Separation and Recovery of Platinum and Palladium from Spent Petrochemical Catalysts Using Activated Carbon, Analysis of Two Kind of Most Used Catalysts in Petro Chemistry

Asadzadeh, M.; Sajadi, Seyed Ali Akbar*+

Institute of Water & Energy, Sharif University of Technology, P.O.Box 11155-8639 Tehran, I.R. IRAN

ABSTRACT: *The goal of this work is the separation and recovery of platinum and palladium from spent catalyst. The recovery consisted of separating the maximum amount of platinum and palladium from catalysts and changing them into usable forms. The petroleum and petrochemical units use Pt and Pd catalyst for reactions such as reforming and hydrogenation. Because these materials contain valuable metals, such as Pt and Pd, these metals should be recycled. Based on economic reasons and the high price of new catalysts, petrochemical companies should solve this problem. The new method in this work may help to recover these metals from spent catalyst. This method may help solve several environmental problems. In this work, the recovery of platinum and palladium from petroleum catalysts has been studied using spent catalysts. Two catalysts were characterized by XRF, XRD, and AAS. Aqua regia, used as a leaching agent, and the effect of dissolution temperature and time, Liquid/Solid (L/S) ratio, size of particles, and elimination of coke were also investigated. Under optimized conditions, the leaching process was done with 98% efficiency. Recovery of platinum and palladium from the leached solutions was done by the adsorption process with Activated Carbon (AC) in an environmentally friendly manner. According to the results, the optimum operating conditions for platinum and palladium removal by activated carbon were a temperature of a solution of 85 and 98 ℃, pH = 0.5 and 2, time of adsorption 180 and 150 min and adsorbent loading capacity = 18.75 mg_{Pt}/g_{AC} and 12.5 mg_{Pd}/g_{AC}, respectively. The activated carbon containing platinum and palladium was decomposed by ignition to produce platinum and palladium powder with commercial purity of 96.5% and 96.3% respectively.*

KEYWORDS: *Platinum; Palladium; Catalyst; Recovery; Separation; Environment; Pollution.*

INTRODUCTION

Platinum (Pt) and Palladium (Pd) are internationally recognized as valuable metals and are widely used as a catalyst in various industries, agriculture, and medicine, because of their special physical and chemical properties [1-2]. Various methods such as hydrometallurgy, which includes adsorption by ion exchange resin, solvent

the extraction and the reduction of the precious metal precipitate by reagents has been utilized more often than the pyro-metallurgical process [3-6].

Because of increasing demand and the increasing cost of production due to decreasing Pt and Pd concentration in remaining naturally occurring ore there is a need to develop an economical method to recover such metals from wastewater i.e. low cost and environmental-friendly. Therefore, it is necessary to process secondary materials, such as spent catalysts, electronic scraps, used equipment, fabricated ware and membrane electrode assemblies, for Pt recovery and recycling [7-12]. Pt is employed as a catalyst in various chemical reactions; thus, spent catalysts are an important secondary source for recovering Pt and other associated metals. A number of platinum-based catalysts are available and applicable for various purposes, such as follows:

- Pt gauze catalyst: Oxidation of ammonia to produce nitric acid

- Pt and Ni catalyst: Acetophenone hydrogenation steam reforming of n-butane to produce hydrogen

- Pt-base metals catalyst: Reforming and isomerization catalyst

- Pt–Sn–In/Al$_2$O$_3$–Li catalyst: n-Paraffin dehydrogenation to produce alpha-olefins

The separation and purification of these metals usually difficult owning to their similar structures and chemical behaviors [13-18]**.** A critical stage in the whole recovery procedure is the efficient and complete separation of Pd. Separation of Pd from solution has been carried out by many researchers utilizing different techniques such as a reduction in phosphoric acid solutions by formalin at 150°C; reduction by aluminum powder; or bioreduction [19-23].

