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INVESTIGATION OF DETERMINATION OF PALLADIUM (II) ION BY CONCENTRATION WITH NN'-DIPHENYL GUANIDINE FRAGMENTED CHELATE FORMING SORBENT

Abstract: The new sorbent was synthesized from maleic anhydride-styrene copolymer modified by the addition of NN' – diphenylguanidine and formaldehyde. The method of fixation of palladium (II) ion with a new synthesized sorbent has been developed. The optimum condition has been determined by the sorption and desorption of Pd (II) ions over obtained sorbent.

Keywords: palladium (II), concentration, sorbent, sorption, photometry.

In modern age determination of traces amount of noble metals in geological objects, on magmatic mountain rocks by concentration with natural and synthetic polymer sorbents are widely used. However, it is well known from the literature that the chelate sorbents have great importance in the concentration of noble metals [1, 243; 2, 256]. It is known that for concentration of elements are used polystyrene-based modified complex sorbents, silica gel, porous glass, poly acryl nitrile fibers and modified complex reagents. However, in the literature there is little information about the determination of Pd (II) ions by the sorbents obtained based on maleic anhydride-styrene copolymer. For this purpose, the new sorbent was obtained based on the maleic anhydride styrene copolymer and modified by formaldehyde and NN' – diphenyl guanidine.

Experimental

The solution of Pd (II) ion of 1000 mg/l was prepared from PdCl₂ salt and was clarified by comparison with standards. The equilibrium concentration of the Pd (II) ion in the solution was determined by the spectrophotometric method with using pyrogallol based 2,2,3,4-tetrahydroxy-3'-sulfo-5'-chlorazobenzene reagent. The KCl salt solution was used to form the required value of the ionic force. Ammonium-acetate buffer solution (pH 3–11) and HCl fiksanal (pH 0–2) were used to maintain the pH constant. The KOH solution was prepared by dissolving the calculated mass of KOH in distilled water and then its concentration determined by titration with standard HCl solution. The optical density of the solutions was measured by KFK-2 type photo colorimeter. The pH of the solution was controlled by pH-25 glass electrode ionomer. The

FTIR – spectrum of sorbent was studied in the Varian 3600.

The new NN' – diphenyl guanidine fragmented chelate forming polymer sorbent was synthesized. For this purpose, the known methodology was carried out with radical copolymerization of maleic anhydride and styrol in benzene solution and at water bath (75–80 °C). Benzoyl peroxide was used as an initiator. The obtained copolymer was dried in vacuum. The calculated amount of the formaldehyde and NN' – diphenyl guanidine was added over obtained copolymer. The reaction was carried out for 2 hours without interruption in the water bath at 65–70 °C. The obtained sorbent was washed with water and dried to a constant weight in vacuum at 50 °C. A photometric method was used to determine the absorbed amount of Pd (II)

ion. For this purpose, the complexon of Pd (II) ion with 2,2,3,4-tetrahydroxy-3-sulfo-5/-chlorazo-benzene was determined by the maximum absorption of the light on the reactive background of the complex $\lambda = 490$ nm.

Sorbent identification. The obtained sorbent was identified by the IQ spectroscopy method. In the FTIR spectra of obtained sorbent there are range of absorption band at 3600–3100 cm^{-1} (valent dances of the –OH group in the carboxyl group), 3400–3200 cm^{-1} (valent dance of the –NH group), 1750–1710 cm^{-1} (valent dances of the group –C=O in the carboxyl group), 1570–1550 cm^{-1} (–CH valent dance and deformed dance of –NH group), 1610–1510 cm^{-1} (C–C valent dance in benzene) and 710–680 cm^{-1} (CC deformation dance in benzene).

Figure 1. FTIR spectrum of sorbent

Potentiometric titration of sorbent was made by known method. In order to determine the ionization constants the exact static sorption capacity

of K^+ ions was determined by the potentiometric titration. Based on the results of the titration, a differential curve was constructed (figure 2).

