Competitive removal of PGMs from aqueous solutions via dendrimer modified magnetic nanoparticles

Joyce T. Khutlane¹ · Klaus R. Koch¹ · Rehana Malgas-Enus¹

Received: 23 March 2020 / Accepted: 15 May 2020 / Published online: 26 May 2020
© Springer Nature Switzerland AG 2020

Abstract

Competitive adsorption of Au(III)- Pd(II)-, and Pt(IV)-chlorido species were carried out using generation 3 diaminobutane poly(propylene) imine dendrimer micelle (**G3-DM15**) and palmitic acid (**C15-acid**) modified superparamagnetic iron oxide nanoparticles (SPIONs). The efficacy of the adsorbents in the recovery of the three metal chlorido species were tested by varying the solution pH and the contact time. SPIONs modified with both the **G3-DM15** and **C15-acid** were not only stable in very acidic conditions (compared to the unmodified SPIONs) but also selective to Au(III)-Cl species with percentage efficiencies of more than 98%. The adsorption of the three metal chlorido species onto the four adsorbents obeyed the Langmuir isotherm. The unmodified SPIONs (**ADS 1**) and dendrimer modified SPIONs (**ADS 2** and **ADS 4**) gave the highest maximum adsorption capacities for Au(III)-Cl species [17.07 mg g^{-1} (**ADS 1**), 6.48 mg g^{-1} (**ADS 2**) and 8.31 mg g^{-1} (**ADS 4**)] compared to SPIONs modified with only C15-acid (**ADS 3**) (1.17 mg g^{-1}). The adsorption kinetics were evaluated using three kinetic models; *pseudo*-first-order, *pseudo*-second-order and intraparticle diffusion. The adsorption kinetics for all the three metal chlorido species best fitted the *pseudo*-second-order kinetics model. Desorption studies showed that all three metal chlorido species can be recovered from the adsorbents.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-020-2922-x>) contains supplementary material, which is available to authorized users.

✉ Rehana Malgas-Enus, rehana@sun.ac.za | ¹Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland, Stellenbosch 7602, South Africa.

SN Applied Sciences (2020) 2:1125 | <https://doi.org/10.1007/s42452-020-2922-x>

Graphic abstract

Schematic representation of adsorbents used to extract PGMs from acidic aqueous media: **ADS 1** (naked SPIONs), **ADS 2** (**G3 DM15**) modified SPIONs), **ADS 3** (**C15-acid** modified SPIONs) and **ADS 4** (SPIONs modified with both **C15-acid** and **G3 DM15**).

Schematic representation of adsorbents used to extract PGMs from acidic aqueous media, and then desorbed from the SPIONs to recover PGMs: **ADS 1** (unmodified SPIONs), **ADS 2** (**G3 DM15**) modified SPIONs), **ADS 3** (**C15-acid** modified SPIONs) and **ADS 4** (SPIONs modified with both **C15-acid** and **G3 DM15**).

Keywords Superparamagnetic nanoparticles · Dendrimer-micelle stabilized nanoparticles · Metal adsorption · Platinum group metals

1 Introduction

Precious metals are widely used in many fields such as catalysis, electrical and electronic industries, biomedicine, jewellery and agriculture because of their remarkable physical and chemical properties [1–3]. Several technologies have been developed to recover precious metals from aqueous solutions and these include precipitation, ion exchange and adsorption [4–7]. Of all the applied technologies, adsorption has been focused on more due to its remarkable efficacy [8–10]. However, separation and recovery of the dissolved precious metals in solution remain a problem and poses a real challenge. Therefore, the search for potentially inexpensive adsorbents to recover precious metals from solution, has acquired attention [3, 11, 12].

Various researchers have examined the potential use of metal oxides, such as iron oxides, manganese oxides and aluminium oxides, as sorbents to recover precious metals from wastewater and leach solutions [13, 14]. Iron oxide nanoparticles in the form of magnetite and maghemite, which are ubiquitous in subsurface environments, have been studied intensively amongst these metal oxides due to their superparamagnetic properties [9, 15]. A few researchers have also studied the use of dendrimers for removal of metal species from aqueous solutions [16–19]. Compared to traditional chelating agents such as triethylenetetraamine, dendrimers have a higher binding capacity [20, 21]. Diallo et al. [22] reported the chelating binding affinities of poly(amidoamine) (PAMAM) dendrimers to Cu(II) ions from an aqueous solution and showed that generation 2, 3, and 6 hydroxyl-terminated PAMAM bind 4, 8, and 64 Cu(II) ions in aqueous solutions, respectively.

The binding affinity of metal species to PAMAM dendrimers indicate that dendrimers could potentially be used as chelating agents to remove metal species from wastewater solutions [16, 22–24]. The encapsulated metal species can be released by deprotonation of the primary and tertiary amine groups on dendrimer scaffolds and the dendrimer recovered for reuse [24]. For instance, Chou and Lien used PAMAM dendrimer-conjugated magnetic nanoparticles (Gn-MNPs) for removal of Zn(II) from aqueous solutions [24]. The Gn-MNPs effectively removed Zn(II) from aqueous solutions, and more than 75% of the total Gn-MNPs were recovered after 10 consecutive cycles.

In this study, we report on the recovery of Au(III)- Pd(II)-, and Pt(IV)- chlorido species from aqueous acidic using unmodified SPIONs as well as SPIONs modified with palmitic acid (**C15-acid**) and/or generation 3 diaminobutane poly(propylene) imine dendrimer micelles (**G3-DM15**). The extraction was carried out in acidic media to mimic the conditions used in the mining industry during extraction

of these metals. **G3-DM15** was prepared by modifying commercially available generation 3 diaminobutane poly(propylene) imine dendrimer with palmitoyl chloride, effectively reducing the cost of using the dendrimer. The adsorption characteristic of the modified SPIONs compared to the unmodified SPIONs were evaluated under various adsorption conditions such as pH and contact time. Desorption studies were conducted using suitable reagent solutions.

2 Experimental

2.1 Materials

All chemicals were purchased from Sigma-Aldrich and Merck and were used without further purification. Deionised water (Milli-Q, 18 M Ω cm) was obtained from the millipore system. Distilled deionised water was deoxygenated by bubbling with pure N₂ gas for 30 min prior to use.

2.2 Characterisation

The pH measurements were carried out using Crison basic 20 plus pH meters that carries a magnetic stirrer and a stand for the sensor. The pH meter was used after calibration with buffer solutions of pH 4.01, 7.01 and 9.01. The pH of the solution was adjusted using 0.1 M NaOH and 0.1 M HCl. A horizontal mechanical shaker (Labcon, BR-30L) was used for agitation of the sample solutions for specified periods. A strong ferrite magnet with a magnetic field strength of ~ 0.35 T was utilised as an external magnetic field for magnetic separation between the aqueous and solid phases. Infrared spectra were recorded using a PerkinElmer spectrum two IR spectrometer. A very small amount of the sample was mixed with dried KBr salt, ground into a fine powder and pressed into a pellet. A pellet of pure KBr was used as the background reference. The spectra were collected between 4000 and 400 cm⁻¹ using 32 scans at a nominal resolution of 4.0 cm⁻¹. All the IR spectra were presented without background correction.

