

Magnetic Iron Oxide Nanoparticles Modified with Moringa Seed Proteins for Recovery of Precious Metal Ions

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Abstract

Precious metals are highly demanded economic value metals that require to be recovered from industrial wastes and electronic used products (e-waste). They are such as gold (Au) as well as Platinum Group Metals (PGMs) for instance palladium (Pd) and platinum (Pt). The study was conducted to test the magnetic iron oxide nanoparticles modified with *Moringa oleifera* seed proteins as adsorbent for recovery of Au(III), Pd(II) and Pt(IV) from aqueous solutions. Different functional groups responsible for adsorption, morphology, thermal stability, and surface charges of the nanoparticles were characterized with FTIR, SEM, TGA and Zeta potential respectively. Batch adsorption method was used, and precious metal ions percentage recovery was measured using ICP-OES. The effects of pH, initial adsorbate concentration, adsorption agitation time and adsorbent dosage were studied at room temperature of 25°C. Au(III) yielded a maximal recovery of 99.8%, followed by Pt(IV) with 87.7%, then Pd(II) with 72.7% at a pH 2.5, 10 mg/L initial adsorbate concentration, 120 minutes agitation time and 0.065 g adsorbent dosage. These results suggested that modified iron oxide nanoparticles were effective in selective recovery of the precious metal ions.

Keywords

Adsorbent, Adsorbate, Adsorption Isotherm, *Moringa oleifera*, Precious Metals, Seed Proteins Extract

1. Introduction

The mining industry has new challenges as many state-of-the-art technologies require precious metals such as gold (Au) as well as Platinum Group Metals

(PGMs) for instance palladium (Pd) and platinum (Pt) [1]-[7]. Platinum and palladium composed of rhodium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os) form up the PGM family. These precious metals possess peculiar physical and chemical characteristics that lead to their significant economic value. Many fields including dental industries, automobile, pharmaceuticals, ornament, jewelry, ornament, medicine and electronics, require these rare naturally occurring precious metals. This rise in demand thus increases the necessity to explore methods to recover them from electronic used products (e-waste) and industrial wastes. However, there are health concerns associated with these precious metal ions, for instance, consumption of contaminated food might lead to conditions such as liver damage, kidney failure among others [8]. Deadly effects are observed on plants, animals and human beings upon bioaccumulation of complexes of platinum ions [7]. Molecular structures of animals and human cells are reported to be negatively affected when gold ions are ingested [6]. Also, carcinogenic effects in plant roots and animals are diagnosed with palladium ions [6] [9]. In turn, the whole food chain is reported to be adversely affected as a result of these precious metal ions, hence making it critical to recover these metal ions from industrial effluent not only because of the rise in demand but also to mitigate the health effects associated with them.

The techniques used in recoveries of precious metals are for instance solid phase extraction, ion exchange, membrane filtration, liquid-liquid extraction, cementation, photocatalytic degradation and chemical precipitation [5] [8] [10]. Nevertheless, there are numerous impediments in applying some of them including excessive costs, poor recovery of precious metal ions and introducing added pollutants other than the ones in the original waste [10]. Among these techniques, solid phase extraction under which adsorption falls is still regarded as a cost-effective method for recovery of low concentrated precious metal from aqueous solutions [11] [12] [13]. Adsorption is referred to as a chemical and physical contact among adsorbent and adsorbate [13]. Adsorbate is defined as a chemical that attaches to the adsorbent which is a solid surface [14]. The magnetic solid phase extraction is the most widespread method that includes magnetic adsorbents in eliminating analytes from solutions [6].

The study was aimed at selective recovery of metal ions using magnetic iron oxide nanoparticles modified with *Moringa oleifera* proteins. The use of a natural adsorbent offers numerous advantages including substantial decrease in sludge volume, quick separation and improved efficiency since this is known to be entirely biodegradable and non-toxic [15] [16]. On the other hand, magnetic iron oxide nanoparticles (Fe_3O_4) are commonly accessible compounds in nature that can also be easily produced in the laboratory, chemically and physically stable, environmentally harmless and biocompatible [17] [18]. Several studies have revealed that it is vital to coat magnetic iron oxide before and after synthesizing to provide stability, avoid oxidation, prevent harmful contaminants and reduce agglomeration in order to optimize their usage [6] [19]-[27]. It is therefore,

against this background that the study aimed at utilizing magnetic iron oxide nanoparticles modified with Moringa seed proteins rather than the naked magnetic iron oxide nanoparticles to determine its effectiveness in selective recovery of Au(III), Pd(II) and Pt(IV) from aqueous solutions. The pH, initial adsorbate concentration, adsorption agitation time and adsorbent dosage were the parameters used to study the adsorption behaviour of Au(III), Pd(II) and Pt(IV) on magnetic iron oxide nanoparticles modified with Moringa seed proteins.

