Article

Recovery of Palladium and Gold from PGM Ore and Concentrate Leachates Using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ Nanocomposite

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Abstract: In this work, we developed a core-shell nanostructured magnetic composite by functionalizing layered double hydroxide (Mg-Al-LDH) microspheres with $\text{Fe}_3\text{O}_4@\text{SiO}_2$, for the recovery of Au(III) and Pd(II). The magnetic Fe_3O_4 nanoparticles provided effective magnetic separation of the adsorbent from aqueous solutions. While silica protected the Fe_3O_4 nanoparticles, increased the adsorption sites and the stability of the material. Finally, Mg-Al-LDH was chosen because of its large anion sorption capacities which lead to the improved adsorption capacity of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite. The morphology and structural composition of the nanocomposite were characterized using various analytical techniques. It was satisfactorily established that silica was coated on iron oxide and layered double hydroxide was immobilized on $\text{Fe}_3\text{O}_4@\text{SiO}_2$. Parameters affecting adsorption of the composite towards Au(III) and Pd(II), such as effects of sample pH, mass of adsorbent, extraction time, eluent type and concentration were investigated using response methodology based on central composite design. Maximum adsorption capacities of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ for Au(III) and Pd(II) were 289 mg g^{-1} and 313 mg g^{-1} , respectively. Under optimum conditions, the proposed method displayed good analytical performance suggesting that the adsorbent is a good candidate for quantitative extraction of Au(III) and Pd(II) from secondary sources. Additionally, %recoveries ranging from 85%–99.6% were obtained revealing that $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ could selectively extract Au(III) and Pd(II) from leaching solutions of SARM 107 PGM ore and SARM 186 PGM concentrate.

Keywords: $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$; magnetic adsorption; PGM concentrates; gold; palladium; ore concentrates

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1. Introduction

The availability of precious metals, such as gold and palladium, is becoming very scarce and natural resources are depleting. This is due to their demand in numerous applications ranging from jewellery to automotive industries [1–6]. Due to their broad application, limited stock and the high price of precious metals make it vital to recycle and recover them from industrial waste [7]. Gold (Au) and palladium (Pd) metals are economically important as investments and as currency. Recovering and recycling precious metals from waste have gained much attention in research industries [8,9]. Mohamed et al. [10], reported in their work that, there is about 300 g per ton of gold in computer motherboards and approximately 200 g in mobile phones [10]. Out of the top six PGMs, Pd plays a key role in manufacturing processes in industries such as fossil fuel refinery, automobile,

electronics and pharmaceutical [11–13]. Several researchers argue that to preserve Au(III) and Pd(II) resources, as well meeting the future market demands, there is a need to develop cheap and eco-friendly processes for the recovery of PGMs from secondary sources.

The most widely used analytical techniques to quantify Pd and Au in industrial waste and natural ore include graphite furnace atomic absorption spectrometry [14,15], X-ray fluorescence spectrometry [16], ultraviolet-visible spectrometry [17], atomic absorption spectroscopy [16,18,19] and inductively coupled plasma techniques [20,21]. Spectrometric methods have attracted attention due to their low cost and simplicity. Among these methods, inductively coupled plasma-atomic emission spectroscopy (ICP-OES) is favourable because it is robust, can handle wide ranges of the sample matrix and has the ability to analyse multi-elements [22,23]. However, due to the low concentration, difficulties in extraction and digestion of precious metals in waste materials, there is a need for the application of sample pre-treatment before ICP-OES determination.

For this reason, several micro-extraction methods have been employed for the effective adsorption of precious metals from waste. These include dispersive liquid-liquid microextraction [24–26], dispersive solid-phase (micro)extraction (DSPME) [27] and magnetic solid-phase extraction (MSPE) [2,28,29]. Among miniaturized SPE techniques, MSPE technology offers remarkable features such as rapid separation of the adsorbent from the sample matrix, effective interaction between the adsorbent and the analytes and elimination of centrifugation step [30,31]. However, in MSPE the sensitivity, affinity and efficiency of an adsorbent depend on the nature of adsorbent material used [31]. For instance, magnetic nanoparticles can provide large surface modification and therefore, an enhancement of adsorption capacity, which can make it to interact with various types of analytes. For instance, in a study reported by Jalilian et al. [18], they investigated the extraction and determination of Au (III), Pd(II) and Ag(I) using a magnetic adsorbent. They used thiourea-HCl to elute metal ions from the adsorbent and quantified those using flame atomic absorption spectroscopy (FAAS). The maximum capacities were ranging between 49–50 mg g^{−1}. They successfully applied the method to extract analytes in wastewater. However, it is critical and significant to search for new materials with high extraction efficiency and adsorption capacity.

