Recovery of Platinum and Rhenium from the Spent Aromatization Catalyst of Naphta Using the Ion Exchange Method and Determining the Operational Parameters

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Abstract

This paper presents the recovery of the nobel metals , platinum and rhenium from the spent aromatization catalyst of naphta using anion exchange resins. the catalyst is solved in a mixture of sulphuric acid and aqua regia , and the produced solution is passed through the columns which contain the ion exchange resins . The platinum and rhenium that exist in the solution are adsorbed on the resin , then the resin is washed by the means of a suitable acid and platinum and rhenium are desorbed from resin. The different parameters which affect the process of desorbtion and adsorption are also considered and the best condition for the maximum efficiency is determined. The efficiency has been 100% in the adsorption process and over 95 % in the desorbtion process.

Key words : Spent Catalyst , Ion exchange , Rhenium , Platinum , Anionic Resin.

Introduction

Catalysts are widely used in different processes related to petroleum and petrochemical industries.Usually the activity of these catalysts decreases after some operations. This is related to different factors like coke formation

on the active sites of the catalyst. In order to increase the activity , the catalyst should be regenerated. In order to regenerate the catalyst , it is usually heated in a high temperature and in the presence of a oxygen containing gas. The regeneration of the catalyst , generally increases its activity to the level of a new catalyst. But after some operation , reduction has no effect on the activity and the catalyst should be replace by a new one.

Patinum,rhenium, and other nobel metals (PMGs) are the most essential active parts of aromatization , reforming, and dehydrogenation catalysts. Every year , oil and petrochemical industries expel a great amount of spent catalysts containing platinum , rhenium and other nobel metals.These spent catalysts have many environmental dangers, because they contain contaminants such as coke, vanadium , nickel , ….On the other hand , the resources of these metals are limited and their production is costy [1] .Therefore , considering these factors and also the extended application of these metals in different industries like oil , and petrochemical industry , although the amount of these metals in the catalyst is as low as 1 % , the processes used for the recovery of nobel metals from spent catalysts would be worthy and considerable.

There are some methods for recovery of platinum , rhenium and other nobel metals from catalysts [1-10] .One effective method for recovery of Pt and Re from spent catalysts containing these metals or from solutions containing the ions of these metals , is using appropriate ion exchange resins [1 , 3 , 5 , 6 ,9] .The nobel metals are separated from the other impurities in solution in the coloumns containing ion exchange resins [3] .

In this paper , separation of platinum and rhenium from spent aromatization catalyst using ion exchange method and ion exchange resin is studied.

Experiments

1-Materials

The spent catalyst is R-62 which is produced in UOP company.Its structure is Pt-Re / Al_2O_3 and is used for the aromatization of naphta. Its properties are mentioned in table (1).

Table 1 – Properties of catalyst R-62

Catalyst suppor	Al_2O_3
	Pt , Re Active metals
Particle shape	Spherical
Particle diameter (mm)	1.6
Bulk (lb/ft^3)	44.3 density
	0.22 Pt (% wt)
(% wt)	0.44 Re
wt)	1-1.1 Cl (%

Sulphuric acid and aqua regia are used to solve the catalyst.In order to separate the nobel metals from catalysts , different resins such as Diaion resins(Mitsubishi Company) [6] , Dow resins (Dow Company) [3 , 5] , Amberjet ,Amberlite and Duolite resins (Rohm and Haas Company) [1,4] have been used.Based on the references , for both platinum and rhenium

recovery a strong anionic resin named Amberjet 4200 Cl (Rohm and Haas,France) is used.The structure of this resin is a copolymer of styrene divinylbenzene.Ionic form of this resin is Cl which in compare with the same resins , has high exchange capacity and is easily regenerated [11] . The properties of this resin is mentioned in table (2).

Table 2 – Properties of Amberjet 4200 Cl resin [12]

Properties	
Matrix	Styrene divinilbenzene copolymer
Functional groups	$-N^{+}(CH_3)_3$
Physical form	Insoluble, white translucent beads
Ionic form as shipped	Cl^-
Total exchange capacity*	≥ 1,30 val/L (Cl^- form)
Moisture holding capacity*	49 to 54 % (Cl^- form)
Specific gravity	1,06 to 1,08 (Cl^- form)
Bulk density	670 g/L
Uniformity coefficient	≤ 1,5
Mean diameter	600 - 800 μm
Maximum reversible swelling	$Cl^- \rightarrow OH^-$: 30 %
* Test methods avialable upon request	
Suggested operating conditions	
Minimum bed depth	800 mm
Service flow rate	5 to 50 BV*/h
Maximum service velocity	60 m/h max.
Regenerants	NaOH
Concentration (%)	2 to 5
Flow rate (BV/h)	2 to 8
Level	40 to 100 g/L
Minimum contact time	30 minutes
Slow rinse	2 BV at regeneration flow rate
Fast rinse	3 to 6 BV at service flow rate
*1 BV (Bed Volume) = 1 m^3 solution per m^3 resin	

The preliminary experiments for determining the best operational condition have been done by using $PtCl_4$ (Platinum (IV)-Chloride 57.5%) (Merck) and Re_2O_7 (Rhenium (VII)-Oxide 77%)(Merck).

