

Composite Polymer-Silicone Adsorbent for Platinum (IV) Ions: Investigation of Models and Absorption Kinetics

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Abstract — The adsorption of platinum (IV) in hydrochloric acid solutions of a composite based on N,N-bis(3-triethoxysilylpropyl)thiourea and 4-vinylpyridine-2-hydroxyethylacrylate copolymer is studied. The value of the static adsorption capacity of the composite for platinum(IV) is found to be 215 mg/g. To describe the nature of the adsorption, Langmuir, Freundlich, and Dubinin–Radushkevich models are used. The adsorption kinetics is estimated using Boyd–Adamson models of pseudo-first and pseudo-second order and the Elovich equation.

Keywords — *adsorption, kinetics, hybrid composites, Langmuir model, Freundlich model, Dubinin–Radushkevich model, Boyd–Adamson model, pseudo-first-order model, pseudo-second-order model, Elovich equation.*

I. INTRODUCTION

Hybrid composites based on organic polymers and organosilicon compounds are materials that combine the best properties of both synthetic and mineral adsorbents [1-3]. The presence of a functionalized organic polymer in their composition is responsible for the chemisorption activity, and the silicon unit determines the morphological characteristics, as well as enhanced mechanical and thermal stability.

- One of the methods for the obtaining silicon–polymer-composite adsorbents is sol-gel synthesis, which makes it possible to influence the composition and structure of the surface layer of sorption materials. A purposeful variation of the nature of the organosilicon monomer, organic component, solvent, temperature, and acidity of the medium makes it possible to obtain polymer systems with predetermined structural characteristics, physicochemical and functional properties.
- To assess the conditions for the practical application of hybrid composites, it is necessary to study kinetic regularities of adsorption processes. Various

parameters of the process will have a determining effect on the sorption capacity of the composites.

- Earlier we have obtained hybrid composites based on silica and 2-hydroxyethylmethacrylate-4-vinylpyridine copolymers, which possess high ion-exchange capacity (2.1 mg-eq/g). Composites based on poly[N,N'-bis(3-silsesquioxanilpropyl)-thiocarbamide] showed complexing activity with respect to Pt(IV) (70 mg/g) [4]. In this connection, it was of interest to create composites that simultaneously combine these two components.

In this work, composites based on 4-vinylpyridine-2-hydroxyethylmethacrylate copolymers and poly[N,N'-bis(3-silsesquioxanilpropyl)thiocarbamide] were obtained by sol-gel synthesis. The mechanism and kinetics of adsorption of platinum(IV) ions from aqueous solutions were studied.

II. METHODS AND MATERIALS

Copolymers of 4-vinylpyridine (4-VP) with 2-hydroxyethylmethacrylate (HEMA) were synthesized according to [5], the composition of the copolymer is 4-VP:HEMA = 70:30 mol %. N,N-bis(3-triethoxysilylpropyl)-thiocarbamide (BTM) was obtained. Sol-gel synthesis of the hybrid composite was carried out in accordance with the methods previously developed by mixing the solution of the 4-VP-HEMA copolymer in ethyl alcohol with BTM. The process was carried out in an alkaline medium (pH 9) while stirring the mixture on an electromagnetic stirrer for 1 h at room temperature. As a result, turbidity of the mixture and formation of an insoluble precipitate are observed. The precipitate formed was washed repeatedly with water and ethyl alcohol and dried in a vacuum desiccator until constant weight was obtained. The yield of the sol-gel product was 76%. Elemental analysis of the reaction product was carried

out on a Thermo Finnigan gas analyzer. The IR spectrum of the composite was obtained using a Specord IR-75 spectrometer in KBr tablets and Vaseline oil, as well as on a Bruker IFS-25 spectrometer. The surface structure of the synthesized composite material was studied by scanning electron microscopy using a Philips 525-M instrument.

The TGA curves of the sample were taken on a NETZSCH STA 449F1 derivatograph. The rate of heating in air was 3°/min, and the maximum temperature was 550 °C. Adsorption of Pt (IV) was carried out from hydrochloric acid (HCl 1 mol/L) solution of hydrogen hexachloroplatinate (H₂PtCl₆ · 6H₂O of the reagent grade) with an initial platinum concentration of 3 × 10⁻² mol/L. Determination of the concentration of platinum ions in the solution was carried out by the spectrophotometric method using a PE-5400B spectrophotometer. Regeneration of the adsorbent was carried out with a 10% solution of thiourea in hydrochloric acid (pH 1). The degree of desorption of platinum upon contact with the desorbent solution for 1 h at the boiling point was 98-99%.