Our previous study, magnetic Fe₃O₄/Mg-Al-layered double hydroxide (LDH) nanocomposite has proven to be effective in the recovery of gold(III) and iridium(IV) from mine soil samples [32]. Promising results that maximum adsorption capacities and recoveries ranging from 115–124 mg g^{−1} and 80%–109% were obtained. The high adsorption capacity and acceptable percentage recoveries were attributed to the incorporation of LDH material. Layered double hydroxide has been extensively studied as a potential adsorbent for the sorption removal of various pollutants [33,34]. This is due to their structural characteristics such as ion exchange and memory effect which makes LDH to be favourable for extraction and adsorption of pollutants (especially anions) in acidic and basic media. However, LDH, on its own, lacks practical applicability due to the difficulties in separation and recovery of the adsorbents from sample solutions media.

Therefore, the aim of this work was to investigate the potential application of core-shell nanostructured magnetic (Fe₃O₄@SiO₂) nanocomposite functionalized with layered double hydroxide (Mg-Al-LDH) nanoflakes for the extraction and recovery of gold(III) and palladium(II) from aqueous leachate solutions of PGM ore and concentrate. The objectives of this article are: (1) to prepare and characterise layered double hydroxide-coated with magnetic nanoparticles (Fe₃O₄@SiO₂@Mg-Al-LDH) nanocomposite, and (2) to apply the Fe₃O₄@SiO₂@Mg-Al-LDH nanocomposite as the adsorbent in the recovery of Au(III) and Pd(II) from aqueous leachate solutions of PGM ore and concentrate prior to ICP-OES quantification. The effect of sample pH, mass of adsorbent, extraction time, eluent type and concentration on the extraction and recovery were investigated using response surface methodology.

2. Materials and Methods

2.1. Materials and Instrumentation

The reagents employed in this study were all of analytical grade unless otherwise specified in the methods and they were used as obtained. Double distilled water (Ultrapure (type 1) supplied by Milli-Q water system (Merk, Darmstadt, Germany) was used for the entire study. Ammonium hydroxide solution (25% *v/v*) was obtained from Associated Chemical Enterprises, (Pty) Ltd., Johannesburg, South Africa) and was used in the synthesis of the adsorbent and pH adjustments. Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), aluminium chloride (AlCl_3), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), absolute ethanol, tetraethylorthosilicate (TEOS) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) used for the synthesis of magnetic Mg-Al-LDH composite were acquired from Sigma-Aldrich (St. Louis, MO, USA). Gold and palladium single element standard (1000 mg L^{-1}) purchased from HG-LGC (Teddington, UK) were used to prepare synthetic samples for adsorption and the calibration of the instrument. South African Reference materials, that is, SARM 186 platinum group metal (PGM) concentrate and SARM 107 PGM ore were obtained from Mintek (Analytical Services Division, Johannesburg, South Africa). The quantification of Au(III) and Pd(II) recovered from sample solutions was determined using an ICP-OES (iCAP 6500 Duo, Thermo Scientific, Loughborough, UK) equipped with a charge injection device (CID) detector. The operating conditions were applied as suggested by the manufacturer. The pH of the solutions was adjusted using H1 9811–5, pH meter (HANNA Instruments, Smithfield, RI, USA). A Scientech ultrasonic cleaner (Labotec, Midrand, South Africa) with a volume of 5.7 L (internal dimensions: $300 \text{ mm} \times 153 \text{ mm} \times 150 \text{ mm}$) was used to facilitate the adsorption, extraction, and recovery (elution) process.

2.2. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ Nanocomposite

The synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al LDH}$ was obtained via sol-gel method. Magnetic nanoparticles were synthesized by following a previously reported method by Munonde et al. with minor changes [35]. The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microsphere was obtained through a sol-gel method which was previously reported by [36]. Briefly, 850 mg magnetic spheres (Fe_3O_4) previously synthesised were dispersed into a round-bottom flask charged with ethanol, water at a ratio of 4:1 (*v/v*) and 3.60 mL concentrated ammonia solution 25%–30% NH_3 basis). The suspension was sonicated in an ultrasonic bath for 30 min to enable uniform dispersion. This was followed by dropwise addition of 2.5 mL of tetraethyl orthosilicate (TEOS), and the mixture was stirred continuously for 8 h at 70°C . The resultant $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres were collected using an external magnetic field, washed with ethanol five times, and dried at 50°C for 2 h.

