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Review

Evolution of Environmentally Friendly Strategies for Metal Extraction

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Abstract: The demand for the recovery of valuable metals and the need to understand the impact of heavy metals in the environment on human and aquatic life has led to the development of new methods for the extraction, recovery, and analysis of metal ions. With special emphasis on environmentally friendly approaches, efforts have been made to consider strategies that minimize the use of organic solvents, apply micromethodology, limit waste, reduce costs, are safe, and utilize benign or reusable materials. This review discusses recent developments in liquid- and solid-phase extraction techniques. Liquid-based methods include advances in the application of aqueous two- and three-phase systems, liquid membranes, and cloud point extraction. Recent progress in exploiting new sorbent materials for solid-phase extraction (SPE), solid-phase microextraction (SPME), and bulk extractions will also be discussed.

Keywords: metal extraction; liquid–liquid extraction; solid-phase extraction; solid-phase microextraction; green extraction methods

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1. Introduction

Metals are ubiquitous in nature serving as essential elements for human health and critical materials for modern industrialization and urbanization. While some metals such as iron are necessary for human health, many metals are toxic, and can cause physical problems such as diarrhea, nausea, asthma, kidney malfunction, different cancers, and even death [1]. Arsenic, cadmium, chromium, mercury, and lead are commonly known as heavy metals—or metalloids in the case of arsenic—and have the greatest toxicity. The maximum limits in drinking water for these metal ions according to the World Health Organization (WHO) are 10, 3, 50, 6, and 10 $\mu g\ L^{-1}$, respectively [2]. The harmful effect of arsenic can mostly affect skin, respiratory, and cardiovascular systems. Elevated risk of skin and lung cancers has been reported among people who were exposed to arsenic from working in mining and smelting areas where inorganic arsenic was inhaled [3]. Cadmium and lead are harmful for the nervous system. Mercury used in electrical devices, dental fillings, Hg vapor lamps, solders, and X-ray tubes has a strong attraction to biological tissues and is carcinogenic, mutagenic, and teratogenic [4]. The Flint water crisis in 2014 affected about 100,000 people when lead from aging pipes leached into the water supply and contaminated the drinking water. This poignant example illustrates the importance of careful monitoring of heavy metals (HMs) in water systems and investigating new technologies to extract and remove them [5,6].

Other metals such as cobalt, copper, iron, and zinc have higher threshold limits. The maximum limit for copper in drinking water is 2 mg L^{-1} according to the WHO [2]. No guideline values are provided for iron and zinc in drinking water, however, high concentrations of these elements may still cause adverse health effects or, at a minimum, an unacceptable taste for consumers [2]. The recovery, removal, and recycling of valuable metals, including gold, platinum, and rare earth elements, from natural and secondary sources such as industrial wastes is also important for their economic, strategic, and national security value. These critical elements have important applications in metallurgy and the biomedical and electronics industries [7–12].

Several methods have been used for extraction and removal of metals from different sources of water, including microfiltration [13], chemical precipitation [14], coagulation and flocculation [15], electrochemical removal [16], liquid–liquid extraction [17,18], osmosis [19], crystallization and distillation [20], photocatalysis [21], and adsorption. In this review, we focus on several techniques for extraction, determination, and removal of metals, including heavy and valuable metals, from water samples. In particular, extraction methods that aim to provide environmentally friendly, simpler and faster techniques are discussed. Approaches include recent advances in primarily liquid–liquid and solid-phase extraction. Comparison of their advantages and disadvantages will be made to illustrate efforts to develop more environmentally friendly methods.

2. Liquid-Based Extraction

Numerous liquid-based techniques like liquid–liquid extraction (LLE) [9,22–24], chemical precipitation [14,25], and cloud point extraction [26] have been utilized for extraction of metal ions from aqueous media. Among the listed methods, LLE is based on analyte partitioning between two immiscible phases. Conventional LLE is widely used for separations and preconcentration, including extraction and recovery of metal species from aqueous media by the addition of organic solvents [24]. This technique has significant advantages. These include rapid extraction kinetics, the ability to choose selective solvents, amenability to large-scale separation, and easy and flexible implementation. In spite of these advantages, traditional LLE has several drawbacks, including the extensive use of volatile and flammable organic solvents, which are potential health and environmental hazards [27]. Moreover, from the economic point of view, LLE is quite expensive because of the cost of organic extractants and their disposal [28]. These drawbacks can be circumvented by embracing new methods that provide simple, low-cost, fast, sensitive, and accurate analyses in a more environmentally friendly manner. Various advancements in liquid-based extraction for metal ions, such as aqueous biphasic and triphasic extraction, cloud point extraction, and liquid membrane extraction, are discussed herein.

2.1. Aqueous Biphasic Systems

Aqueous biphasic systems (ABS, Figure 1) forms when two immiscible aqueous-based solutions are mixed together at a certain temperature [29]. ABS have gained more attention for metal extraction since 1984 when Zvarova and co-workers successfully extracted copper, zinc, cobalt, iron, indium, and molybdenum using a polyethylene glycol (PEG) 2000–ammonium sulfate–water system in the presence of ammonium thiocyanate and sulfuric acid [30]. Because organic solvents are not required in ABS, it has several advantages over traditional solvent extraction. ABS are less toxic, more economical, biocompatible, and have a reduced environmental risk [31]. Furthermore, numerous inorganic anions can be used as water-soluble extractants resulting in metal ion partitioning between two immiscible aqueous phases, which reduces dehydration effects [32].

ABS can be formed by various mechanisms and thus are tunable to the desired extraction. Biphasic systems composed of polymer–polymer [33], polymer–salt [34], salt–salt [35], ionic liquid–salt [36], and surfactant-based systems [37] have been reported. In addition to these, other phase-forming elements are amino acids, alcohols, and carbohydrates. In ABS, factors governing the metal ion extraction include molecular weight and polymer type [38], Gibbs free energy of hydration [32], medium pH [39], presence and absence of an extracting agent [32,40], and temperature [41]. Examples of metal ion extractions using different ABS are given in Table 1.

