metals

MDPI

Review

Bio-Reclamation of Strategic and Energy Critical Metals from Secondary Resources

Sadia Ilyas [1,*], Min-Seuk Kim [2], Jae-Chun Lee [2,*], Asma Jabeen [1] and Haq Nawaz Bhatti [1]

[1] Mineral and Material Chemistry Laboratory, Department of Chemistry,
University of Agriculture Faisalabad (UAF), Faisalabad 38040, Pakistan;
asmajabeen7861@gmail.com (A.J.); profhnbhatti@gmail.com (H.N.B.)
[2] Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM),
Daejeon 305-350, Korea; redkms@kigam.re.kr
* Correspondence: sadiailyas1@yahoo.com (S.I.); jclee@kigam.re.kr (J.-C.L.);
Tel.: +92-41-9200161-69 (S.I.); +82-42-868-3612 (J.-C.L.)

Academic Editor: Peng Cao
Received: 15 April 2016; Accepted: 1 June 2017; Published: 6 June 2017

Abstract: Metals with an average crustal abundance of <0.01 ppm, which are high in supply shortage due to soaring demand, can, under the excessive environmental risk and <1% recycling rate of their production, be termed as 'critical' in a limited geo-boundary. A global trend to the green energy and low carbon technologies with geopolitical scenario is challenging for the sustainable reclamation of these metals from secondary resources. Among the available processes, bio-reclamation can be a sustainable technique for extracting and concentrating these metals. Therefore, in the present paper, the potential reclamation of critical metals (including rare earth elements, precious metals, and a common nuclear fuel element, uranium) via their interaction with microbe/s has been reviewed.

Keywords: bio-reclamation; energy critical metals; microbes-metal interaction; sustainability

1. Introduction

The rare earth elements (REEs) and precious metals (PMs) have remained in metallurgical attraction for a long time. The tendency to occur together in nature, difficulties in their extraction and separation with specific area of applications has placed these metals in the list of critical metals. However, in the recent past, the definition of criticality is certainly not limited to the difficult metallurgy and abundance in the earth's crust (<0.01 ppm). In this technological era, the metals required in advanced materials and technologies for the transition towards a sustainable post-fossil society facing high supply risk due to the market complexities, lack of supply diversity, and geopolitical scenarios are termed as 'critical metals' [1]. Metals in the list of criticality changes with region or country. The organizations like, the American Physical Society and Materials Research Society have termed 'energy-critical elements' (ECEs) as the elements necessary for emerging renewable energy whose unavailability could limit future research & development (R&D) or deployment of a technology [2]. On the other hand, the European Union (EU) has accounted for the political and economic stability of producing countries along with their weak environmental performance to calculate the supply shortage of a particular metal [3]. Hence, commonly a metal can be labelled 'critical' which is facing high shortage in supply, excessive environmental risk and be of significant economic importance under the availability of a limited geo-boundary. In that case, the criticality of metal can simply be presented as follows [4]:

$$\text{Criticality} = \text{Supply risk} \times \text{Vulnerability} = \text{Likelihood of supply disruption} \times \text{Economic Consequences} \quad (1)$$

Notably, the availability of these metals largely influences the energy supply; country's economy, export business, job creation and geopolitical relation of two individual countries [5], hence can also be pronounced as 'strategic critical metals'. Figure 1 presents the list of such metals, including uranium (the major source of non-fossil, nuclear fuel) and gold (widely used for plating other conductor materials besides its economic importance in global trade) [2,3,6]. In the scenario of a mineral deficit country like Korea, all the metals shown in Figure 1 can be on the country's critical-list. Most of these metals are currently being exploited through mining and metallurgy of their fast depleting primary ores in their respective region. Hence, the sustainable and cost-effective processing of these metals from the waste/end-of-life/scrap materials as their alternative sources is an absolute necessity of time. Moreover, metal contamination from waste materials is a major concern because: metals are non(bio)degradable substances which can transform to form their carcinogenic and toxic compounds to transfer across the trophic levels of food-chain and bioaccumulating in living organisms [7–9]. Therefore, reclamation of critical metals from their alternative secondary resources can be a game-changer by overcoming the geo-boundary limitation, mitigating the supply risk and controlling the environmental damage by mining of their primary ores.

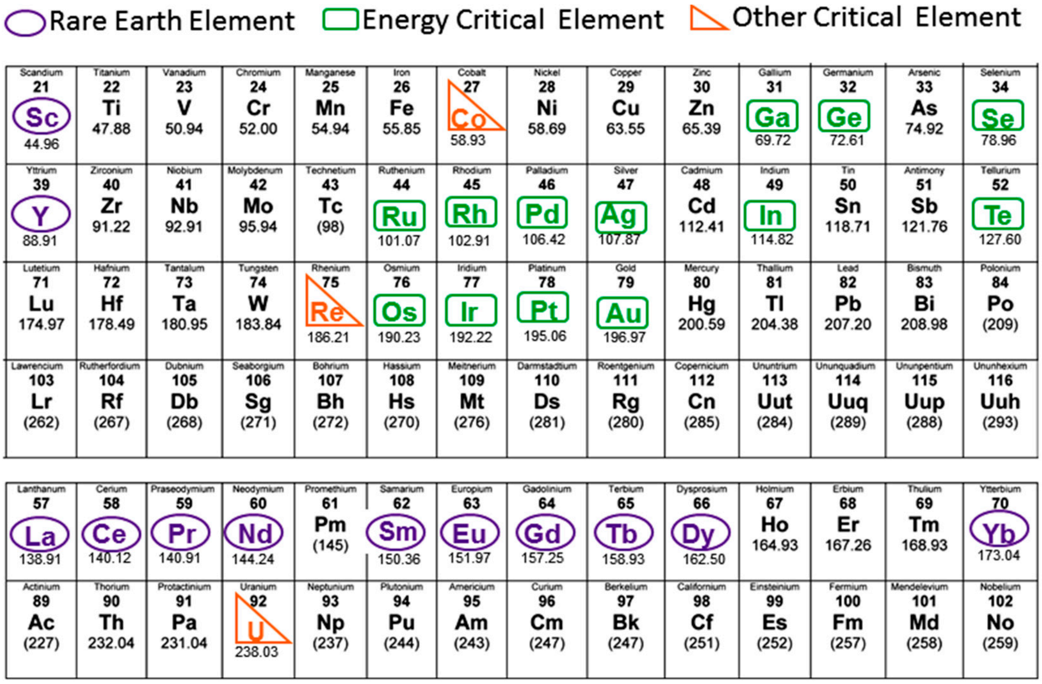

Figure 1. Periodic table indicating the critical and scarce metals taken into this study [1–3].

A variety of reclamation routes have been explored and reviewed so far, including high calorific smelting, large chemical intensive hydrometallurgy, and energy intensive electrometallurgy [6,10–12]. However, the microbe-to-metal/material interactions have attracted renewed attention for a sustainable reclamation of metals from diversified materials [9]. Bio-reclamation including bacterial leaching, control of redox reaction using bacterial treatment, metal adsorption and (impurity) removal by employing dead biomass as the potential sorbents can facilitate the recycling of various critical and valuable metals from diverse secondary materials [13,14]. In this article, we have reviewed the literatures on bio-reclamation techniques (which includes microbial leaching, sorption, reduction and accumulation processes from non-primary sources) of critical metals; wherein the microbes-to-metal interaction, process sustainability and future challenge for the practical implementation of these processes has been discussed.

2. Potentially Important Microbes and Mechanism of Bio-Reclamation

From a bio-reclamation perspective, potentially important bacteria belong to the genus *Acidiphilium*, *Acidithiobacillus*, *Sulfobacillus* and *Leptospirillum* [15]. The most vital bio-reclamating mesophiles belong to *Acidithiobacillus*, including sulfur and iron oxidizing *Acidithiobacillus ferrooxidans* and sulfur oxidizing *Acidithiobacillus thiooxidans*. *Acidithiobacillus ferrooxidans* supplied with a broad metabolic capacity was the first acidophilic bacteria which was used for the bio-metallurgical perspectives. The investigations at the putative boundary of mesophilic and moderately thermophilic conditions at a temperature of 45 °C, showed *Acidithiobacillus caldus* being a dominant sulfur oxidizer; whereas *Leptospirillum* dominates as iron oxidizer. The role of Fe-oxidizing, *Leptospirillum ferrooxidans* in bio-reclamation was lately recognized due to its poor enrichment from samples as compared with the *Acidithiobacillus ferrooxidans*. The prior importance of *Leptospirillum ferrooxidans* in bio-reclamation was due to its mix culture with *Acidithiobacillus thiooxidans*, which could oxidize pyrite on a faster rate than using *Acidithiobacillus ferrooxidans* alone. Such behavior was ascribed to: its high propensity to attach with materials to be leached, a high affinity for Fe^{2+} and the low sensitivity to inhibition by Fe^{3+} [16,17].

Association between the microbial activity and exothermic reaction caused in sulfur containing materials points out the relevance of thermophiles in bio-reclamation process. Moderately thermophilic iron and sulfur-oxidizing microbes were primarily cultured from the mining conditions or hot springs [18,19] and subsequently from the mine-sites of iron ore [20]. Advancement in moderate thermophiles such as *Sulfobacillus thermosulfidooxidans* continues in recent mining operations, including refractory gold heaps undergoing biooxidation [21] and in bio-reclamation of electronic wastes [20,22]. Nowadays extremely thermophilic microorganisms in acidic, sulfidic hot springs have been used for their exceptional ability to oxidize the hard-to-treat materials. These microorganisms have enlarged the bio-reclamation options in terms of temperature and metal tolerance capacity. Figure 2 depicted various modes of microbial-metal interactions for metal mobilization or immobilization.