To desorb the ions from resin , different acids are used like nitric acid (Merck) 95% , perchloric acid (Merck) 70% , hydrochloric acid (Merck) 37%.

2- Equipments

Seperation of the ions from the solution was carried out in a glass fixed-bed coloumn with a length of 40 cm and diameter of 7 mm. A control value is placed at the column exit to control the flow of the solution leaving the column . All the coloumn length is made double-layered ,because the solution inside the coloumn should be heated.

The solution , intering the coloumn are entered through a dosig pump.Calcination of the catalyst is done in a furnace with maximum temperature of 1200°c .

3-Experiments

To solve the catalyst,the required amount of the calcined spent catalyst was solved in the appropriate amount of sulphuric acid 50%wt and then in aqua regia.After around 5 hours ,the catalyst was completely solved and a yellowish solution was formed.Then the solution was diluted and filtered several times so that all the sediments in the solution was separated and the solution has become transparent.

The amount of platinum and rhenium in the solution were determined by using the ICP analysis .

The existing platinum and rhenium in the catalyst solution are separated from other parts of the spent catalyst in a coloumn containing ion exchange resins.The ion exchange resin is Amberjet 4200 Cl which is a strong anionic resin. The glass coloumn was filled by the resin up to 10 cm and then some glasswool is entered the coloumn to avoid the dislocation of resins , when the solution is entered. Before putting the resins in coloumn , they were washed by distilled water and HCl 0.1 normal to ensure replacement of all anions of resin with Cl.After preparation of the coloumn , the solution

containing platinum and rhenium is entered the coloumn to adsorb the platinum and rhenium on resins.

After the complete evacuation of the coloumn from solution , three times as much as the volume of the entered solution , distilled water is added to the coloumn and then it is washed with HCl 0.1 normal to remove the interfering ions and those ions entrapped mechanically by the resin [3] .

Resin is not able to adsorb the ions after it is saturated.At this state the ions which have not been adsorbed gradually increase in the effluent [3] .

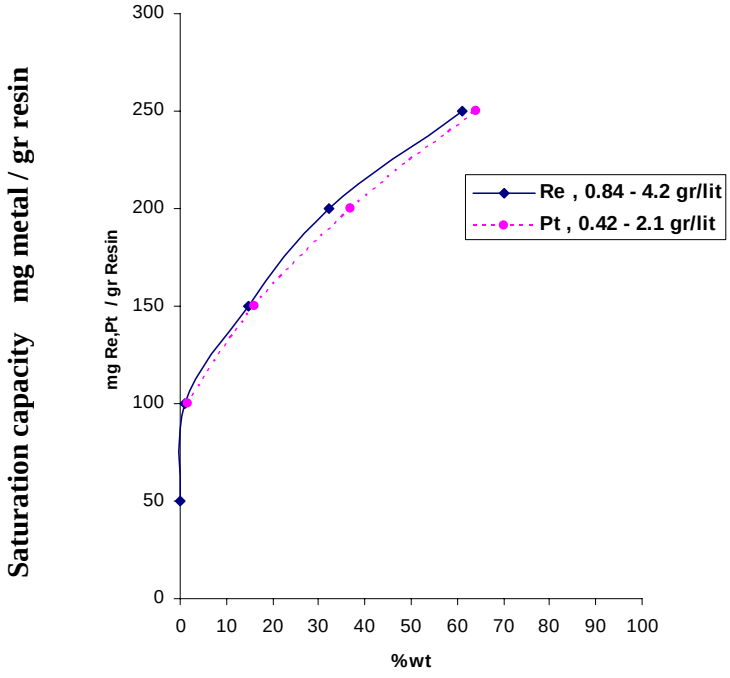
To determine the appropriate solution for washing the resin and desorb the ions from resin , according to references , three acid solutions , nitric acid , hydrochloric acid and perchloric acid were used [4 , 6 , 9] . These acids were used with different normality 3 , 5, 7 and 8 normal [4 , 6 , 9] .After determining the appropriate acid with optimum concentration , the effect of residence time and temperature were also examined. Then according to these results , the obtained conditions were used to desorb the ions from coloumn containing resin.

To determine the saturation capacity of resins , five areas are determined based on the described capacity in the table of the resin properties.Then some experiments are done to obtain the saturation capacity of resins.The areas of 50 , 100 , 150 , 200 and 250 $\frac{\text{mgr metal}}{\text{gr resin}}$ are considered and some experiments were done.Two standard solutions Re_2O_7 (77% Re) and $PtCl_4$ (57.5% Pt) are used in these experiments.Saturation ranges are tested for Re_2O_7 , $PtCl_4$ and the mixture of these two.