III. RESULTS

The sol-gel synthesis of the composite under consideration proceeds as a process of hydrolytic polycondensation of BTM in the presence of 4-VP-HEMA copolymer. This results in the formation of a two component polymer system consisting of poly[N,N'-bis(3-silsesquioxanilpropyl)thiocarbamide], in the three-dimensional structure of which the macromolecules of the copolymer are firmly intercalated:

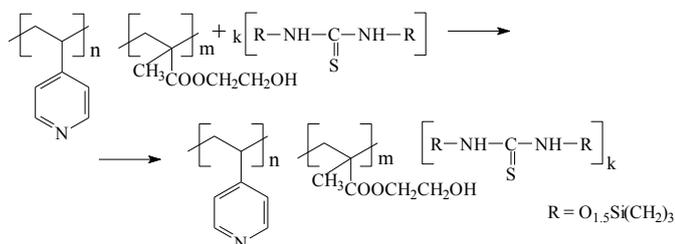


Fig. 1

The composite is a solid powdered substance that is insoluble in water, mineral acids, and organic solvents. The composition and the structure of the composite obtained have been confirmed by IR spectroscopy and elemental analysis data. In the IR spectra of the composite, there are absorption bands at 1100–1250 cm⁻¹, related to the valent vibrations of the siloxane bond, which confirms the formation of the cross-linked structure of the silicon framework during gel formation. Characteristic displacement of the absorption band of the pyridine nitrogen atom in the high-frequency region from 1600 to 1637 cm⁻¹ in comparison with the position in the IR spectra of the initial poly-4-vinylpyridine is observed. The bands of C=O valent vibrations (1740 cm⁻¹), which confirm the presence of HEMA in the composition of the composite, are retained.

High thermal stability of the synthesized composite is due to the presence in its composition of the organosilicon polymer having a three-dimensional structure. According to

thermogravimetric analysis, the TGA curve of the synthesized composite has a steplike character: at the first stage, the aliphatic fragments of the chain are destroyed, while at the second stage aromatic fragments are destroyed. The temperature of the beginning of decomposition of the composite with 10% weight loss from the initial one is 360° C. A significant loss of mass (more than 50%) at temperatures above 400° C corresponds to the complete burnout of the organic part “Fig. 2”.

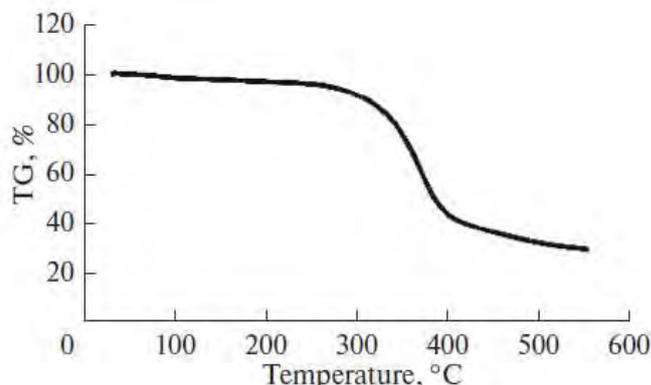


Fig. 2. Thermogravimetric curve of the composite.

According to electron microscopy “Fig. 2”, the structure of the resulting composite is described by aggregated globules of regular shape with a predominant particle size of 0.2-0.4 μm.

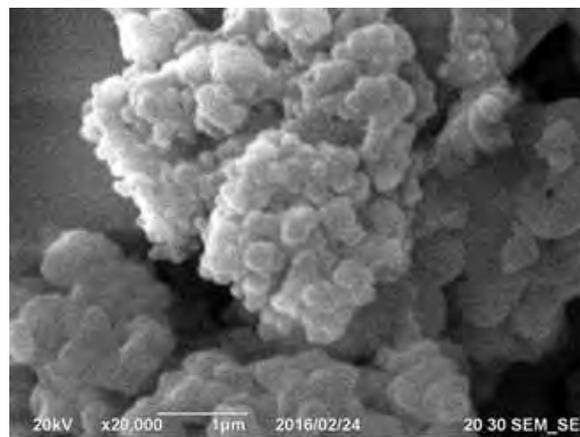


Fig. 3. Electron microscopic image of the composite surface.

The sorption activity of the composite was studied with respect to Pt(IV) ions, in a solution of hydrochloric acid, where this metal is present in the form of acidic complexes of the composition [PtCl₆]⁻². The degree of extraction of metal ions decreases slightly with an increase in the concentration of hydrochloric acid in the interval of 0.25-3.0 mol/L. This may be due to an increase in the competing participation of acid ions in coordination with pyridine nitrogen atom of the composite.