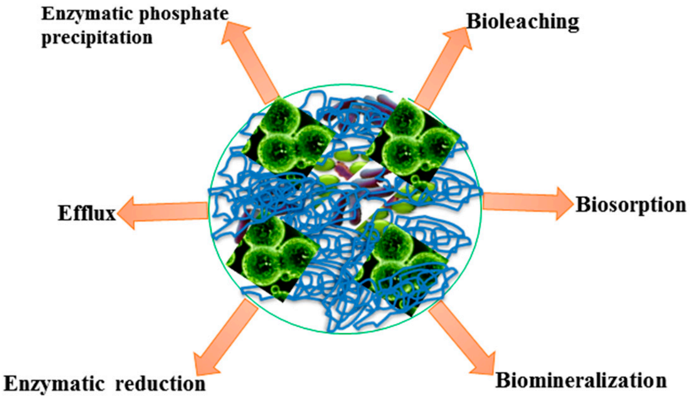

Figure 2. A typical representation of various modes of bio-reclamation process.

Mostly acidophilic autotrophs generate ferric iron and sulfuric acid for biooxidation and enhanced dissolution of associated metals (M) or metal oxide (MO) by direct, indirect, thiosulfate and poly-sulfide mechanisms after additional supplementation of sulfur source as in Equations (2)–(6) and Figure 3 [23,24]. Other than the acidophilic autotrophs, some heterotrophic microbes (*Pseudomonas fluorescens*, *Chromobacterium violaceum*) and fungi (*Penicillium simplicissimum*, *Aspergillus niger*) have also shown potential in bio-reclamation of metals. Employing the heterotrophic microorganisms, metals are usually reclaimed by displacement with H^+ ions or formation of soluble metal species/chelates or the cyanidation with biogenic CN^- [25,26].

$$4FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{bacterial} 2Fe_2(SO_4)_3 + 2H_2O \tag{2}$$

$$2S^0 + 3O_2 + 2H_2O \xrightarrow{bacterial} 2H_2SO_4 \tag{3}$$

$$M + H_2SO_4 + 0.5O_2 \xrightarrow{chemical} MSO_4 + H_2O \tag{4}$$

$$MO + H_2SO_4 \xrightarrow{chemical} MSO_4 + H_2O \tag{5}$$

$$M + 2Fe^{3+} \xrightarrow{chemical} M^{2+} + 2Fe^{2+} \tag{6}$$

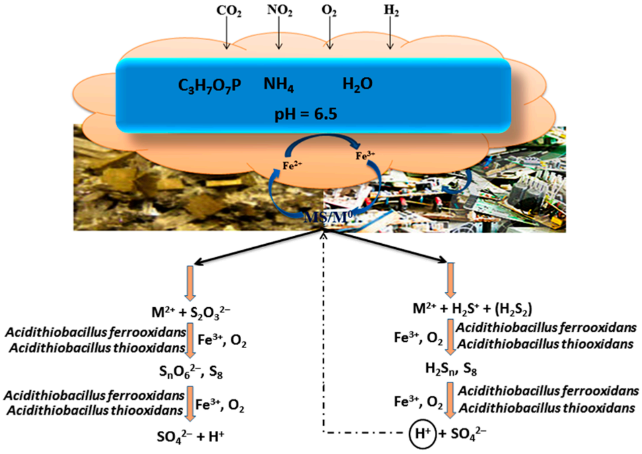

Figure 3. Interaction of *Acidithiobacillus ferrooxidans* with metals on surface of source material [23].

3. Bio-Reclamation of Caritical Metals

3.1. Bio-Reclamation of Rare Earth Elements

The rare earth elements (REEs) are a combination of 17 chemically similar elements, comprised of 15 lanthanides (Z, 57 to 71), scandium (Z, 21) and yttrium (Z, 39), and exhibiting the characteristics of magnetism, fluorescence, and superconductivity. REEs are being used in rechargeable batteries, permanent magnets, catalysts, lamp phosphors, and biomedical applications. Based on the importance, they are sub-grouped as light (La to Sm) and heavy (Eu to Lu) REEs. The heavy REEs are technologically vital for the electronics, defence, and low-carbon renewable energy, and identified as the most critical raw materials with an aggregate demand of ~210,000 tonnes by 2015 [27]. Figure 4 depicts the probable interaction of microbes with REEs and their subsequent leaching. However, exact understanding of the interactions is still not well documented despite a clear interest for developing biotechnology in clean recovery from the mine-sites. Consequently, only a few literatures have reported reclaiming REEs from secondary resources. A study involving the bio-reclamation of REEs from red mud describes the use of *Penicillium tricolor* at 2% (*w/v*) pulp density, could result in the maximum extraction of REEs and radioactive elements [28]. The maximum extraction was achieved under a two-step bio-reclamation process using 10% pulp density. This study provides a basis for seeking the bio-reclamation of REEs from other secondary resources, including the electronic wastes.

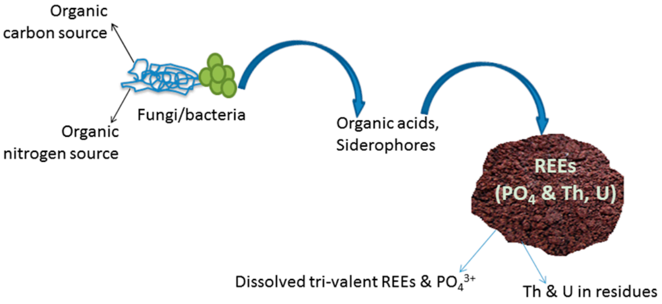

Figure 4. Bio-reclamation of rare earth elements by interactions with heterotrophic microbes.

The bioleaching in presence and absence of Fe/S oxidizing bacteria (*Acidithiobacillus ferrooxidans*) has been studied for yttrium extraction from the waste cathode ray tube (CRT) glass [29]. Notably, the effect of ferric ions can be understood by its ability to influence the redox potential of a bioleaching system [30]. The results revealed a linear enhancement in Y extraction with time, which could reach the maximum yield of 40% and 70% after a 16 days of bioleaching in the presence and absence of ferric ions, respectively [29]. The improved extraction of Y in the absence of ferric ions, attributed to the bacterial activity, was the highest with 3×10^8 cells/mL. A decrease in Y extraction with increase in pulp density indicated its negative effect on bacterial growth. The toxicity generated by the high metal content [31] in CRT (43% Zn and 23% Y) has been identified as the technological limit of this process. Hopfe et al. [32] recently reported the bioleaching of REEs from waste fluorescent powder (12.1% Y, 1.4% Ce, 0.8% Gd, 3.4% La, 0.7% Eu, 0.6% Tb) by using tea fungus Kombucha. The highest leaching yields were obtained in shake cultures either by using the entire Kombucha-consortium or with the supernatant of Kombucha, compared to the leaching yields of isolated *Zygosaccharomyces lentus* and *Komagataeibacter hansenii*. A primarily and effective leaching of Y and Eu indicated the red dye of Y_2O_3:Eu^{3+} could be leached selectively. Approximately 60% and 68% Y was leached after 15 days of bioleaching in stationary and shaken mode, respectively; however, only 0.01% La could be released in both modes. Initially in both cases, a rapid decrease in pH was observed due to the in-situ generation of organic acids, mainly the acetic and gluconic acid. After a prolonged time (over 3 days) it slowed down due to the buffering effect of weak acids. Similar trends on pH profile with in-situ production of organic acids in the bioleaching of electronic waste, red mud, cracked catalysts and monazite ores have been observed in earlier studies [28,33–36]. Reed et al. [36] reported that 60% of the organic acids, mainly gluconic acid, can be produced within the initial 24 h. Using the isolated microbial culture BH1, *Acinetobacter calcoaceticus* GSN8; BH24, *Pseudomonas frederiksbergensis* 37; and A1, *Talaromyces purpureogenus* for producing gluconic acid were however less effective in bioleaching of REE than the bacterium *Gluconobacter oxydans*. Abiotic control experiments showed that an increasing concentration of gluconic acid from 10 to 90 mM could increase the total leaching efficiency of REE from 24% to 45%. The supernatants of *Gluconobacter* B58, containing an average 12.5 mM gluconic acid were more effective for solubilizing the REE from a fluid catalytic cracking (FCC) catalyst than abiotically prepared solutions of 30 and 90 mM gluconic acid (Figure 5) [36].

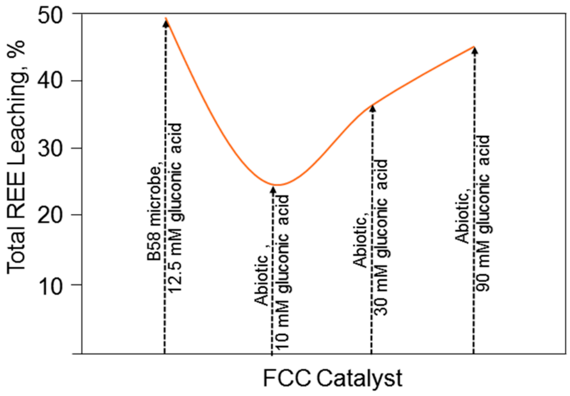

Figure 5. Leaching efficiency of total rare earth elements (REE) from fluid catalytic cracking (FCC) catalyst after 24 h using a four-day B58 culture supernatant producing 12.5 mM gluconic acid and abiotic solution of 10, 30 and 90 mM gluconic acid. Adapted from [36]. Copyright ELSEVIER, 2016.

