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# STUDY OF PALLADIUM (II) ION SEPARATION BY CONCENTRATION WITH P-AMINOSALICYL ACID FRAGMENTED POLYMER SORBENT

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**Abstract.** A new polymer sorbent based on styrene copolymer of maleic anhydride has been synthesized. This sorbent contains an amine fragmented p-aminosalicylic acid. The temperature resistance of the obtained sorbent and its metal-forming polychelates was determined by thermogravimetric analysis. It was found that there are occurs the separation of water from the sample with an endothermic effect, the destruction of macromolecules with a weak exothermic effect at relatively high temperatures and the oxidation (or combustion) of destroyed particles. It is not advisable to use sorbents based on styrene copolymer at temperatures above 100-120°C.

The obtained sorbent was identified by IR spectroscopy. Comparison of IR spectra shows that during the formation of the complex there are shifts in the oscillation frequencies of the groups in the sorbent links. This confirms the participation of these groups in complex reactions with metals. Sorption and desorption of palladium (II) ions under optimal conditions were determined. The optimal pH for the newly synthesized sorbent was determined to be 4.

Experiments have shown that the sorption equilibrium is reached within 120 minutes with a p-aminosalicyl fragmented chelate-containing sorbent based on malein-anhydride styrene copolomer. The maximum absorption density of Pd (II) ion with the new polymer sorbent is 800 mg / m1. (Stmax = 512mq / q). As the density of the metal ion increases, the sorption capacity of the sorbents increases. It was found that for individual systems, an increase in the value of ionic strength in the liquid phase to 0.2-0.8 mol/l does not lead to a significant decrease in the sorption rate.

Experience has shown that $HclO_4$ acid is better able to desorb with a new polymer sorbent. In order to determine the optimal concentration of perchlorotic acid in the desorption process, desorption experiments at different concentrations of acid were performed. After desorption, the adsorbent does not lose its sorption properties. The obtained sorbent can be reused for thickening.

***Keywords:*** *sorption, desorption, p-aminosalicyl, thickening, maleic anhydride, copolymer*.

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## 1. Introduction

Separation and sorption of palladium group metals by various sorbents is one of the most widely used methods. Synthetic sorbents are mainly used in this separation method. Synthetic sorbents differ from natural sorbents in a number of properties. Because, unlike natural sorbents, synthetic sorbents have higher sorption capacity. Polymer chelate sorbents containing functional analytical group are used during the sorption process (Abdrashitov *et al.*, 2015; Ergozhin *et al.*, 2019; Kholmogorova *et al.*, 2018). The selectivity of chelate-forming polymer sorbents against various metal ions is expressed by the ratio of the stability constants of the complexes formed in the sorbent phase. It is known that palladium ion, unlike other metals, has the property of forming a more stable complex with ligands containing nitrogen and sulfur in an acidic environment. In addition, the main sorbents for the sorption of palladium (II) are sorbents containing heterocyclic azo and amino groups (Mokhodoeva *et al.,* 2010; Pavlova *et al.,* 2014; Pavlova *et al.,* 2010).

## 2. Devices and solutions

The palladium (II) solution used in the experiment (1000 mg/1 concentration) was prepared from PdCl2 (k.t.) salt and its concentration was determined by comparing it with the standards. The equilibrium concentration of Pd (II) ion in solution was determined by spectrophotometric method with pyrogallol-based 2,2,3,4 tetrahydroxy3/sulfo-5/chlorazoben-zene (TSCAB) reagent. The pH of the medium was kept constant using ammonium acetate buffer solution and HCl standard titrimetric substance. The pH of the buffer solution was 3-11 and the pH of the HCl solution was 0-2. The KOH solution was prepared by dissolving the calculated mass of KOH in distilled water and titrating with standard HCl solution to determine its concentration. The optical densities of the solutions were measured on a KFK-2 photo calorimeter (λ = 490 nm). The pH of the solutions was monitored using a pHS-25 glass electrode ionomer. The IR spectra and thermogram of the sorbent were studied with the device with Thermo Scientific USA Nicoletisio Spectrometer and NETZSCH STA 449F3 STA449F3A-0836-M.

