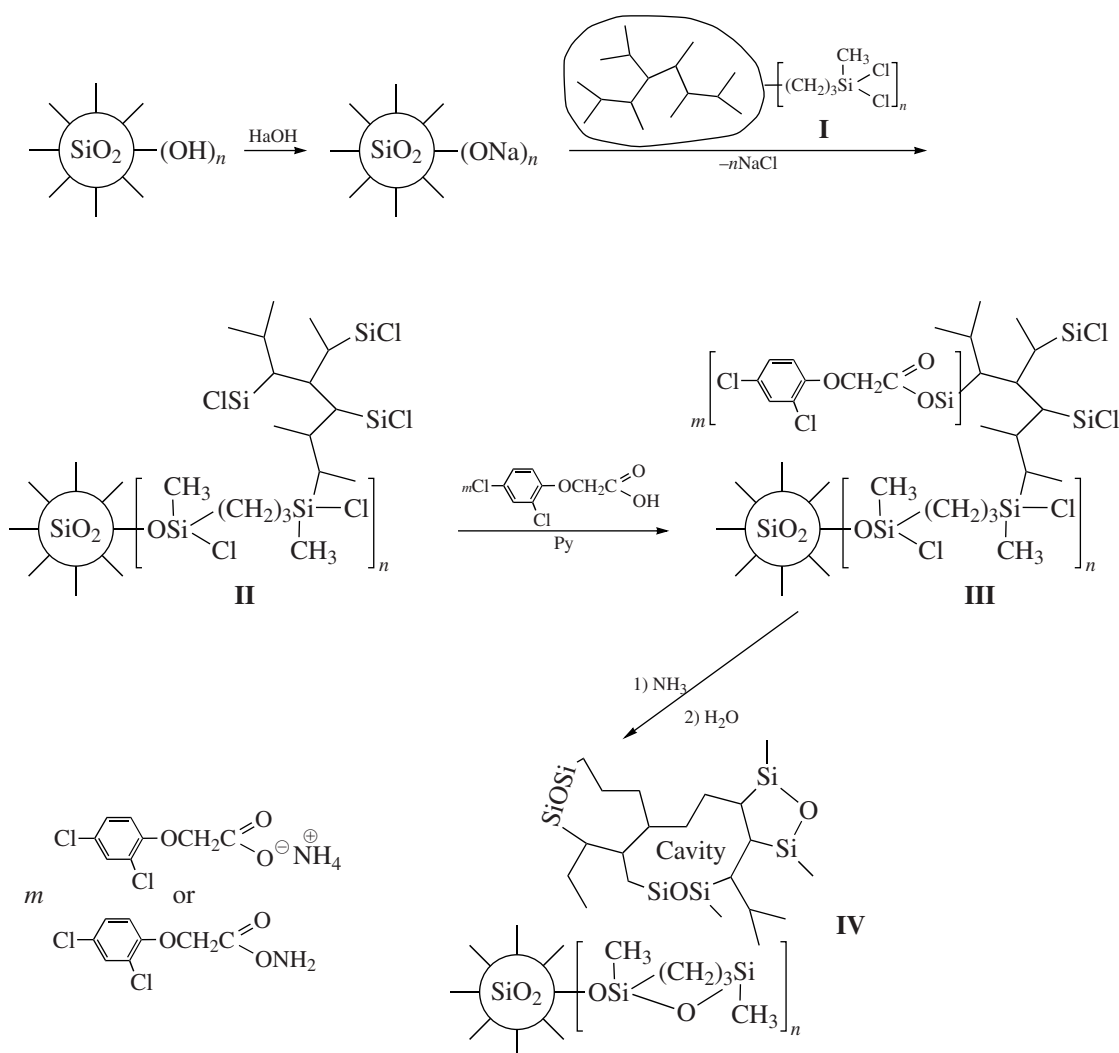
Scheme 1.

The Si–OH groups of silica gel interact with chlorotrimethylsilane to yield the silica gel modified with trimethylsilyl groups. The water contained in the silica gel hydrolyzes chlorotrimethylsilane to form hexamethyldisiloxane. The resulting reaction mixture of chlorotrimethylsilane and hexamethyldisiloxane is readily identified in ^1H NMR spectra, and the integrated intensity ratio for the trimethylsilyl protons in these compounds makes it possible to determine the content of the resulting hexamethyldisiloxane and, hence, water.

