

Macroporous Anion Exchanger Purolite A-500 Loaded with Ferron for Palladium(II) Recovery

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A systematic study on interaction of Pd(II) with 7-iodo-8-hydroxyquinoline-5 sulfonic acid (Ferron) and the strongly basic anion exchange resin Purolite A-500 in its chloride form was carried out. It was found that for Ferron/resin ratio ranging from 0.15 to 0.70 mmol g⁻¹, the retention of chelating reagent on the investigated ion exchanger is practically quantitative. The sorption increase of Pd(II) on Ferron-loaded resin was observed for higher values of parameters like: pH solution, initial concentration and temperature. It was observed that the equilibrium distribution of Pd(II) between sorbent and solution could adequately be described by the Langmuir model with two parameters. The thermodynamic quantities characteristic of Pd(II) sorption process ($\Delta G = -18.4 \text{ kJ mol}^{-1}$; $\Delta H = 11.7 \text{ kJ mol}^{-1}$; $\Delta S = 104.4 \text{ J mol}^{-1} \text{ K}^{-1}$) suggest a strong affinity between Ferron-loaded resin and the tested cation.

Keywords: Ferron, Palladium, Anion exchanger, Sorption, Recovery

INTRODUCTION

Palladium, one of the precious metals is, technologically speaking, highly important due to a number of its properties. Owing to its corrosion resistance nature and alloying ability, palladium is an important element in metallurgy. Its alloys are used in dental and medicinal devices and in jewelry manufacture. The catalytic properties of Pd(II) are presently exerting a positive impact on the environment. Thus, palladium is used in automobile catalyst together with platinum and rhodium. They have the ability to oxidize specific toxic components such as carbon monoxide, hydrocarbons as well as various nitrous oxides in hot gases as they pass through the exhaust system [1].

On the other hand, palladium is one of the most expensive metals. Many processes have been developed to recover this metal in complex solutions or aimed at its recovery from spent

catalysts. Ion exchange and sorption process as well as liquid-liquid techniques have been extensively investigated [2].

Sorption by chelating resins is one of the most important and modern methods for the separation and preconcentration of the platinum metals traces. The rapid and efficient recovery of the microelements from large volumes of solutions with complex saline composition is assured by the high selectivity of chelating sorbents. Sorption capacities are influenced by the nature of the chelating groups bonded on polymer matrix and sorption conditions (pH, temperature, presence of masking compounds *etc.*).

The chelating resins are well-known and extensively used [3-8], but they have major disadvantages, such as specific laborious preparation methods, high cost, difficult regeneration and unsatisfactory kinetic characteristics. In this context, research on a new, simple and rapid synthesis alternative remains a priority. One of these alternatives consists in the sorption of specific organic chelating reagents on the conventional ion exchangers [9-17].

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The resulting chelating agent-loaded ion exchanger accumulates the properties of both modifier agent and initial resin. Materials with excellent sorptive properties have been obtained by loading 8-hydroxyquinoline on different solid supports [18-20]. Similarly, by sorption of a sulfonic acid derivative of 8-hydroxyquinoline, namely Ferron, on anion exchange resins, chelating sorbents with good applicability in separation and preconcentration of some metal cations from aqueous media have been obtained [21-22].

In this connection, a part of this work has focused on the conditions for 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Ferron) retention by the strong basic anion exchange resin Purolite A-500 in its chloride form. Subsequently, the complexing properties of Ferron-resin toward Pd(II) have been investigated. The selection of Ferron as a modifier agent was determined by the presence, in its structure, of two ligand groups: a sulfonic one, able to interact with the anion exchange resin and the 8-hydroxyquinoline group able to chelate with Pd(II).

EXPERIMENTAL

Reagents

The macroporous ion-exchanger of type I, A-500, was supplied from Purolite International Ltd. Its characteristics are given in Table 1. The chelating agent, aqueous solution of 5×10^{-3} M Ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) (Merk) was used. Working solutions were prepared daily by the appropriate dilution with bidistilled water of a stock solution of Pd(II) of 2.25×10^{-2} M prepared by dissolving 1 g PdCl₂ (Merk, Germany) in 10 ml of concentrated HCl, followed by dilution with bidistilled water to 250 ml. The Pd(II) stock solution was complexometrically standardized [23]. The HCl/KCl, CH₃COOH/CH₃COONa and NH₄Cl/NH₃ mixtures were used for adjusting the pH values.