## 3. Methodology

A p-aminosalicylic fragmented chelate-forming polymer sorbent was synthesized. For this purpose, radical copolymerization of maleic anhydride (k.t.) in styrene (k.t.) benzene solution was carried out in a water bath [80-85°C, 120 min]. The obtained copolymer was dried in vacuum. Calculated amounts of formaldehyde and p-aminosalicylic acid (dissolved in water) were added to the obtained copolymer (Qrebneva-Balyk & Kubrakova, 2020). The resulting sorbent is washed with water and dried in a vacuum at 50°C to a constant weight. The weight of the sorbent is determined before and after drying. The photometric method was used to determine the amount of absorbed Pd (II) ion. At equilibrium, the concentration of palladium (II) ions was determined by photometric sorption analysis. At pH 4, Pd (II) interacts with the TSCAB reagent in an acidic environment (maximum light absorption λ = 490 nm at wavelength) to form a color complex (7).

## 4. Results and discussions

***Sorbent identification.*** The obtained sorbent was identified by IR spectroscopy. Comparison of the IR spectra of the obtained sorbents and polychelates shows that during the formation of the complex, shifts in the oscillation frequencies of the groups in the sorbent links are observed. This confirms the participation of these groups in complex reactions with metals. The following results are obtained from the IR spectroscopy of a sorbent with a fragment of P-aminosalicylic acid (Radomskaya *et al.,* 2014).

CONHR binary amides at wavelength 3377.11- (330-3070); 2953,21- (2960) $CH_3$ has two lines of intensity 70 mol l cm-1; 2853,31- (2880-2650), the intensity of the middle line is 2720 $cm^{-1}$; 2359.91 (2440-2350) P-H short, moderate intensity is observed; 1615,33- (1610-1550), where asymmetric and symmetric valence oscillations form five different parts in the CO group with the neutralization of acid and the formation of inorganic matter.1376,65- (1370-1330) 10 for solid compounds -20 cm-1 falls; 1302,96-

(1340-1410) valence oscillations $NO_3^-$ deformation oscillations ONO high-section strong line; 1168,81- (1150-1070) (Aliphatic and cyclic COC) asymmetric valence oscillations in all CO lines It is observed. The diversification is not clear; 965.80- (970-950) N-O valence oscillations are very intensive; 844.45- (850-840) benzene ring; 803.64- (800-810) irregular deformation oscillations; 721.45- (745-705) cm-1; 668,63- (620-690) deformation oscillations correspond to $O\text{-}N_{=}O$ fog and trans form. All aromatic compounds in the range 2000-1600 cm-1; 2850-symmetric valence oscillations $CH_3$; all lines between 900-700 are intense. (Filatova *et al.*, 2018)

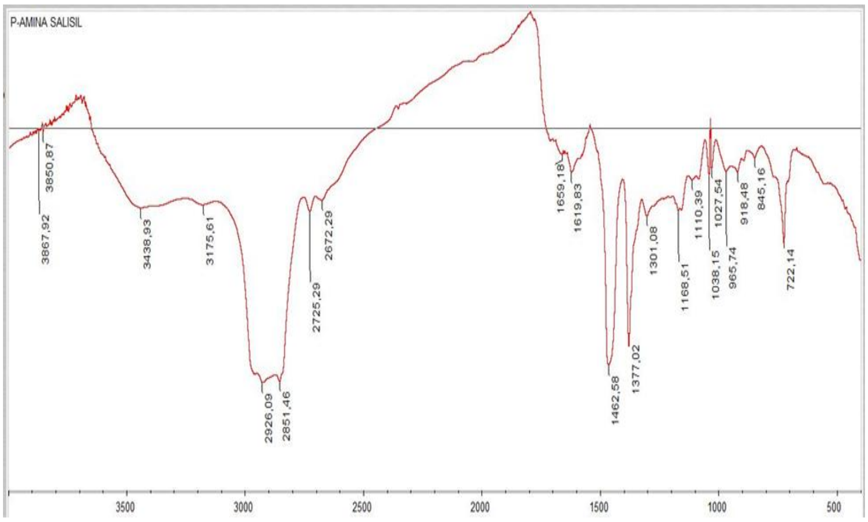

**Figure 1.** IR spectrum of p-aminosalicylic fragment sorbent

Results from IR spectroscopy of chelate complex: 3813.71 (3080) $_{=}CH_2$; The absorption of alkanes is covered in strip 2795; 3438.93- (3400-3200) strong wide band is observed. In the solid and liquid state, a broad band is observed for the substances. In addition, a monomer band is observed in the dissolved substances; 2725,29- (2730) cm-1 weak group lines; 1659,18- (1640-1560) $-NH_2$ straight deformation oscillations (O-N valence oscillations); 1619.83- (1640-1620) other bands $O\text{-}NO_2$; 1462.58 (1460) $CH_3$ groups, double dimethyl groups; 1027,54- (1000-1035) epoxy group. Each strip occurs depending on the condition of the epoxy group; 845,16- (890-820) -C-O-O-C aliphatic group Both bands were weak and difficult to identify.

