

Review

Magnetic Adsorbents for the Recovery of Precious Metals from Leach Solutions and Wastewater

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Abstract: Precious metals which include the platinum group, gold, and silver, play indispensable roles in high technology industries of the modern world due to their outstanding physical and chemical properties. As a result of diminishing availability of mineral sources, increasing demand, and environmental concerns, the recovery of precious metals from both leaching and industrial waste solutions is becoming a very important technology. Magnetic solid phase extraction (MSPE) is a technique that has received substantial consideration in the separation and recovery of precious metals because of the many advantages it offers compared to conventional methods. This technique is based on the extraction of different analytes from solutions using solid adsorbents with magnetic properties. This review focuses on different types of magnetic adsorbents, the main procedures used for synthesis, characterization and their application in precious metals recovery based on recently published literatures.

Keywords: precious metals; solid phase extraction; magnetic adsorbents; aqueous solution

1. Introduction

The rare and naturally-existing metallic chemical elements of high economic value are collectively known as precious metals (PMs). They include the members of the Platinum Group Metals (PGMs) plus gold (Au) and silver (Ag) [1]. Due to their unique physical and chemical properties, precious metals (PMs) are used extensively not only in traditional jewelry and ornamental purposes but also in a variety of advanced applications, such as electronics, chemical and environmental catalysis, dentistry and medicine, and pharmaceutical industries. Since these metals are scarce and exist only in small amounts in the earth's crust, they should be recovered effectively from their natural ores and also from various wastes and secondary sources through recycling [2].

The recovery and removal of precious metals from mineral and wastewater samples are also of great importance due to health and environmental reasons. For instance, high levels of silver are toxic to human cells due to its effect on the rate of wound healing [3]. On the other hand, Pd(II) compounds are highly toxic and carcinogenic and can be easily transported in biological materials through plant roots and the effects can be intensified along the food chain [4]. Therefore, detection and recovery of PMs are essential for economic and environmental reasons.

Precious metals are recovered by commercially available methods including pyrometallurgy and hydrometallurgy. Nowadays, engineers and researchers prefer hydrometallurgical methods for recovery of PMs owing to several advantages including ease and flexibility of operations, clean working conditions, low capital requirement, and low toxic gas emissions. In the case of aqueous PM sources,

separation of target elements from solutions can be directly applied. However, in the case of solid PM sources, dissolution of target metals using suitable solvents or otherwise known as leaching, is required [5].

Amongst various hydrometallurgical techniques to separate PMs from both leaching solutions and waste effluents, solid phase extraction (SPE) offers several advantages over other techniques like liquid-liquid extraction (LLE) [6,7], cloud point extraction (CPE) [8,9], solvent extraction [10], precipitation [11,12], and others. Solid phase extraction is carried out by allowing the desired or target analyte from the solution to adhere or bond, either by ion exchange mechanism or chelating mechanism, at the surface of a solid material known as adsorbents. The adsorbed analyte is stripped from the adsorbent using a suitable eluent and the purified solution undergoes refining. SPE is a widely applied technique in environmental applications, specifically in the separation of metal ions in environmental samples because several reasons including ease of operation, fast kinetics, minimal cost and reagent consumption, and flexibility to combine with different detection techniques whether in on-line or off-line mode [13]. Full recovery and high enrichment factor can be achieved in SPE by careful selection of suitable adsorbents [14]. Various types of material have been employed as solid sorbents for the recovery of PMs. Activated carbon [15–18] is one of the most popular and conventional adsorbents, while graphene oxide [19–21], nanomaterials [22–24], biosorbents, such as chitosan, bacterial biomass, algal, and etc. [25–27], resins [28–30], mesoporous silica [31,32], modified metallic oxides or composite oxides [33], and polymeric materials [34,35] are amongst the more recent and emerging ones. However, these adsorbents use conventional centrifugation or filtration methods for solid-liquid separation or collection which pose operational and practicality issues when the adsorbents used are very fine, particularly in the nanometer size range [36]. Due to this, more focus has been given to the application of magnetic materials as sorbent in SPE in recent years, especially in the recovery of PMs.

Magnetic solid phase extraction (MSPE) is an analytical technique which uses magnetic adsorbents to separate and preconcentrate various organic and inorganic analytes from solution. In MSPE, typically the magnetic adsorbents are added into the solution and contacted with the target analyte for a specified amount of time until adsorption and subsequently, separation of analyte occurs. Following the adsorption process, the magnetic sorbents are separated from the solution by means of an external magnetic field. The loaded magnetic adsorbent is washed and the adsorbed analyte eluted with an appropriate solvent or stripping agent for further purification. MSPE is advantageous over the conventional solid phase extraction techniques for various reasons and among them are the simplicity of sample preparation (does not require prior centrifugation and filtration steps), and ease of solid-liquid separation overcoming the problems associated with conventional filtration and phase separation (column-packing). Due to these, there has been a considerable impetus recently in the exploration of potential adsorbents and novel automation procedures related to MSPE [37].

This review summarizes the different magnetic adsorbents used in SPE for the recovery of precious metals from solutions, their preparation and characterization methods, and also suitable eluents for recycling and reusing of those adsorbents. In addition, factors influencing MSPE of precious metals are also discussed.

2. Precious Metals (PMs)

Precious metals include the members of the Platinum Group Metals (PGMs) (platinum (Pt), palladium (Pd), iridium (Ir), osmium (Os), rhodium (Rh), and ruthenium (Ru)) plus gold (Au) and silver (Ag). Natural sources of these metals are seldom available and unevenly distributed [5]. Platinum, palladium, gold and silver are of major commercial significance [38,39]. The spectacular physical and chemical properties such as lustrous, ductile and non-corrosive and high stability made them indispensable in high technology industries of the modern world. As a result of their increasing demand and their scarcity, acquired skyrocketing prices are never seemed to be come down. Hence the title 'precious' is given to them. The content of the PMs in secondary sources (i.e., electronic and

catalytic waste) was found to be far higher than their content in natural ores. The average concentration of the PMs found in actual and chief natural ores is about 1–30 ppm while secondary sources have higher concentrations around 1–2000 ppm. Hence the spent catalysts, electronic wastes and other secondary sources are also named as the urban mines of the PMs [5].

In industries where gold is processed, produced or utilized, such as metallurgical or electroplating plants, the generation of gold-containing wastewater is inevitable and these waste effluents can be detrimental to the environment. For instance, the contact between Au(III) ions and phospholipid bilayers will result to disturbance of the molecular structure of cells and will affect permeability and biological functions of ion channels, receptors and enzymes consumed in the membrane lipid moiety [14]. Gold production and processing plants generate considerable amounts of waste effluents containing gold species which can negatively impact the environment. For instance, Au(III) can interact with phospholipid bilayers to disturb the molecular structure of cells, affecting structures and behavior such as the permeability and functions of ion channels, receptors and enzymes immersed in the membrane lipid moiety [14]. Therefore, it is essential to recover Au from both secondary sources and primary sources (leach liquors from gold ores) from the economic and environmental points of view.

Silver is present in limited amounts in the earth's crust and is commonly associated with ores of Au, Cu, Pb and Zn. Silver can also be sourced naturally as a co-product of gold or as a byproduct of zinc, copper, antimony, lead and others from metallurgical processing industries [39]. Silver has found many applications in a number of industries because of its useful properties such as excellent malleability, ductility, electrical, and thermal conductivity, catalysis, photosensitivity, and antimicrobial properties [40]. As a result of increasing industrial activities involving silver, it has become a contaminant species of concern for the environment and pose health risks to human. Human contact with soluble silver compounds either through skin, ingestion or inhalation can cause eye and skin irritation, respiratory and other internal organ malfunction (liver and kidney damage) and blood cells mutation [39,41].

Aside from platinum and palladium, other PGMs of commercial significance include rhodium, iridium and ruthenium which are traded in moderate quantities. Osmium is rarely used [38]. Natural deposits of platinum and PGMs can be found in Russia, North America, Canada, and South Africa. Most of the platinum produced in the world can be mined in an area popularly known as the Bushveld Igneous Complex which can be found in South Africa. Usually, PGMs are recovered as byproduct or co-product depending on their abundance in the ore [42]. PGMs have distinguishing characteristics such as high melting point, chemically inert to different substances (even at high temperatures), corrosion resistant, electrical resistivity, catalytic properties, and brilliant color that have been exploited in various industrial applications [38,43,44]. These excellent chemical and physical properties propelled the huge demand and increasing number of applications for PGMs in various fields. Due to large uses of PGMs, accumulation of huge amount of these metals in the environment cannot be avoided and the release of soluble PGM ions in the environment inevitable. The presence of soluble PGM ions in the environment pose hazards to human health and growth of other living organisms [45]. Therefore, due to the declining resources of PMs, increasing worldwide demand, and the growing environmental concern, the recovery of PMs from leaching and waste solutions has become a very important consideration.

3. Magnetic Solid Phase Extraction (MSPE)

As mentioned in Section 2, due to extensive applications, toxicity, and economic significance of precious metals, their separation from leaching solutions and wastewater even in trace amounts is beneficial. Therefore, the development of dependable and efficient methods for the pre-concentration (in the case of ultra-trace concentration of analytes and complex media), determination, separation and recovery of these valuable metals are vital.

Among various separation and pre-concentration techniques, solid phase extraction (SPE) offers a number of advantages including simplicity of sample preparation, faster kinetics, better enrichment factors leading to improved recoveries, enhanced phase separation and reduced energy and solvent consumption leading to lower capital and operating costs. In SPE, the extraction depends on the partition coefficient of analytes between the solid-liquid phases, hence, the selection of the appropriate sorbent material is a crucial factor [46]. Recently, a novel SPE procedure using magnetic or magnetizable materials has been introduced and the new method is called magnetic solid phase extraction (MSPE) [47]. MSPE requires the addition of magnetic sorbent particles to the target ions-containing solution. The target ions are adsorbed onto the surface of magnetic material and the magnetic particles containing the analytes are collected by applying an external magnetic field. The adsorbed analyte is then eluted with a suitable solvent, analysed and the purified solution sent to other downstream processes or refining. MSPE offers several advantages compared to conventional solid phase extraction methods: (i) simplified sample pre-treatment in contrast with the time-consuming column packing; (ii) fast and easy analyte separation since sample pre-treatment (i.e., centrifugation, filtration, etc.) is not required; (iii) magnetic sorbent particles render high selectivity towards environmental and biological compounds treated even with the presence of suspended solids; (iv) typical sample impurities that hinders the adsorption process during the magnetic separation are repelled due to its diamagnetic properties; and (v) opportunity for automation procedures (off- and on-line) with flow injection analysis and other related methods providing fast, selective, sensitive and repeatable methods for conventional analysis [37].

The most significant element to achieve sensitivity and selectivity in MSPE is the choice of the adsorbent material to be used [13]. A competitive adsorbent material is characterized by good selectivity, high specific area, suitable physical and chemical stability, and an improved extraction efficiency. Most of the magnetic particles consist of magnetic elements such as iron, nickel, cobalt or their oxides and alloys that exhibits ferromagnetic or superparamagnetic properties [46,48]. Upon the application of an external field, magnetic particles tend to act as permanent magnets that form lattices or aggregates considering the magnetic interaction. Ferromagnetic particles possess permanent magnetism and results in a lattice form when magnetic field is removed. On the contrary, superparamagnetic particles are attracted to magnetic field however magnetic properties does not remain after the elimination of magnetic field. Magnetic particles come in a wide range of sizes from nanoparticles to micro-sized particles [46].

Generally, various inorganic materials including Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, CoFe_2O_4 , MnFe_2O_4 , CoPt_3 and FePt can be utilized as microparticles that can supply magnetism [48]. Amongst the magnetic particles, iron oxides such as magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), have received considerable attention attributable to their particle size and high surface area which contributes to faster kinetics and improved extraction efficiency for analytes and have considered as novel sorbents materials in SPE. In addition, their superparamagnetic property allows the easy handling of adsorbents upon exposure to an external magnetic field [46].

