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Palladium(II) and cobalt(II) sorption by silica gel sequentially modified by polyhexamethylene guanidine and a nitroso-R salt

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The sorbent prepared by sequential treatment of silica gel by polyhexamethylene guanidine of linear structure and nitroso-R salt is suggested for sorption concentration of palladium(II) and cobalt(II) from aqueous solutions.

Sorption is widely used for concentration of the elements. It allows one to concentrate micro components from bulk concentrated by macro component solutions on relatively small weight of the sorbent. Chemically modified silicas (CMSs)[1,2] with functional groups covalently bound to the surface are the most extensively used sorbents on inorganic oxide supports. The main limitations for their extensive use are inaccessibility of organic silicon modifiers and a complicated synthesis. The sol–gel method and impregnation of the silica surface by reagents are used, as a rule, in non-covalent fixation of the reagents.[3] The first way consists in the putting of appropriate reagents into solution during gelatinization. This way is characterized by long duration of the sorbent synthesis. The reagent distribution in the bulk of a sorbent matrix makes the majority of reagent molecules not easily accessible. Treatment of silicas by aqueous or water-organic solutions of the reagents is in the basis of the second way. This causes not strong enough fixation of the reagents on the silica surface.

It is necessary to make a surface layer with effective positive charge in order to fix reagents with negatively charged groups on the surface. Such a layer can be prepared during the sorption of polyamines, particularly,[4] linear polyhexamethylene guanidine (PHMG), which has convenient amine group configurations. The strong fixation of PHMG on the surface of silica gel proceeds due to formation of multicentered hydrogen bonds between amine groups of PHMG and hydroxyl groups of the surface. Subsequent fixation of organic reagent is provided due to electrostatic interaction between negatively charged sulfonate groups of the organic compound and protonated amine groups of PHMG, which are not evolved in hydrogen bond formation with surface hydroxyl groups. Such an approach allows one to carry out the fixation of any quantity of the reagent on the surface pretreated with PHMG silica. At the low concentration of the reagent on the surface, free amine groups remain. They can interact with extracted metal ions.

In this paper, palladium(II) and cobalt(II) sorption by silica gel sequentially modified by PHMG and 1-nitroso-2-naphthol-disulfo acid (nitroso-R salt) are considered.

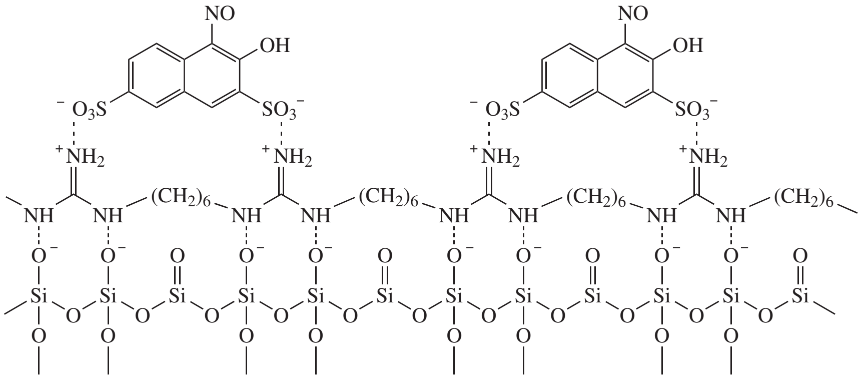
Silica gel 60 Merck (100–230 mesh, specific surface area of 270 $m^2 g^{-1}$, and pore diameter of 12 nm) was used as a support for the sorbent synthesis.

The manner of silica gel modification was as follows: 100 ml of 1% PHMG solution was added to 10 g of silica gel under stirring; then, the sorbent was separated from solution by decantation, washed by distilled water and dried at 80 °C. After that, 100 ml of aqueous solution of nitroso-R salt (NRS) of required concentration was added to silica gel modified by PHMG (SiO_2–PHMG) and the mixture was stirred for 5 min. Prepared sorbent (SiO_2–PHMG–NRS) was washed with distilled water and dried in air. During sequential treatment by PHMG and NRS supramolecular ensemble was generated on the silica gel surface. All three reagents in this ensemble are bound due to nonvalent interactions.

In this case, the surface of the initial silica gel can be considered as a macromolecule (supramolecule)[1] with a large quantity of hydroxyl groups.

Thus, during sorbent synthesis supramolecular ensembles on the silica gel surface have three kinds of groups: surface hydroxyl groups, amine groups of PHMG, and functional groups of NRS, which can interact with extractable metal ions under appropriate conditions.

