

POLYSTYRENE LATEX WITH PARTIALLY HYDROLYZED PNAI GRAFTS AT THE SURFACE AS Pt(IV) SORBENT

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The ability of the polystyrene latex with partially hydrolyzed poly[(N-acetylimino) ethylene] grafts at the surface (PSt-PNAI, h) as a sorbent for Pt(IV) was evaluated. The process characteristics were established by analysis according to the sorption isotherm models (Freundlich and Langmuir) and by kinetic study. It was found that the sorbed amount and percentage of Pt(IV) recovery from the aqueous solutions increase with increasing pH and initial concentration, and reach a maximum at pH = 10, with a sorption capacity of 1111 mg/g and a sorption half-time of about 90 min. The equilibrium distribution of Pt(IV) between the two phases (sorbent and solution) is described by means of Langmuir model of monomolecular layer adsorption. The sorption data indicate the applicability of a pseudo-second order kinetics.

INTRODUCTION

In the last years the preconcentration, separation and determination of platinum group metals (PGM), especially platinum, from industrial, environmental and biotic matrices became of increasing interest due to the potential applications of these valuable metals in various fields.

The sorption method has been frequently used for the solid phase extraction and preconcentration of trace amount of PGM.¹⁻⁵ A high variety of sorbents are suitable for this purpose: silica gels impregnated or chemically modified with complexing ligands,⁶ macroporous chelating resins with covalently attached selective ligands,⁷⁻⁸ fibrous complexing sorbents.⁹ Among them, the sorbents modified with ligands containing nitrogen as a donor atom are successfully applied.^{10,11}

We presented in a previous paper the possibility to prepare stable hybrid platinum nanocatalysts-polymer systems by the reduction of the alcoholic solutions of H₂[PtCl₆] in the presence of poly[(N-acetylimino)ethylene] (PNAI) based graft copolymers or of polystyrene latexes with PNAI surface grafts.¹²

The aim of this work was to study the sorption ability of polystyrene latex with partially hydrolyzed hydrophilic poly[(N-acetylimino)ethylene] shell with respect to Pt(IV) ions from aqueous solutions.

EXPERIMENTAL

Materials

Styrene (St, Merck) was purified by vacuum distillation and was stored on molecular sieves.

The platinum precursor dihydrogen hexachloroplatinate (anhydrous, H₂PtCl₆·6H₂O, Aldrich), the solvents (commercial ethyl and methyl alcohol) and the kalium persulfate (K₂S₂O₈, Aldrich) were used without further purification.

The poly[(N-acetylimino) ethylene] macromere MA₁₅, having a structure of unsaturated polyester, was obtained according to literature data.^{13,14} The average polymerization degrees of the sequences inserted between two polymerizable bonds were of 14.5, and the functionalization degree 95%.

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The polystyrene microparticles with poly[(N-acetylmino)ethylene] shell used as sorbent were prepared according to the previously published procedure,¹² by soapless emulsion polymerization. The following recipe was used: St - 5g, water - 95g, MA₁₅ - 0.5g, K₂S₂O₈ - 0.1g, 75°C, 6h, inert atmosphere (N₂). The resulted microparticles were separated and purified by centrifugation and repeated washings with bidistilled water.

The polystyrene latex with superficial PNAI grafts (Dn = 246nm, Dw = 260, PI = 1.06) was subjected to acid hydrolysis after redispersion in 10 wt% aqueous solutions of HCl, for 6h at 60°C. According to the spectral (H-NMR) and analytical data, the particles resulted after hydrolysis contained 15 wt% ethylenimine units in the hydrophilic shell.

The stock solution of 1 mg Pt(IV)/mL was prepared by dissolving K₂[PtCl₆] (Aldrich) in 1M hydrochloric acid. The working solutions were obtained from the stock solution by dilution with bidistilled water.

The pH values of the solutions were adjusted by adding 0.2 M HCl, 0.2 M sodium acetate or ammonia buffer solutions, respectively.

All reagents were of analytical grade.

Characterization

A S104D spectrophotometer was employed for the determination of Pt(IV). The pH measurements were realized with a Radelkis OP. 205 instrument, equipped with a combined glass electrode.