Homchuen et al. (2016) [43] studied the recovery of platinum, palladium, and rhodium from chloride solution using magnetite as adsorbent. Adsorption experiments were done utilizing reagent-grade synthetic magnetite powder at room temperature, and the effects of various process parameters, such as pH, contact time, chloride concentration, and PGM concentrations were explored. According to the experimental results, the uptake amounts of Pt, Pd, and Rh were greatly influenced by pH. Platinum and palladium were favorably adsorbed at pH 6–7, and while pH 3–4 was found suitable for rhodium at 24 h contact time, 0.1 mol/dm³ chloride concentration and initial PGM concentration of 0.05 mol/m³. The uptake amounts of Pt, Pd, and Rh increased with time and equilibrium was achieved over 24 h. The slow sorption kinetics suggests that the adsorption mechanism does not only involve physical adsorption but chemisorption as well. The results of the study showed the potential of magnetite as a selective adsorbent to recover the metals, such as Pt and Pd, from chloride solution or chloride leach liquors.

The recovery of gold chloride (AuCl_4^-) from chloride solution using synthetic and naturally-occurring magnetite powders was studied by Alorro and his colleagues [49] by conducting adsorption experiments and considering various process parameters that affect the adsorption process (pH, contact time, chloride concentration, etc.). The results of the study indicated that synthetic magnetite demonstrated selectivity towards Au, Pt and Pd, and to a minor extent, Cu and Ni. The natural magnetite was found to be selective towards Au only. Maximum Au adsorption was achieved at pH 6–7 for both types of magnetite. At this pH, maximum Au uptake values of 4.4 mmol/g and 5.0 mmol/g were obtained for synthetic and natural magnetite, respectively. The results also revealed that natural magnetite can recover more Au compared to the synthetic magnetite at 24-h contact time. It was also observed that the Au uptake amounts for both types of magnetite were still at increasing trends even after 24 h indicating that equilibrium was not yet attained. This observation is not common in a typical physical adsorption process. Increased chloride concentration decreased the Au uptake capacity for both synthetic and natural magnetite.

Alorro et al. (2015) [50] also examined the adsorption of gold complexes onto the surface of magnetite and determined the gold adsorption mechanism by conducting electrochemical experiments (potential sweep method). The results of electrochemical studies suggested that gold chloride complexes are reduced to metallic gold on the surface of magnetite and the authors proposed a four-stage uptake mechanism: (i) gold chloride complex was transported from the bulk solution onto the surface of the magnetite; (ii) adsorption of AuCl_4^- ions on magnetite surface by electrostatic attraction; (iii) electrochemical reduction of AuCl_4^- to metallic Au; and (iv) the transport of soluble species to the bulk solution phase. Zeta potential measurements confirm that the surface of magnetite is positive at acidic pH region promoting a favorable environment for electrostatic adsorption of AuCl_4^- ions. However, 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 point of zero charge of magnetite particles was found to be near the neutral pH range and this corresponded well to the optimum pH for adsorption (pH 6–7) presented in their previous study [49]. 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. At alkaline pH, low Au recovery was observed since the surface charge of magnetite is negative inhibiting the approach of gold chloride complexes to the surface of magnetite due to electrostatic repulsion.

Recently, magnetic nanoparticles (MNPs) ranging in size from 1–200 nm and represented by the general formula MFe_2O_4 ($\text{M} = \text{Fe}, \text{Co}, \text{Cu}, \text{Mn}, \text{etc.}$), have attracted much attention for applications related to heavy metals removal as well as recovery of precious metals from wastewater [36]. Among the more known MNPs are magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and cobalt oxide (Co_3O_4). This new application is attributed to their superparamagnetic nature as well as to their unique physical and chemical properties including high dispersibility, large surface area, and high surface to volume ratio resulting to higher adsorption capacity [46]. The application of MNPs in metal separation processes can significantly reduce the reaction time and adsorbent consumption due to faster kinetics and the need for a small adsorbent amount only to achieve high loading capacity [51]. Decreasing the particle size to nanoscale increases its active sites and consequently reduces the total mass required for treatment [52].

In the study conducted by Uheida et al. (2006) [53], Fe_3O_4 nanoparticles of particle size approximately 10 nm were synthesized for the recovery of palladium(II), rhodium(III), and platinum(IV) from dilute hydrochloric acid solutions. Several parameters influencing the adsorption, such as contact time, metal and solute (H^+ , Cl^-) concentrations, were studied. The fast equilibrium time of less 20 min achieved for all metals was accounted to the large surface area and high surface reactivity of the Fe_3O_4 nanoparticles. The maximum loading capacity of Fe_3O_4 nanoparticles for Pd(II), Rh(III), and Pt(IV) was determined to be 0.103, 0.149, and 0.068 mmol/g, respectively. Different eluants were assessed to strip Pt(IV), Pd(II), and Rh(III) from Fe_3O_4 nanoparticles. The authors found that 0.5 mol/L HNO_3 can elute Pd(II), Rh(III), and Pt(IV) ions simultaneously, while 1 mol/L

NaHSO₃ was effective only for Rh(III), and 0.5 mol/L NaClO₄ was applicable for Pt(IV). It was also observed that the nanoparticles exhibited stronger attraction towards Rh(III) than Pd(II) and Pt(IV) in a competitive environment.

Mohammadi et al. (2011) [54] investigated the potential of magnetic Fe₃O₄ nanoparticles as adsorbent for simultaneous separation and preconcentration of trace amounts of palladium and rhodium from Pt-Ir alloy and dust samples, prior to flame atomic absorption spectroscopy [54]. In this research work, the effect of pH on the adsorption of analyte ions was studied by varying the pH from 3 to 12. The analyte ions quantitatively were adsorbed on magnetic Fe₃O₄ nanoparticles in the pH range of 10–12. The magnetic nanoparticles (MNPs) were easily separated from the aqueous solution with the aid of an external magnetic field. In addition, the capacity of the sorbent for palladium and rhodium was determined to be 27.2 and 31.8 mg/g, respectively. After extraction and collection of MNPs, the analyte ions were stripped of precious metals using HCl 1.0 mol/L.

Several researchers synthesized different magnetic composites including magnetic particles, activated carbon, and other materials for the separation of precious metals from solutions. The combination of adsorptive and magnetic properties in one composite allows the preparation of magnetic adsorbent which can be potentially applied in wastewater treatment [55] and metals recovery. For instance, in a research work conducted by Tsyganova et al. (2013) [56], the process of deposition of gold from an aqueous solution of hydrogen tetrachloroaurate(III) on microporous composites synthesized from a blend of sawdust, iron and zinc chlorides was examined. Synthesis of the sorbent was conducted by chemical activation of sawdust modified with iron and zinc chlorides. Composites carbonized at temperatures of 400 and 800 °C as well as industrial activated carbon synthesized from coconut shell at a temperature of 1000 °C were selected as samples. The obtained magnetic samples were of a microporous structure (micropore volume of 0.4–0.6 m³/g). Saturation of samples by gold was performed as follows: a weighed portion (0.3–0.5 g) of the composite was placed in an aqueous hydrogen tetrachloroaurate solution (solution volume, $V_s = 3.0$ mL and Au concentration, $C_{Au} = 14.4$ mg/mL) and maintained for 3 h, then the blend was filtered and the filtrate was analyzed for gold content by atomic absorption. Results showed that synthesized iron-containing sorbents have higher sorption activity compared to industrial activated carbon. This may be caused by the partial dissolution of magnetite, its redox properties, and the formation of the free active surface for the gold precipitation.

In a research by Wang et al. (2012) [57] magnetic nanoparticles/graphitic carbon nanostructures composite were prepared by combining graphitic carbon nanostructures (GCNs) with magnetic nanoparticles for easier recovery of GCN adsorbents from the liquid-phase system compared to traditional technique (filtration or centrifugation). Adsorbents such as graphitic carbon nanostructures (GCNs) are promising due to its excellent physico-chemical properties associated with thermal resistance, chemical stability, rigidity and energy adsorption sites, which leads to improved adsorption performance. The results of the study showed that synthesized MNPs/GCNs composites can be utilized as effective mobile adsorbents for the separation of precious metal ions, specifically Ag⁺ and Au³⁺, from aqueous solution. The obtained uptake amounts for Ag⁺ and Au³⁺ ions were 7.88 mg/g and 7.92 mg/g, respectively, higher than that of activated carbon.

Carbon nanotubes (CNTs) have gained considerable interest as excellent sorbents in the solid phase extraction after their discovery in 1991. CNTs are found to have exceptional properties such as high surface area and inner volume, stability, mechanical strength, possibility of establishing π - π interactions and their capacity for functionalization. However, the use of CNTs is limited due to the following drawbacks: the low solubility of CNTs in water and the intricate recovery of CNTs from dispersing media. In an effort to overcome these downsides, surface modifications of CNTs have been proposed. In order to improve the solubility of CNTs, one of the major considerations was to oxidize the nanotubes. The oxidation process introduces hydroxyl, carbonyl and carboxyl groups onto the nanotube surface and creates bonded surface oxygen-containing radicals that have adsorption capacity for various analytes. The intricate recovery of CNTs from dispersing media can

be addressed by converting CNTs to magnetic materials. Magnetic CNTs (M-CNTs) were prepared by synthesizing magnetic nanomaterials with CNTs and utilizing them as adsorbents in magnetic solid-phase extraction. Numerous metals and metal oxides have been prepared to produce magnetic carbon nanotubes intended for various applications. The iron oxides such as magnetite (Fe_3O_4) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are commonly used as adsorbents in M-SPE and other analytical applications [37]. Herrero-Latorre et al. (2015) [37] reviewed several MSPE applications using M-CNT composites as sorbent. The review also covered the preparation and synthesis of M-CNTs and the different applications of these compounds in MSPE.

3.1. Preparation of Magnetic Adsorbents

Pure inorganic magnetic particles (Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$) are susceptible to accumulation of lattices and aggregates that may alter their magnetic characteristic. The disadvantages of using magnetic particles in the recovery of metal ions include: low selectivity towards target metal ions in complex matrices and unstable particles in strong acidic solutions [46,58–60]. A surface modification of a suitable functional group of the magnetic core has been considered to address these limitations. The magnetic core is coated with a shell that can either be inorganic (e.g., silica or alumina) or organic molecules (e.g., modified with polymer or surfactant, etc.) in order to improve its chemical stability, resistance to oxidation and increase the selectivity towards target metal ions. Furthermore, surface functionalization of magnetic particles can be accomplished by incorporating organic or inorganic functional groups onto inorganic shell improving the sorption capability (Figure 1) [46]. According to the hard-soft acid-base (HSAB) theory by Pearson [61], precious metal ions such as Ag(I) , Au(III) , Pd(II) , and Pt(II) are soft acids and tend to coordinate with functional moieties containing soft atoms such as nitrogen, and sulfur atoms [14].

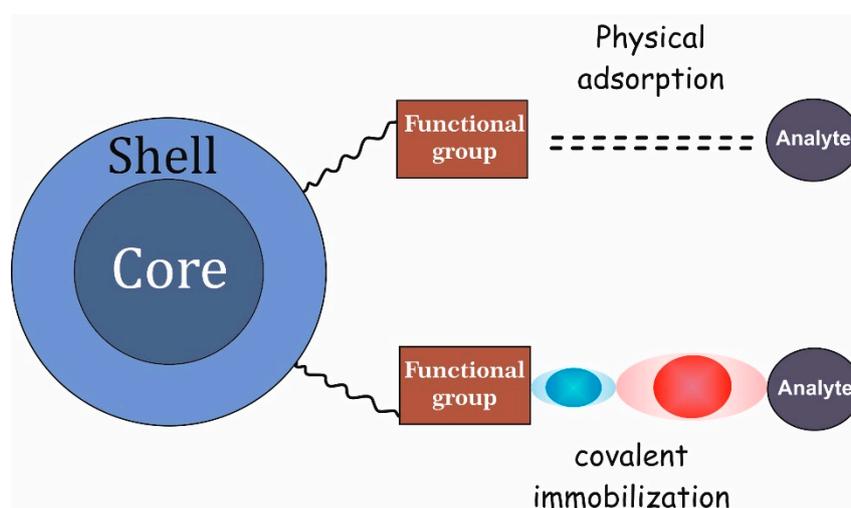


Figure 1. Functionalization of a core-shell type structure of MPs (magnetic particles) [46].