2. Materials and Methods

2.1. Chemicals and Reagents

Reagents used throughout the study were either chemically pure or of analytical grade. Deionized water was obtained from a Rios - DI system supplied by Merck. Whatman No. 1 filter papers with a diameter of 90 mm manufactured by GE Healthcare company were used. Sodium hydroxide (NaOH) was supplied by Skylabs. Sodium chloride was supplied by LD didactic in Germany. Gold (III) chloride by Sigma-Aldrich, platinum (IV) chloride and palladium (II) chloride by Alfa aesar. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and hydrochloric acid (HCl) were supplied by Merck, petroleum ether (40 °C - 60 °C) by Skychem, whereas ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), acetone and ammonium sulphate were obtained from Promark Chemicals. Preswollen Carboxymethyl cellulose was supplied by Biophoretics (USA). Multielement precious metals standard was supplied by Perkin Elmer.

2.2. Instrumentation

The study was based on laboratory experiments, and the following techniques were utilized to characterize the modified iron oxide nanoparticles: The Perkin Elmer UATR spectrum two system Fourier transform Infrared (FTIR) spectrometer was utilized to evaluate the key functional groups present that are accountable for adsorption in the modified magnetic iron oxide nanoparticles. Q600 V20.9 Build 20 Thermogravimetric Analyser (TGA) and Differential Scanning Calorimeter (DSC) was used for the decomposition and thermal stability of the nanoparticles. The morphology of the synthesized nanoparticles was characterized with the Jeol JSM-6010PLUS/LA Scanning Electron Microscope (SEM) equipped with the Oxford X-ray energy dispersive spectroscope (EDS). The surface charge of the nanoparticles was measured with a nanoZetasizer (Nano Zs model) between pH 2-12. A permanent magnet was utilized to assess whether the nanoparticles produced were magnetic. Perkin Elmer Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for quantitative determination of metals.

2.3. Preparation of Adsorbent

2.3.1. Preparation of *Moringa oleifera* Seed Extract

Samples of *M. oleifera* mature dry pods were collected from a tree in Cimbes-

basia, Windhoek. The extraction of the protein was carried out using the method by Maikokera and Kwaambwa [28]. The seeds obtained from the pods were de-shelled skinned and the kernels crushed using a pestle and mortar to obtain a powder. The seeds powder was defatted by mixing with 40°C - 60°C petroleum ether using hot plate magnetic stirrer at a continuous speed for two hours followed by suction filtration. The presence of oil is known to reduce the effectiveness of metals recovery thus necessary to remove it [29] [30]. The powder obtained was then dried in open air. This powder was then continuously stirred in 1M potassium chloride for an hour followed by suction filtration to remove the bigger solid particles followed by gravity filtration to obtain a clear solution. Studies have demonstrated that coagulating component extracted from *M. oleifera* seeds is more efficient using salt solution than tap water [28] [31]. Ammonium sulphate was used to precipitate the proteins in the extract to saturation as a result of “salting out” effect. The precipitated protein was filtered using suction filtration after which it was then re-dissolved in distilled water and dialyzed using Sigma-Aldrich dialysis tubing cellulose membrane of 43 mm width. The carboxymethyl cellulose (CMC) resin was utilized to purify the protein solution. The sodium chloride (1M) was used to elute the protein. The eluted protein solution was then dialyzed. The -80°C Chris Alpha 1-2 LD plus freeze drier was used to freeze-dry the resulting protein solution. The protein powder obtained was kept in an airtight container until ready for use.

2.3.2. Preparation of Modified Magnetic Iron Oxide Nanoparticles

Magnetic iron oxide (Fe_3O_4) nanoparticles were prepared by chemical co-precipitation of Fe^{3+} and Fe^{2+} ions [11] [18] [31] [32]. According to this method, the iron salts solution was prepared by mixing ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) in a ratio of 2:1 in 20 mL 1% aqueous protein solution at room temperature and continuous stirring for 20 minutes. Sodium hydroxide (8 M) solution was prepared in 1% aqueous protein solution under ice water and continuous stirring for 30 minutes at room temperature. The precipitation of magnetic iron oxide (Fe_3O_4) nanoparticles was achieved by dropping the iron salts solution into the NaOH solution at room temperature while continuous stirring for an hour. The magnetic iron oxide nanoparticles obtained with Sodium hydroxide as a base is favoured as they are deemed to possess better magnetic properties [20]. The permanent magnet is utilized to separate the resulting black nanoparticles produced before pouring out the supernatant. Lastly, water and acetone are used to wash the nanoparticles. The obtained fine modified magnetic Fe_3O_4 nanoparticles were finally freeze-dried for 24 hours and stored in an airtight vial ready for use.

2.4. Batch Adsorption Studies

Gold, palladium and platinum precious metal ions solutions were prepared as follows [33] [34]: The stock solutions ($100 \text{ mg} \cdot \text{L}^{-1}$) of predefined quantities of respective metal chloride salts were dissolved in distilled water. The desired

working concentrations were prepared by diluting the stock solutions. Diluted concentrations of 0.1 M HCl and 0.1 M NaOH were used to create acidic and basic environments as required, respectively. The batch experiments were conducted in 50 mL falcon tubes with the modified magnetic iron oxide nanoparticles and the mixture of Au(III), Pd(II) and Pt(IV) solution. The solution was agitated with a Stuart Scientific mechanical shaker at a speed of 150 rpm, allowed to settle overnight before filtration using gravity filtration (Whatmann filter paper No. 1). Perkin Elmer Optima 8000 ICP-OES was used to analyze the equilibrium metal ions concentrations. The experiments were conducted by varying various parameters namely: pH (1.5 - 2.5), initial adsorbate concentration (10 - 100 mgL⁻¹), adsorption agitation time (30 - 240 minutes) and adsorbent dosage (0.005 - 0.065 g) to optimize them. The analysis was done in triplicate and the averages were reported.

