

# Recovery of palladium from palladium phthalocyanine complex adsorbed on silica

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## Abstract

This study presents the feasibility of recovering palladium from the spent silica waste wherein palladium is adsorbed on silica as palladium phthalocyanine complexes. The spent silica having palladium phthalocyanine complexes adsorbed on it is thermally calcined in air to partially burn the organic moiety of the complex followed by palladium dissolution as  $\text{H}_2\text{PdCl}_4$  in hydrochloric acid. The palladium is recovered as  $\text{PdCl}_2$  by judiciously adjusting the pH of filtrate obtained. Recovered silica retains its structure and can be re-used.

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## 1. Introduction

Platinum group metals (e.g., platinum, palladium and rhodium) are in extensive use for catalytic reactions, electronic devices, and space materials (Hoke, 1940; Loewen, 1995; Takanori and Tetsuo, 2005). For example, the platinum group metals are increasingly employed for the manufacture of auto exhaust catalysts (Clàudia et al., 2003) and the coordination metal complexes of Pd, Pt, Ru and Rh are extensively used as commercial catalysts in homogeneous conditions for hydroformylation and hydrogenation reactions (Srivastava et al., 2005). However, owing to difficulties in

separation of metal complexes from product mixtures, increasing research efforts are being directed to develop heterogeneous catalysts where coordination metal complexes are supported on polymeric or inorganic solid supports like silica, carbon, zeolite, and alumina. Commercially, it is important to recover the precious metals or metal complexes from their support to the maximum extent possible once the catalyst is deactivated. Consequently, growing efforts are put to develop processes for complete recovery of such metals from spent catalysts/materials (Boricha et al., 2006; Edward, 1996; Benguerel et al., 1996; Van Der Puy et al., 1987; Demopoulos et al., 1987; Dimmit et al., 1986; Melka et al., 1984; Edwards et al., 1978; Shanton and Grant, 1982). The hydrometallurgical processes employed for the separation and recovery of the platinum group metals, typically, involve dissolving the metal ions by oxidative acidic chloride leach, normally with aqua regia or hydrochloric acid/chlorine gas followed by

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reduction of palladium (Schreier and Edtmaier, 2003). Solvent extraction has been in practice for the preparation of highly pure precious metals (Narita, 1997; Barnes and Edwards, 1982; Cleare and Charlesworth, 1979; Reavell and Charlesworth, 1980). However, during the recovery of precious metals from ore or scrap including spent catalysts, the use of metal selective solvent extraction to separate the precious metals from one another and from base metals that may also be present is becoming more widespread. Palladium complexes find diverse commercial applications (Hartley, 1991; Khaled et al., 2005; Yu Cai Cao and Xuan Zhen Jiang, 2002; Wolleb, 1997). During the past decades phthalocyanines (Pc) and their derivatives have been extensively studied and found numerous applications in widely different areas due to their distinct properties (Leznoff and Lever, 1996). A mixture of palladium chloride and phthalonitrile (1:8 mole ratio) was heated at 300 °C for 2 h for the synthesis of palladium phthalocyanine complex. The reaction mixture was cooled and the product obtained was purified by silica gel column chromatography using chloroform as eluting solvent. Palladium complexes of phthalocyanine, Bromo phthalocyanine and Irgaphor green (Scheme 1), which find applications as pigment material for compact disc coating are purified using silica gel (Hartley, 1991). However, significant quantity of these complexes (up to 0.5 wt.% Pd) is adsorbed in the pores of silica gel and is difficult to recover from the pores of silica after use by conventional extraction with solvents like dichloromethane and chloroform. Furthermore, the quantity of solvent required for solvent extraction is very high and is not cost effective. Being low boiling solvents, these also are lost as volatile organic compounds to the environment. The other commonly used technique for recovery of Pd from palladium complexes involves the treatment of the complexes with aqua regia followed by reduction of palladium chloride with an organic reductant like borohydride, formaldehyde or ascorbic acid. It is difficult

to precipitate out palladium as palladium chloride after treating with aqua regia.