The deposition of nanoflakes of Mg-Al-LDH onto $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres via ultrasonication to form $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ were carried out as reported by Zhao et al. [36]. Briefly, 0.10 g $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanocomposite was dispersed in 50 mL deionized water-methanol mixture at pH 10. via ultrasonication. The pH of the deionised water-methanol mixture (1:1) was adjusted to 10 addition 0.53 g Na_2CO_3 and 0.4 g NaOH solids. 20 mL 1:1 methanol:water containing 1.13 g AlCl_3 , 1.476 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was added dropwise to the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ suspension at a constant rate using a burette under vigorous stirring. It should be noted that the pH of the solution was maintained at pH 10. When the reaction was completed, the mixture was further agitated via ultrasonication for 1 h. The product was collected via an external magnet and redispersed in 70 mL of deionized. The product was further exfoliated under ultrasound dispersion for another 1 h. The $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite was separated from the supernatant using an external magnet, washed with ethanol, and dried at 50°C under vacuum for 2 h.

2.3. Characterization

The crystalline structure of Fe_3O_4 Mg-Al-LDH, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite were investigated using a PANalytical X'pert Pro X-ray diffraction crystal analyser (XRD, PANalytical, Almelo, The Netherlands) with nickel-filtered $\text{CuK}\alpha$

radiation. The transmission electron microscopy (TEM, JEM-2100, JEOL, Tokyo, Japan) was used to record the TEM images of the adsorbents. The morphological studies of the prepared adsorbent were also assessed using scanning electron microscopy (SEM, TESCAN VEGA 3 XMU, LMH instrument coupled with energy dispersive X-ray spectroscopy (EDS) to confirm the elemental composition of the composite. The nitrogen adsorption–desorption (Brunauer–Emmett–Teller (BET)) analysis (ASAP2020 V3. 00H, Micrometrics Instrument Corporation, Norcross, GA, USA) was used to determine the surface properties of the adsorbent. The zeta potential of the nanocomposite was measured by analysing suspension of 0.1 g adsorbent at different pH (1–12) using a Nano ZS Zetasizer (Malvern Instruments Limited, Malvern, Worces, UK).

2.4. Extraction and Recovery of Au(III) and Pd(II) from Synthetic Samples

2.4.1. Selection of Eluent Type

The elution or desorption of Pd(II) and Au(III) was studied using the analyte-loaded adsorbent and different elution solvents. Briefly, 0.15 g $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite was placed in sample bottles containing 50 mL of $500 \mu\text{g L}^{-1}$ adjusted to pH 3.5 with 0.01 mol L^{-1} HCl or NaOH and sonicated for 20 min. The supernatant solution was carefully discarded with aid of an external magnet. 5.0 mL of 3.0 mol L^{-1} HNO_3 , HCl, and aqua regia was replaced in the sample bottle containing an analyte-loaded adsorbent. The elution or desorption process was carried by allowing the adsorbent to interact with the eluent solvent under ultrasonication for 10 min. The supernatant and the adsorbent were separated using magnetic separation and the supernatant was filtered and analysed using ICP-OES.

2.4.2. Optimization Using Central Composite Design (CCD)

The extraction and recovery of Pd(II) and Au(III) was carried by placing different masses of the adsorbent (50–200 mg) in as sample bottles containing 50 mL of $500 \mu\text{g L}^{-1}$ of Pd(II) and Au(III) solution (pH 2–9 adjusted with 0.01 mol L^{-1} HCl or NaOH). The adsorption process was achieved by ultrasonication for 5–30 min. Aqueous solutions and the adsorbent were separated via magnetic decantation. The adsorbed analytes were recovered using 3.0 mol L^{-1} HCl acid after sonication for 10 min, magnetically separated, filtered and analysed with ICP-OES. The optimization of the extraction and recovery process was achieved using central composite design (CCD). The most influential variables were mass of adsorbent (MA) sample pH and extraction time (ET), their minimum (–), central (0) and higher (+) levels are presented in Table 1.

Table 1. Range of independent variables.

Parameters	Lower Level (–)	Central Point (0)	Higher Level (+)
mass of adsorbent (mg)	50	125	200
extraction time (min)	5.0	17.5	30
pH	2.0	5.5	9.0

2.5. Determination of Adsorption Capacity

The adsorption equilibrium experiments were carried out under optimized conditions. Briefly, 112 mg of adsorbents were added into 100.0 mL model solution (pH 4.0) containing Pd(II) and Au(III) at initial concentrations ranging from 2–10 mg L^{-1} (prepared using a single stock solution of each analyte) for 17.5 min. Four commonly used isotherms, i.e., Freundlich, Langmuir, Toth and Sips models were applied to interpret the experimental data obtained for ICP-OES analyses. The concentration of Au(III) and Pd(II) in the procedure blanks and model sample solution (before adsorption) was determined using ICP-OES. The analytical data from the ICP-OES was used to calculate adsorption capacity (q_e , mg g^{-1}) (Equation (1)).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are initial and equilibrium concentrations (mg L^{-1}) of Au(III) and Pd(II), V is the volume of the sample (L), and m is the mass of the adsorbent (g).