Complete dissolution of palladium was achieved by leaching with a solution contains 7% HCl and 5% H$_2$O$_2$ at 60 8C for 2 hwith a liquid/solid ratio of 10/1. The leach liquor contained 0.04% palladium and 0.5% aluminum and thefiltered solids was a pure aluminum rich residue. Palladium could be separated from the leach liquor by reduction with formic acid solution [22]. Solvent extraction experiments were done to find extraction conditions to selectively extract Pd(II) over Pt(IV) from HCl solutions in the concentration range from 0.5 to 9 M. The separation of platinum and palladium from chloride

solution by solvent extraction, using Alamine 300 as an extractant has been studied. The effect of different parameters such as the concentration of HCl in the feed solution, NaCl concentration, extractant concentration, and platinum and palladium concentrations in the feed solution has been evaluated [24]. The quantitative extraction of approximately 98% platinum(IV) and 36% rhodium(III) was achieved with 0.01 mol L(-1) Alamine 308. The highest separation factor (S.F.=184.7) of platinum(IV) and rhodium(III) was achieved with 0.01 mol/L Alamine 308 at 1.0 mol/L of hydrochloric acid concentration. Alkaline metal salts like sodium chloride, sodium nitrate, sodium thiocyanate, lithium chloride, lithium nitrate, potassium chloride and potassium thiocyanate used for the salting-out effect [25]. Extraction and separation of Pt(IV) and Pd(II) was carried out with Cyanex 923 in chloride media. Pt was quantitatively extracted from 3.0-8.0 M HCl in the presence of 0.01 M SnCl$_2$ while Pd from 4.0-5.0 M HCl with 5x10-3 M Cyanex 923 in toluene. Pt was than quantitatively stripped from the organic phase with 5.0 M HNO$_3$ while Pd was quantitatively stripped with 1:1 HCl + HClO$_4$ in a single step and also with 7.0 M HCl in two steps. Pt was also extracted without using SnCl$_2$ [27].

In this study, the recovery of platinum and palladium from the spent petroleum catalysts has been examined by mixing the catalyst substrates (in liquid solution form) in activated carbon thereby adsorbing platinum and palladium in activated carbon. The effect of temperature and time, the concentration of acid, particle size, and pulp density on the dissolution of the substrate has also been investigated [24-30]. Platinum and palladium dissolved in acid could, to some extent, also be recovered in a cementation process using aluminum powder as a reducing agent [33-35].

EXPERIMENTAL SECTION
Equipment

Atomic absorption instrument, AA 220-Varian; pH meter, ZPH 76 ATC; Electrical furnace, Thermoline; Spectrophotometer UV/Vis, Hach; XRF instrument, Magix-pro, Philips; XRD instrument, Stadi P, Stoe; ICP-OES instrument, Spectro arcos, Amtech; BET instrument, Belsorp mini 1, BEL; TGA/DSC instrument, TGA/DSC 1, Mettler; Potentiograph titrator, Titrino, Metrohm.

Chemicals

H_2PtCl_6 , standard solution 1000 ppm, (pro analysis) Art # 70219, purchased from Fluka Co.

Aluminum metallic powder (pro analysis) Art # 820051; $Pd(NO_3)_2$, standard solution 1000 ppm, from Merck Co. (pro analysis) Art # 14282; Nitric acid 65% from Merck Co. (pro analysis) Art # 100443; Hydrochloric acid 37% , from Merck Co. (pro analysis) Art # 3172500; Sodium hydroxide , from Merck Co. (pro analysis) Art # 106462; Ammonium hydroxide 33%, from Merck Co. (pro analysis) Art # 5426; Ammonium chloride, from Merck Co. (pro analysis) Art # 1142; Sodium nitrate, from Merck Co. (pro analysis) Art # 6537; Sodium thiosulfate, from Merck Co. (pro analysis) Art # 6516; Sodium carbonate, from Merck Co. (pro analysis) Art # 6392; Activated carbon, from Merck Co. (pro analysis) Art # 2186; Buffer solutions 4, 7 & 9 ; all were purchased from Merck Co.. Spent catalyst Pt, RG-582 (a catalyst containing Pt (see Tab. 1&3 for details)), Axens and Spent catalyst Pd, LD-265 (a catalyst containing Pd (see Tab. 2&3 for details)), Axens were received from petrochemical co. and twice distillated water prepared in our lab.

The analysis of used catalysts

In this study the spent catalysts RG-582 and LD-265 from petrochemical companies are used in the recovery of Pt and Pd. The RG-582 catalyst used was cylindrical, shaped like a grain of rice, and contained Pt. It was received from the Tabriz Refinery Co. and had been used for production of gasoline with high octane. The LD-265 catalyst used was spherical particles from a hydrogenation unit in a petrochemical company. It was provided by the Iranian petrochemical research and technology Co.

Both catalysts consisted of approximately 90% alumina silica with some transition metals; alkali- and earth alkali metals. Catalysts have doted only for a few percent novel metals such as Pt and Pd.