Results and discussion

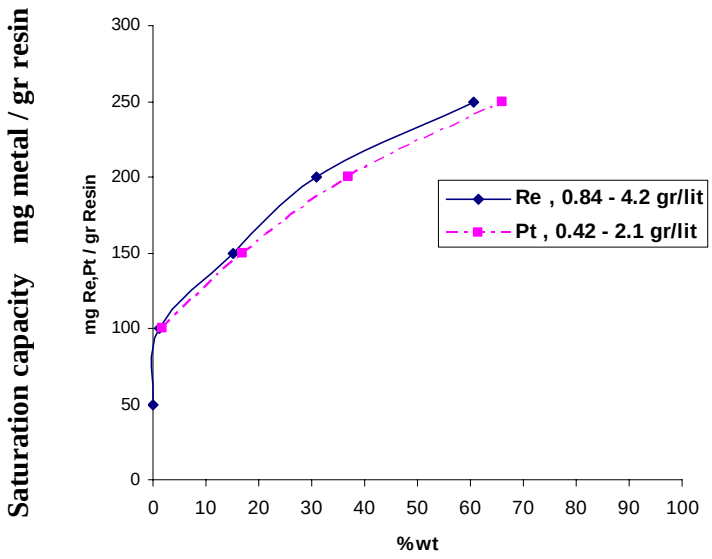
1 – Adsorbtion

The results of the experiments for determining the saturation capacity , with solutions containing chloroplatinate ions , perhenate ions and solutions containing both ions and also the solution of solved spent catalyst are shown in figures (1) and (2).



Amount of Pt and Re in the solution leaving the resin (wt%)

Figure 1 – Saturation capacity of Amberjet 4200 Cl for Pt and Re at 25 °c



Amount of Pt and Re in the solution leaving the resin (wt%)

Figure 2 – Saturation capacity of Amberjet 4200 Cl for the mixture of Pt and Re at 25 °c (Re / Pt = 2/ 1)

According to these results , when the volume of the solution intering the coloumn increases , the amount of Pt and Re leaving the coloumn increase simultaneously.In the other hand the amount of Pt and Re which are adsorbed on resin are increased and the resin is saturated.

According to the results of figures (1) and (2) , the saturation capacity of the resin is 100 $\frac{\text{mgr metal}}{\text{gr resin}}$ .In order to consider the effect of time that solution is contacted with resin , the adsorbtion operation is tested at different periods.

At the adsorption stage , some solutions with completely similar conditions and with saturation capacity of 100 $\frac{\text{mgr metal}}{\text{gr resin}}$, are in contact with similar resins , for 5 , 10 , 12 , 14 , 15 , 17 and 20 hours.The results are shown in figure (3).

According to figure (3) when residence time increases , adsorbtion recovery of both Pt and Re increase too.When the maximum recovery is obtained (this

is when the saturation capacity of resin is reached) , increasing the residence time has no effect on recovery.

The saturation capacity of the resin is also tested for the dissolved spent catalyst for five resin saturation capacities 50 , 100 , 150 , 200 and 250 .The results are shown in figure (4) .

Same as the resin saturation capacities which have been obtained in the last experiments , the saturation capacity for the spent catalyst is 100 $\frac{\text{mgr metal}}{\text{gr resin}}$

Also the comparison of figures (2) and (4) shows that interfering ions in the solution of dissolved spent catalyst have no effect on adsorbtion of Pt and Re .It means that the resin is very selective with relation to Pt and Re in the solution.