2.6. Regeneration and Reusability Studies

The desorption of adsorbed Au(III) and Pd(II) was carried out by 3.0 mol L^{-1} hydrochloric acid. Briefly, 10 mL of desorption solution was added to 50 mL reagent bottles containing spent adsorbent loaded with analytes of interest. The samples were sonicated for 20 min to ensure that all the analytes have been desorbed. The desorbed analytes from the spent adsorbent were analysed using ICP-OES. After the desorption process the adsorbent was washed with deionised water followed by ethanol and dried at 50°C in a vacuum oven for 2 h.

2.7. Effect of Interfering Ions

Gold and palladium may coexist with other metals and therefore, the effect of interfering ions was investigated under optimum conditions. Briefly, 50 mL of synthetic samples (pH 4.0 adjusted with 0.01 mol L^{-1} HCl or NaOH) containing analytes of interest was fixed at 1.0 mg L^{-1} and major and trace metals (As, Zn(II), Ni(II), Mn(II), Cr(III), Na(I), Ca(II), Ba, and Cr(III)^-), at 10 mg L^{-1} were added to sample bottles containing 112 mg of the adsorbent. The mixed-ion sample solution was sonicated for 17.5 min and the analytes were eluted using 3.0 mol L^{-1} HCl. The eluent was analysed using ICP-OES.

2.8. Application to Real Samples

Briefly, 1000 mg of SARM 186 PGM concentrate and SARM 107 PGM ore were accurately weighed and placed in 50 mL of polypropylene tube. Then, 10 mL of aqua regia (6 mL of HNO_3 and 4 mL of HCl) and 5-mL of the concentrated H_2O_2 was added. The sample was then digested for 60 min at 60°C using a Digi block. The residue was diluted to 50 mL using deionised water. The extraction and recovery of Pd(II) and Au(III) from leachate samples were carried out under optimum conditions. Briefly, 50 mL leachate solutions at pH 4.0 (adjusted with 0.01 mol L^{-1} HCl or NaOH) was placed in a sample bottle containing 112 mg of the adsorbent. The extraction process was achieved via ultrasonication for 17.5 min. Supernatant and residual adsorbent were separated via an external magnet. The adsorbed analytes were recovered using 3.0 mol L^{-1} HCl acid and the elution process was assisted by ultrasonic power 10 min. The supernatant containing the recovered analytes were separated via magnetic decantation and the liquid was filtered and analysed using ICP-OES.

3. Results and Discussion

3.1. Characterization of Adsorbents

3.1.1. Powder X-ray Diffraction (XRD) Analysis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$

The XRD patterns of (a) Fe_3O_4 , (b) Mg-Al-LDH, (c) $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and (d) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ were recorded in Figure 1. As seen in Figure 1A,C,D, all samples displayed typically diffractions patterns of Fe_3O_4 which are similar to the ones reported in the literature [31,37–39] (JCPDS 19-0629). The diffraction peaks in Figure 1B displayed reflection planes of Mg-Al-LDH [33]. Figure 1C shows the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles XRD profile with reduced crystallinity. An additional broad peak between 15 and 30° which was ascribed to the typical profile of silica, confirmed the successful incorporation of SiO_2 shell on the Fe_3O_4 nanoparticles [40]. Figure 1D, show diffractions patterns of the nanocomposite. As seen in this Figure nanocomposite assemblies exhibit characteristic diffraction peaks of Mg-Al-LDH and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ [34,37,41,42]. The incorporation of magnetic nanoparticles reduced the intensity of the peaks of the LDH. In addition, the results revealed that the XRD patterns of magnetic nanoparticles in the resultant nanocomposite remained unchanged during the incorporation of LDH.

Figure 1. X-ray diffraction patterns of (A) Fe_3O_4 , (B) Mg-Al-LDH, (C) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (D) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ Mg-Al-LDH.

3.1.2. Structural and Morphological Properties of the Composite

The TEM was used to study the morphology and internal porosity of the prepared adsorbents. The TEM images of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ are shown in Figure 2A–C. It is observed in Figure 2A that the displayed darker black isometric structures were ascribed to Fe_3O_4 nanoparticles [39]. Figure 2B displayed distinctive regular core-shell structures with a certain amount of black particles inside the transparent shells. These core-shell structures were assigned to $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanocomposite. These results confirmed that that magnetite (black particles) was coated with SiO_2 [36]. The TEM image for the nanocomposite indicated that the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles decorated with Mg-Al-LDH nanoflakes are presented in Figure 2C. As seen, the presence of numerous fibrous-like, lamellar nanoflakes grafted to the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanocomposite, confirmed the incorporation of Mg-Al-LDH nanoflake. Thus, the TEM images demonstrated that $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite was successfully synthesized, and further confirmed the analytical results of XRD. These findings agreed with reported in the literature [33].