The recovery efficiency (R) was calculated using the equation [35]:

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where, C_i is the initial concentration, C_f is the final concentration of the analyte, and %R is the recovery percentage.

3. Results and Discussion

3.1. Characterisation of Modified Magnetic Iron Oxide Nanoparticles

3.1.1. Fourier Transform Infrared Spectrometer (FTIR)

The FTIR measurements were performed to identify the main functional groups of modified magnetic iron oxide nanoparticles to understand the mechanism for precious metal ions adsorption. The transmittance band ranging from 4000 cm⁻¹ to 400 cm⁻¹ was recorded for the FTIR spectra as depicted in **Figure 1** and **Figure 2** and summarized in **Table 1**. These results and a study by Araujo *et al.* [36] depicted that a band at 3281.9 cm⁻¹ for OH could be as a result of proteins and fatty acids structures in Moringa seeds. In addition, the symmetrical and asymmetrical stretching of C-H bond from the -CH₂ group. The OH (alcohol, carboxylic acid) arises at 2942.6 cm⁻¹ wavenumber. Furthermore, the frequencies 1648.4 cm⁻¹ representing Amide I and 1544 cm⁻¹ for Amide II are part of the bands shown in the spectrum. A study by Nermark [37] confirmed that that these amides largely arise from the amide bonds joining amino acids. The study also reveals that absorption at amide I and II yield to C=O bond stretching vibrations and N-H bond bending vibrations, respectively, and they are primarily allocated to the α -helix of the secondary structure in a protein. This further confirms the protein structure in Moringa seeds. Similar functional groups were attained for *M. oleifera* seed pods and *Sclerocarya birrea* [35] and *Plantago ovata* seeds [38]. On the other hand, typical functional groups for iron oxide are depicted by absorption band at 3664.7 cm⁻¹ that corresponds to the hydroxyl functional group and a band at 543.2 cm⁻¹ that is assigned to Fe-O (iron oxide) group

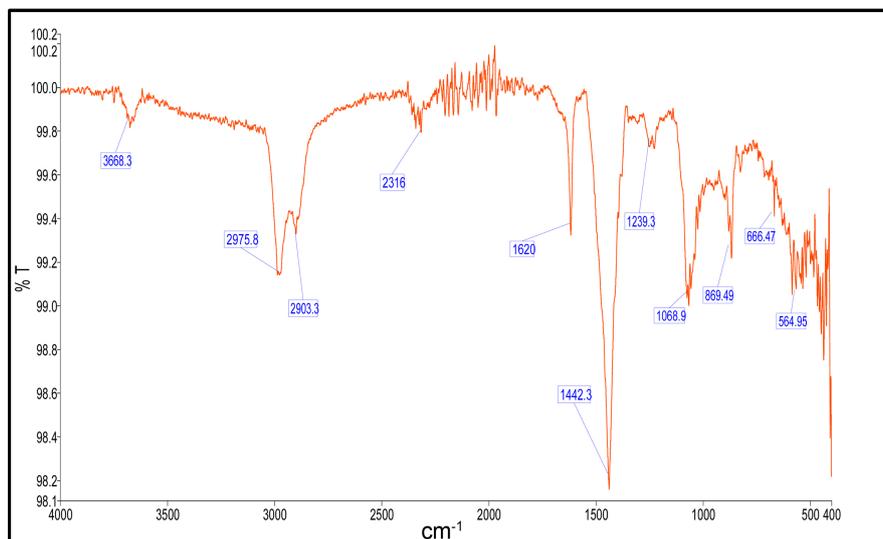


Figure 1. FTIR spectrum of unmodified magnetic iron oxide.

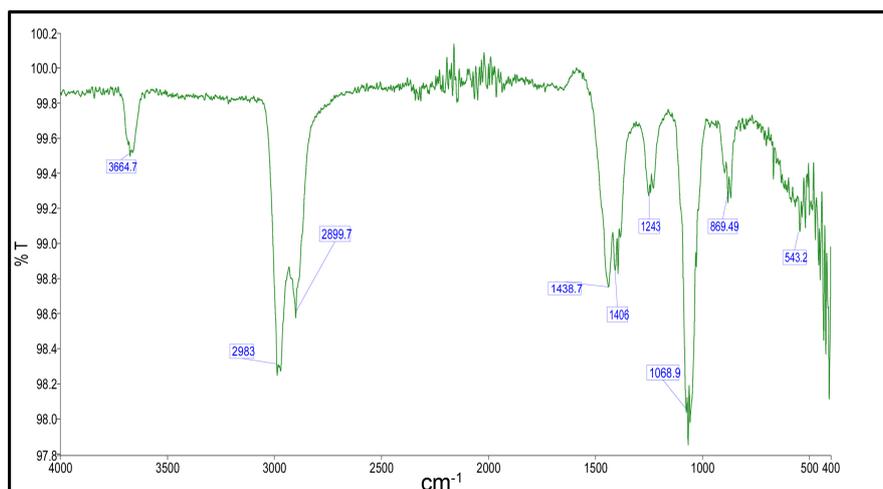


Figure 2. FTIR spectrum of iron oxide modified with Moringa seed proteins extract.

