

Recovery of precious metals from processed wastewater: conventional techniques nexus advanced and pragmatic alternatives

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ABSTRACT

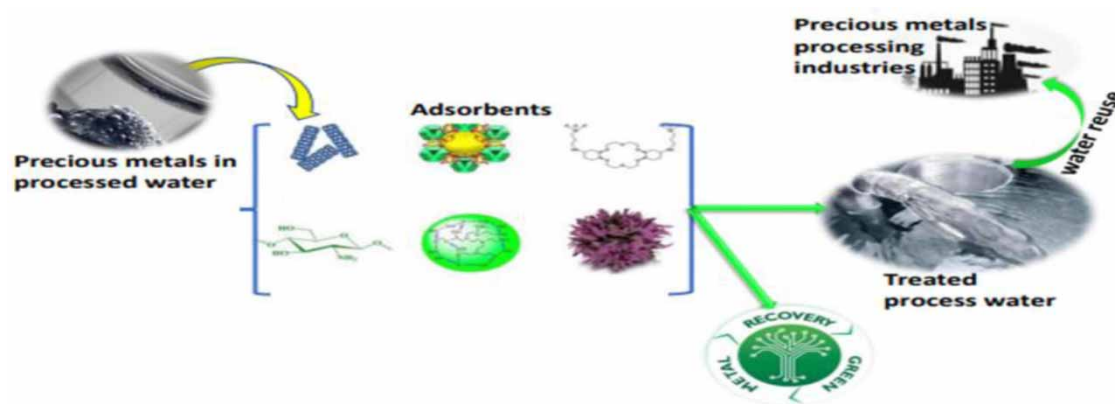
The loss of highly sought metals such as gold, silver, and platinum during extraction processes not only constitutes a significant waste of valuable resources but also contributes to alarming environmental pollution. The ever-growing adverse impacts of these highly valued metals significantly increase the contamination of water bodies on discharge, while reducing the reusability potential of their corresponding processed wastewater. It is, therefore, of great interest to identify pragmatic solutions for the recovery of precious materials from processed water. In this review, pollution from targeted precious metals such as gold, silver, platinum, palladium, iridium, ruthenium, and rhodium was reviewed and analyzed. Also, the hazardous effects are elicited, and detection techniques are enumerated. An insightful approach to more recent treatment techniques was also discussed. The study reveals nano- and bio-sorption techniques as adoptable pragmatic alternatives, among other techniques, especially for industrial applications with merits of cost, time, waste management, and eco-friendliness. The results indicate that gold (46.2%), palladium (23.1%), platinum (19.2%), and silver (11.5%) are of utmost interest when considering recent recovery techniques. High yield and cost analysis reduction are reasons for the observed preference of this recovery process when considering groups of precious metals. The challenges and prospects of nanomaterials are highlighted.

Key words: biosorption, metal recovery, nanomaterials, precious metals, sequestration

HIGHLIGHTS

- Precious metals are present in processed wastewater as pollutants.
- Conventional recovery methods are associated with limitations.
- Bio- and nano-sorption provide pragmatic alternatives to other existing techniques with cost-effectiveness, simplicity of design, and eco-friendly disposal methods.
- The technological approach via trapping and impregnation of precious metals in sorbents is effective in the recovery of precious metals.

GRAPHICAL ABSTRACT



1. INTRODUCTION

The increase in population coupled with rapid economic growth experienced all over the world due to industrialization has placed an ever-increasing demand on the need for both clean and safe water (Ebenstein 2012). Water is an important natural resource for the sustainability of life, especially potable water (Adeeyo *et al.* 2020). However, its unavailability in sufficient quantity and quality is a global concern, though more intense in developing countries (Edokpayi *et al.* 2014). SDG goal 6 anticipates increasing access to clean and safe water for all, globally, in the year 2030. Clean and safe drinking water is essential for the protection of public health, the environment, and the economy of any nation.

Among the wide spectrum of water contaminants, processed wastewater from industrial activities especially in the mining sector has tremendously contributed to environmental pollution and various health-impaired effects in man (Wang *et al.* 2008; Odiyo *et al.* 2012). These harmful impacts stem from the significant presence of mined metals in the discharged water. Furthermore, the recent emphasis on the toxicological impacts of processed wastewater resulting from various precious metal mining has raised a global concern (Birungi *et al.* 2020). Generally, the emphasis and demand for these metals are based on their economic worth and high-valued products (Table 1) that can be realized from them (Chen *et al.* 2021). For instance, materials such as the platinum group metals and gold are highly sought in dental, electronics, automobiles, and the jewellery industries (Takahashi *et al.* 2007; Abisheva *et al.* 2011; Umeda *et al.* 2011). These metals (gold, silver, platinum, palladium, iridium, ruthenium, and rhodium) are often called rare earth metals, having premium economic and industrial demands yet scarce and unevenly distributed in the earth's crust (He & Kappler 2017). Furthermore, this group of metals is ranked as one of the most critical elements with a diminishing supply due to the cost of mining and appreciable loss through processed wastewater, leading to deleterious environmental impacts on discharge (Birungi *et al.* 2020).

The reported losses are basically associated with mining, extraction, purification, and processing (Mannina *et al.* 2020). The disposal of waste or processed water from the aforementioned processes and metallurgical activities, therefore, constitutes the major source for the discharge of valuable metals into the environment (Baysal *et al.* 2013). Large volumes of processed

Table 1 | Major applications of precious metals

Precious metals	Applications
Gold	Jewellery, electronics, pharmaceuticals, superalloys and dental applications
Silver	Jewellery, catalyst, electronics, dental, oil, photovoltaics
Platinum	superalloys, photovoltaics, pharmaceuticals, oil, dental Ceramics, glass, fuel cells, electronics, chemistry, catalysts, jewellery
Palladium	Pharmaceuticals, dental, fuel cells, electronics, chemistry, catalysts, jewellery
Rhodium	Ceramics, glass, fuel cells, electronics, chemistry, catalysts
Iridium	Catalysts, electronics, dental
Ruthenium	Catalysts, electronics, fuel cells, pharmaceuticals, photovoltaics, superalloys

wastewater with substantial amounts of high-value metals have been reportedly discharged indiscriminately into the environment (Khaliq *et al.* 2014; Kaya 2016). These processed wastewaters cause contamination of different environmental media (Bambas-Nolen *et al.* 2018). Hence, valued metals, in themselves, have become pollutants to the environment even as demands for such fast-growing economies are very high. The use of water in industrial mining covers processes from extraction to the transportation of minerals with a subsequent release of significant amounts of the metals as waste to the environment (Van Berkel 2007; García *et al.* 2014). Soil, surface water, and groundwater have been highly polluted by various mining activities due to tailing leaks and disposal into water systems (Akciil & Koldas 2006; Gunson *et al.* 2012; Li *et al.* 2014). The release of precious metals as solid or liquid waste unrecovered is accompanied by huge environmental impacts, but not economical, and poses financial and strong penalties burdens on industries (Ravindra *et al.* 2004; Wei *et al.* 2016). In addition, the mining and processing of precious and heavy metals have subjected human health and the ecosystem to unwarranted risks (Eisler 2004; Tabari *et al.* 2008). Some critical health conditions, above the normal safety concentrations, have been attributed to the accumulation of metals in human bodies. Usually, they accumulate in food chains due to their solubility in aqueous media and their ability to be absorbed by microorganisms (Tabari *et al.* 2008).

To meet up with the growing demand and to minimize the loss during the processing of precious/rare earth metals, it necessitates the need for alternative technologies associated with pragmatic recovery approaches. The pragmatic approach describes the practical emerging technology such as bio-recovery, mechanochemical technology, ionic liquid technology, and nano-biotechnology (Ramachandran *et al.* 2016). The main criteria for the evaluation of these alternative technologies are their significant recovery performance and the capacity to annul secondary pollutants which is a major drawback in conventional techniques (Shin *et al.* 2015; Awasthi *et al.* 2016; Palomo-Briones *et al.* 2016). The recovery of precious metals is, therefore, of great interest vis-a-vis existing recovery technologies for the sequestration of precious metals from processed wastewater. Some reported techniques used in the recovery of valuable metals include chelation, ion exchange, chemical precipitation, solvent extraction leaching, adsorption, and biosorption methods (Golunski *et al.* 2002; Schreier & Edtmaier 2003; Da,browski *et al.* 2004; Wang *et al.* 2007; Birinci *et al.* 2009; Nikoloski & Ang 2014; Firmansyah *et al.* 2018; Lopes Colpani *et al.* 2019). This documentation enumerates cogent toxicological reports, detection and analytical techniques, and different processes of recovery methods for metals, particularly, precious metals. Conventional and recent alternative approaches for the sequestration of valuable metals from processed wastewater are discussed. A brief analysis of previous studies focused on precious metal recoveries is reported with recent limitations. Implication for theory and practice is highlighted.