Methods

The sorption of Pt(IV) on the PSt (modified with PNAI) microparticles was studied by batch experiments. Samples of 0.03 g sorbent were equilibrated with 25 mL solutions containing 10 mL of buffer and various amounts of Pt(IV) ions and then dispersed by ultrasonication (10 min). After a fixed time, usually 24h, the phases were separated by centrifugation (6000 rot/min).

Pt(IV) concentration in the separated filtrate was monitored by spectrophotometric method after pretreatment with SnCl₂. The measurements were performed at $\lambda = 403$ nm.

The sorption capacity of the polymer microparticles was evaluated by the amount of Pt(IV) retained by 1 g polymer or by the percentage of Pt(IV) retained on polymeric microspheres, calculated with the relations (1) and (2):

$$q = \frac{C_o - C}{G} \cdot V \cdot 10^{-3} \text{ (mg / g)} \quad (1)$$

$$R = \frac{C_o - C}{C} \cdot 100 \text{ (\%)} \quad (2)$$

where C_o and C are the Pt(IV) concentration in solution before and after the sorption process.

RESULTS AND DISCUSSION

The influence of experimental factors (pH of the solution, metal ion concentration, phases contact time) on the sorption process was investigated in order to estimate the proper condition for preconcentration of Pt(IV) ions onto polystyrene microparticles with partially hydrolyzed PNAI shell.

Effect of pH

The pH value of the solution can have a significant effect on the Pt(IV) sorption due to the presence of both imine nitrogens and carboxylic groups in the structure of the hydrophilic shell of the microparticles. The experimental data illustrated in Fig.1, show that the Pt(IV) retention on polymeric latex from buffered solutions with an initial concentration of 40 mg/L takes place in both acidic and alkaline (ammoniacal) media. Also, both the sorbed amount and percentage of Pt(IV) recovery from the aqueous solutions increase with increasing pH. Maximum values were observed at pH= 10.

The obtained data suggest that the Pt(IV) ions are retained by different mechanisms. In acidic solutions (pH ≤ 3) the nitrogen atoms from the imine groups are protonated and bind the anionic chlorocomplexes such as [PtCl₆]²⁻ only by ion exchange mechanism. At the increase of solution pH (> 3), Pt(IV) is retained especially by a complexation mechanism (replacement of chloride from coordination sphere of [PtCl₆]²⁻ ions with imine groups of the sorbent followed by the formation of chelate rings). At the same time, the terminal carboxylic groups are susceptible to electrostatic interactions with cationic complexes such as [Pt(NH₃)₆]⁴⁺ in ammoniacal media.

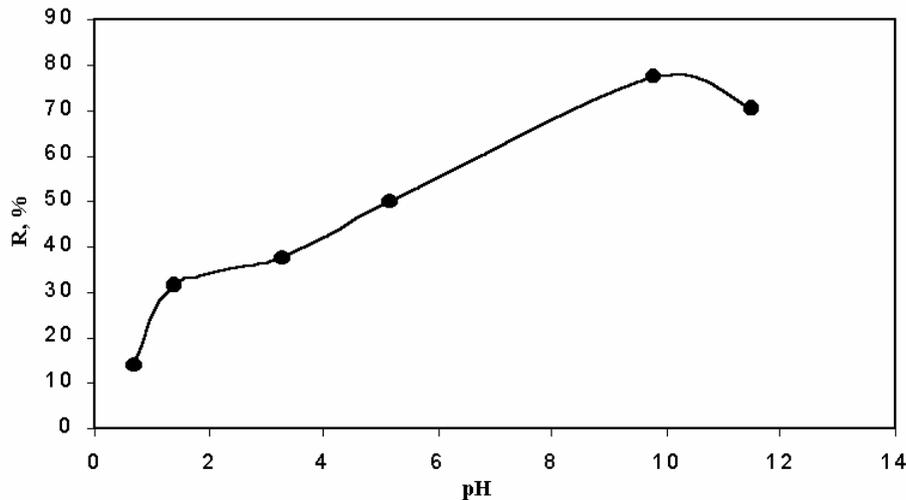


Fig. 1 – The influence of solution pH on Pt(IV) sorption onto PSt-PNAI latex.

Effect of the initial Pt(IV) concentration

The recovery of Pt(IV) on PSt-PNAI latex was determined in solutions of pH = 10 at different initial platinum concentrations (C_0).