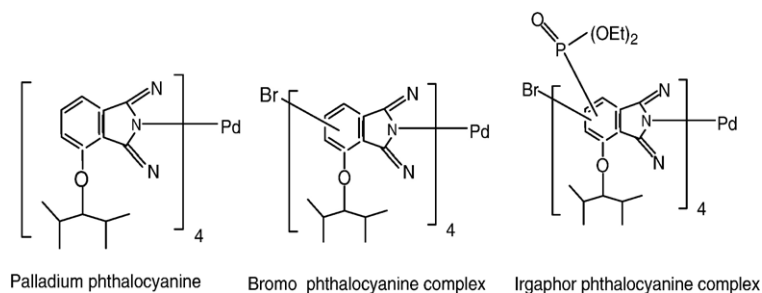
Therefore, it is imperative to search for a more efficient method for the recovery of palladium from its complexes. In this paper, we are describing a three step method without involving any solvent extraction or reduction for the recovery of palladium from palladium phthalocyanine/SiO<sub>2</sub> complex wherein 98–100% palladium can be recovered as PdCl<sub>2</sub> with 99% purity.

## 2. Experimental

### 2.1. Materials

Commercial hydrochloric acid and sodium hydroxide were obtained from S D fine chemicals, Mumbai, India; potassium iodide and ascorbic acid were obtained from E Merck Mumbai, India. De-ionized water was used for the purpose of analysis. A sample of spent silica (having Pd content 0.1 to 0.5 wt.%) was obtained from M/S Strides Arcolab Ltd., Bangalore, India. Pd content in the waste silica gel varies from batch to batch because in the process wherein silica gel is used in column chromatography for the purification of phthalocyanine, the amount of Pd adsorbed on silica will vary depending upon the impurities. Chemical analysis of the spent silica was done after leaching it with HCl and the filtrate was analyzed for Pd content using OES-ICP spectrophotometer (Perkin Elmer Model 2000, USA) and UV–Vis spectrophotometrically as [PdL<sub>4</sub>]<sup>2-</sup> using Shimadzu 3101PC spectrophotometer, Japan.

Thermogravimetric analysis of spent silica was done by Mettler-Toledo, TGA/SDTA 851e thermal analyzer at 10 °C/min. heating rate in the air flow of 40 ml/min. Powder X-ray diffraction (XRD) analysis was carried out with a Phillips powder diffractometer X'Pert MPD using PW3123/00 curved Cu-filtered Cu-Kα (λ = 1.54056 Å) radiation with slow scan of 0.3°/s. Fourier Transform Infrared spectra (FTIR) of samples were measured with



Scheme 1. Structure of various phthalocyanine compounds adsorbed on silica.

Perkin-Elmer-Spectrum GX-Spectrophotometer using KBr pellet. A Shimadzu 3101PC spectrophotometer was employed for recording of DRS UV–Visible spectra. The nitrogen sorption studies were carried out at 77 K on Micromeritics Model 2010ASAP instruments. The sample were dehydrated under vacuum at 373 K for 1 h and then degassed (523 K) for 7 h. The BET surface area, pore volume and the pore size distribution (BJH method) were determined from these data.

## 2.2. Determination of palladium and the recovery percentage

Palladium (II) concentration in the filtrate was determined using the spectrophotometric iodide method which is based on formation of a red-brown  $[\text{PdI}_4]^{2-}$  complex in the presence of an excess of potassium iodide (Marczenko and Balcerzak, 1998). A reducing agent (usually ascorbic acid) is added to the solution in order to avoid oxidation of iodide. The solution under investigation containing not more than 0.2 mg Pd (II) was put into a 50 ml volumetric flask; 5 ml of 6 M HCl, 10 ml of 20% KI solution and 2 ml to 6 ml of the ascorbic acid solution (1%, freshly prepared) were added depending on the model system. The solution was diluted with water to 50 ml. After stirring, absorbance was measured at 410 nm in a 1-cm cell against water as reference.

Amount of palladium in the solution was calculated as

$$\text{Amount of Pd per 100 ml} = \left\{ \frac{A}{\epsilon} \times \text{At. Wt of Pd} \right\}$$

$A$  Absorption of 100 ml solution at 410 nm  
 $\epsilon$  Extinction coefficient,  $\epsilon = 1.02 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$  for  $[\text{PdI}_4]^{2-}$  species at 410 nm

## 2.3. Procedure for the recovery of palladium as $\text{PdCl}_2$

Scheme 2 shows the procedures elaborated in the present work for the recovery of palladium from spent silica as  $\text{PdCl}_2$ . 500 g of spent silica was taken in a china dish and kept at 400 °C for 3 h and then allowed to cool. In a five litre round bottom flask equipped with heating mantle, refluxing condenser to prevent the leaching solution losses due to evaporation and thermocouple to keep the content of the round bottom flask at constant temperature, one litre 2 M HCl solution was taken, to this was added silica calcined at 400 °C. The whole content was treated at 90 °C for 5 h under stirring which was followed by filtering and washed with 500 ml of 0.5 M HCl solution. Silica was dried at 100 °C in the oven. The pH of the filtrate containing palladium was

adjusted to 6 by adding 0.1 to 0.5 M NaOH and the pH of the solution was recorded using pH meter.