2. HAZARDOUS EFFECT OF VALUABLE METALS IN PROCESSED WASTEWATER

Metals that have percolated into the environment and human system have posed a great threat in recent times. Valuable metals have been reported to have toxic effects on aquatic organisms, particularly, when they reach the aqueous environment in their organic forms (Shimada *et al.* 2010). Their volatility and ability to be transported through long ranges have equally increased their presence in the environment (Laliberte 2015). Precious metals generally pose harmful effects on plants and animals at a concentration above their toxicity limits, whereas there are a few that can greatly disturb the balance of the ecosystem and the human body even at very low concentrations. The presence of valuable metals unabated in the environment can result in serious health challenges ranging from mild to chronic ones (Abdul-Wahab & Marikar 2012; Laliberte 2015). A review of different literature has established various toxicological effects of Au, Ag, and the platinum group metals including bone marrow suppression and necrosis, cranial neuropathy, nephrotoxicity, cancer, haemorrhage pulmonary injury, blood dyscrasias among others (García *et al.* 2014). Concerns have been raised on the toxicological impact of untreated metal-laden effluents and the need for an effective recovery procedure was proposed as a very critical topic (Benavente *et al.* 2011; Mondal & Sharma 2016).

3. ANALYTICAL TECHNIQUES FOR DISCOVERY OF METALS IN PROCESSED WASTEWATER

Analytical techniques such as Atomic Adsorption Spectrometry (AAS), Anodic Stripping Voltammetry (ASV), Laser-Induced Breakdown Spectroscopy (LIBS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can be employed in detecting various valuable metals. In the AAS technique, different atomization of samples gives rise to different procedures for analyzing elements. For example, in Flame Atomic Adsorption Spectrometry (FAAS), air or nitrous oxide/acetylene flame can be used with respect to the thermal stability of the metal for analysis (Komendova 2020). Metals such as zinc, tin, silver, rhodium, platinum, nickel, lead, gold, cobalt,

calcium, and antimony among others, can be determined using air/acetylene flame while elements like vanadium, silicon, rhenium, barium, and aluminium among others, can be determined using nitrous oxide/ acetylene flame (Rice *et al.* 2012). FAAS is limited as certain elements require higher temperatures to atomize than is obtainable for this technique.

Another technique used in the detection of precious metals is ICP-OES which uses plasma for the excitation of atoms. Atomization temperature can reach up to 10,000 °C which gives this technique an advantage over AAS (Zeeshan & Shehzadi 2019). Metals can be determined even at low concentrations in this technique and several elements can be analyzed simultaneously in a few seconds. Other recent techniques that have been employed include LIBS and ASV, ICP-MS which are characterized by better detection limits ranging in part per trillion (ppt) (Nebeker & Hiskey 2012). The major limitation attached to these techniques is the cost associated while running them.

4. APPROACHES/PROCESSES FOR THE RECOVERY OF PRECIOUS METALS FROM PROCESSED WASTEWATER

There are several traditional and emerging approaches employed to recover commonly used precious metals such as gold, silver, platinum, palladium, and indium. These traditional approaches are categorized as physical or mechanical, pyrometallurgical, and hydrometallurgical (Zhao *et al.* 2004; Parajuli *et al.* 2006). Advanced and more recent precious metal recovery processes include mechanochemical technologies, solvato-metallurgy (use of ionic liquid), and electrochemical technologies from which bio-electrochemical technology stems and biotechnology or bio-recovery (Binnemans & Jones 2017). A critical and extensive study on the recovery of precious metals from processed wastewater will proffer insights and solutions that will remove contaminants and recover valuable products from processed wastewater (Zhang *et al.* 2010; Benit & Roslin 2015).

4.1. Conventional recovery processes

4.1.1. Physical/mechanical process

This separation and recovery technology is described as being foundational to other conventional techniques (Yoo *et al.* 2009). It involves the mechanical breaking and crushing of precious metals in the processed wastewater followed by separation (Table 2). This process follows three basic steps which are crushing, corona electrostatic separation, and metallic material recovery as described by Huang *et al.* (2009) and Zeng *et al.* (2014). An appreciable benefit of the process is reduced secondary pollution. However, this procedure is not sufficient to facilitate the recovery of a significant amount of metal scraps and tailings in effluents. Hence, the process is only used as a pre-treatment process while other recovery processes are incorporated (Chancerel *et al.* 2009; Marra *et al.* 2018).

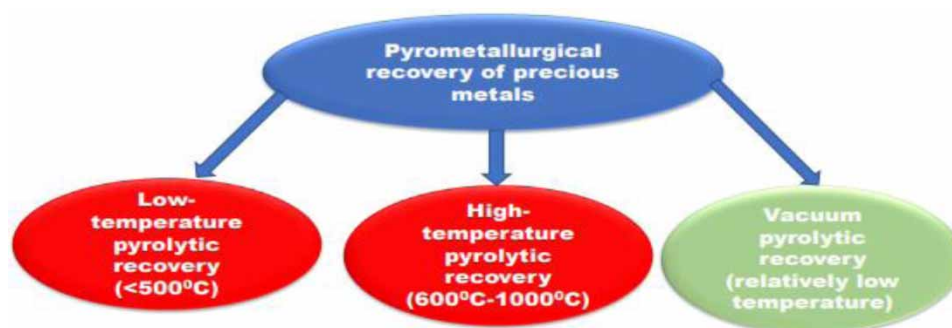
4.1.2. Pyrometallurgical process

Pyrometallurgy is a routine process used for non-ferrous and precious metals recovery from solid mine tailings, electronic wastes, and their corresponding effluents (Ghosh *et al.* 2015). This recovery process can be classified into three main classes as described in Figure 1. However, the process can be described with respect to the thermal breakdown of precious metals at high temperatures in the furnace. This could be through roasting following a solid–gas phase reaction, oxidation, reduction, chlorination, sulphation, and pyro-hydrolysis. Thereafter smelting procedure is introduced to degenerate the solids tailings into a molten state and finally refine them to recover the metals from the molten slag (Cui & Zhang 2008).

Although this process is conventional, the challenges of low and high-temperature pyrolytic recovery technique such as cost implication, generation of toxic slag, and low amount of metal recovery remains a major concern. This brought about the recent investigation on vacuum pyrolytic recovery technique associated with relatively low temperatures and residence time for the recovery process. Also, the technique reduces the generation of toxic secondary reactions which is notable in high and low pyrolytic recovery techniques (Yazici *et al.* 2010). The use of vacuum pyrolytic metal recovery is known for its superiority among other traditional pyrometallurgical techniques because of the low interfacial bond existing between metals and other materials after vacuum pyrolysis. This enhances the separation and recovery of precious metals. However, this approach relates the temperature of metals as a function of their vapour pressure using Clausius–Clapeyron expression

Table 2 | Mechanical/physical process of metal recovery from waste effluents and solid waste

Separation techniques	Useful property	Recovery product	Process mechanism	Material Size (mm)	References
Magnetic	Magnetic susceptibility	Ferrous (ferromagnetic) metals from non-ferrous and non-metals	Uses magnets to separate magnetic materials from their corresponding mixtures	<5	Huang <i>et al.</i> (2009)
Corona Electrostatic	Electrical conductivity	Conductive metallic materials from non-metallic particles	Electrical conductivity separation as a result of different charges on the particles determines different interactive forces existing between them	0.1–5	Zhang <i>et al.</i> (2017)
Eddy-current	Electrical conductivity/specific gravity	Light metals from conductive heavy (base and precious) metals and non-conductive particles	Uses strong magnetic field separation between ferrous and non-ferrous metals	<5	Bas <i>et al.</i> (2013)
Gravity	Specific gravity	Metals from non-metals	Different materials are separated by their relative motion in response to the force of gravity	0.05–10	Duan <i>et al.</i> (2009); Veit <i>et al.</i> (2014)
Flotation	Surface characteristics	Non-metals (non-hydrophilic) from metals		0.075–1	Gallegos-Acevedo <i>et al.</i> (2014); Vidyadhar & Das (2013)
Shredding, washing and sieving	Mechanical vibratory forces	Metals from non-metals	Removal of extraneous impurities by the sieving coupled with the vibratory action of the agitator	3–5	Chancerel <i>et al.</i> (2009)

**Figure 1** | Categories of pyrometallurgical recovery of metals.

(1) and Antoine Equation (2), respectively:

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2} \quad (1)$$

$$\ln P = A - \frac{B}{C + T} \quad (2)$$

where P refers to the vapour pressure, ΔH refers to the standard molar enthalpy of evaporation or sublimation, T refers to the temperature, R is the gas constant, and A , B , C are specific metal constants.