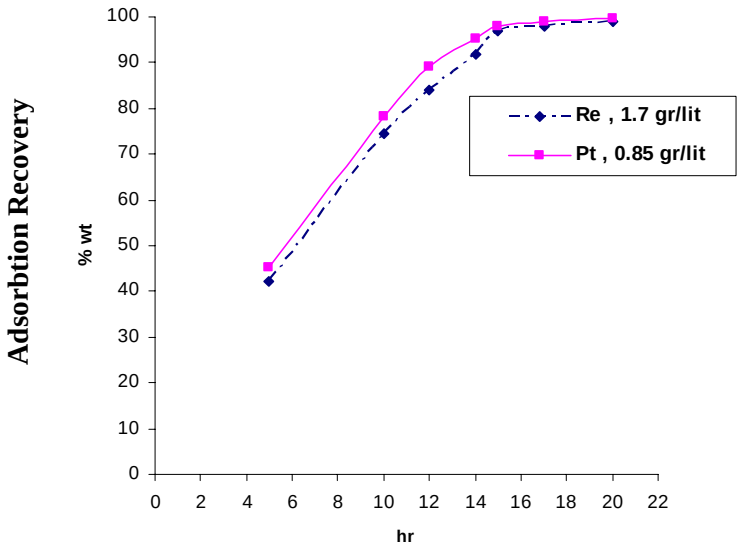
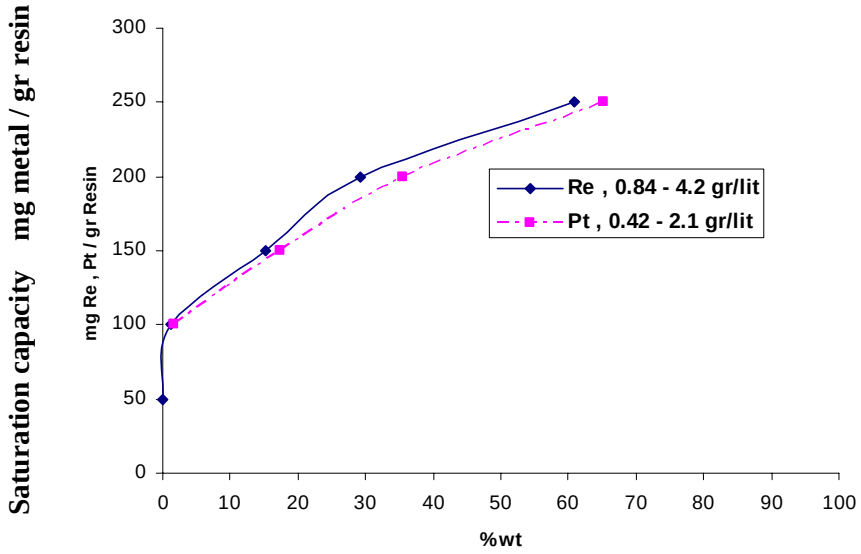


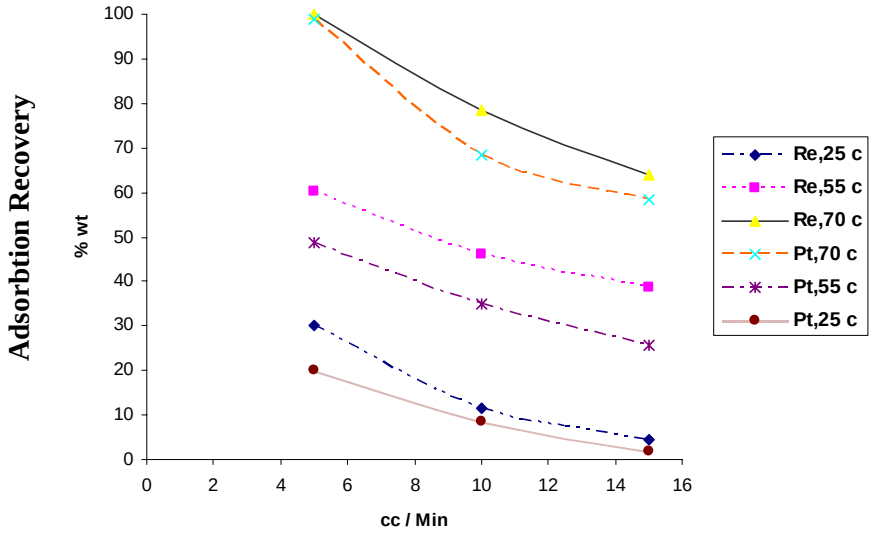
Figure 3 – Effect of residence time of the solution containing Pt and Re on adsorbtion recovery at 25 °c



Amount of Pt and Re in the solution leaving the resin (wt%)

Figure 4 – Saturation capacity of Amberjet 4200 Cl for the solution of dissolved spent catalyst at 25 °c

To study the parameters that affect the adsorbtion process – flow rate of the interring solution and temperature (residence time) – some experiments in saturation capacity 100 $\frac{\text{mgr metal}}{\text{gr resin}}$ at different temperatures (25 , 55 and 70 **°c**) and different flow rates (5 , 10 and 15 $\frac{cc}{\text{min}}$) were done and their effects on the process were tested.The results are shown in figure (5).



Flow rate of interring solution to the coloumn

Figure 5 – Effect of different flow rate of interring solution on Pt and Re adsorbtion recovery at different temperatures 25,55 and 70 °c

According to figure (5) , adsorbtion of Pt and Re on resin at 70 °c and flow rate 5 $\frac{cc}{\min}$ has the maximum adsorbtion recovery. Also this figure shows that when the flowrat of interring solution to the coloumn increases , the adsorbtion ability for Pt and Re of the resin decreases , because of deduction of residence time of the solution on resin.

Now , at the presence of the best condition , the solution of dissolved spent catalyst is passed through the coloumn.

In this state as well , the adsorbtion recovery of both metals is maximum.The adsorbtion recovery is 100% for Pt and 99.91% for Re.