Figure 2. TEM image of (A) Fe₃O₄, (B) Fe₃O₄@SiO₂ and (C) Fe₃O₄@SiO₂@Mg-Al-LDH nanocomposite.

Figure 3 illustrates the SEM image and EDS spectrum of nanocomposite Fe₃O₄@SiO₂@Mg-Al-LDH. It can be seen that Fe₃O₄ were agglomerated and particles were distributed uniformly, which was in agreement with the images reported in the literature [33]. EDS spectrum displays all the expected elements, Fe, Si, O, Al and Mg. The appearance of O, Si and Fe elements suggest the presence of Fe₃O₄ and SiO₂ in the nanocomposite. While Mg and Al confirmed the incorporation of LDH layers in the nanocomposite. The presence of C might be from carbon coating, whereas forms part of the impurities. The result above further demonstrated that Mg-Al-LDH was coated on the surface of the magnetic nanocomposite and they are in agreement with TEM and XRD results.

Figure 3. SEM and EDX images of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ composite.

3.1.3. Surface Area and Pore Sizes Analysis

Table 2 portrays the BET specific surface area, pore volume and pore size of the adsorbents. The BET surface area of Fe_3O_4 was $85.1 \text{ m}^2 \text{ g}^{-1}$ and the incorporation of SiO_2 coating dramatically increased the surface area of the nanocomposite to $235 \text{ m}^2 \text{ g}^{-1}$. However, upon the incorporation of Mg–Al-LDH (surface area $93.4 \text{ m}^2 \text{ g}^{-1}$), the surface area of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ was decreased to $220 \text{ m}^2 \text{ g}^{-1}$. In all adsorbents the pore sizes were above 2 nm (Fe_3O_4 , 4.20 nm; $\text{Fe}_3\text{O}_4@\text{SiO}_2$, 5.75 nm, Mg–Al-LDH, 6.34 nm and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$, 7.85 nm) showing that the adsorbents exhibited mesoporous structures. The smaller pore sizes correlate to the small pore volumes justifying for blockage of pores on the surface of the adsorbent.

Table 2. Porous characteristics of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite.

Adsorbent	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Fe_3O_4	85.1	0.107	4.20
$\text{Fe}_3\text{O}_4@\text{SiO}_2$	235	0.149	5.75
Mg–Al-LDH	93.4	0.357	6.34
$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$	220	0.294	7.85

3.1.4. Zeta Potential of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ Nanocomposite

The surface charge of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite was investigated to obtain information about the surface charge of the adsorbent and pH of point of zero charge (pH PZC) was determined. The zeta potential results against pH of the solution, between pH 1 and pH 12 are presented in Figure 4. As seen, the surface charge of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite is positively charged from pH 1 up to about pH 7. In addition, the pH at point of zero charge (pH_{PZC}) of the nanocomposite was found to be 7.1.

Figure 4. Zeta potential of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$.

3.2. Extraction and Recovery of Au(III) and Pd(II) from Synthetic Samples

3.2.1. Selection of Eluent Type

The selection of the eluent type plays a critical role in the recovery of Au(III) and Pd(II) on the surface of the adsorbent. This is because the recovery of metals on the adsorbents depends on how they are adsorbed. Three eluents were used to determine the extraction/desorption behaviour of Pd and Au from the nanocomposite surface. The concentration of the solutions was fixed at 3.0 mol L^{-1} for all the eluents. Figure 5 shows the results obtained when the desorption abilities of HNO_3 , HCl, and aqua regia were investigated. As seen, 5.0 mL HCl at 3.0 mol L^{-1} was found to be the most suitable solution followed by aqua regia. Therefore, hydrochloric acid was used throughout the studies.

Figure 5. Choice of suitable eluent type for desorption study: Experimental conditions: mass of adsorbent = 150 mg; Extraction time = 20 min; elution time = 10 min; sample pH = 3.5.

3.2.2. Optimization Using Central Composite Design (CCD) Statistical Analysis

The response surface methodology (RSM) based on CCD was used to determine the factors affecting the adsorption process. The design matrix was computed using Statistica software. The study of the significant parameters affecting the adsorption process was done using the RSM obtained from CCD. A Pareto chart reproduced from the analysis of variance (ANOVA) was used to assess the significance interactive (Figure 6). In the Pareto chart graphs, the red line represents the 95% confidence limit while the bars represent the parameters that were optimised. In Figure 6, it can be seen that pH of the solution was significant in the adsorption of Au(III) and Pd(II) as the bar of the pH crossed the 95% confidence limit [43]. Other factors (mass of adsorbent and contact time), as well as their interactions were insignificant at 95% confidence level in both removal of Pd and Au, this indicates that pH of the solution had greater influence in the removal of these precious metals.