4.1.3. Hydrometallurgical process

Hydrometallurgy possesses advantages such as reduced power consumption and lower cost of pre-treatment. Hydrometallurgy systems are relatively small in capacities coupled with a controlled recovery process when compared to pyrometallurgy (Ranjbar *et al.* 2014). Hydrometallurgy is concerned with the use of aqueous solutions known as leaching reagents (cyanide, thiourea, thiosulphate, acids) to isolate, purify, and recover precious metals from its attendant effluents (Tuncuk *et al.* 2012). There is a wide spectrum of leaching reagents used for this process as described in Table 3. Table 4 describes the chemistry involved vis-a-vis the leaching solvent selected for the leaching process. The choice of solvent used by these techniques categorizes the method into either green or conventional (Kumari *et al.* 2015). Cyanide leaching may be used for gold recovery; however, cyanide is a very toxic compound that requires intensive care and treatment during usage and disposal (Konyratbekova *et al.* 2015). In this process, methods such as adsorption using activated carbon, cementation, solvent extraction, and ion exchange may be used as recovery technology.

Table 3 | Summary of the leaching process in hydrometallurgy

Leaching Methods	Lixiviant	Metal recovered	Advantage(s)	Disadvantages	References
Cyanide leaching	Cyanide	Au, Ag, Pt	Cost-effectiveness of reagent. Less dosage and its operation in an alkaline solution	Slow leaching reaction, generation of toxic wastewater	Huang <i>et al.</i> (2009)
Thiourea leaching	Thiourea	Au, Ag	Very efficient in the separation of Au from wastewater and electronic waste	Chemically the Stability is low and requires a high amount of reagent	Xu & Li (2011)
Thiosulphate leaching	Thiosulphate	Au, Ag Pt etc.	Faster leaching rate. High selectivity. Nontoxic and non-corrosive	Chemically the Stability is low and requires a high amount of reagent	Zhang <i>et al.</i> (2012)
Other leaching techniques	Mineral acids (H ₂ SO ₄ , HNO ₃ or HCl) Bases (NH ₃ , NaOH) Chelating agents (EDTA or citric acid)	Varieties of precious metals	-	Difficulty in the dissolution of some metals eg gold	Binnemans & Jones (2017)
Organosulphur leaching	Organosulphur compounds	Precious metals	biodegradability and the low toxicity	The reaction may be slow	Kaya (2016); Khaliq <i>et al.</i> (2014)

Table 4 | Chemistry of leaching in pyrometallurgy

S/N	Type of leaching	Leaching reagent(s)	Leaching reaction
1.	Acid leaching	Nitric Acid (HNO ₃) Aqua Regia (HNO ₃ :HCl) H ₂ SO ₄ : H ₂ O ₂	$4\text{HNO}_3 + \text{Cu} \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$ $2\text{Au} + 11\text{HCl} + 3\text{HNO}_3 \rightarrow 2\text{HAuCl}_4 + 3\text{NOCl} + 6\text{H}_2\text{O}$ $\text{Cu} + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + 2\text{H}_2\text{O}$
2	Cyanide leaching	NaCN	$4\text{Au} + 8\text{CN}^- \rightarrow 4\text{Au}(\text{CN})_2^{2-} + 4\text{e}^-$
3	Thiourea leaching	CS(NH ₂) ₂	$\text{Au} + 2\text{CS}(\text{NH}_2)_2 \rightarrow \text{Au}(\text{CS}(\text{NH}_2)_2)_2^{2+} + \text{e}^-$
4	Thiosulphate	(S ₂ O ₃) ₂ ²⁻	$\text{Au} + 5\text{S}_2\text{O}_3^{2-} + \text{Cu}(\text{NH}_3)_4^{2+} \rightarrow \text{Au}(\text{S}_2\text{O}_3)_2^{3-} + \text{Cu}(\text{S}_2\text{O}_3)_3^{5-} + 4\text{NH}_3$
5.	Halide leaching	Bromine, chlorine, iodine	$2\text{Au} + \text{I}_3^- + \text{I}^- \rightarrow 2\text{AuI}_2^-$ $\text{Au} + 4\text{Br}^- \rightarrow \text{AuBr}_4^- + 3\text{e}^-$ $\text{Au} + 4\text{Cl}^- \rightarrow \text{AuCl}_4^- + 3\text{e}^-$
6	Organosulphur leaching	Organosulphur compounds	$2\text{Ag} + 2\text{CH}_3\text{SO}_2\text{OH} + \text{HO}_2\text{O}_2 \leftrightarrow 2\text{AgO}_3\text{SCH}_3 + \text{H}_2\text{O}$

4.1.4. Solvent extraction system

The solvent extraction system stands alone as a versatile technique, although some researchers classify this system of metal recovery under hydrometallurgy. However, the recovery system/process is commonly called a liquid–liquid extraction system. The extraction system uses the process of solute (metal ion) distribution between the immiscible aqueous and organic phases in contact with each other (Ebenstein 2012). The solvent extraction process takes place by either cross-current batch extraction, counter-current batch extraction, or continuous-current batch extraction (Park *et al.* 2014). In addition, these different approaches used in solvent extraction systems follow a sequential order of extraction, scrubbing, and stripping. However, cross-current batch extraction is known with an appreciable advantage of generating the least amount of residual solute concentration in the raffinate (Nguyen & Lee 2021; Kozhevnikova *et al.* 2022). The process involves the replacement of the water molecules and the removal or reduction of the ionic charge (Zhang *et al.* 2012). This process can be actualized through the use of any of the three classes of extractants, which are acidic, basic, and solvating, which extract metals according to the equilibrium reaction in Table 5. It is needful to add that there are vital parameters such as the maximum degree of separation between a precious metal (*A*) and other co-metallic substance (*B*) in a single equilibrium, the phase ratio (*r*), and the distribution ratio (*D*) (Park *et al.* 2014). The maximum degree of separation is determined by the separation factor (α), which define as the ratio of the distribution ratios (*D*) of the two metals, expressed by the following equation.

$$\alpha = \frac{D_{AB}}{D_A + D_B} \quad (3)$$

The phase ratio (*r*) is the ratio of the volume of the organic phase to the volume of the aqueous phase. Hence, the ratio of metal *A* extracted (R_A) and the fraction of *B* extracted (R_B), is expressed as R_A/R_B . However, the recovery factor ratio is an expression of the degree of separation. Equation (4) expresses the relationship between these parameters.

$$\frac{R_A}{R_B} = \alpha \left(\frac{D_B + (1/r)}{R_B + (1/r)} \right) \quad (4)$$

Despite the industrial application of the solvent extractions, the toxicological impacts of these solvents, cost, and lack of adequate recovery of precious metal tailings from the processed wastewater of mining have led to search of other improved technologies.

4.1.5. Ion exchange technology

The ion exchange method is a reversible chemical reaction used in the recovery of metals from pregnant solutions. This technology is sometimes classed under hydrometallurgy. It uses Ion Exchange Resins (IEXRs), or activated carbon as its porous media for the separation and recovery of metals. The resins used in this technology can be organic or inorganic, however, their source can be natural or synthetic (Figure 2). Research attention has recently focused on the use of this technology in the recovery of precious metals from processed water using IEXRs than activated carbon. The selective interest is based on the higher capacity for metal ion loading, elimination of thermal regeneration, and low amount of contamination by solvent for the preferred resins (Edokpayi *et al.* 2020). Furthermore, IEXRs are composed of the polymeric matrix as an inert resin backbone and selective functional groups. The resin backbone can be either of gel or a macroporous-type structure

Table 5 | Extraction mechanism in a solvent extraction system

S/ N	Types of extractants	Examples	Extraction mechanism
1.	Acidic	Carboxylic acids, organophosphorus acids, β -diketones, 8-hydroxyquinoline and hydroxyoximes	$M_{(aq)}^{z+} + zHA_{(aq/org)} \rightleftharpoons MA_{z(org)} + zH^+$
2.	Basic	Alkylammonium species	$(n-z)R_4N_{(aq/org)}^+ + MXn_{(aq)}^{(n-z)-} \rightleftharpoons (n-z)R_4N^+MXn_{(org)}^{(n-z)-}$
3.	Solvating	Alcohols, ethers, esters and ketones with compounds such as dibutylcarbitol, nonyl phenol and methyl isobutyl ketone (MIBK)	$MXz_{(aq)} + mS_{(org)} \rightleftharpoons MXZSm_{(org)} + mH_2O$