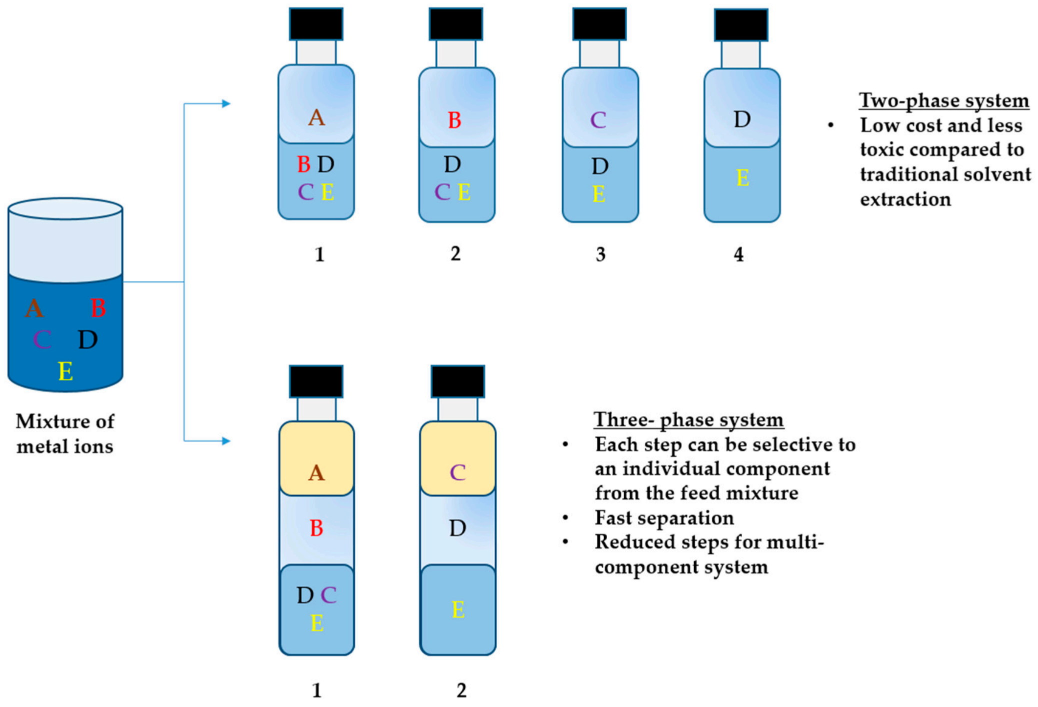

Figure 1. Schematic representations of a two- versus three-phase system for metal ion extraction.

Table 1. Aqueous biphasic systems for metal ion extraction.

Targeted Metal(s)	ABS Composition	Extraction Agent	Detection	Ref.
	Surfactant–Salt			
Zn^{2+}	Triton X-100 [a], $MgSO_4$	PAN [n]	UV–Vis	[42]
Mo^{6+}, W^{6+}	Triton X-100, $(NH_4)_2SO_4$	None	ICP–AES [r]	[43,44]
	Polymer–Salt			
Hg^{2+}, Zn^{2+}, Co^{2+}	PEG 6000 [b], Na_2CO_3	None	AAS [s]	[45]
Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Li^{+}	PEG 4000, Na_2SO_4	None	AAS	[46]
Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	L35 [c], Na_2SO_4	1N2N [o], SCN^-, I^-	AAS	[47]
Cd^{2+}, Ni^{2+}	L35, $LiSO_4$	KI, TTL [p]	AAS	[48]
Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}	PEG 1550, Na_2SO_4, $NaNO_3$, $(NH_4)_2SO_4$	NaX, X = I^-, Cl^-, Br^-, SCN^-	FTIR [t]	[49]
Co^{2+}, Fe^{3+}, Ni^{2+}	PEO [d] 1500, $(NH_4)_2SO_4$, H_2O	KSCN	FAAS [u]	[50]
Hg^{2+}	PEG 5000, Na_2SO_4	NaX, X = I^-, Cl^-, Br^-	Packard Cobra II Auto-Ɣ-Spectrometer	[51]
Co^{2+}, Ni^{2+}, Cd^{2+}	L64 [e], $Na_2C_4H_4O_6$	1N2N	FAAS	[52]
Ca^{2+}	L64, sodium tartrate	None	FAAS	[53]
As^{3+}	L64, $(NH_4)_2SO_4$, H_2O	APDC [q]	ICP–OES [v]	[54]

Table 1. *Cont.*

Targeted Metal(s)	ABS Composition	Extraction Agent	Detection	Ref.
	Salt–Salt			
Cd^{2+}	TBAB [f], $(NH_4)_2SO_4$	None	AAS	[55]
	Ionic Liquid–Salt			
Ni^{2+}, Co^{2+}	(P44414) [g](Cl), NaCl	None	NR	[56]
Co^{2+}, Fe^{3+}, Nd^{3+}, Sm^{3+}	Cyphos IL 101 [h], NaCl	None	ICP–OES, TXRF [w]	[57,58]
Sc^{3+}	$(P_{444}C_1COOH)Cl$ [i], NaCl	None	TXRF	[59]
Au^+	1-alkyl-3-methylimidazolium bromide, K_2HPO_4	None	AAS	[60]
Co^{2+}	$(HMIM)(BF_4)$ [j], NaCl	None	ICP–OES	[61]
Pr^{3+}	$(A336)(NO_3)$ [k], $NaNO_3$	None	UV–Vis	[62]
Nd^{3+}	(P4444) [l](NO_3), NaCl	None	ICP–MS	[63]
	Miscellaneous			
Au^{3+}	$(C_6mim)(C_{12}SO_3)$ [m], PEG 6000	None	UV–Vis	[64]

[a] octylphenolpolyethoxylene, [b] polyethylene glycol (average molecular mass 6000), [c] (ethylene oxide)$_{11}$ (propylene oxide)$_{16}$ (ethylene oxide)$_{11}$, [d] poly(ethylene oxide), [e] (ethylene oxide)$_{13}$-(propylene oxide)$_{30}$-(ethylene oxide)$_{13}$, [f] tetrabutylammonium bromide, [g] tributyl(tetradecyl)phosphonium, [h] tri(hexyl)tetradecylphosphonium chloride, [i] tri-*n*-butyl(carboxymethyl)phosphonium chloride, [j] 1-hexyl-3-methylimidazolium tetrafluoroborate, [k] tricaprylmethylammonium nitrate, [l] tetrabutylphosphonate, [m] 1-hexyl-3-methylimidazole dodecyl sulfonate, [n] 1-(2-pyridylazo)-2-naphthol, [o] 1-nitroso-2-naphthol, [p] tie-line length, [q] ammonium pyrrolidine dithiocarbamate, [r] inductively coupled plasma atomic emission spectrometry, [s] atomic absorption spectrophotometry, [t] fourier transform infrared spectrophotometry, [u] flame atomic absorption spectrophotometry, [v] inductively coupled plasma optical emission spectrometry, [w] total reflection X-ray fluorescence.