Analysis of catalyst's components by XRD

The XRF technique was used for quantitative analysis of spent catalysts RG-582 and LD-265. The obtained results are shown in Tables 1 and 2.

Quantitative analysis of components of the spent catalysts by atomic absorption technique

The sample solution was measured by the atomic absorption method, it should be clear and free of precipitation used filter. For this purpose, 2 g of each catalyst, RG and LD, were dried at 105°C for five hours in an oven and then cooled to room temperature in a desiccator and weighted. The catalysts were then mixed with 15 mL HCl 37% and 5 mL HNO_3 65% and heated under reflux at 109°C for two hours.

The content of the balloon was cooled to room temperature and filtered. Then the precipitate was washed several times with water. Finally, the obtained solution was inserted in a 250mL balloon and used for the quantitative analysis. The obtained results of the quantitative analysis of the catalysts RG and LD by atomic absorption are listed in Table 3.

XRD investigation of RG and LD

Both catalysts RG and LD were also investigated by the XRD technique. The obtained diagram is shown in Figs. 1 and 2.

Recovery of Pt from the spent catalyst RG-582 and Pd from LD-265

After an initial analysis, the catalysts were investigated by different methods for separation and recovery of Pt from RG-582 and Pd from LD-265.

The first stage consisted of acid leaching, dissolution of Pt and Pd from the solid structure of the catalysts. The second stage was the separation of Pt and Pd from the obtained solution and conversion to their useable compounds such as metallic Pt and Pd or Pt- and Pd-oxides.

Factors that can affect the efficiency of the leaching process are temperature, leaching time process, the catalyst particle size distribution, the acid volume ratio to the mass of catalysts (L/S) and initial calcination of catalysts.

The effect of temperature on the efficiency of the leaching process:

Catalyst leaching kinetics of the process can be influenced by temperature and therefore the optimization of the leaching process temperature is necessary in order to reduce energy consumption.

For this reason, in both catalysts, particle size distribution of 100 mesh was separated and dried in an oven and cooled in a desiccator. Seven samples, each weighting 1g., were prepared from this, and 10mL nitrohydochloric acid (aqua regia) (7.5mL HCl 37% +

Table 1: Results of the analysis of RG-582 by XRF technique.

component	w/w %	component	w/w %	component	w/w %
Al_2O_3	90.80	SO_3	0.10	Pt	0.20
SiO_2	2.00	TiO_2	0.11	Re	0.20
Fe_2O_3	0.10	ZnO	0.11	L.O.I	5.47
K_2O	0.12	Cl	0.70	…	…

Table 2: results of the analysis of LD-265 by XRF technique.

component	w/w %	component	w/w %	component	w/w %
Al_2O_3	90.80	SO_3	0.10	Pt	0.20
SiO_2	2.00	TiO_2	0.11	Re	0.20
Fe_2O_3	0.10	ZnO	0.11	L.O.I	5.47
K_2O	0.12	Cl	0.70	…	…

Table 2: Results from quantitative analysis of RG-582 and LD-265 by atomic absorption.

Catalyst*	% Fe_2O_3	% ZnO	% CaO	% MgO	% Pt	% Re	% Pd
RG-582	0.11	0.01	…	…	0.30	0.22	…
LD-265	0.95	…	2.20	0.06	…	…	0.30

**The other compounds of RG-582 and LD-265 are listed in tables 1 and 2.*

Fig. 1: XRD diagram of RG-582.

Fig. 2: XRD diagram of LD-265.

2.5mL HNO_3 65%) was added to each sample. These samples were then placed in reflax balloons and heated for two hours at different temperatures of 25, 40, 55, 70, 85, 100, and 109°C.

After completion of the leaching, the solution was cooled to room temperature and a Wattman filter paper was used for smooth filtering. The insoluble materials were washed with distilled water and the filtrate was transferred to a 100 ml balloon for forthcoming analysis of Pt and Pd.

