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ADSORPTION OF Pd (II) ON *N*- AND *S*- MODIFIED SILICA SORBENTS

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ABSTRACT

In this study two silica gel sorbents with different mobilization agents were applied for solid phase extraction of palladium(II) from 0.1 mol L^{-1} - 3 mol L^{-1}aqueous HCl solution. The first sorbent was prepared by immobilization of 4 - aminoantypyrine Schiff base (Schiff B-4-AAP) and the second one - by introduction of S-containing amino acid analog, N-benzyloxycarbonyl-L-methionine (Z-Met-OH) on the silica gel surface through physical adsorption. Thus, the obtained two silica sorbents were functionalized with nitrogen (Sig ~ Schiff B-4-AAP) and nitrogen and sulfur (Sig ~ Z-Met-OH) chelating groups.

The role of various chemical parameters was studied for quantitative sorption of Pd(II) through batch adsorption experiments. It was found that the extraction efficiency of the newly prepared sorbents toward Pd(II) depends on the concentration of HCl in the sample solution and the contact time between Pd ions and the sorbents as well as on the type and concentration of the eluent. The optimal acid concentration for quantitative adsorption of Pd(II) was 1 mol L^{-1} HCl. The experiments showed that the coexisting ions - base metals exhibited little interference on the Pd(II) separation.

Keywords: Pd (II) recovery, noble metals preconcentration, chelating sorbents for noble metals.

INTRODUCTION

Palladium as a noble metal possesses remarkable chemical and physical properties such as high corrosion and mechanical resistance, high melting point, excellent catalytic activity, which determines its wide application. The demand for palladium has been continuously increased owing to its use in electrical equipment, dental materials, jewelry, in chemical catalysis, with the greatest Pd application in car industry [1 - 3]. The main use of Pd along with Pt and Rh is in the production of automotive catalytic converters for the reduction of harmful gases released during the fuel combustion. Due to the mechanical abrasion catalytic converters wear out over time, liberating Pd which concentration in the environment is continuously enhanced [4].

Although the metal is released from converters, mainly as insoluble nanoparticles [5, 6], fall into the environment under favorable conditions Pd may be transformed into water-soluble species and spread in all environmental compartments.

However, the direct quantification of Pd in environmental samples by the majority of instrumental methods is a difficult task due to its low concentrations in water, soil, and ambient air [7]. The low environmental content accompanied by interference from matrix elements requires separation and enrichment of palladium before its instrumental determination.

There are various methods, such as ion exchange [8], liquid-liquid extraction [9], coprecipitation [10, 11] and adsorption, for the removal of Pd(II) from aqueous solutions. Amongst them, the adsorption on an inert solid phase with high surface area, immobilized with specific functional group plays an important role in the separation and recovery of Pd ions from aqueous solutions [6, 12, 13].

Silica gel is a suitable solid phase due to its high sorption capacity, reversibility and reusability, low cost, and possibilities to enhance its selectivity mobilizing reagents with suitable functional groups [14, 15].

In order to improve the sorption selectivity towards Pd ions a great number of sorbents have been prepared by introducing different chelating agents on the material surface [6, 7, 16, 17]. Since palladium(II) is a soft acid, the selective extraction is feasible with soft base extractants containing *S* - and *N* - donor atoms [18].

In the literature, several mechanisms were proposed to explain the adsorption of precious metals on *N*- and *S*- modified sorbents, such as electrostatic attraction, ion exchange, and chelation. Because in HCl palladium is mainly present in anionic form as $[PdCl_4]^{2-}$ [19] which is easily adsorbed on the positively charged active centers on sorbent surface, many authors suppose that in case of sorption of platinum and palladium, electrostatic interaction plays a major role [20 - 23]. Chassary et al. [24] reported that in acidic solution the protonation of the amine groups diminishes their ability for Pd (II) chelation and according to these authors the metal sorption can be mainly explained by the electrostatic attraction of anion metal complexes by protonated amine groups.

