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## RESEARCH ARTICLE

# SORPTION AND SEPARATION OF Pd(II) AND Pt(IV) FROM WASTEWATER WITH DIFFERENT CHELATING RESINS CONTAINING SULPHUR ATOM(S)

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### ABSTRACT

S-bearing chelating resins have been successfully employed for the recovery of Pd(II) and Pt(IV) from a variety of sources including wastewater. In the present study, four different chelating resins each containing sulphur as the donor atom(s) viz., R1, R2, R3 and R4 as synthesized in this laboratory and two commercially available chelating resins viz., C1 containing thiol group and C2 containing thio-uronium group procured from Ion-Exchange India Pvt. Ltd., Mumbai, were taken for carrying out sorption studies of Pd(II) and Pt(IV) and their separation from wastewater obtained from Johnson Matthey Company, Taloja, Mumbai. The resin R1 contains hexylthioglycolate functional group supported on poly-(styrene-DVB-methylmethacrylate). The resin R2 also contains hexylthioglycolate functional group but supported on poly-(ethylacrylate-acrylonitrile-DVB). The resins R3 and R4 possess diphenyldisulphide functional group supported on poly-(styrene-DVB-methyl-methacrylate) and poly-(ethylacrylate-acrylonitrile-DVB), respectively. The sorption studies using synthesized and commercial resins with aqueous solutions of Pd(II) and Pt(IV) have been performed using batch equilibration method. The recovery of Pd(II) and Pt(IV) from an industrial wastewater sample using R1, R2, R3, R4, C1 and C2 have also been accomplished. The concentration of metal ions in solutions was determined using ICP-AES technique. The percent recovery values from industrial wastewater for Pd(II) have been found to be 95 and those for Pt(IV) 93 with resins R1, R2, R3, R4, C1 and C2. Furthermore, the percent recovery values of Pd(II) and Pt(IV) ions using synthesized resins R1, R2, R3 and R4 appear to be somewhat better as compared to those obtained with the commercial resins (C1 and C2).

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### INTRODUCTION

The development of catalytic systems has led to an increasing industrial demand for precious metals viz., the platinum group metals (PGMs) [1]. Platinum group metals play a key role in modern society, as they are of specific importance for clean technologies and other high-tech equipment. For some of these, the demand for PGMs is not balanced by supply. Due to limited resources, a number of metallurgical processes have been investigated during recent decades for recovering precious and strategic metals from low-grade ores and more specifically from industrial waste (spent catalysts, electronic devices, wastewater etc.).

Because of increasing application of palladium and platinum in industry and depleting of their natural sources, ion-exchange methods have acquired great importance for their recovery [2]. On the basis of hard and soft acids and bases (HSAB) theory, the ion-exchangers having the functional groups with sulphur donor atoms interact strongly with the soft acids like precious metal ions [3].

Numerous selective chelating resins for Pd (II) and Pt (IV) ions containing functional groups such as thiol [4], tri-isobutylphosphine sulphide [5], dithizone [6], thiourea [7] and dithiocarbamate [8] are known. The ion-exchange capacities as well as recovery factors of Pd (II) employing the two commercial ion-exchangers containing S-donor atoms (Duolite GT-73 and Lewatit TP-214) have been calculated [2].

The present paper deals with a comparative study of four S-bearing resins (R1, R2, R3 and R4) synthesized in this laboratory vis-à-vis two S-bearing commercial resins (C1 and C2) with regard to sorption behaviour of Pd(II) and Pt(IV) ions based on optimum pH and time of equilibration.

Chromatographic column separation also was carried out in order to recover Pd(II) and Pt(IV) from industrial wastewater as obtained from Johnson Matthey Company, Taloja, Mumbai. The determination of Pd (II) and Pt (IV) were done using ICP-AES technique.

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## Experimental

### Reagents

A standard stock solution (1000 ppm) of Pd (II) was prepared by dissolving AR grade palladium chloride (1.667g) in double distilled water in the presence of minimum volume of 1M HCl solution and diluting it to 1000 mL.

A standard stock solution (1000 ppm) of Pt (IV) was prepared by dissolving AR grade hexachloroplatinic acid (1.0g) in double distilled water in the presence of minimum volume of 1M HCl solution and diluting it to 1000 mL.

A solution of 0.2M acetate buffer of pH 5.0 was prepared by dissolving 13.6 g of sodium acetate and 6 mL of glacial acetic acid in minimum volume of double distilled water and diluting it to 1000 mL.

The commercial chelating resins (C1 and C2) containing thiol group and thio-uronium group respectively were procured from Ion-exchange India (Pvt.) Ltd., Mumbai.