The interactions of REEs with biogenic phosphates and specific transporter uptake are two recently disclosed processes having the potential to recover the REEs from aqueous waste streams. Firstly, the sorption on, or the encapsulation into the biogenic phosphate nano-minerals and the formation of REE-phosphate complexes were demonstrated using biofilms of *Serratia* strains [37,38]. Using an extremophile, acidophilic methanotrophic *Methylacidiphilum fumariolicum*, Pol et al. [39] observed that the function of methanol dehydrogenase (MDH) in this bacterium strictly depends on the presence of REEs. The analysis of protein structure and alignment of amino acid sequences has revealed that the REE-binding motifs in this particular MDH were also present in other MDH enzymes. This largely indicated that many MDHs are lanthanide dependent. It was assumed that by modifying the structure of protein, the specificity and binding efficiency of protein towards the substrate could be improved [40,41]. Henceforth, a REE-specific transporter to only recognize one particular REE could artificially evolve to concentrate REE in its cell. These approaches may be especially useful in recovering REEs from the aqueous waste streams.

Working with a mixed solution of La, Eu and Y, Texlier et al. [42] observed a preferential adsorption of europium ions onto the dead biomass of *Pseudomonas aeruginosa*. An investigation on the influential presence of metal cations viz. Al^{3+}, Ca^{2+}, Na^{+}, K^{+} and anionic salts viz. NO_3^-, SO_4^{2-}, Cl^- exhibited that the Al^{3+} was more inhibitive cation for adsorbing REEs by *Pseudomonas aeruginosa*. Nevertheless, the presence of thorium or uranyl ions could greatly decrease lanthanum adsorption (at pH $\approx$ 1.0) by *Mycobacterium smegmatis* [43]. Fungal biomasses of *Rhizopusarrhizus*, *Saccharomyces cerevisiae*, *Aspergillus niger* were also examined for biosorption of REEs from various solutions. It has been observed that the presence of glutamate, sulfate, phosphate, chloride, carbonate and ethylenediamine tetraacetate (EDTA) in sorbate solution with metal ratios up to 15, can greatly affect the sorption of lanthanum onto fungal biomass [44]. Table 1 summarizes the R&D works for the biosorption of rare earth elements from various solutions.

Table 1. A summary of various biosorption processes of rare earth elements (*T* = temperature; *t* = contact time; B.D. = biomass dosage).

Microorganism	Composition of Treated Solution	Optimum Condition	Efficacy of Metal Recovery %	References
Pseudomonas aeruginosa	3 mM nitrate solution of: Ca, La, Eu, Yb and Gd	*T*, 20 °C; *t*, 2 h; pH, 5.0; B.D., 0.5 g/L	>90% Gd, and 77% Ca, La, Eu and Yb	[45,46]
Pseudomonas putida	10^{-8} M Ca, Sr, Eu, Zn, Cd, Hg in solution	*T*, 25 °C; *t*, 24 h; pH, 6.4; B.D., 0.075 mg/mL	90% Eu	[47]
Bacillus subtilis	Synthetic nitrate solution containing La	*T*, 25 °C; *t*, 30 min; pH, 4.0; B.D., 3 mg/mL	98% La	[48]
Pseudomonas aeruginosa	Chloride solution containing 0.25–2.0 mM REEs	*T*, 30 °C; *t*, 4 h; pH, 5.0; B.D., 0.124 g/L	Up to 97% REEs	[49]
Shewanella putrefaciens	Synthetic solution containing 0.14 mM Pm	*T*, 15 °C; *t*, 17 h; pH, 5.5; B.D., 5.6×10^{11} cells/L	90% Pm	[50]
Mycobacterium smegmatis and *Bacillus subtilis*	Synthetic Gd-nitrate solution	*T*, 20 °C; *t*, 1 h; pH, 5.0; B.D., 50 g/L	≥98% Gd	[45]
Myxococcus xanthus and *Saccharomyces cerevisiae*	0.4 mM nitrate solution of: La, Co, Mn, Pb, Ag, Zn, Cd	*T*, 28 °C; *t*, 1 h; pH, 4.5; B.D., 0.4 g/L solution	>95% La	[51]
Mycobacterium smegmatis	Nitrate solution of 30 mM Th, U, Yb, Eu, and La	*T*, 20 °C; *t*, 3 h; pH, 1.0–1.5; B.D., 50 g/L	99% REEs	[52]
(a) Saccharomyces cerevisiae; *(b) Rhizopusarrhizus;* *(c) Aspergillus terreus;* *(d) Saccharomyces cerevisiae*	In synthetic solution (mg/L): 1.7 Sc, 7.9 Y, 2.0 Al, 1.7 Fe, 0.35 Ti, 2.1 Ca	*T*, 25 °C; *t*, 30 min; pH, 4.5; B.D., 0.5 g/L	(a) >98%; (b) 87%; (c) 87%; (d) 99% Y	[44]

Using bioaccumulation technique, an acidophilic fungal strain *Penidiella* sp., isolated through enrichment procedures to accumulate Dy, revealed the occurrence of REEs' accumulation onto the cell surfaces. Except for Sc, the strains were found to be accumulated with Dy, Nd, Y, Eu, Pr, Yb, and Tb. The fungal cells, however, did not accumulate the base metal ions viz. Mn^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}, Zn^{3+}, Ga^{3+} [53]. The accumulation of lanthanum onto the surface of *Pseudomonas aeruginosa* inducing crystalline precipitation has been reported by Mullen et al. [48].

Regarding the bio-remediation of rare earths, Ce^{3+} and La^{3+} are primarily required in the oxidation of methanol in microbes thriving on plant leaves via utilizing the methanol exudates [54]. The presence of La^{3+} supports the enrichment and isolation of methylotrophic bacteria, and uses single carbon compounds for energy acquisition to growth. A better knowledge of the microbial role of REEs and their acquisition by microbes will certainly lead to the development of the bioremediation strategies for a clean-up job of rare earth's mine-sites and their recovery from divergent waste streams.

3.2. Bio-Reclamation of Precious Metals

Commercial bioprocessing units use oxidizing conditions and iron or sulfur oxidizers (such as *Acidithiobacillus ferrooxidancs*, *Acidithiobacillus thiooxidans*, *sulfobacillus thermosulfidooxidans*) to generate ferric iron and sulfuric acid to accelerate metals dissolution via direct, indirect, thiosulfate and poly-sulfide mechanisms of biooxidation [24,55]. After initial removal of heavy metal impurities using biooxidation, the precious metals are subjected to biogenic cyanidation as depicted in Figure 6. Precious metals include palladium, Pd; platinum, Pt; rhodium, Rh; iridium, Ir; osmium, Os; ruthenium, Ru and gold, Au can be extracted through biogenic cyanide leaching of wastes/secondary materials. Glycine is a direct precursor of biogenic cyanide that can be produced via the oxidative decarboxylation of glycine performed by the cyanogenic bacteria. The biogenic cyanidation leaching has the advantages to replace the chemical cyanidation in gold leaching under an alkaline condition, making metal's recovery much more efficient, reducing the reagents and transportation costs, and minimizing the environmental issues of chemical cyanidation. This stems from the fact that the cyanogenic bacteria yielded cyanide from glycine for short periods at the late exponential or early stationary phase of its growth. The CN^- produced by *Chromobacterium violaceum*, a cyanogenic bacteria, is substantially used for gold recovery from the various waste streams, as with Equation (7) [26,55].

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \tag{7}$$

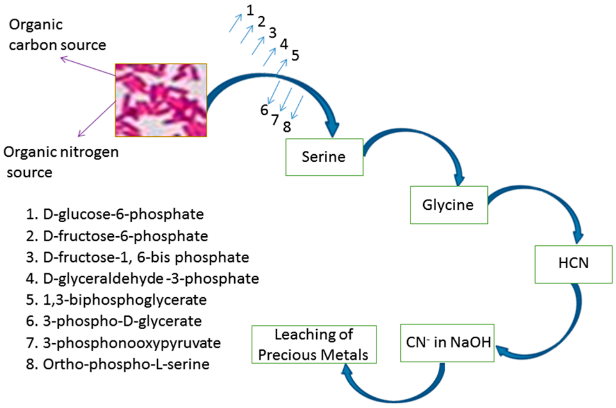

Figure 6. The production route of cyanide by microorganism with the subsequent use in cyanidation of precious metals (arrows are denoting the metabolic pathway of *Chromobacterium violaceum*).