Structural properties of the samples were analysed using powder X-ray diffraction (XRD) with a Siemens D8 Advance diffractometer using Cu K α radiation ($\lambda = 1.540$ Å) operated at 40 kV and 30 mA. XRD patterns were recorded in the range 20°–80° (2 θ) with a scan step of 0.02°. The average crystallite size ($\langle D \rangle$, nm) was calculated from line broadening analysis using the Debye–Scherrer formula (Eq. 1). The full width at half maximum height (FWHM) of the three intense diffraction peaks indexed at (311), (511) and (440) were used to determine the particle size.

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D_{hkl} is the crystallite size (nm), λ is the radiation wavelength, β is the full width at half maximum height (FWHM), θ is the Bragg angle (degrees). The average particle size, particle distribution and morphology were determined using a JEOL-1200EXII electron microscope, high resolution transmission electron microscopy (HRTEM). An accelerating voltage of 250 kV was used throughout. A drop of sample was placed on a carbon-coated 200 mesh copper grid, dried under the UV lamp and then attached to the sample holder. From HRTEM images, more than 250 individual particles were counted using Image J software, a public domain image processing program. The magnetic properties of the adsorbent materials were carried out using the LDJ 9600 Vibrating Sample Magnetometer (VSM) operating at room temperature. A known volume of the sample was placed into the VSM sample holder. A maximum field of approximately 1.3 Ka/M was used. Densities of the samples were determined using an Anton Paar AP DMA 38 density meter.

The metal chlorido species concentration was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with a Liberty Series II spectrometer (Varian, Australia). A standard solution containing a mixture of gold and PGMs with the concentration of 1000 mg L⁻¹ was used. Standards (traceable to NIST) were matrix matched to acid concentrations of the samples. After calibration and a quality check analysis to verify the accuracy of standards, samples were analysed without dilution.

2.3 Synthetic procedures

Unmodified SPIONs (**ADS 1**) were prepared using chemical co-precipitation of FeSO₄·7H₂O (1.16 g) and FeCl₃·6H₂O (2.26 g) in the molar ratio of 1:2. The metal precursors were dissolved in degassed distilled deionised water at 60 °C. Upon dropwise addition of an excess amount of NH₄OH (33%, 12.99 mL), a black precipitate was formed, immediately signifying the formation of the adsorbent, **ADS 1**. The reaction was stirred for a further 30 min to ensure complete precipitation of the metal precursor ions. The black solid was separated by magnetic decantation and washed several times with deionised water until the pH of the supernatant was 7.0. The final product was washed with ethanol (50 mL × 2) and dried at 40 °C in the oven.

The **G3-DM15** modified SPIONs (**ADS 2**) were prepared by dispersing 100 mg of unmodified SPIONs in a degassed chloroform solution containing 25 mg of the generation 3 diaminobutane poly(propylene) imine dendrimer micelles

(**G3-DM15**). The **G3-DM15** was synthesised using the method reported by Stevelmans et al. [25] [see supporting info]. The mixture was stirred for three days at 60 °C. The final product was then separated from the reaction mixture via magnetic decantation and dried in the oven at 40 °C.

The synthesis of **C15-acid** modified SPIONs (**ADS 3**) was performed using the method adapted from Hatton and co-workers [26]. The metal precursors, FeCl₃·6H₂O (2.26 g) and FeSO₄·7H₂O (1.16 g) (molar ratio of 2:1, the total iron concentration was 0.125 M) were dissolved in 100 ml of degassed deionised water. A solution of neat **C15-acid** (0.966 g) in 10 mL acetone was added to the solution and the temperature was increased to 60 °C. This was followed by addition of NH₄OH (33%, 12.99 mL). The temperature was further increased to 90 °C. Formation of a black precipitate was observed signifying the formation of the nanoparticles. The reaction mixture was stirred for 60 min and finally cooled slowly to room temperature. This was followed by washing the resultant nanoparticles with distilled water until the pH of the water was 7 (to remove unreacted salts). To remove an excess of the unreacted **C15-acid**, the product was washed with a mixture of methanol and acetone (3 × 5 mL). Lastly, the product was dried in the oven at 40 °C.

The adsorbent, **ADS 4**, was prepared using freshly produced **C15-acid** (1.00 g) modified SPIONs. The latter was dispersed in 50 mL of degassed methanol/chloroform and the mixture was heated to 35 °C. A solution of **G3-DM15** (200 mg in 20 mL) was added dropwise to the slurry and the reaction mixture was stirred overnight under nitrogen. The resulting product was recovered using magnetic-decantation and dried in the oven at 40 °C.

2.4 Adsorption-desorption experiments

These experiments were carried out in 100 mL reagent bottles. A solution containing a mixture of the three metal chlorido species (Au(III)-Cl, Pd(II)-Cl, Pt(IV)-Cl) species, with appropriate concentration and pH, was added to pre-weighed adsorbent (**ADS 1**, **ADS 2**, **ADS 3** and **ADS 4**). The samples were agitated at 150 rpm for a prescribed period and the adsorbents were recovered from the solution using magnetic decantation and centrifugation. For desorption experiments, 1.0 M HNO₃, 0.5 M thiourea, and a mixture of 1.0 M HNO₃/0.5 M thiourea were used as stripping solutions. A quantity of 10 mL of the stripping solution was added to the appropriate amount of metal-loaded adsorbent. The resultant mixture was shaken at 150 rpm for 2 h. The resultant adsorbent was separated from the solution using magnetic decantation and centrifugation.

Fig. 1 Schematic representation of adsorbents: **ADS 1** (unmodified SPIONs), **ADS 2** (**G3 DM15** modified SPIONs), **ADS 3** (**C15-acid** modified SPIONs) and **ADS 4** (SPIONs modified with both **C15-acid** and **G3 DM15**)

The concentration of the metal chlorido species was determined using ICP-OES. The adsorption capacity was calculated using Eq. 2, the removal efficiency using Eq. 3 and the desorption efficiency by using Eq. 4 [10, 27].

$$q = (C_i - C_{aq}) \frac{V}{m} \quad (2)$$

$$\text{Re}(\%) = \frac{(C_i - C_{aq})}{C_i} \times 100\% \quad (3)$$

$$\text{De}(\%) = \frac{C'_e V}{qm} \times 100\% \quad (4)$$

where q is sorption capacity (mg g^{-1}), %Re is the percentage of the metal removed from solution, C_i is initial metal chlorido species concentration (mg L^{-1}), C_{aq} represents metal chlorido species concentration in aqueous solution (mg L^{-1}) after sorption, V represents volume of the aqueous phase (L), m mass of the adsorbent (g) and C'_e (mg L^{-1}) is the concentration of metal chlorido species after desorption.

Fig. 2 Infrared spectra of **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4** **Fig. 3** TGA and DTA analysis of **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4**

3 Results and discussion

3.1 Synthesis of the adsorbents

ADS 1 was prepared using the chemical co-precipitation method, while the other adsorbent materials (**ADS 2**, **ADS 3** and **ADS 4**) were prepared by modifying the surface of unmodified SPIONs with **G3-DM15** and/or **C15-acid**, as discussed in the experimental section of this paper. The schematic representation of the four adsorbents are shown in Fig. 1.