We found that the most efficient method of water removal from silica gel is refluxing in toluene with a Dean–Stark trap: the residual water content in silica gel is 0.13 (method 1), 0.12 (method 2), and 0.08% (method 3).

The chemical activation of the silica gel surface was carried out by treatment of dry silica gel with a sodium hydroxide solution in methanol, which leads to the formation of silanolate groups instead of silanol groups.

The sorbent based on silica gel modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane with 2,4-D molecular imprints was obtained according to Scheme 2. At the first stage, the silica gel activated with sodium hydroxide was modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane **I**. The ratio of activated silica gel to polymer **I** was chosen such that only one half of the chlorosilyl groups of the polymer was involved in the reaction.

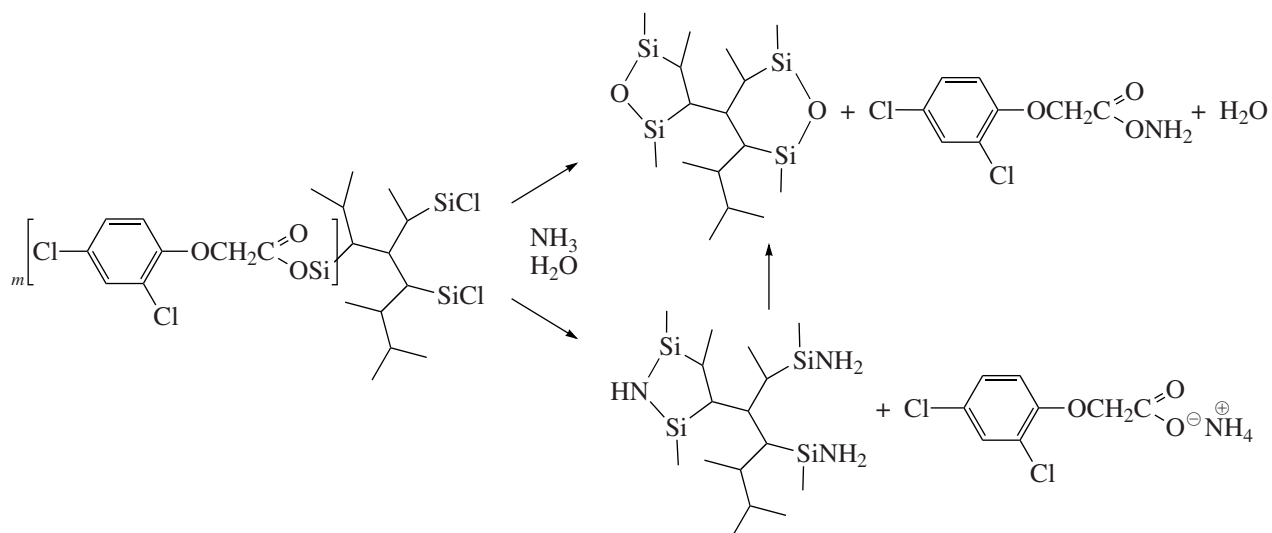


Scheme 2.

After the end of the reaction, unreacted polymer **I** was washed out with a solvent, and the degree of modification was determined from the difference between the amounts of the loaded and collected polymer. As a result, we obtained sorbent **II**, silica gel modified with the hyperbranched polymer containing in the surface layer active chlorosilyl groups capable of further transformations. The resulting silica gel **II** was divided into two portions: one of them was used for obtaining template silica gel with 2,4-D molecular imprints (**IV**, SG-MI), and the other portion was used for preparing the reference sample (SG-M).

The template sorbent (SG-MI) was obtained as follows: first, silica gel **II** with chlorosilyl groups was treated with the template, 2,4-dichlorophenoxyacetic acid. The reagent ratio was chosen such that only one half of the chlorosilyl groups of silica gel **II** was

involved in the reaction. Product **III** was treated with dry ammonia. This treatment made it possible to complete the formation of a crosslinked polymer layer containing template molecules and break chemical bonds between the template and the polymer. Further treatment of silica gel with a THF–water mixture completed the formation of the template sorbent. During this treatment, the template was washed out from the sorbent so that the silazane crosslinks in the crosslinked network structure of the surface layer are exchange for siloxane crosslinks. Thus, the above sequence of operations results in the formation of cavities in the surface layer with memory of the shape and structure of the template, which are fixed in a rigid network structure. The process of breaking of the chemical bonds of the template with silica gel **III** is shown in Scheme 3.