During investigation of palladium(II) and cobalt(II) sorption using a batch equilibrium technique, 0.1 g of the sorbent was



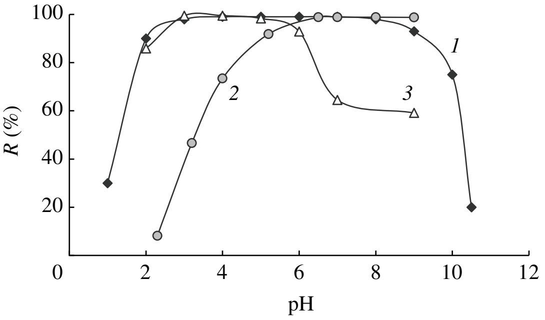


Figure 1 Batch equilibration of nitroso-R salt with (*1*) SiO_2–PHMG, (*2*) cobalt(II) and (*3*) palladium(II) SiO_2–PHMG–NRS as a function of pH. (C_{Me} = 10 mg cm^{-3}; V = 10 ml; sorbent weight of 0.1 g).

put into the solution of adjusted pH, which contained one of the elements and stirred for 1–10 min at 20 °C. The sorbent was isolated from solution by decantation, moved into fluoroplastic cuvette, and a diffuse reflectance spectrum was measured. The analysis of metal distribution was carried out by flame (acetylene–air) atomic absorption spectrometry using a Saturn-2M spectrometer (λ_{Pd} = 340.4 nm, λ_{Co} = 241.0 nm).

The maximum extraction of nitroso-R salt by the SiO_2–PHMG sorbent at room temperature was observed at pH 2–9 (Figure 1). The equilibration time was 2 min. Increase or decrease of pH cause destruction of the surface supramolecular complex. This may be connected with protonation of sulfonate groups of the reagent at pH < 2, and deprotonation of amino groups of PHMG at pH > 9. The surface layer is stable at the optimum pH even at high saline background (up to 5 g dm^{-3} NaCl). SiO_2–PHMG–NRS quantitatively extracts (extraction ≥99%) palladium(II) over pH 3–6, and cobalt(II) over pH 5–9 (Figure 1). The equilibration time is less than 5 min and independent of the nature of metal ion. pH range of maximum metal ions extraction coincides with pH range of maximum degree of complex formation of metal ions and NRS in solutions.[5,6]

Isotherms of palladium(II) sorption by SiO_2–PHMG–NRS with different quantity of fixed NRS are represented in Figure 2. Complex of palladium(II) with the ratio Pd:NRS = 1:2 is formed (Figure 2, curve *1*) on the SiO_2–PHMG–NRS over maximum concentration of nitroso-R salt on the surface and maximum metal capacity. It corresponds to composition of palladium(II) complex in the solutions.[5] Complex with the ratio Pd:NRS = 2:1 (Figure 2, curve *2*) is formed over low concentration of NRS on the sorbent surface. Excess of sorption capacity in comparison with fixed NRS connected with the fact that over the low concentration of the reagent on the surface of SiO_2–PHMG–NRS, the sorption of palladium(II) occurs by both complexing mechanism as a result of interaction with NRS and ion-exchange mechanism as a result of interaction of chloride complex of palladium(II) with protonated amine groups of PHMG.

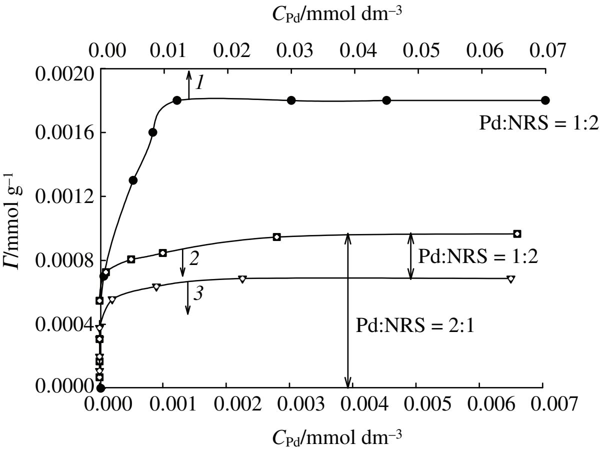


Figure 2 Isotherms of palladium(II) sorption by SiO_2–PHMG–NRS. C_{NRS}, 10^{-4} mmol g^{-1}: (*1*) 26.5, (*2*) 5.3, (*3*) 0.0.

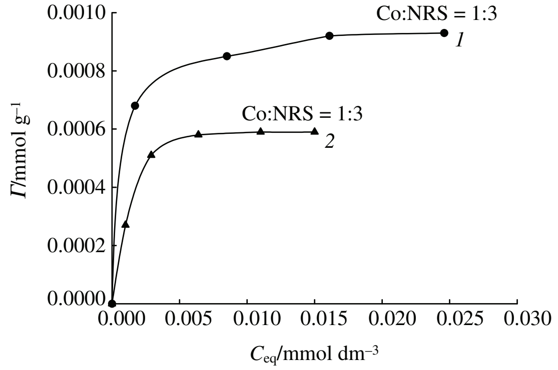
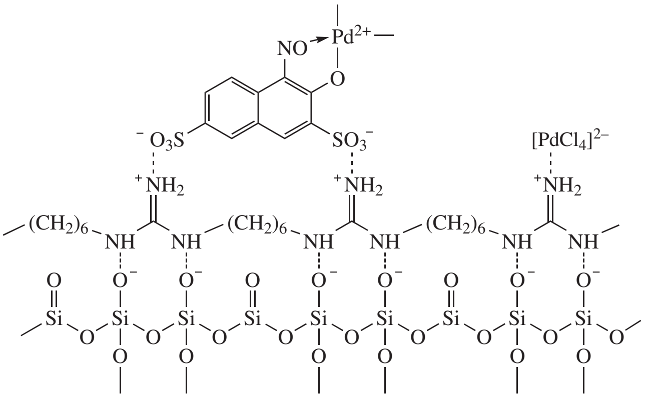