The temperature resistance of the sorbent was determined by the thermogravimetric method (Fig. 3, 4). The thermogram of the sorbent shows that the separation of water with an endothermic effect, the destruction of macromolecules with a weak exothermic effect at relatively high temperatures and the oxidation (or combustion) of destroyed particles. Thermolysis of polychelates shows that they are more durable than a suitable sorbent. Can be explained by the acquisition of phase-resistant chelate complexes. Application of sorbents based on styrene copolymer of maleic anhydride at temperatures above 100-120°C is not advisable (Simanova *et al.*, 2006).

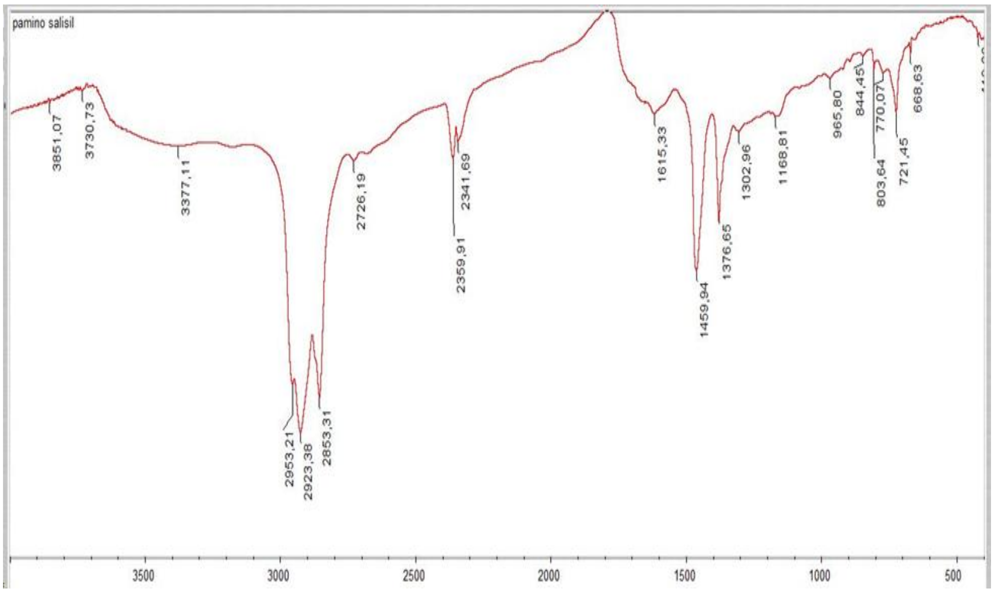

**Figure 2.** IR spectrum of Pd (II) ion with p-aminosalicylic fragment sorbent

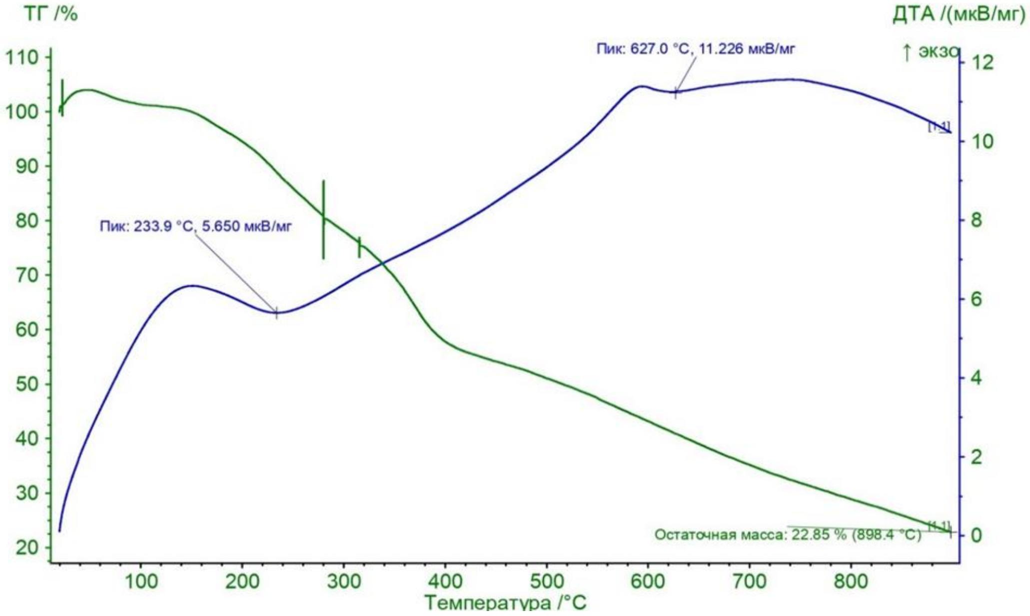

**Figure 3.** Thermogram of a sorbent with a p-aminosalicylic fragment 22.85% of the sorbent remains at 898.40°C

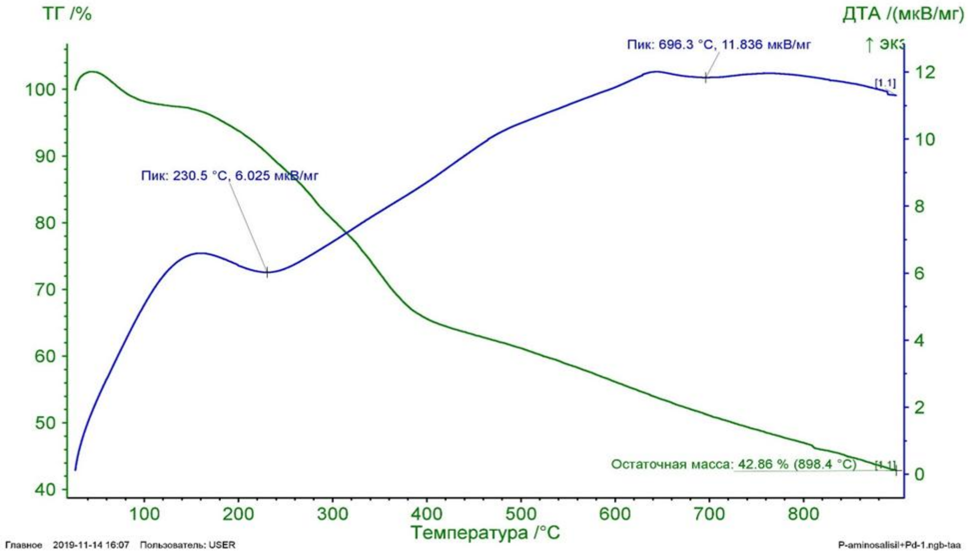

**Figure 4.** Thermogram of Pd (II) ion with p-aminosalicylic fragment sorbent. At a temperature of 898.40°C, the polychelate complex remains 42.86%

***The effect of hydrogen ions on the sorption process***. One of the important factors influencing the balance of the complex reaction of palladium ions with sorbents is the concentration of hydrogen ions in the liquid phase. Most organic reagents and chelate-forming polymer sorbents used for the separation, thickening, and determination of elements are weakly acidic compounds. That is, the proportion of ionized and non-ionized functional groups in macromoleculesvaries depending on the pH value. Also, depending on the pH value, the position of metal ions in solution varies. In each case, the sorption of palladium ions by the sorbent exceeds the maximum in a certain range of the pH of the liquid phase. The acid-base properties of chelate-forming sorbents significantly determine the selectivity of sorbents. Properties are affected by the state of all ionic groups it contains (Filatova *et al.,* 2018). It was studied the effect of pH of the medium on the sorption process of Pd (II) ions with a p-aminosalicylic fragmented chelate-forming sorbent. As a result of the experiment, it was observed that in the studied heterogeneous system, the value of the distribution coefficient of Pd (II) ions increases from acidic to weakly acidic and neutral medium. This is due to the fact that the functional groups in the macromolecules are in a protonated form and the degree of swelling of the polymer sorbent is small. In addition to metal ions in the aqueous solution in the pH-4 range, it also exists in the form of hydroxy complexes. The fact that the optimal sorption pH of the studied metal ions is in the range of 4-6 and indicates that the sorption takes place mainly in the ionized form (HR-, R2-). The optimal pH of the obtained sorbent is observed in the pH-4 range (Simanova *et al.,* 2016).