It is worth noting that the RG-582 needed no preparation before measuring the samples. In contrast, 0.01 M EDTA
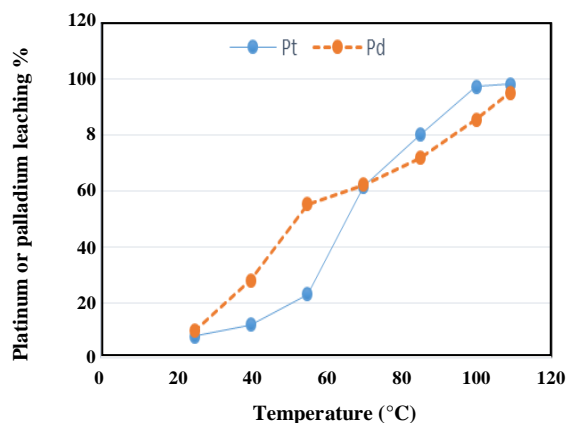
Fig. 3: Relation of the effect of temperature on the efficiency of the leaching process of Pt and Pd, t=120 min, partile size=100 mesh, L/S=10.

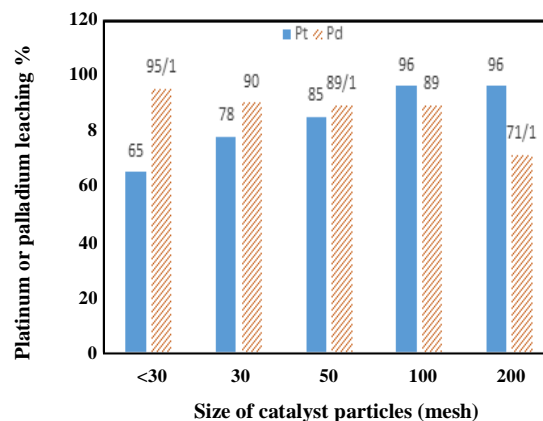
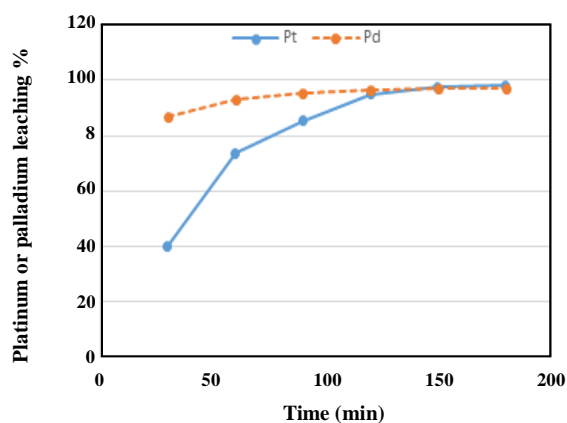*Fig. 5: Relation of the particle size on the efficiency of the leaching process of Pt and Pd, T=109°C, leaching time=180 min, L/S=10.*

Fig. 4: Relation of the effect of leaching time on the efficiency of the leaching process of Pt and Pd, T=109°C, partile size=100 mesh, L/S=10.

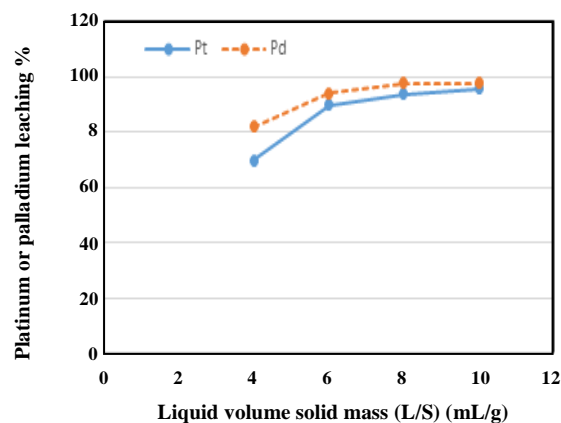*Fig. 6: Relation of the acid volume ratio on the efficiency of the leaching process of Pt and Pd, T=109°C, leaching time=180 min, particle size=100 mesh.*

should be added to the LD-265 for the elimination of interference. The results of the effect of temperature on the efficiency of the leaching process of Pt and Pd are shown in Fig. 3.

The effect of the leaching time process:

The same experiments as in the last section were carried out to determine the optimal time range of maximal leaching. The temperature for these experiments was kept constant at 109°C. The leaching time was in order 30, 60, 90, 120, 150, and 180 min. The results are shown in Fig. 4. As we can see from Fig. 4, the optimal time for a successful and maximal extraction was 180 min.

Effect of the catalyst particle size distribution:

Experiments similar to the previous sections were made

under the following conditions: Temperature=109°C, leaching time= 180 min, particle size= <30, 30, 50, 100, 200, and >20 mesh.