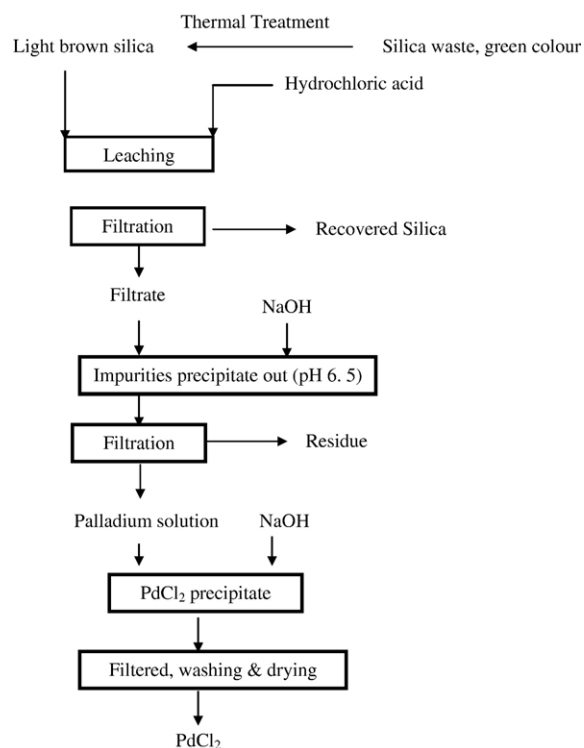
The resulting solution was filtered again to remove the impurities especially of iron due to the use of commercial HCl. Then the pH of the filtrate obtained at pH 6 was raised to 9.3 to precipitate Pd as  $\text{PdCl}_2$  followed by filtration to collect the palladium salt which was then dried.

The percentage recovery of palladium was 98–100%. The percentage recovery of palladium is calculated based on the leaching of the palladium from the standard sample of Pd-silica prepared by impregnation of known wt.% of Pd-phthalocyanine on silica gel. The product obtained is 99% pure as analyzed by OES-ICP spectrophotometer analysis and UV–Vis spectrophotometric iodide method based on formation of a red-brown  $[\text{PdI}_4]^{2-}$  complex in the presence of an excess of potassium iodide (Marczenko and Balcerzak, 1998).

## 3. Results and discussion

### 3.1. Recovery of palladium as $\text{PdCl}_2$

Recovery of palladium as palladium chloride is based on the fact that organic moiety can be burnt out by heat treatment and then palladium can be recovered as its salt



Scheme 2.

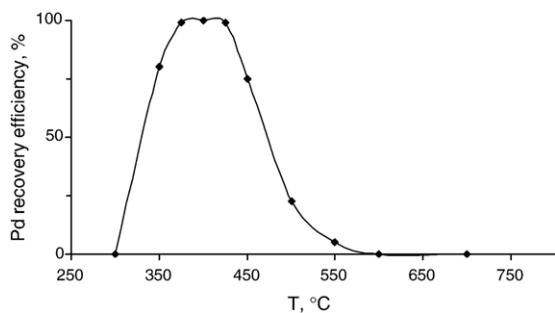
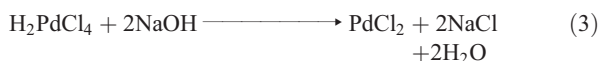


Fig. 1. Effect of calcination temperature on the percentage recovery of palladium from spent silica.

by its digestion with mineral acid and further purification by simple precipitation techniques (Eqs. (1) (2) (3)).



In order to optimise the maximum palladium recovery, the effect of calcination temperature, mineral acid concentration, and time of acid digestion along with solid to liquid ratio for acid digestion are studied in detail.