At the chosen acidity value of the medium (1 mol/L), complete sorption equilibrium in the system is achieved after 3 h of contact of the composite with Pt(IV) solution.

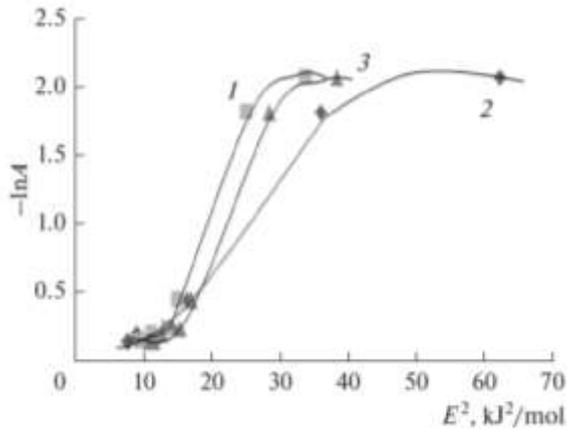


Fig. 8. Pt(IV) adsorption isotherms in the coordinates of the linear Dubinin-Radushkevich equation with (1) 298, (2) 318, and (3) 338 K.

The value of the average free energy of adsorption (E) according to the Dubinin-Radushkevich model “Fig. 4” (Table 1) was calculated using Eqs. 1-3:

$$E = (-2k)^{-0.5} \quad (1)$$

$$\ln a - \ln a_m - k\varepsilon^2 \quad (2)$$

$$\varepsilon = RT \ln(1 + 1/C) \quad (3)$$

where k is the adsorption process constant (mol^2/kJ^2) and ε is the Polanyi potential (kJ/mol).

Analysis of the parameters of the adsorption models used (Table 1) shows that the process under consideration in the studied temperature range is most adequately described by the Freundlich model of monomolecular adsorption, as well as the Dubinin-Radushkevich equation [8].

TABLE I. PARAMETERS OF ADSORPTION MODELS

Parameters of models	Temperature, K		
	298	318	338
<i>Langmuir model</i>			
R^2	0,982	0,721	0,833
<i>Freundlich model</i>			
R^2	0,9546	0,9707	0,9847
ΔG , kJ mol	-5,713	-9,971	-13,985
<i>Dubinin-Radushkevich model</i>			
E	8,2539	18,904	19,1938
R^2	0,9114	0,9114	0,9517

The integral kinetic curves of adsorption of platinum(IV) are shown in “Fig. 9”. Taking into account the heterogeneity of the studied processes, several kinetic models were used to describe them. To assess the contribution of the diffusion stages to the overall rate of the sorption, the experimental kinetic data were processed in the framework of the Boyd-Adamson diffusion model [9], which made it possible to estimate the influence of intra- and externally diffusion processes on the total adsorption rate.

Within the framework of the Boyd-Adamson model, when external diffusion is limited, the kinetic curve should be linear in the coordinates $-\lg(1-a/a_e)=f(\tau)$ [11], where a_e is the amount of sorbed platinum in the equilibrium state, mmol/g “Fig. 9”.

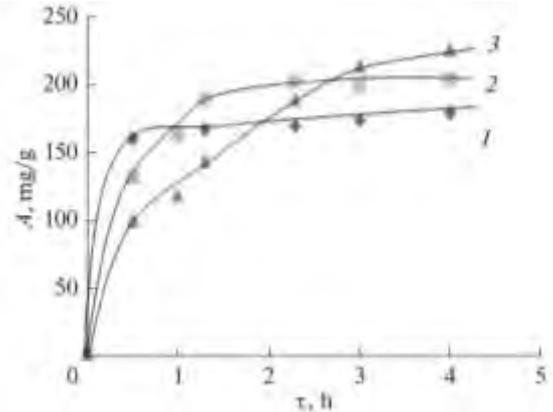


Fig. 9. Kinetic curves of adsorption of platinum(IV) ions.

If the sorption in the grain of the sorbent (internal diffusion) is the limiting stage of the process, the linearity of the kinetic curves should be observed in coordinates $(a/a_e) = f(\tau^{1/2})$ [9] “Fig. 10”.