Surface modification processes of magnetic particles are generally comprised of three steps: (i) preparation of the magnetic sorbent (magnetite or maghemite); (ii) layering of the magnetic core with a shell-like framework and (iii) functionalization of the resultant core-shell structure [46]. Typical methods of producing magnetic sorbent include co-precipitation, pyrolysis, hydrothermal and solvothermal methods. Other methods such as sol-gel and microemulsion are applied to coat the magnetic particle (Xiao et al., 2016).

The most common and efficient technique of preparing iron oxide (Fe_3O_4 , Fe_2O_3 , etc.) and ferrite (Zn-Mn ferrite, Ni-Zn ferrite, Co-Zn ferrite) is the co-precipitation method. This procedure consisted of the addition of alkaline solution (ammonia, sodium, hydroxide solution) to the metallic salt solution as

precipitant which will cause the metal ions to precipitate out from the solution. The advantages of this method include simple preparation, simpler reaction conditions and higher product purity. However, this method is limited by the occurrence of agglomeration during the washing, filtering, and drying phases. The size and shape of the nanoparticles produced using this method are dependent on the following: type of salt used (chlorides, sulfates, nitrates, perchlorates, etc.), ratio of ferric and ferrous ions, reaction temperature, solution pH, ionic strength of the media and other reaction factors (stirring rate, mode of solution addition, etc.) [46,48,62].

Mwilu et al. (2014) [63] synthesized magnetic particles for the capture and concentration of AgNPs in aqueous media. The magnetic particles used in the study were synthesized by co-precipitation method. A mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (13.9 g) and $\text{Fe}_2(\text{SO}_4)_3$ (20 g) was dissolved in 500 mL water in a 1000 mL beaker. Ammonium hydroxide (25%) was added slowly to adjust the solution to pH 10. The mixture was then continuously stirred for 1 h at 60 °C. The unmodified magnetic particles (UMPs) were magnetically separated, washed with water until a pH of 7 was obtained, and then vacuum-dried at 60 °C for 2 h. When examined under SEM, it was found that suspensions of these partially dispersed particles showed spherical morphology with a size range of 10–25 nm.

Another way of preparing magnetic particles is through pyrolysis method. In this method, magnetic micro/nano particles are prepared by thermal decomposition of precursors such as metal compounds ($\text{Fe}(\text{acac})_3$, $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$ and $\text{Fe}(\text{Cup})_3$ (acac and Cup are acetyl acetone and cup ferrate respectively)) at elevated temperature and pressure. The particles are then oxidized to magnetic metal oxide nanoparticles. Pyrolysis method has the advantages of producing particles with high nano-crystallinity, tunable size and narrow diameter distribution [48,64].

An alternative way of synthesizing magnetite is by hydrothermal method. Hydrothermal synthesis is carried out under high temperature and pressure in an autoclave with water as the reaction medium, promoting dissolution and reaction of usually sparingly soluble and insoluble substances followed by product recrystallization. Both high temperature and high pressure offer several benefits including improvement in magnetic property and product purity. Hydrothermal synthesis can also effectively control the size and shape of particles and particles and minimizes particle agglomeration. Subsequently, the method is capable of generating particles with good dispersibility and uniform size [48]. The method can be done either with or without the use of specific surfactants [62,65,66].

Solvothermal method is also a popular method developed to prepare magnetic particles containing ethylene glycol, oleic acid and trioctylphosphine oxide or hexadecylamine [46]. Yu et al. (2010) [67] successfully synthesized superparamagnetic magnetite microspheres with hydrophobic surface using the conventional solvothermal technique based on the hydrolysis of iron-oleate complex in diphenyl ether in the presence of oleic acid as ligand. The Transmitting Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) results showed that the synthesized spherical nanostructures were about 140 nm in size and were self-assembly or agglomerates of the 10 nm primary magnetic nanoparticles. The X-ray diffraction (XRD) analysis confirmed that the magnetic microspheres were composed of magnetite. Magnetic measurements demonstrated that the spherical nanostructures are superparamagnetic at room temperature with no magnetic residual and coercive force. In addition, the microspheres can be appropriately diffused in different non-polar solvents, a characteristic brought about by their hydrophobic surface coating.

The synthesis of maghemite, another known magnetic adsorbent, was described by Giakisikli and Anthemidis [46] in their review article. Nanoparticles of maghemite were prepared by dissolving magnetite particles using acid and then roasting at 90–100 °C for 0.5 h for oxidation [46]. Sun et al. (2004) [68] also reported the synthesis of maghemite particles using magnetite (Fe_3O_4) nanoparticles as the precursor. The magnetite with mean diameter of about 7–23 nm was prepared by partial reduction coprecipitation and modified Massart method, respectively, and then transformed to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles by aerated oxidization of acidified magnetite nanoparticles aqueous suspension [68].

The layering of the magnetic core can be prepared through integration of the magnetic core by silica, alumina or other metal oxides as well as organic polymers/non-polymers [46]. In the following subsections, the classification of magnetic particles according to the type of shell is presented. For precious metal determination and separation, several works have been reported using different magnetic materials (with or without organic and inorganic coating and functional groups) as summarized in Table 1.

3.1.1. Magnetic Particles with Inorganic Coating

Various kinds of inorganic materials have been used in recent years as surface coating for magnetic particles. These materials include silica, alumina, zirconium, and ferrites [46,69,70]. Among these coating materials, silica and alumina have been reported with most applications in precious metals determination and separation via SPE.

The strong affinity of silica towards magnetite particles has been exploited to impart surface modification on MPs. The procedure is commonly done using Stöber method through a sol-gel reaction, which incorporates alkoxy silane (mainly tetraethoxysilane, TEOS) in acidic or basic media in a nitrogen environment. Generally, the silica coating is relatively stable and no primer is required for improved deposition and adhesion. Functionalization of the surface of silica coated MPs is usually done by silanation using silane coupling agents like amine, thiol, carboxylic and C_{18} [46,51]. Inorganic coating material, such as silica (SiO_2), has outstanding physical and chemical properties such as nontoxic and stable to redox reactions [60], chemically inert in acidic solution and viable for modification, prevents the agglomeration and inhibit the dissolution in acidic solution [71]. Another benefit of amorphous silica coating on MPs is providing strength and stability to magnetic cores and offering suitable platforms for chemical derivatization, thus making functionalization easier [72].

In a research work conducted by Ranjbar et al. (2014) [73], the recovery of gold from copper anode slime by means of a novel process utilizing magnetite nanoparticles (MNPs) was studied. All the gold content of copper anode slime was dissolved in thiourea solution as leachant and a positive complex of gold and thiourea was obtained as a result. The gold complex was present as $Au(CS(NH_2)_2)_2^{2+}$ in solution. MNPs were prepared using the co-precipitation method, and the silica-coating process was carried out according to the Stöber method to be used for recovery of gold from thiourea solution. TEM images illustrated that the particle size for MNPs and silica-coating MNPs was about 8 and 10 nm, respectively. Gold adsorption onto the NPs occurred according to the electrostatic attraction between the negative charged MNPs and positive complex of gold. Finally, Au complex adsorbed on MNPs could be desorbed effectively using ammonia to increase the pH, and this is because of the low stability of gold complex in alkaline solutions. The results suggest that MNPs can be an effective alternative to conventional adsorbents for the adsorption of gold complex from its solution at recovery efficiency as high as 100% and very short contact time.

Thiol-functionalized $Fe_3O_4@SiO_2$ nanoparticles ($Fe_3O_4@SiO_2-SH$) were synthesized for the recovery of gold from dilute solutions by Zhang et al. (2013) and Roto et al. (2016) [59,71]. Fe_3O_4 nanoparticles were produced by coprecipitation method, and the surface modification with SiO_2 was performed through hydrolyzation of Na_2SiO_3 to prevent the core from being oxidized or dissolved under acid solution after the silanization reaction of $Fe_3O_4@SiO_2$. The stable Au-S bond formed between the thiol group and gold ion served as the basis of the adsorbent's application in gold recovery from solution. According to the study conducted by Zhang et al. (2013), the maximum adsorption capacity was found to be 84.75 mg/g at pH 5. Complete gold recovery was observed using an initial gold concentration of 5 mg/L and $Fe_3O_4@SiO_2-SH$ as the adsorbent. However, increasing the gold concentration to 10 mg/L reduced the gold recovery to 98.8%. At pH 3 to 7, the adsorption capacity exhibited a decreasing trend but shifted to increasing mode in alkaline pH region. Desorption of the gold-loaded adsorbents was achieved by using 1 M or 2 M HCl containing 2% thiourea. Good adsorbent reusability was also noted after 5 recycles. According to the results from the work of Roto et al. (2016), the maximum adsorption capacity of modified adsorbent was 115 mg/g at an initial

concentration of 55 mg/L and pH 3. In addition, the thiourea solution in 1 M HCl can desorb 60% of initial $[\text{AuCl}_4]$ adsorption amount.

The synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microspheres carrying thiols with high magnetization and their adsorption properties for Au(III) separation from aqueous solutions were reported by Peng et al. (2016) [74]. The maximum adsorption capacity of Au(III) on thiol-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ microspheres was 43.7 mg/g. Since gold usually coexists with copper in e-wastes and copper concentrate, the effect of Cu(II) ions on the selective separation of Au(III) from aqueous solutions was also investigated. The results showed that Cu(II) ions have little interference in the adsorption of Au(III) on the adsorbent. To examine the recovery of Au(III) and the reusability of the magnetic adsorbent, different eluents were used to recover the Au(III) species including 1 M $\text{Na}_2\text{S}_2\text{O}_3$; 0.5 M thiourea; 0.5 M thiourea + 5% HNO_3 ; 1 M thiourea + 5% HNO_3 ; and 1 M thiourea + 5% HCl. A satisfactory recovery of 89.5% was achieved by using an eluent consisting of 1 M thiourea and 5% HCl, in spite of thiols having high affinity to Au(III) ions based on the hard-soft acid-base (HSAB) theory by Pearson.

Ye et al. (2014) [75] successfully synthesized and characterized crown ether-functionalized magnetic silica nanoparticles. The magnetic particles were used for on-line determination of gold, palladium, and platinum in mine samples based on a method known as flow injection micro-column preconcentration coupled with graphite furnace atomic absorption spectrometry (GFAAS). The magnetic Fe_3O_4 nanoparticles were synthesized following solvothermal reaction functionalized with 4'-aminobenzo-15-crown-5-ether and then packed into a micro-column and eluted with a solution consisting of 2% thiourea and 0.1 M HCl prior to GFAAS. The utility of the synthesized magnetic adsorbents in GFAAS coupled with flow injection technique (FI-column) for the determination of Au, Pd, and Pt was able to enhance the level of detection even to trace amounts and limits of 0.16, 0.28, and 1.01 ng/mL were achieved. Consequently, the combined method has shown to be highly efficient in terms of enrichment factor, sensitivity, and accuracy for the determination trace Au, Pd, and Pt.

The growing number of applications for silver nanoparticles (AgNPs) has led to increase in production and generation of waste effluents containing the metal. As silver contamination pose risk to human and the environment due to its toxic effects, the removal of AgNPs from wastewater is a must. Zhang et al. (2017) [76] synthesized a nitrogen rich (~10% nitrogen content) core-shell magnetic mesoporous silica adsorbent for the removal of AgNPs. The study was able to demonstrate the potential of the prepare adsorbent for such purpose. The adsorbent preparation included a poly(ethylenimine) functionalization stage of the core-shell magnetic mesoporous silica composites ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PEI}$). The choice of using poly(ethylenimine) (PEI) as a functional group for surface functionalization of metal oxides (alumina, silica, ad zirconia), according to the study, was due to its possession of a cationic polymeric with branched chains containing a large number of amino groups providing good metal chelation properties. The results of the study indicated that the adsorption capacity of the prepared magnetic adsorbent for AgNPs was 909.1 mg/g and with good regeneration and reusability up to at least five cycles.