Some authors combined several possible mechanisms concluding that in acidic solutions the adsorption mechanism of Pd(II) on N- and S-modified sorbent is assumed to be electrostatic attraction and ion exchange [25, 26]. Furthermore, Fujiwara et al. [26] reported that the electrostatic sorption of chloro-anion complexes of Pt(II) and Pd(II) was simultaneously accompanied by chelation of the metal ion on sulfur containing groups.

Although the electrostatic mechanism seems to be generally accepted, chemical mechanisms and redox reactions were proposed in case of platinum and palladium sorption on tannin [20].

Palladium and platinum, according to Pearson's acid base concept, belong to soft metals that possess high affinity for the soft donors, such as *S*- and *N*-atoms. Dobrzyńska et al. [6] suggest that in 0.1 mol L^{-1} HCl $[PdCl_4]^{2-}$ forms Pd-S bonds with surface –SH groups. Other investigations demonstrate formation of coordinative bonds and suppose that the adsorption is caused by chelating [7, 16, 27].

Guibal et al. [28] also pay attention to the fact that the functional groups that contain *N* and *S* donor atoms strongly interact with soft acids like noble metals. Moreover the autors suggest that the sorption mechanism is pH dependent - ion exchange mechanism is predominant in acidic solutions while the coordination mechanism predominates in less acidic solutions.

Lim et al. [15] compare palladium ion uptake on the silica functionalized with amine and thiol groups. Based on the experimental data they demonstrate that the palladium ion chemisorption by thiol predominates compared to the electrostatic attraction of palladium by the amine groups. Feng et al. [29] described the adsorption behavior of Au^{3+}, Pd^{2+} and Pt^{4+} towards MoS_2 nanoflakes, indicating a chemisorption process which occurs via M^{n+}─S bonding.

In the present study, the adsorption of Pd(II) onto *N*- and *S*- modified silica surface was studied. The aim is synthesis and characterization of two cost-effective sorbents for Pd(II) by immobilization of ligands with *N*- and *S*- donor groups on the silica gel surface.

As a first step, *N*-benzyloxycarbonyl-*L*-methionine or Schiff base derived from syringaldehyde and 4-aminoantipyrine were non-covalently immobilized on the surface of silica gel and respective sorbents Sig ~ Z-Met-OH or Sig ~ Schiff B-4-AAP were obtained. As a second step extraction efficiency of both sorbents toward Pd(II) was studied bearing in mind high selectivity and sorption affinity of Pd(II) to amino- and thio- functional groups. The influence of various chemical parameters such as pH, amount of sorbent and contact time, eluent type, and elution kinetics was examined. In addition, the selectivity of both sorbents toward other noble metals and base metals was defined.

EXPERIMENTAL

Instruments, materials and methods

ICP-OES measurements were performed on an ICP-OES spectrometer Ultima 2, Jobin Yvon under optimized instrumental parameters. The centrifuge K-1000 (KUBOTA Corporation, Osaka, Japan) was used for the centrifugation of modified silica sorbent in batch experiments.

The pH measurements were conducted on a pH-meter (Hanna Instruments). All chemicals were of analytical reagent grade and were used without further purification. The stock standard solution 1000 mg L^{-1} of Pd(II) in 10 % HCl was purchased by Sigma-Aldrich

(Germany). Working standard solutions for Pd ions were prepared daily by appropriate dilution of the stock standard solution. Methionine analog (Z-Met-OH, Fig. 1) was obtained previously, following the known procedure described by Paquet [30]. The Schiff base (Fig. 2) derived from syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) and 4-aminoantipyrine (4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one; 4-AAP) was sonochemically synthesized as reported earlier [31].

Preparation of modified silica gels

The silica gel modified with Z-Met-OH (Sig ~ Z-Met-OH) and silica gel modified with 4-aminoantipyrine Schiff base (Sig ~ Schiff B-4-AAP) were prepared following the procedure described by Bartyzel et al. [32] and further optimized by Petrova et al. [31].

