PALLADIUM RECOVERY BY ADSORPTION ON ALUMINUM HYDROXIDE

Mihaela CIOPEC[1], Adina NEGREA[1], Narcis DUTEANU[1], Petru NEGREA[1], Nicoleta NEMES[1], Gheorghe DOBRA[2], Sorin ILIEV[2], Lucian COTET[2], Alina BOIANGIU[2], Laurentiu FILIPESCU[3]

Palladium is a precious metal which has a very large utilization in different industrial fields, such as catalysts in different industries, in electronics, dental alloys and into different environmental applications. Recovering and reusing palladium are healthy for the environment and productive for the industry. In this paper it is presented an easy technology used for palladium recovery, by adsorption on dry hydrated alumina (HA, aluminum hydroxide) produced by Alum SA Tulcea, Romania. First, HA was characterized by chemical and mineralogical analysis, and also by scanning electron microscopy. After that, there were determined its adsorptive properties by kinetic, thermodynamic and equilibrium studies. Also, there was proposed the kinetic mechanism for palladium adsorption on HA. In order to perform these studies, the following issues were carefully monitored: the effect of pH, of contact time, of solid/liquid ratio and of temperature on the material (HA) adsorption capacity.

Keywords: palladium, recovery, adsorption, hydrated alumina, aluminum hydroxide

1. Introduction

Palladium is a precious metal from platinum metallic group (PGMs) [1], having a large number of industrial applications: catalysis and energy, petrochemical industry, jewelry and electronic industry, printed circuits, preparation of different dental alloys, heat and corrosion resistance systems, brazing alloys. In organic chemistry palladium is a well-known catalyst, For example, it's used as catalyst for: the Suzuki cross-coupling of halo-benzenes and the phenyl-boronic acids [2], the ethylene polymerization and copolymerization with polar monomers [3] for biaryl - compounds fabrication [4], as well as catalyst for Suzuki-Miyaura reaction, catalyst for control of polyethylene topology, catalyst in Heck coupling reaction, hydrogenation of alkyl-antraquinones and methane combustion [5]. Production of active pharmaceutical ingredients has become possible by development of palladium-catalyzed

[1] Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, University POLITEHNICA of Timisoara, Romania, e-mail: mihaela.ciopec@upt.ro
[2] Vimetco Alum SA Tulcea, Romania, e-mail lcotet@alum.ro
[3] Doctoral School of Chemical Engineering, University POLITEHNICA of Bucharest, Romania, *Corresponding author, e-mail: laurentiu_filipescu@yahoo.co.uk

reactions, but a main issue it is represented by the product contamination with palladium [5]. Production of active pharmaceutical ingredients has become possible by development of palladium-catalyzed reactions, but here a main issue is represented by the product contamination with palladium. Due to its spread usage as catalyst, it is vital to develop new stable catalyst, where palladium remains bound to the support, thus eliminating a further product contamination [5]. Experimental data proved that palladium has no biological role, however its compounds present an extreme toxicity being carcinogenic, causing asthma, allergy, rhino-conjunctivitis, etc. [6]. Increasing demand for palladium and palladium compounds due to the electronic industry and other special applications has led to a rapid increase in its price. Such high price, correlated with the expectation that palladium market will go in some deficit, make the recovery of palladium a secondary resource able to fulfill the needs of human society [7]. For example, palladium contributes at approximately 50% from the value of PCBs after recycling of personal computers. In this context it is very important to proper separate the palladium form other metals. Main constituent of these metallic wastes is copper, which has similar chemical properties with palladium [8]. Copper solutions with palladium content are enriched after the wastes leaching with different solutions and then the extraction of palladium is made by different methods, such as: solvent extraction. Zhang et al. [8] reported the recovery of palladium form PCBs using a solution of copper sulfate and sodium chloride followed by solvent extraction. Some different approach was presented by Prabaharan et al. [8, 9], which used aqua regia for the palladium dissolution, followed by the palladium cementation with zinc. Fontana et al. [9] proved that the palladium recovery from scrap is possible by leaching with aqua regia, followed extraction with Aliquant 336 in limonene. Faisal et al. [10] found that the usage of CO_2 with TBP-HNO_3 ligands is an effective method for palladium extraction from the spent automobile catalytic converters. Yousif [11] proved that palladium recovery can be done by leaching spent catalytic convertors with an eco-friendly solution (H_2O_2 + HCl) followed by further precipitation with $NaClO_3$. Uheida et al. [12] developed a new adsorbent material based on magnetite nanoparticles coated with nonyl-thiourea, for palladium recovery from diluted aqueous solution Sharififard et al. [13] used activated carbon and bio-polymer activated carbon as adsorbent for palladium recovery from aqueous solutions. Adsorption at level of different interfaces represents a concern of the scientists for such a long time. This process presents a high importance for a large number of biological, ecological, technological and industrial processes. During last decades the applications of adsorption in industry and environmental protection becomes relatively important, leading at production of new classes of solid adsorbents with a large number of applications in different industries such as: catalysis, water purification and sewage treatment. In all adsorption processes an important

