



Evaluation of novel ligand dithiodiglycolamide (DTDGA) for separation and recovery of palladium from simulated spent catalyst dissolver solution



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ABSTRACT

Novel ligand, namely, *N,N,N,N*-tetra-(2-ethylhexyl)-dithiodiglycolamide (DTDGA) has been evaluated for separation and recovery of palladium from simulated spent catalyst dissolver (SSCD) solution. Liquid–liquid batch extraction studies were carried out to understand the influence of various parameters on the extraction behavior of palladium. Extraction equilibrium studies showed near complete extraction of palladium within 5 min. With the increase in hydrochloric acid concentration, the extraction of palladium increased up to 3.0 M HCl and then remained constant on further increase in acidity. Stoichiometry of the extracted species was determined to be PdCl₂·DTDGA by mole ratio plot. The effect of various diluents on the extraction of palladium was studied and it was found that there is quantitative uptake in *n*-paraffinic diluents and the extraction decreases with increase in polarity of diluent. More than 99% of palladium was back extracted in single contact using 0.01 M thiourea in 0.1 M HCl. Extraction studies with SSCD solution showed negligible uptake of Fe, Cr, Ni, and Pt, thus showing very high selectivity and extractability of DTDGA for palladium.

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1. Introduction

Palladium has found enormous applications in various fields like catalysis, pharmaceuticals, petroleum industry, electronics, telecommunication, heat and corrosion resistance apparatus, dental alloys, jewellery, etc. [1–3]. The natural abundance of palladium in the earth crust is very low and the present deposits will not be enough to meet its growing demand in near future. This has necessitated exploring the options of the separation and recovery of palladium from secondary resources. Among the various secondary resources of Pd the major ones include, high level waste (HLW) solutions generated from reprocessing of spent nuclear fuel [4,5] and, palladium group metals (PGM) based spent catalysts from automotive and petroleum industries [6–9]. While the use of Pd recovered from HLW solution will have some reservations in public domain, those recovered from spent catalyst will have no such issues. Moreover, the option of recycling the recovered Pd from spent catalysts could minimize the environmental hazards associated with their direct disposal. In this regard separation and recovery of palladium from the spent catalysts is attempted worldwide.

Liquid–liquid extraction is generally used for the separation and recovery of palladium from spent catalysts in hydrometallurgical

processes [10,11]. Palladium being a soft metal, will have preference for ligands having soft donor atoms like ‘S’ and ‘N’. Based on this presumption several extractants, namely, 2-hydroxy-4-*s*-octanoyl diphenyl-ketoxime [11], dialkyl sulphoxides [12], 8-hydroxyquinoline [13], dioctyl sulphides [14] 4-acylpyrazolone [15], pyridine-carboxamides [16], Cyphos®IL-101 [17], and bis-(2,4,4-trimethyl pentyl)-phosphinodithioic acid [18] have been explored at various laboratories. The utilization of these ligands has been hampered by several limitations like pH sensitivity, chemical stability, slower kinetics of extraction, poor solubility in paraffinic diluents, etc. These limitations have necessitated the development of new ligands. Recently a novel ligand, namely, *N,N,N,N*-tetraoctylthiodiglycolamide (TOTDGA) has been explored for the separation and of Pd from HCl medium [19,20]. The ligand has shown high extractability and selectivity for Pd over other metal ions. However, to recover palladium from lean aqueous streams even more effective extractant is desirable.

Recently, we have reported a novel ‘S’ donor ligand, namely, *N,N,N,N*-tetra-(2-ethylhexyl)-dithiodiglycolamide (DTDGA) [5] which has shown its remarkable extractability and selectivity for palladium over other metal ions present in nitric acid medium. The chelation occurs through more than one donor sites of thio-etheric sulfur and amidic moiety placed appropriately in the ligand, accounting for its high selectivity and extractability for palladium [21]. Since DTDGA molecule possesses two thioetheric ‘S’

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atoms as compared to the single 'S' atom in TOTDGA molecule, it is expected that this ligand will chelate more effectively with palladium and therefore, would be more effective for Pd recovery from lean aqueous streams. With this presumption it was thought to explore the potential of DTDGA for the separation and recovery of Pd from HCl medium.

The present work deals with the evaluation of novel ligand DTDGA for the extraction and recovery of palladium from HCl medium and finally from the simulated leach liquor of spent automotive catalyst.

2. Experimental

2.1. Reagents and instruments

2.1.1. DTDGA

DTDGA (Fig. 1) was synthesized by the condensation reaction of potassium salt of ethane-1,2-dithiol with *N,N*-bis-(2-ethylhexyl)-2-chloroacetamide according to the procedure described earlier [5]. The purity of the product was ~99% and the yield of the reaction was ~95%.