The results are summarized in Fig. 5. These results show that a particle size 100 mesh was optimal for successful leaching.

Effect of acid volume ratio:

In this section, the effect of acid volume ratio to the mass of catalyst (L/S) is studied. The experiment was carried out in the following conditions: T=109°C, t=180 min, PS= 100 mesh and an acid volume ratio (L/S) of 4, 6, 8, and 10 mg/L. The results are shown in Fig. 6. As we can see the reasonable ratio was L/S=8 with an efficiency of about 98%.
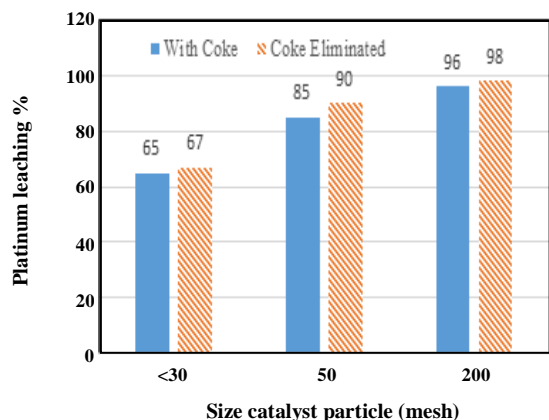
Fig. 7: Relation of calcination on the efficiency of the leaching process of RG-582, T=109°C, leaching time=180 min, L/S=10.

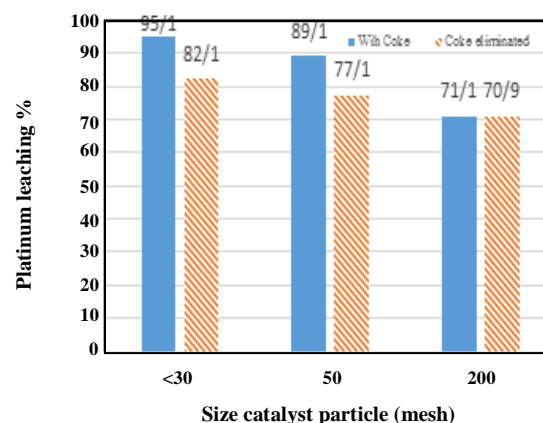*Fig. 8: Relation of calcination on the efficiency of the leaching process of LD-265, T=109°C, leaching time=180 min, L/S=10.*

Effect of initial calcination of catalysts

The spent catalysts normally have organic and inorganic materials as pollution on their surface organic materials, such as carbon, from the refining and petrochemical processes can cover the surface of the catalyst. To determine any pollutants the catalyst was heated at a temperature of 700°C for 4 hours.

In this stage, the experiments were conducted under the following conditions: T=109°C, t=180 min, PS=100 mesh, L/S=8. The obtained results are shown in Figs. 7 and 8. The results confirmed the increased leaching of about 2-5% of Pt and Pd.

Separation of Pt and Pd from the acid solution by activated carbon

Some researchers have investigated the adsorption of heavy metals such as Pt by activated carbon [24,25]. This part of the experiments is aimed at optimizing the factors influencing the adsorption of Pt and Pd catalysts in the leaching solutions of RG-582 and LD-265. Factors that can affect the adsorption process are: temperature of the solution in the adsorption process, time of adsorption, the amount of activated carbon used for a given volume and the concentration and pH of the leaching solution during the process.

Characteristic of used activated carbon:

The activated carbon used was purchased from Merck, Darmstadt, insoluble in water, and its density and particle size was 150-440 kg/m^3. The BET experiments were carried out to obtain detailed information. The results are shown in Table 4 and Fig. 9.

RESULTS AND DISCUSSION

As Fig. 3 shows the leaching of Pt from RG-582 was greatly affected by temperature. It can be seen that 8 and 12% Pt was leached from the catalyst, under the same conditions, at 25 and 40°C, respectively. While the leaching process at temperatures of 100 and 109°C yielded satisfactory results of 97 and 98%. The catalyst LD-265 obtained the best result i.e. 95% at the temperature of 109°C.