2 - Desorbtion

To determine the appropriate material for rinsing the resin to desorb the platinum and rhenium ions , some experiments were done which are shown

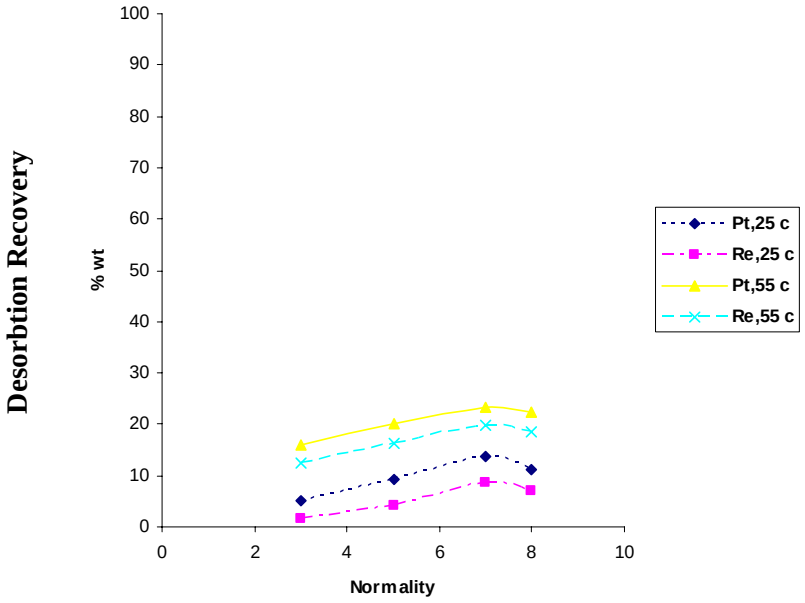
in table (3) and the results for HCl , HNO_3 and $HClO_4$ are reported in figures (6) and (7) , (8) and (9) , (10) and (11) respectively.

Table 3 – Experiments for the desorbtion stage

acid	normality	Temperature(°c)
HCl	3-8	25 , 55
HNO_3	3-8	25 , 55
$HClO_4$	3-8	25 , 55 , 75

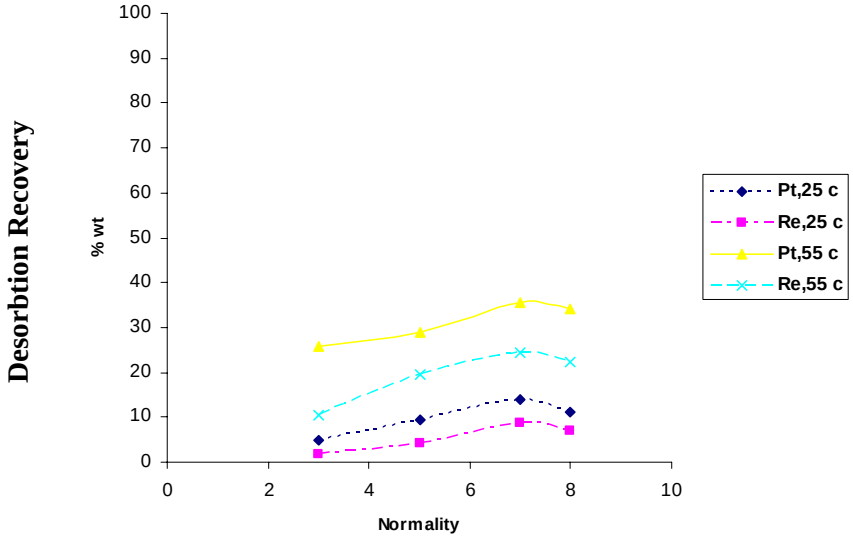
According to figure (7) , for the mixture of Pt and Re , the maximum desorbtion recovery for HCl is 33% for Pt and 18% for Re at 25°c and 36% for Pt and 20% for Re at 55 °c .SO this acid has a very low desorbtion ability for Pt and Re , even at high temperatures.

According to figures (6) to (11) , 7 normal perchloric acid with 85% desorbtion recovery for Pt and 89% for Re at 25°c in comparison with the other acids , has the maximum desorbtion recovery for both Pt and Re. when the best concentration and also the suitable kind of acid is found , time and temperature were also tested.In order to consider the effect of time and temperature at this stage , desorbtion operation is examined by $HClO_4$ of 7 normal at different times and temperatures.The results are shown in figure (12).