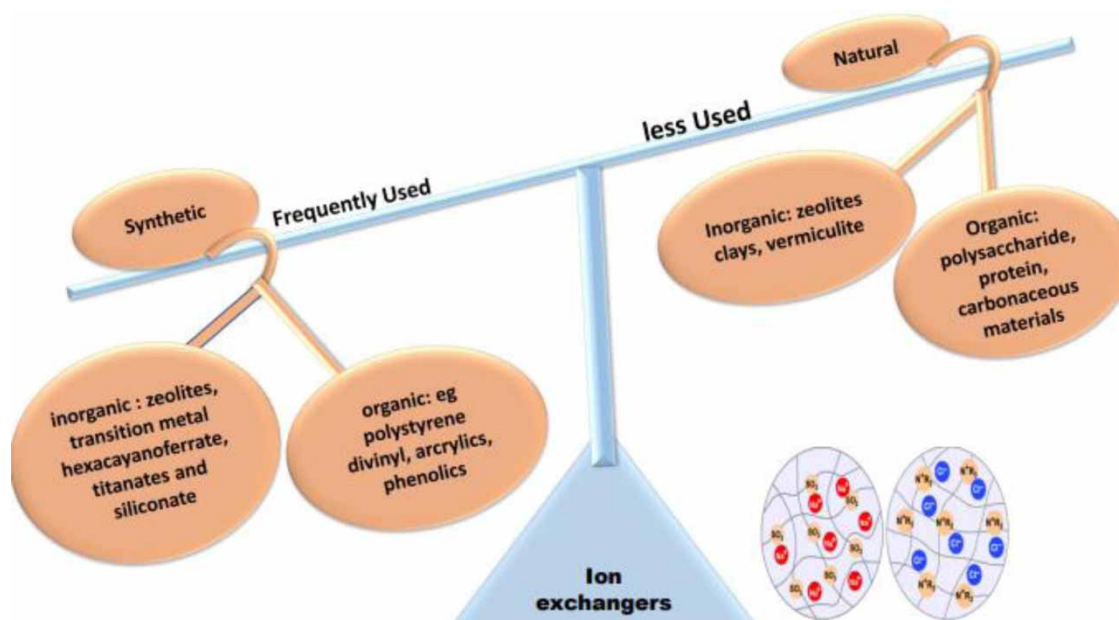


Figure 2 | Categories of IEXRs, structure, and chemical composition.

with distinct chemical composition. However, recent reports have identified the novel use of IEXRs resin adsorption for gold recovery, especially processed wastewater from mining based on its fast adsorption rate, high loading capacity, simultaneous elution, and regeneration at ambient temperature operation (Eisler 2004; Wei *et al.* 2016).

The mechanism for the recovery of precious metals like gold in pregnant solutions primarily depends on its oxidation state. For instance, gold in pregnant solution exists in two different oxidation states (anion forms) of $[\text{Au}]^-$ and $[\text{Au}]^{3-}$ and the resins used in gold recovery are all weak, medium, and strong base anion exchange resins (Akciil & Koldas 2006; Birinci *et al.* 2009; Wei *et al.* 2016). From Figure 3, the complex metal cyanide on the resin can be eluted by either conversion of the metal ions to cationic complex (by using thiourea) or by an ion exchange method which consequently shifts the equilibrium towards the left-hand side (Dabrowski *et al.* 2004; Eisler 2004; Zakhar'yan & Gedgagov 2013; He & Kappler 2017). The reaction mechanism for weak base resins is described in Equations (5) and (6):

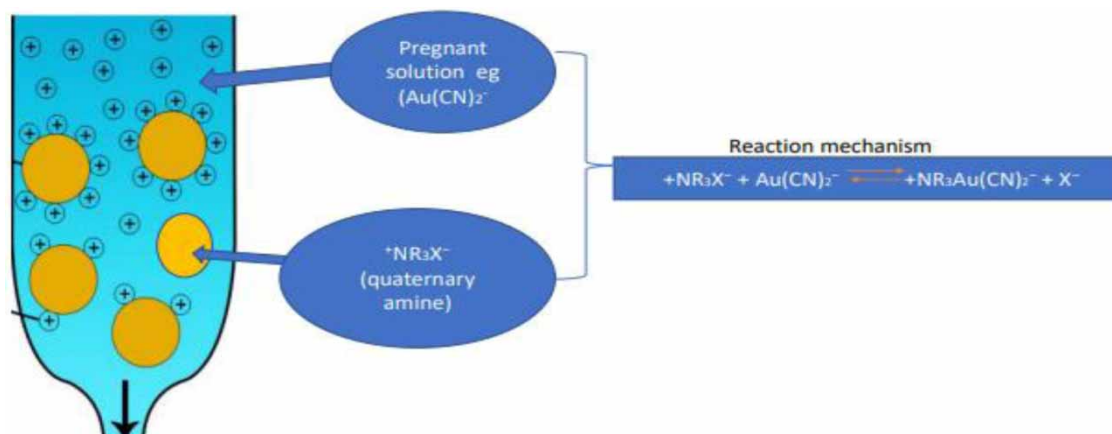


Figure 3 | Ion exchange recovery mechanism for precious metal.

Also, the optimization of the performance and kinetics of the process depends on parameters such as the mass transfer rate, the film thickness, the reaction between counterions and fixed groups, and sorption conditions.

4.2. Selected advanced and emerging alternatives for precious metal recovery

There are justifications and a quest for highly selective and efficient emerging processes to effectively clean up and recover precious metals from processed wastewater other than the known traditional methods. These emerging processes include mechanochemical technologies, the use of ionic liquid (Solvato-metallurgy) (Binnemans & Jones 2017), and others as discussed in the following.

4.2.1. Bio-recovery technology

This technology is also referred to as bioleaching, which involves the extraction or metal recovery through the use of living organisms (Kumari *et al.* 2015; Ramachandran *et al.* 2016). Living organisms such as acidophilic bacteria with examples like *Thiobacillus ferrooxidans* is used for the recovery of precious metals in processed wastewater (Bas *et al.* 2013). The recovery of metals using this method depends on the chemical composition of the culture media, the particle size of the metal tailings, and the pH of the solution. Consequently, these factors affect the leaching rate and kinetics of the reaction (Chand *et al.* 2009). Various approaches such as bio-based leaching, precipitation, sorption, reduction, flotation, flocculation, oxidation, and accumulation are commonly used in this technology (Watling 2006; Ramachandran *et al.* 2016). For instance, in bioleaching, a unique bacterial strain called *Chromobacterium violaceum* (CV) has been reported to have great potential in the recovery of gold and silver tailings in processed wastewater. This bacterial strain generates the needful CN^- which efficiently recovers up to 70% of the desired precious metals from the pregnant solution (Sicupira *et al.* 2010). The reaction mechanism in Equation (7), shows the recovery of gold via the CN^- generated by this bacterial strain.



Although, the challenges in the use of the bacterial strains are the limiting factor of the cyanide lixiviant and the difficulty in getting CV due to its growth in stringent living conditions (Asere *et al.* 2019); however, recent studies have pointed out the use of a new mode of bacterial strain for the leaching of these precious metals, one of which is *Pseudomonas chlororaphis* (PC), which produces CN^- for the leaching process (Mincke *et al.* 2019). This new bacterial strain is easily obtainable and can be employed for a continuous industrial system. However, *C. violaceum* (CV), still has higher strength for the generation of CN^- when compared with the *P. chlororaphis* (PC). This justifies the low recovery yield of 8.2, 12.1, 52.3% for Au, Ag, and Cu, respectively (Nebeker & Hiskey 2012).

Other examples involve the sulphate-reducing bacteria reduction of Platinum(II) to Platinum (Riddin *et al.* 2009; Homchuen *et al.* 2016). These bacteria include *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum ferrooxidans*. Among the fungi microbial class, a notable microorganisms used in the bio-recovery of precious metals are *Penicillium* sp. and *Aspergillus niger*. The use of fungi is an example of eukaryotes engaged in leaching technology for recovering metals of concern from their wastes (Ha *et al.* 2010). Soluble precious metals can be recovered with biosorption and reduction (Colica *et al.* 2012; Maes *et al.* 2016). *Trichoderma harzianum* was reported for the efficient removal of silver from metal-polluted waste-rock tips or processed wastewater (Cecchi *et al.* 2017). In addition to this, *Stenotrophomonas* sp. a magnetotactic microbe removes gold(III) from waste effluents to reduce the gold(III) to gold and deposit nanocrystals particles of gold on the surface of the cell (Song *et al.* 2008).

4.2.2. Electrochemical technology

Electrochemical technology involves the plating-out of metal ions on the cathode surface with the use of electric current (Karn *et al.* 2021). This process is categorized into electrodeposition/electrowinning or electrorefining. The recovery of precious metals via electrowinning involves the use of direct current between the anode and cathode electrodes so aid the reduction of the targeted metals specie in the effluent of the cathode and to extract the metal in its metallic form (Subbaiah *et al.* 2022). However, in electrorefining, the anode consisting the metals associated with impurities is dissolved in an aqueous state by either direct or indirect electrooxidation, leading to the selective deposition of leached metal ions unto the cathode in its pure form (Rai *et al.* 2021; Subbaiah *et al.* 2022). This precious metal recovery approach has notable significant merits such as uniform selective and uniform deposition of metals, high purity grade, automation, faster reaction kinetics, and cost-

effectiveness. However, the demerits of this recovery approach remain the deposition of non-electroactive particles on the electrode, variation of current density in the electrode surface and nucleation rate distribution step, ultimately leading to recovery of a smaller concentration of target metal in leachates. Recent studies on the use of electrochemical technology for extraction and recovery of precious metals recovery have proposed electrochemically mediated optimized processes for metals extraction and recovery (Lister *et al.* 2014). Although, the recovery technology comes in different forms such as electrocoagulation, electrodeposition and electrodialysis (Fu & Wang 2011). However, the supply of adequate electrical potential and effective distribution of the current at the electrode enhances its uniformity leading to homogeneity in the optimal metal deposition of uniform thickness (Zhang & Huang 2020). The thermodynamic study and mechanism of electrochemical recovery of precious metals in electrodeposition/electrowinning involve the use of three electrodes namely a reference, a working, and a counter electrode. The cathodic electrode is the working electrode while the anodic electrode is the counter electrode. The process of deposition involves the dissolution of the metal ions (M^{n+}), in a liquid or molten state and its reduction to metal electrodeposit (M^0) known as a cathodic deposit when an external electrical potential is supplied. The reversible reaction is expressed by Equations (8) and (9) known as the Nernst equation as shown in the following:



$$E^{eq} = E^0 + \frac{RT}{nF} \ln \frac{a(M^{n+})_{ox}}{a(M)_{red}} \quad (9)$$

where R represents the gas constant ($R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$), T (K) is the temperature, F is the Faraday constant ($F = 96,485.339 \text{ C mol}^{-1}$), and E^0 is the measured standard electrode potential at standard conditions (Karvelas *et al.* 2003).