Graphene oxide (GO), a highly oxidized form of graphene, has been described as an ideal material for adsorbent preparation due to many oxygen-containing functional groups it contain including carboxyl, hydroxyl and epoxide groups on its edges and surface. The increasing application of GO-based materials as adsorbent has been driven by sweeping increase in porosity, surface area and the possibility of inner-pore diffusion of pollutants [77]. In terms of its application in the recovery of precious metal ions, GO has been utilized in combination with magnetic particles to generate a composite adsorbent. One example is the study reported by Jalilian et al. (2017) [14] which described the preparation of a nanosorbent for fast magnetic solid phase extraction of trace levels of Ag(I), Au(III), Pd(II) and Pt(II). The nanosorbent included graphene oxide sheets functionalized with silica and magnetite nanoparticles (mGO) as the core. Further modifications were done by a polypyrrole-polythiophene copolymer via oxidative polymerization to produce a material of the type $\text{mGO}@\text{SiO}_2@\text{PPy-PTh}$. Magnetic GO (mGO) nanocomposites are advantageous for its particle size,

high water dispersability and the avoidance of conventional solid-liquid separation techniques, such as centrifugation and filtration during the solid phase extraction. The formation of strong complexes between the target precious metal ions and the surface of the sorbent is made possible due to nitrogen- and sulfur-containing functional groups found on both sides of the nanocomposite sheets. It was determined that the maximum sorption capacities were 49, 50, 45, and 50 mg/g for Ag(I), Au(III), Pd(II) and Pt(II), respectively. Elution of the loaded adsorbents was carried out using thiourea-HCl solution. Successful applications in the extraction and determination of analytes in wastewater (electroplating, radiological and photographic wastewater), sea water, and road dust were reported.

Anbia and Mehrizi (2016) [60] synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core/shell magnetic nanostructure and modified it by *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane for the adsorption of hexachloro platinate anion. The results demonstrated that the adsorption process was dependent on pH, temperature, contact time, and background electrolyte. The optimal conditions of platinum adsorption were obtained at temperature of about 25 °C, pH of about 2.5 and equilibrium time of 30–20 min. The maximum adsorption capacity (q_{max}) under the optimal conditions was equal to 74 mg/g.

In a study by Lopes et al. (2016) [72], findings on the strong affinity of magnetite particles to precious metals through chemical functionalization of the surface with silica was presented. The study described the preparation of dithiocarbamate functionalized Fe_3O_4 particles into two steps: (i) synthesis of the magnetic core (Fe_3O_4) by alkaline hydrolysis of the iron salt ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$); and (ii) surface modification via hydrolytic condensation of TEOS with a siloxydithiocarbamate precursor (SiDTC) of the magnetic particle. The prepared adsorbent was applied in the recovery of colloidal precious metal nanoparticles (Au, Ag, Pt, Pd). The process involved treating respective hydrosols with the magnetic sorbents and allowing their uptake from water under a magnetic gradient. The magnetic particles were found to be very efficient sorbents for Au colloids primarily due to the strong affinity of sulfur containing groups at the magnetite surfaces for this metal [72].

Another surface modification of magnetic nanoparticles through functionalization with poly(2-amino thiophenol) was studied by Sedghi et al. (2015) [78] for the recovery of heavy metal ions such as lead(II), copper(II) and silver(I). The synthesized sorbents loaded with target metals were separated from the solution through the application of an external magnetic field. The extracted ions were analyzed using flame atomic absorption spectrophotometry (FAAS). The effects of pH, adsorption and desorption time, type, concentration and volume of eluent, breakthrough volume, and effects of impurities influencing the adsorption were studied. At optimum conditions, an extraction efficiency of >95% was achieved. The measured limits of detection were 2.1, 0.4 and 1.1 ng/mL for lead, copper and silver ions, while the adsorption capacities for these ions were 78.2, 68.1 and 52.3 mg/g, respectively. The study concluded that the magnetic particles functionalized with poly(2-amino thiophenol) generated are reliable, sensitive to competitive analytes, and selective towards trace amounts lead(II), copper(II) and silver(I) in various food applications [78].

Recent investigations of Karimi et al. (2011) [79] studied the possibility of 2-mercaptobenzothiazol/sodium dodecyl sulfate immobilized on alumina-coated magnetite nanoparticles (MBT/SDS-ACMNPs) as SPE sorbents for the recovery of trace amounts of silver ions from environmental samples prior to analysis using flame atomic absorption spectrometry. Initially, the Fe_3O_4 NPs (MNPs) were synthesized by a chemical co-precipitation procedure. The ACMNPs were prepared by dissolving aluminum isopropoxide (1.0 g) in ethanol (60 mL) to form a clear solution. MNPs (0.1 g) were then dispersed in freshly prepared solution for 5 min with the aid of ultrasonic waves. Optimum conditions for pH, sample volume, eluent concentration and volume, and co-existing ions, have been obtained and studied. The experimental results showed that the maximum Ag uptake by MBT/SDS-ACMNPs was found to be 11.6 mg/g. Prepared adsorbents are found to be highly monodisperse, magnetically separable and competitive adsorbents for the magnetic solid-phase extraction of Ag(I) ions from high volume of water samples in environmental applications.

3.1.2. Magnetic Particles with Organic Coating

Magnetic particles as sorbents can offer an effective separation/pre-concentration method for precious metals recovery. Moreover, they can be easily altered by structural surface modifications to form highly effective and robust adsorbent materials [63]. Coating magnetic micro- and nanoparticles with organic compounds containing various functional groups such as, iminodiacetic acid, thiols, amines, and etc., has offered several benefits to improve the properties and effectiveness of the adsorbents including affinity towards target metal ions, capacity, selectivity, and reusability [36]. A variety of magnetic particles enclosed with organic shells have been utilized as adsorbents for the separation and purification of precious metals from solutions and are presented in Table 1.

Solid-phase extraction based on reusable magnetic chitosan microspheres coupled with Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was studied by Tolessa et al. (2017) [80] for separation and quantification of silver nanoparticles (AgNPs) in the presence of silver ions in environmental water samples. The monodisperse magnetic chitosan microspheres with an average size of 2 μm were synthesized using suspension cross-linking technique, characterized and investigated for its application as SPE adsorbent. It was found that the chitosan coating improved the dispersibility of magnetic sorbents in aqueous solution making active/binding sites of the biosorbents accessible for analytes and reduced the interference of natural organic macromolecules in complex samples which might be caused by size exclusion frequently encountered due to aggregation. Parameters affecting the SPE were optimized, and the best performance was achieved by extracting a 20 mL sample (pH 4.5) with 10 mg adsorbent for 90 min, followed by elution with 1 mL 1% (*w/v*) thiourea in 10% (*v/v*) nitric acid for 10 min.

The recovery of platinum(IV) and palladium(II) from aqueous solutions using ethylenediamine-modified magnetic chitosan nanoparticles (EMCN) as sorbent was studied by Zhou et al. (2010) [81]. The preparation of magnetic chitosan nanoparticles involved the addition of basic precipitant solution (NaOH) into a W/O microemulsion system. Chitosan is an *N*-deacetylated derivative of chitin, a cationic polysaccharide composed of β -D-glucosamine and acetyl- β -D-glucosamine residues with a 1,4 linkage. Chitosan is a biopolymer reported to be suitable in the removal of metal ions from aqueous solution due to the presence of amino and hydroxyl functional groups that serve as chelation sites. Metal adsorption is governed by various mechanisms such as chelation and electrostatic attraction which depend on pH, solution composition and formation of the metal ions. The prepared EMCN was analyzed using transmission electron microscope (TEM) and was found to have a diameter in the range of 15 to 40 nm. Adsorption experiments indicated that pH 2.0 was favorable for both Pt(IV) and Pd(II) and the maximum adsorption capacity was obtained at this pH. The maximum loading capacities of EMCN for Pt(IV) and Pd(II) were determined to be 171 and 138 mg/g, respectively. The study also reported that the sorbents have greater affinity for Pt(IV) than for Pd(II). Elution was performed by using an appropriate solvent of 0.4 M HNO_3 –1.0 M thiourea solution to desorb Pt(IV) and Pd(II) from EMCN.

In the research conducted by Chang and Chen (2006) [82], monodisperse chitosan-coated Fe_3O_4 nanoparticles with a mean diameter of 13.5 nm and containing 4.92 wt % chitosan were used as adsorbent for the recovery of Au(III) ions from aqueous solutions. A fast and efficient Au(III) ion adsorption was observed and the protonation of the amino groups led to the increased adsorption capacity with decreasing pH. A maximum adsorption capacity of 59.52 mg/g (1210 mg/g based on the weight of chitosan) was noted. The adsorption kinetics and thermodynamic studies revealed that the adsorption process followed the pseudo-second-order kinetic model. The authors explained that a shorter adsorption time was observed and equilibrium was easily attained when nanoparticles were used owing primarily to the large surface area available for the target ions [82].

A novel magnetic sorbent, an ion imprinted polymer(IIP) was synthesized and studied by Ebrahimzadeh et al. (2012) [83] for the speedy extraction, preconcentration and determination of trace amounts of gold ions. The effects of sample pH, adsorption time, type of eluent, eluent concentration and minimum volume required for desorption of gold ions were determined. The effects of various

cationic interferences on the adsorption of gold, specifically Pt(II) and Pd(II) ions were assessed. The maximum capacity of the IIP modified magnetic nanoparticles was determined to be greater than 76 mg/g.

A small-scale (0.1 m³) extraction of gold and platinum at high dilution (milligram to gram per ton \equiv ppb to ppm) using metal-based carbon-coated magnetic particles was investigated by Rossier et al. (2010) [84]. The adsorbents known as acid-stable nanomagnets, were prepared following two steps: (i) synthesis by reducing flame method using graphene-like carbon-coated cobalt metal nanoparticles (20–40 nm diameter) with an onion-like core/shell structure; and (ii) surface coating with a standard noble metal extraction resin-like polymer (thiourea groups on a poly (ethylene imine)). The authors reported that the use of metal core enhanced the saturation magnetization of the material, while carbon shells protect the material from harsh chemical conditions. The synthesized adsorbents were tested for the recovery of Au and Pt at laboratory scale and in a tank model (4 m height, 0.1 m³ volume). Laboratory scale experiments returned Au and Pt removal efficiency results of >95%. Tank model experiments reported Pt extraction of >80% at 50 mg/ton of acid water. Permanent magnets were used to collect the nanomagnet adsorbents from the bottom of the tank. The authors have noted that applications in fixed bed or column systems for precious metals can be possible using the nanomagnets.

Mattila et al. (2014) [85] synthesized magnetic cobalt nanoparticles coated with a thin carbon shell (Co@C NPs) using a scalable method based on hydrogen reduction synthesis and the particles were applied in the adsorption of gold ions from solutions. The carbon shell of these cobalt nanoparticles served as a guard to prevent the release of cobalt into water at neutral pH and contained oxidized components promoting a flexible surface chemistry for further modification or functionalization. The adsorption experiments showed that the Co@C NPs modified with a silane containing a thiol group could effectively recover Au from both simulated solutions containing gold and thiocyanate-leaching solutions of crushed electronic circuit boards.

In the research work conducted by Lin and Lien (2013) [86], a novel magnetic nano-adsorbent was used for the effective and selective adsorption of gold(III), palladium(II) and platinum(IV) from acidic aqueous solution. The surface of magnetite nanoparticles was coated with thiourea and the resulting adsorbent was named MNP-Tu. A short contact time of less than 30 min was reported for the adsorption of precious metals using MNP-Tu. The adsorption data was reported to obey the Langmuir model with maximum adsorption capacity calculated as 43.34, 118.46 and 111.58 mg/g for Pt(IV), Au(III) and Pd(II), respectively, at pH 2 and 25 °C. It has been noted that the adsorbent exhibited high adsorption selectivity towards precious metals, especially Au(III), even with the coexistence of impurity ions, such as Cu(II). A mixture of 0.7 M thiourea and 2% HCl was found to be effective to elute and regenerate the loaded magnetic nanoadsorbent. The researchers also conducted a multi-cycle adsorption-desorption test and the results indicated that MNP-Tu is reusable for the recovery of precious metals.