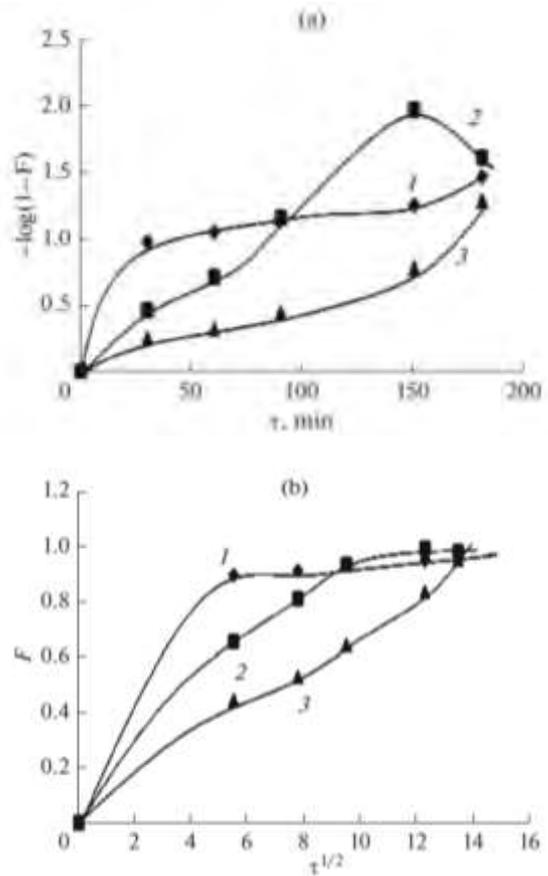


Fig. 10. Kinetic curves of adsorption of platinum(IV) ions in the framework of the Boyd-Adamson diffusion model: (a) external diffusion, (b) internal diffusion.

The character of the kinetic dependencies in the coordinates of the Boyd–Adamson model “Fig. 10” indicates the significant influence of the external diffusion stage of mass transfer (film kinetics) in the overall adsorption rate at the initial stage of the process and the predominance of intradiffusion interaction (gel kinetics) at the final stage.

TABLE II. EQUATIONS OF MODELS OF CHEMICAL KINETICS

Kinetic model	Integral form of equation*	Linearized form of equation*
<i>Pseudo-first-order</i>	$a_i = a_e \cdot (1 - e^{-k_1 \tau})$	$\ln(a_e - a_i) = \ln a_e - k_1 \tau$
<i>Pseudo-second-order</i>	$a_i = \frac{\tau}{\frac{1}{k_2 \cdot a_e^2} + \frac{\tau}{a_e}}$	$\frac{1}{a_e - a_i} = k_2 \tau + \frac{1}{a_e}$
<i>Elovich</i>	$a_i = \frac{1}{\beta} \cdot \ln(1 + \alpha \cdot \beta \cdot \tau)$	$e^{\beta a_i} = 1 + \alpha \cdot \beta \cdot \tau$

* τ is time, min; a_e is the equilibrium value of the adsorption, mmol/g; a_i is the value of the adsorption at a given time, mmol/g; k_1 is a rate constant of the pseudo-first-order model, min⁻¹; k_2 is the rate constant of the pseudo-second-order model, g/(mmol min)⁻¹; α is initial rate of sorption, g/(mmol min)⁻¹; and β is the constant of the Elovich equation, g/mmol.

The total adsorption rate was characterized within the framework of the pseudo-first- and pseudo-second-order kinetic models, as well as the Elovich equation [10] (Table III).

As the values of determination coefficients R² show (Table III), the pseudo-second-order model, which assumes that the chemical reaction limits the sorption process under the condition of interaction between sorbate and adsorbent in the ratio of 1:1, is the most applicable for describing the processes under study.

TABLE III. KINETIC PARAMETERS OF ADSORPTION

Kinetic model	Rate constant			Determination coefficient, R ²		
	298 K	318 K	338 K	298 K	318 K	338 K
<i>Pseudo-first-order</i>	0,00019	0,00021	0,00007	0,6836	0,8087	0,4550
<i>Pseudo-second-order</i>	0,0013	0,0031	0,0009	0,9085	0,9919	0,9498
<i>Elovich</i>	0,00011	0,00023	0,00018	0,909	0,6835	0,9694

IV. CONCLUSIONS

The formation of hybrid composites as a result of sol-gel synthesis involving N,N-bis(3-triethoxysilylpropyl) thiocarbamide and 4-vinylpyridine-2-hydroxyethyl-methacrylate copolymer was studied. It was shown that composites possess high thermal and chemical stability.

Composite materials showed a sorption ability with respect to platinum(IV) ions, which is the result of chemisorption, which results from the formation of ion-coordinated Pt(IV) complexes with functional groups of the composites.

The value of the static sorption capacity of the composite for platinum(IV) reaches up to 215 mg/g, which will make it possible to use it as a material for extraction of platinum salts from process solutions.

The most adequately adsorption process is described by the Freundlich model of monomolecular adsorption, as well as the Dubinin–Radushkevich equation. The rate of chemical interaction of platinum ions with heteroatomic groups of the composites is described by a pseudo-second-order equation.

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