In a preliminary study, Faramarzi et al. [26] reported the feasibility of gold recovery from waste printed circuit boards (PCBs) by *Chromobacterium violaceum*. The biogenic cyanidation of 5 mm × 10 mm sized PCBs, containing 10 mg of gold in each piece, could mobilize 15% gold as dicyanoaurate, $Au(CN)_2^-$ in an alkaline solution. However, the microbe-mediated gold dissolution in presence of *Chromobacterium violaceum* with low metal mobilization did not show the formation of $Au(CN)_2^-$ [56]. Further studies done by Brandl and Faramarzi [57] showed a better performance of *Chromobacterium violaceum* for mobilizing 68.5% gold in 7 days from waste PCBs. In contrast, *Pseudomonas fluorescens* and *Pseudomonas plecoglossicida* formed lower amount of dicyanoaurate. The gold complex was more specifically unstable with *Pseudomonas fluorescens* due to the sorption of dicyanoaurate onto dead biomass or metal-cyanide's degradation [57]. A substantial amount of copper dissolution from e-waste was also obtained due to its high content in the waste and a faster kinetics of cyanidation. Recovery of other precious metals viz. silver and platinum from the e-waste was not very promising because of their resistance and toxic effects on microorganisms. Using wild culture of *Chromobacterium violaceum*, Chi et al. [58] obtained 13% gold and 37% copper in 8 days from mobile phone PCBs of content 0.025% Au and 34.5% Cu. They suggested an improved bio-reclamation of gold can be achieved by reducing the cyanide consumption from the copper containing material, and hence, proposed to substantially decrease copper content prior to undergo for biogenic cyanidation of precious metals. Recently, Tay et al. [59] could produce 70% more cyanide by metabolically-engineered strains of *Chromobacterium violaceum*, pTAC and pBAD in as compared to the cyanide generated by wild culture of *Chromobacterium violaceum*. Such a high amount of cyanide yielded more than twice the amount of gold leaching as well. Moreover, the cyanide production could be decoupled from quorum control by using the exogenous promoters. Modulations in proteome, resulting in a decreased cyanogenesis and an enhanced cyanolysis, may lead to a high amount of cyanide production. Moreover, the increase in cyanide production by the engineered strain does not change the protein levels of these enzymes, associated either directly or indirectly with the cyanolytic pathways. The study demonstrated that for the sustainable and effective bio-reclamation of precious metals from secondary sources, the genetically engineered microbes would be beneficial within their inherent capacity of cyanide production.

Other than the bacterial leaching of precious metals from secondary sources, bio-reduction of metal oxides to their metallic phase has also been studied in some cases. It has been observed that the microbial activity is helpful to generate an in situ reducing environment for metal ion reduction and the subsequent catalytic reactions as well [60–62]. Lenz et al. [63] showed the important role of metal species in reduction potential and bacterial uptake efficiency. For example, bio-reduction of various palladium species has shown the influence of reduction potential for obtaining the reduced Pd^0 nanoparticles using microbes (viz. *Geobacter*), biofilms, and granular sludge [60,64]. In a continuous recovery of palladium from granular sludge in an up-flow anaerobic bed reactor, Pat-Espadas et al. [61] showed the practical feasibility of the bio-recovery. Using *Serratia* sp. biofilms, developed on the polyurethane foam, palladium was recovered as biofilm-Pd^0 nanocatalyst from industrial wastes [65]. The biorecovery of Pd(II) occurs in three concomitant steps: (i) biosorption with biomass via interactions with surface functional groups viz. carboxyl, phosphoryl, and amines; (ii) initial reduction to form Pd^0 nucleation sites; and (iii) the growth of Pd^0 on nuclei surfaces via the autocatalytic reduction of Pd(II) [66]. The results were in line with microbial activity of enzymes such as formate dehydrogenase and hydrogenase used for the bioreduction of Pd(II) [67–70]. Subsequent studies demonstrated that the metabolic activity of microorganisms is not essential to form the bio-Pd^0 [60,66]. The applicability of metal-reducing bacteria like *Shewanella alga*, *Desulfovibrio vulgaris* in manufacturing the nanoparticles of gold and platinum has also been explored, but yet to be explored with waste streams [71]. The uses of native and palladized *Desulfovibrio desulfuricans* in recovery of precious metals have shown selectivity for Au over Pt and Pd from an e-waste leachate [72].

Employing the biosorption technique for ruthenium recovery from a metal-plating effluent and process streams of acetic acid production by *Rhodopseudomonas palustris* and *Corynebacterium glutamicum* strains has given inspiring results. The experimental results showed that an acid pre-treatment of *Rhodopseudomonas palustris* cells could improve Ru-loading from 86 to 145 mg/g dry cells along with good selectivity over the co-existing metals Ni and Zn in effluent [73]. Polyethyleimine (PEI)-coated *Corynebacterium glutamicum* fibers yielded 110 mg/g Ru-loading from an acetic acid solution. This result was a 16.5-fold higher efficiency than the commercially used ion-exchange resin [73], and 6.9-fold higher with the surface modified biomass blended with chitosan [74]. The R&D works performed on reclamation via biosorption of precious metals from various secondary sources have been summarized in Tables 2–5. By analyzing the presented Tables, it can be stated that the use of specific microbes along with their surface modification strategies may lead to the selective binding of these critical metals from their waste streams of complex nature.

Table 2. A summary for the biosorption studies of gold by dead biomass of algae (T = temperature; t = contact time; B.D. = biosorbent dosage).

Algae	Composition of Treated Solution	Optimum Process Conditions	Efficacy of Gold Recovery %	Remarks	References
Chlorella vulgaris	A solution containing 10^{-4} M of each Cr^{3+}, Cu^{2+}, Zn^{2+}, Au^{3+}, Hg^{2+}	T, 30 °C; t, 12 h; pH, 2; B.D., 5 mg/mL solution	90%	Lab scale study; except the $AuCl_4^-$ and $Cr(H_2O)_6^{3+}$ all other metals taken in oxidized form	[75]
Sargassum natans	8.5–1000 mg gold with other metal ions UO_2^{2+}, Pb^{2+}, Zn^{2+}, Ag^+ in solution	T, 30 °C; t, 2 h; pH 2.5	420 mg/g gold	Various cationic species of gold was used in lab scale study	[76]
Sargassum fluitans	2.2 mM gold in cyanide solution	T, 30 °C; t, 4 h; pH 2.0; B.D., 20 mg/150 mL solution	97%	Gold ions, Laboratory Scale Laboratory Scale	[77]
Alginate cross-linked with $CaCl_2$	Synthetic solution containing 25–500 ppm gold as $HAuCl_4$	T, 25 °C; t, 4 h; pH, 2.0; B.D., 0.075 g/75 mL solution	98%	Colloidal gold Laboratory Scale	[78]
Alginate cross-linked with $CaCl_2$	Synthetic solution containing 25–500 mg/L silver as $AgNO_3$	T, 25 °C; t, 4 h; pH, 2.0; B.D., 0.075 g/75 mL solution	85%	Colloidal Siver Laboratory Scale	[78]
De-alginated Seaweed Waste	Synthetic solution of gold	T, 25 °C; pH, 3.0; B.D., 0.5 g/mL solution	92%	Colloidal gold Laboratory Scale	[79]

Table 3. A summary of the biosorption studies of gold and silver by dead biomass of fungi and yeast (T = temperature, t = contact time, B.D. = biosorbent dosage).

Microbe Used	Composition of Treated Solution	Optimum Process Conditions	Efficacy of Metal Recovery %	Remarks	References
Cladosporium cladosporioides	Synthetic solution of gold	T, 30 °C; t, 30 min; pH, 4.0; B.D., 0.05 g/25 mL	96.6 mg Au/g biomass dosage	Lab study recovering the colloidal gold	[80]
Cladosporium cladosporioides	Synthetic solution containing Ag^+	T, 30 °C; t, 30 min; pH, 4.0; B.D., 0.05 g/25 mL	15.2 mg Ag/g biomass dosage	-	[80]
Rhizopus arrhizus	8.5–1000 mg gold with other metal ions UO_2^{2+}, Pb^{2+}, Zn^{2+}, Ag^+ in solution	T, 30 °C; t, 30 min; pH 2.5; B.D., 0.5 mg/mL	92–95% gold	Lab study recovering the colloidal gold	[76]
PVA-immobilized biomass (*Fomitopsis carnea*)	10–100 mg/L gold solution	T, 25 °C; t, 33.3 h; pH, 1.0–13.0; B.D., 5 g/100 mL	~80% gold	Lab study recovering the colloidal gold	[81]
Aspergillus niger	2.5–1000 mg/L silver as $AgNO_3$	T, 30 °C, t, 1 h; pH, 7; B.D., 2 g/25 mL solution	75% silver	Lab study recovering the colloidal silver	[82]
Neurosporacrassa	2.5–1000 mg/L silver as $AgNO_3$	T, 30 °C; t, 1 h; pH, 7.0; B.D., 2 g/25 mL solution	68.2% silver	Lab scale study recovering the colloidal silver	[82]
Fusarium oxysporium	2.5–1000 mg/L silver as $AgNO_3$	T, 30 ; t, 1 h; pH, 7.0; B.D., 2 g/25 mL solution	57.5% silver	Lab scale study recovering the colloidal silver	[82]

Table 4. A summary of the biosorption studies of precious metals using protein biomass (T = temperature, t = contact time, B.D. = biosorbent dosage).