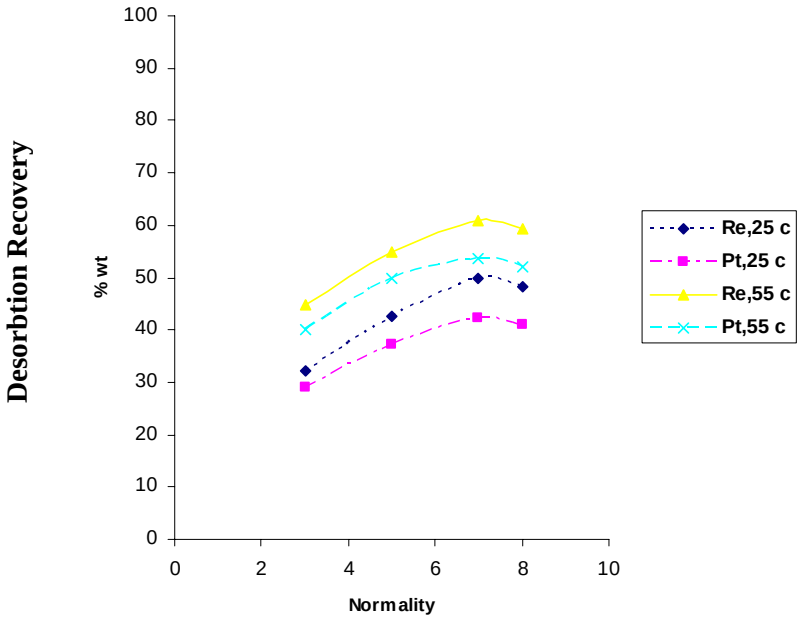
HCl Normality

Figure 6 – Effect of different normality of HCl on desorbtion recovery of Pt and Re at 25 and 55°c



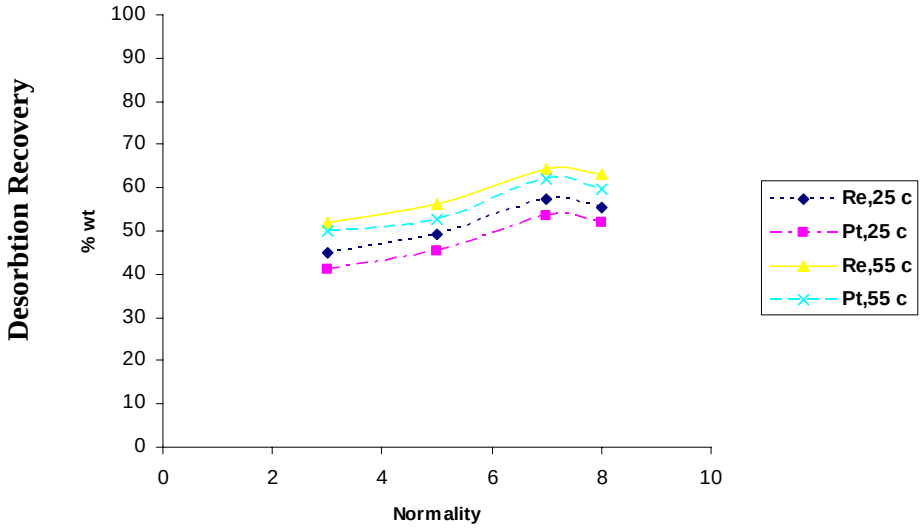
HCl Normality

Figure 7 – Effect of different normality of HCl on desorbtion recovery of mixture of Pt and Re (Re / Pt = 2/ 1) at 25 and 55°c



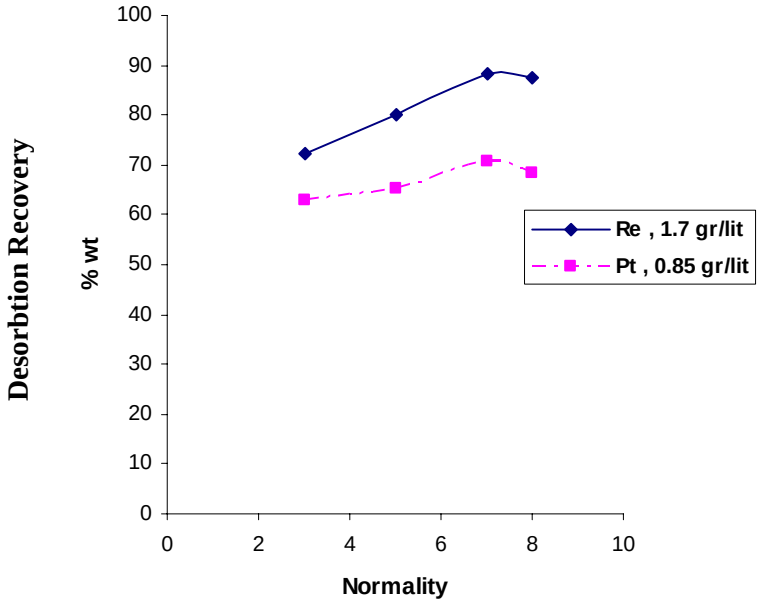
HNO_3 Normality

Figure 8 – Effect of different normality of HNO_3 on desorbtion recovery of Pt and Re at 25 and 55°c



HNO_3 Normality

Figure 9 – Effect of different normality of HNO_3 on desorbtion recovery of mixture of Pt and Re (Re / Pt = 2/ 1) at 25 and 55°c