Eluant for Pd(II): 1% thiourea in 0.1M HCl and eluant for Pt(IV): 5% thiourea in 0.1M HCl.

All other chemicals, solvents and indicators used were of AR grade. Double distilled water was used throughout the present work.

R1, R2, R3 and R4 have been synthesized in this laboratory and the procedures for their preparation are available in literature [9, 10, 11 and 12].

The concentration of Pd(II) and Pt(IV) in the industrial wastewater as supplied by Johnson Matthey Company were found to be 489.98 ppm and 50.07 ppm, respectively.

### Batch Experiment

With the help of batch equilibration technique, the amount of metal ions adsorbed on the resin phase was determined by the equation:

$$N_f = \frac{X - Y}{Z}$$

Where, X is the initial amount of metal ions, Y is the amount of metal ions in the supernatant,  $N_f$  is the amount of metal ions adsorbed and Z is the amount of chelating resin.

### Optimum pH for maximum metal ion uptake

In order to determine the optimum pH of metal ion uptake with each of the four synthesized resins (R1, R2, R3 and R4) and the two commercial resins (C1 and C2), 0.5 g of dry resin was added to 25 mL of each of the Pd(II) and Pt(IV) solutions each having 1mg/mL of the metal buffered at the requisite pH. After equilibrating for 24 hrs, the mixtures were filtered and the resin beads thoroughly washed with distilled water. The sorbed metal

ions were then completely eluted using 40 mL of 2N HCl solution.

The amount of metal ions present in the solution and retained on the resin were determined using ICP-AES technique in each case. All the reported values are the mean of three determinations made during the study.

### Sorption kinetics

In order to estimate the rate of loading of Pd(II) and Pt(IV) ions on each of the four synthesized (R1, R2, R3 and R4) and the two commercial resins C1 and C2, a series of experiments were carried out in which the dry resin (0.5g) was added to 25 mL of each of the Pd(II) and Pt(IV) metal ions solution each having 1 mg/mL concentration, buffered at an optimum pH. After equilibrating for different intervals of time, each mixture was filtered off and the resin was thoroughly washed with double distilled water. The sorbed metal ions were completely eluted by using 40 mL of 2N HCl solution in each case.

The amount of metal ions present in the solution and retained on the resin were determined by ICP-AES technique in each case. All the reported values are the mean of three determinations made during the study.

### Chromatographic recovery of Pd(II) and Pt(IV) from Industrial wastewater

Prior to use, the resins were converted into sodium form as per the procedure [13] as cited in literature. The resin beads were rinsed with 1N HCl and then washed with 1N NaOH and finally washed repeatedly with double distilled water until the pH of the effluent in each case dropped to 10.

A compact column of 50 cm length and 1 cm i.d. was prepared with 3.0 g of the resin beads in the sodium form. The column was conditioned at pH 5.0 using 0.2M acetate buffer. Then 20 mL of the industrial wastewater sample was introduced into the column at a flow rate of 0.5 mL min<sup>-1</sup>. Next, approximately 150 mL of 1% thiourea in 0.1M HCl eluting agent for Pd(II) and 150 mL of 5% thiourea in 0.1M HCl for Pt(IV) was passed respectively through the column at a flow rate of 0.5 mL min<sup>-1</sup>; the concentration of each metal ion in the eluant was determined by ICP-AES technique.

## RESULTS AND DISCUSSION

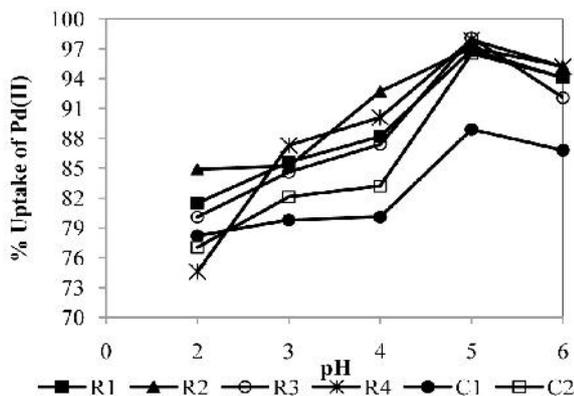
### Effect of pH on metal ions uptake

The sorption characteristics of four synthesized resins (R1, R2, R3 and R4) and two commercial resins (C1 and C2) towards Pd(II) metal ions have been investigated by batch equilibration method over a pH range of 2-6 as reported in Table 1 and the data thus generated have been plotted in Fig.1. It is evident that the adsorption of Pd(II) metal ions in all the four synthesized and two commercial resins increases with increase in pH, reaching a limiting value in each instance followed by a decrease in adsorption, beyond the limiting value. Thus, the optimum pH for Pd(II) ions in the aqueous solution is evaluated

to be 5. The uptake of Pd(II) metal ions among four synthesized resins is found to be 97%, whereas in case of C1 and C2 it is about 87% and 94%, respectively.