Protein Used	Composition of Treated Solution	Optimum Condition	Efficacy of Metal Recovery %	References
Hen egg shell membrane	1 g/L $KAu(CN)_2$, $HAuCl_4$	T, 25 °C; t, 2 h; pH, 3.0; B.D., 0.25–0.35 g/50 mL	147 mg Au^+/g 618 mgAu^{3+}/g	[83]
Lysozyme from hen egg white	Cu-refining solution containing 82 g/L Au, 3.8 b/L Pt and 21 g/L Pd	T, 25 °C; t, 1 h; pH, 4.0; B.D., 2 mg/10 mL	165 g/kg Au; 11 g/kg Pt; 1 g/kg Pd	[84]
Alfalfa	0.3 mM of each metal ions: Au^{3+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Pb^{2+}, Ni^{2+}, Zn^{2+}	T, 30 °C; t, 1 h; pH, 5.0; B.D., 5 mg/mL	58% Au	[85]
Condensed-tannin gel	Synthetic solution of Pd	T, 25 °C; t, 3 days; pH, 2.0; B.D., 3–35 mg/150 mL	95% Pd	[86]
Bayberry tannin immobilized collagen fiber membrane	Chloride solution containing 48.8 mg/L Pd and Pt each	T, 40 °C; t, 4 h; pH, 4.0; B.D., 0.1 g membrane	97.4% Pd and 94% Pt	[87]
Acid-washed *Ucides cordatus* (waste crab shells)	Synthetic cyanide solution containing 2.2 mM gold	T, 25 °C; t, 24 h; pH, 3.4; B.D., 40 mg/20 mL solution	92% Au	[88]
Sulfur derivative of chitosan	Synthetic gold solution in 1 M HCl	T, 25 °C; t, 5 days; pH, 2.0–3.0; B.D., 8 mg/150 mL solution	400 mg Au/g B.D.	[89]
Glutaraldehyde crosslinked derivatives of chitosan (GCC, RADC)	Synthetic gold solution in 1 M HCl	T, 25 °C; t, 5 days; pH, 2.0–3.0; B.D., 8 mg/150 mL solution	600 mg Au/g B.D.	[89]
Thiourea derivative of chitosan	20 mg/L Pt solution	T, 25 °C; t, 72 h; pH, 2.0; B.D., 10 mg/100 mL solution	120 mg Pt/g B.D.	[90]
Glutaraldehyde crosslinked chitosan	50 mg/L Pd and 20 mg/L Pt	T, ~20 °C; t, 72 h; pH, 2.0; B.D., 10 mg/100 mL solution	400 mg Pd and 120 mg Pt/g B.D.	[91,92]
Chitosan derivatives	10–20 mg/L Pd and 20–40 mg/L Pt	T, ~20 °C; t, 3 days; pH, 2.0; B.D., 3–35 mg/150 mL solution	1.3 mM Pd and 0.8 mM Pt/g B.D.	[93]

Table 5. A summary of the biosorption studies of precious metals using dead bacterial biomass (T = temperature, t = contact time, B.D. = biosorbent dosage).

Bacteria Used	Composition of Treated Solution	*Optimum Condition	Efficacy of Metal Recovery %	References
Streptomyces erythraeus and *Spirulina platensis*	1 g/L $KAu(CN)_2$, $HAuCl_4H_2O$	T, 25 °C; t, 2 h; pH, 3.0; B.D., 0.25–0.35 g/50 mL	99% and 98% Au, respectively	[83]
Desulfovibrio desulfuricans	Synthetic solution: 5–50 mg/L Pd and Pt	T, 30 °C; t, 4 days; pH, 3.0; B.D., 50 mg/L solution	90% Pd and 92% Pt	[93]
Bacillus subtilis	Synthetic CN^- containing 2.2 mMAu	T, 30 °C; t, 4 h; pH, 2.0; B.D., 40 mg/20 mL solution	97% Au	[77]

3.3. Bio-Reclamation of Other Critical Metals

Due to the extensive uses of selenium and tellurium in electronics, semi-conductors and solar cells, their scarcity and uneven distribution, it necessitates the recovery methods of these metals from waste materials/solutions [94,95]. The microorganism *Pseudomonas mendocina* can reduce tellurium from its higher oxidation states (+2, +4 and +6) to Te^0 [96,97]. In an integrated process of recovery of critical metals from used CdTe solar cells, Rajwade and Paknikar [96] firstly employed fungal strains for selective removal of silver and cadmium from acidic solution. Then, *Pseudomonas mendocina* could lead to reductive precipitation of Te^0. In a recent study, Te^0 was directly recovered using *Pseudomonas* sp. (strain EPR3) from the divergent sources, anode slime of copper, and TeO_2/CdTe/Bi_2Te_3 used material [97]. The occurrence of several inter-related and coupled processes was observed during the bacterial speciation of tellurium. In the presence of microbial cultures, the soluble metal species diffuse across the cell membrane, inside which a reversible redox reaction simultaneously takes place with the methylation. As a result of this, an internal bacterial precipitation of Te^0 occurs. Some of the gaseous species of tellurium diffused out through the cell membrane which may volatize to atmosphere or reform the soluble tellurite by following the Challenger mechanism [97]. However, the microbial volatilization of metals like Te and Se poses serious risks to the environment and human health.

Uranium from its resources including the waste materials is processed by chemical/bacterial leaching in sulfuric acid by following Equation (8) below.

$$UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+} \tag{8}$$

Extraction of uranium from various sources has been a long-term quest due to its strategic importance in defence, and civil nuclear industry. The anthropogenic activities from mining to generation of spent fuel have led to uranium contamination in the environment [98–100]. Therefore, the microbial strategy has been explored not only to reclaim but also for remediation purposes. The interactions between uranium and bioorganism involve different mechanisms, certainly not limited to biosorption on the cell surface, bioprecipitation as hydrogen uranyl phosphate (HUO_2PO_4), bioaccumulation in polyphosphate granules, and bioreduction as uraninite (UO_2). Bio precipitation of uranium as HUO_2PO_4 from waste streams using bacterial phosphate has long been studied for hydrolytic release of inorganic phosphates [100]. To improve the economy of bioprecipitation, Paterson-Beedle et al. [38] used phytic acid, a waste product of plants as the phosphate source in the system. Furthermore, the phosphatase activity of microbial cultures was improved by the overexpression of phosphatase through genetic engineering. The bacterial reduction of uranium from the +6 to +4 state is a potent method of bioremediation for in situ immobilization and remediation of subsurface environment [101]. This approach is cost-effective compared to the pump and treat remediation; however, supply of electron donors, maintenance of proper redox environment and long durability of bio reduced uranium (+4) precipitates have been found to be challenging. The exploitation of 349 mg U/kg black shale using *Acidithiobacillus ferrooxidans* has been investigated by comparing the effect of inoculation and non-inoculation reactor [102]. It was observed that the batch-type reactor inoculated with microbial cells exhibited a higher redox potential, lower pH and higher quantity of ferric ions than that which was observed for the non-inoculated reactor until 200 h. The condition facilitated by microbial activity could efficiently improve the bioleaching of uranium; however, with sufficient nutrients and Fe^{3+} as energy source, the indigenous microorganisms in non-inoculated black shell could also be activated over time. The study revealed a scope of cost reduction by the means of lower consumption of Fe^{2+} and nutrients in the system [102].

Rhenium, one of the energy-critical elements has a prime use in Pt-Re catalysts [103]. A study on rhenium extraction from spent Pt-Re catalyst using *Bacillus megaterium* as a cyanogenic bacterium has been reported by Motaghed et al. [104]. The response surface methodology was applied by keeping pulp density and initial glycine concentration as two main influential parameters for extracting the critical metals; however, it was found to be better only to extract the Re. After seven days of bioleaching under the optimal condition of 40 g/L pulp density and 12.8 g/L initial concentration of glycine, 98% Re could be leached with only 16% Pt in leach liquor. During the bioleaching, an increase in free cyanide concentration to 3.6 mg/L under the varied pH (6.7 to 9.0) and dissolved oxygen concentration (2 to 5 mg/L) clearly demonstrated the growth characteristics of *Bacillus megaterium*. A lower leachability of Pt can be attributed to its resistance to being mobilized using the cyanogenic microorganisms [26,105]. Recovery of Re from a waste water employing biosorption technique has also been studied. Using the brown algae *Laminaria japonica* in its modified cross-link gel structure exhibited a maximum 97% sorption with the capacity 37.2 mg/g at pH 6.0 [106]. The result showed a higher affinity for Re in comparison with the earlier used sorbents of persimmon and orange peel [107,108]. This indicated the positive effect of H_2SO_4-modified structure on rhenium adsorption that was resultant of the increased surface area of the sorption sites on algae cell walls.

4. Prospects for the Bio-Reclamation of Critical Metals from Secondary Resources

The stringent regulations on environmental pollutions and constraints on practicing the current operations will create demand for new methodologies to recover the critical metals from waste streams, providing an ideal situation for bio-reclamation approaches. Notably, the particular microbe-to-REE interactions and leaching mechanism have hardly been focused upon and we are facing challenges as their bio-geo-chemistry is stable towards the redox transformations. For such a challenging task, a multidisciplinary approach of various research communities belonging microbiology, metallurgy, and chemistry to unfold the complexation of critical metals with biogenic lixiviants and/or their enrichment/separation using the bio-accumulation/sorption/reduction would be much needed.

Reclamation of critical metals by heterotrophic bioleaching is far less discussed, despite its distinctive potential. Heterotrophic bio-reclamation using indigenous fungal species could be feasible to recover REEs from solid wastes. Biogenic organic acids coupled with biogenic chelators could be efficiently employed to liberate the REEs from divergent wastes. Extensive uses of microorganisms in leaching of precious metals have been restricted by the limited exploitation of cyanogenic microbes only to *Chromobacterium violaceum*. Therefore, the construction of a metabolic engineered strain of related microbial cultures can produce more cyanide in lixiviant that may enhance the recovery by several fold compared to using the wild culture. Immobilization of bacterial cells on supports, like polyurethane foam and design of integrated-column operations can lead to efficient recovery of metals. The critical metals able to form insoluble phosphates can be amenable for recovery via the precipitation-crystallization route through the biogenic production of high phosphate ligands locally. Employing the biosorption technique, the microbial biomass and its constituents (viz. bacteria, yeast, fungi, algae, derived from activated sludge or fermentation waste, including fast growing microorganism crab shells and seaweeds) can be potential sorbent material for critical metals recovery.

