Recovery of Pt and Pd From Aqueous Solutions by N,N-di(trimethoxysilylpropyl)-N′-benzoylthiourea Modified Silica Gel

Malehlogonolo R.R. Mphahlele, Alseno K. Mosai, Hlanganani Tutu, Izak A. Kotzé

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag X3, WITS, Johannesburg, 2050, South Africa

Abstract

Platinum and palladium are scarce precious metals that can end up in waste streams during mineral processing. There is therefore a need to develop efficient recovery methods. In this study, a novel silica-anchored acylthiourea adsorbent was prepared by first synthesizing the N,N-di(trimethoxy-silyl-propyl)-N′-benzoylthiourea (DTMSP-BT) ligand followed by its immobilization onto silica gel. The recovery of Pt and Pd aqueous solutions by DTMSP-BT-SG was investigated at different conditions that mimic mining wastewaters. The significant recovery (>95%) of Pt and Pd observed at pH 2, 0.5 mg L-1 dosage and 5 mg L-1 concentration makes the adsorbent an excellent extracting agent that can be utilized by mining wastewater industries.

Keywords: Adsorption, Acylthioureas, Mining wastewater, Platinum group metals

Introduction

The platinum group metals (PGMs) are known for their excellent physical and chemical properties which make them important components in applications such as catalysts, electronics, medical equipment and jewellery (Bernardis *et al*. 2005). These precious metals also form critical components of the renewable energy revolution which is currently underway and is a result of the global push to reduce greenhouse emissions (Wang *et al*. 2017). However, the rising industrial demand of these metals coupled with their depleting natural resources and the complex processes associated with their recovery has made them scarce (Bernardis *et al*. 2005). Thus, great emphasis has been placed on the recovery of PGMs from alternative sources such as refinery wastewater and to develop economically feasible recovery methods (Barakat 2011; Mosai *et al*. 2020).

The adsorption process, which utilizes a solid support such as zeolite, chitosan, silica gel, bentonite is known to be an effective technique for the removal of metal ions from waste solutions with low metal concentrations (Mosai *et al*. 2020; Barquist 2009). Furthemore, adsorption has advantages including low operating costs, high removal efficiency, short operation times and tunability of the solid support (Jal 2004). These reasons have motivated this study to develop an efficient adsorbent that can be utilized in the recovery of PGMs from waste solutions in order to meet the surging demands and to reduce pollution (Barakat 2011).

Silica gel is an amorphous and porous form of silicon dioxide that is characterized by the siloxane ($\equiv$Si-O-Si$\equiv$) and the silanol ($\equiv$Si-OH) functional groups (Barquist 2009). It has a high thermal and mechanical resistance, and its surface can be modified with various organic ligands with metal chelating abilities that will act to improve its efficiency, sensitivity, and selectivity in analytical applications (Jal 2004). Acylthioureas serve as a class of organic compounds that can be immobilized onto the silica surface. They have a rich coordination chemistry since they contain multiple hard and soft donor atoms (O, N, S) that can bind to metal ions such as Pt and Pd, thus allowing for efficient recovery (Nkabyo *et al*. 2021). Acylthioureas are also non-toxic, non-sensitive, odourless and can be readily prepared from cheap reagents in high yields through a facile two-step, one pot synthetic procedure (Douglas and Dains 1934).

Methods

Chemicals and instruments

The synthetic reagents and analytical grade Pt and Pd standard solutions (5% w/w of c(HCl)) used in the experiments were purchased from Sigma Aldrich. To characterize the DTMSP-BT ligand, ^{1}H and ^{13}C NMR spectroscopy (Bruker Avance III 400 MHz) were used. ^{13}C Solid State NMR was also used for characterization of the DTMSP-BT-SG adsorbent. The functional groups of both DTMSP-BT and DTMSP-BT-SG were determined using Fourier transform infrared spectroscopy (FT-IR) (Bruker Tensor 27 spectrometer). The chemical composition of the unmodified silica gel and DTMSP-BT-SG were determined using X-ray fluorescence (XRF).

Synthesis of DTMSP-BT and its immobilization onto silica gel

The synthetic procedure described by Douglas and Dains (1934) was adopted and modified in preparation of the acylthiourea ligand. Benzoyl chloride (1.2 mL/ 10 mmol) in dry acetonitrile (15 mL) was added into a solution of potassium thiocyanate (1 g/ 10 mmol) and anhydrous acetonitrile (20 mL). The reaction mixture was refluxed for 1 h at 80 °C to yield a benzoyl isothiocyanate intermediate which was cooled down to room temperature. The acetonitrile was removed under vacuum to isolate the intermediate. Anhydrous dichloromethane (DCM) (20 mL) was added to the intermediate followed by the addition of bis(3-(trimethoxysilyl)propyl) amine (3.12 mL/ 9.5 mmol) in DCM (20 mL). The reaction mixture was stirred overnight at 40°C and the resultant product was cooled to room temperature and filtered. The DCM

of the filtrate was removed under reduced pressure and the product was obtained as an orange viscous liquid.