parameter is represented by adsorbent selectivity and anti-interference ability, which are determined by adsorbent structure and properties. In this context it is crucial to develop proper adsorbents possessing good selectivity or to develop advanced functional materials with adsorbent properties [14]. Recovery of different valuable compounds by adsorption has been possible by using different adsorbent materials such as: activated carbon, silica gels, carbon fibers, molecular sieves, metallic oxides, activated alumina, carbon micro and nano-tubes, synthetic polymers, metallic hydroxides, zeolites, inorganic materials and by using different extractants such as: amines, quaternary ammonium salts, oximes, alkyl phosphates, phosphonic salts, derivatives of thioamides, etc. Powder activated alumina represents a good and efficient adsorbent, obtained by dehydroxilation of aluminum hydroxide. Because of the presence of Lewis acid sites on activated alumina surface, this material presents the capacity to withdraw electrons, having beneficial effects on adsorption rate. Kannan et al. [15] used alumina as effective adsorbent for removal of malachite green dye. In other study, Asim et al. [16], alumina has been used as effective adsorbent for removal of direful black dye from waste water by when, 1 g alumina was able to remove 85 % of dye from concentrated solutions.

Present study aims to recover palladium ions from aqueous solutions by using hydrated alumina as adsorbent. In the experimental part have been highlighted the adsorptive properties of used adsorbent material, as well as the adsorption mechanism by kinetic, thermodynamic and equilibrium studies.

2. Materials and methods

2.1. Materials

Hydrated alumina (HA) (aluminum hydroxide) dried and classified grade has been produced by Alum SA Tulcea, Romania. The fraction below 45 μm of the industrial product was preliminary dried at 80°C. In order to set up the optimum conditions for palladium recovery by adsorption, it has been used as a stock solution of 1000 mg/L $Pd(NO_3)_2$ in HNO_3 0.5 mol/L, purchased from Merck, Germany.

2.2. Adsorbent characterization

Samples of aluminum hydroxide were collected from the new experimental pilot-size installation for research and development of a technology to obtain the dried and classified grade aluminum hydroxide, built up by implementation of the "Endow the Research and Development Department of SC ALUM SA Tulcea with independent and efficient research facilities to support the economic competitiveness and business development", project co-funded by the European Regional Development Fund through the Competitiveness Operational Program 2014–2020.

Samples were characterized by chemical analyses (using ICP-OES and ISP-MS methods) [17], by mineralogical analysis (using a BRUKER D8 ADVANCE diffraction instrument with all the programs for data processing [18] and by scanning electron microscopy (using a SEM: Quanta FEG 250, FEI, The Netherlands) with back scattered electron detector (BSD) coupled with energy dispersive X-ray spectroscopy (EDS) [17].

2.3. Pd(II) recovery by adsorption

Adsorptive performances of HA were demonstrated by performing kinetics, thermodynamic and equilibrium studies, by determining the influence of specific adsorption parameters (pH, sorbent dose, contact time, Pd(II) initial concentration) on maximum adsorption capacity. By correlating data obtained from these studies has been suggested a possible mechanism for palladium adsorption on HA.

Adsorption capacity has been determined using equation 1:

$$q = (C_0 - C_f)V/m \quad (1)$$

where: C_o – initial concentration of Pd(II) from solution, (mg/L); C_f – residual concentration of Pd(II) from solution, (mg/L); V–solution volume, (L); m–adsorbent mass, (g).

Efficiency of adsorption process has been determined using equation 2:

$$\eta = 100\ (C_0 - C_f) / C \quad (2)$$

where: C_o – initial concentration of Pd(II) from solution, (mg/L); C_f – residual concentration of Pd(II) from solution, (mg/L).

2.3.1. pH effect

The pH represents a variable with a significant influence in the case of adsorptive processes, having a large effect on adsorbent material affinity for palladium ions. In order to settle the influence of pH on palladium adsorption process, there were weighed samples of 0.1 g of adsorbent material, which were mixed with 25 mL solution of Pd(II) with an initial concentration of 10 mg/L, and the pH between 1 and 6. All samples were maintained in contact for 60 minutes, and after that there were filtered. Palladium residual concentration in the filtrated solutions has been determined by atomic adsorption spectrometry using a Varian SpectrAA 280 FS instrument. Solution pH has been determined using a Seven Compact S 210 Mettler Toledo pH-meter.