### 3.2. Effect of calcination temperature

Spent silica is calcined in air at constant temperature for sufficient time to burn out the organic moiety. In order to optimise the calcination temperature, the spent silica samples were calcined at different temperature, i.e., from 250 to 800 °C and analyzed using TGA, powder XRD, DRS, surface area analysis and FTIR spectroscopy. Effect of calcination temperature on the percentage recovery of palladium is given in Fig. 1. It is seen from the data that more than 99% palladium recovery is observed in the temperature range of 375 to 425 °C. There is a sharp decrease in Pd recovery when the calcination temperature is higher than 425 °C. This clearly reflects that for maximum palladium recovery, palladium phthalocyanine/silica complex is required to be calcined in this temperature range only.

The TGA of spent silica sample calcined at different temperature along with un-calcined sample and the Pd phthalocyanine complex alone is given in Fig. 2. It is observed from TGA of palladium phthalocyanine complex that the highest weight loss (40%) is observed in the temperature range 325 to 400 °C beyond which

there is a further increase in weight loss (6%). The data show that phthalocyanine complex decomposes at around 325 °C and most (46%) of the volatile organic compounds produced due to decomposition are lost up to 640 °C. This is also supported from the weight loss data (TGA) observed for samples which have been calcined at different temperatures. For example, maximum weight loss is observed for the un-calcined green silica which is due to the decomposition of Pd-phthalocyanine complex. However, the sample calcined at 450 °C shows an insignificant weight loss (TGA) and the weight loss is almost negligible for the sample calcined above 650 °C.

### 3.3. Powder XRD analysis

The powder XRD of spent silica sample calcined at different temperatures along with un-calcined sample and the Pd phthalocyanine complex alone is given in Fig. 3. The XRD of the sample calcined at different temperature shows the features pertaining to amorphous silica. It was expected that samples calcined at temperature  $\geq 650$  °C could show XRD reflections at  $2\theta=40$  for palladium oxide as once the complex is completely oxidized further calcination is expected to oxidize palladium present in silica to palladium oxide. However, XRD reflections due to palladium oxide were not observed, probably due to its very low concentration in the silica. The intensity of the PdO peaks in the PXRD depends upon the concentration, crystallite size and the dispersion of the PdO particles in the silica matrix. If the concentration and the crystallite size of the PdO particle are high, it is possible to observe PdO peak in the XRD (Simplício et al., 2005). However we could not observe PXRD peak due to PdO in our sample.

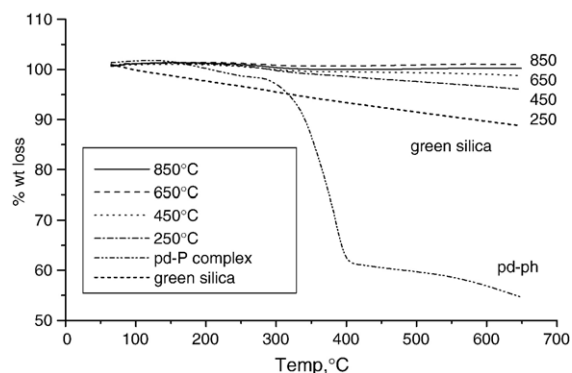


Fig. 2. TGA of spent silica sample calcined at different temperatures along with un-calcined sample.

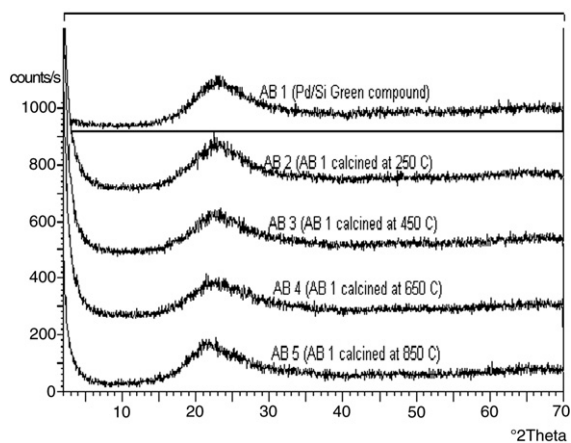


Fig. 3. Powder XRD of spent silica sample calcined at different temperatures along with un-calcined sample.

### 3.4. Surface area analysis

The surface areas values of the spent silica samples calcined at different temperatures (250–850 °C) are given in Table 1. From these data, it is clear that BET surface area of the samples calcined below 650 °C remains almost constant ( $\approx 360 \text{ m}^2 \text{ g}^{-1}$ ). The surface area of the sample calcined at 850 °C decreases to  $272 \text{ m}^2 \text{ g}^{-1}$ . This decrease could be due to the sintering of silica particles at higher temperature. The pore volume values of these samples also show trend similar to surface area values.