Figure 6. Pareto chart of standardized effects on the recovery of (A) gold and (B) palladium: 2Lby3L = interaction between mass of adsorbent (MA) and sample pH; 1Lby3L = interaction between extraction time (ET) and sample pH; 1Lby2L = interaction between extraction time (ET) and MA.

Response Surface Methodology (RSM)

Three-dimensional (3D) response surface methodology was used to study the interaction between two parameters to obtain maximum extraction efficiency and percentage recovery (%R). The 3D response surfaces plots (Figure 7) were combined to show the interaction of independent variables [43]. The effect of pH was best described in Figure 7, it was investigated by varying pH ranging from 2.0 to 10.0 on Au(III) and Pd(II) adsorption ion using the initial Au(III) concentration of 50 mg L⁻¹. Dilute HCl and NaOH (0.01 mol L⁻¹) solutions were used for the adjustment of the aqueous solutions to obtain the desired pH. It was seen that at a low pH, the adsorption recoveries were high and decreases with the increase with pH. According to the speciation diagram of Au(III) [1,2,44], the neutral AuCl₃ species is only present in aqueous solution with higher acidities and low chloride concentration. By looking at the speciation data, [AuCl₄]⁻ will have a negative charge from lower pH up until it precipitates at a pH around 10. The adsorption/extraction will occur at a lower pH since the surface charge of the material is positive at low pH as demonstrated in Figure 4 [1,2,45]. Pd(II) ions forms chloro-palladium complexes (PdCl₄²⁻ and PdCl₃⁻) in a solution and are dominated at a pH of a range between 1.0–4.0 [1,46]. At a low pH, the adsorption of gold(III) and palladium(II) is high due to the electrostatic attraction between the positively charged of the material and anionic complexes. The surface charge of the material has pH_{pzc} value of 7.1 meaning, at pH lower than pH_{pzc} the surface is positively charged and at the pH higher that that the surface is negatively charged. Since

the pH_{pzc} of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ is 7.1, Au(III) and Pd(II) ions will be advantageous for adsorption.

Figure 7. The 3D response surface plots of Pd(II) and Au(III). Experimental conditions: MA = Mass of adsorbent, 50–200 mg; sample pH, 2–9; sample volume, 50 mL; extraction time, 5–30 min, eluent volume, 5.0 mL, eluent (HCl) concentration, 3.0 mol L^{-1} and number of replicates = 3; %R = percentage recovery.

Figure 8 shows the desirability of 1.0 was assigned for maximum recoveries (93.7%), at 0.0 there was no recovery (20.7%) and 0.5 for the middle (57.1%). It also shows the individual desirability scores for the extraction of Au(III) and Pd(II). In this study, the desirability value of 1.0 was selected for the estimation of optimum conditions. Therefore, on the desirability value of 1.0, the optimal conditions were 112 mg (mass of adsorbent), 17.5 min (extraction time), 5.0 mL 3.0 mol L^{-1} HCl and a sample pH of 4.0.

Figure 8. Profile of predicted values and desirability for the recovery of precious elements.

3.3. Determination of Adsorption of Capacity

Adsorption equilibrium is referred to the ratio between the concentration of the target analyte adsorbed and residual amount in solution [32]. This is achieved when the sample solution containing an analyte of interest is in contact with the adsorbent for a specific time. This interaction can be described using different isotherms models. In this study, the adsorption isotherms of Au(III) and Pd(II) onto $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ was done under the obtained optimum conditions. As shown in Figure 9 the adsorption or binding capacity of both Au(III) and Pd(II) onto $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ increased with increasing the initial concentration until the saturation point was achieved. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms models were used to exam the adsorption behaviour between $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ and the two analytes. The linear equations of the models and their constant parameters are presented in Table 3. The correlation coefficient (R^2) values were used to decide on the isotherm model that best describes adsorption equilibrium data, which was done by comparing the correlation coefficients (R^2) in Table 3. The adsorption data followed the Langmuir isotherm model with correlation coefficients of 0.9924 and 0.9907 for Au(III) and Pd(II) respectively, which were higher than other models. The q_{max} values for Au(III) and Pd(II) were found to be 289 mg g^{-1} and 313 mg g^{-1} respectively. These results suggest that the adsorption process was dominated by monolayer sorption meaning that the adsorption was homogenous. Dubinin–Radushkevich is typically used to differentiate between chemisorption and physisorption by using the mean energy (E). The calculated E value for both (Au(III) and Pd(II)) was 22.4 kJ mol^{-1} that shows chemisorption process [47].

Figure 9. Equilibrium studies for Au(III) and Pd(II) absorption onto the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite.

Table 3. Adsorption isotherms and parameters.