Analytical Procedure

The preparation of the chelate-forming resin and the subsequent Pd(II) sorption were made in batch conditions

Table 1. The Physico-Chemical Characteristics of the Anion Exchanger Purolite A-500

Parameter	Characteristics
Matrix	Polystyrene crosslinked with
Functional group	DVB
Ionic form	-(CH ₃) ₃ N ⁺
Bead size	Cl ⁻
Sorption capacity ^a (mequiv. g ⁻¹)	14-15 mesh 3.9

^aDetermined by pH-metric titration of the dried resin in ambient conditions, over 72 h.

according to the procedures presented in Fig. 1.

Apparatus

Absorbance measurements were made on a S104D-WPA Linton Cambridge spectrophotometer. The pH-measurements were recorded with a Radiometer pH-meter, M-64.

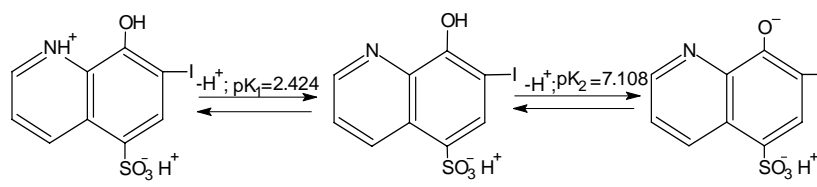
RESULTS AND DISCUSSION

Sorption Study of Ferron on Anionic Resin

To establish the proper conditions of the chelating ion exchanger preparation, the interaction of anion exchange resin with Ferron, in different conditions of acidity and organic reagent concentration was studied. The experimental results concerning the pH effect on the retention of Ferron by anion exchange resin Purolite A-500 are given in Table 2.

The immobilization of Ferron on anion exchanger Purolite A-500 easily increased with the increase of the solution pH. The retention degree was maximum in neutral (Ferron solution neutralized with NaOH) to slightly alkaline (ammoniacal buffer) medium. Such a behavior could account for by the dissociation of hydroxyl group in this pH domain.

The low sorption level in acidic region (pH < 4) is probably due to a protonation process according to Eq. (1) [25]:



