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Bio-derived Materials as a Green Route for Precious & Critical Metal Recovery and Re-use

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To meet the global challenges of elemental sustainability a holistic approach to the extraction, use and recovery of precious and critical metals must be developed. Biosorption is a key technology for the benign recovery of diffuse elements from liquid effluents and hydrometallurgy processes. There is the opportunity to go beyond the remediation of heavy metals and pollutants, by utilising biosorption within a circular economy approach for the cycling of precious and critical metals in higher-value applications. This review provides an overview of the current research in the area of critical and precious metals recovery using biosorption, its application to real-life wastes and the potential uses for these metal-loaded materials for catalysis or functional materials.

Introduction

There are rising concerns around the world about the issue of ‘critical’ elements; elements that are of critical importance for our economies and lifestyles but demonstrate supply-chain risks.[1-6] These include elements with: rising demand; low substitutability; high scarcity; production as ‘hitchhiker’ elements, or restricted reserve distributions (geopolitical risks).[1, 6] The assessment of the criticality of elements varies around the world, frequently depending on national concerns, but there is a consensus that elements of high concern include the rare earth elements (REEs), platinum group elements (PGMs) and a variety of others including niobium, indium, gallium and molybdenum.[2, 3, 6]

These elements are of vital importance to chemistry, both for the development of new advanced materials and as catalysts and reagents in the chemical and related industries.[6, 7] Moving towards the use of more abundant elements is vital, however, many of these critical elements have particular attributes which make them difficult to substitute. It was for this reason that we developed the vision of elemental sustainability;[8, 9] the need to develop circular routes for the recovery and re-use of all elements to ensure their availability to future generations. Previously the closed-loop recovery of elements from municipal wastes, E-waste and degraded land have been discussed,[10-12] but an area that has received less attention is the recovery of elements from low concentration and diffuse sources, particularly dilute liquid effluents.

A variety of traditional methods can be used to recover elements from these sources including chemical precipitation, chemical coagulation, electrochemical technologies, ion exchange, and membrane technologies.[13] However, they suffer from many disadvantages including the need for large quantities of chemical additives forming by-product sludges, high energy usage, high cost and their poor efficiency at very low metal concentrations.[13-15] Researchers have therefore been studying the potential of bio-derived materials for biosorption of elements from dilute solutions, as sustainable metal recovery technologies.[13, 16-18]

For the purposes of this review “biosorption” is defined as the removal or binding of substances from solution by non-living bio-derived materials (referred to as biosorbents). Biosorbents have several advantages, alongside being renewable materials, including easy handling, high metal uptake rates even in trace conditions, minimal sludge production and potential for regeneration and reusability.[13, 19, 20] Over the past decade, there have been several review articles focusing on biosorption for the recovery of heavy metals and for the removal of dyes and organic compounds from wastewater.[13, 16, 19, 21-30] However, in general, the use of biosorption has been viewed solely as an environmental remediation technique to capture toxic and harmful substances. It is our view that there is an opportunity to go beyond this, by recovering these metal containing materials after remediation and utilising them for higher-value applications such as catalysts and in electronic applications (Figure 1).

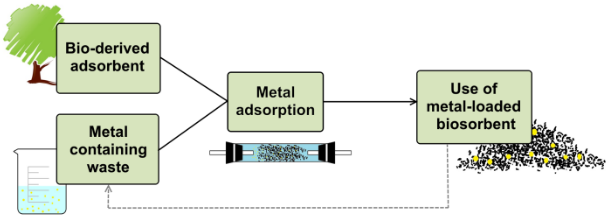

Fig. 1 Schematic representing of the proposed route for metal recovery and reuse using biosorption

The focus of this review is to discuss: (1) bio-derived materials, (2) biosorption of precious and critical elements, with special attention to real life waste sources, (3) use of these metal loaded biosorbents in value added applications and finally (4) the future potential for use of biosorbents to close the loop on metal recovery and use.

Bio-derived Materials

A wide variety of bio-derived materials have been studied as potential biosorbents including fungi, bacteria, algae, agricultural residues and components that can be extracted from these, particularly polysaccharides such as chitosan and alginic acid and also proteins. Preferable biosorbents are those that are abundant and cheap.

Preparation of Bio-derived adsorbents

Adsorption can be carried out either by native, immobilized or modified biosorbents. In general, biosorbents used in their native form are prepared by washing and drying of the biomass,[21] followed by cutting or grinding into stable adsorbent particles.[24] Agricultural wastes, commonly lignocellulosic materials, can act as excellent adsorbents as they require minimal processing, thus reducing production costs and the environmental impacts of preparation.[31, 32-33-35] However, the use of biomass in its native form has some disadvantages, e.g. difficulty in separation from the reaction mixture, mass loss after regeneration, poor mechanical strength and small particle size, resulting in difficulties using it in batch and continuous systems.[36, 37] Various authors have discussed various technical challenges related to biosorption in more detail.[16, 24, 38-40]

The use of immobilized biomass particles in packed- or fluidized-bed reactors can minimize these disadvantages. A suitable immobilization method improves mechanical strength, rigidity, porosity and the overall metal ion removal capacity, as well as lifetime of the biosorbent.[41-43] Polymeric matrices used in immobilization include polysulfone, polyurethane, polyacrylamide, polyethyleneimine, and alginates.[44-47] Marayuma *et al* used corn protein and hexamethyl diisocyante to shape egg-shell membrane to a flat sheet to improve handling.[48] Immobilized adsorbents are usually expensive due to the extra processing required and they can result in higher mechanical diffusion resistance and present mass transfer limitations, which can lead to a reduction in metal-adsorbent contact and overall lower metal adsorption capacity. Ngah *et al.* found that glutaraldehyde cross-linked chitosan beads had lower adsorption capacities (30-50 mg/g Fe compared to 55-60 mg/g Fe for un-crosslinked) and slower rates of metal uptake.[49]

An alternative method of immobilization is the use of a highly rigid biomass as support. Raw or unprocessed seaweeds are good adsorbents for metal ions and thus can be used in adsorption processes without immobilization.[50] Alginate, a polysaccharide extracted from seaweed, can also be combined with other bio-polymers to create stable adsorbents; chitosan-alginate beads have been seen to improve stability and metal uptake in comparison to pure chitosan beads.[51] Zhang *et al.* have investigated the immobilisation of chitosan using cotton fibre improving both the lifetime and the adsorption capacity of the adsorbent.[52] Work by Clark *et al.* has demonstrated the production of expanded mesoporous materials from a range of polysaccharides including starch, alginic acid, pectin and directly from seaweeds or using silica derived from waste biomass ashes, which are rigid and can promote adsorption due to improved diffusion.[53-57] Care must be taken to assess the impact of extraction and modification steps to ensure that they do not severely negatively impact the sustainability of the biosorption technology, ideally through full life-cycle and social impact assessments.