Solutions with desired concentration of DTDGA were prepared by dissolving appropriate amount of DTDGA in diluents, namely, *n*-dodecane, toluene, chloroform, isodecyl alcohol, etc.

2.1.2. Palladium feed solution

Stock solution containing 10^{-2} M Pd(II) in 3.0 M HCl was prepared by dissolving appropriate amount of PdCl₂ in hydrochloric acid. Aliquots were taken from this stock solution and properly adjusted for Pd(II) and hydrochloric acid concentration, and were used for different experiments.

2.1.3. Simulated spent catalyst dissolver (SSCD) solution

SSCD solution was prepared by dissolving metal salts in concentrated HCl and diluting the stock solution to appropriate concentration of metal ions and acid. The concentrations of the metal ions present in SSCD solution are given in Table 1.

2.1.4. Instruments

Quantitative determination of various metal ions present in SSCD solution was carried out using Atomic Emission Spectrometry technique (ICP-AES). An Ultima-2 sequential scan instrument with axial ICP (Horiba Jobin Yvon, France), operated at 40.68 MHz, and was used in this study. The error on the measured concentrations was within ±5.0%.

Table 1

Simulated spent catalyst dissolver (SSCD) solution, aqueous phase = aq., organic phase = org., and A/O = aqueous/organic.

S. No.	Element	Concentration (mg/L)
1	Pd	88.1
2	Cr	81.8
3	Fe	1002.4
4	Mn	528.6
5	Ni	1138.2
6	Pt	85.8

2.2. Extraction studies

Liquid–liquid extraction experiments were carried out under ambient conditions by shaking equal volume (5 mL each) of organic and aqueous phase in a separatory funnel. After phase separation, the aqueous phase was analyzed for palladium concentration. The concentration of palladium in the organic phase was calculated by mass balance. The contact time for all the batch extraction studies were 10 min, whereas in the case of extraction equilibration studies the contact time was varied. For the extraction studies of palladium and other SSCD solution elements, equal volume of DTDGA/*n*-dodecane was equilibrated with aqueous feed solution and after phase separation the aqueous phase was analyzed for metal ion concentration. The concentration of metal ion in the organic phase was calculated by mass balance.

The distribution ratio ' D_M ' of the metal was determined as the ratio of metal ion concentration in organic phase to that in aqueous phase. Separation factor of palladium with respect to other metal ion ($SF = D_{Pd}/D_M$) was determined. Percentage extraction of metal ion was determined by equation:

$$\%E = \frac{D_M}{D_M + 1} \times 100 \quad (1)$$

Errors in D_M and %E values were within ±5.0% and ±2.0% respectively. However, for elements with very small distribution ratios in the range of 10^{-2} – 10^{-3} , the error was within ±10.0%.

The contact time required to attain extraction equilibrium was determined by shaking 0.0025 M DTDGA/*n*-dodecane with 10^{-3} M palladium in 3.0 M hydrochloric acid at different time intervals. To evaluate the effect of HCl concentration on extraction of palladium, 0.0025 M DTDGA/*n*-dodecane was equilibrated with aqueous solution containing 10^{-3} M palladium at varying hydrochloric acid concentrations. The concentration of HCl was varied from 0.5 M to 6.0 M. The influence of DTDGA concentration on the distribution ratio of palladium was determined by equilibrating the organic

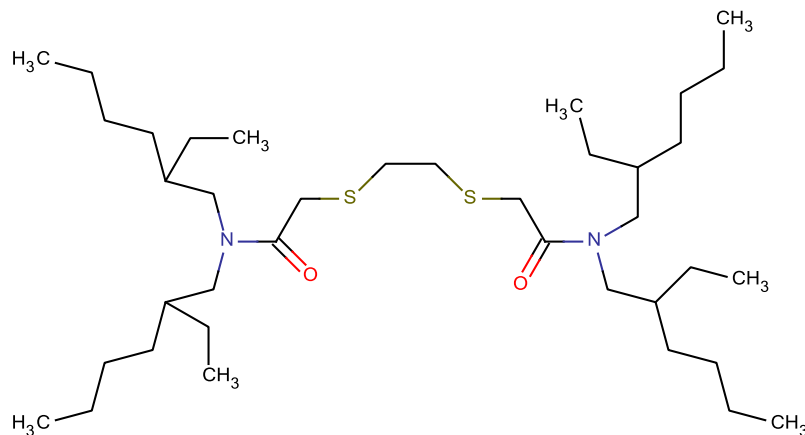


Fig. 1. *N,N,N',N'*-tetra-(2-ethylhexyl)-dithiodiglycolamide (DTDGA).

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