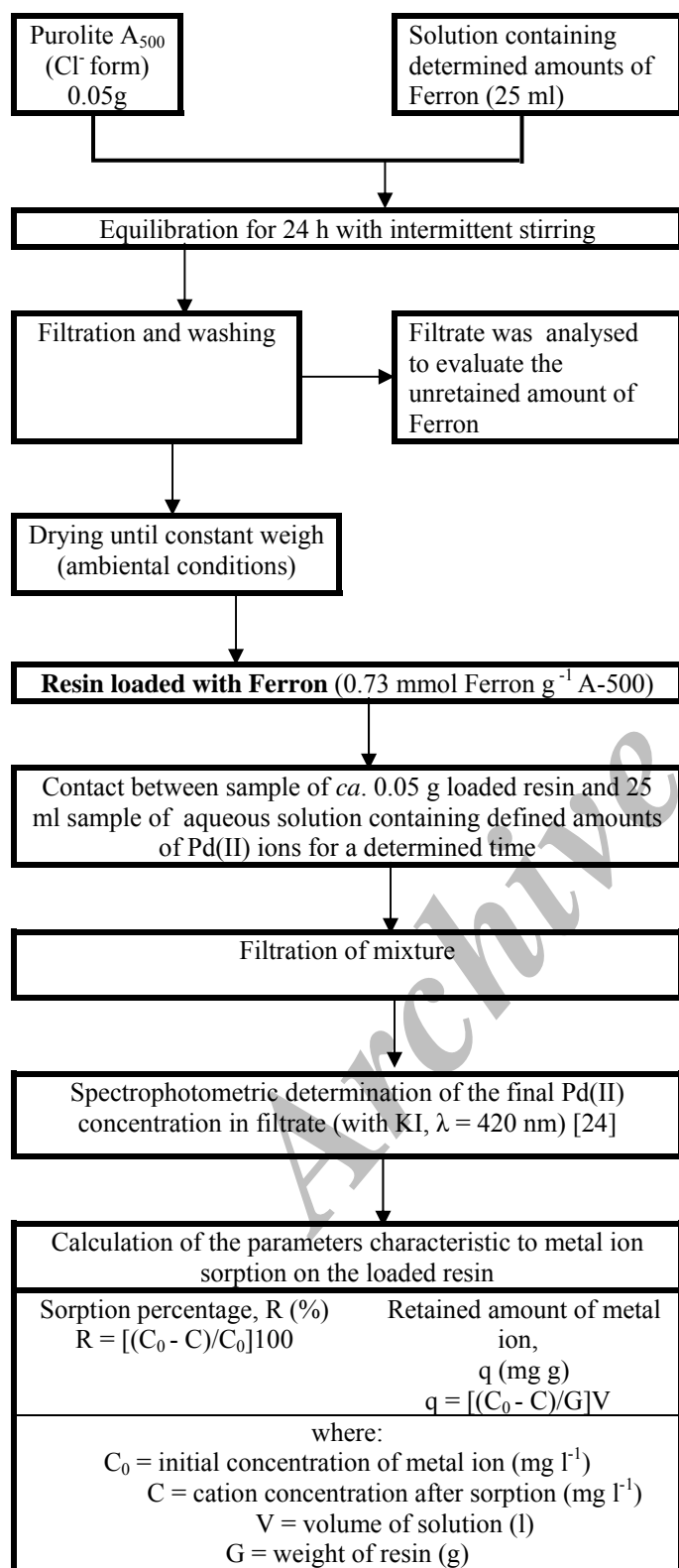


Fig. 1. Schematic representation of the analytical procedures.

Table 2. Immobilization of Ferron on Anion Exchanger Purolite A-500 as Function of Solution pH

pH	q (mmol g ⁻¹)	R (%) ^a	lgK _d ^b
2.0	0.206	68.66	3.039
4.0	0.257	88.60	3.578
4.5-5.0	0.252	85.33	3.456
5.5-6.0	0.280	93.33	3.845
7.0	0.284	96.66	4.152
9.0	0.276	95.00	3.963

^aR is the retention degree. ^bK_d is the distribution coefficient calculated as ratio between mmol Ferron g⁻¹ resin and mmol Ferron ml⁻¹ solution at equilibrium.

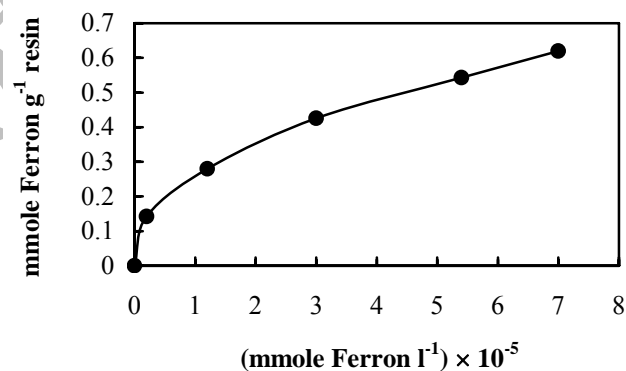


Fig. 2. Sorption isotherm of Ferron on anion-exchanger Purolite A-500 (t = 20 °C; time = 24 h; 0.05 g resin).

By the addition of ammoniacal buffer, the concentration of Cl⁻ ions increases and the exchange equilibrium of Ferron is retrograded.

The influence of Ferron concentration was investigated for values of initial ratio Ferron/resin ranging from 0.15-0.70 mmol g⁻¹. The Ferron distribution at equilibrium between the solution and resin phases, represented in Fig. 2, indicates that the reagent is retained on ion exchanger almost quantitatively.