Bio-derived carbonaceous materials can improve the stability of the materials and their porous stucture, promoting increased adsorption capacities and selectivity. Activated carbons with high surface areas and significant microporosity, made from waste agricultural residues by pyrolysis at high temperatures with activators such as steam, phosphoric acid or $ZnCl_2$, are the mostly widely studied system.[58, 59] Activated carbons can suffer from diffusion limitations, especially for bulkier adsorbates. Mesoporous carbonaceous materials from polysaccharides have shown excellent recoveries of pollutants such as dyes and phenolic compounds, but need to be demonstrated for metal-containing wastes.[60, 61] The ability to tune the surface functionality of these materials to promote selectivity towards certain elements is also a benefit.[62]

Precious, Critical Metal and Selective Biosorption

Table 1 summarises the literature that is available on the biosorption of precious and critical metals from single-element synthetic solutions. From this data it is clear that a wide-range of biosorbents are of interest for critical element recovery. Chitosan and cellulose-modified adsorbents have gained substantial attention in this area with some excellent adsorption capacities, whilst adsorption of REEs using algae and algae derivatives is also relatively popular. Amongst the precious metals gold is the most widely studied, likely due to its high economic value,[63] whilst lanthanum has had the most detailed analysis amongst the REEs. Although almost all species have been tested for their uptake by some form of biosorbent and demonstrate the ability to be recovered via this technique, in general the majority of elements have only been examined in one or two studies and with little comparison of competing element effects or extensive analysis of the most appropriate biosorbent.

More applicable to real life metal samples the work of Chen *et al.* has demonstrated the selective adsorption of Au from binary (Au-Cu), five (Au-Cu-Ni-Co-Zn) and six (Au-Pd-Co-Ni-Cu-Zn) component solutions using silk sericin and chitosan derived adsorbents.[64] For both materials Au was selectively recovered from each of the solutions, the silk sericin showed the most selective adsorption as Au was the only metal removed from each of the solutions – whereas chitosan also adsorbed Pd from the six component mixture. This demonstrates the potential for selective precious metal recovery from WEEE waste, mine ores and wastewaters where these mixtures of metals will be present.

Mechanisms for precious and critical element adsorption

Metal adsorption on these biosorbents depends upon physicochemical interactions between the metal and functional groups on the biosorbent surface.[21, 50, 65] Surface functionalities can include hydroxyl, carbonyl, carboxylate, thiol, sulfonate,

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Table 1: Literature data for the recovery of precious and globally important critical metals (based on UNEP and BGS assessment)[6] using biosorbents

Element	**Biosorbent**		**Max Ads. Capacity (mg/g)**	**Ref.**
Precious metals				
Ag	Chemically modified chitosan resin		226.5	66
	Fungi:	*Cladosporium cladosporioides*	118.2	67
		Aspergillus niger	177.3	68
		Neurospora crassa	118.2	68
		Fomitopsis carnea	98.5	68
		Brewery waste yeast	78.0	69
Au	Chitosan:	Chitosan	650	70
		Chemically modified chitosan	669.7	66
		Crosslinked chitosan resin (modified with l-lysine)	70.3	71
		Sulphur derivative of chitosan	223.1	72
		Glutaraldehyde crosslinked chitosan	333.0	72
		4-amino-4´ -nitro azobenzene modified chitosan	69.9	73
	Algae:	*Fucus vesiculosus*	66.6	74
		Sargassum fluitans	0.3	75
		Chllorella vulgaris	53.2	76
		Sargassum natanss	409.7	77
		Ascophyllum nodosum	29.3	77
		Chlorella vulgaris	51.5	78
		Dealginated seaweed waste	42.6	79
		Calcium alginate beads	290.0	80
		Sulfuric acid modified alginic acid gel	1111	81
	Fungi:	*Cladosporium cladosporioides*	51.5	67
		Fomitopsis carnea	48.5	82
		Aspergillus niger	140.1	77
		Rhizopus arrhizus	112.1	77
	Bacteria:	*Corynebacterium glutamicum*	50.2	83
		Decarboxylated *Corynebacterium glutamicum*	86.2	83
	Protein:	Hen eggshell membrane	108.9	84
		Chicken egg shell membrane	250	48
		Silk seracin	200	70
		Ovalbumin	36	85
		Lysozyme	40	85
		Bovine serum albumin (BSA)	19	85
	Alfalfa		29.3	86
	Buckwheat hulls		297	87
	Silk (Au-CN ions)		23.6	88
	Wool (Au-CN ions)		98.1	88
	Aminated cross-linked lignophenol		606.8	89
	Sulfuric acid modified cellulose gel		1491	81
	Sulfuric acid modified cotton cellulose gel		1042	90
	Sulfuric acid modified paper cellulose gel		994.9	91
	Sulfuric acid cross-linked cellulose modified with N-aminoguanidine		1814	92
	Sulfuric acid modified dextran gel		1418	81
	Sulfuric acid modified pectin ge		945.6	81
	Condensed-tannin gel		5605	93
	Rice husk carbon		106.5	94
Platinum Group Metals				
Ir	Chitosan:	Glutaraldehyde cross-linked chitosan beads	220	95
		Thiourea derivative of chitosan	170	95
		PEI-grafted chitosan beads	340	95
Os	Chitosan:	Glutaraldehyde cross-linked chitosan beads	550	95
		Thiourea derivative of chitosan	100	95
		PEI-grafted chitosan beads	650	95
Pd	Aquatic plant:	*Racomitrium lanuginosum*	37.2	96
	Chitosan:	Chitosan derivatives	486.2	97
		Rubeanic acid derivative of chitosan	450.1	98
		Thiourea derivative of chitosan	325.8	98
		Glutaraldehyde crosslinked chitosan	338.9	98
		4-amino-4-nitro azobenzene modified chitosan	58.6	73