3.2 Characterisation of the adsorbents

The IR analysis was used to study the coordination of the organic moieties to the surface of the SPIONs. Figure 2 shows the overlaid IR spectra of **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4** respectively. The spectrum of **ADS 1** shows

Fig. 4 Powder XRD analysis of **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4**

absorption bands at around 3450 cm^{-1} and 1636 cm^{-1} ascribed to water molecules absorbed during sample preparation. The IR spectrum of **ADS 2** shows absorption bands at 1629 cm^{-1} and 1467 cm^{-1} due to the C=O stretch of the amide. Compared to the absorption bands of the neat **G3-DM15** [see supporting info, Fig S1], the absorption bands observed shifted to lower wavenumbers indicating that **G3-DM15** bound to the surface of **ADS 1** through the C-O functional group [28]. Due to the large density of the alkyl chains of the dendrimer micelle, it is possible that the nanoparticles were also stabilised by electrostatic interactions of the alkyl chains of the dendrimer micelles. The absorption bands corresponding to $\nu_{as}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ stretches can be seen at 2922 cm^{-1} and 2852 cm^{-1} respectively.

The spectrum of **ADS 3** shows absorption bands corresponding to $\nu_{as}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ at 2918 cm^{-1} and

2850 cm^{-1} respectively whereas absorption bands of $\nu_{as}(\text{-COO}^-)$ and $\nu_s(\text{-COO}^-)$ can be seen at 1407 cm^{-1} and 1571 cm^{-1} respectively. The spectrum of **ADS 4** displayed the absorption bands at 1641 cm^{-1} and 1551 cm^{-1} which is consistent with carbonyl amide groups and the 1560 cm^{-1} which is attributed to C-N stretches of **G3-DM15**. The C=O stretching band observed in the spectrum of **ADS 4** at around 1716 cm^{-1} shows that the dendrimer did not replace the **C15-acid** chemisorbed onto the surface of the SPIONs but rather formed a second layer. All the spectra show a strong absorption band at around 580 cm^{-1} assigned to the Fe-O stretching vibrational mode of SPIONs. The band broadening observed in the spectra of modified SPIONs compared to the spectrum of neat **G3-DM15** indicates that these organic moieties were coordinated to the surface of the SPIONs [29–32].

Fig. 5 HRTEM images and the corresponding histogram of **ADS 1**, **ADS 2** and **ADS 3**

Fig. 6 HRTEM images of **ADS 4** **Table 1** The saturation magnetisation and average particle sizes of the adsorbents determined from PXRD diffraction data and HRTEM analysis

Sample	PXRD mean particle size (nm)	HRTEM mean particle size (nm)	Ms (emu g ⁻¹)
ADS 1	11.4 ± 0.1	11.6 ± 1.7	80.41
ADS 2	13.2 ± 0.3	13.5 ± 2.0	79.78
ADS 3	13.5 ± 0.3	13.7 ± 1.9	77.38
ADS 4	10.3 ± 0.5	–	71.66

Thermal analysis (TGA and DTA) was done to corroborate the infrared results, the weight loss profile of the four adsorbents are shown in Fig. 3. All the curves show broad weight losses indicating decomposition of the organic moieties from the surface of the nanoparticles. The weight loss profile of **ADS 1** exhibited one significant weight loss ranging from 50 to 100 °C which can be assigned to the loss of moisture absorbed during sample preparation. The TGA curves of **ADS 2** shows weight loss from 250 to 500 °C. The weight loss profile of **ADS 3** shows weight loss in the range of 200–400 °C which is ascribed to the **C15-acid** found on the surface of the nanoparticles. However, the weight loss profile of **ADS 4** shows two distinct weight losses indicating that **ADS 4** was supported with two layers of organic moieties. The first weight loss can be attributed to the **G3-DM15**, while the second weight loss can be assigned to the **C15-acid** as it forms a coordinate bond with the surface of the SPIONs. The corresponding differential thermal analysis (DTA) curves of the three adsorbents clearly indicate the decomposition of the organic moieties in the temperature range of 250–500 °C compared to **ADS 1** which does not show any decomposition in that temperature range.

Powder XRD analysis was used to determine the crystal structure and size of the adsorbents. Figure 4 shows overlaid diffractograms of all four adsorbents. As seen in the figure, all the samples exhibit diffraction peaks with Miller

Fig. 7 The concentration of iron leached from 30.43 ± 0.05 mg of **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4** at pH 1.0, 2.0, and 3.0 at room temperature 25 ± 2 °C. The volume of the samples was 10 mL and the shaking speed was 150 rpm

index (*hkl*) values of (220), (311), (400), (422), (511) and (440). These diffraction peaks matched that of the standard magnetite sample, as per JCPDS cards No. 00-016-0653. The absence of other diffraction peaks that do not correspond to magnetite is an indication that all the samples were single phase with spinel cubic structure. Hence, all the four adsorbents maintained their crystal structure after modification.

The HRTEM images of all the adsorbents and their corresponding particle size histograms are shown in Fig. 5. All three images show nanoparticles that are mostly spherical. Comparing the HRTEM images of unmodified **ADS 1** and the modified SPIONs (**ADS 2** and **ADS 3**), the shape of the particles looks similar. The average particle sizes of **ADS 2** and **ADS 3** were 13.5 ± 2.0 nm and 13.7 ± 1.9 nm respectively. Comparing the average particle size of **ADS 1** which is 11.6 ± 1.7 nm to **ADS 4**, the particles slightly increased in size and this is most

probably due to the high temperature (60 °C) used during the modification. At high temperatures, the nanoparticles tend to easily interact with each other and hence agglomerate easily. Therefore, a small increase in the average size of the particles **ADS 2** and **ADS 3** demonstrated the efficacy of **G3-DM15** in preventing the agglomeration of these particles.

The HRTEM image of **ADS 4** clearly shows small nanoparticles trapped within a mesh-like material (Fig. 6). Due to this entrapment, it was difficult to count the nanoparticles. Presumably, this mesh-like material was formed by the intercalation of the alkyl chains of the **G3-DM15** and **C15-acid** as shown in Fig. 1. This confirms the observations made from the infrared and TGA results as discussed earlier, indicating that the **ADS 4** was stabilised with both **G3-DM15** and **C15-acid**, forming a double layer of these two moieties on the surface of the nanoparticles. The average particle sizes of all the adsorbent molecules was determined powder X-Ray diffraction and HRTEM analysis. The results for the particle size analysis of the adsorbents using both techniques are shown in Table 1. The average particle sizes of the four adsorbents determined using PXRD and HRTEM are in good agreement, indicating the accuracy of both techniques for determining the size of SPIONs.

Modification of the magnetic nanoparticles can have a significant effect on their final magnetic moments. Therefore, the magnetic moments of the four adsorbents were evaluated using vibrating Sample Magnetometry before and after modification and the results are as shown in Table 1. The adsorbent, **ADS 1**, exhibited very high saturation magnetisation which is close to the expected value for bulk magnetite. The magnetic saturation of the other adsorbents (**ADS 2**, **ADS 3** and **ADS 4**) which have been modified with the organic moieties were 79.78 emu g⁻¹, 77.38 emu g⁻¹ and 71.66 emu g⁻¹, respectively. The magnetic susceptibility of the latter showed a decrease in values, and this was attributed to the surfaces that might have been masked by these organic molecules.