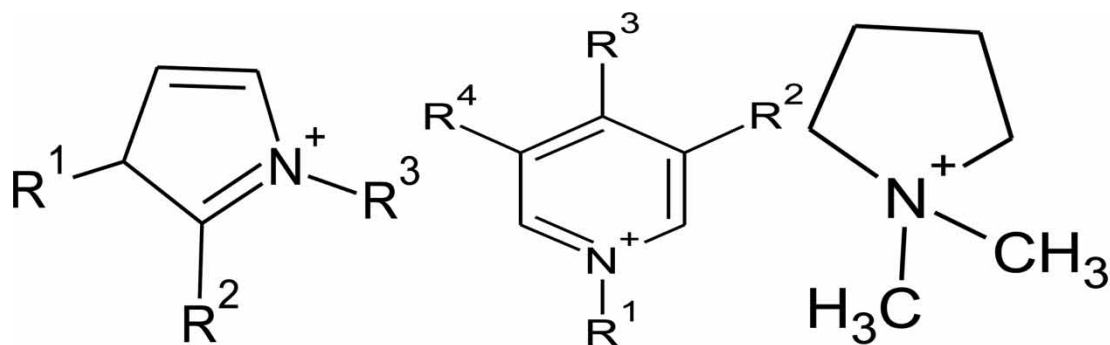
Hydrogen gas is released from the cathode, while the generation of the coagulants metal ions happens at the anode (Azimi *et al.* 2017). Generally, the merits of electrochemical technology include proper controlled process and speed, reduced use of chemicals, improved selectivity, and absence of sludge. The process involves high starting and operational costs since it involves appreciable energy supply and facility demand (Gunatilake 2015).

4.2.3. Mechanochemical technology

Mechanochemical technology involves a chemical reaction that is initiated via mechanical energy in the extraction or recovery of metals from processed wastewater. This technology is carried out by integrating milling and leaching operations into a single step (Nasser & Mingelgrin 2012; Mengmeng *et al.* 2017). In a broader sense, the study of physicochemical transformation brought about by mechanical and chemical action is known as mechano-chemistry (ball milling). Mechanical forces exert energy on metals during ball milling which turns the metals separated from processed wastewater (by physical/ mechanical method) into powder of appreciable surface area and reduced size. The surface area of these reduced metal particles increases to facilitate reaction efficiency (Nasser & Mingelgrin 2012). The distinct difference existing between this technology and thermochemical technology is that mechanochemical technology uses mechanical energy and not thermal energy. Hence, the reaction proceeds without harsh conditions such as increased pressure and temperature (James *et al.* 2013). Baláz (2008) categorized this emerging technology into dry and wet milling. In dry milling, the two processes of milling and leaching are separated distinctly while in wet milling, the processes are performed concurrently together. The recovery of indium (Id) which has its renowned use in indium-tin-oxide (ITO) thin films, mainly in liquid crystal display (LCD) has been investigated based on its increasing scarcity and demand (Hasegawa *et al.* 2018). Investigation on the recovery of this precious metal via mechanochemical technology was carried out by Janiszewska *et al.* (2019), who recovered indium by grinding the representative sample of indium oxide with tin doping. After including alumina powder ($\alpha\text{-Al}_2\text{O}_3$), the result of the leaching yield exceeded 80%.

4.2.4. Ionic liquid technology

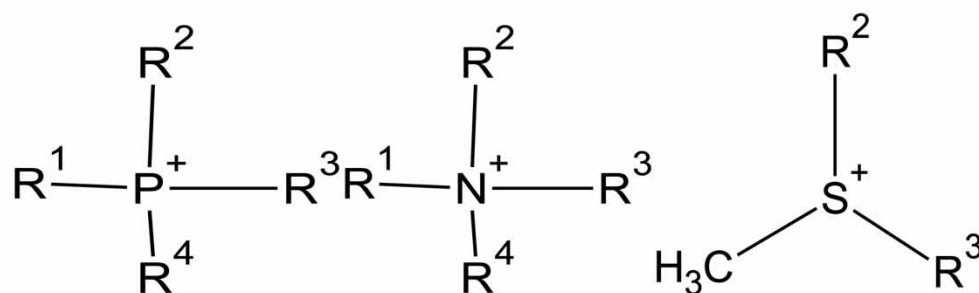
One of the emerging processes that stem out of hydrometallurgy is ionic liquid (IL) removal and recovery of precious metals (Janiszewska *et al.* 2019). Descriptively, a family of molten salts encompassing organic cations as well as organic/inorganic anions is known as ILs (Figure 4). Appreciable advantages of using this technology for precious metal recoveries exist in the literature. These advantages are its non-volatility, low flammability, and, in general, low toxicity (Park *et al.* 2014; Binnemans & Jones 2017). The ionic liquid incorporation aids easy concentration of Pt^{4+} , Pd^{2+} , Rh^{3+} from hydrochloric acid leaching



(a) imidazolium

(b) pyridinium

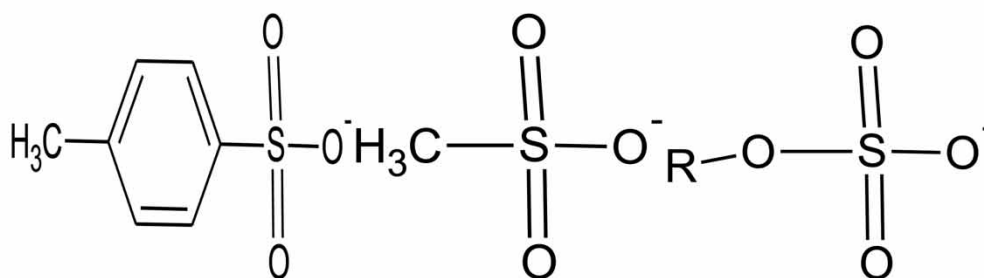
(c) pyrrolidinium



(d) phosphonium

(e) ammonium

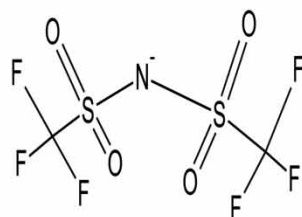
(f) sulfonium



(g) tosylate

(h) methanesulfonate

(i) alkylsulfate



(j) bis(trifluoromethylsulfonyl)amide

(k) Tetrafluoroborate

(l) hexafluorophosphate



(m) halogenate

Figure 4 | (a–m) Examples of some cations and anions of ILs (Owusu-Ansah *et al.* 2015).

solution using [C4mim]PF₆-oil phase (diisopentyl sulphide-nonane organic solution)-aqueous phase (HCl water solution). Cieszyńska & Wisniewski (2011) also confirmed the effective use of ILs during the removal and recovery of platinum group metals when likened to the two-phase solvent extraction systems. There is the possibility of the direct use of ILs as

electrolytes for the electrowinning of liquefied metal ions due to their improved ionic conductivity and potential which enhances the electrolytic reduction of different metals (Cieszyńska & Wisniewski 2011).

5. APPLICATION OF DIFFERENT SORBENTS AS PRAGMATIC ALTERNATIVES FOR THE SEQUESTERING OF PRECIOUS METALS AND OTHER VALUABLE PRODUCTS FROM WASTE EFFLUENTS

The use of sorbents in the adsorption of metals from processed wastewater is a commonly used process due to its clean and fast operation, high productivity, simplicity, and reduced cost-effectiveness. Accessibility and new research into diverse adsorbents has resulted in the high-quality treatment of effluent (Adeeyo *et al.* 2019) with sorbents of various types.