	Protein:	Chicken egg shell membrane	107	48
		Ovalbumin	91	85
		Lysozyme	104	85
		Bovine serum albumin (BSA)	104	85
	Collagen fibre-immobilized bayberry tannin		52.8	99
	Aminated cross-linked lignophenol		22.7	89
	Sulfuric acid cross-linked cellulose modified with N-aminoguanidine		119.2	92
Pt	Chitosan:	Thiourea derivative of chitosan	288.5	100, 101
		Glutaraldehyde crosslinked chitosan	232.0	100, 101
		Chitosan derivatives	450.9	97
	Protein:	Chicken egg shell membrane	50	48
	Collagen fibre-immobilized bayberry tannin		40.2	99
	Aminated cross-linked lignophenol		104.6	89
	Sulfuric acid cross-linked cellulose modified with N-aminoguanidine		119.0	92
Rh	Bacteria:	*Rhodopseudomonas palustris* pre-treated with acid	207.2	102
	Yeast:	*Saccharomyces cerevisiae*	4.0-9.5	103
	Aquatic plant:	*Azolla filiculoides*	5.0-10.5	
	Amine-modified tannin gel		3.0-3.8	104
Ru	Bacteria:	*Rp. palustris* strain CGA009	86.3	102
		Rp. palustris strain CGA009 with acid pretreatment	207.2	102
		Corynebacterium glutamicum	16.0	105
		Polyethylenimine (PEI)-modified *Corynebacterium glutamicum*-chitosan	110.5	105
Rare Earth Elements				
Ce	Algae:	*Turbinaria Conoides*	152.8	106
		Calcium alginate-poly glutamic acid hybrid gels	≈ 450	107
	Grapefruit peel		159.3	108
	Tangerine peel		162.8	109
	Corn style		180.2	110
	Plantanus orientalis leaf powder		32.1	111
	Pinus brutia leaf		62.1	112
	Prawn carapace		218.3	110
	Crab shell		144.9	113
Dy	Algae:	*Parachlorella*	0.5	114
		Carbonised *Parachlorella*	0.25	114
		Calcium alginate-poly glutamic acid hybrid gels	≈ 300	107
	Modified rice husk activated carbon		250.0	115
Er	Algae:	*Sargassum* sp.	136.8	116
		Calcium alginate-poly glutamic acid hybrid gels	≈ 250	107
	Alfalfa native		42.4	117
Eu	Algae:	*Sargassum polycystum*	122-138	116
		Turbinaria conoides	138.2	106
		Sargassum hemiphyllum	118.7	118
		Schizymenia dubyi	148.9	118
		Calcium alginate-poly glutamic acid hybrid gels	≈ 390	107
	Bacteria:	*Pseudomonas aeruginosa*	44.1	119
		Mycobacterium smegmatis	49.0	120
	Crab shell		49.5	113
Gd	Algae:	*Sargassum* sp.	55.0	121
		Parachlorella	0.71	114
		Carbonised *Parachlorella*	0.33	114
		Calcium alginate-poly glutamic acid hybrid gels	≈ 325	107
Ho	Grapefruit peel		171.2	108
	Alfalfa		42.4	117
La	Algae:	*Sargassum polycystum*	111-125	116
		Sargassum fluitans	101.4	122
		Turbinaria conoides	154.7	106
		Desmodesmus multivariabilis	100.0	123
		Chlamydomonas reinhardtii	142.9	123
		Chloroidium saccharophilum	129.9	123
		Scenedesmus acuminutus	111.1	123
		Chlorella vulgaris	74.6	123
		Stichococcus bacillaris	51.02	123
		Sargassum hemiphyllum	97.2	118
		Schizymenia dubyi	90.4	118
		Ulva pertusa	129.2	118
		Calcium alginate-poly glutamic acid hybrid gels	~ 360	107
	Bacteria:	*Pseudomonas aeruginosa*	55.1	119
		Mycobacterium smegmatis	55.0	120
		*Agrobacterium sp.*HN1	35.3	124
	Tangerine peel		154.9	109
	Plantanus orientalis leaf powder		28.7	111
	Bamboo charcoal		163	125