Figure 3 Isotherms of cobalt(II) sorption by SiO_2–PHMG–NRS. C_{NRS}, 10^{-4} mmol g^{-1}: (*1*) 26.5, (*2*) 13.5.



This conclusion is confirmed by the absence of palladium(II) sorption by unmodified silica gel (it is the evidence of non-interaction between chloro complexes of palladium(II) and surface hydroxyl groups under examined conditions), and by isotherm of its sorption by SiO_2–PHMG (Figure 2, curve *3*). The comparison of difference in palladium(II) capacity between sorbents SiO_2–PHMG and SiO_2–PHMG–NRS (Figure 2, curves *2* and *3*) and the quantity of fixed NRS show that palladium(II) coordinated by NRS is in the surface complex with the ratio Pd:NRS = 1:2. Over maximum filling of SiO_2–PHMG surface by nitroso-R salt all amine groups of PHMG are coupled with sulfonate groups of the reagent and sorption of palladium(II) chloride complexes by ion-exchange mechanism is impossible.

During the extraction of cobalt(II), coordinated saturated complexes of cobalt(III) with the ratio Co:NRS = 1:3 (Figure 3) are formed on the SiO_2–PHMG–NRS surface irrespective of NRS concentration on the silica gel surface. Complex of cobalt(III) of the same composition is formed in the solutions.[6] There is no considerable interaction between cobalt(II) and amine groups of PHMG fixed on the surface of silica gel under sorption conditions (pH 5–6).

Thus, the coordinated saturated complexes of palladium(II) and cobalt(III) with NRS are formed irrespective of NRS concentration on the surface because there is no strong fixation of the reagent on the silica gel surface, and reagent molecules can be retracted towards the metal ions.

The obtained complexes of palladium(II) and cobalt(III) with NRS on the SiO_2–PHMG–NRS surface have an intense reddish-brown colour. Spectroscopic characteristics of palladium(II) and cobalt(II) complexes on the SiO_2–PHMG–NRS surface are similar to the characteristics of these metal complexes with NRS in solu-

Table 1 Metrological performance of cobalt and palladium sorption-photometric determination procedure using SiO_2–PHMG–NRS.

Element	Linearity of the calibration curve, mg/0.1 g	Limit of detection, mg/0.1 g	Limit of detection,[a] mg ml^{-1}	S_r
Co	0.3–5	0.1	0.01	0.06
Pd	2–15	0.5	0.05	0.05

[a] Sorption from 10 ml of the solution.

tions.[5,6] Diffuse reflectance spectra of palladium(II) and cobalt(III) complexes have bands at 420 nm and shoulders at 510–515 nm. It is difficult to determine palladium(II) and cobalt(III) if they present together because their complexes with NRS have identical spectroscopic characteristics. However, they are sorbed differently at pH 2. It allows the quantitative separation of palladium(II) from cobalt(II) to be carried out. The separation factor $S_{Pd/Co}$ is 10^3 at pH 2.

SiO_2–PHMG–NRS is characterized by good kinetic properties; so at the ratio $V:m = 10^2$ and $V:m = 10^3$ equilibration time during extraction of palladium(II) and cobalt(II) is less than 5 min. Distribution coefficients under the optimum conditions are 1×10^5 cm^3 g^{-1}.

The formation of palladium(II) and cobalt(III) complex compounds on the surface of SiO_2–PHMG–NRS was used in sorption-photometric determination of these metals. The procedure performance is represented in Table 1. Note that the limits of detection (mg cm^{-3}) decreased proportionally to an increase of the solution volume for sorption. 10^3–10^5-folds quantities of Mg^{II}, Ca^{II}, Sr^{II}, Zn^{II}, Al^{III}, Ga^{III}, In^{III}, Pt^{II}, Cu^{II}, Fe^{II}, Ni^{II} and saline background (up to 10 g dm^{-3} NaCl) do not interfere in sorption pre-concentration and sorption-photometric determination of cobalt and palladium.

The suggested sorbent and procedures are comparable in performance with procedures, based on sorption of complex compound of cobalt(III) with NRS by silica gel chemically modified with quaternary ammonium compounds,[7] and sorption of palladium(II) by silica chemically modified with mercaptopropyl groups.[8]

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