5.1. Conventional materials

Different adsorption procedures have been used over the years for various adsorption purpose with such adsorbent originating from mineral, organic, or biological material. Common adsorbents are activated carbon, zeolite, clay, and silica beads (Ghoul *et al.* 2003). However, the usual economic origin of adsorbents is commonly industrial by-products or agricultural wastes (Netpradit *et al.* 2003). Also, Song *et al.* (2008) reported that adsorbents from polymer and biomass are equally used in the sequestration of metals. For instance, Chand *et al.* (2009) reported the use of barley straw and rice husk at optimized conditions as adsorbents in precious metal recovery. Also, the efficiency of activated carbon as sorbent in the extraction of platinum, gold, and palladium has been studied by Mpinga *et al.* (2014) and Quinet *et al.* (2005) with a report of favourable adsorption capacity, adsorption rate as well as its abrasion resistance. The frequent study of activated carbon as an adsorbent in the recovery process is due to the appreciable properties of extended surface area, porous structures, high adsorption capacity as well as an appropriate functional group that helps its surface reactivity (Chand *et al.* 2009). Mosai *et al.* (2019) reported the recovery of platinum from an aqueous solution using hydrazine-functionalized zeolite. However, a bentonite clay adsorbent was studied by Mosai *et al.* (2019) with a record of high recovery potential for numerous metal ions. Polysaccharides including chitin, starch, cyclodextrin, and chitosan have also been explored as adsorbents and they are cheap and effective (Varma *et al.* 2004). The structure, physicochemical characteristics, chemical stability, high reactivity, and selectivity of polysaccharides give high preference towards aromatic compounds and metals (Crini 2005). Chitosan is greatly used as an adsorbent and its main advantage in the adsorption of precious metals is due to its amino acids that are easily protonated in acid media. Other effective sorbents are tannins which are commonly used for redox capabilities (Ma *et al.* 2006).

A magnetite adsorbent was also used for recovering gold, platinum, and palladium (Tsyanova *et al.* 2013). However, separating magnetic adsorbent should be considerably checked at the post-precious metal recovery phase (Kraus *et al.* 2009). While numerous materials are described as capable of recovery of precious metals from processed wastewater, conventional methods using these materials usually results in operational issue, especially when using sorbents of the nanometer size range (Donia *et al.* 2007). A summary of selected sorbents investigated for precious metal recoveries is presented in Table 6.

5.2. Nanomaterials and biosorption

The emphasis of nanosorbents over conventional sorbents is due to appreciable features such as availability of more active sites and ability to form composite with improved morphological attributes, adsorption capacity, durability, reusability, surface area, crystallite size and distribution, dispersibility, as well as mechanical and thermal stability (Oyetade *et al.* 2022). Predominantly, higher surface-to-volume ratio improves the reactivity of nanomaterials with environmental contaminants (Mincke *et al.* 2019). Other advantages of nano-sorbents include short intra-particle diffusion distance, tunable surface properties and easy reuse (Rickerby & Morrison 2007). Carbon nanotubes, zeolites, and dendrimers have been reported in a few studies for exceptional adsorption properties (Rickerby & Morrison 2007; Theron *et al.* 2008).

Metallic oxide nanomaterials of titanium, zinc, manganese, and iron have been applied for the adsorption of metals in processed wastewater (Amin *et al.* 2014). Unique characteristics of high surface area, reactivity and strong sorption make them suitable adsorbents (Savage & Diallo 2005; Kamali *et al.* 2019). TiO₂ nanoparticle was reported for adsorption in metal recovery (Kim *et al.* 2020). Metal-based nanomaterials were better than activated carbon. Iron-oxide nanomaterials are of low cost for recovering metals from solution (Salipira *et al.* 2007). Carbon-based nanomaterials have been used for the treatment of processed wastewater due to ease of chemical or physical modification and broad affinity for inorganic and organic pollutants (Mayo *et al.* 2007). Application of magnetic material as adsorbent (Kraus *et al.* 2009) in the recovery of platinum (Oliveira *et al.* 2004), iron-carbon composite in the recovery of gold (Banimahd Keivani *et al.* 2010) and modified chitosan magnetite

Table 6 | Selected sorbents used for precious metal recoveries in the literature

Metal	Sorbent	References
Au(III)	Glutaraldehyde-crosslinked chitosan beads	Lin & Lien (2013)
	Chitosan (sulphur-grafted)	Bui <i>et al.</i> (2020)
	Condensed tannin gel particles	Arrascue <i>et al.</i> (2003)
	Calcium alginate beads	Adeeyo <i>et al.</i> (2021)
	Chitosan (glutaraldehyde)	Bui <i>et al.</i> (2020)
	Chitosan-coated magnetic nano-adsorbent	Ogata & Nakano (2005)
	Dealginated seaweed waste	Chang & Chen (2006)
	Thioctic acid-modified Zr-MOF	Romero-González <i>et al.</i> (2003)
Pd(II)	Chitosan (glutaraldehyde crosslinked)	Bui <i>et al.</i> (2020)
	Activated carbon	Wang <i>et al.</i> (2020)
	Chitosan	Wang <i>et al.</i> (2020)
	Chitosan	Ruiz <i>et al.</i> (2000)
	Chitosan-based hydrogels	Sharififard <i>et al.</i> (2013)
	Functionalized chitosan	Mao <i>et al.</i> (2020)
	Pyridine-functionalised graphene oxide	Sicupira <i>et al.</i> (2010)
	Bayberry tannin	Ma <i>et al.</i> (2006)
Pt(IV)	Ion-imprinted chitosan fibre	Kraus <i>et al.</i> (2009)
	Bayberry tannin	Ma <i>et al.</i> (2006)
	Magnetic functionalized cellulose	Mincke <i>et al.</i> (2019)
	Dialdehyde carboxymethyl cellulose crosslinked chitosan	Chen <i>et al.</i> (2019)
	Chitosan-based hydrogels	Sharififard <i>et al.</i> (2013)
	Chitosan flakes	Yousif <i>et al.</i> (2019)
	Activated carbon	Wang <i>et al.</i> (2020)
	Chitosan	Wang <i>et al.</i> (2020)

resin in the recovery of silver (Homchuen *et al.* 2016) have been documented. Silica-based nanomaterials are used in the removal of metals because of their non-toxicity and excellent surface characteristics (Tewari *et al.* 2005). Many advantages of magnesium oxide nanoparticles as adsorbents for metals are listed in literature and include a high adsorption strength, low cost, non-toxicity, availability, as well as an environmentally friendly character (Dresselhaus & Terrones 2013). Biosorption is a promising technology because it is inexpensive and can use inactive or dead microbial cells which are available in large quantities. Biomass properties affect the binding and concentration of metal ions (Bessong *et al.* 2009) and the mechanism of sorption for the metal uptake depends on the biomass type (Mahmoud *et al.* 2016). Also, using biomass is advantageous in that it can be exposed to an environment of high toxicity and bio-augmentation is not required for the process (Maes *et al.* 2016). Biosorption can also be used *in situ* and requires little or no industrial operation when properly designed (Janiszewska *et al.* 2019). Biosorbents including fungi, plant biomass, algae, bacteria, and yeast have been used in the recovery of gold (Chand *et al.* 2009), silver (Homchuen *et al.* 2016), and platinum group of metals (Banimahd Keivani *et al.* 2010).

6. ANALYSIS OF DATA ON PRECIOUS METAL RECOVERY

A total of 242 articles downloaded from reputable sites such as google scholar, science direct, research gate and web of science were reviewed, with 45 literature works satisfying the goal of precious metal recovery. After screening, eighty-six (86) recoveries were reported in 45 literature works targeted at the subject matter reviewed, and seven precious metals including gold, silver, platinum, palladium, iridium, ruthenium, and rhodium were reported in the recovery studies. Both traditional/conventional (chemical precipitation, coagulation, membrane filtration) and some more recent methods (including bio-recovery, photocatalysis, forward osmosis, and co-precipitation) were applicable for recovery of precious metals from waste effluents. Figure 5 presents frequencies and percentage distributions of recoveries made for precious metals in literature (summarized in Table 7).

Traditional techniques have been broadly applied for the recovery of gold, silver, platinum, palladium, iridium, ruthenium, and rhodium; palladium (28.3%), gold (26.7%), silver (20.0%), and platinum (16.77%) were the most recovered under these processes. With regards to the more advanced and recent techniques, gold metal has been mostly recovered (46.2%), followed

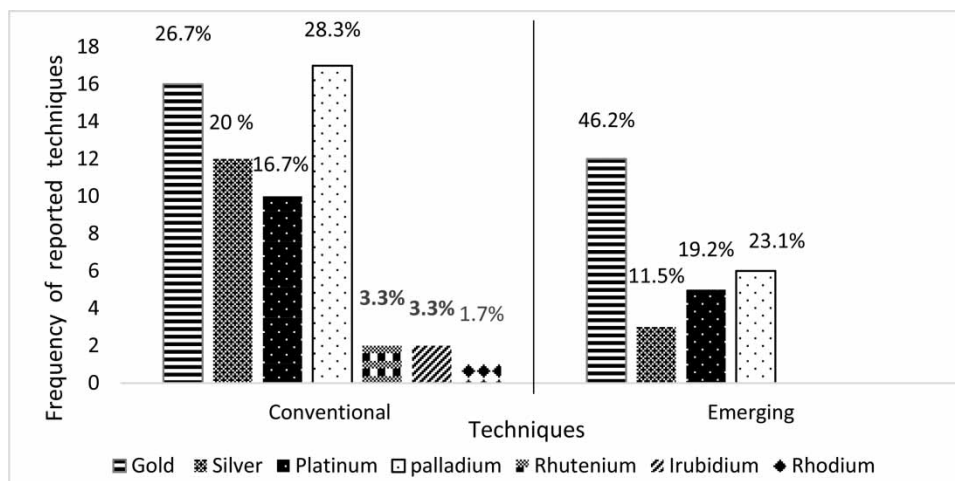


Figure 5 | Frequency and percentage distribution of publications on conventional and advanced alternative/emerging techniques for precious metal recovery.

by palladium (23.1%), platinum (19.2%), and silver (11.5%). The recovery of ruthenium, iridium, and rhodium are poorly reported and there is still a research gap within the recovery of precious metals using the more recent advanced techniques (Figure 5).