	Modified rice husk activated carbon		175.4	115
Lu	Algae:	*Monoraphidium* sp.	136.7	126
		Calcium alginate-poly glutamic acid hybrid gels	~ 175	107
Nd	Algae:	*Monoraphidium* sp.	1511	126
		Phormidium	0.6	127
		Sargassum sp.	53.4	121
		Parachlorella	6.7	114
		Carbonised *Parachlorella*	3.1	114
		Calcium alginate-poly glutamic acid hybrid gels	~ 400	107
	Fungi:	*Penicillium* sp.	178	126
		Bakers' Yeast	313	126
	Activated carbon		61	126
Pm	Algae:	*Sargassum* sp.	40.9	121
Pr	Algae:	*Sargassum* sp.	51.1	121
		Sargassum sp.	40.9	121
		Parachlorella	2.3	114
		Carbonised *Parachlorella*	0.96	114
		Calcium alginate-poly glutamic acid hybrid gels	≈ 500	107
Sm	Algae:	*Sargassum* sp.	51.1	121
		Parachlorella	1.2	114
		Carbonised *Parachlorella*	0.52	114
		Calcium alginate-poly glutamic acid hybrid gels	≈ 400	107
Tb	Algae-derived:	Calcium alginate-poly glutamic acid hybrid gels	≈ 300	107
Tm	Algae:	*Sargassum* sp.	155.7	116
		Calcium alginate-poly glutamic acid hybrid gels	≈ 225	107
Yb	Algae:	*Sargassum polycystum*	121-156	116
		Turbinaria conoides	121.2	106
		Sargassum hemiphyllum	133.1	118
		Schizymenia dubyi	160.2	118
		Ulva pertusa	124.4	118
		Calcium alginate-poly glutamic acid hybrid gels	≈ 190	107
	Bacteria:	*Pseudomonas aeruginosa*	56.4	119
		Mycobacterium smegmatis	69.0	120
Other critical elements				
Ba	-			
Be	Municipal wastewater sludge aerobic granules		14.1	128
Bi	Collagen fibre-immobilized bayberry tannin		72.7	128
	Coconut shell activated carbon		54.4	129
Co	Many materials: *Sargassum sp.*, *Ascophyllum nodosum*, *Streptomyces n*., yeast, sawdust, bark, coir, rice straw, cotton stalks,bagasse, peanut shell, citrus peel etc		0.5-156	39
Ga	Coir		13.8	130
	Coir oxidised with H_2O_2		19.4	130
In	Chitosan:	Chitosan-coated bentonite beads	10	131
	Bacteria:	*Shewanella algae*	53.6	132
Ge	-			
Li	Algae-derived:	Ca-alginate beads	0.56	133
	Bacteria:	*Arthrobacter nicotianae* IAM12342	0.87	134
		Streptomyces albus HUT6047	0.39	134
	Fungi:	*Penicillium chrysogenum* IAM7106	0.05	134
Mo	Aquatic plant:	*Posidonia oceanica*	~ 18	135
	Algae:	Ca-pretreated *Cystoseria indica*	18.3	136
Nb	-			
Sb	Fungi:	Fe-treated *Geotrichum fragrans*	111	137
	Cyanobacteria:	*Microcystis*	7.3	138
	Green bean husk		20.1	139
	Beech (Fagus sylvatica) sawdust		153.3	140
	Lichen (*Physcia tribacia*)		81.1	141
Sc	Algae-derived:	Calcium alginate-poly glutamic acid hybrid gels	≈ 6550	107
	Fungi:	*Saccharomyces cerevisiae*	6.01	142
		Rhizopus arrhizus	16.45	142
Se	Algae:	*Cladophora hutchinsiae*	74.9	143
	Fungi:	*Ganoderma lucidum*	127.0	144
		Aspergillus sp. J2	5.7	145
	Eggshell membrane		37.0	146
	Chicken feathers		20.7	146
Sr	Chitosan:	Chitosan modified sawdust with Fe_3O_4 particles	12.6	147
	Algae:	*Padina* sp.	330.4	148
		Ca-alginate beads	6.7	133

	Fungi:	*Aspergillus terreus*	308.0	[149]
		Aspergillus niger	751.9	[150]
		Baker's yeast	33.0	[151]
		Brewery waste yeast	8.0	[69]
		Magnetically modified fodder yeast (*Kluyveromyces fragilis*) cells	140.8	[152]
	Moss *Rhytidiadelphus squarrosus*		13.1	[153]
	Spent coffee grounds		69.1	[154]
Ta	-			
Te	-			
Y	Algae:	*Parachlorella*	1.6	[114]
		Carbonised *Parachlorella*	0.97	[114]
		Calcium alginate-poly glutamic acid hybrid gels	≈ 180	[107]

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amine, amide, imine and phosphonate groups depending on the biosorbent.[65] For adsorption to occur it is imperative that the metal ion is solvated in solution, either through dissolution of the solid material in which the metal is encased or by the recovery of metals directly from liquids.

The most commonly assumed mechanism for biosorption is via electrostatic interactions, with other mechanisms including chemical reaction, ion exchange and redox reaction.[63] For the adsorption of precious metals such as, gold, platinum and palladium, highly acidic media (i.e. pH 2) are favoured as it leads to protonation of the biosorbent which better interact with metal anions in solution. For instance, the major advantage of using chitosan in acidic media for precious metal adsorption is that the amino sites of the chitosan are easily protonated, accentuating the electrostatic forces often implicated in the initial stages of adsorption.[19, 155] Work by Ogata and Nakano investigating the recovery of gold using tannin gel capsules concluded that the gold was being biosorbed due to a redox reaction occurring between the gel and the $AuCl_4^-$ complex in solution.[93] This resulted in reduction of Au(III) to Au(0) and oxidation of the hydroxyl groups of the tannin gel to carbonyl groups. A similar mechanism has also been proposed for precious metal recovery by calcium alginate beads.[156]

In the case of REE recovery, research into the mechanisms of biosorption are still in their infancy. However, Vijayaraghava *et al.* have carried out some interesting work on the uptake of REE on marine brown algae.[106, 157] It was shown that conversely to precious metal biosorption a less acidic pH was preferred (i.e. pH 4-5). At this pH the lanthanides exist in their 3+ oxidation state and will interact strongly with the negatively charged carboxylate groups of the alga. Below pH 4 the carboxylate groups will become protonated and above pH 5 the lanthanides will begin to precipitate. Due to the trivalent nature of the lanthanides is it understood that biosorption is occurring via an ion exchange mechanism – analysis of the brown alga before and after adsorption showed a significant drop in the concentration of calcium on the surface of the alga, indicating that ion exchange between the REE and calcium was the mechanism of uptake. This strong pH dependence of the lanthanides is advantageous as it allows for easy desorption of the metal simply using HCl to lower the pH.[158]

Challengingly, the way one biomass interacts with an element bears little resemblance to another system with the same element but a different biomass (form or type). Yet, the chemical characteristics of the metal will mean the occurrence of a common mechanistic thread, e.g. the ease of gold reduction from $Au^{(III)}$ to $Au^{(0)}$.

Precious and critical metal biosorption from real-life wastes

As mentioned previously the vast majority of studies in the literature use simulated wastes to test biosorption of metals. However, to utilize these materials industrially, and particularly to create close-looped systems, it is vital to test them on real-life wastewaters and wastes. A variety of challenges occur when transferring tests from synthetic and single-metal uptake to real-life wastes, including contamination by other metals and non-metals and variability of the pH from that preferred. This generally results in the materials performance differing when real wastes are used compared to simulated wastes.