In a study conducted by Ghasemi et al. (2017) [87], Fe₃O₄ nanoparticles were functionalized with ethylene diamine tetraacetic acid (EDTA) to produce a novel and efficient superparamagnetic nanosorbent for the removal of Ag(I), Hg(II), Mn(II), Zn(II), Pb(II) and Cd(II) from different soil samples and environmental water effluent. EDTA forms very strong complexes with metal ions and offers an excellent means of chemical modification for magnetite nanoparticles to generate adsorbents with high adsorption capacity and fast kinetics. The effects of various process parameters, such as pH, contact time, and the amount of magnetic Fe₃O₄@EDTA nanoparticles, on the adsorption efficiency were investigated simultaneously using an experimental design. Box-Behnken design (BBD) combined with desirability function (DF) revealed the highest global adsorption to determine the experimental conditions efficiency. Under the optimum conditions, the adsorption efficiencies and capacities of superparamagnetic Fe₃O₄@EDTA nanoadsorbents for Ag(I), Hg(II), Mn(II), Zn(II), Pb(II) and Cd(II) were in the range of 96–104% and 71–169 mg/g, respectively. The study reported that

the nanoadsorbent exhibited high adsorption efficiency, good reusability, and cost-effectiveness as a material for the removal of heavy metals present in environmental water and soil samples.

The use of gallic acid-modified magnetite particles (Mag-GA) in gold adsorption from solution was investigated by Rahmayanti et al. (2016) [88]. Gallic acid-modified magnetite particles (Mag-GA) were synthesized at pH 4–5 through reverse co-precipitation method. A series of AuCl_4^- solutions (10 mL, 25 mg/L) were adjusted to pH 2, 3, 4, 5, 6, and 7 by adding either HCl or NaOH solution. Optimum AuCl_4^- (about 95%) adsorption on Mag-GA was achieved at pH 3. The mechanism of gold adsorption onto Mag-GA was elucidated through electrostatic interaction between $-\text{COO}-$ group and the surface of magnetite. The study further explained that the mechanism occurs via the formation of hydrogen bonding followed by the reduction of trivalent gold ions to metallic gold, which is accompanied by simultaneous oxidization of the hydroxyl groups of gallic acid.

A chemically modified chitosan resin with magnetic properties was synthesized and examined by Donia et al. (2007) [89] for the recovery of Au(III) and Ag(I) from aqueous solutions using batch and column methods. Surface modification of the magnetite core with chitosan and polymeric Schiff's base of thiourea/glutaraldehyde was an essential part of the preparation of the sorbent material. Maximum metal uptake values of 3.6 and 2.1 mmol/g were reported for Au(III) and Ag(I), respectively. The interaction mechanism between metal ion and active sites has been interpreted as ion pair for gold(III) and chelation for silver(I). The column experiments determined the breakthrough time, critical bed height, and durability of the resin used. Based on the results, the breakthrough point and exhaustion of the resin occurred faster at higher flow rates. Increased flowrate induced the rapid breakout of the metal ions to the effluent. This occurrence was speculated to have been caused by an insufficient residence time of the metal ions to come in contact in the column. It was also found that for all flowrates, Au(III) displayed longer breakthrough time than that of Ag(I). Furthermore, the critical bed height for Au(III) and Ag(I) columns were calculated as 1.1 and 2.2 cm, respectively.

A study by Bagheri et al. (2012a) [90] attempted the application of magnetic nanoparticles (MNPs) with Fe_3O_4 as core and functionalized with pyridine on the solid-phase extraction of trace quantities of Pd(II) ions. The immobilization on the surface of the MNPs by covalent bonding of isonicotinamide was caused by the presence of the pyridine functional group. Separation and regeneration of the modified MNPs from aqueous solution were made possible through the application of an external magnetic field. The main process parameters evaluated in the study were pH, amount of functionalized MNPs, extraction time, type and quantity of eluent, desorption time, and breakthrough volume. The optimum conditions were determined to be pH 3, 15 mg MNPs, and 4 min extraction time. A mixture of 0.5 M thiourea and 0.4 M HCl was found to be an effective eluent. A maximum adsorption capacity of 42.0 ± 2.0 mg/g was obtained for Py- Fe_3O_4 NPs. The authors concluded that magnetic nanoparticles (MNPs) with Fe_3O_4 as core and functionalized with pyridine are viable adsorbents in the determination of Pd(II) in spiked tap water and soil samples.

Further studies were conducted by Bagheri et al. (2012b) [91] where a novel magnetic metal-organic framework (MOF) [(Fe_3O_4 -Pyridine)/ $\text{Cu}_3(\text{BTC})_2$] was synthesized and utilized for the preconcentration of Pd(II). Box-Behnken experimental design was used to establish the optimum conditions for the preconcentration procedure through response surface methodology. The process variables that influenced the adsorption include amount of magnetic MOF, extraction time, and extraction pH. For the desorption experiments, parameters such as type, volume, and concentration of eluent, and desorption time were selected in the optimization study. The extraction time was noted to be fast (6 min) and the optimum pH was found to be 6.9. A solution of $\text{K}_2\text{SO}_4 + \text{NaOH}$ (6 mL, 9.5 (w/v %) + 0.01 mol/L) was used for stripping of the loaded adsorbent. From the results of the experiments, the preconcentration factor (PF), relative standard deviation (RSD), limit of detection (LOD), and adsorption capacity were found to be 208, 2.1%, 0.37 ng/mL, and 105.1 mg/g, respectively. The results also revealed that the adsorption capacity of magnetic MOF is higher than that of the Fe_3O_4 -Py adsorbents [90] studied by the same researchers previously. Conclusively, the magnetic

MOF was successfully applied for the rapid extraction of trace amounts of Pd(II) ions in biological and environmental samples such as fish, sediment, soil, and water.

Tahmasebi and Yamini (2014) [92] developed an efficient technique for the sensitive extraction and determination of silver(I), gold(III), copper(II) and palladium(II) ions with the use of Fe₃O₄ magnetic nanoparticles functionalized with polythiophene (Fe₃O₄@PTh) in the absence of a chelating agent. Subsequently, the ions present on the surface of the adsorbent were determined by flow injection inductively coupled plasma optical emission spectrometry. Different process parameters were investigated and the optimum conditions were determined as follows: that the optimized values of sample pH, type and volume of eluent, amount of adsorbent, sample volume and time of adsorption and desorption were pH 4, 0.01 M HNO₃ solution for the elution of palladium, 1 M thiourea for gold and silver desorption, thiourea (1 M) and HNO₃ (0.01 M) for copper, 60 mg of adsorbent, 8 min adsorption and 1 min elution. Modification of the Fe₃O₄ magnetic nanoparticles with polythiophene (Fe₃O₄@PTh) was advantageous because of the absence of chelating agent and organic solvents that are commonly used in complexation and extraction of metal ions. It also offered a shorter residence time for bulk volume of samples as compared to the conventional SPE methods. Other beneficial features of this novel adsorbent are the high specific surface area, absence of internal diffusion resistance, operation in dispersion mode, and applicability of magnetic separation. The researchers recommended that the extractions of Ag⁺, Au³⁺, Cu²⁺ and Pd²⁺ ions by Fe₃O₄@PTh NPs occur via complex formation reaction mechanism between the sulfur atoms of polythiophene and metal ions according to hard/soft-acid/base theory.

3.2. Characterization of Magnetic Adsorbents

The chemical and physical properties, especially the magnetic properties, of magnetic adsorbents define their intended applications in environmental, analytical, chemical and metal extraction industries. These characteristics are highly dependent on properties such as particle size, morphology, crystal structure and the surface functional groups of the prepared adsorbents. There are a multitude of characterization techniques available nowadays to determine these features. This section describes some of the most common and widely used ones.

3.2.1. Size and Morphology

There are commonly used techniques cited in literature to examine the particle size and morphology of the synthesized magnetic adsorbents. The first one is, Transmission Electron Microscopy (TEM) which is an analytical technique based on detecting differences in electron density and allows observation of the size and shape of the magnetic particles. The second one is the Scanning Electron Microscopy (SEM) which is widely used in the characterization of the morphological characteristics of MPs [46].

3.2.2. Crystal Structure

As with most solids and mineral characterizations analyses, magnetic adsorbents also assessed for mineralogy and crystal structure using the well-known X-ray diffraction (XRD) analytical technique. XRD is used for determining the crystallographic identity of the produced material and phase purity. In order to investigate the structure and composition and verify the presence of magnetite, maghemite or other magnetic adsorbents in the solid matrix, XRD is widely applied [46,93,94].

3.2.3. Magnetic Properties

One of the methods to evaluate the magnetic properties of the MNPs in terms of the applied external magnetic force (H) ranging from −3 to 3 Tesla, is the Vibrating Sample Magnetometry (VSM). The VSM curve can provide details of the magnetic behavior of the MNPs at different temperatures. For instance, the zero magnetic remanence (when H is zero) at room temperature, and the anhysteretic loop feature indicates that the MNPs are superparamagnetic. The saturation magnetization (M_s) can

be observed from the plateau part of the VSM curve. It should be noted that the core-shell structure should be dominated with sufficient magnetic and superparamagnetism properties for industrial applications. The use of VSM is relevant in the estimation of a shell's influence on M_s .

For the measurement of extremely weak magnetic fields, Superconducting Quantum Interference Device (SQUID) magnetometry is routinely used. Monitoring magnetization as a function of temperature for particles cooled with or without an applied magnetic field followed by warming the particles in the presence of a magnetic field determines the characteristic blocking temperature [93]. Ye et al. (2014) [75] conducted magnetization measurements of the crown ether-coated magnetic nanoparticles (CEMNs) and Fe_3O_4 they synthesized using SQUID to investigate the magnetic behaviors of the magnetic particles at room temperature. The maximum saturation magnetization value of CEMNs was found to be 53.3 emu/g which is lower than that of the bulk Fe_3O_4 (61.9 emu/g). The authors reported that this was due to the fact that CEMNs were purposely prepared with the surface modification resulting to a lower saturation magnetization. In the test, the magnetic particles in ethanol were placed in a glass vessel and its magnetic separability was examined by placing small neodymium permanent magnet near them. The black magnetite particles were attracted toward the magnet for a few seconds indicating the good magnetic response of CEMNs.

3.2.4. Surface Characterization

The two very familiar methods for detecting the surface functional groups of solids and investigating the adsorption mechanism of target metals are Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photo-Electron Spectroscopy (XPS) [46]. XPS is a highly valuable technique to study reaction mechanisms that occur on the surface of MNPs. The XPS spectra are very useful tools to determine the nature of the bonds that exist amongst different elements involved through measurements of binding energy and other properties. It can also be applied to confirm the structure as well as the speciation of elements contained in MNPs [93]. FTIR is usually utilized to examine the surface groups of the synthesized materials [59].

Analytical techniques such as Thermal Gravimetric Analysis (TGA) have been employed to verify the layering of surfactant or polymers and to estimate the binding efficiency on the surface of MPs. A research work carried out by Bagheri et al. (2012b) [91] evaluated the thermal stability of the magnetic metal-organic framework ((MOF) = $\text{Cu}_3(\text{BTC})_2$ (BTC = benzene-1,3,5-tricarboxylate)) and MOF using TGA. According to the TG analysis results, weight loss for MOF was about 72%, and the remaining 28% was related to the presence of Cu^{2+} in the MOF structure. The decrease in weight for magnetic MOF was about 68% and the remaining 32% was related to Cu^{2+} (28%) and due to the presence of Fe^{2+} and Fe^{3+} ions (4%) in the structure of magnetic MOF. The analytical results confirmed that the magnetic MOF was formed or synthesized successfully.