[39]. These identified functional groups might therefore explain the adsorption process thus recovery of precious metal ions in the current study.

3.1.2. Scanning Electron Microscopy

The surface morphology of the unmodified (left) and modified (right) magnetic iron oxide nanoparticles to understand the surface characteristics of the nanoparticles was studied using SEM as shown in **Figure 3**. The surface morphology is porous with various pore sizes as observed in the scanning electron micrograph and this might therefore facilitate the adsorption of the precious metal ions [35] [36]. As depicted in the micrographs, modified magnetic iron oxide nanoparticles appears to have better porosity in comparison to the unmodified magnetic iron oxide nanoparticles. However, the nanoparticles appear to have agglomerated and this might be due to strong bonding of nanoparticles, Van der Waals forces and magnetic dipoles [21] [42].

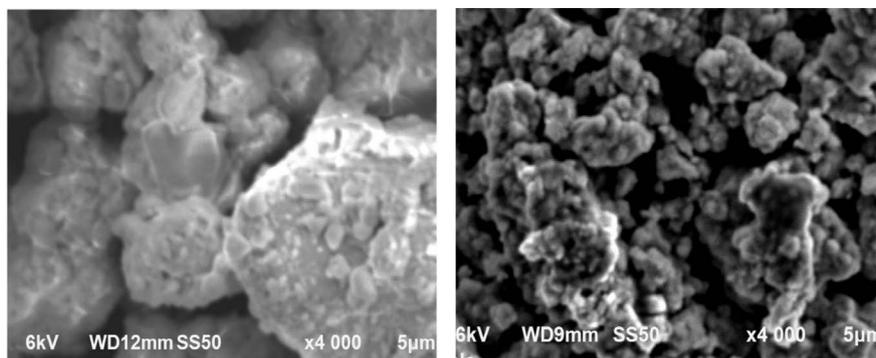


Figure 3. SEM unmodified and modified magnetic iron oxide nanoparticles.

Table 1. Analysis of the IR spectra for unmodified magnetic iron oxide nanoparticles and iron oxide modified with Moringa seed proteins extract (MoFe_3O_4).

Functional group	Reference frequency range (cm^{-1}) [35] [36] [39]-[44]	Observed IR frequency (cm^{-1}) for iron oxide	IR frequency (cm^{-1}) for MoFe_3O_4	Peak shift (cm^{-1})
OH stretching	3700 - 3500	3668.3	3664.7	3.6
OH (Alcohol)	3400 - 2400	2903.3 2975.8	2899.7 2983.3	3.6 -7.5
OH bend (Carboxylic acid)	1440 - 1400	-	1438.7 1406	-
H-O-H (Adsorbed water)	1652 - 1429	1442.3; 1620	1438.7 -	3.6
CO stretching (Carboxylic acid)	1320 - 1210	-	1243	-
OH stretching vibration	1092 - 1060	1068.9	1068.9	0
CO stretching (Alcohol)	1260 - 1000	1239.3	1243	-3.7
Alkenes (CH bend)	~890	889.49	869.49	20
Aromatics (CH bend)	~880	889.49	869.49	20
Fe-O	588 - 535	564.95	543.2	21.75

3.1.3. Thermogravimetric Analysis

Thermal stability of unmodified and modified magnetic iron oxide nanoparticles was studied when the nanoparticles were heated from 30.86°C to 794.80°C as shown in **Figure 4** and **Figure 5**. The different thermal decomposition stages in terms of percentage weight loss and their respective derivatives weight loss percentage per $^\circ\text{C}$ were obtained [36]. The first stage between 30°C to 100°C is associated with water loss. The second stage ranging from 100°C to 350°C could be due to loss of organic matter that might include proteins amino acid residues with various functional groups and other low molecular weight compounds. The third stage between 350°C to 795°C might be from compounds with higher boiling point. At the end of the decomposition stage (795°C), the total residue was therefore attained with overall weight loss of 17.7% and 17.2% for unmodified

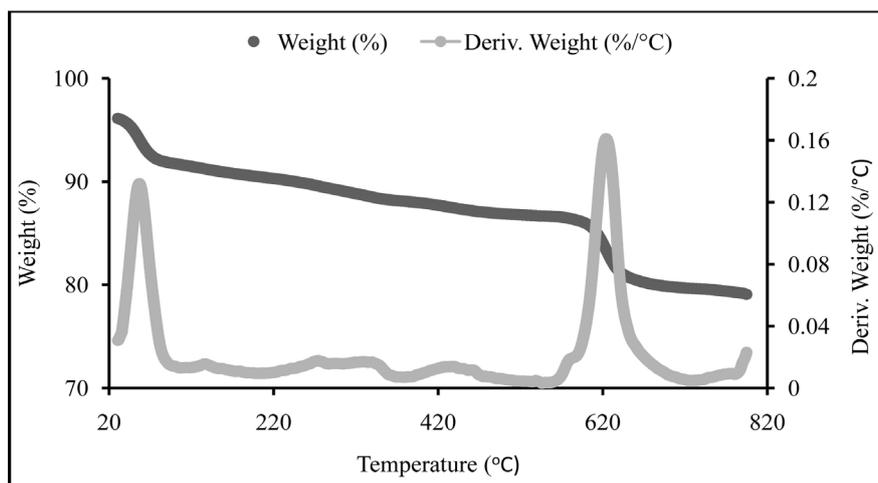


Figure 4. TGA curve for unmodified magnetic iron oxide nanoparticles with weight loss and derivative weight loss.