The complex processing required to recover PGMs from the base metal, sulfide ores and from each other results in large quantities of waste solvent and water streams containing trace levels of precious metals.[159] These effluents are currently concentrated in holding ponds for recovery, however, the lower density of the co-solvents used can prevent solar water evaporation making biosorption an ideal solution.[159] Mack provides one of the only detailed investigations comparing biosorption of a synthetic precious metal containing waste source with refinery wastewater.[160] The yeast *Saccharomyces cerevisiae* immobilised using polyethyleneimine and glutaraldehyde was capable of high platinum uptake (150 – 170 mg/g), or close to 100% Pt removal, at low pH in a single-metal solution. However, transfer to the platinum refinery wastewater (~18 mg/L Pt) resulted in only 20% Pt removal (4 mg/g), attributable to competition with chloride and nitrate anions, complexation with ammonium ions or speciation of the platinum into less extractable forms. The authors suggest that pre-treatment of wastewaters to remove contaminants such as chloride ions may be necessary prior to metal recovery. Interestingly, the kinetic data indicated that chemical sorption mechanisms were involved in the metal uptake, making desorption difficult but providing opportunities for higher value applications of the materials.

Maryuyama *et al* provide a detailed study using egg shell membrane on the recovery of precious metals from eight different industrial waste solutions including from electronic materials, vapour deposition, cyanogen and plating processes.[48] Gold was selectively recovered, however, much lower levels of metal adsorption were observed compared to the synthetic solution (10-65 mg/g from industrial samples vs 250 mg/g).

Flat Screen Displays utilize 50-70% of the world's indium output as Indium Tin Oxide (ITO). Large quantities of dilute indium wastewaters are generated though cleaning and etching of the glass surfaces, which may be discharged from semi-conductor or optoelectric plants.[161, 162] Kwon and Jeon studied the recovery of In(III) from wastewater from the Toricom company in Korea containing In (19.1 mg/L), Zn (140,600 mg/L) and Sn (~0.01 mg/L), using waste sawdust.[163] Without modification the sawdust displayed some selectivity towards In over Zn (15% vs 9%). Phosphorylation of the sawdust resulted in improved selectivity and increased recovery of In(III), reaching nearly 100% at a pH of 3.5.[163]

Won *et al.* investigated the recovery of Pt from inductively coupled plasma (ICP) wastewater using *E. coli,* a byproduct of L-phenylalanine production.[164] The ICP wastewater was collected and tested without modification. Analysis showed that it contained 1554 ppm Pt along with a mixture of other inorganic elements. After some modification the *E. coli* achieved Pt adsorption capacities of 108 mg/g.

Electroplating produces metal-containing waste effluents variously containing Au, Zn, Cu and Cd. Gold plating bath effluents are treated to remove complexing agents (e.g. cyanides, citrate) and to neutralise the solutions, but may contain significant quantities of gold (up to 50 mg/L). Paknikar and Pethkar studied the fungal isolate *Cladosporium cladosporioides* for the adsorption of gold from extroplating effluent with a 55% removal efficiency and loading capacity of 36 mg/g, though this was much lower than a single-metal pure solution at 100-110 mg/g.[165] Again, the presence of anionic species (carbonate, citrate, sulphite and thiosulfate) significantly affected gold adsorption. Soleimani and Kaghazchi used activated carbon produced from Iranian apricot stones for the removal of gold from electroplating wastewater.[166] Gold recovery ranged from 40-100% depending mainly on the adsorbent loading in solution.[166] Suyama *et al.* used eggshell membrane for the removal of Au(I) and Au(III) ions from solutions and electroplating wastewater, with preference for the latter demonstrated (618 mg/g Au(III) vs 147 mg/g Au(I)).[84] Column recovery of the mixed metal electroplating wasterwater gave recoveries in the order Au (98%) > Ag (97%) > Co (94%) > Cu (17%) > Pb (15%) > Ni (4%) > Zn (3%).[84]

Effluents from hospitals contain platinum from excreted anti-neoplastic drugs, currently generally discharged to sewers, as well as elements from dental treatment and other medical treatments with an estimated 84-99 kg PGMs released per annum from hospitals in Germany.[167, 168] Adani *et al.* demonstrated the recovery of silver from medical photographic and X-ray effluents using activated carbons.[169] Ag concentrations of 4050 ppm and 4196 ppm were found in these wastes, respectively, with the activated carbons giving >90 % recoveries.

Wood shaving fly ash and coconut shell activated carbon have also been utilized for Au recovery from gold jewellery manufacturing slag.[170] The Au was washed from the slag using sodium cyanide and the dissolved gold was adsorbed. The coconut shell activated carbon proved the most effective with a maximum Au adsorption capacity of 76.78 mg/g, whilst the wood shaving fly ash reached only 8.68 mg/g.

Although a wide-range of liquid effluents already contain low levels of critical and precious elements, biosorption can be extended to other wastes by dissolution of metals into solution from solids, using hydrometallugical processes.[171, 172] Hydrometallurgy is the use of aqueous and/or organic solutions to extract, concentrate, separate or refine metals. Waste Electronic and Electrical Equipment (WEEE) offers a prime opportunity for selective critical element recovery, with items such as discarded mobile phones containing up to approx. 30% rare and precious metals amongst a broad-range of elements (>60 different elements).[173, 174] Gurung *et al.* have demonstrated a method for integrating hydrometallurgical treatment of mobile phone printed circuit boards (PCB) with adsorption by biosorbents (Figure 2).[172] The adsorbent material used was persimmon tannin powder treated with acid to obtain a cross-linked persimmon tannin gel (CPT gel). The CPT gel was stable for use directly in the leach liquor containing: Ag, Au, Fe, Cu, Ni, Zn and Pb. Recovery of Au and Ag reached 100% whilst the recovery of the other metals present was < 20%. The Au and Ag were also reduced to the metallic form on the CPT gel, an additional advantage of this adsorption process.[172] Overall, this process shows the potential for development of integrated systems where selective metal recovery can be achieved, thus increasing the value and attractiveness of recovery from highly contaminated and mixed metal waste streams.