**Table 1.** The effect of pH on the sorption of palladium (II) ions

| pH | pH-1 | pH-2 | pH-3 | pH-4 | pH-5 |
|---|---|---|---|---|---|
| Sorption capacity, mg/ml | 66,61 | 66,62 | 66.64 | 66,66 | 66.66 |
| Sorption rate, % | 99,94 | 99,95 | 99,96 | 99,99 | 99,99 |

***Time dependence of the sorption process***. Sorption experiments were performed at a constant value of ionic strength under optimal pH (pH-4) under static conditions, and the aliquot fraction of the liquid phase was determined at different time intervals to determine the concentration of the metal ion in the solution. Experience has shown that the sorption equilibrium is reached within 120 minutes with a p-aminosalicyl fragmented chelate-containing sorbent based on maleic anhydride styrene copolymer (Vasilyeva *et al.*, 2010).

**Table 2.** Effect of time on sorption of palladium (II) ions

| Time, min | 30 | 60 | 90 | 120 |
|---|---|---|---|---|
| Sorption capacity, mg/ml | 66,64 | 66,65 | 66,65 | 66,65 |
| Sorption rate, % | 99,97 | 99,98 | 99,98 | 99,98 |

***Concentration effect***: The maximum absorption concentration of Pd (II) ion by sorbent is 800 mg/m1. (Stmax = 512mq/q). As the density of the metal ion increases, the sorption capacity of the sorbents increases, and the sorption capacity of the sorbent does not change after a certain value of the density of the metal ion.

**Table 3.** Dependence of the sorption process formed by the Pd (II) ion with a p-aminosalicylic fragment sorbent on the concentration of the metal

| C $Pd^{2+}$ mq/ml | 50 | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 |
|---|---|---|---|---|---|---|---|---|---|---|
| Sorption capacity, mg/ml | 26,95 | 59,57 | 124.46 | 184.04 | 247,86 | 314,18 | 381,91 | 452,48 | 512,05 | 511,07 |
| Sorption rate, % | 80,85 | 89,36 | 93,35 | 92,02 | 92,95 | 94,25 | 95,47 | 96.96 | 96,98 | 96,98 |

***The effect of ionic strength***: The effect of ionic strength of the solution on the sorption process was studied. For this purpose, potentiometric titration of the sorbent was carried out against the background of KCl at a constant ionic strength $\mu$=1 mol/l. Thus, 8 flasks were taken and 0,03 mg of sorbents and 2 ml of PdCl solution were added to each of the flasks. After that, different volumes of 1 M KCl solution were added to the flasks and measurements were made after one day. It was found that for individual systems, an increase in the value of ionic strength in the liquid phase to 0.2-0.8 mol/l does not lead to a significant decrease in the sorption rate. Subsequent increases in ionic strength do not affect the sorption rate of Pd (II) ions (Volchkova *et al.*, 2016).

***Effect of desorption****:* Equivalent mass sorbent samples containing the same amount of metal ions are added to containers of the same capacity and shape. Desorption experiments were performed by changing the volume of the liquid phase and the concentration of acids. The effect of $HClO_4$, $HNO_3$, $H_3PO_4$, HCl and their concentrations of various mineral acids on the desorption of absorbed Pd (II) ions from the polymer sorbent was studied. Experience has shown that $HClO_4$ acid has a better ability to desorb. In order to determine the optimal concentration of perchlorotic acid in the desorption process, desorption experiments at different concentrations of acid were performed. After desorption, the adsorbent does not lose its sorption properties. The obtained sorbent can be reused for thickening.

**Table 4.** Dependence of Pd (II) ion ionic strength of sorption process formed by p-aminosalicylic fraction sorbent

| $V_{KCl}$,ml 1M | - | 2 | 4 | 6 | 8 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|
| $V_{Me,Pd}$ ml | 4 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| V pH-4 | 16 | 14 | 12 | 10 | 8 | 6 | 4 | 2 |
| $V_{alkv.}$ | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| ΔA 490 nm | 0,16 | 0,2 | 0,19 | 0,21 | 0,22 | 0,22 | 0,22 | 0,22 |

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