Overall, the most important factor is the practical implementation of lab scale technology to the actual systems. Indeed, microbe-to-metal interactions have been efficiently employed in exploitation of primary ores, but are not sufficiently investigated to be commissioned for reclamation of strategic and energy critical metals from secondary sources. In an actual system, the conditions of waste streams like extreme acidic/alkaline pH, high amount of total dissolved solids, strong ionic strength, presence of organics and undesired toxic metals are the bottlenecks which can deviate the reclamation efficiency of critical metals, because most of the lab studies are performed under ideal conditions using synthetic solutions. Notably, critical/scarce metals in the waste solutions remain in trace amounts, sometimes as micro-sized colloids, and are sorbed onto suspended materials or as complex compound in solid wastes like alloys, scraps, metallurgical slags; hence, bio-reclamation should furthermore focus on "unfavorable" conditions and combination of metals that cannot be separated well by either the pyro or hydro(chemical) route of metallurgy.

5. Conclusions

Bio-reclamation of critical metals from the secondary/urban mine resources can be attractive in economic and technical terms. The microbial approach does not require high capital to invest, energy for smelting or electro-reduction; and a minimized generation of new waste compared to the conventional extraction route of REEs and other critical metals are major advantages which can mitigate their supply risk in a sustainable manner. However, the complex nature of secondary materials with a minor amount of critical metals compared to the other co-engineered metals is the most difficult challenge. Bioleaching of REEs from the urban mined sources is quite different than using the phosphate solubilizing bacteria in the case of primary ores, despite the organic acid producing microorganisms being useful to leach the REEs. In the case of precious metals like Au, Ag, Pt, and Pd, the biogenic cyanidation is the promising one. Reclaiming the precious metals of very low concentration from various waste stream solutions, biosorption and bioaccumulation techniques have been employed frequently to get the prominent recovery of critical metals. In some cases, like for Pd and Te, the bio-reduction has also been reported to directly recover the critical metals in nano-sized metallic form. Nevertheless, the reported literature on bio-reclamation critical metals belongs to only lab scale basic research; therefore, a lot of efforts are needed to get the real benefit of microbial strategy for treating the urban mined secondary materials.

Acknowledgments: This work was supported by the Basic Research Project (GP2015-013) of the Korea Institute of Geoscience and Mineral Resources (KIGAM), funded by the Ministry of Science, ICT and Future Planning of Korea.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hurd, A.J.; Kelley, R.L.; Eggert, R.G.; Lee, M.-H. Energy-critical elements for sustainable development. *MRS Bull.* **2012**, *37*, 405–410. [CrossRef]
2. Jaffe, R.; Price, J.; Ceder, G.; Eggert, R.; Graedel, T.; Gschneidner, K.; Hitzman, M.; Houle, F.; Hurd, A.; Kelley, R.; et al. *Energy Critical Elements: Securing Materials for Emerging Technologies*; Materials Research Society/American Physical Society: Washington, DC, USA, 2011.
3. Catinat, M. *Critical Raw Materials for the EU—Report of the Ad-Hoc Working Group on Defining Critical Raw Materials*; EC: Brussels, Belgium, 2010.
4. Glöser, S.; Espinoza, L.T.; Gandenberger, C.; Faulstich, M. Raw material criticality in the context of classical risk assessment. *Resour. Policy* **2015**, *44*, 35–46. [CrossRef]
5. Hennebel, T.; Boon, N.; Maes, N.; Lenz, M. Biotechnologies for critical raw material recovery from primary and secondary sources: R&D priorities and future perspectives. *New Biotechnol.* **2015**, *32*, 121–127.
6. Srivastava, R.R.; Kim, M.; Lee, J.; Jha, M.K.; Kim, B.-S. Resource recycling of superalloys and hydrometallurgical challenges. *J. Mater. Sci.* **2014**, *49*, 4671–4686. [CrossRef]
7. Kumar, A.; Tripathi, Y.C.; Singh, S.; Tripathi, G. Metal pollutants in living environment: Threat and challenges. In *Dimensions of Environmental Threats*; Kumar, A., Ed.; Daa Publishing House: New Delhi, India, 2003; pp. 1–20.
8. Pathak, P.; Srivastava, R.R.; Ojasvi. Assessment of legislation and practices for the sustainable management of waste electrical and electronic equipment in India. *Renew. Sustain. Energy Rev.* **2017**, *78*, 220–232. [CrossRef]
9. Abdi, O.; Kazemi, M. A review stud of biosorption of heavy metals and comparison between different biosorbents. *J. Mater. Environ. Sci.* **2015**, *6*, 1386–1399.
10. Jha, M.K.; Lee, J.; Kim, M.; Jeong, J.; Kim, B.-S.; Kumar, V. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: A review. *Hydrometallurgy* **2013**, *133*, 23–32. [CrossRef]
11. Jha, M.K.; Kumari, A.; Panda, R.; Kumar, J.R.; Yoo, K.; Lee, J.Y. Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* **2016**, *165*, 2–26. [CrossRef]
12. Ilyas, S.; Lee, J. Biometallurgical recovery of metals from waste electrical and electronic equipment: A review. *Chem. Bioeng. Rev.* **2014**, *1*, 148–169. [CrossRef]
13. Ilyas, S.; Lee, J.; Kim, B.-S. Bioremoval of heavy metals from recycling industry electronic waste by a consortium of moderate thermophiles: Process development and optimization. *J. Clean. Prod.* **2014**, *70*, 194–202. [CrossRef]
14. Ilyas, S.; Lee, J. Bioprocessing of electronic scraps. In *Microbiology for Minerals, Metals, Materials and the Environment*; Abhilash, Pandey, B.D., Natrajan, K.A., Eds.; CRC Press: Boca Raton, FL, USA, 2015; pp. 307–328.
15. Norris, P.R.; Burton, N.P.; Foulis, N.A. Acidophiles in bioreactormineral processing. *Extremophiles* **2000**, *4*, 71–76. [CrossRef] [PubMed]
16. Markosyan, G.E. A new iron-oxidizing bacterium: *Leptospirillum ferrooxidans* gen. et sp. nov. *Biol. Zh. Arm.* **1972**, *25*, 26–29.
17. Sand, W.; Rohde, K.; Sobotke, B.; Zenneck, C. Evaluation of *Leptospirillum ferrooxidans* for leaching. *Appl. Environ. Microbiol.* **1992**, *58*, 85–92. [PubMed]
18. Brierley, J.A. Thermophilic iron-oxidizing bacteria found in copper leaching dumps. *Appl. Environ. Microbiol.* **1978**, *36*, 523–525. [PubMed]
19. Brierley, C.L. Biogenic extraction of uranium from ores of the grants region. In *Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena*; Murr, L.E., Torma, A.E., Brierley, J.A., Eds.; Academic Press: New York, NY, USA, 1978; pp. 345–351.