The commercially available silica gel was activated by refluxing with concentrated HCl for 4 h, because the commercial silica gel possesses a low concentration of suitable surface silanol groups, required for further modification. Thereafter it was filtered, washed with deionized water until the filtrate was neutral and dried in an oven at 150^{o}C for 12 h to remove surface adsorbed water. The activated silica gel was refluxed separately with the derivatives as Z-Met-OH or 4-aminoantipyrine Schiff base in ratio 9:1 w/w in an acetone media for 8 h. Finally, the mixture was vigorously stirred at room temperature to complete the solvent evaporation and then dried at 40^{o}C for 1 h.

Pd(II) ions adsorption studies

The palladium ion sorption was evaluated by introducing 50 mg of surface functionalized silica into

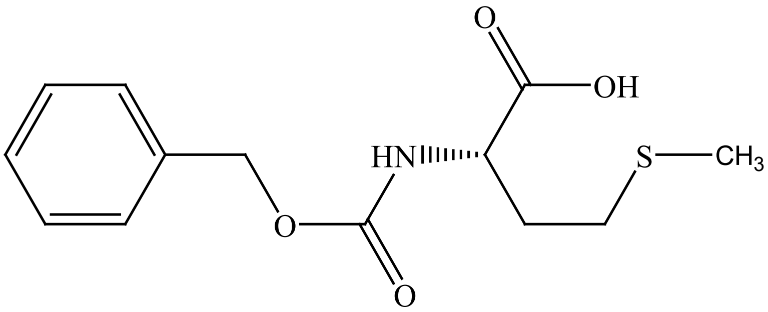

Fig. 1. Structure of *N*-benzyloxycarbonyl-*L*-methionine.

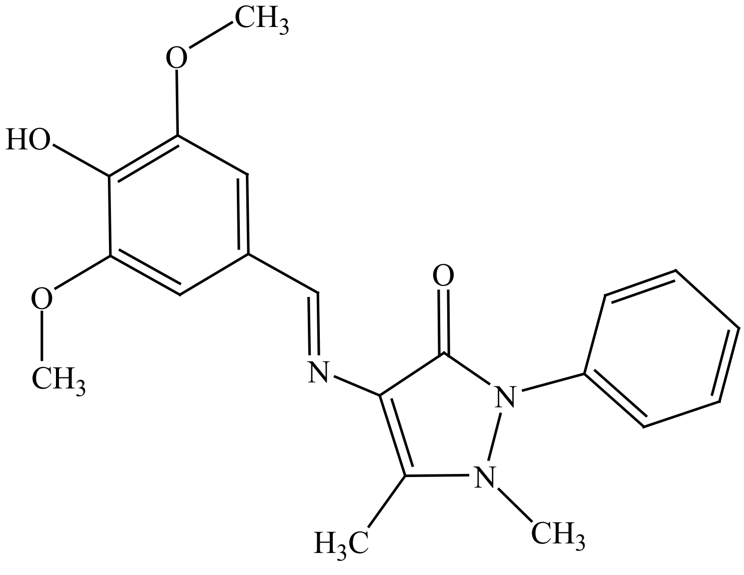

Fig. 2. Chemical structure of 4-aminoantipyrine Schiff base.

10 mL palladium ion solution with a concentration 10 mg L^{-1}. The sample pH was adjusted to the desired pH value with HCl solution. The mixture was shaken for 5-100 min with a mechanical shaker and then centrifuged. After filtration, the resulting supernatant solution was collected as effluat to measure the remaining palladium ion concentration by ICP-OES.

The sorbent was washed with deionized water and Pd (II) was recovered from the sorbent with solution of a suitable eluent. In order to investigate the degree of elution, metal ion content in eluate solution was determined by ICP-OES after sorbent centrifugation.

The sorption degree, *D*, %, was obtained by Eq. (1):

$$D\% = \frac{C_0 - C_{effluate}}{C_0} * 100 \qquad (1)$$

The extraction efficiency, *E*, % can be calculated using Eq. (2):

$$E\% = \frac{C_{eluate}}{C_0 - C_{effluate}} * 100 \qquad (2)$$

where C_0 is the initial amount of Pd, $C_{effluate}$ is the amount of Pd measured in the effluate solution and C_{eluate} is the amount of Pd measured in the eluate solution.