To elucidate the sorption mechanism of Ferron on anionic resin A-500, the correlation between the amount of reagent retained and the amount of removed chloride (Fig. 3) was studied. As is shown in Fig. 3, the dependence is linear, with a slope of about 1 ($y = 1.0069x + 0.0046$, $R^2 = 0.9998$),

Table 3. The pH Influence in A-500-Pd(II) ($C_0 = 4.8 \mu\text{g Pd ml}^{-1}$) and A-500-Ferron-Pd(II) ($C_0 = 11.36 \mu\text{g Pd ml}^{-1}$) Batch Sorption Systems

pH (buffer)	Amount of Pd(II) retained q (mg g ⁻¹)		Sorption percentage R (%)	
	A-500	A-500-Ferron (0.73 mmol g ⁻¹)	A-500	A-500-Ferron (0.73 mmol g ⁻¹)
2.2 (HCl + KCl)	1.60	2.55	66.58	35.2
3.6 (Acetate)	1.14	5.68	47.62	50.48
4.8 (Acetate)	0.73	7.31-7.19	30.38	64.75; 63.73
5.0-6.0 (Acetate)	0.44	8.30	12.5	74.69
8.2 (Ammoniacal)	0	8.82	0	80.3
9.0 (Ammoniacal)	0	8.74	0	77.99

Pd(II) retained on Ferron-loaded resin (0.73 mmol Ferron g⁻¹) increases by increasing the metallic ion initial concentration (Fig. 4(●)). Higher initial concentrations might be closely associated with high values of the ratio between the initial number of mmoles of Pd(II) cation and the limited number of available binding sites, thus resulting in an enhancement of the metal ion sorption [28].

Conversely, as the Pd(II) amount increases, the sorption percentage decreases. Occupation of the total active sites on Ferron-loaded sorbent probably hinders the access to Pd(II), consequently decreasing the sorption percentage. These findings seem to indicate that Ferron-loaded resin under study can be efficiently used for the quantitative recovery of Pd(II) from aqueous diluted solutions ($R \approx 80\%$).

Increasing the temperature of initial solution (pH = 5.6) has a favorable effect on Pd(II) sorption by Ferron-loaded resin (0.73 mmol g⁻¹). For one degree of rise in temperature, the increase of Pd(II) sorption percentage is about 1.2%.

The equilibrium distribution of Pd(II) ions between the solid and aqueous phases, respectively, was investigated for the anionic resin loaded with 0.73 mmol Ferron g⁻¹, at pH = 5.6 (acetate buffer); phases ratio- 2 g sorbent l⁻¹ solution. The

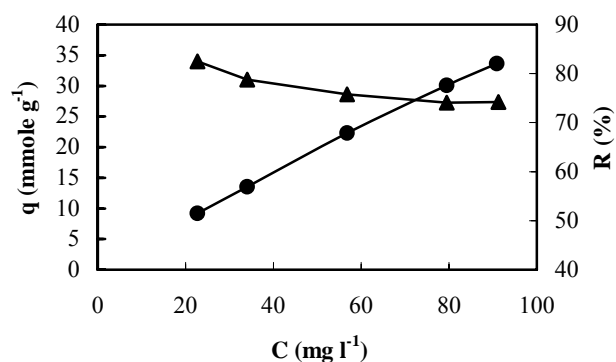


Fig. 4. The influence of initial concentration on Pd(II) sorption by Ferron-loaded resin. (●) q, mmol g⁻¹; (▲) R%; (time = 24 h; 0.05 g resin)

sorption isotherms have been plotted for three different temperatures each time (Fig. 5).

The experimental data were processed (Table 4) by means of linear Langmuir Eq. (3) [8]:

$$q = K_L C q_0 / (1 + K_L C) \quad (3)$$

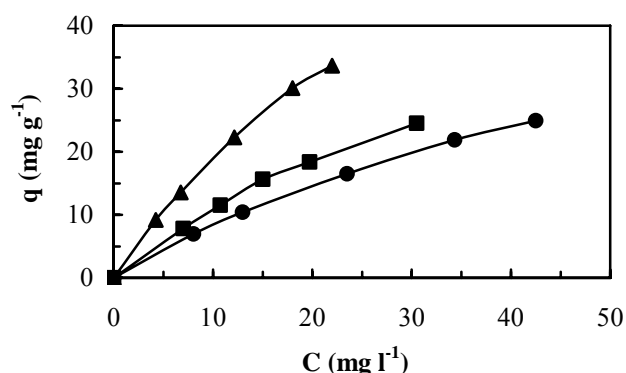


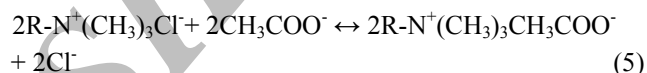
Fig. 5. The Pd(II) sorption isotherms on Ferron-loaded resin A-500 at 5 °C (●), 15 °C (◆) and 27 °C (▲) (pH = 5.6, time 24 h, 0.05 g sorbent)

where C is the solution concentration at equilibrium (mM); q is the amount of sorbed Pd(II) on modified resin (mmol g^{-1}); q_0 is maximum capacity of sorption and K_L is the sorption constant. The experimental data were also statistically processed by linear regression. The regression equations of $y = ax + b$ type and the obtained values of the correlation coefficients, R^2 , are given in Table 4. The results indicate that the experimental data fit the Langmuir model well with two parameters (q_0 and K_L).

With reference to the maximum capacity of sorption (q_0), it is obvious from Table 4 that its values increase with an increase in temperature. The results are examined on the

assumption that the interaction between Pd(II) and the functional group of sorbent takes place with a 1:1 molar ratio of 1 Pd(II):Ferron. The spatial distribution of functional groups and low values of their concentrations exclude the formation of a 1:2 complex, as shown in Eq. (4).

At the same time, the high concentrations of Cl^- ions inside the resin phase can be attributed to a possible formation of Pd(II) negative chlorocomplexes, retainable by anionic exchange by the quaternary ammonium groups of the basic resin, as follows:

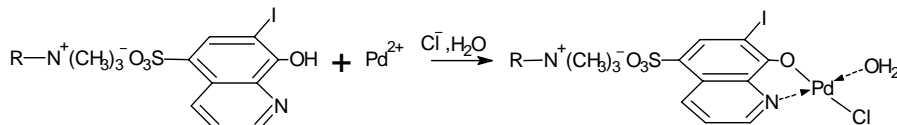


The high values of sorption constants, K_L , reflecting the strength of sorbed Pd(II)-sorbent bonds, confirm the existence of a complexation reaction.

The thermodynamic parameters characteristic of the process of Pd(II) sorption on Ferron-loaded resin (Table 5) were determined using the usual relations for ΔG and ΔS calculations and the plot of van't Hoff equation. The negative value of apparent Gibbs energy at all working temperatures point to the spontaneous character of the sorption process (a

Table 4. Quantitative Description of the Sorption Systems Purolite A-500-Ferron-Pd(II) on the Basis of Langmuir Model

Temperature (K)	Linear regression equation	R^2	q_0 (mmol g^{-1})	K_L (l mol^{-1})
278	$y = 1.8099x + 1.0185$	0.9928	0.5525	1777.02
288	$y = 1.6234x + 0.7746$	0.994	0.616	2095.76
300	$y = 1.0879x + 0.4227$	0.9924	0.919	2573.74



(4)

Table 5. Thermodynamic Parameters for the Pd(II) Sorption Process on Ferron-Loaded Resin

Temperature (K)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
278	-17.3		104.2
288	-18.3	11.7	104.1
300	-19.8		104.7

high affinity of chelating agent loaded resin toward Pd(II)). The positive value of the apparent enthalpy of sorption, ΔH , is characteristic of an endothermic process, favored by temperature increase. The positive value of entropy, ΔS , reflects the increase of system disorder by Pd(II) sorption on loaded resin, while hydration water molecules are liberated.

CONCLUSIONS

A chelating sorbent with a high affinity for Pd(II) has been obtained by loading strongly basic anionic resin Purolite A-500 with 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Ferron). The sorption of Pd(II) on Ferron-loaded resin becomes higher with solution pH, initial concentration and temperature increase. The sorption isotherms of Pd(II) on Ferron-loaded resin at different temperatures fit well the Langmuir model. The obtained results are significant for the future development of the tested sorbent into beneficial material for industrial and environmental applications.

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