One of the important surface properties of adsorbent materials that governs their applications is the surface charge and this can be determined by zeta potential analysis. In the analysis, an important information is usually measured and that is the isoelectric point, also referred to as PZC (point of zero charge), which is the pH at which the particles in suspension have a net charge of zero and no mobility in the electric field [93]. Zeta potential analysis is also a useful tool to evaluate the dispersibility and stability of magnetic particles in aqueous solution. The surface charge characteristics of solid particles can be deduced from their zeta potential plots. In the study conducted by Peng et al. (2016) [74], the isoelectric point (ip) of the Fe_3O_4 microspheres has been determined to be at pH 5.1. The ip of thiol functionalized- $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was determined to be at pH 3.1, close to that of 3.0 for thiol functionalized silica. In comparison to that of bare Fe_3O_4 , the shift of ip to the left for thiol functionalized- $\text{Fe}_3\text{O}_4/\text{SiO}_2$ indicates a more negatively charged surface of the composite sample. In other words, thiols and silanols are more prone to deprotonation compared to hydroxyls upon Fe_3O_4 in aqueous solution. This observed shift is in agreement with the isoelectric points measured for Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, and thiol-functionalized- $\text{Fe}_3\text{O}_4/\text{SiO}_2$. It was also observed that positive surface charges dramatically increase with decreasing solution pH to the left of the ip . This is attributed to the protonation of surface

thiols and silanols. To the right of the *ip*, negative surface charges rapidly increased as the solution pH increases to 4 and then leveled off in the pH range of 4–10. This is probably due to the gradual deprotonation of surface thiols and silanols with increasing solution pH, rendering an increasing negatively charged surface that repels the OH[−] in solution.

The specific surface area of particles is determined by BET (Brunauer, Emmett and Teller) method. Lin and Lien (2013) [86] applied the BET analysis to determine the specific surface area of magnetite nanoparticles (MNP) and thiourea-modified magnetite nanoparticles (MNP-Tu). The analysis revealed that the specific surface area of MNP and MNP-Tu was 81.4 and 64.3 m²/g, respectively. The authors noted a decrease in the surface area of the synthesized magnetic adsorbents and explained that the aminosilanization of MNP contributed to such phenomenon. They discussed further that aminosilanes were anchored onto the inner pore volume of MNPs and contributed to the change in the surface area. Although the effect was not highly desirable in terms of surface area, aminosilanization is a key step in the process since it stabilizes thiourea at the surface of MNPs [86].

3.3. Modeling of Adsorption Systems

3.3.1. Adsorption Kinetic Studies

Studies on sorption kinetics provide valuable understanding of the reaction pathways and useful information to establish the mechanism of sorption reactions. Kinetic studies determine solute uptake rates and the factors that govern rate-controlling steps in a chemical reaction. These information are beneficial in process and plant optimization and control. Better understanding of rate laws and kinetic principles is essential and this can only be verified by laboratory experiments and studies [95].

The adsorption of precious metal ions on solid phase or adsorbents can be described by kinetic data. Kinetic calculations can also define the mechanism that governs the adsorption process. Several models can be used to study the kinetic mechanism of the adsorption process [57]. The most widely used kinetic models for precious metals adsorption systems are the pseudo first-order (Equation (1)), pseudo second-order (Equation (2)), and intraparticle diffusion models (Equation (3)), [57,82]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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

$$q_t = k_{id} t^{0.5} \quad (3)$$

where q_e and q_t are the amount of metal ions adsorbed per unit adsorbent at equilibrium (mg/L) and any time (t), respectively. The k_1 , k_2 and k_{id} represent the respective first-order, second-order and intraparticle diffusion rate constants.

The three basic considerations for pseudo-first and pseudo-second models include external film diffusion, intraparticle diffusion and interaction step for the adsorption process. One of these adsorption reactions can be kinetically limited and serves as the rate controlling step for the process. The kinetics of the reaction can be enhanced by mixing or stirring especially when external film diffusion is the bottleneck. This leaves the intraparticle diffusion or interaction step as the main factor that controls the adsorption rate. The kinetic parameters for the pseudo-first and pseudo-second models are determined from the linear plots of $\ln(q_e - q_t)$ vs. t or (t/q_t) vs. t , respectively. The suitability of each model can be evaluated by the fitness of the straight lines (R^2 values) [89]. Another important consideration is that the calculated equilibrium adsorption capacity values of q_e (cal.) must be in agreement with the experimental q_e (exp.) values [57].

In the study reported by Zhang et al. (2013) [59], the kinetics of gold adsorption on thiol-modified Fe₃O₄@SiO₂ was conducted by contacting the adsorbent with 20 mg/L of gold solution at pH 5. Pseudo-second order kinetic model was used to describe the adsorption of gold on the magnetic adsorbent. The adsorption data was found to fit well with the model with R^2 over 0.993. The study

described that based on the kinetic analysis, the rate limiting step might be chemical adsorption involving valency forces through sharing or exchange of electrons between thiol group of adsorbent surface and Au(III), which conformed with the HSAB theory [59].

The adsorption kinetics of Ag(I) and Au(III) on polystyrene-coated CoFe₂O₄ magnetic particles functionalized with 2-(3-(2-aminoethylthio)propylthio)ethanamine were studied by Jainae et al. (2010) [58]. Pseudo-first order and pseudo-second order kinetic models were adopted. The optimal pH for the extraction of Ag(I) and Au(III) ions was pH 5.0 and pH 4.0, respectively. The experiments include the addition of 5.0 mg adsorbent to 5 mL of metal solution with an initial concentration of 50mg/L or 40 mg/L. The adsorption of metal ions on the magnetic adsorbent was found to be very rapid and equilibrium was within 60 min. The pseudo-second order kinetic model was determined to be most suitable to describe the experimental and this was confirmed by the calculated adsorption capacity values at equilibrium which were in agreement with both kinetic equations ($q_{e,cal}$) and experimental values ($q_{e,exp}$). In addition, the kinetic constants obtained for Ag(I) and Au(III) are high and similar to each other, signifying that the adsorption of these metal ions is kinetically favorable. The adsorption was also found to follow the Langmuir isotherm model with the maximum adsorption capacity of 0.44 mmol Ag(I)/g and 0.19 mmol Au(III)/g. The Ag and Au loaded magnetic adsorbent can be effectively eluted using 1.0 M thiourea in 1% HNO₃ and 1.0 M thiourea in 2% HCl, respectively [58].

3.3.2. Adsorption Isotherm Studies

In attempts to explore novel adsorbents for efficient adsorption systems, it is indispensable to establish the most suitable adsorption equilibrium correlations for effective and dependable prediction of adsorption parameters and quantitative comparison of adsorbent behavior in various adsorbent systems or experimental conditions [96]. According to Foo et al. (2010) [96], equilibrium relationships, generally known as adsorption isotherms, are crucial for the optimization of adsorption mechanism pathways, description of surface properties and effective design of the adsorption systems. An adsorption isotherm as defined in the report by Foo et al. (2010) [96], is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium is achieved when the adsorbent has been allowed to come in contact with the adsorbate or solution containing target analytes for an ample amount of time until a dynamic balance between the adsorbate concentration in the bulk solution and the interface concentration [96]. A number of equilibrium isotherm models have been formulated and reported and these include Langmuir, Freundlich, Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Sips, Khan, Hill, Flory-Huggins and Radke-Prausnitz isotherms [96]. Amongst these models, Langmuir and Freundlich have been widely applied to determine the adsorption behavior of precious metals on magnetic adsorbents.

The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [47,96]. The mathematical expression of linearized Langmuir isotherm model is as follows:

$$\frac{C_e}{q_e} = \frac{1}{k_1 q_m} + \frac{C_e}{q_m} \quad (4)$$

where C_e is the equilibrium concentration of the analyte in solution (mg/L), q_e is the amount of adsorbed analyte on the sorbents (mg/g), k_1 is the constant related to free energy of adsorption (L/mg), and q_m is the maximum adsorption capacity (mg/g). The Freundlich isotherm assumes the exponential distribution of adsorption sites and the multilayer adsorption. The linearized expression of this model is given by Equation (5) [47,96]:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (5)$$

where k_f ($\text{mg/g (L/mg)}^{1/n}$) and n are the Freundlich constants; C_e is the equilibrium analyte ion concentration in solution (mg/L). The linear Langmuir and Freundlich plots for the adsorption of analyte on the sorbents are obtained by plotting C_e/q_e vs. C_e and $\ln q_e$ vs. $\ln C_e$, respectively.

In order to interpret the adsorption isotherm data of silver ions onto superparamagnetic carbon material (Cmag), Condomitti et al. (2014) [41] tested both the Langmuir and the Freundlich isotherm models. Based on the data obtained from the linearization of the adsorption isotherm, it was possible to determine the adsorption capacity of Cmag for Ag^+ ions. The comparison between the Langmuir and Freundlich models revealed that the Langmuir model provided a better fit for the data obtained for the adsorption of silver ions on Cmag with a determined adsorption capacity of 61.5 mg/g at 298 K.

Peng et al. (2016) [74] analyzed the adsorption behaviors of the thiol-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$) with the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models. According to the Langmuir isotherm equation, the plot of C_e/q_e versus C_e exhibited a straight line, and linear fitting of this plot presented a high correlation coefficient ($R^2 = 0.9998$). In addition, the calculated q_m value of 43.7 mg/g is very close to the experimental value of 44 mg/g . In relation to the high correlation coefficient, it was concluded that the Langmuir model can well describe the adsorption behaviors of Au(III) upon the adsorbent. The Freundlich equation was found unsuitable to describe the adsorption behaviors of Au(III) upon $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ due to very low values of R^2 (0.236) and n (40.6). The Temkin and D-R isotherm models were also applied to explain the adsorption behaviors of Au(III) upon $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$. However, linear fittings of the adsorption data according to their models gave bad correlation coefficients, indicating that the adsorption of Au(III) upon $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ follows neither the Temkin nor the D-R isotherm model. Generally, the results revealed that the adsorption mechanism of Au(III) upon $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ follows the Langmuir isotherm model and acetate anions play an important role in the adsorption process involving Au(III) complex anions.

In the study conducted by Zhang et al. (2017) [76], Langmuir and Freundlich models were used to evaluate the experimental data of Ag nanoparticles adsorption from water by poly(ethylenimine) functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PEI}$). The results suggested that both Langmuir and Freundlich models closely fitted the experimental data with good correlation coefficients. The Langmuir adsorption constant k_1 (L/mg) was used to determine the separation factor (R_L), represented by the following equation (Equation (6)):

$$R_L = \frac{1}{1 + k_1 C_0} \quad (6)$$

where C_0 is the initial concentration of the AgNPs (mg/L). The value of R_L indicates the nature of the adsorption process: $R_L < 1$ suggests a favorable adsorption, while $R_L > 1$ indicates an unfavorable adsorption. In this study, for a C_0 of 1.8 to 21.6 mg/L , the corresponding R_L values were calculated to be in the range of 0.09–0.55, indicating that the adsorption of AgNPs onto $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PEI}$ is favorable. The parameter n in Freundlich model was also found to be greater than 1, suggesting a favorable adsorption and strong adsorption behavior between $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PEI}$ adsorbent and AgNPs. The maximum adsorption capacity based on Langmuir model was determined to be 909.1 mg/g .

3.4. Factors Influencing Magnetic Solid Phase Extraction of Precious Metals

The adsorption and removal efficiencies of precious metals from aqueous solution are influenced by several process parameters. Knowing and understanding how these factors affect the process and how their interactions contribute to high removal efficiency are essential for process control and optimization. The most important process parameters that significantly affect MSPE are as follows.

Table 1. Magnetic adsorbents for the recovery of precious metals from solutions.