**Table 1** % Uptake of Pd (II) at various pH values

pH of Equilibration	% Uptake of Pd(II)					
	R1	R2	R3	R4	C1	C2
2	81.50	84.90	80.1	74.60	78.20	77.04
3	85.60	85.20	84.6	87.30	79.80	82.12
4	89.2	92.70	87.4	90.10	80.10	83.17
5	96.90	97.09	98.1	97.90	88.90	96.52
6	94.1	95.25	92.1	95.20	86.80	94.12

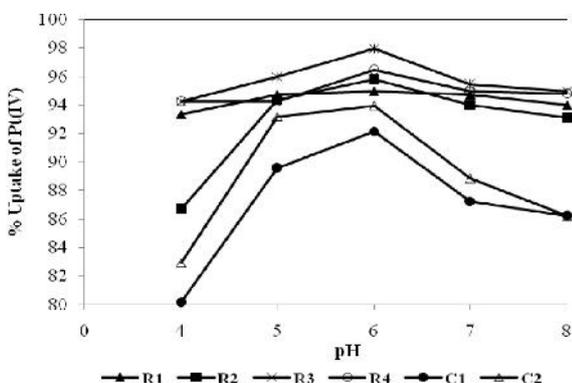


**Figure 1** Effect of pH on Pd(II) uptake by R1, R2, R3, R4, C1 and C2

In case of Pt(IV), the sorption characteristics with four synthesized resins (R1, R2, R3 and R4) and two commercial resins (C1 and C2) have been investigated over a pH range of 4-8 as reported in Table 2 and the data thus gathered have been plotted in Fig.2. It is evident that the adsorption of Pt(IV) metal ions in all the four synthesized and two commercial resins increases with increase in pH, reaching a limiting value in each instance followed by a decrease in adsorption, beyond the limiting value. Thus, the optimum pH for Pt(IV) ions in the aqueous solution worked out to be 6. The uptake of Pt(IV) metal ions among four synthesized resins is found to be 95%, whereas in case of C1 and C2 it is about 92% and 94%, respectively.

**Table 2** % Uptake of Pt(IV) at various pH values

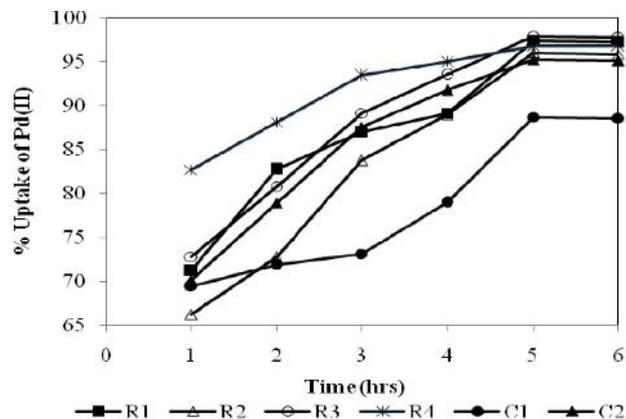
pH of Equilibration	% Uptake of Pt(IV)					
	R1	R2	R3	R4	C1	C2
4	93.35	86.68	94.26	92.23	80.19	82.94
5	94.72	94.38	96.00	94.26	89.56	93.17
6	94.99	95.78	97.96	96.44	92.15	93.95
7	94.70	94.03	95.43	94.98	87.23	88.84
8	93.98	93.09	94.97	94.76	86.19	86.19



**Figure 2** Effect of pH on Pt(IV) uptake using R1, R2, R3, R4, C1 and C2

**Table 3** % Uptake of Pd(II) at various time intervals

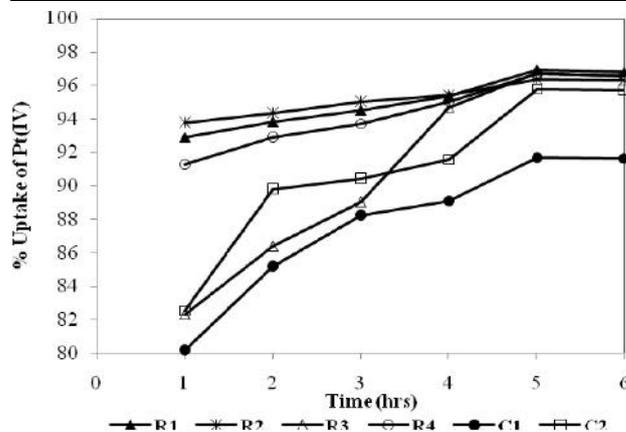
Time of Equilibration (hrs)	% Uptake of Pd(II)					
	R1	R2	R3	R4	C1	C2
1	71.17	66.18	72.77	82.70	69.42	70.09
2	82.72	72.75	80.80	88.14	71.87	78.93
3	87.00	83.72	89.13	93.39	73.13	87.56
4	89.10	88.93	93.50	94.98	78.96	91.71
5	97.26	95.97	97.87	96.77	88.65	95.15
6	97.16	95.78	97.79	96.70	88.58	95.05