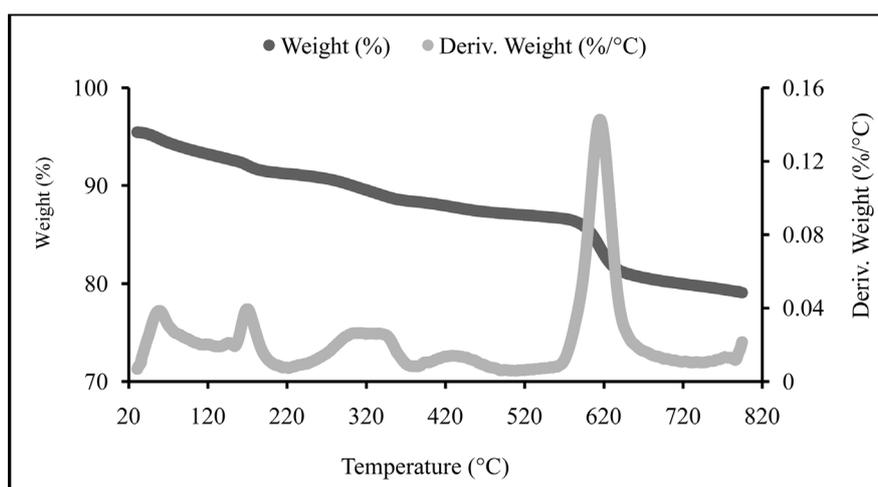


Figure 5. TGA curve for modified magnetic iron oxide nanoparticles with weight loss and derivative weight loss.

and modified iron oxide, respectively. As observed from the curves, the weight loss was slow and a study by Sneha and Sundaram [45] obtained a similar weight loss of about 17% on naked Fe_3O_4 . Other studies by Padmavathy *et al.* [40] and Araujo *et al.* [36] also attained similar mass loss curve as in the current study.

3.1.4. Zeta Potential

The nanoZetasizer was used to characterize the surface charge of the unmodified and modified iron oxide nanoparticles in the pH range of 2 to 12 as shown in **Figure 6**. The zeta potential was pH-dependent. The point of zero charge (isoelectric point) for modified iron oxide nanoparticles and unmodified iron oxide nanoparticles was found to 3.69 and 6.12, respectively. The curves show that at pH ranges below the isoelectric points of the nanoparticles, the surfaces are positively charged and negatively charged at pH ranges above the isoelectric points. The modified magnetic iron oxide nanoparticles is highly negatively

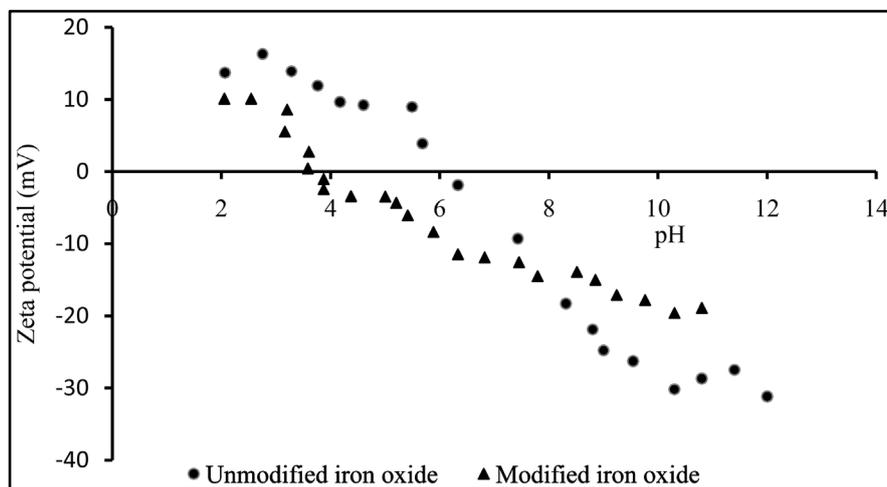


Figure 6. Zeta potential trends for unmodified and modified magnetic iron oxide nanoparticles.

charged, *i.e.* lower zeta potential, compared to unmodified magnetic iron oxide nanoparticles at high pH but less positively charged at lower pH. Similar studies on the characterization of magnetic iron oxide by Aghaei *et al.* [6] and Yang *et al.* [20] obtained isoelectric points in the pH range of 6 - 7 as well. In the current study, the surface charge values obtained therefore explain the dependency of adsorption on pH and the recovery of precious metal ions.