Analyte	Adsorbent	Eluent	Maximum Loading Capacity	Reference
Pt Pd Rh	Magnetite (Fe ₃ O ₄)	-	3.0 µmol/g 2.8 µmol/g 4.2 µmol/g	[43]
AuCl ₄ ⁻	Synthetic magnetite Natural magnetite	-	4.4 µmol/g 5.0 µmol/g	[49]
Pd(II) Rh(III) Pt(IV)	Fe ₃ O ₄ nanoparticles	0.5 M HNO ₃ for all of metal ions simultaneously; 1 M NaHSO ₃ for Rh(III); 0.5 M NaClO ₄ for Pt(IV)	0.103 mmol/g 0.149 mmol/g 0.068 mmol/g	[53]
Pd Rh	Fe ₃ O ₄ nanoparticles	1.0 M HCl	27.3 mg/g 31.8 mg/g	[54]
Au	Iron-carbon composite	-	0.52 g/g	[56]
Au ³⁺ Ag ⁺	Magnetic nanoparticles/graphitic carbon nanostructures composite	-	7.92 mg/g 7.88 mg/g	[57]
Au(CS(NH ₂) ₂) ₂ ⁺	Fe ₃ O ₄ @SiO ₂ nanoparticles	Ammonia	-	[73]
AuCl ₄ ⁻	Fe ₃ O ₄ @SiO ₂ nanoparticles modified with thiol group	thiourea + 1 M HCl	115 mg/g	[71]
Au(III)	Thiol-functionalized Fe ₃ O ₄ @SiO ₂ microspheres	1.0 M thiourea + 5% HCl	43.7 mg/g	[74]
Au Pd Pt	Fe ₃ O ₄ @SiO ₂ functionalized with 4'-aminobenzo-15-crown-5-ethet	2% thiourea + 0.1 M HCl	-	[75]
AgNPs	Fe ₃ O ₄ @SiO ₂ functionalized with poly(ethylenimine)	-	909.1 mg/g	[76]
Ag(I) Au(III) Pd(II) Pt(II)	Fe ₃ O ₄ -graphene oxide composite coated with silica-modified with polyrrrole-polythiophene	Thiourea + HCl	49 mg/g 50 mg/g 45 mg/g 50 mg/g	[14]
Au	Thiol-modified Fe ₃ O ₄ @SiO ₂ nanoparticles	1 or 2 M HCl + 2% thiourea	84.75 mg/g	[59]
Pt (Hexachloro platinate anion)	Fe ₃ O ₄ @SiO ₂ modified by N-(2-aminoethyl)-3-aminopropyltrimethoxysilane	-	74 mg/g	[60]
Au, Ag, Pt, Pd	Dithiocarbamate functionalized-Fe ₃ O ₄ @SiO ₂	-	-	[72]

Table 1. Cont.

Analyte	Adsorbent	Eluent	Maximum Loading Capacity	Reference
Pb(II) Cu(II) Ag(I)	Fe ₃ O ₄ @SiO ₂ modified with poly(2-aminothiophenol)	-	78.2 mg/g 68.1 mg/g 52.3 mg/g	[78]
Ag(I)	Fe ₃ O ₄ @Al ₂ O ₃ nanoparticles modified with 2-mercaptobenzothiazole/sodium dodecyl sulfate	-	11.6 mg/g	[79]
AgNPs	Fe ₃ O ₄ modified with chitosan	1% (w/v) thiourea + 10% (v/v) HNO ₃	-	[80]
Pt(IV) Pd(II)	Magnetic cross-linking chitosan nanoparticles modified with ethylenediamine	0.4 M HNO ₃ + 1.0 M thiourea	171 mg/g 138 mg/g	[81]
Au(III)	Chitosan-coated Fe ₃ O ₄ nanoparticles	-	59.52 mg/g	[82]
Au	Dipyridyl amine-coated Fe ₃ O ₄ nanoparticles	-	>76 mg/g	[83]
Au Pt	Graphene-like carbon-coated cobalt metal nanoparticles	-	-	[84]
Pd(II)	Pyridine- functionalized Fe ₃ O ₄ nanoparticles	0.5 M thiourea + 0.4 M HCl	42.0 ± 2.0 mg/g	[90]
Pd(II) Au(III) Ag(I) Cu(II)	Modified Fe ₃ O ₄ nanoparticles with polythiophene	0.01 M HNO ₃ 1 M thiourea 1 M thiourea 0.01 M HNO ₃ + 1 M thiourea	-	[92]
Ag Cd Cu Zn	Fe ₃ O ₄ nanoparticles coated by 3-(trimethoxysilyl)-1-propanol modified with 2-amino-5-mercapto-a,3,4-thiadiazole	-	10.4 mg/g 4.7 mg/g 3.8 mg/g 5.3 mg/g	[97]
Au	Magnetic cobalt nanoparticles coated with carbon and functionalized with 3-aminopropyltriethoxysilane and 3-mercaptopropyltrimethoxysilane	-	-	[85]
Pt(IV) Au(III) Pd(II)	Thiourea modified Fe ₃ O ₄ nanoparticles	0.7 M thiourea + 2% HCl	43.34 mg/g 118.46 mg/g 111.58 mg/g	[86]
Ag(I), Hg(II), Mn(II), Zn(II), Pb(II), and Cd(II)	Ethylene diamine tetraacetic acid (EDTA) functionalized Fe ₃ O ₄ nanoparticles	0.5 M HCl	71–269 mg/g	[87]

Table 1. Cont.

Analyte	Adsorbent	Eluent	Maximum Loading Capacity	Reference
AuCl ₄ ⁻	Gallic acid-modified Fe ₃ O ₄ particles	-	-	[88]
Au(III) Ag(I)	Modified chitosan magnetite resin	0.5 M thiourea + 0.2 M H ₂ SO ₄	3.6 mol/g 2.1 mol/g	[89]
Pd(II)	(Fe ₃ O ₄ -pyridine)/Cu ₃ (BTC) ₂ BTC = benzene-1,3,5-tricarboxylate	K ₂ SO ₄ + NaOH	105.1 mg/g	[91]
Pd ⁴⁺ Au ³⁺ Pd ²⁺ Ag ⁺	Magnetite nanoparticles modified by third-generation dendrimers and further modified by EDTA	1.0% HCl	3.6 mg/g 3.58 mg/g 2.75 mg/g 2.84 mg/g	[98]
Ag ⁺ Zn ²⁺	Fe ₃ O ₄ modified with ethylenediamine	1 M HNO ₃	90.3 mg/g 80.8 mg/g	[40]
Ag(I)	Activated carbon/γ-Fe ₂ O ₃ nanocomposite modified with 4,4'-bis-(3-phenylthiourea)diphenyl methane(BPDM)	0.5 M thiourea	32.6 mg/g	[47]
Ag(I) Au(III)	Polystyrene-coated CoFe ₂ O ₄ functionalized with 2-(3-(2-aminoethylthio)propylthio) ethanamine	1.0 M thiourea + 1% HNO ₃ 1.0 M thiourea + 2% HCl	0.44 mmol/g 0.19 mmol/g	[58]
Ag(I) Au(III)	Tris(2-aminoethyl)amine- functionalized Fe ₃ O ₄ nanoparticles	2 M HCl 0.1 M thiourea + 1 M H ₂ SO ₄	>97.3 mg/g >167 mg/g	[3]
Ag ⁺	Superparamagnetic magnetite carbon materials (Cmag)	-	61.5 mg/g	[41]
AgNPs	Fe ₃ O ₄ nanoparticles coated with either dopamine or glutathione	-	-	[63]
Au(III)	Cobal ferrite magnetic nanoparticles (CoFe ₂ O ₄) coated with (3-mercaptopropyl)trimethoxysilane(MPTS)	1 M thiourea + 1 M HCL	120.5 mg/g	[36]
Au(III) Pd(II) Ag(I)	A magnetized grapheme oxide by MnFe ₂ O ₄ nanoparticles modified with 2-mercaptopbenzothiazole	0.75 M thiourea + 15 mM HNO ₃	37 mg/mg 28 mg/mg 45 mg/mg	[13]

3.4.1. pH

The pH of the solution plays a key role in the MSPE of precious metals. For instance, Roto et al. (2016) [71] investigated the effect of pH on the AuCl_4^- ion adsorption by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles modified with thiol group. Based on their results, the adsorption capacity (q_e) increased from 32 mg/g at pH 2, to 54 mg/g at pH 3 and dropped to 17 mg/g at pH 6. The $[\text{AuCl}_x]^{-y}$ complex assumes different forms at depending on pH. At pH 2–3, AuCl_4^- species is predominant gold chloride complex and at pH 4–6, $[\text{AuCl}_3(\text{OH})]^-$ is the major species followed by $[\text{AuCl}_2(\text{OH})_2]^-$. At pH 2–3, AuCl_4^- species is prevalent, contributing to a higher q_e value. The q_e reached a maximum value at pH 3 and started to decrease at pH 4 [71].

The effect of pH on the adsorption of Pt(IV) and Pd(II) by ethylenediamine-modified magnetic chitosan nanoparticles (EMCN) was examined by Zhou et al. (2010) [81]. The results of the study revealed that maximum adsorption occurred at highly acidic regions for both Pt(IV) and Pd(II). The metal uptake increased at pH < 2.0 but decreased at pH > 3.0. The influence of pH was also reflected in the mechanism proposed by the authors: (a) coordination on amino groups in a pendant fashion or in combination with vicinal hydroxyl groups; (b) electrostatic attraction (in acidic media); and (c) ion exchange with protonated amino groups through proton exchange or anion exchange, the counter ion being exchanged with the metal anion. Aside from pH, the adsorption of Pt(IV) and Pd(II) on EMCN was also dependent on other parameters such as the chemistry of the metal ion including the ionic charge and the ability to be hydrolyzed and to form polynuclear species. The point of zero charge for EMCN was found to be 4.8 using standard potentiometric methods, verifying that EMCN was positively charged at pH < 4.8. It seems that around pH 2–3, most of the amino groups were protonated. The authors also described the significant role played by pH in the speciation of Pt(IV) and Pd(II). Solution pH coupled with chloride concentration dictate the form of Pt and Pd in solution. At low pH, platinum and palladium are usually present in solution in its most stable form, i.e., Pt(IV) and Pd(II). Due to this, Pt and Pd can form stable complexes especially with amino group chelation sites of EMCN, due to their characteristics of soft acid [81].

Tahmasebi and Yamini (2014) [92] evaluated the extraction efficiency of silver(I), gold(III), copper(II) and palladium(II) on Fe_3O_4 magnetic nanoparticles modified with polythiophene as a function of solution pH. The results demonstrated that the maximum adsorption efficiency occurred at pH 2 for Au^{3+} and pH 3 for Pd^{2+} . On the other hand, the extraction efficiencies for Cu^{2+} and Ag^+ increased when the pH was increased from 2 to 4 and reached maximum values at pH 4. The extraction efficiency decreased at pH > 4. The decrease in the extraction efficiency at higher pH values may be explained by the formation and precipitation of hydroxide species of target metal ions on the surface of the adsorbent. The authors explained that in strong acidic solutions, the decrease in the extraction efficiency was probably due to the surface protonation of the adsorbent (sulfur donor atoms) and occupation of active sites by protons rather than target metal ions. Subsequent experiments were conducted using a pH value of 4 to achieve better extraction efficiencies for all metal ions studied.

3.4.2. Adsorbent Amount

Compared to traditional sorbent in micrometer size, nanoparticles are considered superior due a variety of reasons but the most prominent one is their higher surface area-to-volume ratio and a short diffusion route which consequentially led to high extraction capacity, rapid extraction kinetics and high extraction efficiencies. Magnetic nanoparticles can also be rapidly harvested from aqueous solutions after the adsorption process by employing magnetic separation techniques. This can significantly reduce the time required for extraction and solid-liquid separation. Due to this highly beneficial characteristic, only a small amount of magnetic nanoparticles are required for a maximum capacity. To evaluate this, Bagheri et al. (2012a) [90] carried out optimization studies by varying the amount of adsorbent used to separate ultra-trace Pd ions. Magnetite nanoparticles functionalized with pyridine (Py- Fe_3O_4 NPs) were used and the added amount was varied from 5–30 mg. The results showed that increasing the amounts of the Py- Fe_3O_4 NPs increased the surface area and accessible sites for

the adsorption of analytes, thus the increase in the extraction efficiency. Quantitative extraction of palladium ions was achieved using only 15 mg of the Py-Fe₃O₄ NPs. No significant effect on the extraction efficiency was observed at higher adsorbent amounts.

In a similar study, the amount of magnetic iron oxide nanoparticles for complete extraction of 50 mL solution containing 2.5 µg palladium and rhodium at pH 10.5 was studied [54]. The results showed that the recovery percent increased to 4 mg and remained constant. Therefore, 20 mg of the adsorbent was used in all subsequent experiments.