The recovery of palladium among other precious metals has been highly researched because of the low availability of the metal in natural reserves and high market demand. Moreover, high yield and cost analysis reduction established reasons for the high recovery of gold and other precious metals such as palladium using the advanced and more recent alternative processes (Dwivedi *et al.* 2014). In their experiment, Dwivedi *et al.* (2014) studied the recovery of gold species from aqueous solutions using taurine modified cellulose which were concluded to be promising material for the treatment of gold-polluted waters. Their experiment revealed that pyro-crystallization is an effective technique in the recovery of gold as it has a high yield of recovered gold. This agrees with what has been earlier opined in this review that advanced process of metal recovery is preferred for the high yield of metals recovered. Additionally, data gathered showed that chemical precipitation and electrolysis are methods highly reported for recovery of silver due to the simplicity of the processes and diverse leaching reagent available. The performance of the recovery techniques is important since precious metals usually exist at low concentrations in media of interest (Bas *et al.* 2013; Masebinu & Muzenda 2014). Figure 6 shows the percentage of published articles studied on the recovery of precious metals between 2006 and 2021. The results reveal a progressive growth pattern in the archives of publications that indicate interest in recent years (2012, 2014, 2019, 2020, and 2021). With regard to influencing parameters and thermodynamics, important parameters influencing most of the processes include pH, time and temperature.

7. RECENT LIMITATIONS AND IMPLICATIONS FOR THEORY AND PRACTICE

Methods such as hydrometallurgical processes, ion exchange, solvent extraction, (Cai *et al.* 2017) as well as pyrometallurgical methods have been used in precious metal recovery. The methods when engaged in industrial cycling, are expensive, time-consuming, and generate large waste. Some of the metal recovery methods are less efficient in the recovery of precious metals, toxic, and cause secondary pollution (Jacobsen 2005; Cai *et al.* 2017). Though recent techniques for activated carbon preparation have made it cheap, it is still relatively costly, requiring high temperatures and entails special kilns usage to reactivate the carbon (Colica *et al.* 2012). When using magnetic particles, the disadvantages include little selectivity towards the metal ions of choice in complex matrices and instability of the metal particles in strongly acidic solutions (Jacobson 2005). In the Merrill Crowe method, the pregnant solution needs clarification and deoxygenation based on free cyanide concentration and pH. The use of ion-exchange resins is also costly and has a low loading capacity and the resin must be regenerated in an acid medium. The use of solvent extraction in this field of study is also comparatively costly when compared to other procedures (Anbia & Mehrizi 2016). These limitations are part of what research must further focus on regarding precious metal recovery from processed wastewater.

Table 7 | Alternative techniques for precious metal recovery

Metal	Methods of recovery	Merit	Demerit	Influencing parameters	Mechanism(s)	References
Traditional Methods						
Platinum	Precipitation	Solving environmental-related issues and high purity of the metal is generated High percentage recovery	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, Stirring rate and temperature	Sedimentation	De Vargas <i>et al.</i> (2004)
Palladium and Platinum	Precipitation	Simple efficient and eco-friendly methods for solving environmental-related issues and high purity of the metal is generated	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, Stirring rate and temperature	Sedimentation	Lee <i>et al.</i> (2010)
Platinum, Selenium, Irubidium, Ruthenium,	Precipitation through leaching	High percentage removal	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, Stirring rate and temperature	Sedimentation/leaching	Génand-Pinaz <i>et al.</i> (2013)
Gold and silver	Precipitation	High percentage recovery, Simplicity, speed and low capital investment requirement	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, Stirring rate and temperature	Sedimentation	Mulwanda & Dorfling (2015)
Gold	Precipitation with nitric acid water leachate and aqua regia	An effective method of recovering	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, Stirring rate and temperature	Sedimentation	Sheng & Etsell (2007)
Gold	Ion exchange	High purity and high recovery efficiency	Reagent and material cost Environmental impact of process Inefficient at high concentration of metals	pH, elution time	Cationic and anionic exchange	Murakami <i>et al.</i> (2015)
Silver	Precipitation	Potent and High selectivity for silver	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, Stirring rate and temperature	Sedimentation	Yazici <i>et al.</i> (2010)
Silver	Precipitation	Feasibility of estimated profit and high removal efficiency	Generation of high-water content sludge.	pH, Stirring rate and Temperature	Sedimentation	Gu <i>et al.</i> (2020)

(Continued.)

Table 7 | Continued

Metal	Methods of recovery	Merit	Demerit	Influencing parameters	Mechanism(s)	References
Silver and Gold	Coagulation and flocculation	Reduced cost and maximum removal of metal	Inefficient at low pH and presence of other salts High operational cost due to chemical consumption and treatment of sludge generated	Coagulant and flocculant dosage, pH, Residual metal concentration	Coagulation and flocculation	Folens <i>et al.</i> (2017)
Silver and gold	Ion exchange	Does not need: washing, revitalization or heat treatment. High abrasion resistance in tanks of adsorption. High selectivity	Reagent and material cost Environmental impact of process Inefficient at high concentration of metals	pH, elution time	Cationic and anionic exchange	Parga <i>et al.</i> (2012)
Silver and gold	Coagulation	Low residence time (minutes). Does not use chemicals. Handles solutions containing lower or high silver and gold contents. Energy costs per m ³ of pregnant solution are lower than conventional treatment systems	The sacrificial anode must be replaced periodically. High operational cost due to chemical consumption and treatment of sludge generated	pH, Residence time	Oxidation/Reduction	Parga <i>et al.</i> (2012)
Gold, palladium, and platinum	Coagulation	High selectivity	High operational cost due to chemical consumption and treatment of sludge generated	Coagulant dosage, pH, Residual metal concentration	Coagulation and flocculation	Kawakita <i>et al.</i> (2008)
Gold, silver and palladium	Precipitation	An efficient and fast leaching process	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, Stirring rate and temperature	Sedimentation	Behnamfard <i>et al.</i> (2013)
Gold	Adsorption	Economical technology and feasible method	Low selectivity, recovery efficiency and production of waste products	pH, temperature, contact time, adsorbent dosage, initial metal concentration	Adsorption/reduction, electrostatic interaction, ion exchange	Panda <i>et al.</i> (2020)
Gold, palladium, and platinum	Ion exchange	An efficient and sustainable recovery method	Reagent and material cost Environmental impact of process	pH, elution time	Cationic and anionic exchange	Ilyas <i>et al.</i> (2021)

Silver and gold	Ion exchange with Potassium Thiocyanate	High elution of metals	Inefficient at high concentration of metals Reagent and material cost Environmental impact of process Inefficient at high concentration of metals	pH, elution time	Cationic and anionic exchange	Gámez <i>et al.</i> (2019)
Gold and palladium	Adsorption	High selectivity of gold recovery.	Low selectivity, recovery efficiency and production of waste products	pH, temperature, contact time, adsorbent dosage, initial metal concentration	Adsorption/reduction, electrostatic interaction, ion exchange	Liu <i>et al.</i> (2021)
Silver and palladium	Adsorption	Simplicity high-efficiency recovery of metal without the use of redundant	Low selectivity, recovery efficiency and production of waste products	pH, temperature, contact time, adsorbent dosage, initial metal concentration	Adsorption/reduction, electrostatic interaction, ion exchange	Biswas <i>et al.</i> (2021)
Palladium	Adsorption	High selective method of separation	Low selectivity, recovery efficiency and production of waste products	pH, temperature, contact time, adsorbent dosage, initial metal concentration	Adsorption/reduction, electrostatic interaction, ion exchange	Mao <i>et al.</i> (2020)
Platinum and Palladium	Adsorption process (activated carbon)	High adsorption capacity, good resistance to abrasion	Low selectivity, recovery efficiency and production of waste products	pH, temperature, contact time, adsorbent dosage, initial metal concentration	Adsorption/reduction, electrostatic interaction, ion exchange	Ghomi <i>et al.</i> (2020)
Silver	Precipitation process	Selective recovery from cyanide leaching solution. Fast and easy recovery up to 99%	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, stirring rate and temperature	Sedimentation	Yazici <i>et al.</i> (2017)
Gold	Membrane filtration	High-value utilization of waste for high selectivity recovery of gold.	Loss of valuable metals to the retentate Membrane fouling	pH, initial metal concentration	Reverse osmosis, nanofiltration	Zhou <i>et al.</i> (2021)
Palladium	Membrane filtration	Efficient recovery and safe storage medium.	Loss of valuable metals to the retentate Membrane fouling	pH, initial metal concentration	Reverse osmosis, nanofiltration	Monroy-Barreto <i>et al.</i> (2021)
Platinum	Membrane separation	High percentage recovery		pH, initial metal concentration	Reverse osmosis, nanofiltration	Ren <i>et al.</i> (2021)

(Continued.)