Isotherm & Equation		Description	Parameters	Au(III)	Pd(II)
			Q_e (experimental)	288	312
Langmuir			$Q_{\max}$ (mg mg^{-1})	289	313
$\frac{1}{q_e} = \frac{1}{q_{\max} K_L} \cdot \frac{1}{C_e} + \frac{1}{q_{\max}}$	$q_{\max}$: maximum monolayer adsorption capacity, mg g^{-1} , K_L : Langmuir constant, L mg^{-1} and C_e : concentration of the target analyte at equilibrium, mg L^{-1}		K_L ($\text{L} \cdot \text{mg}^{-1}$)	0.37	0.32
$R_L = \frac{1}{1 + K_L C_0}$			R^2	0.9924	0.9907
			R_L	0.23–0.73	0.25–0.766
Freundlich			n	1.33	1.4
$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	where q_e is the target analyte adsorbed at equilibrium (mg g^{-1}), K_f and n are Freundlich constants including the factors affecting the adsorption capacity and adsorption intensity respectively		K_F ($\text{L} \cdot \text{mg}^{-1}$)	87.8	107
			R^2	0.9882	0.9429
Temkin			B_T	122	144
$q_e = B \ln A + B \ln C_e$	where q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}); C_e is the concentration of adsorbate in solution at equilibrium (mg L^{-1}). B is a constant related to the heat of adsorption and A is the Temkin isotherm constant (L g^{-1})		K_T (L mg^{-1})	2.14	2.03
			R^2	0.9538	0.8823
Dubinin-Radushkevich			Q_s (mg g^{-1})	292	302
$\ln q_e = \ln q_s - \beta \epsilon^2$ $\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$	where q_e is the amount of target analyte adsorbed at equilibrium (mg g^{-1}), q_s is the maximum adsorption capacity, β is the activity coefficient useful in obtaining the mean sorption energy E (kJ mol^{-1}) and ϵ is the Polanyi potential.		β ($\times 10^{-9}$)	−1.0	−1.2
			E (kJ mol^{-1})	22.4	20.4
			R^2	0.9779	0.9256

3.4. Regeneration and Reusability Studies

The regeneration and recyclability of a spent adsorbent are important for practical applications and industrial development of large-scale adsorbents. In addition, the regeneration of a spent adsorbent will make the recovery process to be economical. Therefore, in this study, the reuse of the spent adsorbent was tested for other cycles of adsorption and desorption applications. The adsorption capacity of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite for five subsequent adsorption-desorption cycles are shown in Figure 10. According to Figure 10A, the adsorption efficiency of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite after five cycles could retain up to 80% of the original adsorption capacities. Therefore, these results suggest that $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite could be successfully reused in the adsorptive recovery of Au(III) and Pd(II) from acidic leachates of the secondary resources. Moreover, the resultant filtrates after regeneration were analysed using ICP-OES to determine the concentration of Mg, Al and Fe. This is because strong acids like HCl are likely to destroy the nanomaterial structure, thus resulting in the high release of Al, Fe, and Mg and the poor adsorption of Au(III) and Pd(II). The results obtained are summarized in Figure 10B. As seen very low concentrations of Al, Fe, and Mg leached out of the material. This could be attributed to the incorporation of silica which enhanced the stability of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite under acidic conditions. Silica tends to remain unchanged during redox reactions and due abundance of hydroxyl groups on its surface it tends to be stable in acidic conditions. Similar observations have been reported in the literature [48–50].

Figure 10. (A) Reusability and regeneration of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite and (B) leaching studies.

3.5. Analytical Figures of Merit

The analytical performance of the proposed method was authenticated by evaluating the limits of detection (LOD), limits of quantification (LOQ), linearity, coefficient of determinations (R^2), precisions (intraday and interday) and enrichment factors (Table 4). These were investigated to assess where the MSPE method will be able to extract Au(III) and Pd(II) at low concentrations. Limits of detection of the proposed method were found to be 0.10–0.13 concentration/ $\mu\text{g L}^{-1}$ in aqueous solutions and 0.21–0.27 concentration/ $\mu\text{g g}^{-1}$ in ore concentrates. The linear range of the calibration curve was found to be 0.4–550 concentration/ $\mu\text{g L}^{-1}$ and 0.7–500 concentration/ $\mu\text{g g}^{-1}$ in aqueous and ore concentrates, respectively. Enrichment factors were calculated and found to be 55.0 for Au(III) and 46.6 for Pd(II). As seen in Table 4, the intraday and interday (%RSD) values ranged between 1.3%–2.5% for intraday and 3.5%–5.1% for interday, suggesting that the developed method was precise.

Table 4. Analytical figures of merit of Au(III) and Pd(II) in deionised water and ore concentrates ($n = 3$).