It is important to note that to extract a single target metal in each extraction step with a biphasic system, the extraction process for a specific metal from a mixture of metal ions must be highly selective, resulting in a potentially lengthy and costly method. A well-designed three-liquid-phase extraction system may overcome this disadvantage by selective separation and extraction of two or more targeted metals during a single extraction step.

2.2. Three-Liquid-Phase Extraction

Three-liquid-phase extraction (TLP, Figure 1) has been used for the isolation of organic macromolecules such as cellulose, enzymes, proteins, and metals [65,66]. This approach is based on the use of three immiscible liquid phases composed of different organic solvents, polymers, inorganic salts, water, or ionic liquids [67,68]. As the number of non-miscible phases is increased from two (biphasic) to three (triphasic), the steps required for separation decrease. Therefore, three metal cations can be separated simultaneously in a single step as shown in Figure 1. For example, in the case of a biphasic system, a mixture of five metals may require four steps for the separation, whereas for TLP, two steps may be sufficient. Different approaches have been considered to design a TLP system for metal extraction. These include one aqueous and two organic phases [69], one organic and two aqueous phases [70], and ionic liquid-based systems [71]. One recent study showed an improved extraction efficiency for Co^{2+} with a TLP system when directly compared to an ionic liquid ABS approach [61]. However, in TLP, the challenges associated with the use of organic phases are reintroduced. Examples of metal ion extraction using different TLP systems are tabulated in Table 2.

Table 2. TLP systems for metal ion extraction.

TLP Phases	TLP Component			Metal Extracted			Ref.
	Top	Middle	Bottom	Top	Middle	Bottom	
1 Organic 2 Aqueous							
	TRPO [a]	PEG-2000	$(NH_4)_2SO_4$, H_2O	Ti^{4+}	Fe^{3+}	Mg^{2+}	[72]
	S201 [b]	EOPO [j]	Na_2SO_4, H_2O	Pd^{2+}	Pt^{4+}	Rh^{3+}	[73,74]
	D2EHPA [c]	PEG	$(NH_4)_2SO_4$, H_2O	Cr^{3+}	Cr^{6+}	None	[75]
	Cyanex272 [d]	PEG	$(NH_4)_2SO_4$, H_2O	Yb^{3+}	Eu^{3+}	La^{3+}	[76]
	Cyanex272	PEG 2000	$(NH_4)_2SO_4$, H_2O	Yb^{3+}, Eu^{3+}	Fe^{3+}, Si^{4+}	La^{3+}, Al^{3+}	[77]
	PC-88A [e]	PEG 2000	$(NH_4)_2SO_4$, H_2O	Eu^{3+}	Al^{3+}, Si^{4+}, Fe^{3+}	La^{3+}, Yb^{3+}	[78]
	Xylene, (D2EHPA)	PEG	$(NH_4)_2SO_4$, H_2O	Mn^{2+}	Co^{2+}	Ni^{2+}	[79]
	N1923 [f]	PEG	$(NH_4)_2SO_4$, H_2O	V^{5+}	Cr^{6+}	Al^{3+}	[80]
2 Organic 1 Aqueous							
	S201	(Sugaring out) CH_3CN	glucose, H_2O	Pd^{2+}	Pt^{4+}	Rh^{3+}	[81]
	S201	(Salting out) CH_3CN	NaCl, H_2O	Pd^{2+}	Pt^{4+}	Rh^{3+}	[69]
TLP Systems with Ionic Liquids							
	H_2O	(HMIM) (BF_4) [k]	NaCl	None	Co^{2+}	None	[61]
	TOPO [g]	H_2O	(Bmim) (PF_6) [l]	Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	None	Cu^{2+}, Ni^{2+}	[71]
	S201	H_2O	(C_4mim) (PF_6) [l]	Pd^{2+}	Rh^{3+}	Pt^{4+}	[82]
	TBP [h], (P66614) (Tf_2N) [i]	H_2O	(Hbet) (Tf_2N) [m]	Sn^{2+}	Sc^{3+}	Y^{3+}	[66]

[a] trialkylphosphine oxide, [b] diisoamyl sulfide/nonane, [c] di(2-ethylhexyl)phosphoric acid, [d] bis(2,4,4-trimethylpentyl)phosphinic acid, [e] 2-ethylhexylphosphoric acid mono(2-ethylhexyl)ester, [f] primary amine, [g] tri-n-octylphosphine oxide, [h] tri-n-butyl phosphate, [i] trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide, [j] polyethylene oxide-polypropylene oxide, [k] 1-hexyl-3-methylimidazolium tetrafluoroborate, [l] 1-butyl-3-methylimidazolium hexafluorophosphate, [m] betainium bis(trifluoromethylsulfonyl) imide.

2.3. Cloud Point Extraction (CPE)

The cloud point is the point where a solution mixture turns cloudy due to diminished solubility of one component after changes to experimental conditions such as pressure, temperature, and inclusion of additives [83]. For example, this clouding process can result in the formation of two distinct phases of nonionic and zwitterionic surfactants in which one is a surfactant-rich phase and the other has a concentration close to the critical micelle concentration [84]. The surfactant-rich phase obtained at the cloud phase condition functions to extract and preconcentrate various inorganics [85]. This phase extracts metal cations and is dispersed in the aqueous phase formed after phase separation. Detection of the cloud point occurs by various techniques (e.g., light scattering or particle counting, turbidimetry, refractometry, thermo-optical methods, and viscometry) [86]. CPE shows great promise as a more environmentally friendly method for heavy metal extractions [87]. Kazi et al. have studied extraction of Al^{3+} by the cloud point technique where 8-hydroxyquinone was added to coordinate Al^{3+} while the surfactant octylphenoxypolyethoxyethanol (Triton X-114) was added to extract and entrap the complex [88]. Similarly, Zhao et al. studied the extraction of Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Cu^{2+} using a dual-CPE technique [89]. The main advantage of CPE over other techniques is the use of water instead of organic solvents [90]. CPE is also easy to manipulate, is fast, requires minimal expense, and offers high analyte recovery [85,91].

2.4. Liquid Membrane Extraction

Membrane-based extraction is a non-equilibrium process that has been developed as an important green strategy for recovery of rare earth elements [92]. Different types of liquid membranes (LM) have been reported, such as bulk liquid membrane (BLM) [93], emulsion liquid membrane (ELM) [94], supported liquid membrane (SLM) [95], and hollow fiber-supported liquid membrane (HFSLM) [96]. Their advantages and disadvantages are summarized in Table 3. Various metal ions from common metals (copper, nickel, and cobalt) [97] and valuable metals (platinum, gold) [98,99] to radioactive species (uranium) [100] have been extracted using LM techniques. As noted in Table 3, there are several concerns regarding membrane stability when organic solvents are used.