### 3.5. FTIR analysis

The FTIR spectra of spent silica sample calcined at different temperatures along with un-calcined sample and the Pd phthalocyanine complex alone are given in Fig. 4. The FTIR spectra of the un-treated spent silica sample gave peaks at 465 and  $801 \text{ cm}^{-1}$  due to Si–O–Si bending vibration. The peak at  $1100 \text{ cm}^{-1}$  is due to Si–O stretching vibration while the peak at  $970 \text{ cm}^{-1}$  is ascribed to Si–OH stretching vibration. The peak in the range  $3400\text{--}3500 \text{ cm}^{-1}$  is due to hydroxyl group on the silica surface. The peaks at 1633 and  $1536 \text{ cm}^{-1}$

(isoindole stretch,  $1407 \text{ cm}^{-1}$  (pyrrole stretch), 970 and  $964 \text{ cm}^{-1}$  (C–H bending and out of plane mode respectively) are the characteristic peaks of phthalocyanine complex (Gaffo et al., 2002). As the spent silica is calcined in the temperature range 250–450 °C, the characteristic peaks due to phthalocyanine complex start disappearing and only the characteristic peaks of silica remain at calcination temperature  $>450 \text{ °C}$ . From the FTIR spectra, it is evident that for the sample calcined at 650 and 850 °C, no phthalocyanine moiety is left in the silica and the intensity of the peaks at  $3440 \text{ cm}^{-1}$  due to hydroxyl group in the silica also starts decreasing.

### 3.6. Diffuse reflectance spectroscopy

The diffuse reflectance spectra (DRS) of untreated spent silica sample as such and calcined at different temperature are given in Fig. 5. The DRS spectra of the spent silica sample as such gave a solet peak of around 300–330 nm and the Q band peak in the range of 650–750 nm due to palladium phthalocyanine complexes (Gaffo et al., 2002). These peaks persist even when the sample is calcined at 250 °C but are not observed when the sample is calcined at  $\geq 450 \text{ °C}$ . This indicates that the phthalocyanine complex decomposes between 250 and 450 °C. From the diffuse reflectance spectra of the samples calcined at different temperatures it is evident that the samples that calcined at 450, 650 and 850 °C do not exhibit the broad band (Q band due to phthalocyanine complex) between 650 and 750 nm observed for such samples and the sample calcined at 250 °C.

### 3.7. Effect of acid concentration and solid/liquid ratio

In order to optimise the amount of acid required to recover 99–100% palladium from the calcined silica, experiments were done with varied amounts of acid keeping the total solution volume the same so that the effect of concentration of acid can clearly be observed on the recovery of palladium from calcined silica. In each experiment, 1 kg of spent silica calcined at 400 °C for 5 h, was digested with different amounts of HCl keeping total volume of the digestion solution constant. The palladium

Table 1  
Surface area analysis of the spent silica samples calcined at different temperatures

Sample	Calcination temperature, °C	Surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Pore size (4V/A by BET), Å	Pore volume $\text{cm}^3/\text{g}$
1.	250	360	64	0.58
2.	450	360	64	0.57
3.	650	359	62	0.56
4.	850	272	64	0.43