Scheme 3.

To compare the sorption capacity of the synthesized sorbent, it was necessary to obtain silica gel modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane but not containing template molecules. To do this, the second portion of silica gel **II** was treated with a THF–water mixture, which allowed us to obtain a network of siloxane bonds at the silica gel surface. This network results from hydrolysis of the chlorosilyl groups in the polymer and subsequent condensation. The chemical constitution of the reference sorbent thus obtained was analogous to that of silica gel **IV** modified

with hyperbranched poly(dichloromethylsilylpropyl)carbosilane with 2,4-D molecular imprints.

Study of the Properties of the Sorbent Based on Silica Gel Modified with Hyperbranched Poly(dichloromethylsilylpropyl)carbosilane with 2,4-D Molecular Imprints

Specific surface. The specific surface of samples was determined from low-temperature nitrogen adsorption data by the thermal desorption method. We found that SG-MI has a less developed surface than SG-M (415 and 544 m²/g, respectively). The specific surface of the initial silica gel after water trace removal was 534 m²/g.

Sorption properties. The estimated sorption capacities of initial silica gel 60 (SG), silica gel modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane (SG-M), and silica gel modified with hyperbranched poly(dichloromethylsilylpropyl)carbosilane with 2,4-D imprints (SG-MI) were compared. To determine the time required for achieving sorption equilibrium, we studied the sorption coefficients of 2,4-D on SG, SG-M, and SG-MI as a function of the phase contact time. We found that, for all three sorbents, this time does not exceed 60 min.

2,4-Dichlorophenoxyacetic acid ($pK_a = 2.98 \pm 0.20$) can exist in solution in the molecular and ionized forms; therefore, one of the factors that influence its sorption is the pH of a solution. The specific features of dependence of the 2,4-D sorption coefficient on pH are evidence that this compound is sorbed in the molecular form. All sorbents maximally extract 2,4-D from acid solutions (pH 1–2) where the carboxyl group in not dissociated. As the pH increases, sorption decreases: at pH > 5, the compound is virtually not sorbed. The sorp-

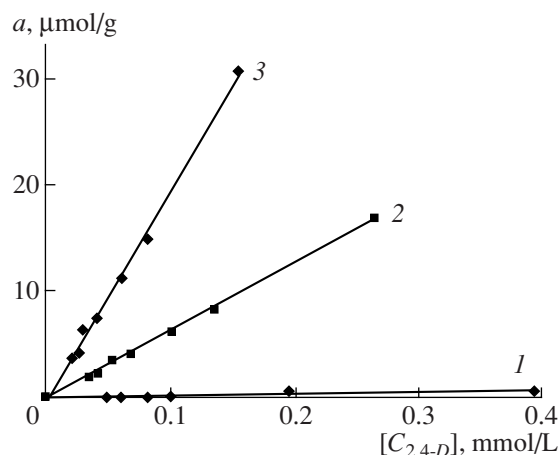


Fig. 1. Sorption isotherms of 2,4-dichlorophenoxyacetic acid on (1) silica gel, (2) silica gel modified with hyperbranched dichlorocarbosilane polymer, and (3) silica gel modified with hyperbranched dichlorocarbosilane polymer with molecular imprints of 2,4-dichlorophenoxyacetic acid ($C_{HCl} = 0.01$ mol/L, $V = 5$ mL, $m_s = 0.04 \pm 0.001$ g, $t = 60$ min).