Figure 2. Differential titration curve

Thus, the ionization process of the purchased polymer sorbent will occur in two stages:

During titration, the amount of alkaline used to obtain the first peak is pK_1 and the amount of alkaline used to obtain the second peak characterizes pK_2 . Based on the potentiometric titration, the cost of ionization constants is calculated by the modifier

equation of Henderson-Hasselbach. It is known that in a wide range of α dependence $\text{pH} - \lg \frac{\alpha}{1-\alpha}$ is a line, and this linear dependence is determined by the graph and calculation of ionization constants of ionogenic groups in sorbent sleeves. The results needed to calculate the ionization constant are shown in Table 1. Investigation of sorption properties was carried out in static conditions.

Table 1. – Determination of sorbent ionization constants ($m_{\text{sorb.}} = 100.000 \text{ mg}$, $C_{\text{KOH}} = 0.1 \text{ M}$, $\text{pK}_1 = 4.07$, $\text{pK}_2 = 8.53$)

α	$\frac{\alpha}{1-\alpha}$	$\lg \frac{\alpha}{1-\alpha}$	$V_{\text{KOH}}, \text{ml}$	pH	pK_1	α	$\frac{\alpha}{1-\alpha}$	$\lg \frac{\alpha}{1-\alpha}$	$V_{\text{KOH}}, \text{ml}$	pH	pK_2
0.1	0.(1)	-0.954	0.13	2.87	6.23	0.1	0.(1)	-0.954	1.41	7.78	9.74
0.2	0.25	-0.602	0.26	3.07	5.40	0.2	0.25	-0.602	1.52	7.90	9.27
0.3	0.43	-0.368	0.39	3.29	4.84	0.3	0.43	-0.368	1.63	8.06	8.96
0.4	0.(6)	-0.176	0.52	3.58	4.39	0.4	0.(6)	-0.176	1.74	8.26	8.70
0.5	1.00	0.000	0.65	3.97	3.97	0.5	1.0	0.000	1.85	8.47	8.47
0.6	1.5	0.176	0.78	4.53	3.55	0.6	1.5	0.176	1.96	8.71	8.24
0.7	2.(3)	0.368	0.91	5.21	3.10	0.7	2.(3)	0.368	2.07	8.98	7.98
0.8	4.0	0.602	1.04	6.00	2.54	0.8	4.0	0.602	2.18	9.30	7.67

The effect of pH on the Pd (II) ion in the sorption process was studied by NN'-diphenyl guanidine fragmented chelate sorbent. Experimental data shows that in the investigated heterogeneous system the value of Pd (II) ions distribution coefficient is increased from the acid environment to the weak acid environment and then to neutral environment.

The low value of the pH in the fluid phase (pH 0–3) is because the functional groups in the macromolecules are in protonated form and that the polymer sorbent is inflated. The aqueous solution is present in the form of hydroxocomplexes along with the metal ions shown in the pH-4 range. The optimal sorption of the investigated metal ions at the pH range of 4–6

indicates that the sorption mainly goes to the ionized form (HR^- , R^{2-}).

In static conditions, the optimum pH environment (pH-4) was experimented with a constant rate of ionic force, and the aliquot fraction from the liquid phase at different time intervals determined the concentration of metal ion in the solution. Experiments show that the sorption balance over NN'-diphenyl guanidine fragmented chelate-forming sorbent based on maleic anhydride styrene copolymer forms within 1–2 hours.

The dependence of the sorption process on the ionic force was investigated. Increasing the ionic force of the fluid phase to 0.8 mol/l does not have a significant effect on the degree of sorption. The subsequent increase in ionic force leads to a reduction in Pd (II) ions' sorption rate.

When the concentration of Pd (II) ion is 800 mg/l, the sorbent's sorption capacity is maximal.

Effects of the absorbed Pd (II) ion of the various solids (HClO_4 , HNO_3 , H_3PO_4 , HCl) and their concentration were investigated from the polymer sorbent desorption. Experience shows that HClO_4 acid has better desorption capability. Desorption experiments have been performed in different layers of perchloric acid to determine the optimum condition of desorption. The obtained results are shown in

Table 2. – Effect of acid concentration and volume to desorption of Pd (II) from polymer sorbent

Density and volume of HClO_4	Desorption degree (%)
0.5 M, 5 ml	96.81
1 M, 5 ml	98.32
1.5 M, 5ml	98.40

Thus, it has been established that the determination of the palladium (II) ion can be accomplished by using sorption-photometric methods in rocks, electrodes, standard alloys.

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