	Deionised Water			Real Samples	
	Au	Pd		Au	Pd
Linearity ($\mu\text{g L}^{-1}$)	0.4–500	0.5–550	Linearity ($\mu\text{g g}^{-1}$)	0.7–450	1.0–500
R^2	0.9989	0.9969	R^2	0.9912	0.9923
LOD ($\mu\text{g L}^{-1}$)	0.10	0.13	LOD ($\mu\text{g g}^{-1}$)	0.21	0.27
LOQ ($\mu\text{g L}^{-1}$)	0.34	0.45	LOQ ($\mu\text{g g}^{-1}$)	0.68	0.90
Intraday (%RSD)	1.3	1.6	Intraday (%)	2.3	2.5
Interday (%RSD)	3.5	4.3	Interday (%)	4.7	5.1
PF	55.0	46.6			

The analytical performance of the synthesized sorbent for extraction of Au(III) and Pd(II) is shown in Table 5. The LODs and %RSD of the developed methods were comparable with previous works [30,47]. However, the LODs were lower than those reported elsewhere (Table 5). Furthermore, preconcentration factors were lower than those reported in the literature [19,30,46–49]. These findings suggest that the developed method has low LODs and acceptable precision when compared to the previous studies.

Table 5. Comparative study of the developed method with literature.

Analyte	Adsorbent	Detection Techniques	LOD ($\mu\text{g L}^{-1}$)	PF	%RSD	Refs.
Au, Pd, Pt		LEP-OES	0.8, 3.1, 57.3	250	≤ 5	[19]
Au(III), Pd(II) and Pt(IV)	$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}$	graphite furnace	0.197, 0.223 and	197, 174 and	2.1, 1.4 and	[16]
Pd	C18 modified silica	AAS	1.070	168	1.5	
		HR-CS-GF-AAS	1.110	100	1.5	[51]
Au^{3+} , Pd^{2+} and Ag^+	mag-GO@MBT/SDS NPs	ICP-OES	0.045–0.076	160, 160 and 140	3.1	[30]
Au(III), Pd(II) and Ag(I)	2,3-Bis(2-formylphenoxy)-propan-1-ol	FAAS	0.12, 0.28 and 0.17	-	-	[52]
Au(III)	CNT	HR CS GF AAS	2.24	264	8	[53]
Au(III) and Pd(II)	N-(6-morpholin-4-ylpyridin-3-yl)-N'-phenylthiourea		1.75 and 1.65 $\mu\text{g L}^{-1}$		2.8	[54]
Au(III) and Pd(II)	$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$	ICP-OES	0.10–0.13	47–55	2.3–5.1	This work

3.6. Effect of Interfering Ions

To assess the selectivity of the sorbent and the influence of other ions in respect to the target metal ions extraction capability was investigated. The analytical results obtained are presented in Figure 11. This figure disclosed that the effect of co-existing ions has no significant disturbance and significant interference in the absorption process of Au(III) and Pd(II), under optimum conditions. This might be because most of these coexisting ions were repelled due to their positive charge. Therefore, the proposed method could be characterised as an appropriate procedure for the analysis of complicated sample matrices. Additionally, the method exhibited good selectivity for Au(III) and Pd(II) in this study.

Figure 11. Effect of co-existing ions on the recovery of gold and palladium using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Mg-Al-LDH}$ nanocomposite. The cocktail means that model solution contained all the investigated co-existing ions at approximately 10 mg L^{-1} .

3.7. Application to Real Samples

To investigate the accuracy of the method, South African Reference Materials (SARM 186 and 107) were digested and then analysed using the developed method. As presented in Table 6, there was a good agreement between obtained values and the certified values. The percentage recoveries ranged from 85%–87.7% and 82%–99.6% for Au(III) and Pd(II), respectively.

Table 6. Analytical results for Au(III) and Pd (II) ions in the South African reference materials (SARM 186 and 107).

	Au(III)			Pd(II)		
	Certified value	Recovered	%R	Certified value	Recovered	%R
SARM 186	2.58 ± 0.8	2.21 ± 0.15	85.6	28.1 ± 1.4	28.0 ± 0.22	99.6
SARM 107	0.046 ± 0.010	0.040 ± 0.020	87.7	0.926 ± 0.036	0.758 ± 0.050	81.9

4. Conclusions

In the present work, a nanocomposite composed of layered double hydroxide and silica-coated magnetic nanoparticles were successfully synthesized through a combination of two-methods sol-gel and co-precipitation method. The synthesized material was characterized by various characterization methods and successfully employed as an adsorbent in ultrasound-assisted dispersive magnetic solid phase extraction for selective extraction of gold and palladium from aqueous samples. The applicability of the proposed method was validated by analysing the South African reference material target analytes and percentage

recovery values ranged from 81 to 100%. Looking at these results, we can safely say that the synthesized layered double hydroxide magnetite nanoparticles may be successfully used as a sorbent for the extraction of Pd and Au from the waste.

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