Table 3. Liquid membrane systems for metal ion extraction.

Type of LM	Overview	Advantages	Disadvantages	Ref.
SLM	Hydrophobic membrane impregnated with an organic solvent is squeezed between an aqueous feed and stripping solution	Simplicity of operation Low operating cost	Emulsion formation of liquid membrane phase in water Instability	[95]
HFSLM	Hollow fiber is used as microporous hydrophobic membrane and impregnated with LM phase	High interfacial area-to-volume ratio	Lower transport rate than SLM	[96]
ELM	Water/organic/water (W/O/W) or organic/water/organic (O/W/O) with a thin middle LM phase	High transfer rates	Continuous operation is difficult to achieve as settling stage is performed after extraction. Long contact of emulsions with water in feed stream results in swelling and rupture due to the difference in osmotic pressure, shear forces, and static pressure between the feed and stripping phase	[101]
BLM	An aqueous feed and stripping phase separated by bulk organic LM phase	High transfer rate	Less interfacial area-to-volume ratio results in low fluxes	[93]

2.5. Summary

In summary, LLE methods often require several extractions for complete recovery of targeted metals. Thus, LLE is often replaced by solid-phase extraction (SPE) methods to achieve higher efficiency and recovery. SPE is advantageous because consumption of organic solvent can be minimized [102]. Additionally, errors from inaccurately measured extraction volumes, especially when multiple extraction steps are required with LLE, are minimized with SPE as it does not require phase separation [103].

3. Solid-Phase Extraction

Solid-phase extraction (SPE, Figure 2) is one of the most popular sample pretreatment and separation techniques because of its simplicity, low cost, high preconcentration factors, selectivity, and versatility. Furthermore, the availability of a wide variety of sorbent materials and the ability to use only minimal amounts, or in some cases, no organic solvents, makes SPE a very environmentally friendly technique [102,104,105]. Most of the benefits of SPE methods are governed by the physical and chemical nature of the sorbent [104,106]. Recent development and applications of a number of new sorbent materials for metal extraction, such as nanosorbent materials, polymers, metal oxides, magnetic materials, metal organic frameworks (MOFs), and bioadsorbents, are discussed herein.

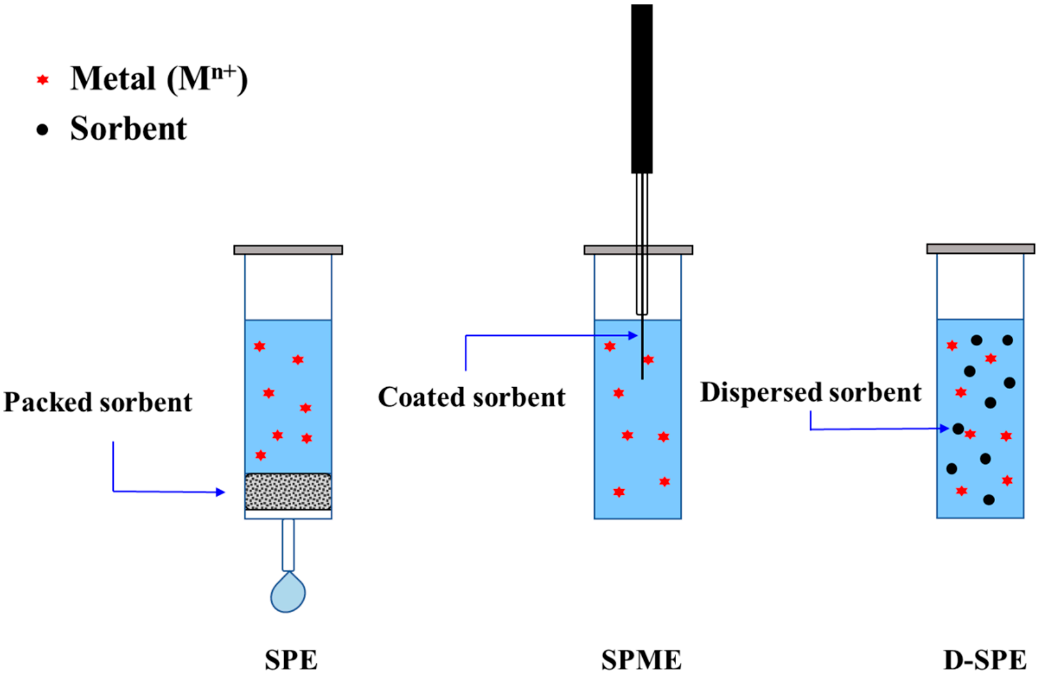

Figure 2. Schematic representation of solid-phase extraction (SPE), solid-phase microextraction (SPME, direct immersion only), and dispersive solid-phase extraction (D-SPE).

3.1. Nanosorbent Materials

Nanosorbent materials such as carbon nanotubes (CNTs) [107], graphene oxide (GO), silica [108], chitosan [109], and activated carbon [110,111] are particularly useful due to their large surface areas compared to their particle volume. Thus, they are excellent candidates as sorbent materials for metals since the high surface area provides a greater number of active sites leading to enhanced extraction efficiency. Recently, Gouda et al. developed a sorbent material based on multiwalled carbon nanotubes impregnated with 2-(2-benzothiazolylazo)orcinal (BTAO) for preconcentration of cadmium, copper, nickel, lead, and zinc from food and water samples prior to determination by flame atomic absorption [112]. Similarly, carbon nanotubes impregnated with tartrazine [113], polyaniline [114], and di-(2-ethyl hexyl phosphoric acid) [115] have been utilized as sorbent materials for preconcentration, separation, and determination of metals. Moreover, Awual et al. synthesized ligand-impregnated conjugate nanomaterials for the extraction of mercury from aqueous solution [116]. Metal oxides such as Al_2O_3 [117], TiO_2 [118], and SiO_2 [119] have been used for metal extraction due to their physical stability, cost-effectiveness, and high surface area [118]. Other examples are shown in Table 4. The utilization of nanosorbent materials is attributed to their high surface area, ease of modification, and nonspecific adsorption with metals [120,121]. However, limitations include low selectivity and, in some cases, low stability and limited reusability of the material.

Table 4. Nanomaterial-based solid sorbents.