2.3,2. Effect of sorbent dose

In order to settle the optimum ratio adsorbent (dried HA/Pd(II) solution, it has been varied the quantity of adsorbent between 0.05 and 0.5 g. Each adsorbent sample has been mixed with 25 mL Pd(II) solution with an initial concentration of 10 mg/L, and maintained in contact for 60 minutes. After that, the samples were filteredand the solution was analyzed for determination of Pd(II) residual concentration by AAS.

2.3.3. Contact time and temperature effect

Contact time and temperature represent another two important factors with a great influence over adsorptive processes. In order to describe the influence of contact time and temperature on the adsorption process, quantities of 0.1 g of HA were weighed and were mixed with 25 mL Pd(II) solution with an initial concentration of 10 mg/L. Prepared samples were mixed for different time durations (15, 30, 60, 90 and 120 minutes) and also at different temperatures using a thermostatic bath. In all cases the pH was lower than 4. After filtration, Pd(II) residual concentration has been determined by AAS.

Kinetics equation used to describe Pd(II) adsorption on HA were: pseudo-first-order model (Lagergren model) [19] and pseudo-second-order model (Ho and McKay model) [20].

Pseudo-first-order kinetic model is described by equation [19]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where: q_e – equilibrium adsorption capacity, (mg/g); q_t – adsorption capacity at time t, (mg/g); k_1 – rate constant for pseudo-first order (min^{-1}); t – contact time, (min).

In this case the equation (3), the process is represented by a linear dependence between ln(qe-qt) versus t. This dependence can be evaluated from the rate constant (k_1) and adsorption capacity ($q_{e,calc}$).

Pseudo-second-order kinetic model is described by equation [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where: q_e – equilibrium adsorption capacity, (mg/g); q_t - adsorption capacity at time t, (mg/g); k_2 – rate constant for pseudo-second order (g/mg·min; t – contact time, (min).

For pseudo-second-order kinetic model, the process has been represented a linear dependence between t/q_t and t. From this linear dependence, there were calculated the values of rate constant (k_2) and adsorption capacity ($q_{e,calc}$).

In order to determine if the rate determinant stage is intra-particles diffusion, the obtained experimental data were processed using Weber and Morris kinetic model [21]:

$$q_t = k_{diff} \cdot t^{1/2} + C \tag{5}$$

where: q_t – adsorption capacity at time t; k_{diff} – intra-particles diffusion rate constant (mg/g· $min^{1/2}$); C - constant correlated with the thickness of the liquid film surrounding the adsorbent particles. The obtained experimental data were better described by pseudo-second-order model, so based on this, it has been evaluated the activation energy for Pd(II) adsorption on HA using the following equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (6)$$

where: k_2 – rate constant, (g/min·mg); A - Arrhenius constant, (g·min/mg); E_a – activation energy, (kJ/ mol); T – absolute temperature, (K); R - the ideal gas constant, (8.314 J/mol·K).

Activation energy for Pd(II) adsorption on HA has been calculated from the linear representation of $\ln k_2$ versus 1/T.

In order to determine if Pd(II) adsorption on HA it is a spontaneous process, it has been calculated the value of free Gibbs, using Gibbs – Helmholtz equation [22]:

$$\Delta G^o = \Delta H^o - T \cdot \Delta S^o \quad (7)$$

where: ΔG°- standard variation of Gibbs free energy (kJ/mol); ΔH° - the standard variation of enthalpy, (kJ/mol); ΔS°- standard variation of entropy, (J/mol·K); T– absolute temperature, (K).

Standard entropy and standard enthalpy variations were determined form linear dependence between $\ln K_d$ versus 1/T:

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (8)$$

where: K_d - equilibrium constant; ΔS°- the standard variation of entropy, (J/mol·K); ΔH°- the standard variation of enthalpy, (kJ/mol); T - absolute temperature, (K); R - the ideal gas constant, (8.314 J/mol·K).

Equilibrium constant (K_d) represents the ratio between adsorption capacity at equilibrium and concentration at equilibrium:

$$K_d = \frac{q_e}{C_e} \quad (9)$$

where: q_e – equilibrium adsorption capacity, (mg/g); and C_e– equilibrium concentration, (mg/L).

For all the equilibrium studies, there were weighed 0.1 g of HA and mixed with 25 mL of Pd(II) solutions with different concentrations (5, 10, 20, 30, 40, 50 and 60 mg/L). All the samples were maintained in contact for 90 minutes at 298 K. In all cases, the solutions have had a pH lower than 4. After filtration, the residual concentration of palladium has been determined by AAS.