Table 2 Speciation of Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species at different pH

Metal chlorido species	pH 1.0	pH ≤ 2.5 and 3.0	pH = 3.0–5.0
Au(III)-Cl	AuCl ₄ ⁻	AuCl ₄ ⁻	AuCl ₄ ⁻ , AuCl ₃ OH ⁻ , AuCl ₂ (OH) ₂ ⁻ , AuCl(OH) ₃ ⁻
Pd(II)-Cl	PdCl ₄ ²⁻	PdCl ₄ ²⁻ , PdCl ₂ (H ₂ O) ₂	PdCl ₃ (H ₂ O) ⁻ , Pd(OH) ₂
Pt(IV)-Cl	PtCl ₆ ²⁻	PtCl ₅ (H ₂ O) ⁻	PtCl ₅ (OH) ²⁻

3.3 Stability of the adsorbents

The stability of the adsorbents in acidic solutions were investigated by conducting Fe leaching experiments. The adsorbents were dispersed in aqueous HCl solutions at a pH of 1.0, 2.0 and 3.0. The mixture was shaken at 150 rpm for 2 h. The concentration of Fe leached into solution was determined by ICP-OES. From Fig. 7, it is clear that for **ADS 1** at the pH of 1.0, a high concentration of Fe was leached into the solution. The same was observed for **ADS 2** and **ADS 3**, albeit to a lesser extent, indicating that modification of the naked SPIONs improved nanoparticle stability. The adsorbent, **ADS 4**, shows no leaching of Fe at a pH of 1, demonstrating its stability at very low pH's. At the pH of 2.0 and 3.0, the dissolution of all the four adsorbents, including **ADS 1** was significantly reduced. Vatta et al. [33] also reported that the stability of unmodified SPIONs was improved after their functionalisation with silica.

3.4 Adsorption studies

All four adsorbents were used in the competitive adsorption of Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species from acidic aqueous solution.

3.4.1 Effect of pH

The effect of pH in adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species by **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4** was evaluated by conducting competitive batch experiments at a pH range of 1.0–6.0. The pH of the solution plays a vital role in the sorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species by **ADS 1** from aqueous solutions. The pH affects the distribution of active sites and the hydroxyl groups (-OH) found on the surface of **ADS 1** where the cations or anions bind. The pH_{ZPC} of **ADS 1** is in the range of 6.0–8.2 [34]. At pH less than the point of zero charge (pH_{ZPC}), the surface of **ADS 1** is positively charged, whereas at a pH > pH_{ZPC}, the surface of **ADS 1** is negatively charged.

The pH of the solution alters the speciation of the Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl. At pH < 4, Au(III)-Cl species exist as a square planar complex, AuCl₄⁻ [9, 15]. Increasing the pH to pH > 4.0 changes Au(III)-Cl species to negatively charged anions (AuCl₃OH⁻, AuCl₂(OH)₂⁻, AuCl(OH)₃⁻ etc.) [14, 34, 35]. Similarly for Pd(II)-Cl and Pt(IV)-Cl species, at pH ≤ 3.0, Pd(II)-Cl and Pt(IV)-Cl species forms the following species: PdCl₄²⁻, PdCl₂(H₂O)₂, PtCl₆²⁻ and PtCl₅(H₂O)⁻ respectively. A pH of pH ≥ 3.5 to basic conditions causes hydrolysis of these species to PdCl₃(H₂O), Pd(OH)₂, PtCl₅(H₂O)⁻ and PtCl₅(OH)²⁻ species respectively [36, 37]. Therefore, under the experimental conditions employed, the anionic complexes formed by Au(III)-Cl,

Fig. 8 Effect of pH in adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using 30.99 ± 0.59 mg **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4** from acidic aqueous solutions at room temperature 25 ± 2 °C. Initial

metal chlorido species concentrations [(Au(III)-Cl: 9.78 ± 0.20 ppm, Pd(II)-Cl: 10.61 ± 0.59 ppm, Pt(IV)-Cl: 10.24 ± 0.59 ppm]. The volume of the samples was 10 mL and were shaken at 150 rpm

Pd(II)-Cl and Pt(IV)-Cl species have been summarised in Table 2.

ADS 1 removed 100% of Au(III)-Cl species from solution at all pH's (Fig. 8). This shows that **ADS 1** has a high adsorption affinity towards the Au(III)-Cl species. On the other hand, removal efficiencies of the Pd(II)-Cl species increased significantly with an increase in pH. However, during the sample preparation, it was observed that at pH > 4.0, Pd(II)-Cl species precipitated out of solution. Hence, the high adsorption efficiency observed at pH 5.0 and pH 6.0 cannot be solely attributed to adsorption of the Pd(II)-Cl species. The adsorption efficacies for Pt(IV)-Cl species by **ADS 1** reached a maximum of about 60% at pH 3.0 and remained constant until pH 6.0. Therefore, the optimum adsorption of Pt(IV)-Cl species using **ADS 1** is at pH 3.0.

ADS 2 shows higher adsorption affinities towards Au(III)-Cl species than Pd(II)-Cl and Pt(IV)-Cl species. However, the figure also shows improved adsorption efficiency for Pd(II)-Cl and Pt(IV)-Cl species compared to **ADS 1**. Therefore, an increase in adsorption efficiency of Pd(II)-Cl and Pt(IV)-Cl species suggest that the **G3-DM15** plays a

vital role in adsorption of these precious metal chlorido species. Chassary et al. [8] reported that in acidic solution, although amine groups may contribute to metal chelation, their protonation significantly reduces their ability to react with Au, Pt and Pd species. Based on this finding, in acidic medium, the adsorption mechanism of these species on **ADS 2** is assumed to be electrostatic and via ion exchange.

ADS 3 selectively adsorbed Au(III)-Cl species at pH 1.0. However, increasing the pH resulted into a decrease in percentage efficiency. Higher adsorption efficiency for Pd(II)-Cl species are observed at pH > 4.0. As stated earlier, this might be attributed to the precipitation of the Pd(II)-Cl species. It was also observed that only a fraction of **ADS 3** dispersed into the solution. This was ascribed to the hydrophobicity of the adsorbent, due to the large mass of alkyl chain functionalities from the **C15-acid**.

ADS 4 removed 100% of Au(III)-Cl species, showing a higher adsorption affinity for these species over Pd(II)-Cl and Pt(IV)-Cl species. Compared to **ADS 3** which was also modified with only **G3-DM15**, **ADS 4** showed improved adsorption efficiency for Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl

Fig. 9 Effect of contact time on adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using 30.23 ± 0.01 mg of **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4** at room temperature (25 ± 2 °C). Initial metal chlorido species concentrations (Au(III)-Cl: 12.01 ± 0.50 ppm, Pd(II)-Cl: 12.50 ± 0.59 ppm, Pt(IV)-Cl: 12.03 ± 0.40 ppm), aqueous phase 10 mL and shaking speed was 150 rpm

species at all pH values. The improvement in adsorption efficiency of Au(III)-Cl species by **ADS 4** as compared to **ADS 3** indicates that **G3-DM15** played a crucial part in the competitive adsorption of these species. At the pH range of pH 1.0 to pH 3.0, adsorption could be ascribed to electrostatic attraction between the protonated amines and the negatively charged Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species. However, adsorption efficiency of Pd(II)-Cl species using **ADS 4** increased with an increase in solution pH due to the precipitation of Pd(II)-Cl at pH > 4.0.