Sorbent	Extraction Method	Target Metal(s)	Reusability	SC [f] (mg g^{-1})	Ref.
Tyre-based activated carbon	SPE-FAAS [d]	As^{5+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}	NR	NR	[122]
Dowex 50W-x8 & Chelex-100	SPE	Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}	Stable up to 150 elution cycles	NR	[123]
$ZnFe_2O_4$ nanotubes (ZFONTs)	DMSPE [e]	Co^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}	NR	Co^{2+}-30.09 Ni^{2+}-28.4 Mn^{2+}-35.4 Cd^{2+}-27.9	[124]
Agarose-g-PMMA [a]	DMSPE	Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	NR	Cd^{2+}-31.8 Ni^{2+}-42.5 Cu^{2+}-48.3 Zn^{2+}-34.3	[125]
Activated carbon	DSPE	Cu^{2+}	Stable up to 6 cycles	1.6	[126]
MWCNTs [b]	DMSPE	Cr^{6+}	NR	NR	[127]
GO-MWCNTs-DETA [c]	SPE	Cr^{3+}, Fe^{3+}, Pb^{2+}, Mn^{2+}	NR	Cr^{3+}-5.4 Fe^{3+}-13.8 Pb^{2+}-6.6 Mn^{2+}-9.5	[128]

[a] poly(methyl methacrylate) grafted agarose, [b] multiwalled carbon nanotubes, [c] diethylenetriamine, [d] flame atomic absorption spectrometry, [e] dispersive magnetic SPE, [f] sorption capacity, NR: not reported.

3.2. *Polymer-Based Materials*

Some of the limitations found with nanosorbent materials have been addressed by employing specially designed sorbent materials based on chelating resins [129–132], polymers with chelating units [133,134], ion imprinted polymers [135–138], and polymeric ionic liquids [135,139,140].

Polymeric chelating materials, unlike the inorganic nanosorbents, have the advantage of tunability in functionalization using unique chelating groups to obtain enhanced selectivity and extraction efficiencies for metals. Recently, Nunes et al. developed a greener SPE approach for the extraction of Zn and Ni by employing nylon-6 nanofibers modified with di-(2-ethylhexyl) phosphoric acid [141]. The experimental results suggested that these polymeric nanofibers were cost-effective because of their reusability even after ten cycles of extraction in addition to being ecofriendly due to the absence of organic solvents. The same polymeric material was also used for SPE of indium from LCD screens [142]. Furthermore, polymeric materials based on ionic liquids also were utilized as effective sorbent materials for extraction of metals. For example, a polymeric ionic liquid containing 3-(1-ethyl imidazolium-3-yl)propyl-methacrylamido bromide and ethylene dimethacrylate was specifically developed by Zhang et al. for extraction of antimony employing a stir cake sorptive extraction method [143]. Table 5 summarizes several additional examples of polymer sorbents including ion-imprinted polymer (IIP) materials for SPE of metals.

Table 5. Polymer-based sorbent materials for metal ion extraction.

Sorbent Material	Extraction Method	Target Metal(s)	Flow Rate	Extraction Time	Ref.
Copolymer Strata^{TM}-X resin	On-line SPE	Cd^{2+}, Pb^{2+}, Cu^{2+}, Cr^{6+}	NR	1.5	[144]
mGO/SiO_2@coPPy-Th [a]	MSPE [b]	Cd^{2+}, Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}	NR	6.5 min	[145]
Thallium ion-imprinted polymer	SPE [c]	Tl^{3+}	NR	30 min	[146]
Copolymer of 4-Vinylpyridine and Ni-Dithizone	SPE	Ni^{2+}	0.2 mL min^{-1}	NR	[147]
(EGDMA-MAH/Ni) [d] imprinted polymer	SPE	Ni^{2+}	0.5 mL min^{-1}	NR	[148]
Double imprinted chitosan-succinate polymer	SPE	Cu^{2+}	NR	NR	[149]
Dual imprinted polymers of Cd	SPE	Cd^{2+}	3.0 mL min^{-1}	20 min	[150]
Poly(GMA [e]-co-EDMA [f])-IDA [g]	SPE	Cu^{2+}, Pb^{2+}, Cd^{2+}	10 μL s^{-1}	NR	[151]
Nylon 6-DEHPA [h]	SPE	Zn^{2+}, Ni^{2+}	NR	7.5 min	[141]

[a] SiO_2-coated magnetic graphene oxide modified with polypyrrole–polythiophene, [b] magnetic solid-phase extraction, [c] solid-phase extraction, [d] ethyleneglycoldimethacrylate-methacryloylhistidinedihydrate nickel(II), [e] glycidyl methacrylate, [f] ethylene dimethacrylate, [g] iminodiacetate, [h] di-(2-ethyl)phosphoric acid.

3.3. Metal–Organic Frameworks

Metal–organic frameworks (MOFs) consist of metal ions and organic linkers that are strongly bonded together. These materials have been used as effective sorbents in various applications due to their highly porous structure and the ability to be synthesized in various shapes and sizes [152,153]. Recently, Tadjarodi et al. designed a magnetic nanocomposite sorbent from HKUST-1 MOF combined with Fe_3O_4@4-(5)-imidazoledithiocarboxylic acid (Fe_3O_4@DTIM) for SPE of Hg^{2+} in canned tuna and fish samples [154]. The sorbent selectivity towards Hg^{2+} was due to the presence of sulfur atoms in DTIM. Also, the magnetic Fe_3O_4 nanoparticles facilitated separation from samples by simply applying an external magnetic field while the MOF prevented aggregation of Fe_3O_4 nanoparticles by acting as spacers and a support matrix with the MOF cavities providing increased surface area to enhance sorption capacity. Similarly, Esmaeilzadeh developed a MOF with iron-based magnetic nanoparticles decorated with tetraethyl orthosilicate to create a silica layer on the surface [155]. The nanoparticles were subsequently functionalized with morin (2-(2,4-dihyroxyphenyl)-3,5,7-trihydroxychromen-4-one) as a chelating agent to develop a MIL-101(Fe)/Fe_3O_4@morin nanocomposite for the selective extraction and speciation of V^{4+} and V^{5+}. In this case, the silica layer provided stability for the Fe_3O_4 nanoparticles in acidic conditions as well as allowed for further functionalization. MIL-101(Fe) also prevented aggregation of the nanoparticles by acting as a spacer and support. In addition, Nasir et al. developed a two dimensional leaf shaped zeolite imidazolate frame work (2D ZIF-L) for arsenite adsorption [156]. Table 6 shows recently reported MOFs as effective sorbents for the SPE of metals.

Table 6. MOF sorbent materials for metal extraction.