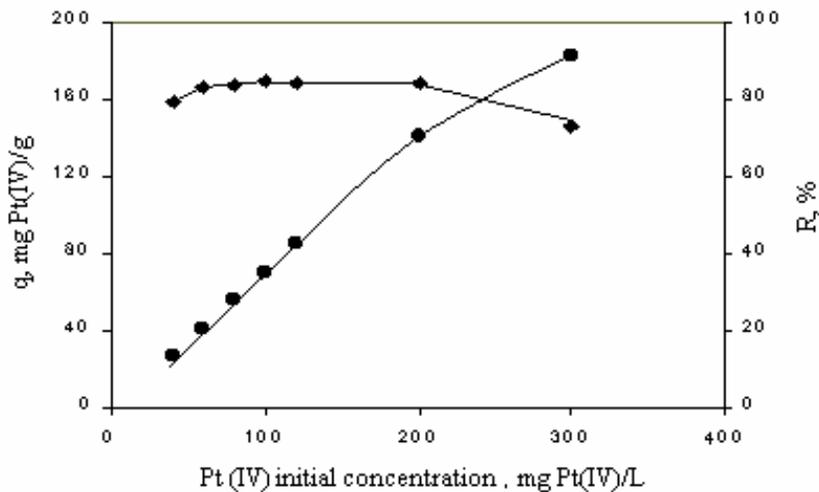


Fig. 2 – Effect of initial Pt(IV) concentration on the sorption process. (●) q, mg/g; (◆) R%.

The results represented in Fig. 2 show that the amount of the sorbed Pt(IV) increases with increasing initial concentration, while the percentage of Pt(IV) recovery has an insignificant variation with the initial concentration.

Sorption isotherms

The equilibrium distribution of Pt(IV) ions between the sorbent solid phase and the aqueous phase determined from the solutions of pH = 10 and increasing initial concentrations is plotted as a sorption isotherm in Fig. 3.

The experimental equilibrium sorption data were analyzed according to the traditional sorption isotherm models, the Freundlich and the Langmuir ones.

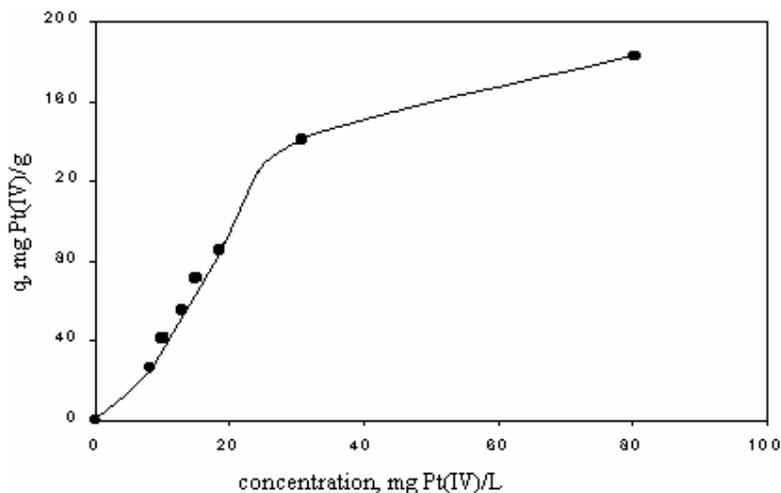


Fig. 3 – Isotherm of Pt(IV) sorption onto PST-PNAI latex.

The Freundlich isotherm is given by the linearised equation (3):

$$\log q = \log K_F + 1/n \log C \quad (3)$$

where K_F parameter is related to the adsorption capacity and n is a measure of sorption energy (a value $1 < n < 10$ corresponds to a favorable sorption).

The Langmuir isotherm is expressed by the linearised equation (4):

$$1/q = (1/q_0 K_L C) + 1/q_0 \quad (4)$$

where K_L is related to the intensity of the sorption process and q_0 is the maximum value of sorption capacity.

The values of Freundlich and Langmuir constants calculated from the intercept and slope of the corresponding linear plots together with their coefficients of correlation (R^2) are listed in Tab. 1.

Table 1

Freundlich and Langmuir constants

Freundlich isotherm			Langmuir isotherm		
K_F (mg/g)(L/mg) ^{1/n}	n	R^2	q (mg/g)	K_L (L/g)	R^2
9.658	1.409	0.9069	1111	4.098	0.9612

The values of correlation coefficients (R^2) from Tab. 1 show that the experimental Pt(IV) sorption data better fitted by Langmuir isotherm model. The high K_L values, which reflect the binding energy between functional groups of sorbent and metal ions, confirm a chelating mechanism for Pt(IV) sorption (pH = 10).