3.4.2 Effect of time

The effect of contact time is another important parameter when describing adsorption of metal chlorido species from aqueous solution. Batch adsorption experiments were carried out to study the effect of contact time (5–160 min) in adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4**. The results are shown in Fig. 9. Adsorption efficiency of each respective metal chlorido species increase with time. Nonetheless, the adsorption equilibrium for adsorption of Au(III)-Cl species using **ADS 1** was reached after 80 min, while

adsorption equilibrium for Pd(II)-Cl and Pt(IV)-Cl species was reached within 5 min. **ADS 1** achieved 100% removal of Au(III)-Cl species confirming its high affinity for Au(III)-Cl species. On the contrary, adsorption efficiency of Pd(II)-Cl and Pt(IV)-Cl species only reached a maximum removal of 30%. The adsorption equilibria for the three metal chlorido species was reached after 120 min. **ADS 2** is more selective towards Au(III)-Cl than Pd(II)-Cl and Pt(IV)-Cl species as 100% of Au(III)-Cl species was adsorbed compared to about 70% adsorption efficiency of Pd(II)-Cl and Pt(IV)-Cl species. **ADS 3** exhibited lower adsorption efficiency for Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species. This can be attributed to poor interaction between the adsorbent and the metal chlorido species solution as this adsorbent did not disperse in solution like the other three. In comparison, competitive adsorption of Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species using **ADS 4** at pH 3.0 showed improved adsorption efficiency and was more selective towards Au(III)-Cl species.

Fig. 10 *Pseudo*-first-order kinetic plots for adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 1** at room temperature (25 ± 2 °C). Initial species concentrations [(Au(III)-Cl: 12.01 ± 0.50 ppm, Pd(II)-Cl: 12.50 ± 0.59 ppm, Pt(IV)-Cl: 12.03 ± 0.40 ppm], aqueous phase; 10 mL, shaking speed; 150 rpm

3.4.3 Adsorption kinetics

Adsorption of the Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 1** was fitted using three kinetic models namely the *pseudo*-first-order, *pseudo*-second-order and intraparticle diffusion kinetic model. These kinetic models are normally used to describe the adsorption of metal species using different solid supports [10, 23, 38, 39]. The *pseudo*-first-order kinetics model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The rate of the adsorptive interactions can be calculated by using the Lagergren equation shown in Eq. 5, integrating the equation between the limits $t=0$ to $t=t$ and $q=0$ to $q=q_e$ gives a linear equation shown in Eq. 6,

$$\frac{dq}{dt} = K_1 (q_e - q_t) \quad (5)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where q_e and q_t are the amounts of adsorbed metal chlorido species (mg g^{-1}) on the adsorbent at equilibrium and at any time t , respectively, and k_1 (min^{-1}) is the *pseudo*-first-order rate constant. The *pseudo*-first-order plot of $\log(q_e - q_t)$ versus time for Au(III)-Cl, Pt(IV)-Cl and Pd(II)-Cl species using **ADS 1** is shown in Fig. 10. The data points were fitted for the whole sorption period and the correlation coefficients (R^2) were 0.8329, 0.8277 and 0.4060 for Au(III)-Cl, Pt(IV)-Cl and Pd(II)-Cl species, respectively. This suggests that adsorption of Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species using **ADS 1** does not follow the *pseudo*-first-order kinetics model.

The R^2 values and other *pseudo*-first-order kinetics model parameters for adsorption with the four adsorbents are shown in Table 3. The R^2 values for competitive adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 2**, **ADS 3**, and **ADS 4**, are in the range of 0.5173–0.8543, 0.0212–0.4493 and 0.0864–0.8268 respectively. Furthermore, calculated q_e values do not match the experimental q_e values. For instance, the calculated q_e values for the adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 1** which were 2.182 mg g^{-1} , 0.506 mg g^{-1} , and 0.506 mg g^{-1} , do not match the experimental values. Therefore, the low R^2 values and disagreement between the calculated q_e values and experimental q_e values suggest that adsorption of these three metal chlorido species cannot be described by the *pseudo*-first-order kinetics model.

The *pseudo*-second-order kinetics model can be described using Eq. 7, which on integration becomes Eq. 8,

$$\frac{dq}{dt} = K_2 (q_e - q_t)^2 \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the rate constant of *pseudo*-second-order kinetics, q_e and q_t are the amount of metal chlorido species adsorbed (mg g^{-1}) at equilibrium and time t respectively. The slope and intercept of the linear plot t/q_t versus t yielded the values of q_e and k_2 . Again, the initial sorption rate (h) can be determined from k_2 and q_e values using $h = k_2 q_e^2$. The *pseudo*-second-order kinetics plot for competitive adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 1** is shown in Fig. 11. The

Table 3 Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models for competitive adsorption of Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species

ADS	Metal chlori- dospecies	Pseudo-first-order (mg g^{-1})		Pseudo-second-order kinetics		Pseudo-second-order kinetics		Intraparticle diffusion	
		$q_{e(\text{exp})}$	k_1 (min^{-1})	$q_{e(\text{cal})}$ (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	h ($\text{mg g}^{-1} \text{min}^{-1}$)	k_d ($\text{mg g}^{-1} \text{min}^{-0.5}$)	R^2
ADS 1	Au(III)	3.98	0.039	2.182	0.8329	0.004	0.65	0.282	0.8088
	Pd(II)	1.23	0.080	0.506	0.406	0.25	0.18	0.0572	0.5802
	Pt(IV)	1.49	0.022	0.506	0.8277	0.21	0.46	0.0518	0.8869
ADS 2	Au(III)	3.98	0.03	1.48	0.5173	0.08	1.23	0.291	0.6694
	Pd(II)	2.72	0.04	2.58	0.8543	0.07	0.55	0.255	0.8220
	Pt(IV)	5.45	0.02	3.74	0.7346	0.04	1.23	0.514	0.8979
ADS 3	Au(III)	0.69	0.004	0.064	0.0212	3.12	1.48	-0.025	0.5364
	Pd(II)	0.48	0.001	0.210	0.0083	0.74	0.15	-0.001	0.0031
	Pt(IV)	0.07	0.014	0.064	0.4493	0.48	0.07	0.0025	0.0376
ADS 4	Au(III)	3.89	0.024	3.940	0.8268	0.05	0.68	0.560	0.8014
	Pd(II)	0.91	0.046	1.023	0.8203	0.88	0.76	0.142	0.6026
	Pt(IV)	0.66	0.020	1.118	0.0864	0.44	0.20	0.140	0.8726

Fig. 11 Pseudo-second-order kinetic plots for adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using 30.15±0.05 mg of ADS 1 at room temperature (25±2 °C). Initial species concentrations [(Au(III)-Cl: 12.01±0.50 ppm, Pd(II)-Cl: 12.50±0.59 ppm, Pt(IV)-Cl: 12.03±0.40 ppm], aqueous phase; 10 mL, shaking speed; 150 rpm

Fig. 12 Intraparticle size kinetic plots for adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using 30.15±0.05 mg of ADS 1 at room temperature (25±2 °C). Initial species concentrations [(Au(III)-Cl: 12.01±0.50 ppm, Pd(II)-Cl: 12.50±0.59 ppm, Pt(IV)-Cl: 12.03±0.40 ppm], aqueous phase; 10 mL, shaking speed; 150 rpm

R^2 values for Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species were 0.9950, 0.9912, and 0.9946 respectively.