Sources of Critical and Precious Metals for Recovery

The details above highlight the need for more in-depth studies on biosorption using real-life wastes due to the contrast with synthetic solution studies. A much wider variety of liquid effluents than those studied in the literature have the potential to be analysed for the recovery of critical and precious metals from point (e.g. mines, industry) and diffuse sources (e.g. sewage plants, surface runoff) (Table 2). The increasing demand worldwide for precious and critical metals is resulting in increased mining, whilst a move towards aqueous or organic solvent metal extraction is producing increasing quantities of liquid effluents still containing appreciable quantities of metal from mining and industrial processes.[19] Diffuse waste samples are likely to be less concentrated and contain a greater mixture of pollutants (metal, organic and inorganic) than point sources.

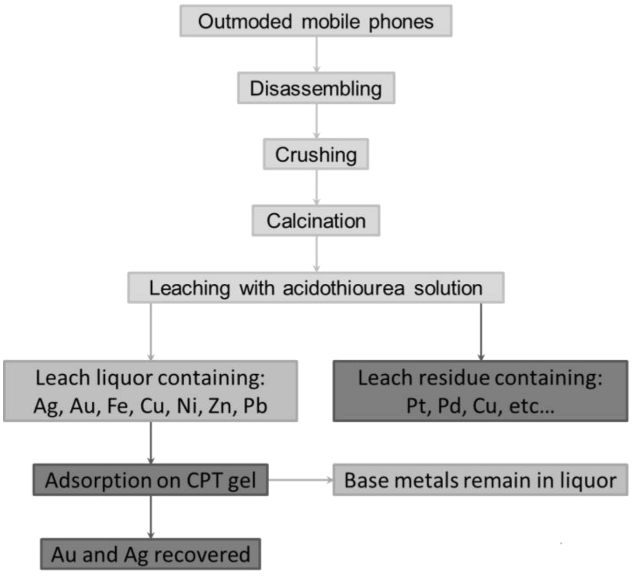

Fig. 2 Recommended methods for the leaching and recovery of precious metals from mobile phone printed circuit boards. (Adapted from Ref.[172])

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Table 2 Caption Industrial point sources and diffuse emissions of some precious and critical elements

Element	Point sources	Diffuse Sources	Ref
Precious and platinum group metals			
Ag	Electroplating and metal surface treatment processes, photographic operations, E-waste leaching liquids, geothermal fluids from heat production	Small scale photography, household products such as polishes, domestic water treatment devices	13, 171, 172, 175-177 178
Au	Heap leach pads and waste dumps, E-waste leaching liquids, Geothermal fluids from heat production, Electroplating wastewaters	Leaching from goldsmiths, jewellery stores, sewage sludge	13, 84, 171, 172, 179 180
Ir	Precious metal refining, spent acetic acid catalysts		159, 181
Os	Precious metal refining	Medical and clinical uses (anti-neoplastic drugs)	159, 176, 180
Pd	Precious metal refining, E-waste leaching liquids, Geothermal fluids from heat production	Leaching of autocatalysts, dental alloys, electronics, jewellery, cancer drugs and catalysts, dust emissions from smelters, medical and clinical uses (mainly as anti-neoplastic drugs), synthetic fibres production, chemical industry	13, 171, 172, 159, 180, 182
Pt	Precious metal refining, E-waste leaching liquids, catalysts used in petroleum/ammonia processing, Geothermal fluids from heat production	Leaching of autocatalysts, from small electronic shops, jewellery shops, laboratories and glass manufacturing, medical and clinical uses, mainly as anti-neoplastic drugs (cisplatin and carboplatin)	13, 159, 171, 172, 180
Rh	Precious metal refining, spent acetic acid catalysts	Leaching of autocatalysts	159, 180, 181
Rare Earths and other Critical elements			
Co	Mining activities		176
Eu,	Nuclear industry, Geothermal fluids from heat production	Nuclear weapons testing, nuclear fuel reprocessing	13, 176, 183
Ga	Etching wastewater of the semiconductor industry	^{67}Ga medical waste from nuclear medicine	184, 185
In	Indium tin oxide (ITO) etching wastewater		161
Li	Geothermal fluids from heat production	Leaching of lithium hypochlorite pesticide	13
REEs	Production of catalysts, hybrid vehicles, rechargeable batteries, mobile phones, plasma televisions, disk drives and catalytic converters, geothermal fluids from heat production	Contrasting agent in magnetic resonance imaging (Gd only)	13, 186
Se		Food products and supplements, shampoos and cosmetics, old paints and pigments, concrete leaching	180

More data is also needed on the actual levels of critical and precious metals in wastewaters.

Green Applications of Recovered Materials

As discussed previously, the biosorption of metals has been the subject of much research, however, little attention has been paid to further use of the metal-loaded biosorbents. Although biosorption is considered a low-cost and environmentally-friendly remediation method, the safe disposal of the loaded biosorbent is an issue. Therefore, in order to move towards a circular economy, applications of the remediated materials should be investigated.

Recovery of Metals from Bio-derived materials

Currently, the most explored "application" for metal loaded biosorbents is metal desorption, enabling the reuse of the biosorbent and recovery of the metals. The preferred method is acid washing.[187] Tsuruta showed that lithium could be quantitatively desorbed from immobilised *A. nicotianae* cells using 1 mM HCl in a column system.[134] Ponou *et al*. investigated the adsorption and desorption of REEs from the dried and carbonised alga, *Parachlorella*. Quantitative desorption of La, Pr and Nd occurred under acidic conditions, up to 76.4 % Sm desorption with 1 M HNO_3, but limited or no desorption of Gd or Dy.[114] Vijayaraghavan *et al.* quantitatively desorbed La, Ce, Eu and Yb using 0.05 M HCl from the algae *T. conoides*, with repeated efficiency over three cycles.[188] For the precious and platinum group metals recovery via these methods can be difficult as the metals are frequently reduced on the surface, or strong chelating agents such as acidified thiourea solution are required to recover the metal.[16, 19] These methods use large amounts of energy and hazardous materials and can decrease the adsorption capacity of the material.[189] In some cases, the amount of waste produced during metal recovery and adsorbent regeneration is equal to the amount of waste treated in the first instance, resulting in no overall benefit.[190] An alternative option for recovery of the metals is combustion of the biomass to produce energy, with the metal extracted from the ash using traditional pyro- or hydrometallurgical processes. Won *et al.* achieved 98.7% recovery of platinum adsorbed on *E. coli* via incineration.[164] However, this does not enable recycling of the biosorbent.