2.3.4. Pd(II) initial concentration effect. Adsorption Isotherms

For understanding the adsorption mechanism, it is necessary to find a model to match the obtained experimental data concerning the adsorption isotherms. In the present study, there were investigated the possibilities to fit the experimental data to models like Langmuir and Freundlich adsorption isotherms. Langmuir adsorption isotherm is specific for homogenous adsorption, when superficial active centers are identical and homogenously distributed on adsorbent surface. This isotherm is used to describe monolayer adsorption processes, in

which the capacity of one molecule to be adsorbed on one active center is independent on the occupancy of neighbors' centers. Nonlinear form or Langmuir isotherm is [23]:

$$q_e = \frac{q_L K_L C_e}{1 + K_L C_e} \tag{10}$$

where: q_e – equilibrium adsorption capacity (mg/g); C_e - equilibrium concentration for Pd(II) ions from solution (mg/L); q_L – Langmuir maximum adsorption capacity (mg/g); K_L - Langmuir constant. Separation factor (R_L) represent a principal characteristic for Langmuir isotherm and has been computed using the following equation:

$$R_L = \frac{1}{1 + K_L Co} \tag{11}$$

where: R_L – separation factor; K_L - Langmuir constant; C_o – Pd(II) initial concentration (mg/L). The Freundlich isotherm assumes that the adsorbent surface is a heterogeneous one, which leads to multilayer adsorption, due to some unlimited number of active centers. The nonlinear form of Freundlich isotherm is [24]:

$$q_e = K_F C_e^{1/n_f} \tag{12}$$

where: q_e - equilibrium adsorption capacity, (mg/g); C_e - equilibrium concentration of Pd(II) from solution (mg/g); K_F and n_F - characteristic constants, which may be associated with the relative adsorption capacities of the adsorbent respectively, the adsorption intensity.

In accordance with the Langmuir and Freundlich isotherms, it has been developed Sips isotherm which at lower concentrations becomes a Freundlich one and at higher concentrations becomes a Langmuir one isotherm. Nonlinear form of Sips isotherm is [25]:

$$q_e = \frac{q_s K_S C_e^{1/n_S}}{1 + K_S C_e^{1/n_S}} \tag{13}$$

where: q_S- maximum equilibrium adsorption capacity (mg/g); K_S - constant related to the adsorption capacity of adsorbent; n_S– heterogenic factor.

These three types of isotherms, described above, were obtained by representing the dependence between qe and Ce. In conformity with the associated equations, there were determined the specific parameters for each adsorption isotherm type.

3. Results and discussion

3.1. pH effect

Graph depicted in Fig. 1 presents the influence of pH on Pd(II) adsorption capacity on HA. Relying on presented data in Fig. 1, it can be noticed that the

solution pH is one of the control parameter of studied adsorption process. Thus, it is evident that simultaneously with pH increase, the adsorption capacity of HA is increasing, until pH 4 when the maximum adsorption capacity has been reached. Further increase of pH does not lead to know any supplementary increase in the maximum adsorption capacity. No other studies were carried out at pH values higher than 6, because at these values the palladium precipitation occurs [26].

3.2. Effect of sorbent dose

Quantity of adsorbent material is an important parameter in adsorption processes, so further has been studied the influence of sorbent dose over adsorption process efficiency (obtained experimental data are depicted in Fig. 2).

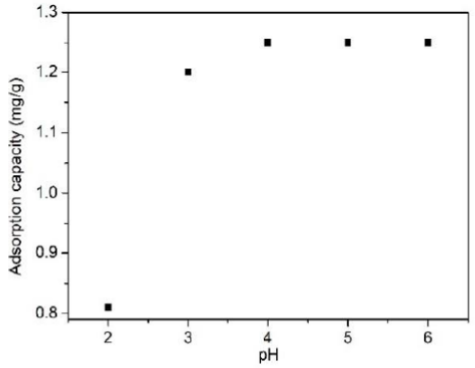

Fig. 1. pH effect

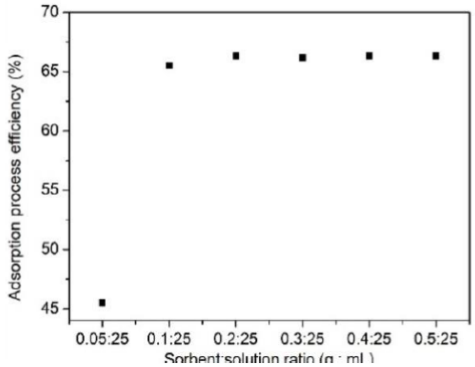

Fig. 2. Effect of sorbent dose

Analyzing the obtained data depicted in Fig. 2, it can be observed that the increase in sorbent dose lead at increase of adsorption efficiency. Maximum adsorption efficiency (65 %) has been obtained for a sorbent dose of 0.1 g used for 25 mL of Pd(II) solution. Further increase in solvent dose does not lead to any increase of maximum adsorption capacity. Based on this observation all further studies were carried out for a ratio sorbent: solution = 0.1 g: 25 mL.