The apparent free energy of adsorption was calculated from the Langmuir constant using the following equation:

$$\Delta G = - RT \ln K_L \quad (5)$$

The negative value of free energy changes ($\Delta G = -20.53$ KJ/mol) indicates that the process is feasible and spontaneous.

Effect of contact time (sorption rate)

The effect of the contact time on the Pt(IV) sorption onto sorbent microparticles was studied in solution of pH = 10 and at an initial concentration of 100 mg Pt(IV)/L. The kinetic curves are represented in Fig. 4.

As seen in Fig. 4 the equilibrium time required for maximum removal of Pt(IV) from solution was found to be of 10 - 12 hours. However the sorption half-time ($t_{1/2}$) was of ≈ 90 min.

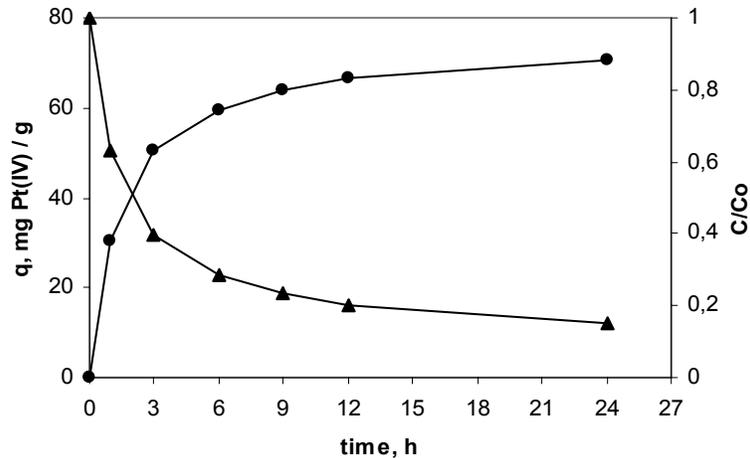


Fig. 4 – Variation of sorbed Pt(IV) amount (●) and of removal degree (C/C_0) (▲) versus time.

The kinetic data were interpreted using two kinetic models: pseudo-first order (Lagergren models) and pseudo-second order models, expressed by the equations:

$$\log (q_0 - q) = \log q - K_1 t \quad (6)$$

and respectively

$$t/q = (1/K_2 q_0^2) + t/q_0 \quad (7)$$

where K_1 (mg/g min) is the Lagergren rate constant of the first order sorption, K_2 (g/mg min) is the rate constant of the second order sorption and $K_2 \cdot q_0^2 = h$ is the initial sorption rate (mg/g min).

The rate constants calculated from the kinetic plots according to the two models and the correlation coefficients are presented in Tab. 2.

Table 2

Kinetic parameters of the Pt(IV) sorption on PSt-PNAI latex

Pseudo-first order		Pseudo-second order		
K_1 (mg/g.min)	R^2	K_2 (g/mg.min)	h (mg/g.min)	R^2
0.016	0.961	0.000146	0.8257	1

The results of Tab. 2 showed that the second order equation model provided the best correlation with experimental results. This fact indicates that the sorption of Pt(IV) ions on PSt-PNAI latex follows the pseudo-second order kinetic model and the intraparticle diffusion (respectively the diffusion through the chains of the polymeric shell) is the rate-controlling step.

CONCLUSION

The study of the sorption process on PSt-PNAI latex¹² indicated that this new polymeric material can be used as an effective sorbent material for the treatment of Pt(IV)-bearing aqueous streams.

The sorption of Pt(IV) on polystyrene latex with partially hydrolyzed PNAI grafts depends on solution pH, on initial Pt(IV) concentration and contact time. The maximum retention was obtained for a pH = 10, at $C_0 = 300$ mg Pt(IV)/L after 10-12hours.

The equilibrium distribution of Pt(IV) between the sorbent and solution can be described by using the Langmuir model of monomolecular layer adsorption.

The apparent free energy of sorption process suggests the affinity of chelating resin against Pt(IV) ions.

The sorption data indicated the applicability of a pseudo-second order kinetics.

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