3.2. Effect of Experimental Parameters on Adsorption of Precious Metal Ions on Modified Magnetic iron Oxide Nanoparticles

3.2.1. Effect of pH

The zeta potential of solid surface is an important factor to determine the electrostatic adsorption of metal ions onto the surface. The adsorption of precious metals ions from aqueous solutions is studied to be pH dependent [5] [43] [46] [47]. The selective recovery of precious metal ions on modified magnetic iron oxide nanoparticles was investigated in the pH range of 1.5 to 2.7 at constant agitation time of 120 minutes, 10 mg/L initial concentration and 0.065 g dosage. Several studies have suggested that adsorption of metal ions from wastewater is more efficient at low pH [38] [43] [46] [48]. The pH values were adjusted to desired values using 0.1 M HCl. **Figure 7** shows that as pH value increased, percentage recovery of precious metal ions increased until an optimal pH value is reached after which percentage recovery decreased. At pH 1.5, percentage recovery of precious metal ions were 2.1%, 5.7% and 0.9% for Au(III), Pt(IV) and Pd(II), respectively. When compared to unmodified magnetic iron oxide nanoparticles, the values of 2.1%, 3.8% and 0% for Au(III), Pt(IV) and Pd(II), respectively, were obtained. These percentage recoveries increased to 99.8%, 88.6% and 77.2% for Au(III), Pt(IV) and Pd(II), respectively, at pH 2.5 which was taken to be optimal pH value. For unmodified magnetic iron oxide nanoparticles, the percentage recoveries were 99.8%, 51.8% and 80.4% for Au(III), Pt(IV) and Pd(II), respectively. Lastly the percentage recoveries decreased

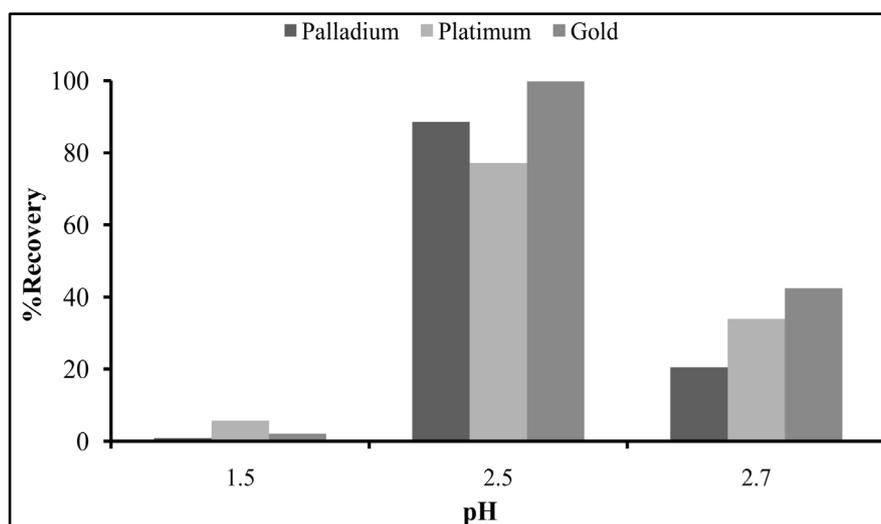


Figure 7. Recovery of precious metal ions at $10 \text{ mg}\cdot\text{L}^{-1}$ using 0.065 g modified iron oxide nanoparticles at different pH values.

to 42.5%, 33.9% and 20.5% for Au(III), Pt(IV) and Pd(II), respectively, at pH 2.7. On the other hand, unmodified magnetic iron oxide nanoparticles gave recoveries of 36.2%, 33.9% and 0.7% for Au(III), Pt(IV) and Pd(II), respectively. A study by Ju *et al.* [48] using a red alga, *Galdieria sulphuraria* also recovered gold and palladium precious metals ions with high efficiency at pH 2.5. The adsorption capacity tends to decrease with increase in pH because at a high pH; there might be less absorption of metal ions due to decreasing chloride anions from the metal salts [46]. On the other hand, at a pH of 1.5 the competition between positively charged hydrogen and precious metal ions might be higher therefore resulting in the lower recoveries observed [34].

At low pH, the dominant species of the PGMs are AuCl_4^- , PtCl_6^{2-} and PdCl_4^- [49] and the zeta potential measurements confirm that the surface of modified and unmodified magnetite particles are positively charged in acidic pH region which actually coincides with pH range below point of zero charge. This promotes a favorable environment for electrostatic adsorption of AuCl_4^- , PtCl_6^{2-} and PdCl_4^- ions. According to Homchuen *et al.* [49], at highly acidic pH, the dissolution of Fe^{3+} is promoted generating ions that compete with AuCl_4^- complex for electrons in active sites of the surface of magnetite. The interaction between AuCl_4^- ions and the magnetite surface through physical adsorption stimulated active sites for electron transfer necessary for the reduction of gold chloride complexes to elemental gold. This may explain why modified iron oxide recovered more PGMs than the unmodified magnetite although the later was more positively charged at low pH. The small uptake of PGMs by the unmodified iron oxide could be due to the presence of the Fe^{3+} dissolved from magnetite, a process that is somehow inhibited in the case modified magnetite. The presence Fe^{3+} as an oxidizer competes with Au(III), Pt(IV) and Pd(II) on the surface of magnetite.