Table 7 | Continued

Metal	Methods of recovery	Merit	Demerit	Influencing parameters	Mechanism(s)	References
			Loss of valuable metals to the retentate Membrane fouling			
Palladium	Membrane filtration	High percentage recovery	Loss of valuable metals to the retentate Membrane fouling	pH, initial metal concentration	Reverse osmosis, nanofiltration	Wen <i>et al.</i> (2021)
Palladium	Adsorption	High percentage recovery	Low selectivity, recovery efficiency and production of waste products	pH, temperature, contact time, Adsorbent dosage, initial metal concentration	Adsorption/reduction, electrostatic interaction, ion exchange	Seto <i>et al.</i> (2017)
Gold, Palladium, Platinum	Macrocyclic equipped-Solid phase extraction system	Non-destructive approach for rapid recovery	High cost of design	pH	Selectivity of ion via electrostatic attraction	Hasegawa <i>et al.</i> (2018)
Recent/Pragmatic alternatives						
Platinum and Palladium	Bio-adsorption	Good resistance to abrasion	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Adsorption/reduction, electrostatic interaction, ion exchange	Sharififard <i>et al.</i> (2012)
Gold	Co-precipitation	High efficiency	Generation of high-water content sludge. Inefficient at low pH and presence of other salts	pH, stirring rate and temperature	Sedimentation	Ranjbar <i>et al.</i> (2014)
Silver, gold, palladium, platinum, Iridium, rhodium and ruthenium	Photocatalytic	Reduced energy consumption and environmental costs. Contributing circular economy, and technology sustainability	The high capital cost of photocatalysts. Long duration time and limited applications	Recovery time, light intensity	Reduction	Chen <i>et al.</i> (2021)
Gold	Bio-electrosorption	Due to the long-term decline of gold ore, sustainable clean gold recovery is made easy.	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Gunson <i>et al.</i> (2012)

Gold	Biosorption	Sustainable clean gold recovery is made easy.	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Ju <i>et al.</i> (2016); Romero-González <i>et al.</i> (2003)
Gold and Silver	Ferritization and delafossite	Selective recovery from cyanide leaching solution. Fast and easy recovery up to 99%	High cost of design	pH, temperature, process time	Precipitation	John <i>et al.</i> (2019)
Gold	Biosorption	High yield	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Dwivedi <i>et al.</i> (2014)
Silver, Gold, Palladium, Platinum	Biosorption	Reduction in cost	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Ghomi <i>et al.</i> (2020)
Platinum, Palladium	Bio-adsorption	Platinum (Pt) and palladium (Pd) have widespread applications, such as in catalysts, jewellery, fuel cells, and electronics because of their favourable physical and chemical properties.	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Mincke <i>et al.</i> (2019)
Gold, platinum group metals	Biosorption	Selective recovery	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Amuanyena <i>et al.</i> (2019)
Gold	Biosorption	High Selective recovery	Early saturation No biological control over characteristics of biosorbent No potential for	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Dwivedi <i>et al.</i> (2014)

(Continued.)

Table 7 | Continued

Metal	Methods of recovery	Merit	Demerit	Influencing parameters	Mechanism(s)	References
Silver, palladium and platinum	Biosorption	High Selective recovery	biologically altering the metal valency state Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Bratskaya <i>et al.</i> (2012)
Gold	Biosorption	High Selective recovery	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Mata <i>et al.</i> (2009)
Gold and Palladium	Biosorption	Recovery within a short period of time	Early saturation No biological control over characteristics of biosorbent No potential for biologically altering the metal valency state	pH, temperature, contact time, biosorbent dosage, initial metal concentration, ionic strength	Complexation, chelation, microprecipitation, electrostatic interaction, ion exchange	Cai <i>et al.</i> (2017)

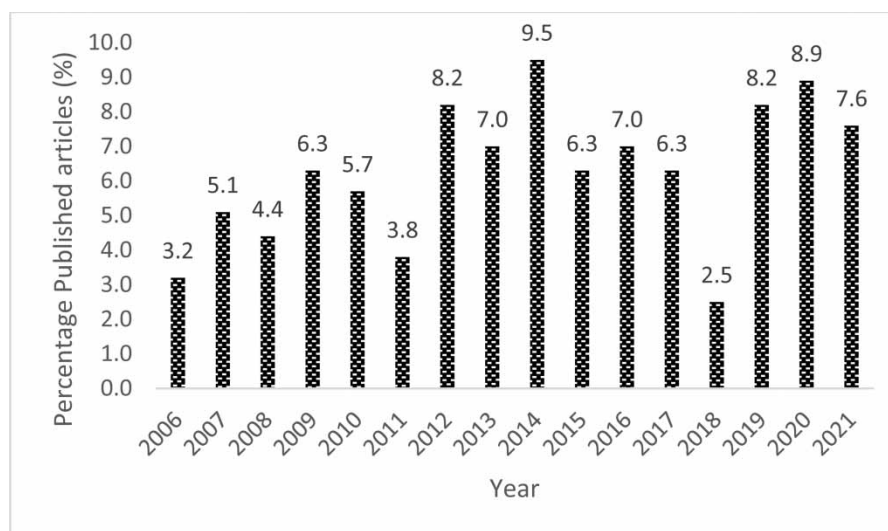


Figure 6 | Percentage of published articles on the recovery of precious metals.

The practical implication of bio- and nano-sorbents as envisaged in this study would be in cost reduction, selectivity and improved yield, environmental friendliness and application in very toxic waste. Biosorption has been reported as a cost-effective recovery process, leading to a lesser cost for the product (Das 2010; Rana *et al.* 2020). The structure, selectivity and high reactivity of the procedure may be adapted for specific and optimal metal recovery which also implies an improved yield of the process (Crini 2005; Ma *et al.* 2006; Adeeyo *et al.* 2019). When considering nano-sorbents, easy re-use may result in long-term cost reduction (Rickerby & Morrison 2007). Nanosorbents synthesized through the green routes come with the merits of eco-friendliness and less toxicity following sustainable development goals. These procedures also have the merits of the possibility of being applied in highly toxic waste for the recovery of useful materials where other processes may fail. When used in situ and properly designed, these techniques require little or no industrial operations. The development of facile, reliable and green chemistry procedures for nanosorbent production is recommended for future studies as the production of some of these nanosorbents materials requires the use of toxic and highly reactive reducing agents which in turn elicit undesirable effect on the environment. The use of treatment train strategy is encouraged for future studies as no single recovery technique can be efficient for complete recovery of valuable metals from processed wastewaters.

8. CONCLUSIONS

This study has put forward recovery procedures implying cost reduction, improved yield and eco-friendliness which are basic factors in appraising the effectiveness of different procedures in industrial applications. The performance of various conventional treatments was analytically compared with more recent, advanced, and pragmatic alternatives. The study identified the simplicity of most conventional techniques. However, they are associated with high-water sludge content and generation of secondary pollutants coupled with its low selectivity for highly valued metals in the presence of competing ions, and high operational cost. Although has an advantage of simplicity, especially, the identified limitations of the conventional techniques are the predominant strength of the pragmatic approach for the recovery of these metals. The flexibility, cost-effectiveness and selectivity of the pragmatic approach (especially the use of bio- and nano-materials) account for the high recovery performance for metals such as gold, platinum and palladium as compared to the traditional technologies. These appreciable advantages serve the SDG goals such as: no poverty (1), good health and well-being (3), clean water (6), affordable energy (7), climate action (13), life below water (14), life on land (15) which will consequently lead to decent work and economic growth (8) and sustainable cities and community (11), and the recovery factor ratio.

AUTHOR CONTRIBUTIONS

A.O.A., J.O.O., O.S.B., J.N.E., J.A.O., and R.M. conceptualized the study, R.O.A., A.O.A., and O.S.A. worked on the methodology, software and formal analysis, and data curation, O.S.B., J.N.E., R.M., and J.O.O. supplied resources, R.O.A., A.O.A.,

O.S.A., and O.S.B. developed the original draft, A.O.A., O.S.B., O.S.A., R.O.A., J.A.O., J.O.O., R.M., and J.N.E. reviewed and edited the draft, J.N.E., O.S.B., R.M., and J.O.O. supervised, R.M. and J.N.E. are involved in project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript. Please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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