Metal-loaded Bio-derived materials for Added Value Applications

In a few cases, predominantly focusing on heavy metals, researchers have already demonstrated the direct use of metal-loaded biosorbents in further applications. An interesting application is the degradation of phenols in aqueous samples; common pollutants with high bioaccumulation levels produced in a wide range of industrial processes, from pharmaceuticals to petrochemicals. Ma *et al.* used sawdust for the adsorption of nickel,[189] with the metal-loaded complex employed as a catalyst on the ozonation of 2-chlorophenol. Wu *et al.* conducted a similar study using graphene oxide/sawdust composites for the adsorption of nickel and subsequent degradation of phenols using metal-loaded bio-derived adsorbents as catalysts.[191] Ge *et al.* studied dithiocarbamate functionalized lignin in the adsorption Cu (II) and Pb (II),[192] with the metal-loaded adsorbent tested as an antioxidant for the inhibition of hydroxyl radicals. Liu *et al.* used fir sawdust as a copper adsorbent, and proved that the Cu(II) adsorbed on the sawdust could catalyse the fast pyrolysis by which the sawdust is turned into bio-oil.[193] A Cu(II) enriched bio-char was obtained as a by-product of the fast pyrolysis, from which the metal could be recovered.

These initial studies demonstrate the potential for the direct use of biosorbents loaded with metals, particularly for catalysis. However, they by no means demonstrate the full potential of these materials, with no current examples of this circular economy approach found for the precious and critical elements. There is a huge-range of research focused on the use of metals supported on bio-derived materials, particularly carbonaceous materials, for applications ranging from catalysts to electronics. Instead of creating separate materials for these applications, the direct use of the precious and critical metal-loaded bio-adsorbents for the applications highlighted in the sections below would create an ideal closed-loop system.

Future uses of Metal-Loaded Bio-derived adsorbents

Supported metal-catalysts

Many of the highlighted critical metals of global importance have found widespread applications in catalysis.[194] The REEs, Ga, In, Sc and Y are predominately used as ions in complexes, and although the precious/PGMs can be used in complexes they are more often utilised as nanoparticles. In both instances there would be possibilities to use the materials resulting from the capture of these metals on biosorbents within catalytic applications.

Numerous examples exist where precious metal nanoparticles are supported on thermally stable supports such as silica, alumina, titania, zeolites etc for the purpose of catalysis. However, the nature of the biomass derived supports suggested for capturing these metals means that the introduction of stability via carbonisation may be necessary and that initial research should target those applications where precious metals on carbon/graphite are currently used. Auer *et al.* reviewed carbons as supports for industrial precious metals, including a section on major uses of supported complexes.[195] However, activated carbons are not the only support for metals. Chitosan has been reviewed as a metal support by Guibal *et al.*,[196] whilst lignin sulfonate has been used to support scandium triflate (Sc) complexes and subsequently applied to Michael addition reactions.[197] During the capture of metals via biosorption it is common to observe reduction of the metal down to nanoparticles, though further research is required to fully characterise the size, form (including oxidation state) and location of these valuable catalytic sites, and more specifically how each selected biomass derived support behaves in this regard. Of particular importance is whether the catalysts are truly heterogeneous or instead function in a release and capture mechanism.[198] Figure 3 shows some examples of major chemical transformations currently catalysed by carbon-supported precious or critical metals where biosorbent-supported metals could be substituted.

Precious and critical metals captured and supported on biosorbents will also ultimately play a key role in the conversion of biomass to higher value chemicals, therefore becoming a technology pillar in the progression towards a sustainable bio-based chemical industry.[199] Examples of potential future sustainable applications for these catalysts are highlight in Figure 4; all of the examples shown have been demonstrated at laboratory scale and could become key transformation. The key metals used here are Au, Pt, Pd and Sc.

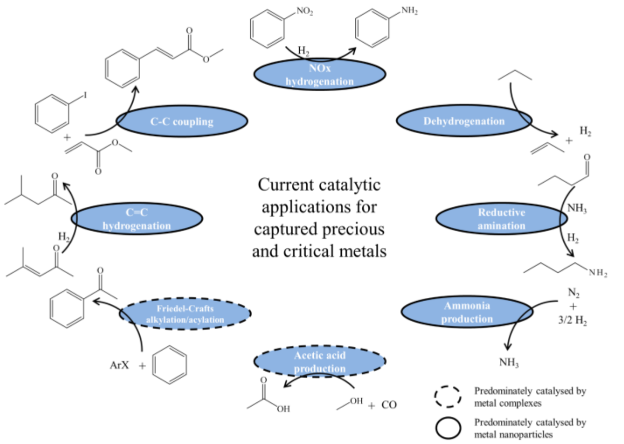

Fig. 3 Examples of current chemical transformation catalysed by precious/critical metals supported on carbonaceous materials. (For each general chemical transformation one specific example is also shown.)[200-205]

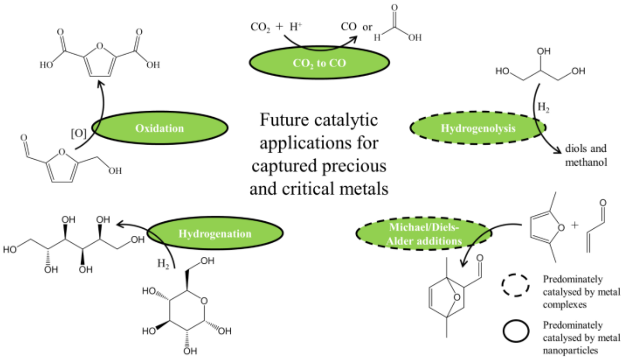

Fig. 4 Examples of potential future applications which could be catalysed by precious/critical metals supported on carbon. (For each general chemical transformation one specific example is also shown.)[199, 206-208]

Functional materials

Metal nanoparticles supported on biopolymers have been extensively researched for a range of functional materials for medical and sensing applications.[209] Polysaccharides used for biosorption, including chitosan, starch and alginates, have been studied due to their high biocompatibility, ease of functionalisation, responsiveness to physiological changes, ease of processing into different structures and role in the reduction of the ions to the metal *in situ*.[209, 210] Metals that have been studied extensively supported on these biopolymers include gold and silver. This therefore offers an excellent opportunity for the re-use of metal-loaded biosorbents.