20. Ilyas, S.; Ruan, C.; Bhatti, H.N.; Ghauri, M.A.; Anwar, M.A. Column bioleaching of metals from electronic scrap. *Hydrometallurgy* **2010**, *101*, 135–140. [CrossRef]
21. Brierley, J.A. Heap leaching of gold bearing deposits, theory and operational description. In *Biomining: Theory, Microbes and Industrial Processes*; Rawlings, D., Ed.; Springer: New York, NY, USA, 1997; pp. 103–115.
22. Ilyas, S.; Anwar, M.A.; Niazi, S.B.; Ghauri, A. Bioleaching of metals from electronic scrap by moderately thermophilic acidophilic bacteria. *Hydrometallurgy* **2007**, *88*, 180–188. [CrossRef]
23. Valdes, J.; Pedroso, I.; Quatrini, R.; Dodson, R.J.; Tettelin, H.; Blake, R., 2nd; Eisen, J.A.; Holmes, D.S. *Acidithiobacillus ferrooxidans* metabolism: From genome sequence to industrial applications. *BMC Genom.* **2008**, *9*, 597.
24. Ilyas, S.; Lee, J.; Shin, D.; Kim, B.-S. Biohydrometallurgical processing of non-ferrous metals from copper smelter slag. *Adv. Mater. Res.* **2013**, *825*, 250–253. [CrossRef]
25. Bosshard, P.P.; Bachofen, R.; Brandl, H. Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. *Environ. Sci. Technol.* **1996**, *30*, 3066–3070. [CrossRef]
26. Faramarzi, M.A.; Stagars, M.; Pensini, E.; Krebs, W.; Brandl, H. Metal solubilization from metal-containing solid materials by cyanogenic *Chromobacterium violaceum*. *J. Biotechnol.* **2004**, *113*, 321–326. [CrossRef] [PubMed]
27. Binnemans, K.; Jones, P.T.; Van, G.T.; Blanpain, B.; Yiannis, Y.P. Towards zero-waste valorisation of rare-earth-containing industrial process residues: A critical review. *J. Clean. Prod.* **2015**, *99*, 17–38. [CrossRef]
28. Qu, Y.; Lian, B. Bioleaching of rare earth and radioactive elements from red mud using *Penicillium tricolor* RM-10. *Bioresour. Technol.* **2013**, *136*, 16–23. [CrossRef] [PubMed]
29. Beolchini, F.; Fonti, V.; Dell'Anno, A.; Rocchetti, L.; Veglio, F. Assessment of biotechnological strategies for the valorization of metal bearing wastes. *Waste Manag.* **2012**, *32*, 949–956. [CrossRef] [PubMed]
30. Cordoba, E.M.; Munoz, J.A.; Blazquez, M.L.; Gonzalez, F.; Ballester, A. Leaching of chalcopyrite with ferric ion. Part II: Effect of redox potential. *Hydrometallurgy* **2008**, *93*, 88–96. [CrossRef]
31. Sugio, T.; Domatsu, C.; Tano, T.; Imai, K. Role of ferrous ions in synthetic cobaltous sulfide leaching of *Thiobacillus ferrooxidans*. *Appl. Environ. Microbiol.* **1984**, *48*, 461–467. [PubMed]
32. Hopfe, S.; Flemming, K.; Lehmann, F.; Mockel, R.; Kutschke, S.; Pollmann, K. Leaching of rare earth elements from fluorescent powder using the tea fungu Kombucha. *Waste Manag.* **2017**, *62*, 211–221. [CrossRef] [PubMed]
33. Brandl, H.; Bosshard, R.; Wegmann, M. Computer-munching microbes: Metal leaching from electronic scrap by bacteria and fungi. *Hydrometallurgy* **2001**, *59*, 319–326. [CrossRef]
34. Hassanien, W.A.G.; Desouky, O.A.N.; Hussien, S.S.E. Bioleaching of some rare earth elements from Egyptian monazite using *Aspergillus ficuum* and *Pseudomonas aeruginosa*. *Walailak J. Sci. Technol.* **2013**, *11*, 809–823.
35. Shin, D.; Kim, J.; Kim, B.-S.; Jeong, J.; Lee, J. Use of phosphate solubilizing bacteria to leach rare earth elements from monazite-bearing ore. *Minerals* **2015**, *5*, 189–202. [CrossRef]
36. Reed, D.W.; Fujita, Y.; Daubaras, D.L.; Jiao, Y.; Thompson, V.S. Bioleaching of rare earth elements from waste phosphors and cracking catalysts. *Hydrometallurgy* **2016**, *166*, 34–40. [CrossRef]
37. Handley-Sidhu, S.; Hriljac, J.A.; Cuthbert, M.O.; Renshaw, J.C.; Pattrick, R.A.D.; Charnock, J.M.; Stolpe, B.; Lead, J.R.; Baker, S.; Macaskie, L.E. Bacterially produced calcium phosphate nanobiominerals: Sorption capacity, site preferences, and stability of captured radionuclides. *Environ. Sci. Technol.* **2014**, *48*, 6891–6898. [CrossRef] [PubMed]
38. Paterson-Beedle, M.; Readman, J.E.; Hriljac, J.A.; Macaskie, L.E. Biorecovery of uranium from aqueous solutions at the expense of phytic acid. *Hydrometallurgy* **2010**, *104*, 524–528. [CrossRef]
39. Pol, A.; Barends, T.R.M.; Dietl, A.; Khadem, A.F.; Eygensteyn, J.; Jetten, M.S.M.; Op den Camp, H.J.M. Rare earth metals are essential for methanotrophic life in volcanic mudpots. *Environ. Microbiol.* **2014**, *16*, 255–264. [CrossRef] [PubMed]
40. Kuroda, K.; Ueda, M. Molecular design of the microbial cell surface toward the recovery of metal ions. *Curr. Opin. Biotechnol.* **2011**, *22*, 427–433. [CrossRef] [PubMed]
41. Moriwaki, H.; Koide, R.; Yoshikawa, R.; Warabino, Y.; Yamamoto, H. Adsorption of rare earth ions onto the cell walls of wild-type and lipoteichoic acid-defective strains of *Bacillus subtilis*. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 3721–3728. [CrossRef] [PubMed]
42. Texier, A.C.; Andrès, Y.; Illemassene, M.; Le Cloirec, P. Characterization of lanthanide ions binding sites in the cell wall of *Pseudomonas aeruginosa*. *Environ. Sci. Technol.* **2000**, *34*, 610–615. [CrossRef]

43. Andrès, Y.; MacCordick, H.J.; Hubert, J.C. Adsorption of several Actinide (Th, U and Lanthanide (La, Eu, Yb) ions to Mycobacterium smegmatis. *Appl. Microbiol. Biotechnol.* **1993**, *39*, 413–417. [CrossRef]
44. Karavaiko, G.I.; Kareva, A.S.; Avakian, Z.A.; Zakharova, V.I.; Korenevsky, A.A. Biosorption of scandium and yttrium from solutions. *Biotechnol. Lett.* **1996**, *18*, 1291–1296. [CrossRef]
45. Andrès, Y.; Thouand, G.; Boualam, M.; Mergeay, M. Factors influencing the biosorption of gadolinium by microorganisms and its mobilization from sand. *Appl. Microbiol. Biotechnol.* **2000**, *54*, 262–267. [PubMed]
46. Texier, A.C.; Andrès, Y.; Le Cloirec, P. Selective biosorption of lanthanide (La, Eu, Yb) ions by *Pseudomonas aeruginosa*. *Environ. Sci. Technol.* **1999**, *33*, 489–495. [CrossRef]
47. Ledin, M.; Pedersen, K.; Allard, B. Effects of pH and ionic strength on the adsorption of Cs, Sr, Eu, Zn, Cd and Hg by *Pseudomonas Putida*. *Water Air Soil Pollut.* **1997**, *93*, 367–381. [CrossRef]
48. Mullen, M.D.; Wolf, D.C.; Ferris, F.G.; Beveridge, T.J.; Flemming, C.; Bailey, G.W. Bacterial sorption of heavy metals. *Appl. Environ. Microbiol.* **1986**, *55*, 3143–3149.
49. Philip, L.; Iyengar, L.; Venkobachar, C. Biosorption of U, La, Dy, Pr, and Eu by *Pseudomonas aeruginosa*. *J. Ind. Microbiol. Biotechnol.* **2000**, *25*, 1–7. [CrossRef]
50. Pedersen, K.; Albinsson, Y. Effect of cell number, pH and lanthanide concentration on the sorption of promethium by *Shewanella putrefaciens*. *Radiochim. Acta* **1991**, *54*, 91–95. [CrossRef]
51. Omar, N.B.; Merroun, M.L.; Penalver, J.M.A.; Munoz, M.T.G. Comparative heavy metal biosorption study of Brewery yeast and *Myxococcus Xanthus* biomass. *Chemosphere* **1997**, *35*, 2277–2283. [CrossRef]
52. Texier, A.C.; Andrès, Y.; Le Cloirec, P. Selective biosorption of lanthanide (La, Eu) ions by *Mycobacterium smegmatis*. *Environ. Technol.* **1997**, *18*, 835–841. [CrossRef]
53. Horiike, T.; Yamashita, M. A new fungal isolate, *Penidiella* sp. strain T9, accumulates the rare earth element dysprosium. *Appl. Environ. Microbiol.* **2015**, *81*, 3062–3068. [CrossRef] [PubMed]
54. Skovran, E.; Martinez-Gomez, N.C. Just add lanthanides. *Science* **2015**, *348*, 862–863. [CrossRef] [PubMed]
55. Valenzuela, L.; Chi, A.; Beard, S.; Orell, A.; Guiliani, N.; Shabanowitz, J.; Hunt, D.F.; Jerez, C.A. Genomics, metagenomics and proteomics in biomining microorganisms. *Biotechnol. Adv.* **2006**, *24*, 197–211. [CrossRef] [PubMed]
56. Kita, Y.; Nishikawa, H.; Takemoto, T. Effects of cyanide and dissolved oxygen concentration on biological Au recovery. *J. Biotechnol.* **2006**, *124*, 545–551. [CrossRef] [PubMed]
57. Brandl, H.; Faramarzi, M.A. Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste. *China Particuol.* **2006**, *4*, 93–97. [CrossRef]
58. Chi, T.D.; Lee, J.-C.; Pandey, B.D.; Jeong, J.; Yoo, K.K.; Huynh, T.H. Bacterial cyanide generation in presence of metal ions (Na^+, Mg^{2+}, Fe^{2+}, Pb^{2+}) and gold bioleaching from waste PCBs. *J. Chem. Eng. Jpn.* **2010**, *44*, 692–700.
59. Tay, S.B.; Natarajan, G.; Rahim, M.N.A.; Tan, H.T.; Chung, M.C.M.; Ting, Y.P.; Yew, W.S. Enhancing gold recovery from electronic waste via lixiviant metabolic engineering in *Chromobacterium violaceum*. *Sci. Rep.* **2013**, *3*. [CrossRef] [PubMed]
60. Suja, E.; Nancharaiah, Y.V.; Venugopalan, V.P. Biogenic nanopalladium production by self-immobilized granular biomass: Application for contaminant remediation. *Water Res.* **2014**, *65*, 395–401. [CrossRef] [PubMed]
61. Pat-Espadas, A.M.; Field, J.A.; Razo-Flores, E.; Cervantes, F.J.; Sierra-Alvarez, R. Continuous removal and recovery of palladium in an upflow anaerobic granular sludge bed (UASB) reactor. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 1183–1189. [CrossRef]
62. Chidambaram, D.; Hennebel, T.; Taghavi, S.; Mast, J.; Boon, N.; Verstraete, W.; Van der Lelie, D.; Fitts, J.P. Concomitant microbial generation of palladium nanoparticles and hydrogen to immobilize chromate. *Environ. Sci. Technol.* **2010**, *44*, 7635–7640. [CrossRef] [PubMed]
63. Lenz, K.; Koellensperger, G.; Hann, S.; Weissenbacher, N.; Mahnik, S.N.; Fuerhacker, M. Fate of cancerostatic platinum compounds in biological wastewater treatment of hospital effluents. *Chemosphere* **2007**, *69*, 1765–1774. [CrossRef] [PubMed]
64. Quan, X.; Zhang, X.; Xu, H. In-situ formation and immobilization of biogenic nanopalladium into anaerobic granular sludge enhances azo dyes degradation. *Water Res.* **2015**, *78*, 74–83. [CrossRef] [PubMed]
65. Yong, P.; Liu, W.; Zhang, Z.; Beauregard, D.; Johns, M.L.; Macaskie, L.E. One step bioconversion of waste precious metals into *Serratia* biofilm-immobilized catalyst for Cr(VI) reduction. *Biotechnol. Lett.* **2015**, *37*, 2181–2191. [CrossRef] [PubMed]