3.3. Contact time and temperature effect

Other important parameters for adsorptive processes on HA are represented by the contact time and temperature at which the system is reaching the equilibrium. In the Fig. 3 is depicted the dependence of adsorption capacities versus contact time at three different temperatures (298, 308 and 318 K). Analyzing experimental data depicted in Fig. 3, it can be noticed that the increase of contact time leads to increase in the maximum adsorption capacity of HA. Maximum adsorption capacity has been obtained when the contact time has been 90 minutes. Assuming these findings, all further experiments were carried out at a contact time of 90 minutes. By increasing the temperature from 298 at 318 K, the significant increases in the maximum adsorption capacity were proving that the studied adsorption process is influenced by temperature. For a optimum contact time of 90 minutes, temperature increase from 298 at 318 K leads to an increase in

maximum adsorption capacity from 1.59 mg/g to 1.74 mg/g. Kinetics of adsorption process depends on the interactions between adsorbent and adsorbate. In order to find more about the kinetic mechanism of the studied adsorption processes, the experimental data were processed using pseudo-first-order and pseudo-second-order kinetic models. Results of the above experiments are depicted in Fig. 4.

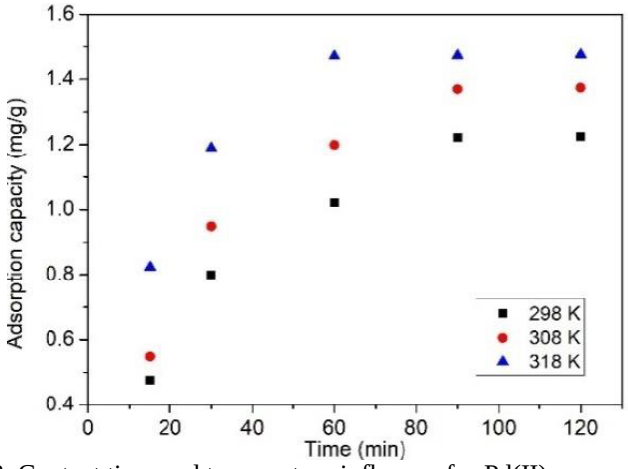

Fig. 3. Contact time and temperature influence for Pd(II) recovery onto HA

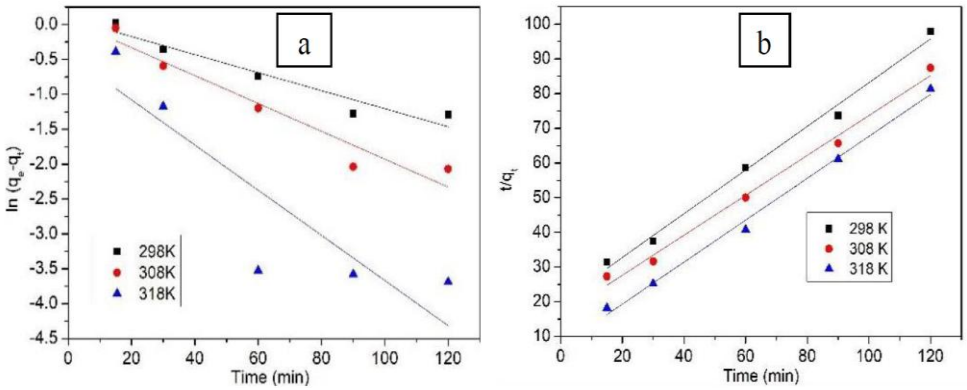

Fig. 4. Kinetic models. a) Pseudo-first-order; b) Pseudo-second-order

Based upon these data, there were determined the kinetic parameters specific for the used models (parameters are presented in the table 1). Constant k_1 value associated with pseudo-first-order model has been calculated from the slope of the linear dependence of $\ln(q_e-q_t)$ versus time. Likewise, de value of the constant k_2 associated with pseudo-second-order model has been determined form the slope of linear dependence of t/qt versus time. On the grounds of these correlation coefficients, we can notice that the studied adsorption process is better

described by the pseudo-second-order model (value of the correlation coefficient is near 1).