**Figure 3** Effect of time of equilibration on Pd(II) uptake using R1, R2, R3, R4, C1 and C2

**Table 4** % Uptake of Pt(IV) at various time intervals

Time of Equilibration (hrs)	% Uptake of Pt (IV) metal ion					
	R1	R2	R3	R4	C1	C2
1	92.91	93.73	82.30	91.3	80.14	82.54
2	93.81	94.31	86.40	92.88	85.16	89.76
3	94.51	95.00	89.02	93.70	88.20	90.4
4	95.34	95.44	94.68	94.99	89.10	91.59
5	96.90	96.34	96.74	96.67	91.7	95.78
6	96.83	96.30	96.54	96.60	91.62	95.71



**Figure 4** Effect of time of equilibration on Pt(IV) uptake using R1, R2, R3, R4, C1 and C2

**Table 5** % Recovery of Pd(II) and Pt(IV) from industrial wastewater

Resins	Pd(II)	Pt(IV)
R1	95.53	93.78
R2	95.87	93.99
R3	96.21	94.47
R4	96.01	94.21
C1	94.89	92.77
C2	95.02	93.66

**Effect of time of equilibration on metal ion uptake**

To determine the rate of loading of Pd(II) and Pt(IV) metal ions

on all the six resins (R1, R2, R3, R4, C1 and C2) batch equilibration experiments were carried out at optimum pH of 5 and 6, respectively. The data thus generated have been set out in Tables 3 and 4 and plotted in Figs.3 and 4, respectively. The time required for maximum adsorption of both Pd(II) and Pt(IV) metal ions was thus found to be 5.0 hrs (Tables 3 and 4 and Figs 3 and 4).

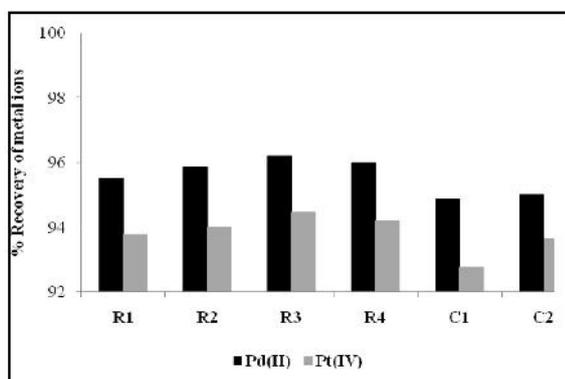


Figure 5 % Recovery of Pd(II) and Pt(IV) from industrial wastewater

#### Recovery of Pd(II) and Pt(IV) from industrial wastewater

The recovery of Pd(II) and Pt(IV) metal ions from industrial wastewater has been effected with all the six resins (R1, R2, R3, R4, C1 and C2). Pd(II) was eluted with 1% thiourea in 0.1M HCl while Pt(IV) was eluted with 5% thiourea in 0.1M HCl each at a flow rate of 0.5 mL min<sup>-1</sup>. The % recovery values of metal ions as determined by ICP-AES technique have been set out in Table 5. Thus, the recovery values of Pd (II) and Pt (IV) were found to be 95.53% and 93.78%; 95.87% and 93.99%; 96.21% and 94.47%; 96.01% and 94.21%; 94.89% and 92.77%; and 95.02% and 93.67 for R1, R2, R3, R4, C1 and C2, respectively.

#### CONCLUSIONS

On the basis of the data as reported in Table 5 and the bar diagrams (Fig. 5), the following conclusions can be drawn:

- (i) In case of synthesized resins (R1, R2, R3 and R4), the recovery of Pd(II) is slightly higher (95-96%) as compared to that for Pt(IV) which is about 94%. Likewise, in case of resins C1 and C2 the recovery of Pd(II) is slightly greater (94-95%) in comparison to that for Pt (IV) (93-94%). Thus, Pd(II) metal ion are preferentially sorbed by all the resins as compared to Pt(IV) metal ions.
- (ii) The recovery values for Pd(II) and Pt(IV) ions appear to be somewhat higher in case of synthesized resins (R1, R2, R3 and R4) as compared to those for commercial resins (C1 and C2).

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