The procedure (fig. 1) reported by Erdem *et al.* (2011) was used to functionalize the silica gel with DTMSP-BT. Silica gel (0.50 g) and 0.01 M acetic acid (20 mL) were mixed for 10 min to activate the silanol groups on the silica surface. The mixture was filtered using suction and washed with distilled water before added to a solution of toluene (20 mL) and DTMSP-BT (0.30 mL). The reaction mixture was left to reflux for 20 h at 110°C and the resultant product was a yellow liquid containing the silica particles. The reaction mixture was cooled and filtered. The functionalized silica particles were washed with toluene and dried at 80 °C for 8 h.

Batch adsorption studies

Batch experiments were carried out by adding the relevant adsorbent mass and 20 mL of the metal solution into centrifuge tubes (50 mL) to study the effect of adsorbent dosage (5-50 mg), pH (2-9), concentration (0.5-50 mg L-1) and contact time (10-1440 min) on the recovery of Pt and Pd by DTMSP-BT-SG. The samples were agitated until equilibrium using an elliptical benchtop shaker. The samples were filtered and the concentration of Pt and Pd was determined with inductively coupled plasma optical emission spectroscopy (ICP-OES). The adsorption capacity, qe (mg g-1) and efficiency were determined using Eq. 1, and Eq. 2, respectively.

$$q_e = \left(\frac{(C_0 - C_e)V}{M} \right) \qquad (1)$$

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (2)$$
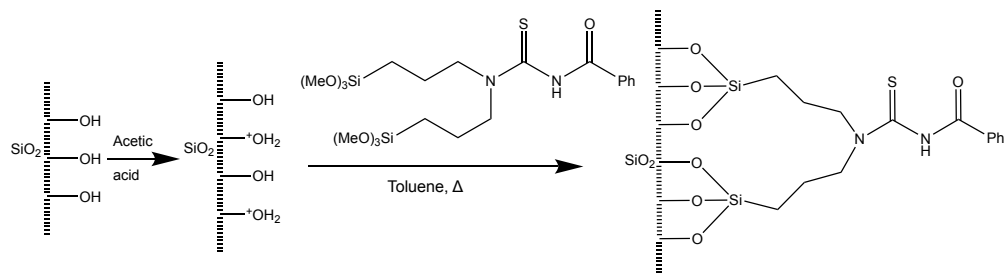

Figure 1 Functionalization of silica gel with DTMSP-BT

where C_0 (mg L^{-1}) is the initial metal concentration, C_e (mg L^{-1}), is the equilibrium metal concentration, V (L) is the solution volume, M (g) is the adsorbent mass used.

Results and Discussion

Characterisation

The successful ligand synthesis was confirmed using 1H NMR and ^{13}C NMR spectroscopy (fig. 2a) which showed the presence of the expected 20 carbon signals of DTMSP-BT and the deshielded thiocarbonyl (C = S) and carbonyl (C = O) signals at 180.18 and 163.57 ppm, respectively. The successful addition of DTMSP-BT onto the silica gel was confirmed by the ^{13}C Solid-State NMR spectra in fig. 2b that illustrates the appearance of the carbon signals as well as the C = S and C = O groups onto the silica gel.

The FT-IR spectra (fig. 3) of both DTMSP-BT and DTMSP-BT-SG also confirmed the synthesis of the ligand and its functionalization onto silica gel. This was noted by the C = O stretch at 1685 cm^{-1}, and the N-H stretch at 3256 cm^{-1} in both the free ligand (DTMSP-BT) and adsorbent (DTMSP- BT-SG) spectra. The C = S stretch of acylthiourea ligands is known to occur around 800-1500 cm^{-1} (Nkabyo *et al.* 2021).

The broad siloxane group (Si-O/Si-O-Si) of the silica gel was observed around 1000-1200 cm-1 and its strong infrared absorption masks other functional groups in this region (Issa and Luyt 2019). XRF indicated that the unmodified silica gel was dominantly composed of SiO_2 (89.2%), which decreased to 68.6% upon functionalization of the silica gel with DTMSP-BT.