Table 1

Kinetic parameters for Pd(II)adsorption on HA

Pseudo-first order				
Temperature (K)	$q_{e,exp}$ (mg/g)	k_1 (1/min)	$q_{e,calc}$ (mg/g)	R^2
298	1.22	0.0175	1.08	0.9296
308	1.37	0.0278	1.15	0.9348
318	1.47	0.0458	1.06	0.8859
Pseudo-second order				
Temperature (K)	$q_{e,exp}$ (mg/g^-)	k_2 (g/mg·min)	$q_{e,calc}$ (mg/g)	R^2
298	1.22	0.1248	1.38	0.9927
308	1.37	0.1867	1.52	0.9920
318	1.47	0.3767	1.65	0.9949

This remark is in good agreement with the data found into the scientific literature. In this case, the rate limiting stage in the first part of the adsorption process is played by the chemical reactions. Experimental data were further processed according with the Weber and Morris kinetic model. The results are presented in Fig. 5. Data presented in the Fig. 5 show that the first 10 minutes can be attributed to the mass transfer, which is taking place by diffusion at grain boundary. The linear part observed after 10 minutes indicates a intra-particle diffusion, which can be associated with the diffusion into the material pores. Also, we can conclude that the studied adsorption process is a rapid one. After the linearization of experimental points, the straight line does not pass through origin, which means that the diffusion of metallic ions into the adsorbent material pores is certainly interfering with kinetics of the studied adsorption. Using the value of rate constant determined for pseudo-second-order model, we can compute the value of adsorption energy associated with Pd(II) adsorption onto HA. This value has been determined form the slope of linear dependence between ln k_2 and 1/T (Fig. 6). According to literature data, there was computed a value of 43.3 kJ/mol for activation energy and a correlation coefficient of 0.9381. Because the activation energy value is higher than 40 kJ/mol, we conclude that the Pd(II) adsorption onto HA is a chemical one.

In the present study, it has been determined the influence of Pd(II) ions initial concentration on the maximum adsorption capacity. Experimental data were processed using Langmuir, Freundlich and Sips isotherms models (Fig. 7). Grounded on the data depicted in Fig. 7, there were determined the associated parameters with used isotherms models and the correlation coefficients (table 2). Data presented in the table 2 put on view that the correlation coefficient has the highest value when the experimental data were fitted using Sips model (0.9981).

Taking into account this value, we can conclude that the studied adsorption process is described by Sips isotherm. Moreover, the calculated adsorption capacity in case of Sips model (2.26 mg/g) is near the experimental one (2.19 mg/g). Thus, we can conclude that adsorbent surface is a heterogeneous one and the Pd(II) adsorption on HA is a multilayer adsorption.

Table 2.

Parameters of isotherm model for adsorption of Pd(II) onto AH

Langmuir isotherm			
$q_{m,exp}$(mg/g)	K_L (L/mg)	q_L (mg/g)	R^2
2.19	0.181	2.52	0.96822
Freundlich isotherm			
K_F (mg/g)	$1/n_F$		R^2
0.800	0.277		0.82802
Sips isotherm			
K_S	q_S (mg/g)	$1/n_S$	R^2
0.086	2.26	0.56	0.99813

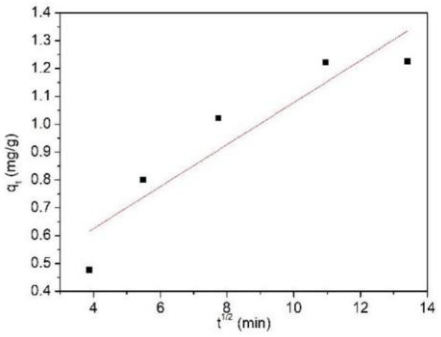

Fig. 5. Intraparticle diffusion process

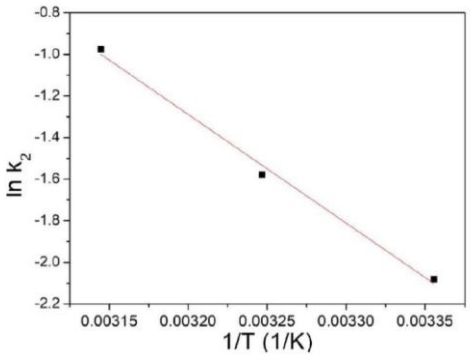

Fig. 6. Arrhenius plot

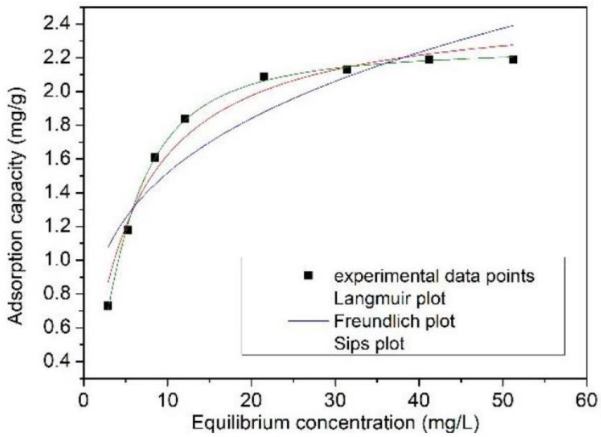

Fig. 7. Isotherm model for adsorption of Pd(II) onto AH surface

Hereinafter, the thermodynamic parameters associated with Pd(II) adsorption onto HA were determined from linear dependence between ln Kd versus 1/T (Fig. 8). From the slope of the line depicted in Fig. 8, it has been computed the value of free Gibbs energy, which indicate that the studied process is a spontaneous one. Computed thermodynamic parameters are given in the table 3.