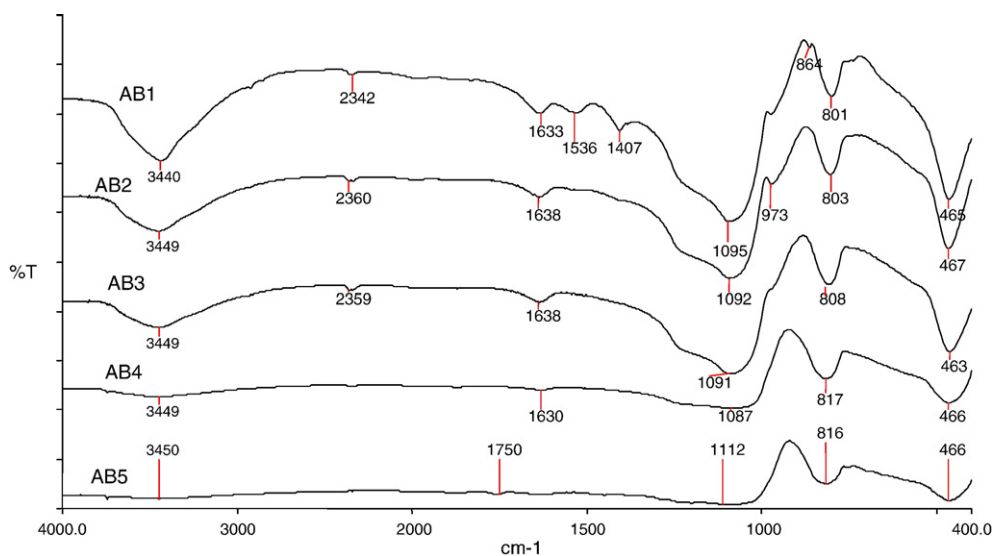


Fig. 4. FTIR spectra of spent silica sample calcined at different temperature, AB1: Pd/Si green sample; AB2: Pd/Si green sample calcined at 250 °C; AB3: Pd/Si green sample calcined at 450 °C; AB4: Pd/Si green sample calcined at 650 °C and AB5: Pd/Si green sample calcined at 850 °C.

recovery was calculated from the precipitate obtained at pH 9.3. Fig. 6 shows the effect of varying hydrochloric acid concentration from 1 to 10 M. The percentage recoveries of palladium increased with increasing HCl concentration up to a certain value and then remained constant with further increase in concentration. A maximum of 99% recovery was observed with 2 M acid concentration. We have also tried to vary the solid to liquid ratio to see its effect on palladium recovery. As such solid to liquid ratio is not expected to be a critical parameter as long as one keeps the HCl content constant, i.e., 330 ml [Conc. HCl]/kg of spent silica. However, minimum solid:liquid ratio of 1:2 must be maintained in order to have effective stirring of the slurry.

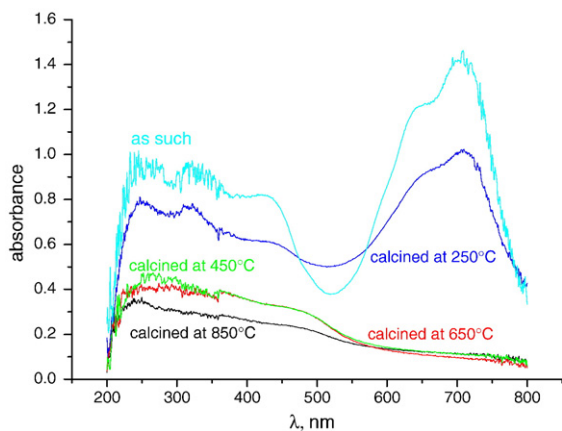


Fig. 5. Diffuse reflectance spectra of spent silica sample calcined at different temperatures.

### 3.8. Effect of digestion time

After optimising the calcination temperature, few experiments were done to optimise the digestion time. 500 g of spent silica calcined at 400 °C was digested in two litre 2 M HCl for 1 to 5 h. Silica was filtered and the pH of the filtrate was raised to 9.5 to precipitate Pd as PdCl<sub>2</sub>. Fig. 7 shows the effect of digestion time on the recovery of palladium. It is observed from the data that palladium recovery does not increase linearly with the digestion time; the dependence is an S-shaped curve. 100% palladium recovery is achieved in 5 h under the studied digestion conditions. The calculated rate constant for the recovery of palladium is  $1.04 \times 10^{-4} \text{ h}^{-1}$  from these data.

Based on the TGA, DRS, FTIR and XRD data, it is evident that phthalocyanine complex decomposes in the temperature of 325 to 400 °C. It can be further seen from

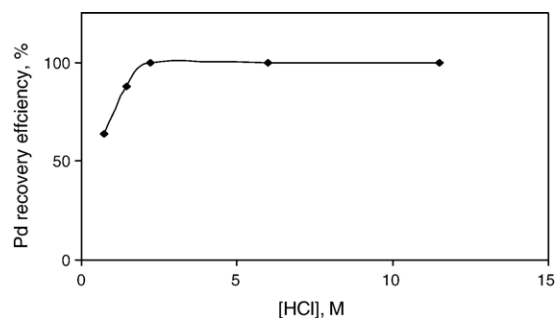


Fig. 6. Effect of hydrochloric acid concentration on the percentage recovery of palladium; liquid/solid ratio=2 L/kg at 100 °C, leaching time=5 h.