RESULTS AND DISCUSSION

Palladium adsorption

Batch tests with Pd(II) solution were used to estimate the amount of palladium adsorbed by *S*- and *N*-loaded sorbents.

Effect of HCl concentration

The concentration of HCl has a significant effect on the adsorption process because it can influence on metal ion chloride complexes formed and the surface properties of adsorbents [33].

In order to evaluate the effect of HCl concentration on the extraction efficiency, the acidity of the sample solutions containing 10 mg L^{-1} of palladium ions was adjusted in the range from 0.1 mol L^{-1} to 3 mol L^{-1} HCl. The retained Pd(II) ions were then eluted from the sorbent with acidic thiourea solution. Pd ions content in the effluate solution was determined by ICP-OES and the data graphed as a function of HCl concentration, are shown in Fig. 3. As can be seen, the sorption is quantitative for Sig ~ Z-Met-OH and Sig ~ Schiff B-4-AAP in the presence of 0.5 - 1 mol L^{-1} HCl followed by decreased Pd sorption in more concentrated HCl solution.

Many authors suggest that the sorption equilibrium is strongly affected by the presence of anions such as Cl^-, that compete $[PdCl_4]^{2-}$ for the active sites, which results in reducing sorption capacity with increasing competitor ion concentration [28, 33, 34]. Our results are consistent with these data, and 1 mol L^{-1} HCl was chosen as optimal acidity and was sustained throughout the experimental study. For comparison, some authors indicated that highest adsorption capacity for Pd (II) was obtained at pH 1.0 - 4.0 [26, 35 - 37] and 1.0 - 6.0 [29].

In our research we found that in hydrochloric acid solutions, palladium sorption performances are comparable for both sorbents Sig ~ Schiff B-4-AAP

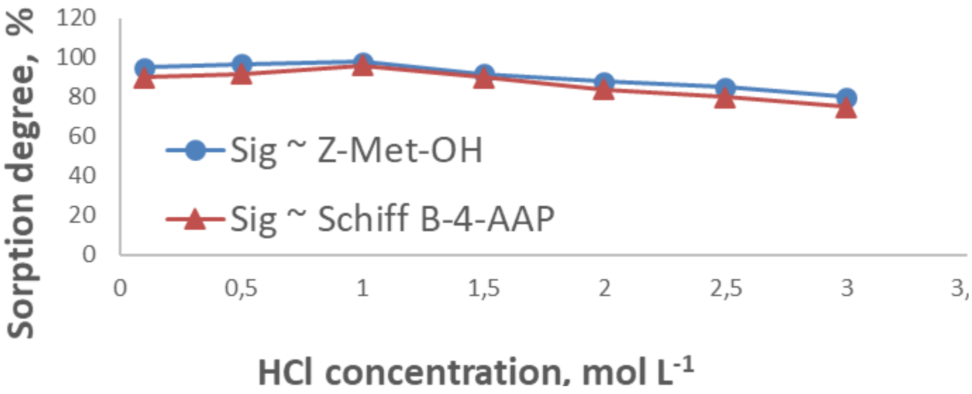

Fig. 3. Effect of HCl concentration on Pd(II) sorption by Sig ~ Z-Met-OH and Sig ~ Schiff B-4-AAP. Adsorbent mass - 50 mg, initial metal concentration - 10 mg L^{-1}, contact time - 1 h. The data represent the average values of three replicates under the identical conditions with error < 5 %.

and Sig ~ Z-Met-OH however slightly higher for Sig ~ Z-Met-OH (Fig. 3), but the difference between them is not so significant.

Kinetics

In the practice, it is preferable that Pd (II) sorption/ recovery is not only quantitative but also if possible rapid process, so the analyte uptake kinetics is an important characteristic that defines the applicability of the sorbent.