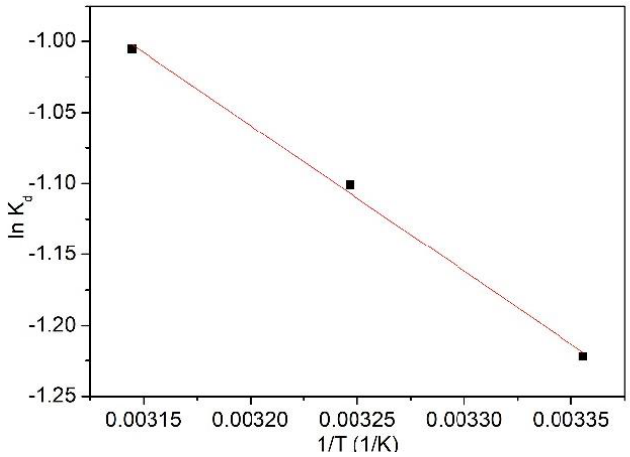

Fig. 8. Plot of ln Kd vs 1/T for the estimation of thermodynamic parameters for recovery Pd(II) onto AH

Table 3.

Thermodynamic parameters for adsorption of Pd(II) onto AH

ΔH^o (kJ/mol)	ΔS^o (J/mol·K)	ΔG^o (kJ/mol)			R^2
3.28	18.49	298 K	308 K	318 K	0.9975
		-2.22	-2.41	-2.59	

Positive value of free enthalpy (ΔH°) proves that the energy needed for adsorption process is the energy used for contacting the Pd(II) ions with adsorbent material surface. Pd(II) ions adsorption generate electrostatic interactions. Negative value of free Gibbs energy (ΔG°) suggest that the studied adsorption process it is a spontaneous process. Because value of the free Gibbs energy becomes more negative when the temperature increases, we can conclude that the increase of temperature is beneficial for studied adsorption process. Considering all these facts, we can attest that the Pd(II) adsorption on HA is an endothermic and spontaneous process.

4. Conclusions

In the present study was investigated the adsorption efficiency of hydrated alumina, produced by Alum SA Tulcea, for Pd(II) recovery process from aqueous solutions. Hydrated alumina has been characterized by chemical, mineralogical

and microscopically methods. According to the obtained experimental data, we can conclude that the Pd(II) adsorption onto hydrated alumina is a spontaneous and endothermic process, which can be assigned to some chemo-sorption processes involved at the interface adsorbent – adsorbate.
Experimental data are better described by Sips isotherm, meaning that the studied process is a multilayers adsorption. Maximum adsorption capacity of hydrated alumina was 2.19 mg Pd(II) per gram of adsorbent material.

Acknowledgement:

This study was possible by implementation of the "Endow the Research and Development Department of SC ALUM SA Tulcea with independent and efficient research facilities to support the economic competitiveness and business development" project, co-funded by the European Regional Development Fund through the Competitiveness Operational Programme 2014 – 2020. Under this project were purchased and commissioned: "Independent equipment/Installation for research and development of the technology of wet aluminum hydroxide classification", "Independent equipment/Installation for research and development of technology to obtain the dried aluminium hydroxide" and "Independent equipment/Installation for research and development of the technology of grinding and screening the dried aluminium hydroxide". Also, this work was supported from the research grant BC 13 / 14.02.2020 - University Polytechnica Timisoara.

R E F E R E N C E S

1. *C. C. C. Johansson Seechurn, M. O. Kitching, D.T. J. Colacot, V. Snieckus,* Palladium-Catalyzed Cross-Coupling: A Historical Contextual Perspective to the 2010 Nobel Prize. Angewandte Chemie International Edition, 51, 5062-5085, 2012.
2. *P. Ruiz-Castillo, S.L.Buchwald,* Applications of Palladium-Catalyzed C–N Cross-Coupling Reactions. Chemical Reviews, **116**,12564-12649, 2016.
3 *Y. Zhangand Z. Jian,* 2-Phosphine-pyridine-N-oxide palladium and nickel catalysts for ethylene polymerization and copolymerization with polar monomers. Polymer, 194, 122410. 2020.
4. *T. N. Baran, Y, Baran, A. Menteş,* Highly active and recyclable heterogeneous palladium catalyst derived from guar gum for fabrication of biaryl compounds. International Journal of Biological Macromolecules, 132,1147-1154, 2019.
5. *C.E. Garrett, and K. Prasad,* The Art of Meeting Palladium Specifications in Active Pharmaceutical Ingredients Produced by Pd-Catalyzed Reactions. Advanced Synthesis & Catalysis, 346, 889-900. 2004.
6. *K., Köhler, RG Heidenreich, SS Soomroet and S.S Procki,* Supported Palladium Catalysts for Suzuki Reactions: Structure-Property Relationships, Optimized Reaction Protocol and Control of Palladium Leaching. Advanced Synthesis & Catalysis, 350, 2930-2936,. 2008.
7. *H.U. Sverdrup, and K.V. Ragnarsdottir,* A system dynamics model for platinum group metal supply, market price, depletion of extractable amounts, ore grade, recycling and stocks-in-use. Resources, Conservation and Recycling, 114, 130-152, 2016..
8. *Z. Zhang, and F.S. Zhang,* Selective recovery of palladium from waste printed circuit boards by a novel non-acid process. Journal of Hazardous Materials, 279, 46-51, 2014.