Sorbent Material	Extraction Method	Target Metal(s)	Reusability	SC [f] ($mg\ g^{-1}$)	Ref.
UiO-66 [a] -NH_2	SPE	Cd^{2+}, Cr^{3+}, Pb^{2+}, Hg^{2+}	NR	Cd^{2+}-49 Cr^{3+}-117 Pb^{2+}-232 Hg^{2+}-769	[157]
KNiFC [b] Fe_3O_4/KNiFC	MSPE	Cs^+	5	153 and 109	[158]
Fe_3O_4@ZIF-8 [c]	SPE	As^{5+}	NR	0.035–0.036	[159]
ZIF-8@cellulose	SPE	Cr^{6+}	NR	NR	[160]
FJI-H12 [d]	SPE	Hg^{2+}	NR	440	[161]
Fe_3O_4/IRMOF-3 [e]	MSPE	Cu^{2+}	10	2.4	[162]
UiO-66-OH	SPE	Th^{4+}	25	47.5	[163]

[a] zirconium-based, [b] potassium nickel hexacyanoferrate, [c] zeolitic imidazolate framework-8, [d] Co(II) and 2,4,6-tri(1-imidazolyl)-1,3,5-triazine, [e] iso-reticular MOFs, [f] sorption capacity.

3.4. Magnetic-Based Materials

In the process of developing more environmentally friendly methods, incorporation of magnetic materials such as iron oxide nanoparticles into sorbent composites has increased in recent years. Magnetic materials are utilized to readily extract target metal ions from complex matrices followed by sorbent separation from samples by an external magnetic field. Following desorption of the metals, the sorbent can be recovered and effectively recycled. Magnetic nanoparticles have been combined with carbon-based [164], ionic liquid [165,166], MOF [167], and polymer [168] materials for magnetic SPE of metals. Several such examples are given in Tables 4–6, while other unique recent studies using magnetic-based materials are described below and in Table 7.

Shirani et al. developed a magnetic sorbent based on an ionic liquid linked to magnetic multiwalled carbon nanotubes for simultaneous separation and determination of cadmium and arsenic in food samples using electrothermal atomic absorption spectrometry [169]. Habila et al. synthesized a sorbent material based on Fe_3O_4@SiO_2@TiO_2, which shows unique magnetic, photocatalytic and acid resistant properties, and was used for the preconcentration of copper, zinc, cadmium, and lead prior to ICP–MS analysis [170]. The advantage of this sorbent material was it not only allowed extraction of toxic heavy metals from complex matrices, but also assisted the simultaneous degradation of the organic matrix to aid preconcentration. Additionally, Molaei et al. utilized a copolymer based on polypyrrole and polythiophene (PPy–PTh) layered on the surface of SiO_2-coated magnetic graphene oxide for the extraction of trace amounts of copper, lead, chromium, zinc, and cadmium from water and agricultural samples [145].

Table 7. Magnetic-based sorbent materials for metal ion extraction.

Sorbent Material	Extraction Method	Target Metal(s)	WS [f] pH	SC [g] (mg g^{-1})	Ref.
CEMNPs [a]	MSPE	Cu^{2+}, Co^{2+}, Cd^{2+}	9.0	Cu^{2+}-3.21 Co^{2+}-1.23 Cd^{2+}-1.77	[171]
Co-IDA [b]	MSPE	Cu^{2+}	7.5	NR	[172]
M-PhCP [c]	MSPE	Cd^{2+}, Pb^{2+}	6.0	NR	[173]
Fe_3O_4@MOF-235(Fe)-OSO_3H	MSPE	Cd^{2+}	3.0	NR	[167]
(Fe_3O_4-ethylenediamine)/ MIL-101(Fe)	MSPE	Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}	6.1	Cd^{2+}-155 Pb^{2+}-198 Zn^{2+}-164 Cr^{3+}-173	[174]
Fe_3O_4@TAR [d]	MSPE	Cd^{2+}, Pb^{2+}, Ni^{2+}	6.2	185–210	[175]
MOF Fe_3O_4-Pyridine	MSPE	Cd^{2+}, Pb^{2+}	6.3	186–198	[176]
SH-Fe_3O_4/$Cu_3(BTC)_2$ [e]	MSPE	Pb^{2+}	6.0	198	[177]

[a] carbon-encapsulated magnetic nanoparticles, [b] magnetic cobalt nanoparticles functionalized with iminodiacetic acid, [c] magnetic phosphorous-containing polymer, [d] thiazolylazo resorcinol, [e] mercapto groups modified with benzene tricarboxylic acid, [f] working solution pH, [g] sorption capacity.

3.5. Ion Exchange

Ion exchange is another technique that can be used for the removal of metals, though it depends on the solution composition [178]. Moreover, other factors like the capacity and selectivity of sorbent material, pH, temperature, and solution salinity also play important roles in the ion exchange process [179]. Recently Murray et al. studied the removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} from natural water with polymeric submicron ion exchange resins [180]. Similarly, Vergili et al. found good extraction properties with a weak acid cation resin for the sorption of Pb^{2+} from industrial wastewater [181].

3.6. Ligand Binding

Simple coordination chemistry, where a ligand with affinity for a metal binds and forms a complex, is a useful method to selectively isolate a metal from aqueous solution. There are numerous organic chelating agents for heavy and precious metal extraction. The overall challenge is achieving selectivity for a single metal or class of metals. Depending on the strength of binding, recovery of the isolated metal ion can also be difficult. Recent studies show dithiocarbamate ligands as one of the most useful materials to coordinate and extract transition metals from aqueous solution [182]. Because of the presence of various hybridized states of nitrogen and sulfur and the tendency to share electrons between the nitrogen and sulfur with metal ions, the removal of heavy metals by these ligands has been demonstrated [183–186]. They also are known to form colored metal complexes, which makes detection and analysis relatively easy [187]. Table 8 provides examples of ion exchange and ligand binding techniques for metal extraction.

Table 8. Ion exchange and ligand binding techniques for metal ion extraction.