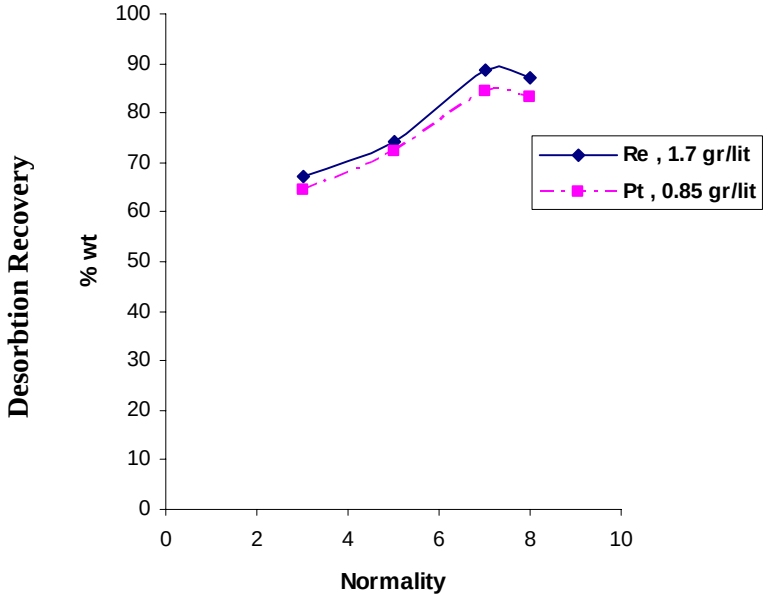
$HClO_4$ Normality

Figure 10 – Effect of different normality of $HClO_4$ on desorbtion recovery of Pt and Re at 25°c

According to figure (12) , when residence time decreases , desorbtion recovery of Pt and Re decreases simultaneously until the maximum desorbtion recovery is obtained.After this point , increasing the residence time has no effect on recovery.

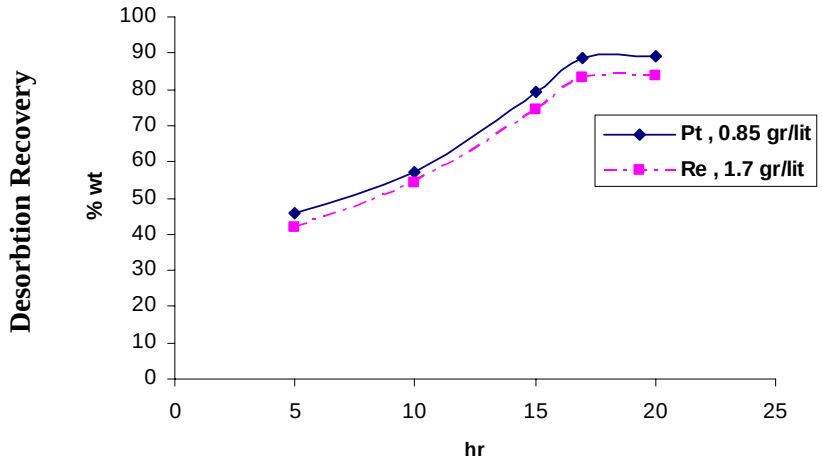
To study the effect of temperature on desorbtion , some experiments were done and their results are shown in figure (13).

According to figure (13) , 7 normal perchloric acid at 75 °c with 96.5% desorbtion recovery for Pt and 95% for Re has the maximum desorbtion recovery in comparison with two other acids.



$HClO_4$ Normality

Figure 11 – Effect of different normality of $HClO_4$ on desorbtion recovery of mixture of Pt and Re (Re / Pt = 2/ 1) at 25°c



Time

Figure 12 – effect of residence time for $HClO_4$ 7 normal on resin , on Pt and Re desorbtion recovery(Re / Pt = 2/ 1) at 25°c