3.2.2. Effect of Initial Adsorbate Concentration

Several studies have demonstrated that initial adsorbate concentration plays a role in the adsorption process of metal ions [35] [39] [40] [47]. **Figure 8** shows the effect of initial adsorbate concentration as varied from 10 to 100 mg·L⁻¹ using modified magnetic iron oxide nanoparticles at constant pH (2.5), agitation time of two hours, and 0.065 g dosage. As initial adsorbate concentration increased, recovery decreased from 83.2% to 42.3% for Au(III), 49.7% to 32.0% for Pt(IV), and 40.9% to 35.1% for Pd(II). In comparison to unmodified magnetic iron oxide, nanoparticles percentage recoveries varied from 60.2% to 43.3% for Au(III), 4.1% to 26.8% for Pt(IV) and 91.4 to 62.4% for Pd(II). This implies that low initial adsorbate concentration increases the ratio of available sites on the surface of adsorbent to the adsorbate concentration thus higher recovery percentage [36] [49]. The opposite is true when initial concentrations are higher. However, Obuseng *et al.* [34] varied initial adsorbate concentration from 1 to 14 mg·L⁻¹ and the results showed that as the initial adsorbate concentration rises, the recovery percentage of metal ions rise until an optimal concentration where biomass is saturated is achieved after which a steady decline is detected when the initial adsorbate concentration is increased. Maina *et al.* [35] concur with these findings. The current study therefore suggest that the initial adsorbate concentration considered could have been toward the optimal concentration thus a decline in recovery percentage of precious metal ions when the initial adsorbate concentration was increased.

3.2.3. Effect of Agitation Time

The effect of agitation time on adsorption of precious metal ions using modified magnetic iron oxide nanoparticles was studied between 0 - 240 minutes at constant pH (2.5), initial adsorbate concentration of 10 mg·L⁻¹, agitation time of two hours, and 0.065 g dosage. **Figure 9** depicts that the percentage recoveries both increased and decreased within the first 120 minutes after which percentage

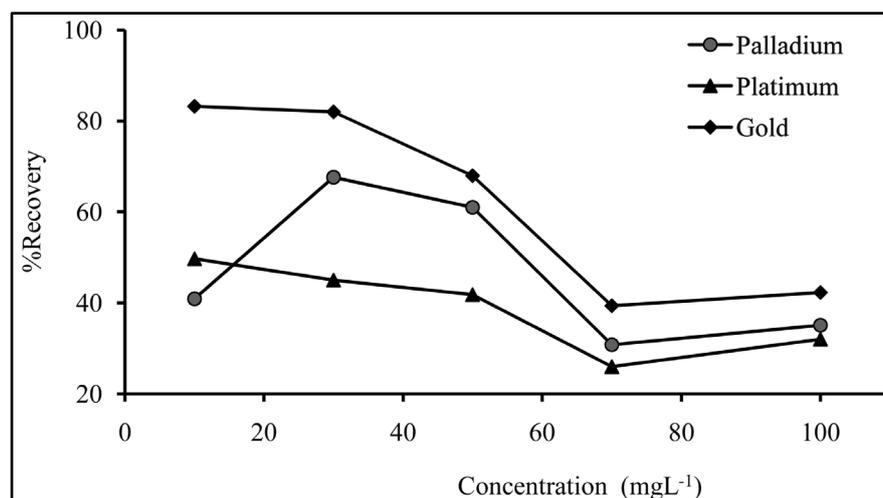


Figure 8. Effect of initial concentration on the recovery of precious metal ions using modified nanoparticles at 10 - 100 mg·L⁻¹.

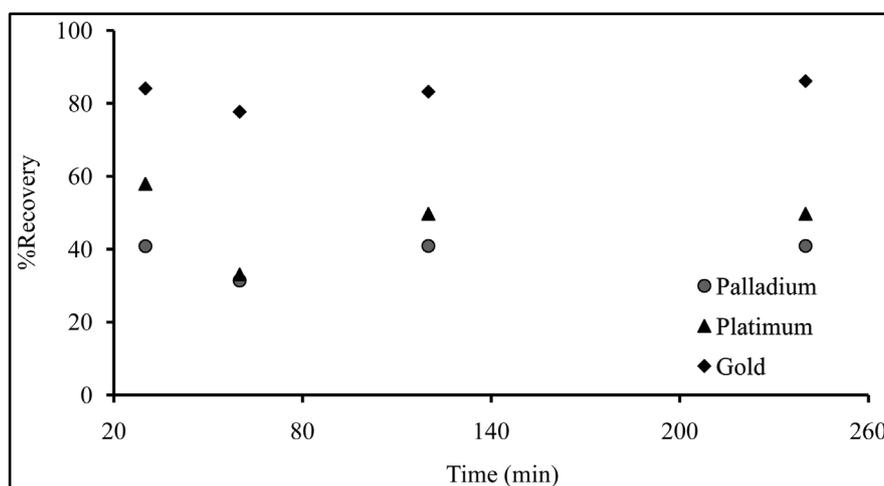


Figure 9. Effect of agitation time on recovery of precious metal ions using modified nanoparticles between 0 - 240 minutes.

recoveries remain almost constant or just slightly increased. The equilibrium was, therefore, reached in 120 minutes. Similar results were attained with unmodified magnetic iron oxide nanoparticles. Studies by Padmavathy *et al.* [40] and Candice *et al.* [50] on similar adsorbent materials also concur with adsorption equilibrium of 120 minutes. These studies suggest that during the initial stages of adsorption there are more vacant sites on the surface of the adsorbent resulting in higher percentage recoveries of precious metals ions and these tend to get saturated at equilibrium thus declined adsorption rate.