Techniques	Substance Used	SC [h]	Target Metal(s)	Ref.
Ion Exchange Membrane	Cellulose nanofiber modified with PAA [a] and PGMA [b]	160 mg g^{-1}	Cd^{2+}	[188]
	Chitisan/PVA [c]/Zeolite nanofiber	NR	Cr^{6+}, Fe^{3+}, Ni^{2+}	[189]
	PAN [d]/GO [e]/Fe_3O_4 nanofiber	799.4 mg g^{-1} of Pb^{2+}, 911.9 mg g^{-1} of Cr^{6+}	Pb^{2+}, Cr^{6+}	[190]
Ligand Binding	PMHS [f]-*g*-PyPz [g] PMHS-*g*-PyPz(OEt)$_2$	0.24 mmol (Co^{2+}) and 1.48 mmol (Cu^{2+}) g^{-1} of polymer	Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}	[191]
	N,*N*′-dialkyl-*N*,*N*′-diaryl-1,10-phenanthroline-2,9-dicarboxamides	NR	Lanthanides	[192]
	N,*N*′-dimethyl-1,4-piperazines	NR	Zn^{2+}, Cu^{2+}, Mn^{2+}, Li^{+}, Ni^{2+}, Mg^{2+}	[193]

[a] poly(acrylic acid), [b] poly(glycidylmethacrylate), [c] polyvinyl alcohol, [d] polyacrylonitrile, [e] graphene oxide, [f] poly(methylhydrosiloxane), [g] pyridine–pyrazole, [h] sorption capacity.

3.7. Solid-Phase Microextraction

Although SPE has advantages over LLE, more progress is needed in the development of more ecofriendly and cost-effective approaches to further reduce the amount of organic solvents and sorbent material, as well as to minimize cost, analysis time, and disposal of waste chemicals. Such considerations have led to the development of greener alternatives such as SPME (Figure 2), which was developed and introduced by Pawliszyn in 1990 [194]. SPME is a fiber-based version of SPE that has benefits over other extraction techniques because the sample and solvent amounts are reduced, liquid, solid and gas samples can be analyzed with higher sensitivity and cost-effectiveness, and the use of organic solvents is minimized. Briefly, a fiber-based material is used as the sorbent to extract molecules by direct immersion of the fiber into the sample solution (Figure 2) or into the headspace above the solution. Once analytes partition into the sorbent, the fiber is removed for desorption and analysis. Direct coupling to analytical instrumentation is then possible to achieve simultaneous preconcentration and determination of target species, thus reducing the analysis time [195–199].

There are limited reports on the use of SPME for metal ion detection and analysis using HPLC and GC [200,201]. For SPME–HPLC, determination of metal ions is limited to commercial adsorbents [200]. Derivatization is required to obtain a hydrophobic organometallic compound to achieve adsorption onto the fibers and desorption after injection into a SPME–HPLC chamber. Difficulties with slow analyte diffusion in HPLC complicate the analysis of metals. One notable example of SPME–HPLC was reported by Kaur et al., in which a complex of thiophenaldehyde-3-thiosemicarbazone with cobalt, nickel, copper, and palladium was followed by UV detection [202]. SPME coupled to GC is limited to volatile species, which also often requires derivatization prior to detection [203]. Apart from the need for derivatization, there are other challenges including fiber-to-fiber variation, carry over problems, relatively high cost, reusability and recycling of the coating material, instrumental compatibility and, most importantly, delicate fibers or fragile coatings [152,199,204].

A recent goal is the desire to use SPME for the direct extraction and analysis of metal ions without the need for derivatization or complicated procedures. Rahmi et al. developed a novel SPME approach for trace metal analysis by modifying the inner wall of a syringe filter tip with a monolithic chelating moiety [205]. Twenty-two elements, including titanium, iron, cobalt, nickel, copper, gallium, cadmium, tin, and rare earth elements, were extracted prior to ICP–MS analysis with extraction efficiencies higher than 80%. Rohanifar et al. developed a versatile, easily tunable, cost-effective, greener approach for SPME of heavy metals from natural waters [133]. In this study, pencil lead was used as a substrate as an alternative to a commercially available SPME fiber or a metal wire, which significantly reduced the cost. The pencil lead was coated by electropolymerization with a sorbent composite containing polypyrrole, carbon nanotubes, and different metal chelating ligands. The resultant fiber was then used for direct immersion SPME of heavy metals followed by determination by ICP–MS (Figure 3). The chelating ligand was trapped inside the polymer matrix, which effectively captured the metal from the solution. Metals were therefore preconcentrated onto the fiber and then released in an analysis solution by treatment with acid. A composite containing polypyrrole/carbon nanotubes/1,10-phenanthroline demonstrated exceptional extraction efficiencies for silver, cadmium, cobalt, iron, nickel, lead, and zinc in several sample matrices. The accuracy of the method was validated by the analysis of a certified reference standard. Analyses were accomplished in a minimum amount of aqueous solution and were thus very environmentally friendly.

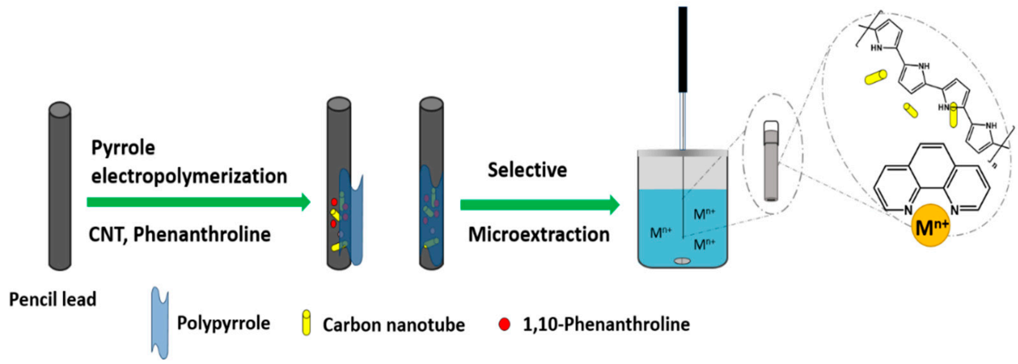

Figure 3. Schematic representation of the creation of an SPME fiber by electropolymerization and its application for metal extraction. Reprinted with permission from [133].

3.8. Dispersive Solid-Phase Extraction

Dispersive solid-phase extraction (D-SPE, Figure 2) is another variation of solid-phase extraction where a micron-sized sorbent is dispersed in the sample solution. This approach eliminates the need to optimize the flow rate and potential backpressure issues with a packed SPE cartridge, especially with newer nano-based materials. Enhanced contact between the analytes and sorbent results in very efficient extractions [206]. New sorbents for D-SPE for metals are beginning to be reported that utilize materials that effectively and selectively capture metal ions by chelation. Sitko et al. described the synthesis of a graphene oxide sorbent modified with (3-mercaptopropyl)-trimethoxysilane for determination of Co^{2+}, Ni^{2+}, Cu^{2+} As^{3+}, Cd^{2+}, and Pb^{2+} by total reflection X-ray fluorescence [207]. Preconcentration and metal capture is quite straightforward, while the analysis step is solvent free. Similarly, dithiocarbamate functionalized $Al(OH)_3$–polyacrylamide was prepared and characterized for extraction of Cu^{2+} and Pb^{2+} [208]. As with SPME, the goal for D-SPE applications is to enhance selectivity for metal analysis with new selective sorbent materials. Recently, pyrrole was derivatized with carbon disulfide and chemically polymerized to obtain an air stable, water-insoluble, chelating polymer for extraction of soft metal ions [209]. Application of this new sorbent for D-SPE of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} demonstrated excellent removal and recovery of these ions. The chelating polymer is reversible, releasing the captured metals after acid treatment for preconcentration prior to analysis by ICP–MS. D-SPE is also amenable to magnetic sorbent particles as demonstrated by the references in Table 4. Therefore, D-SPE shows tremendous promise for developing simple environmentally friendly methods to extract metals.