3.4.3. Sample Volume

Large sample volumes are normally required to obtain higher enrichment factors. The effect of sample volume on extraction efficiency of silver(I), gold(III), copper(II), and palladium(II) was studied by Tahmasebi and Yamini (2014) [92] in the range of 40–200 mL. Their results indicated that increasing the sample volume until 100 mL had no obvious influence on the extraction efficiency of the target analytes and that further increase in sample volume resulted to a decrease in efficiency. The observation was attributed to the more difficult transport of target analytes onto the adsorbent surface in larger sample volume due to lower amount of adsorbent per unit volume. A volume of 100 mL was selected as optimum in the study.

Mashhadizadeh and Karami (2011) [97] also studied the effect of sample solution volume on the extraction of Ag, Cd, Cu, and Zn ions using modified magnetic nanoparticles. Different volumes (50–300 mL) of aqueous solution spiked with a fixed 5 µg of each metal ion were used in the experiments. Metal recovery values of 84–97% were obtained for all the metal ions studied when sample volume was less than 250 mL. Subsequent experiments used a sample volume of 200 mL for a theoretical enrichment factor of 200.

The effect of sample volume on the adsorption of silver ions on modified magnetite nanoparticles was investigated using different feed volumes of water samples, ranging between 50–1000 mL [79]. The optimum sample volume which corresponded to a higher percent recovery was determined. The recovery of silver ions was quantitative up to 500 mL of sample solution. A preconcentration factor of 250 mL was obtained by applying 500 mL sample volume under optimum conditions.

3.4.4. Interfering Ions

Yen et al. (2017) [98] investigated the adsorption efficiency of magnetic nanoparticles modified by third-generation dendrimers (MNP-G3) for Pt, Au, Pd and Ag ions in the presence and absence of a competing Zn(II) ion. The results showed that the adsorption efficiency decreased from around 80–90% to 50% for Pt(IV) and Au(III), from 65 to 45% for Pd(II) and 60 to 40% for Ag(I), in the presence of Zn(II). It was also observed that the adsorption efficiency of MNP-G3 for Zn(II) was not affected by the coexistence of the precious metal ions in the solution, an indication that the adsorption affinity for Zn(II) is stronger than that of the precious metals.

The extraction efficiency of modified magnetic particles functionalized with 2-(3-(2-aminoethylthio)propylthio)ethanamine (AEPE-PS-MPs) for Ag(I) and Au(III) in the presence of different salts was evaluated by Jainae et al. (2010) [58] in the presence of foreign ions. The sample solution used was a wastewater containing NaNO₃, Na₂SO₄, KNO₃, Mg(NO₃)₂, Ca(NO₃)₂, Cd(NO₃)₂, and Ni(NO₃)₂ with different concentrations. The resulting ions from these salts may influence the extraction efficiency of AEPE-PS-MPs due to the competition for the binding sites between Ag(I) or Au(III) ions and other ions. In the presence of alkali metal ions (Na⁺ or K⁺), the experimental results confirmed that there was no effect on the extraction efficiency of Ag(I) and Au(III) ions. On the other hand, there was a slight decrease in the extraction efficiency when alkali earth metal ions (Mg²⁺ or Ca²⁺) were present. This minor decrease is likely due to the high ionic strength of the solution containing alkali earth metal ions which could lead to a change in adsorption equilibrium. Nevertheless, the authors explained that the results indicated that the extraction of Ag(I) or Au(III) ions onto the AEPE-PS-MPs occurs via complex formation between the AEPE ligand and

Ag(I) ions or Au(III) ions according to hard/soft- acid/base theory. The results also showed that NO_3^- and SO_4^{2-} did not influence the extraction of Ag(I) and Au(III) ions, whereas slight effect was noted when Ni^{2+} and Cd^{2+} coexisted.

3.4.5. Type of Eluent

The regeneration and reusability of magnetic adsorbents depends largely on how the adsorbed metal ions are efficiently desorbed/stripped without damaging the structure of the adsorbents. Various desorbing reagents have been reported in literature including HNO_3 , HCl, thiourea, and thiosulfate. A summary of these reagents is given in Table 1. According to the work of Roto et al. (2016) [71], the acid solution can desorb AuCl_4^- ion from the magnetic adsorbent of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles modified with thiol group. The desorption process may use strong acids such as HCl, H_2SO_4 , and HNO_3 . The AuCl_4^- ion is believed to form complex coordination bonds with the surface, and separation of them from the surface of the adsorbent is difficult. On the other hand, desorption by concentrated acid may damage the structure of adsorbent. Therefore, the use of elution agent in mild acidic solution is usually attempted. Gold and thiourea are known to form a stable complex, solutions containing thiourea is commonly used as eluant for gold desorption [59]. Thiourea solution in 1 M HCl was employed to release AuCl_4^- ions that had been adsorbed by the adsorbent. This compound has a better affinity to gold than thiol and amine groups. It can form a complex ion with AuCl_4^- ion. According to the HSAB theory, both thiol and AuCl_4^- ions are among the weak bases. Thiourea can form strong coordination bond or even covalent bond with the AuCl_4^- [71].

In another research work [59], Zhang et al. (2013) tried to apply HCl solution containing thiourea to desorb gold loaded on thiol-modified $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles. A HCl (1–2 M) solution containing different amounts of thiourea was mixed with the adsorbents for gold desorption. Only about 19% and 17% of gold was stripped off the adsorbent with 1 M and 2 M HCl without thiourea. But when thiourea was added in the mixture, it was observed there was a sharp increase in the desorption efficiency. A desorption efficiency of 96.2% was achieved when 1 M HCl containing 2% of thiourea was utilized, and 98.5% for 2 M HCl with 2% thiourea addition. The study concluded with 1 M HCl containing 2% thiourea as the optimum desorption solution concentration.

The paper by Tahmasebi and Yamini (2014) [92] on precious metals adsorption on magnetic nanoparticles modified with polythiophene, reported that 0.01 M HNO_3 solution was suitable for the elution of palladium from polythiophene-coated Fe_3O_4 nanoparticles as a selective adsorbent, and 1 M thiourea for gold and silver desorption, while, copper can be eluted by both thiourea (1 M) and HNO_3 (0.01 M). Since all metals can be eluted using 1 M thiourea and 0.01 M HNO_3 , these solution concentrations were used in other parts of the experiments. The authors have noted that the acidity of the sample solution plays a significant role in the extraction of target metal ions by affecting their adsorption due to both the chemistry of target metal ions in solution and the protonation of the adsorbent donor atoms.

3.4.6. Adsorption Time

The time required to achieve adsorption equilibrium is dependent on several factors including type of adsorbent, metal ions and their initial concentrations, pH of the solution, particle size, temperature, and so on. Generally, adsorption on magnetic adsorbents is characterized by fast kinetics as most studies reported equilibrium and maximum adsorption capacity was reached approximately after 60 min [3,14,53,58,60,81], although 12–24 h was also reported [49,76,82]. The kinetics of Au(III) ion adsorption on chitosan coated magnetic nano-adsorbent at pH 2 was investigated by Chang and Chen (2006) [82]. The major findings of the study include achievement of about 90% of equilibrium adsorption capacity after 30 min and complete adsorption equilibrium after 6–22 h, and increasing adsorption capacity with higher initial Au(III) ion concentration. Due to smaller adsorbent particle size and larger specific surface area, higher adsorption rate was obtained and the contact time required to reach the equilibrium was shorter.

The adsorption and desorption of silver(I) from a modified magnetic nanocomposite was investigated by Ghanei-Motlagh et al. (2016) [47] by considering ultrasonic treatment times in the range 1–8 min. The experimental results showed that the adsorption of silver ions occurred within 3 min and were desorbed quantitatively with a suitable eluent in 3 min. Meanwhile, due to the superparamagnetic property of the modified nanocomposite, the sorbent could be separated rapidly (less than 2 min) from the sample solution using a strong magnet instead of conventional filtration or centrifugation.

Tolessa et al. (2017) [80] developed a reusable magnetic chitosan microspheres adsorbent for selective extraction of silver nanoparticles. In this research work, the effect of extraction time over various intervals (5–300 min) was also investigated. At the end of each time interval, the amount of AgNPs captured was calculated by the difference between the initial and final AgNP concentration in suspension. According to their results, the adsorption of AgNPs rapidly increased with time and then reached an equilibrium until no more AgNPs were further removed from the suspension. The initial high extraction rate was probably due to the abundant available binding sites on the surface of the adsorbent. The adsorption efficiency increased to 74.7% with agitation in 90 min and then leveled off. Therefore, a contact time of 90 min was selected for further studies.

3.5. Recovery of Magnetic Adsorbents

The removal of magnetic adsorbents should be considered crucial in post-precious metal separation stage since they need to be regenerated without damaging their structure and then recycled/re-used. Conventional adsorption and desorption processes are usually performed by immobilizing the magnetic materials into a column using an external uniform magnetic field, and then flowing the fluid phase either the feed or the regeneration solutions through the fixed bed column. On-line column extraction using magnetic adsorbents and analysis techniques such as flow injection analysis (FIA), sequential injection analysis (SIA) has been used to obtain fast, repeatable and dependable results [46,75,99]. However, in the case of processes including MNPs as an adsorbent, fixed bed configuration is not suitable due to the high pressure drop caused by the fluid flow. Therefore, in-series stirred tanks or fluidized beds that allow the solids to be suspended in the liquid are preferably used. Nanoscale magnetite exhibits superparamagnetic properties so they interact rather strongly with magnets [99,100].

Magnetic particles from slurry or aqueous solution can be captured using magnetic separation technique. Conventional magnetic separation devices are widely applied for the removal of magnetic materials such as tramp iron from various feed streams and also in the mineral processing of iron ores [101]. Depending on the plant and process design, magnetic separators can be applied to harvest the magnetic adsorbents after the precious metal separation stage. Amongst the conventional devices that can be employed are the magnetic grate separator, magnetic drum separator, and the magnetic belt separator. Recently, a number of “high intensity” magnetic separators are also available. This type of separators differ from the conventional designs by the employment of magnets of greater strength than usual [101].

4. Conclusions

Due to scarcity, extensive applications, and environmental concerns brought about by release of precious metals, several determination and separation methods for these metals from aqueous solutions generated by various industries and processes have been explored and applied. However, the common methods do not have acceptable sensitivity and selectivity required for real solution samples which normally contain trace amounts of precious metals. Therefore, a suitable separation or preconcentration method is needed to recover precious metals from solutions for economic and environmental reasons.

Magnetic solid phase extraction (MSPE) technique which uses adsorbents with magnetic properties (generally Fe_3O_4), synthesized and modified by coating or functionalization using a

multitude of organic and inorganic compounds, has been shown to be effective in the preconcentration and separation of precious metals from aqueous solutions. In this method, the target analytes (i.e., precious metal ions) are recovered by magnetic adsorbents and the adsorbents loaded with target analytes, can be separated by applying an external magnetic field, avoiding the problems associated with conventional filtration techniques. The harvested magnetic adsorbents are then isolated and eluted with appropriate solvents such as, HCl, thiourea, HNO₃, and H₂SO₄ to recover the target metals and recycle the adsorbent. MSPE minimizes the use of additional steps such as, precipitation, centrifugation, and filtration which significantly decreases the time required for sample manipulation, solvent consumption, and consequently the cost of operation. The technique, as discussed in the present article, is characterized by faster adsorption kinetics and high degree of selectivity towards precious metal ions. A number of literatures also confirmed the flexibility, efficiency and applicability of the method to real samples.

Various types of magnetic adsorbents were prepared and utilized for precious metals separation from aqueous solutions. Among the magnetic particles, iron oxides especially nano-meter sized ones like magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) have received considerable attention. Several researchers also attempted to combine adsorptive and magnetic properties of materials to synthesize different magnetic composites with potential applications in metals recovery. Iron and other metal oxides, activated carbon, graphene oxide, and others have been used for such purpose. However, due to limitations of using pure inorganic magnetic particles including formation of large aggregates, low selectivity toward target metal ions in complex matrices, and low stability of the particles in strong acidic aqueous media, suitable modification of the magnetic particles by coating or functionalization using inorganic components or organic molecules is usually needed.

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