The calculated q_e values which are 4.13 mg g^{-1} , 0.85 mg g^{-1} and 1.49 mg g^{-1} agree with the experimental q_e values (3.98 mg g^{-1} , 1.23 mg g^{-1} and 1.49 mg g^{-1}). The pseudo-second-order kinetics parameter for adsorption of the three metals species using ADS 2, ADS 3, and ADS 4 are also presented in Table 3. The R^2 values for pseudo-second-order kinetics linear plot are in the following ranges: 0.9977–0.9994, 0.9927–0.9983, and 0.9814–0.9959 for adsorption using ADS 2, ADS 3, and ADS 4, respectively. The calculated q_e values correlates well with the

experimental q_e values. For example, the calculated q_e values for adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 3** were 0.69 mg g^{-1} , 0.46 mg g^{-1} , and 0.06 mg g^{-1} corresponds with the experimental q_e which are 0.69 mg g^{-1} , 0.48 mg g^{-1} , and 0.07 mg g^{-1} , respectively. The *pseudo*-second-order kinetics model seems to be the best kinetic model used to describe adsorption of metal species using various nano-materials [10, 40, 41]. For instance, Liu et al. [10] studied the adsorption kinetics of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using graphene oxide (GO) and this could be described by the *pseudo*-second-order kinetic model. In another study, Kraus et al. [42] studied adsorption of Au(III)-Cl species using cobalt ferrite (CoFe_2O_4) modified with (3-mercaptopropyl)trimethoxysilane (MPTS). The adsorption kinetics data best fitted the *pseudo*-second-order kinetic model with correlation

coefficients higher than 0.999. The *pseudo*-second-order kinetics model assumes that there is transfer of electrons between adsorbent and adsorbate.

The third model is also used as a basis to study whether the intraparticle diffusion is the rate determining step during the sorption process. This model assumes that the movement of sorbate molecules into the interior of sorbent particles is the rate determining step in the sorption process [41]. According to the model, the mass transfer rate can be expressed as a function of the square root of time and can be described using Eq. 9,

$$q_t = k_{id}t^{0.5} \quad (9)$$

where k_{id} ($\text{mg g}^{-1} \text{ min}^{-0.5}$) is the intraparticle diffusion rate constant, which can be obtained from the slope of the plot q_t versus $t^{0.5}$.

If the plot is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. The adsorption kinetics model for adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species was also fitted on intraparticle diffusion model. Figure 12 shows intraparticle diffusion kinetics linear plot for adsorption of Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species using **ADS 1**.

As seen in the figure, the data points showed multi-linearity with two different stages of adsorption, suggesting that the intraparticle diffusion kinetics model is not a limiting step. All the kinetics parameters extrapolated from the intraparticle diffusion equation are shown in Table 3.

Fig. 13 Langmuir isotherm linear plots of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species adsorption using $30.15 \pm 0.05 \text{ mg}$ of **ADS 2** at room temperature ($25 \pm 2^\circ \text{C}$). Other experimental conditions: $[\text{M}-\text{Cl}]$: $1.00\text{--}90 \text{ mg L}^{-1}$, aqueous phase; 10 mL , shaking speed; 150 rpm

3.4.4 Adsorption isotherms

Langmuir and Freundlich isotherm equations have been used to predict adsorption abilities of Au(III)-Cl, Pt(IV)-Cl and Pd(II)-Cl species by the four adsorbent materials (**ADS 1**, **ADS 2**, **ADS 3** and **ADS 4**) from acidic solutions.

Table 4 Langmuir and Freundlich parameters for the adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species from acidic aqueous solutions

Adsorbents	M-Cl	Langmuir			Freundlich		
		q_{max} (mg g^{-1})	b	R^2	K_F	n	R^2
ADS 1	Au(III)	17.01	0.039	0.9999	13.78	10.11	0.7973
	Pd(II)	2.01	0.17	0.9991	3.23	6.38	0.6425
	Pt(IV)	4.02	0.07	0.9981	2.94	20.49	0.2363
ADS 2	Au(III)	6.48	0.052	0.9973	4.03	5.65	0.6044
	Pd(II)	3.97	0.08	0.9982	2.78	7.12	0.6580
	Pt(IV)	4.02	0.07	0.9975	3.23	7.84	0.5002
ADS 3	Au(III)	1.17	0.46	0.9647	2.99	3.093	0.4045
	Pd(II)	1.15	0.63	0.9384	2.02	6.22	0.4534
	Pt(IV)	1.12	0.41	0.9642	3.28	2.65	0.3767
ADS 4	Au(III)	8.31	0.04	0.9949	3.67	4.35	0.7538
	Pd(II)	2.26	0.15	0.9874	1.97	1.63	0.3342
	Pt(IV)	3.82	0.06	0.9231	0.61	1.36	0.9944

Fig. 14 Freundlich isotherms linear plots of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species adsorption using 30.15 ± 0.05 mg of **ADS 2** at room temperature (25 ± 2 °C). Other experimental conditions: [M-Cl]: $1.00\text{--}90$ mg L⁻¹, aqueous phase; 10 mL, shaking speed; 150 rpm

These two models are the most frequently used equilibrium adsorption isotherm models in the literature. The Langmuir model is based on monolayer adsorption on the active sites of the adsorbent. Theoretically, therefore, a saturation value is reached, beyond which no further adsorption can take place. The Freundlich model explains the adsorption on a heterogeneous (multiple layers) surface with uniform energy.

The linear form of Langmuir sorption model is given as Eq. 10,

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (10)$$

where q_e is the amount of adsorbed metal species per unit weight of adsorbent (mg g⁻¹), C_e is the concentration of the free metal species in solution (mg L⁻¹), $q_{\max}$ the maximum adsorbed metal species per unit weight of the adsorbent (mg g⁻¹), and k_L is the Langmuir constant (L mg⁻¹) which is related to the energy of sorption. This

Fig. 15 Desorption of Au, Pd, and Pt from 30.22 ± 0.85 mg of **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4** loaded with the metals. Other conditions: room temperature (25 ± 2 °C), total aqueous phase: 10 mL, shaker speed; 150 rpm

constant can be calculated from the intercept and slope of the linear plot, with C_e/q_e versus C_e .