The effect of contact time was monitored with an initial Pd (II) concentration of 10 mg L^{-1} onto 50 mg adsorbent for the time period 5 - 100 min, by adjusting the optimal HCl concentration at 1 mol L^{-1} HCl. As can be seen in Fig. 4 the adsorption efficiency is increased with increasing the contact time and reached the maximum value for Sig ~ Z-Met-OH and Sig ~ Schiff B-4-AAP of 98 % and 96 %, respectively at t = 40 minutes. The kinetic curves showed that the amount of palladium (II) adsorbed on Sig ~ Schiff B-4-AAP and Sig ~ Z-Met-OH increased rapidly with the contact time and then tended to equilibrium with the time. This can be explained with the large surface of the silica gel which is covered with a significant number of reactive sites available for adsorption in a short time. A period of 40 min was chosen as a suitable contact time for the adsorption of Pd (II) ions.

Desorption study

The quantitative recovery of the element of interest can be achieved only if a suitable type of eluent is chosen. Additionally, the concentration and volume of the selected eluent are also important factors for complete elution. The acidity of the eluent solution finally determines the efficacy of the elution process. In this study obviously, eluents containing N- and S- donor atoms are recommendable. Taking into account that the desorption mechanism of Pd(II) depends on the same factors as its sorption, acid desorbing solution has to ensure more favorable conditions for quantitative elution. For this purpose, an eluting agent with both *N*- and *S*- atoms such as thiourea in HCl media was studied. Elution efficiency at various thiourea and HCl concentrations was studied and presented in the Table 1 and Table 2. As can be seen, 0.7 mol L^{-1} thiourea in 2 mol L^{-1} HCl ensures a quantitative desorption of Pd(II) from both Sig ~ Z-Met-OH and Sig ~ Schiff B-4-AAP and was chosen as eluent for Pd recovery.

In order to obtain a larger enrichment factor, as little as possible eluent volume has to be used. In our investigation, we found that 2 ml eluent volume extracts quantitatively Pd(II) from the sorbent.

Influence of interfering ions

Various metal ions, noble and base metals with the properties of soft acids have affinity toward *N*- and *S*- containing ligands, which would make it difficult to separate Pd(II) from environmental samples. In such cases the acidity of the sample solution is an important factor for differentiation and selective separation of Pd(II) and precious metal ions [26, 35].

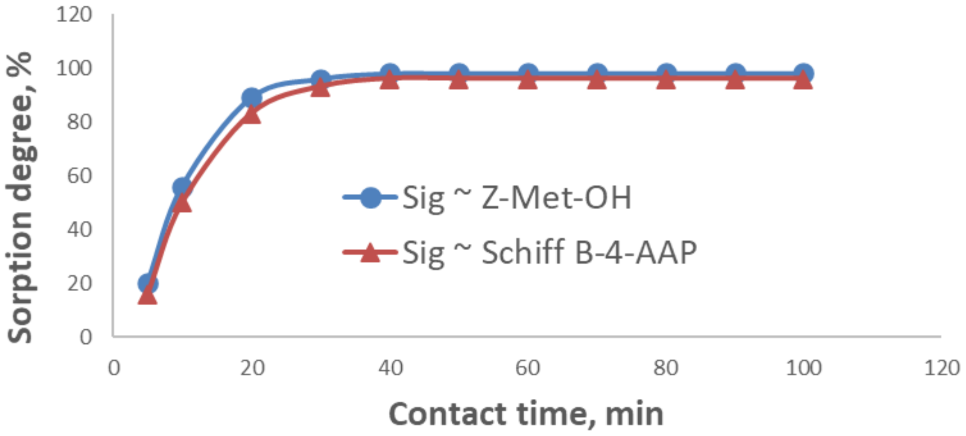

Fig. 4. Influence of contact time on the adsorption of Pd(II) onto Sig ~ Z-Met-OH and Sig ~ Schiff B-4-AAP. Metal ion concentration - 10 mg L^{-1}, HCl concentration - 1 mol L^{-1}, adsorbent mass - 50 mg.

Table 1. Effect of HCl and thiourea (TU) concentration on Pd(II) desorption from Sig ~ Z-Met-OH. Adsorbent masse: 50 mg, Pd(II) concentration on the sorbent: 100 µg, contact time: 1 h. The data represent the average values of three replicates under the identical conditions with error < 5 %.