4. Bulk Sorbent Methods

4.1. Chemical Precipitation

Wastewater is a common medium that regularly is contaminated with heavy metal ions. To ensure safe re-entry into the environment, treated water must contain metal concentrations below an accepted level called the maximum contaminant level (MCL) for each metal ion [210,211]. Chemical precipitation is a useful approach to remove large amounts of heavy metals from inorganic waste materials and prevent contamination of the environment [211]. This technique removes ionic metal components after adding counter-ions to reduce their solubility in aqueous solution [212]. Dissolved metals are turned into insoluble components by a precipitating agent under favorable pH conditions [212]. Much research on chemical precipitation for metal extraction has been conducted because of the low cost and ease of implementation for large volumes of wastewater. However, disadvantages such as the inability to maintain pH for optimum precipitation, high volume of sludge production [213], and low selectivity of metal extraction [214] limits widespread use. The treatment method should not produce toxic chemical sludge such that disposal remains ecofriendly and cost-effective [215]. Several examples on the use of precipitating agents to extract various metals have been reported [216–219].

4.2. Biosorbent Extraction

Biosorbent extraction is particularly important for the removal of heavy metals from industrial effluents as this process utilizes readily available and inexpensive dead biomass compared to conventional sorbents [220]. Aquatic organisms like yeast, algae, and bacteria adsorb dissolved heavy metals and even radioactive elements found in their surroundings [221]. Dead fungal material, for example, does not result in increased toxicity with the extracted metal or adverse operating conditions. Furthermore, no nutrients are needed for dead mass and relatively simple non-destructive treatments are used for the recovery of bound metals, which are often in their anionic forms [220,222]. Natural biosorbents can be valuable low-cost alternatives for metal removal and cleanup, especially for developing countries with limited financial resources. In addition, recent review articles have discussed progress related to the development of ecofriendly phytoremediation and phytoextraction approaches for the removal of metals from contaminated environmental sites [223–225].

Kratochvil et al. studied the removal of molybdate (MoO_4^{2-}) with chitosan beads for up to 700 mg g^{-1} of molybdate [220]. Similarly, removal of Cr^{6+} by peat moss [226] and corncobs [227] was achieved with excellent results. Marine green algae, due to presence of different proteins, lipids, or polysaccharides on the cell wall surface, show good metal binding strength [228]. Hence, for effective removal of heavy metals even at low levels, biosorbents are considered as an emerging technology [229]. However, despite the availability of large quantities of biomass, selection of the most suitable type of biomass is still a challenge. Slight variations in biomass properties can result in considerably different affinities for various metals, which also offers an opportunity to alter biomass properties to design new biosorbent materials. For example, Mallakpour et al. developed a new hydrogel nanocomposite biosorbent by embedding calcium carbonate nanoparticles into tragacanth gum for the removal of Pb^{2+} ions from water samples [230]. Similarly, pine (*Pinus sylvestris*) sawdust was modified with thiourea groups and utilized for the extraction of precious metals from industrial solutions [231]. Table 9 shows additional examples of recently reported natural biosorbent materials for extraction of metals.

Table 9. Biosorbent materials for metal ion extraction.

Biosorbent	SC [a]	Target Metal(s)	Ref.
Rice husk, palm leaf, water hyacinth	NR	Cu^{2+}, Co^{2+}, Fe^{3+}	[232]
Rhizopus arrhizus	180 mg g^{-1}	U^{6+}, Th^{4+}	[233]
Ascophyllum and *Sargassum*	30% of dry weight of biomass	Pb^{2+}, Cd^{2+}	[234]
Tobacco dust	39.6, 36.0, 29.6, 25.1, and 24.5 mg g^{-1}	Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}	[235]
Sargassum filipendula	NR	Ag^{+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}	[236]
Chlorella vulgaris	161.41 mg g^{-1} of Cr^{4+} and 169 mg g^{-1} of Pb^{2+}	Cr^{6+}, Pb^{2+}	[237,238]
Saccharomyces cerevisiae and *Rhizopus arrhizus*	Ranges from 31 to 180 mg g^{-1} for different metals	Cu^{2+}, Zn^{2+}, Cd^{2+}, U^{6+}	[239]
Alcaligenes sp.	66.7 mg g^{-1}	Pb^{2+}	[240]
Olive mill	Varies with pH and other conditions	Hg^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	[241]
Parachlorella	NR	Y^{3+}, La^{3+}, Sm^{3+}, Dy^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+}	[242]

[a] sorption capacity.

5. Conclusions

Recovery of metals often requires extraction from complicated matrices in large quantities, while metal analysis is routinely sought at the trace level. In either case, strategies that are considered greener and minimize their impact on the environment drive development of emerging methods for metal extraction and analysis, many of which are described in this review. Much of the evolution of metal extraction and sample preparation has benefitted from the development and use of new materials. Aqueous two- and three-phase systems reduce the amount of organic solvents needed in LLE and include the use of ionic liquids, which offer the advantageous properties of low flammability and volatility, excellent solvating ability, and high thermal stability. Solid-phase extraction further reduces the need for organic solvents and utilizes novel materials based on adsorption, biosorption, ligand binding, and ion exchange. Extension of SPE into the micro-regime shows exciting promise for effective and selective SPME of metals. Initially, limited by the derivatization of metal ions to generate volatile or hydrophobic organometallic species for gas and liquid chromatographic analysis, new SPME coatings and materials take advantage of classical coordination chemistry to permit direct analysis of metal ions. Development of unique coordination type polymers, magnetic materials, and thin-film coatings for SPE and SPME shows great promise for highly selective and ecofriendly extraction methods for the recovery of valuable metals and for efficient sample preparation and preconcentration of a range of metals from complex matrices.

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