A review by Daniel-da-Silva and Trindade, highlights the wide variety of uses of metals-supported on polysaccharides for biomedical applications.[209] Silver nanoparticles supported on polysaccharides, particularly modified chitosan and alginates,[211] have been extensively studied for their antimicrobial properties, including in wound dressings, with the polysaccharide promoting stability and preventing nanoparticle aggregation.[212, 213] In some cases, polysaccharide-silver interactions, have had positive synergistic effects.[214] Supported gold nanoparticles have tunable optical properties, which stem from the size, shape, composition and environment of the nanoparticle.[209] This could make them applicable for labelling, imaging, sensing and diagnostic applications, and photothermally triggered drug release (due to heat generation during light absorption at specific wavelengths).

Biotechnological applications of polysaccharide-supported metal nanoparticles include biosensing and bioseparation.[210] Gold and silver nanoparticles supported on chitosan and alginate have been used for the detection of trace and single molecules from biological fluids and cells using Surface-enhanced Raman spectroscopy and for glucose sensing, with other metals including platinum and palladium of interest.[215, 216]

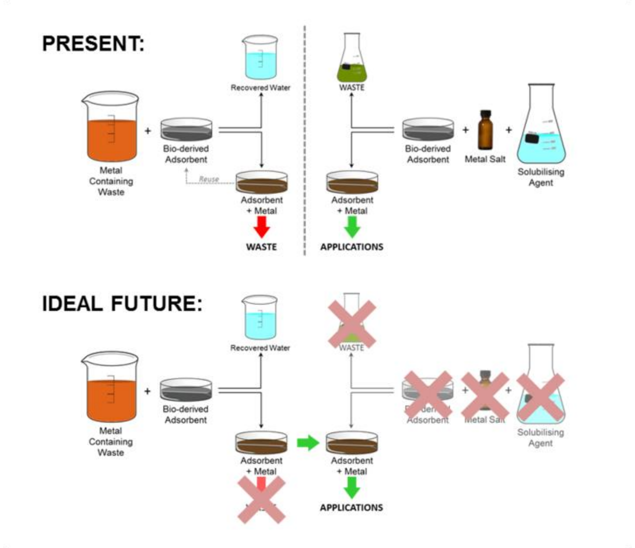

Fig. 5 Schematic showing the present research involving bio-derived adsorbents where there appears to be a divide between research into metal recovery from waste and metal-loaded adsorbents for applications, and the ideal future where the two fields will become interlinked.

Closing the loop

Challenges related to the incorporation of these applications with the metals captured using biosorbents discussed in this review, include control over the shape, size and distribution of the metal nanoparticles, which have a huge impact on the properties of the supported metal. More research into the nature of the metals present in the dissolved streams and the structure of the metals on the surface of the biosorbents following capture is necessary to direct future applications. A further concern will be the toxicity of the materials where mixed metal waste streams are used, especially for biomedical applications. Nevertheless, the potential applications of precious and critical elements within catalysis and for functional materials indicates a new direction of research to develop high-value applications for the metal loaded biosorbents from the remediation of metal wastes. The challenge will be to combine these two strands of research, remediation of critical and precious metals and uses of supported-critical and precious materials, to enable a new closed-loop approach (Figure 5).

Conclusion

To meet the global challenges of elemental sustainability a holistic approach to the extraction, use and recovery of metals must be developed.[6] The use of bio-based methods for the capture, recovery and utilisation of elements (phytoextraction, chelation and adsorption) will become an important topic for green chemistry over the coming years.[11, 217, 218] Biosorption has long been regarded as a low cost method for the remediation of wastes or polluted environments, however, this technique has far greater potential than remediation alone. Bio-derived adsorbents can enable the recovery of elements (many of which are regarded as being of critical importance) and additional value can be obtained by applying these materials in a variety of applications including catalysis, biomedical, antibacterial and energy applications to name but a few. To reach its full potential as a green method for elemental recovery, bio-derived materials must be further developed to include;

- The ability to use flow systems using materials with hierarchical pore structures and good flow characteristics
- Enhancing selectivity by modification with bio-chelates, surface modification or careful selection of the parent biomass (those with specific chemical properties, morphologies or functionalities)
- Exploit the properties of any nanoparticle or nanomaterials that are formed during the adsorption process
- Exploit synergistic effects from mixed metal species
- Develop further industrially relevant examples of biosorbents and their use in green chemistry technologies
- Design materials that are robust and can deal with variable and “emerging” waste streams

By shifting the emphasis from remediation towards the development of efficient, selective adsorption for metal recovery combined with the use of these metal-loaded adsorbents for various applications will aid in closing loops towards the development of a circular economy.[8, 10] This offers real opportunities for the chemical industry to move closer to new efficient systems that will enable the sustainable use of these elements far into the future.

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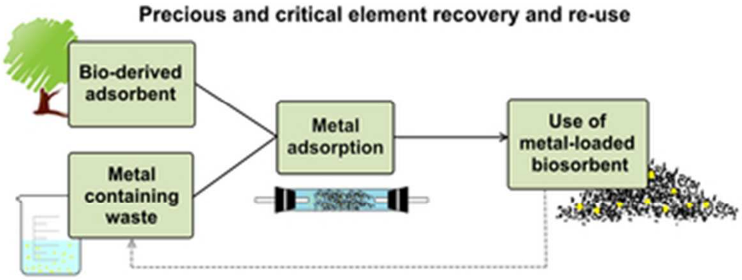

Overview of research in critical and precious metal recovery using biosorption, application to real-life wastes and uses of the metal-loaded materials.
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