Determination of the adsorption capacity of the activated carbon for Pt and Pd:

Each type of activated carbon has a different capacity depending on their nature, synthesis, and activation. Determination of their adsorption capacity was made the following experiments. Leachate of RG-582 and LD-265 was prepared with 25, 50, 75, 100, 200 and 300 ppm. The pH of the samples was adjusted with HCl and NaOH at about 0. Then 25 ml of the above solution was mixed with 1 g activated carbon separately in a 100 ml flask and placed on a magnetic stirrer at 25°C for 1, 2, and 3 hours. After filtering the concentration of Pt and Pd were measured by atomic absorption and ICP. The percent adsorption efficiency for Pt and Pd was obtained as follows:

$\%E = (C_0-C_1)*100/C_0$

Where C_0 is the initial concentration of Pt or Pd, C_1 is the concentration of Pt or Pd after adsorption, and %E is the percent adsorption efficiency. The obtained results are shown in Figs. 10 and 11.

Table 4: Results of BET experiment on used activated carbon.

parameter	V_m (cm³/g)	BET	Mean pore diameter (nm)	Total pore volume (cm³/g)	Specific surface area (m²/g)
amount	191.41	1597.1	2.6494	0.5518	833.12

V_m: volume of adsorbed gas, single layer.

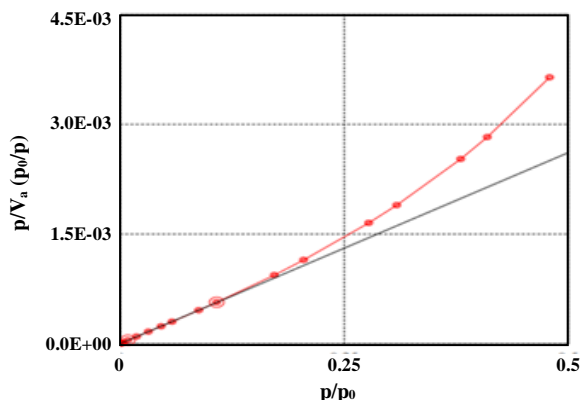***Fig. 9: BET diagram of activated carbon, condition: N_2 77 K, t=15 min, T=120°C.***

In the present study, aqua regia was used for leaching of both catalysts RG-582 and LD-265. The essential factors were investigated such as temperature, leaching time, particle size, acid ratio, and calcination. The end results of the best condition for optimal leaching are as follows: T=109°C, t=180 min, PZ= 100 mesh, L/S=8, and calcination temperature=700°C. Optimal conditions yield a rate of about 98% in the leaching process.

In this study, different methods for the recovery of Pt from the leachate of RG-582 and Pd from LD-265 were evaluated. Some methods can be used for the reduction of Pt(IV) and Pd(II) by using Al powder to convert them to elemental Pt and Pd (direct chemical precipitation of ammonium chloride to remove disturbing ions). Some of the methods described in the literature [36-39] have not shown satisfactory results for RG-582 and LD-265, because of their complicated texture.

Previous investigations have shown, that Al powder was able to reduce Pt(IV) (in a 300 ppm standard solution) and convert it to Pt. But the RG-582 catalyst leachate did not produce even at a higher concentration of Pt, unfortunately, no black Pt was considered. The reason for this is related to the acid solution of Pt metal. The catalyst LD-265 obtained identical experimental results. Thus the use of powdered metals such as Fe, Zn, Al, Mg, and ascorbic acid, etc. cannot help us recover Pt and Pd from leachate. This method could be effective in pure Pt and Pd solutions.

In some references, the precipitation was used in ways to obtain ammonium chloride complexes $(NH_4)_2PtCl_6$ and $(NH_4)_2PdCl_4$ [38-41]. Our results showed the failure of this method. The saturated solution of ammonium chloride in water or alcohol was not capable of precipitating Pt and Pd chloride complexes because the solubility of these salts is significantly high in water (at 10°C, 7 g/l). Two additional obstacles were identified. First, this method is not economical because of the high solubility of Pt and Pd. Secondly, due to the high solubility of the precipitation, the leachate requires a very concentrated solution of Pt and Pd, 30 g/l. This is not practical because of the small concentration of Pt and Pd in RG-582 and LD-265. The leachate should be significantly more concentrated and this is us not optimal from an economic point of view. This method allows the removal of Al ions or the main interfering ions by using alkaline to precipitate as $Al(OH)_3$ by keeping the pH constant.