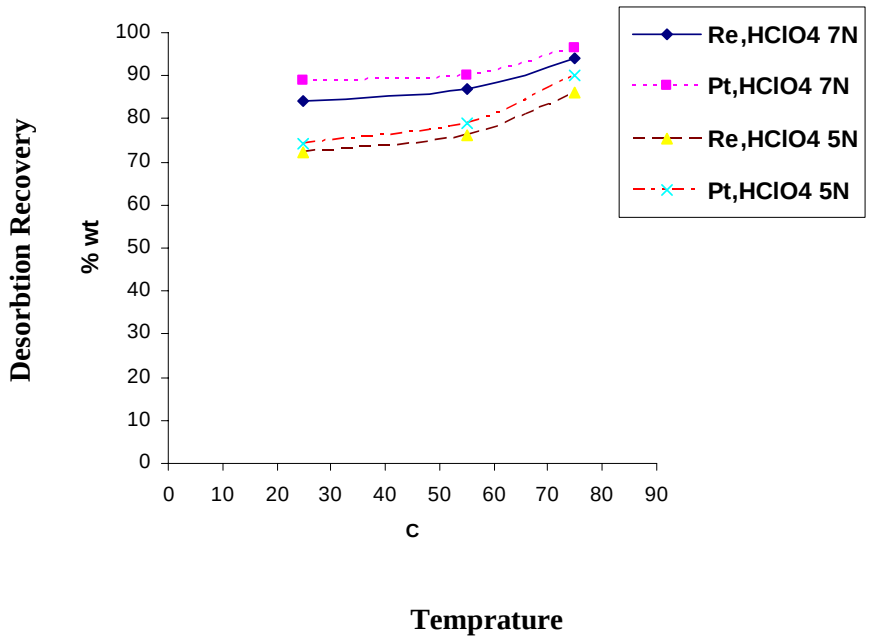


Figure 13 – effect of temperature on desorbtion recovery of resin with $HClO_4$

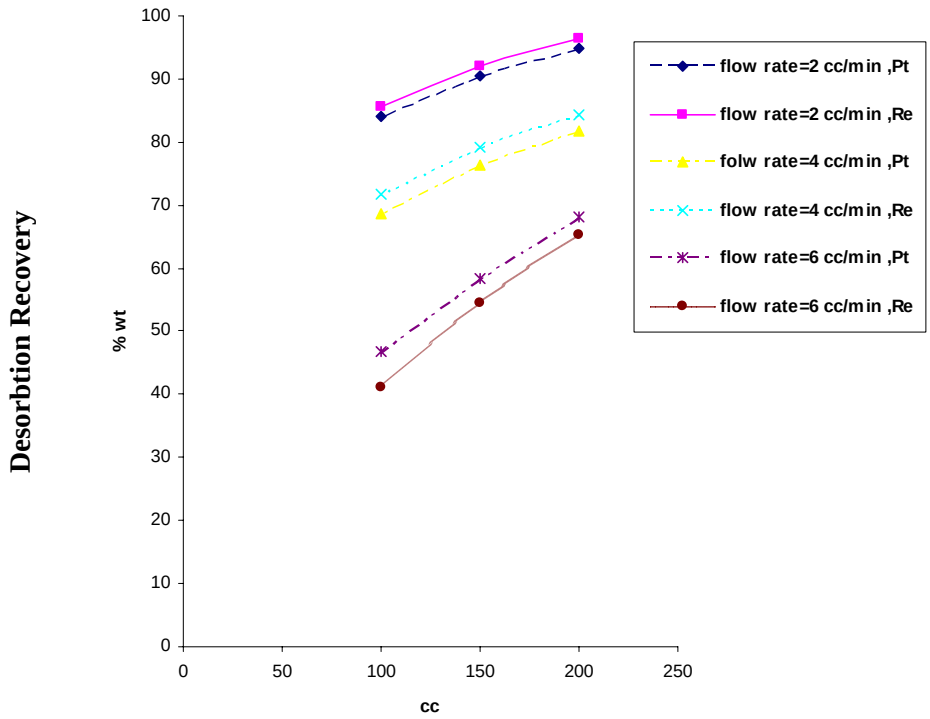


Figure 14 – effective parameters on desorbtion recovery of coloumn containing resin using $HClO_4$ 7normal at 75 °c and saturation capacity

Now the results of these experiments should be examined for recovery of Pt and Re from the coloumn containing resin which has adsorbed the Pt and Re from interring solution.the results of these experiments are shown ih figure (14).

According to figure (14) , when the flow rate of interring acid solution to the coloumn (increasing the residence time) and also the volume of acid increases , the desorbtion recovery of Pt and Re increase too.In this state at 75 °c , 200 cc acid volume and 2 cc/min flow rate , the maximum desorbtion recovery is obtained.

Conclusion

Reccovery of nobel metals platinum and rhenium from spent aromatization catalyst using ion exchange resin was studied and following results were obtained :

- Ion exchange method using strong anion exchange resin Amberjet 4200 Cl can completely adsorb the platinum and rhenium from solution (100% for Pt and 99.91% for Re).
- Temprature and flowrate (residence time) of interring solution to the coloumn are the main parameters which affect the adsorbtion and desorbtion process.
- Whatever the temperature is higher and the flowrate of interring solution to the coloumn is lower , adsorbtion and desorbtion of ions from resin is better.
- interfering ions in the solution of solved spent catalyst , have no effect on adsorbing Pt and Re on resin.In the other hand this resin is very selective in relation with Pt and Re.
- Perchloric acid 7 normal is the most appropriate material for separation of Pt and Re from resin Amberjet 4200 Cl .Desorbtion recovery with this acid for both Pt and Re at ambient temperature is higher than 85% and at 75°c higher than 95% for both metals.
- In the desorbtion stage of the coloumn , the maximum separation recovery of Pt and Re is obtained at 75°c , 200 cc acid volume and 2 cc/min acid flow rate.
- In the adsorbtion stage of the coloumn , the maximum adsorbtion recovery is obtained at 70°c and 5 $\frac{cc}{\min}$ interring solution flow rate.

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