Eluting agent concentration, mol L^{-1}		Degree of elution, %
TU concentration, mol L^{-1}	HCl concentration, mol L^{-1}	
0.1	1	50
	2	52
	2.5	53
0.5	1	70
	2	80
	2.5	80
0.7	1	95
	2	100
	2.5	97
1	1	95
	2	97
	2.5	96

Table 2. Effect of HCl and thiourea (TU) concentration on Pd(II) desorption from Sig ~ Schiff B-4-AAP. Adsorbent mass - 50 mg, Pd(II) concentration on the sorbent - 100 µg, contact time - 1 h. The data represent the average values of three replicates under the identical conditions with error < 5 %.

Eluting agent concentration, mol L^{-1}		Degree of elution, %
TU concentration, mol L^{-1}	HCl concentration, mol L^{-1}	
0.1	1	49
	2	50
	2.5	51
0.5	1	67
	2	72
	2.5	75
0.7	1	92
	2	99
	2.5	95
1	1	94
	2	98
	2.5	95

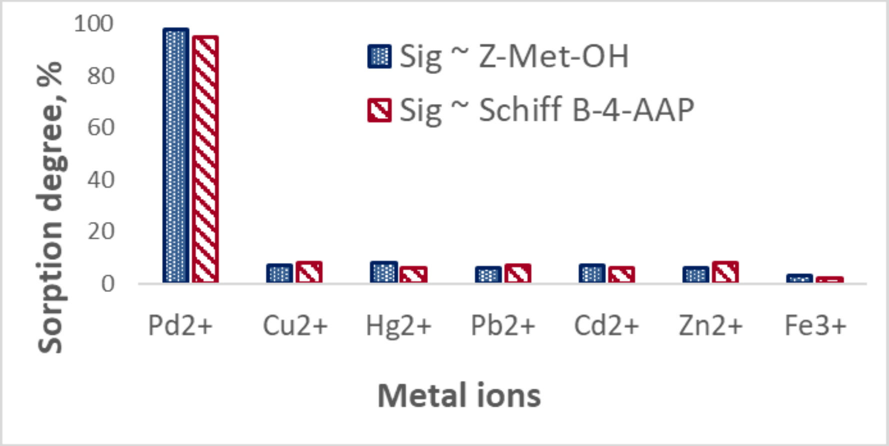

Fig. 5. Competitive sorption of Pd^{2+} in presence of commonly associated base metals.

Fig. 5 shows the results for the competitive sorption of Pd (II) on Sig ~ Z-Met-OH and Sig ~ Schiff B-4-AAP in the presence of several base metals. Among all the ions, Pd (II) was adsorbed selectively in acidic media with minimal absorption of the other base metal ions. However, Sig ~ Z-Met-OH and Sig ~ Schiff B-4-AAP are not capable to extract selectively Pd(II) in presence of other noble metals, such as Pt and Au [30, 38, 39].

CONCLUSIONS

In this study, silica gel sorbents functionalized with *N*- and *S*- functional groups were developed by simple physical immobilization of 4-aminoantipyrine Schiff base (Sig ~ Schiff B-4-AAP) and *N*-benzyloxycarbonyl-*L*-methionine (Sig ~ Z-Met-OH) on the silica surface. The obtained systems, used to extract Pd(II) in acid media, showed an excellent extraction efficiency and fast sorption kinetics. Additionally, the use of relatively low volume of eluent allowed to achieve high enrichment factor, which makes possible the separation and determination of trace Pd(II). Sig ~ Z-Met-OH showed slightly better sorption recovery properties in comparison with Sig ~ Schiff B-4-AAP but the difference is not significant. *N*-benzyloxycarbonyl-*L*-methionine and Schiff base of 4-aminoantipyrine proved to be selective extractants for separation of palladium(II) from commonly associated base metal ions. However, the sorbents are not selective for Pd(II) in presence of other noble metals, such as Pt and Au. Thiourea in acidic media was the eluent reaching quantitative desorption of Pd(II) from the sorbents.

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