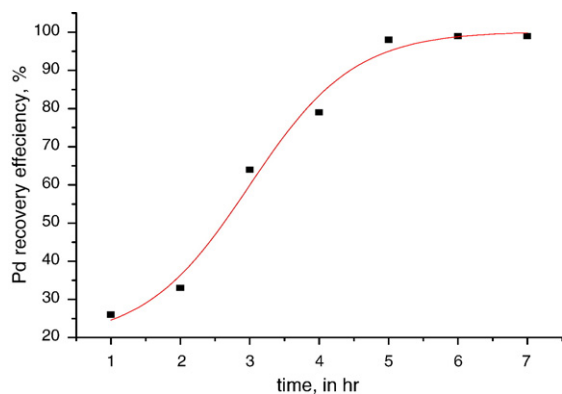


Fig. 7. Effect of leaching time on the percentage recovery of palladium; liquid/solid ratio=2 L/kg at 100 °C; acid concentration=2 M HCl.

FTIR data that up to calcination temperature of 450 °C, there is decomposed organic residue present on silica surface whereas at higher calcination temperatures silica does not retain any organic moiety. The observation that highest palladium recovery is obtained in the temperature range of 375 to 475 °C can be explained in terms of the observations from TGA, FTIR and DRS data. On calcining the palladium phthalocyanine/silica complex, the phthalocyanine moiety decomposes and parts of it get oxidized to carbon dioxide or get removed as volatile organic compounds. However, it is seen from the above data that some organic compounds are retained on the silica surface up to 475 °C. Palladium metal released from the complex can also get oxidized to palladium oxide on calcination. However, as long as organic compounds are present on silica surface, the oxidation of palladium metal is hindered, as in the presence of carbon compounds, PdO may get reduced to Pd<sup>0</sup> as shown below.



However, at higher calcination temperature (>475 °C), above reaction can not occur due to lack of organic compounds on silica surface and hence palladium is present as PdO at temperature above 500 °C. It is well known that dissolution of Pd<sup>0</sup> is easier in hydrochloric acid/aqua regia than that of PdO (Mellor, 1953). As Pd remains in Pd<sup>0</sup> state in the temperature range of 375 to 475 °C due to the presence of organic residue, the palladium recovery is highest in this temperature range. At higher temperatures >500°, Pd starts getting oxidized to PdO while at lower temperatures (~<350°), it is present as Pd phthalocyanine complex and is difficult to recover fully. Even to have complete recovery of palladium while digesting with aqua regia, it is common practice to add some compounds like chlorine gas, sodium borohydride,

ascorbic acid, and formaldehyde to keep palladium in Pd<sup>0</sup> state (Awadalla, 1994). The organic moiety left on silica plays the similar role in the present case.

It is also observed from the structural (X-ray diffraction, FTIR) and textural (surface area, pore volume) characteristics of the recovered silica that it can be re-used as surface area and structural groups like silanol groups are retained during palladium recovery process.

From the data given in Figs. 1, 6 and 7), it is clear that palladium can be completely recovered from spent silica under optimum conditions of silica calcinations temperature, acid content, digestion time and silica to liquid ratio. Once palladium is digested in the acidic solution, it can be recovered in the pure form by properly adjusting the pH of the solution and filtering off the impurity. Finally, palladium can be recovered as PdCl<sub>2</sub> by precipitating it at pH 9.3 and then drying it at 110 °C in oven. Further purification can be done by re-dissolving the recovered Pd containing sample in slightly warm 1 M HCl solution and then adjusting its pH to 6.3 and filtering off the impurity (if any) and then precipitating the pure PdCl<sub>2</sub> at pH 9.3. The PdCl<sub>2</sub> was then filtered using filter paper washed with distilled water and dried in oven. Pd was analyzed spectrophotometrically as [PdL<sub>4</sub>]<sup>2-</sup> for Pd content. We could recover 99% pure Palladium chloride with 99% Pd recovery using the above method.

#### 4. Conclusions

A process for the complete recovery of palladium as palladium chloride from spent silica gel used for the purification of phthalocyanine compounds has been established. Hydrochloric acid (2 M) digestion of spent silica calcined at around 400 °C for 5 h at 90 °C with a liquid/solid ratio of 2 was established as optimum process parameters for 99% Pd recovery. Palladium was separated from the digested liquor as palladium chloride by judiciously adjusting the pH of the solution.

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