

Rapid Separation of Platinum Group Elements with Hydrous Zirconium Oxide as an Ion-Exchange Material

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Summary: This paper describes the adsorption behaviour (K_d) of platinum group elements on hydrous Zirconium Oxide in $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer, of pH 2-10 in batch technique. Then Pt^{2+} , Ni^{2+} and Pd^{2+} were separated from one another with the help of buffers of pH 7.5, 6.0 and 2.0 respectively from HZO column.

Introduction

The term platinum group elements (elements of group 10 according to new IUPAC group notation [1] refers to very closely related elements, i.e., nickel, palladium and platinum which form similar compounds and consequently, recovery of platinum and palladium from nickel ore and waste solutions, was done by tedious method of fractional crystal-

lization or by adsorption of these metal on activated carbon [2] until the advent of ion exchangers. The efficiency of organic anion [3-7] and cation [8] exchangers for the recovery of platinum and palladium was reported by many workers. Solvents extraction [9-12] of platinum group elements with various organic reagents was also attempted suc-

cessfully. Thin layer chromatographic behaviour of these metals on cellulose impregnated with inorganic material [13-18] demonstrated rapid separation which encouraged the authors to try hydrous zirconium oxide as ion exchange material in column technique. This paper describes the adsorption behaviours of platinum group elements on hydrous zirconium oxide at different pH values in a batch technique for the determination of selectivity coefficient (Kd), planning their separation by a column technique and their percentage recovery from their mixtures.

Experimental

Distribution Coefficient

The determination of distribution coefficient (Kd) of each metal ion was carried out by batch equilibrium technique. 16 cleaned, dried flasks of 25 ml capacity each were taken and divided into set (a) measuring and (b) reference. The flasks of measuring set were numbered 2,3 8 and those of reference set were marked 2',3' 8'. 0.25 grams of hydrous zirconium oxide, 80-100 mesh fraction [19-21] were put in each flask of measuring set. 10 ml of Ni^{2+} solution of 50 [ppm] concentration were put in each flask of both the sets and their volumes were made upto the mark with buffer solutions of CH_3COONa/CH_3COOH [22], of respective pH i.e. 2,3 8. Flasks were stoppered and shaken in orbital shaker made by Gallen Kamp, for 72 hours at $30^\circ C$ till an equivalency of exchange was established.

The amounts of Ni^{2+} present in clear supernatant solutions of measuring and reference sets were determined with the help of Atomic Absorption spectrophotometer, "Varian AA-1275". pH values of all the solutions in measuring and reference were recorded with the help of pH meter, "Corning-EEL model 5". Kd values for Ni^{2+} at various pH were calculated as follows and plotted against respective pH values. Fig. 1.

$$K_d = \frac{\text{Ion Conc. in ref. sol.} - \text{ion conc. in measuring sol.}}{\text{Ion conc. in measuring sol.}} \times \frac{\text{Vol. of sol.}}{\text{Wt. of Resin.}}$$

Similar procedure was adopted for Pt^{2+} and Pd^{2+} and results were incorporated in Fig. 1.

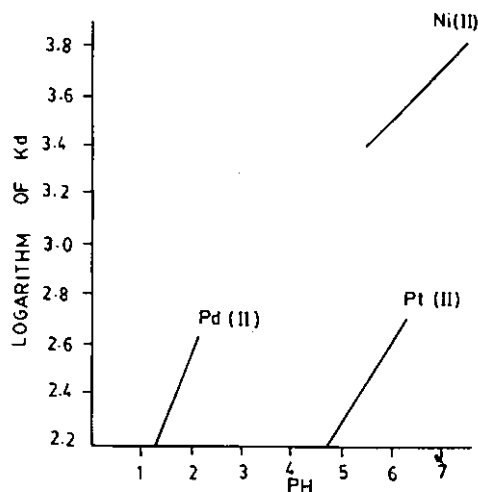


Fig.1: Logarithm of Kd. values of group 10 elements against final pH.

Elution Curves for the metal of group 10

Column technique was used for the separation of Ni^{2+} , Pd^{2+} and Pt^{2+} to attain more precise order of selectivities of competing ions. Slurry of hydrous zirconium oxide was prepared in water in a beaker and poured down the column (15 x 1.5 cm) which was mounted in vertical position. 100 ml of 0.1M HCl was allowed to percolate through the resin to convert it to hydrogen form. The resin was washed with de-ionized water until the elute gave no precipitate with $AgNO_3$. 5ml of solution containing 0.1 mg of Ni^{2+} , and Pd^{2+} and Pt^{2+} , each were loaded in the column. The column was then first eluted with buffer solution of pH 7.5 at the rate 2.0 ml per minute in 8 tubes placed in fraction collector type 301 B.No. 0213, until the last traces of Pt^{2+} were eluted. Then the column was eluted at the same rate with buffer solutions of pH 6.0 and 2.0 in 13 tubes and 12 tubes until the eluents were free from Ni^{2+} and Pd^{2+} respectively. (Table-1). A plot between absorbance of cation, and volume of eluents was shown in Fig. 2.

Discussion

The platinum group elements are becoming increasingly important in electric arc, electrode, catalytic and atomic energy field. But their general

Table-1

Ion	Pt ²⁺	Ni ²⁺	Pd ²⁺
Amount loaded	0.100 mg	0.100 mg	0.100 mg.
Amount recovered	0.0968 mg	0.096 mg	0.095 mg.
% recovery	96.8	96.0	95.0

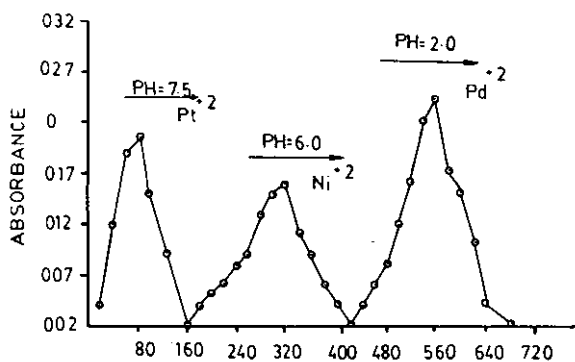


Fig.2: Elution of cations of group 10 with eluents of different pH values on H₂O

behaviour resembles very closely and their separation was difficult. For planning separation, K_d values of metal ions with respect to their relative equilibrium towards hydrous zirconium oxide at different pH were determined by batch technique. Plot of log K_d values vs respective pH, adsorption isotherms indicate that selectivities of these metals on H₂O decreases in the order Pd²⁺ > Ni²⁺ > Pt²⁺ which correspond reactivity of these metals towards free acid.

The column technique was used to obtain a more precise selectivity sequence of competing ions and to establish the applicability of an effective separation. The order of elution of metal ions agrees exactly with the affinity sequence of competing ions. Repeated experiments indicate a clean cut separation with no interference of competing ions. Metal recovery is an outstanding one.

The material presented in this paper indicates that application of H₂O for enrichment, concentration and recovery of Pt²⁺ and Pd²⁺ from Nickel ore has reached a point where the process is techni-

cally sound. However, there is still some questions of its economy justification for the utilization of this process on a commercial basis in large ion-exchange units.

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