3.2.4. Effect of Adsorbent Dosage

The effect of adsorbent dosage on adsorption of precious metal ions using modified magnetic iron oxide nanoparticles was studied between 0.005 g to 0.085 g, equilibrated for two hours with $10 \text{ mg}\cdot\text{L}^{-1}$ at pH 2.5. As shown in **Figure 10**, precious metals ions recoveries rise with dosage until 0.065 g optimal dosage is attained after which a decline in percentage recoveries was obtained. At the optimal dosage, maximal recovery of 99.8% Au(III) was obtained followed by 87.7% Pt(IV) and then 72.7% Pd(II). Comparisons with unmodified magnetic iron oxide nanoparticles yielded percentage recoveries of 100% Au(III), 88.1% Pt(IV) and 67.3% Pd(II). Studies by Mavhungu *et al.* [46] and Hariani *et al.* [47] obtained similar results. These studies demonstrate that increase in percentage recoveries with increase in adsorbent dosage result from rise in vacant active sites on the adsorbent surface. Another study by Maina *et al.* [35] explained further that increase in percentage recoveries with increase in adsorbent dosage is observed until an optimal adsorption level is attained after which the percentage recoveries are reduced due to the decline in vacant active sites on the surface of the adsorbent.

4. Conclusion

In this study, the effectiveness of modified magnetic iron oxide nanoparticles in

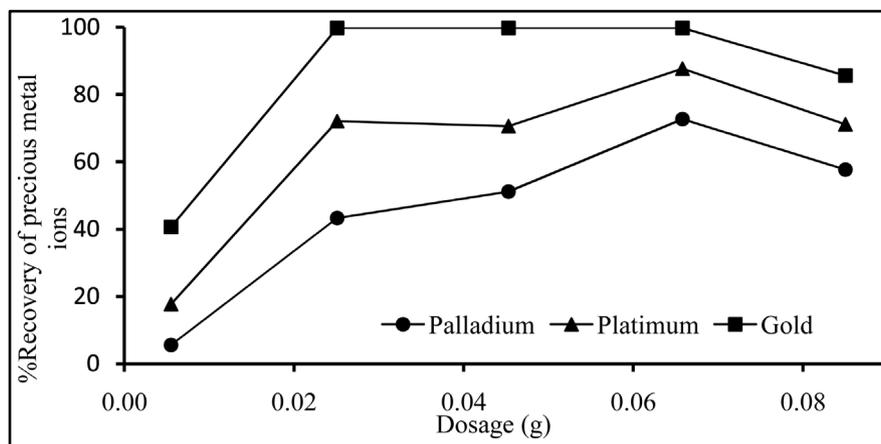


Figure 10. Recovery of precious metal ions at $10 \text{ mg}\cdot\text{L}^{-1}$ using different dosages of modified nanoparticles.

recovery of Au(III), Pt(IV) and Pd(II) precious metal ions from aqueous solutions was investigated. The nanoparticles were prepared by chemical co-precipitation of Fe^{3+} and Fe^{2+} (2:1) in aqueous protein solution (1%) extracted from *M. oleifera* seed. The parameters that studied the adsorption behaviour of the precious metal ions on the nanoparticles on a laboratory scale were pH, initial adsorbate concentration, agitation time and adsorbent dosage. Various characterization techniques namely, FTIR, SEM, TGA, and zeta potential were applied to assess diverse functional groups responsible for adsorption, morphology, thermal stability, and surface charge of the nanoparticles. The FTIR confirmed various functional groups such as amine/amide, carbonyl, hydroxyl, carboxylic and iron oxide on modified magnetic iron oxide nanoparticles that could be responsible for selective recovery of precious metal ions. SEM depicted porous morphology with various pore sizes that might be responsible for retention of precious metal ions. TGA showed a slow weight loss of about 17.2% suggesting stability for the nanoparticles. The isoelectric (point of zero charge) for modified iron oxide nanoparticles was around 3.69, thus the dependency of adsorption on pH and recovery of precious metal ions could be explained by the surface charge values obtained. The optimal conditions for recovery of the precious metal ions obtained from the study were: pH 2.5; 120 minutes agitation time; $10 \text{ mg}\cdot\text{L}^{-1}$ initial concentration; adsorbent dosage 0.065 g. At these conditions, maximum recoveries of 99.8% Au(III), 87.7% Pt(IV), and 72.7% Pd(II) were obtained. The results obtained in the study therefore suggest that modified magnetic iron oxide could be effective in recovery of Au(III), Pt(IV) and Pd(II) precious metal ions. The results clearly show that the recovery of precious metals is not solely due to electrostatic interactions, otherwise the recoveries would have been high for unmodified iron oxide system since it is more positive at low pH as observed from zeta potential measurements. Further studies are needed to determine the mechanism for precious metals recovery by iron oxide nanoparticles modified with Moringa seed proteins.

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Conflicts of Interest

None.

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