The adsorption of all three chlorido species using **ADS 2** were fitted onto a linear Langmuir equation as shown in Fig. 13. As depicted by the figure, the Langmuir model represents a good fit of the experimental data. The corresponding Langmuir parameters along with corresponding coefficients (R^2) for adsorption of the three chlorido species by adsorbent **ADS 2**, **ADS 3** and **ADS 4** are listed in Table 4. All the R^2 values were above 90% and this indicates that the adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using all the four adsorbents followed the Langmuir adsorption isotherm. The maximum adsorption capacity for adsorption of Au(III)-Cl, Pd(II) and Pt(IV) species using **ADS 1** were 17.007 mg g⁻¹, 2.01 mg g⁻¹ and 4.02 mg g⁻¹ respectively.

The Freundlich model explains the sorption on a heterogeneous (multiple layers) surface with uniform energy. This model can be represented using the linearized equation (Eq. 11).

$$\log q_e = \log K_F + \frac{1}{n} \times \log C_e \quad (11)$$

where q_e is, the equilibrium loading capacity (mg g⁻¹), C_e is the equilibrium metal concentrations in the aqueous phase (mg L⁻¹), K_F is the Freundlich constant (L mm⁻¹ g⁻¹), and n is the heterogeneity factor associated with the Freundlich model. k_F and n are related to the sorption capacity and intensity, respectively. These constants can be calculated from the slope and intercept of the linear plot, with $\log q_e$ versus $\log C_e$.

Figure 14 shows the Freundlich linear plot for adsorption of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species using **ADS 2**. The R^2 values and the other parameters are presented in Table 4. The R^2 values for adsorption of Au(III), Pd(II) and Pt(IV) species using **ADS 1**, **ADS 3** and **ADS 4** are in the range of [(0.2432–0.7700), (0.0254–0.5921), and (0.00588–0.9474)] respectively. All the R^2 values are generally very low except for the linear adsorption of Pt(IV)-Cl species using **ADS 4**, suggesting that adsorption of these three metal chlorido species cannot be described using Freundlich adsorption isotherm.

3.5 Desorption studies

The adsorbents recovered from these adsorption experiments were dried in the oven at 40 °C. A batch method was used to study the desorption of Au(III), Pd(II)-Cl, and Pt(IV)-Cl species from **ADS 1**, **ADS 2**, **ADS 3** and **ADS 4**. The results are shown in Fig. 15. This was carried out using the following stripping solutions: 1.0 M HNO₃, 0.5 M thiourea, and a mixture of 1.0 M HNO₃/0.5 M thiourea solution. Several researchers used similar stripping solutions to recover

Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species [10, 27]. The graph shows that the three stripping solutions released different amounts of metal chlorido species from the adsorbent. For instance, 1.0 M HNO₃ selectively stripped Pd(II)-Cl and Pt(IV)-Cl species from **ADS 1** over Au(III)-Cl species. This suggests that Au(III)-Cl species were bound to the adsorbent **ADS 1**. Therefore, 1.0 M HNO₃ was not aggressive enough to strip it from the surface of **ADS 1**.

On the other hand, 0.5 M thiourea released 55%, 65% and 62% of Au(III)-Cl, Pd(II)-Cl, and Pt(IV)-Cl species respectively from **ADS 1**. The mixture of the two stripping solutions (1.0 M HNO₃/0.5 M thiourea) desorbed all three metal chlorido species equally from **ADS 1**. Desorption of the metal chlorido species from **ADS 2** with 1.0 M HNO₃ only released Pt(IV)-Cl species. The other stripping solutions released all three metal chlorido species into the solution and the desorption efficiency of 1.0 M HNO₃/0.5 M thiourea is higher than 0.5 M thiourea. These results suggest that the mixture of 1.0 M HNO₃/0.5 M is the best stripping solution. As for adsorbent **ADS 3** and **ADS 4**, only 1.0 M HNO₃/0.5 M thiourea released some of the metal chlorido species into the solution. This solution was the best solvent for adsorbent **ADS 3** which is selective to Au(III)-Cl species.

4 Conclusion

The unmodified and modified SPIONs proved to be efficient adsorbent materials for the competitive adsorption of Au(III)-Cl, Pd(II)-Cl and Pt(IV)-Cl species from acidic aqueous solutions. Successful modification of the unmodified SPIONs was confirmed using infrared spectroscopy, TGA, PXRD and HRTEM analysis. Leaching experiments in aqueous HCl solutions at the pH range of 1.0–6.0 confirmed that modified SPIONs (**ADS 2**, **ADS 3** and **ADS 4**) were more stable than the unmodified **ADS 1**, with **ADS 4** being the most stable adsorbent (at pH 1.0) demonstrating the efficacy of using both **C15-acids** and **G3-DM15** as stabilisers for unmodified SPIONs. All four adsorbents were evaluated in adsorption of the three metal chlorido species by varying the solution pH and the contact time. All the adsorbents generally removed higher percentiles of Au(III)-Cl species over Pd(II)-Cl and Pt(IV)-Cl species. **ADS 1** was selective towards Au(III)-Cl species at a pH of 1.0 but was very unstable at this low pH. On the contrary, **ADS 4** was not only more selective to Au(III)-Cl species at the pH of 1.0 but was also stable at this pH. Furthermore, comparing the adsorption efficiency of Pd(II)-Cl and Pt(IV)-Cl species using **ADS 1** and **ADS 2** showed that the presence of **G3-DM15** improved adsorption of these species. The adsorption data was evaluated using the *pseudo-first-order*, *pseudo-second-order* and intraparticle diffusion kinetics models. The adsorption kinetics for all

three metal chlorido species best fitted the *pseudo*-second-order kinetics model. Moreover, experimental adsorption capacities (q_e) and the calculated q_e values were very close. The desorption studies showed that Au, Pd and Pt can be recovered from all the adsorbents.