Effect of adsorbent dosage and pH

The effect of adsorbent dosage on the adsorption of Pt and Pd by DTMSP-BT-SG was investigated at pH 2 and 5 mg L^{-1}. The results indicated that the adsorption efficiency increased with adsorbent dosage due to increased amount of the binding sites (Ramakul *et al.* 2012). The adsorption efficiency was found to be >98% for Pt and >95% for Pd, thus there was favourable adsorption of both metals onto DTMSP-BT-SG. The pH of a solution is known affect the speciation of metals and adsorbent surface charge (Mosai *et al.* 2020). The effect of pH on the adsorption of Pt and Pd by DTMSP-BT-SG was investigated at 5 mg L^{-1} and 10 mg. The results in fig. 4b, indicated that the adsorption efficiency for Pt decreased with increasing pH until pH 5, thereafter increased from pH 5-8, whilst for Pd the efficiency
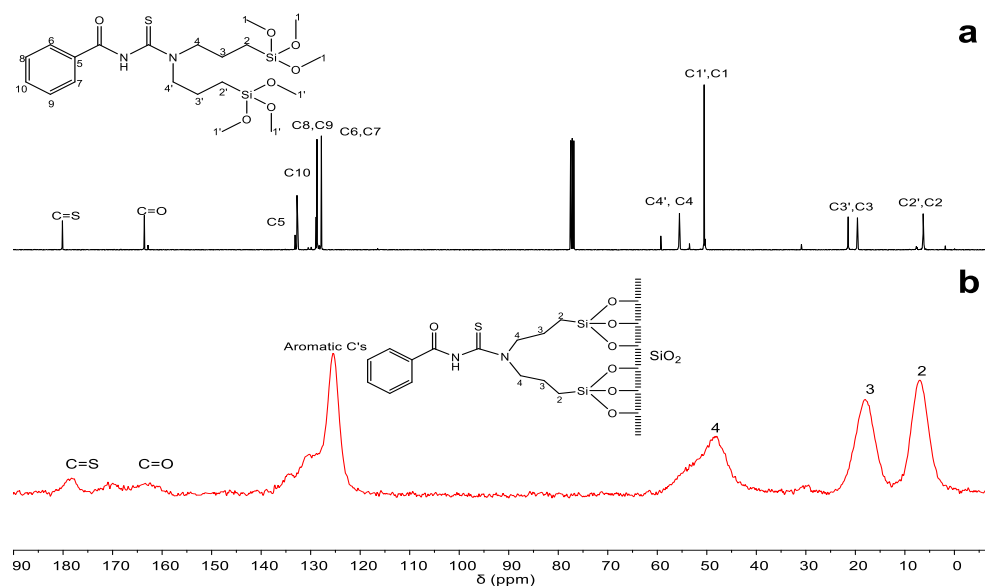

Figure 2 (a) ^{13}C solution NMR spectrum of DTMSP-BT (b) stacked with the ^{13}C solid-state NMR spectrum of the DTMSP-BT-SG.
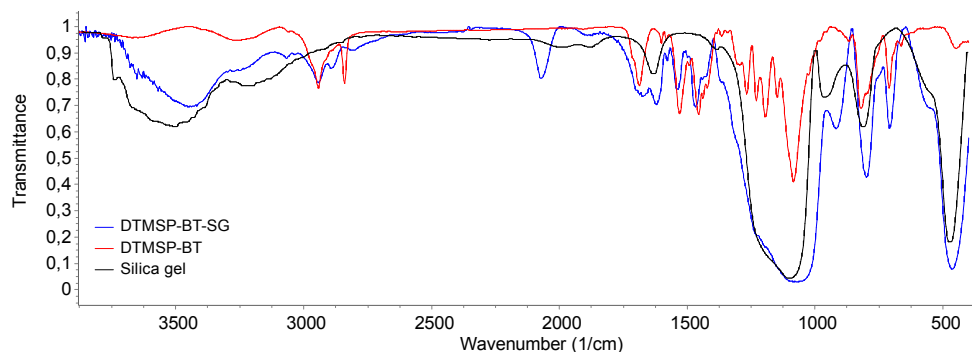
Figure 3 The superimposed FT-IR spectra of silica gel, DTMSP-BT, and DTMSP-BT-SG.

decreased from pH 2-8. The high adsorption of Pt and Pd observed at pH 2-3, can be deduced to occur through ion-pairing, where the dominant and stable Pt and Pd species (PtCl62-, PtCl42-, PdCl42) are attracted to the positively charged adsorbent surface. As the acidity of the metal solution decreases beyond pH 3, aquo chloro complexes i.e. (PtCl5(H2O)-, PtCl4(H2O)2, PdCl3(H2O)– and PdCl2(H2O)2) begin to form, hence the observed decrease in adsorption (Zhou *et al.* 2010). However, the recovery was still significant (>95%). At higher pH values, the donor atoms (O,S,N) no longer function as ion-exchangers or form ion-pairs with the metals but coordinate to the metal species through their lone pairs, hence adsorption still takes place (Tu *et al.* 2011).