Recovery levels (R , %) of 2,4- and 3,4-dichlorophenoxyacetic acids, 4-hydroxybenzoic acid, 2,4-dichlorophenol, 2-chlorophenol, phenol, and 4-chlorophenol on silica gel 60 (SG), silica gel modified with hyperbranched dichlorocarbosilane polymer (SG-M), and silica gel modified with hyperbranched dichlorocarbosilane polymer with molecular imprints of 2,4-dichlorophenoxyacetic acid (SG-MI). $C_C = 1 \times 10^{-4}$ mol/L, $C_{HCl} = 0.01$ mol/L, $V = 5$ mL, $m_s = 0.040 \pm 0.001$ g, $t = 60$ min, $n = 5$, $P = 0.95$

Compound	R , % (S_{sp} , m ² /g)		
	SG (534)	SG-M (544)	SG-MI (415)
2,4-Dichlorophenoxyacetic acid	2.0 ± 0.8	31 ± 2	61 ± 4
3,4-Dichlorophenoxyacetic acid	2.0 ± 0.8	35 ± 2	50 ± 3
2,4-Dichlorophenol	7 ± 2	23 ± 1	24 ± 2
2-Chlorophenol	3 ± 1	7.0 ± 0.9	8.0 ± 0.9
4-Chlorophenol	3 ± 1	8.0 ± 0.9	7 ± 1
Phenol	2.0 ± 0.8	1.0 ± 0.2	1.0 ± 0.2
4-Hydroxybenzoic acid	1.0 ± 0.4	10 ± 1	8 ± 1

tion coefficients of 2,4-D in the range of pH 1–2 (parenthesized, %) increase in the series SG (2 ± 1) < SG-M (31 ± 2) < SG-MI (61 ± 1) ($n = 5$, $P = 0.95$). The difference in the sorption behavior of 2,4-D on different sorbents is observed in a wide range of acid concentrations (from 5×10^{-5} to 4×10^{-4} mol/L), as follows from comparison of sorption isotherms (Fig. 1). The slope of the sorption isotherms increases in going from SG through SG-M to SG-MI, which is evidence that the efficiency of the sorbents increases in this order.

To estimate the selectivity of SG-MI, we compared the sorption of structurally related compounds: 3,4-dichlorophenoxyacetic acid (3,4-D), 2,4-dichlorophenol (2,4-DCP), 2- and 4-chlorophenol (2-CP, 4-CP),

phenol (P), and 4-hydroxybenzoic acid (4-HBA). Comparison was carried out with respect to SG and SG-M. The table gives the recovery levels, and Fig. 2 shows the imprinting factors. As follows from the experimental data, the molecularly imprinted sorbent best sorbs the 2,4-D template molecule. This sorbent is also able to recognize structural analogues, although these compounds (e.g., 3,4-D or 2,4-DCP) are sorbed in smaller amounts.

Thus, our findings show that hyperbranched polycarbosilanes can be used as promising polymer modifiers of silica gels for producing new materials capable of molecular recognition.

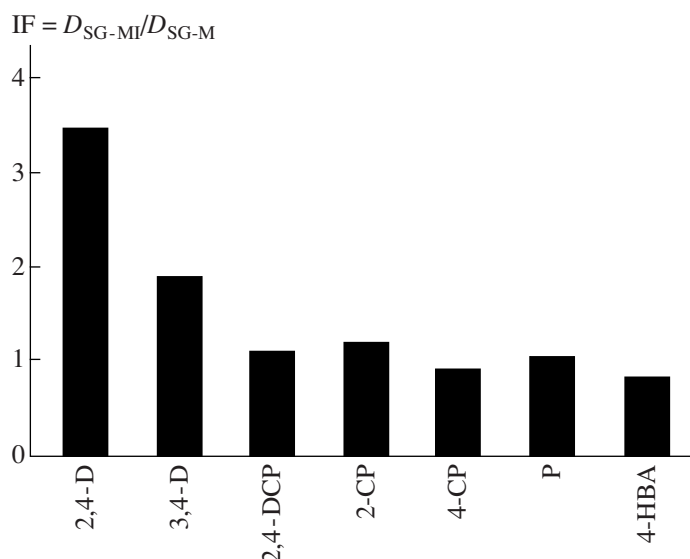


Fig. 2. Imprinting factors of different organic compounds on silica gel modified with hyperbranched dichlorocarbosilane polymer with 2,4-dichlorophenoxyacetic acid imprints ($C_C = 10^{-4}$ mol/L, $C_{HCl} = 0.01$ mol/L, $V = 5$ mL, $m_s = 0.04 \pm 0.001$ g, $t = 60$ min).

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