Acknowledgements The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed, and conclusions arrived at, are those of the authors and are not necessarily to be attributed to the NRF.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Dong H, Zhao J, Chen J, Wu Y, Li B (2015) Recovery of platinum group metals from spent catalysts: a review. *Int J Miner Process* 145:108–113
- Bernardis FL, Grant RA, Sherrington DC (2005) A review of methods of separation of the platinum-group metals through their chloro-complexes. *React Funct Polym* 65:205–217
- Taylor P, Nikoloski AN, Ang K (2014) Mineral processing and extractive metallurgy review: an international review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. *Miner Process Extr Met Rev* 35:369–389
- Mahmoud ME, Khalifa MA, Al-sherady MA, Mohamed AK, El-Demerdash FM (2019) A novel multifunctional sandwiched activated carbon between manganese and tin oxides nanoparticles for removal of divalent metal ions. *Powder Technol* 351:169–177
- Gautam J, Tran DT, Singh TI, Kim NH, Lee JH (2019) Mesoporous iron sulfide nanoparticles anchored graphene sheet as an efficient and durable catalyst for oxygen reduction reaction. *J Power Sources* 427:91–100
- Perez JPH, Folens K, Leus K, Vanhaecke F, Van Der Voort P, Du Laing G (2019) Progress in hydrometallurgical technologies to recover critical raw materials and precious metals from low-concentrated streams. *Resour Conserv Recycl* 142:177–188
- Bhateria R, Singh R (2019) A review on nanotechnological application of magnetic iron oxides for heavy metal removal. *J Water Process Eng* 31:100845
- Ramesh A, Hasegawa H, Sugimoto W, Maki T, Ueda K (2008) Adsorption of gold(III), platinum(IV) and palladium(II) onto glycine modified crosslinked chitosan resin. *Bioresour Technol* 99:3801–3809
- Machesky ML, Andrade W, Rose AW (1991) Adsorption of gold (III)-chloride and gold(I)-thiosulfate anions by goethite. *Geochim Cosmochim Acta* 55:769–776
- Liu L et al (2013) Adsorption of Au(III), Pd(II), and Pt(IV) from aqueous solution onto graphene oxide. *J Chem Eng Data* 58:209–216
- Charlesworth BP (1981) Separating the platinum group metals by liquid–liquid extraction. *Platin Met Rev* 25:106–112
- Odio OF et al (2014) Sorption of gold by naked and thiol-capped magnetite nanoparticles: an XPS approach. *J Phys Chem C* 118:2776–2791
- Alorro R, Hiroyoshi N, Ito M, Tsunekawa M (2010) Recovery of precious metals from chloride solution by magnetite. In: XXV international mineral processing congresses, pp 263–271
- Uheida A et al (2006) Sorption of palladium(II), rhodium(III), and platinum(IV) on Fe_3O_4 nanoparticles. *J Colloid Interface Sci* 301:402–408
- Karasyova ON, Ivanova LI, Leonid Z (1998) Complexation of gold(III)-chloride at the surface of hematite. *Aquat Geochem* 4:215–231
- Diallo MS, Balogh L, Shafagati A, Johnson JH, Goddard WA, Tomalia DA (1999) Poly(amidoamine) dendrimers: a new class of high capacity chelating agents for Cu(II) ions. *Environ Sci Technol* 33:820–824
- Al-rabe K (2004) Characterization of Co(II) binding to PAMAM G4- NH_2 dendrimer in aqueous solutions using UV and EPR spectroscopy
- Niu Y et al (2014) Synthesis of silica gel supported salicylaldehyde modified PAMAM dendrimers for the effective removal of Hg(II) from aqueous solution. *J Hazard Mater* 278:267–278
- Barakat MA, Ramadan MH, Alghamdi MA, Algarny SS, Woodcock HL, Kuhn JN (2013) Remediation of Cu(II), Ni(II), and Cr(III) ions from simulated wastewater by dendrimer/titania composites. *J Environ Manag* 117:50–57
- Niu YH, Crooks RM (2003) Preparation of dendrimer-encapsulated metal nanoparticles using organic solvents. *Chem Mater* 15:3463–3467
- Zhang Q, Wang N, Zhao L, Xu T, Cheng Y (2013) Polyamidoamine dendronized hollow fiber membranes in the recovery of heavy metal ions. *ACS Appl Mater Interfaces* 5:1907–1912
- Diallo SM, Christie S, Swaminathan P, Johnson HJ, William AGI (2005) Dendrimer enhanced ultrafiltration. 1. Recovery of Cu(II) from aqueous solutions using PAMAM dendrimers with ethylene diamine core and terminal NH_2 groups. *Environ Sci Technol* 39:1366–1377
- Ma YX, Xing D, Shao WJ, Du XY, La PQ (2017) Preparation of polyamidoamine dendrimers functionalized magnetic graphene oxide for the adsorption of Hg(II) in aqueous solution. *J Colloid Interface Sci* 505:352–363
- Chou C-M, Lien H-L (2011) Dendrimer-conjugated magnetic nanoparticles for removal of zinc(II) from aqueous solutions. *J Nanopart Res* 13:2099–2107
- Stevelmans S, van Hest JCM, Jansen JFGA, van Boxtel DAFJ, de Brabander-van den Berg EMM, Meijer EW (1996) Synthesis, characterization, and guest–host properties of inverted unimolecular dendritic micelles. *J Am Chem Soc* 118:7398–7399
- Shen L, Laibinis PE, Hatton TA (1999) Bilayer surfactant stabilized magnetic fluids: synthesis and interactions at interfaces. *Langmuir* 15:447–453
- Liu L et al (2012) Preparation and characterization of chitosan/graphene oxide composites for the adsorption of Au(III) and Pd(II). *Talanta* 93:350–357
- Chandra S, Noronha G, Dietrich S, Lang H, Bahadur D (2015) Dendrimer-magnetic nanoparticles as multiple stimuli responsive and enzymatic drug delivery vehicle. *J Magn Magn Mater* 380:7–12
- Mendoza-Garcia A, Sun S (2016) Recent advances in the high-temperature chemical synthesis of magnetic nanoparticles. *Adv Funct Mater* 26:3809–3817
- Lenin R, Joy PA (2016) Role of primary and secondary surfactant layers on the thermal conductivity of lauric acid coated magnetite nanofluids. *J Phys Chem C* 120:11640–11651
- Sun W, Mignani S, Shen M, Shi X (2016) Dendrimer-based magnetic iron oxide nanoparticles: their synthesis and biomedical applications. *Drug Discov Today* 21:1873–1885
- Petcharoen K, Sirivat A (2012) Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method. *Mater Sci Eng B* 177:421–427
- Vatta LL, Kramer J, Koch KR (2007) Diethylenetriamine functionalized silica coated magnetite nanoparticles for selective

- palladium ion extraction from aqueous solutions. *Sep Sci Technol* 42:1985–2002
34. Colvin CB (1962) Kinetics of ligand substitution for platinum(II) complexes. *Retrospective Theses and Dissertations*. 2047
  35. Ivar EL (1970) The stepwise dissociation of the tetrachloroplatinate(II) ion in aqueous solution. *Acta Chem Scand* 24:1331–1340
  36. Cox LE, Peters DG, Wehry EL (1972) Photoaquation of hexachloroplatinate(IV). *J Inorg Nucl Chem* 34:297–305
  37. Tait CD, Janecky DR, Rogers PSZ (1991) Speciation of aqueous palladium(II) chloride solutions using optical spectroscopies. *Geochim Cosmochim Acta* 55:1253–1264
  38. Wang L, Peng H, Liu S, Yu H, Li P, Xing R (2012) Adsorption properties of gold onto a chitosan derivative. *Int J Biol Macromol* 51:701–704
  39. Li X et al (2013) Efficient adsorption of gold ions from aqueous systems with thioamide-group chelating nanofiber membranes. *Chem Eng J* 229:420–428
  40. He Z, He L, Yang J, Lu Q (2013) Removal and recovery of Au(III) from aqueous solution using a low-cost lignin-based biosorbent. *Ind Eng Chem Res* 52:4103–4108
  41. Pang S, Yung K (2014) Prerequisites for achieving gold adsorption by multiwalled carbon nanotubes in gold recovery. *Chem Eng Sci* 107:58–65
  42. Kraus A, Jainae K, Unob F, Sukpirom N (2009) Synthesis of MPTS-modified cobalt ferrite nanoparticles and their adsorption properties in relation to Au(III). *J Colloid Interface Sci* 338:359–365
- Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.