Effect of concentration

The effect of initial concentration on the recovery of Pt and Pd by DTMSP-BT-SG was investigated at pH 2 and 5 mg L^{-1} (fig. 5a). The adsorption efficiency for Pt and Pd was high between 2-10 mg L^{-1} and thereafter decreased, with increasing concentration (Ramakul *et al.* 2012; Tu *et al.* 2011).

Adsorption Isotherms

The Langmuir, Freundlich, and Dubinin-Radushkevic (D-R) isotherm models were used to fit the concentration data in order to describe the equilibrium relationship that is established between the adsorbed metals and DTMSP-BT-SG. The Langmuir isotherm (Eq. 3) assumes that the surface of the adsorbent is homogenous with a finite number of sites that have equal energies and are equally available for adsorption, therefore monolayer adsorption of the elements onto the adsorbent sites will be assumed (Sevim *et al.* 2020). The Freundlich (Eq. 4) assumes that the adsorbent's active sites are unequal and have different energies, therefore adsorption takes
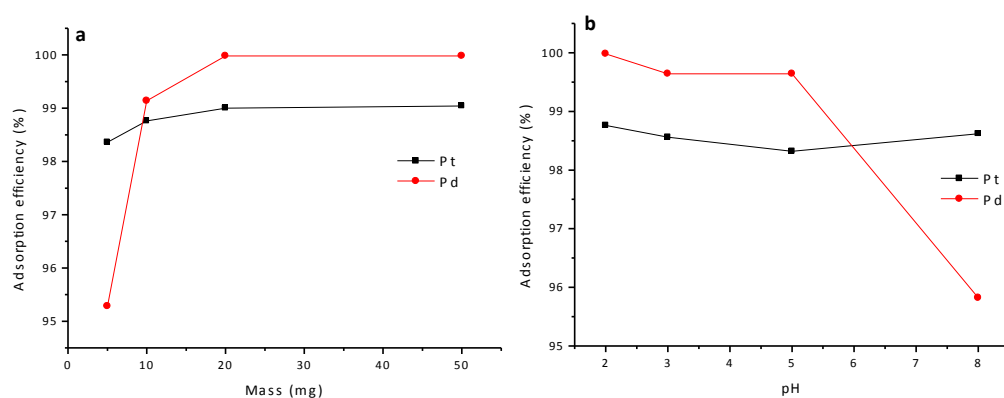

Figure 4 Effect of (a) mass and (b) pH on the recovery of Pt and Pd (time = 4 h, temp = 25 °C)

place onto a heterogeneous surface (Sevim *et al.* 2020). Lastly, the D-R isotherm (Eq. 5) describes the adsorption mechanism between elements and adsorbents with Gaussian energy distribution onto a heterogenous adsorbent surface, furthermore, this model can also be used to confirm whether adsorption takes place through chemical or physical adsorption (Tu *et al.* 2011).

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right) C_e + \left(\frac{1}{K_L q_m}\right) \quad (3)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

$$\ln q_e = \ln X_m - K_{ad} \varepsilon^2 \quad (5)$$

where qm (mg g^{-1}) is the maximum monolayer coverage, K_L (L mol^{-1}) is the Langmuir isotherm constant, K_f ((mg g^{-1})/mol L^{-1})$^{1/n}$) is the Freundlich isotherm constant, n is adsorption intensity, X_m (mg g^{-1}) is the D-R theoretical saturation capacity, K_{ad} (mol^2 (kJ)^2)$^{-1}$) is the D-R isotherm constant and ε (Eq. 6) is the Polanyi constant calculated as:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

where R (8.314 J (mol. K)$^{-1}$) is the universal gas constant and T (K) is the absolute temperature.