9. *D. Fontana, M. Pietrantonio, S. Pucciarmati, G. N.Torelli, C. Bonomi and F. Masi,* Palladium recovery from monolithic ceramic capacitors by leaching, solvent extraction and reduction. Journal of Material Cycles and Waste Management, 20, 1199-1206, 2018.
10. *M., Faisal, Y. Atsuta, H. Daimon K. Fujie,* Recovery of precious metals from spent automobile catalytic converters using supercritical carbon dioxide. Asia-Pacific Journal of Chemical Engineering, 3, 364-367, 2008.
11. *Yousif, A.M.* Recovery and Then Individual Separation of Platinum, Palladium, and Rhodium from Spent Car Catalytic Converters Using Hydrometallurgical Technique followed by Successive Precipitation Methods. Journal of Chemistry, 2019, P. 2318157.
12. *A Uheida, M. Iglesias, C. Fontàs, Y. Zhangand M. Muhammad,* Adsorption Behavior of Platinum Group Metals (Pd, Pt, Rh) on Nonylthiourea- Coated Fe_3O_4 Nanoparticles. Separation Science and Technology, 41, 909-923., 2006.
13. *H. Sharififard, M. Soleimani, and F.Z. Ashtiani*, Evaluation of activated carbon and bio-polymer modified activated carbon performance for palladium and platinum removal. Journal of the Taiwan Institute of Chemical Engineers 43, 696-703 , 2012.
14. *M. He, L Huang, B Zhao, B Chen and B Hu.* Advanced functional materials in solid phase extraction for ICP-MS determination of trace elements and their species - A review. Analytica Chimica Acta, 973, 1-24, 2017.
15. *C., Kannan, T. Sundaram, and T. Palvannan,* Environmentally stable adsorbent of tetrahedral silica and non-tetrahedral alumina for removal and recovery of malachite green dye from aqueous solution. Journal of Hazardous Materials, 157, 137-145, 2008.
16. *T. Asim, Mamoona, A. Tahir; N. Nisar; A. Ali; A. Sheikh,* Alumina as environmentally stable adsorbent for the removal of diresul black dye from waste water. Water Practice and Technology, 14, 62-70, 2018.
17. *G. Dobra, S. Iliev, L. Cotet, A. Boiangiu I, Hulka, L. Kim, G.A. Catrina and L. Filipescu*, Heavy metals as impurities in the Bayer production cycle of the aluminum hydroxide from Sierra Leone bauxite. Preliminary study (under press).
18. *G. Dobra, V. Badilita, S. Iliev, L. Cotet, A. Boiangiu, L. Filipescu,* Identification of the crystalline and amorphous phases in the dried raw alumina hydroxide, U.P.B. Sci. Bull., Series B, 81, 163-174, 2019,
19. *S. Lagergren,* About the theory of so-called adsorption of soluble substabces. Kungl. Svenska Vetenskapsakademiens Handlingar 24, 1-39, 1898.
20. *Ho, Y.S. Review of second-order models for adsorption systems.* Journal of Hazardous Materials, 136, 681-689, 2006.
21. A.M. Aljeboree, A.N. Alshirifi, and A.F. Alkaim, *Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon.* Arabian Journal of Chemistry, 10, S3381-S3393, 2017.
22. *P. Atkins and J. de Paula*, Atkins Physical Chemistry, Oxford University Press, Oxford: 2005.
23 . *I. Langmuir,* The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical Society, 40, 1361-1403, 1918.
24. *H.M.F. Freundlich,* Over the adsorption in solution. J. Phys. Chem., 57, 385 – 470, 1906.
25. R. Sips, On the Structure of a Catalyst Surface. The Journal of Chemical Physics, 16, 490-, 1948.
26. *Conţescu, C. and M.I. Vass*, The effect of pH on the adsorption of palladium (II) complexes on alumina. Applied Catalysis, 33, 259-27, 1987.