Potentiometric titration of leachate was made, but what was seen in the act at the loss of 6.5 to 30 percent of the Pt when using a filtering Buchner or centrifuge. The main reason for the loss of Pt or Pd was the adsorption of the gelatinous precipitation $Al(OH)_3$ onto the surface. Thus, we were required to change the method. Due to the above ineffectual methods for the recovery of Pt and Pd from leachate the adsorbent, eco-friendly, inexpensive and accessible method of activated carbon was used. When using activated carbon you should consider certain required factors, such as pH, amount of activated carbon, contact time (adsorption time), and temperature. The obtained experimental results for optimal adsorption was found to be: 18.75 mg Pt/ 1g activated carbon, 85°C, 180 min, pH=0.5, and 12.5 mg Pd/ 1g activated carbon, 98°C, 150 min, pH=2. The end result was that the optimal condition yield for the adsorption of Pt and Pd was from a leachate rate of 96.5 and 96.3 %.

Precipitation of metallic Pt or Pd
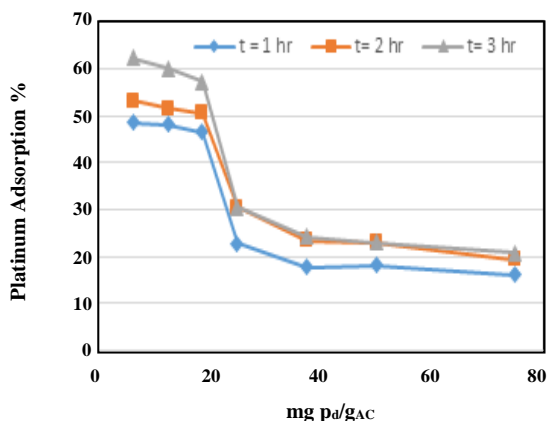In the final stage, a solid compound of Pt and Pd should be prepared. For this purpose activated carbon

Fig. 9: Determination of the adsorption capacity of the activated carbon for Pt from leachate, 1 g activated carbon, T=25°C, and pH=0.

Fig. 10: Determination of the adsorption capacity of the activated carbon for Pd from leachate, 1 g activated carbon, T=25°C, and pH=0.

containing Pt and Pd was calcinated. The condition for ashing temperature was 3-4 h, 1100°C, and air atmosphere. The XRD and ICP-OES techniques for elemental analysis were used in order to evaluate the composition obtained from the calcinations process. XRD results confirmed the existence of Platinum- and palladium oxides II , IV, and α-SiO₂. By using the ICP technique we were able to determine the amount of Pt and Pd as 96.8 and 86.7%, respectively. These compounds with the above purity are of commercial value.

CONCLUSIONS

The recovery of platinum and palladium from spent catalysts of petrochemical companies endeavored through the total dissolution of catalyst substrate in nitrohydochloric acid (aqua regia). The optimum dissolution conditions for the platinum catalysts RG-582 were: nitrohydochloric acid 6.0 mol/L, dissolution temperature 109°C, dissolution time 180 min, pulp density 220 g/L. The optimum dissolution conditions for the palladium catalyst LD-265 were: nitrohydochloric acid 8.0 mol/L, dissolution temperature 109°C, dissolution time 180 min, pulp density 220 g/L.

During the nitrohydochloric acid (aqua regia) dissolution of spent catalyst, platinum, and palladium was found to dissolve to some extent. The percent dissolution of Pt was 98% in the case of RG-582 and LD-265, respectively. Rapid recovery of platinum and palladium was possible by the cementation using aluminum powder at 60°C. For the complete recovery of platinum
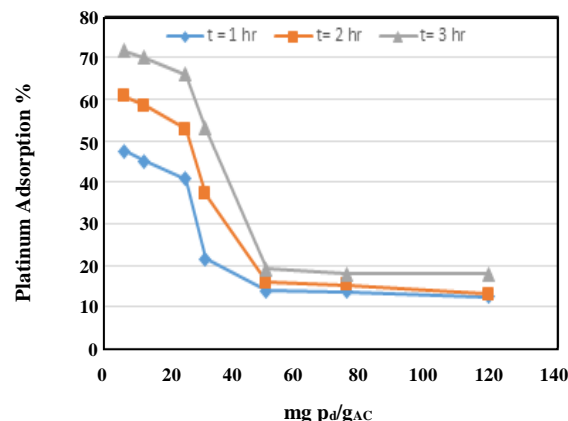
and palladium, 96% equivalents of aluminum were required for RG-582 and LD-265, respectively. In conclusion, the complete recovery of Pt from RG-582 and Pd from LD-265 catalysts was possible by the proposed method.

Acknowledgements

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