The D-R isotherm constant can also be used to estimate the mean free energy (E$_s$) (Eq. 7) of adsorption (Tu *et al.* 2011). The value of E$_s$ (kJ mol^{-1}) can be used to validate the type of adsorption process that takes

place (Sevim *et al.* 2020). The adsorption isotherm data presented in tab. 1 indicated that the Langmuir isotherm best described the experimental data for both Pt and Pd, given the high value of the coefficient of determination (R^2). Thus, there was monolayer adsorption of Pt and Pd onto the adsorbent's surface. The mean free energy for Pt and Pd indicated that the mechanism of adsorption was chemisorption (Mosai *et al.* 2020).

$$E_s = \frac{1}{\sqrt{2K_{ad}}} \quad (7)$$

Effect of time

The effect of contact time on the adsorption of Pt and Pd by DTMSP-BT-SG was investigated at pH 2 (fig. 5b). There was a rapid adsorption of Pt and Pd within the first 60 min, beyond which equilibrium was reached. The rapid increase can be attributed to the high number of active sites that are readily available at the start of the adsorption process (Ramakul *et al.* 2012).

The kinetic models deduced from the time contact data of the elements with the adsorbent can be used to determine whether the adsorption process takes place through chemisorption or physisorption (Ramakul *et al.* 2012). The pseudo-first order (Eq. 8) model assumes that bonding of the elements to the adsorbent occurs via weak Van der Waals forces thus physical adsorption takes
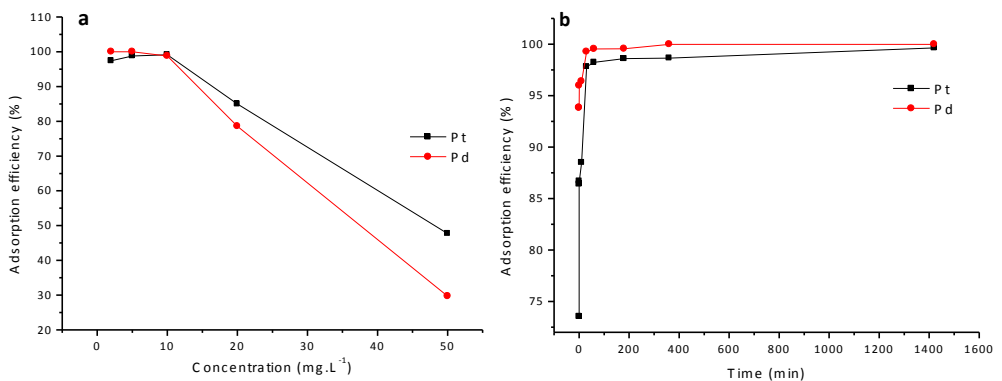

Figure 5 Effect of (a) concentration and (b) contact time on the recovery of Pt and Pd (temp= 25 °C).

Table 1 The isotherm models parameters for the adsorption of Pt and Pd onto DTMSP-BT-SG.

Metal	Langmuir			Freundlich			D-R		
	q_m mg g^{-1}	K_L L mol^{-1}	R^2	n	K_F (mg g^{-1})/ (mol L^{-1})$^{1/n}$	R^2	E_s kJ mol^{-1}	X_m mg g^{-1}	R^2
Pt	48.52	1.85	0.99	3.31	20.86	0.62	3841.69	44.35	0.77
Pd	29.68	-26.74	0.99	7.26	22.86	0.94	14425.55	25.77	0.93

place (Ramakul *et al.* 2012). The pseudo-second order model (Eq. 9) describes the adsorption process to be largely controlled by chemisorption (Sevim *et al.* 2020).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

where q_t (mg g^{-1}) is the amount of metal adsorbed per unit mass of adsorbent at time t, k_1 (min^{-1}) is the pseudo first-order rate constant and k_2 (g mg^{-1}min^{-1}) is pseudo second-order rate constant.

The pseudo second-order model best described the kinetic data since the R^2 was found to be >0.99 for both Pt and Pd. This indicated that chemisorption was the dominant mechanism of adsorption between the metal ions and DTMSP-BT-SG (Mosai *et al.* 2020). The k_2 of Pd uptake by DTMSP-BT-SG was higher than that of Pt, indicating favourable adsorption of Pd than Pt (Zhou *et al.* 2010).

Conclusions

The DTMSP-BT-SG adsorbent was successfully synthesised and efficiently recovered Pt and Pd from aqueous solutions at various conditions mimicking mining wastewater. DTMSP-BT-SG displayed a high Pd and Pt recovery at low concentrations, thus indicating that it can be used to remove these metals from mining wastewaters where the precious metal concentration is low. The ability of DTMSP-BT-SG to remove a considerable amount of Pt and Pd in both the acidic and basic pH makes it a good and competitive potential recovery agent that can applied to remove Pt and Pd from mining wastewaters.

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