66. Rotaru, A.E.; Jiang, W.; Finster, K.; Skrydstru, T.; Meyer, R.L. Non-enzymatic palladium recovery on microbial and synthetic surfaces. *Biotechnol. Bioeng.* **2012**, *109*, 1889–1897. [CrossRef] [PubMed]
67. Lloyd, J.R.; Yong, P.; Macaskie, L.E. Enzymatic recovery of elemental palladium by using sulfate-reducing bacteria. *Appl. Environ. Microb.* **1998**, *64*, 4607–4609.
68. De Windt, W.; Aelterman, P.; Verstraete, W. Bioreductive deposition of palladium (0) nanoparticles on *Shewanella oneidensis* with catalytic activity towards reductive dechlorination of polychlorinated biphenyls. *Environ. Microbiol.* **2005**, *7*, 314–325. [CrossRef] [PubMed]
69. Mikheenko, I.P.; Rousset, M.; Dementin, S.; Macaskie, L.E. Bioaccumulation of palladium by *Desulfovibrio fructosivorans* wild-type and hydrogenase-deficient strains. *Appl. Environ. Microbiol.* **2008**, *74*, 6144–6146. [CrossRef] [PubMed]
70. Bunge, M.; Sobjerg, L.S.; Amelia-Elena, R.; Delphine, G.; Lindhardt, A.T.; Hause, G.; Finster, K.; Kingshott, P.; Skrydstrup, T.; Meyer, R.L. Formation of palladium(0) nanoparticles at microbial surfaces. *Biotechnol. Bioeng.* **2010**, *107*, 206–215. [CrossRef] [PubMed]
71. Capeness, M.J.; Edmundson, M.C.; Horsfall, L.E. Nickel and platinum group metal nanoparticle production by *Desulfovibrio alaskensis* G20. *New Biotechnol.* **2015**, *32*, 727–731. [CrossRef] [PubMed]
72. Creamer, N.J.; Baxter-Plant, V.S.; Henderson, J.; Potter, M.; Macaskie, L.E. Palladium and gold removal and recovery from precious metal solutions and electronic scrap leachates by *Desulfovibrio desulfuricans*. *Biotechnol. Lett.* **2005**, *28*, 1475–1484. [CrossRef] [PubMed]
73. Kwak, I.S.; Won, S.W.; Chung, Y.S.; Yun, Y.S. Ruthenium recovery from acetic acid waste water through sorption with bacterial biosorbent fibers. *Bioresour. Technol.* **2006**, *128*, 30–35. [CrossRef] [PubMed]
74. Won, S.W.; Kwak, I.S.; Yun, Y.S. The role of biomass in polyethylenimine-coated chitosan/bacterial biomass composite biosorbent fiber for removal of Ru from acetic acid waste solution. *Bioresour. Technol.* **2014**, *160*, 93–97. [CrossRef] [PubMed]
75. Darnall, D.W.; Greene, B.; Henzl, M.T. Selective recovery of gold and other metal ions from an algal biomass. *Environ. Sci. Technol.* **1986**, *20*, 206–208. [CrossRef] [PubMed]
76. Kuyucak, N.; Volesky, B. Biosorbents for recovery of metals from industrial solutions. *J. Biotechnol. Lett.* **1988**, *10*, 137–142. [CrossRef]
77. Niu, H.; Volesky, B. Characteristics of gold biosorption from cyanide solution. *J. Chem. Technol. Biotechnol.* **1999**, *74*, 778–784. [CrossRef]
78. Torres, E.; Mata, Y.N.; Bl'azquez, M.L. Gold and silver uptake and nanoprecipitation on calcium alginate beads. *Langmuir* **2005**, *21*, 7951–7958. [CrossRef] [PubMed]
79. Romero-Gonz'alez, M.E.; Williams, C.J.; Gardiner, P.H.E.; Gurman, S.J.; Habesh, S. Spectroscopic studies of the biosorption of gold (III) by dealginated seaweed waste. *Environ. Sci. Technol.* **2003**, *37*, 4163–4169. [CrossRef]
80. Pethkar, A.V.; Paknikar, K.M. Recovery of gold from solutions using *Cladosporium cladosporioides* biomass beads. *J. Biotechnol.* **1998**, *63*, 121–136. [CrossRef]
81. Khoo, K.M.; Ting, Y.P. Biosorption of gold by immobilized fungal biomass. *Biochem. Eng. J.* **2001**, *8*, 51–59. [CrossRef]
82. Akthar, M.N.; Sastry, K.S.; Mohan, P.M. Biosorption of silver ions by processed *Aspergillus niger* biomass. *J. Biotechnol. Lett.* **1995**, *17*, 551–556. [CrossRef]
83. Ishikawa, S.; Suyama, K.; Arihara, K. Uptake and recovery of gold ions from electroplating wastes using eggshell membrane. *Bioresour. Technol.* **2002**, *81*, 201–206. [CrossRef]
84. Maruyama, T.; Matsushita, H.; Shimada, Y.; Kamata, I.; Hanaki, M.; Sonokawa, S.; Kamiya, N.; Goto, M. Proteins and protein-rich biomass as environmentally friendly adsorbents selective for precious metal ions. *Environ. Sci. Technol.* **2007**, *41*, 1359–1364. [CrossRef] [PubMed]
85. Gamez, G.; Gardea-Torresdey, J.L.; Tiemann, K.J. Recovery of gold(III) from multi-elemental solutions by alfalfa biomass. *Adv. Environ. Res.* **2003**, *7*, 563–571. [CrossRef]
86. Volesky, B. Removal of heavy metals by biosorption. In *Harnessing Biotechnology for the 21st Century*; Ladisch, M.R., Bose, A., Eds.; American Chemical Society: Washington, DC, USA, 1992; pp. 462–466.
87. Ma, H.-W.; Liao, X.-P.; Liu, X. Recovery of platinum (IV) and palladium (II) by bayberry tannin immobilized collagen fiber membrane from water solution. *J. Membr. Sci.* **2006**, *278*, 373–380. [CrossRef]
88. Niu, H.; Volesky, B. Characteristics of anionic metal species biosorption with waste crab shells. *Hydrometallurgy* **2003**, *71*, 209–215. [CrossRef]

89. Arrascue, M.L.; Garcia, H.M.; Horna, O.; Guibal, E. Gold sorption on chitosan derivatives. *Hydrometallurgy* **2003**, *71*, 191–200. [CrossRef]
90. Guibal, E.; Vincent, T.; Mendoza, R.N. Synthesis and characterization of a thiourea derivative of chitosan for platinum recovery. *J. Appl. Polym. Sci.* **1999**, *75*, 119–134. [CrossRef]
91. Guibal, E.; VonOffenberg, N.S.; Vincent, T.; Tobin, J.M. Sulfur derivatives of chitosan for palladium sorption. *React. Funct. Polym.* **2002**, *50*, 149–163. [CrossRef]
92. Chassary, P.; Vincent, T.; SanchezMarcano, J.; Macaskie, L.E.; Guibal, E. Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives. *Hydrometallurgy* **2005**, *76*, 131–147. [CrossRef]
93. De Vargas, I.; Macaskie, L.E. Biosorption of palladium and platinum by sulfate-reducing bacteria. *J. Chem. Technol. Biotechnol.* **2004**, *79*, 49–56. [CrossRef]
94. Nancharaiah, Y.V.; Lens, P.N. Ecology and biotechnology of selenium-respiring bacteria. *Microbiol. Mol. Biol. Rev.* **2015**, *79*, 61–80. [CrossRef] [PubMed]
95. Turner, R.J.; Borghese, R.; Zannoni, D. Microbial processing of tellurium as a tool in biotechnology. *Biotechnol. Adv.* **2012**, *30*, 954–963. [CrossRef] [PubMed]
96. Rajwade, J.M.; Paknikar, K.M. Bioreduction of tellurite to elemental tellurium by *Pseudomonas mendocina* MCM B-180 and its practical application. *Hydrometallurgy* **2003**, *71*, 243–248. [CrossRef]
97. Bonificio, W.D.; Clarke, D.R. Bacterial recovery and recycling of tellurium from tellurium-containing compounds by *Pseudoalteromonas* sp. EPR3. *J Appl. Microbiol.* **2014**, *117*, 1293–1304. [CrossRef] [PubMed]
98. Campbell, K.M.; Gallegos, T.J.; Landa, E.R. Biogeochemical aspects of uranium mineralization, mining, milling, and remediation. *Appl. Geochem.* **2015**, *57*, 206–235. [CrossRef]
99. Nancharaiah, Y.V.; Joshi, H.M.; Mohan, T.V.K.; Venugopalan, V.P.; Narasimhan, S.V. Aerobic granular biomass: A novel biomaterial for efficient uranium removal. *Curr. Sci.* **2006**, *91*, 503–509.
100. Newsome, L.; Morris, K.; Lloyd, J.R. The biogeochemistry and bioremediation of uranium and other priority radionuclides. *Chem. Geol.* **2014**, *363*, 164–184. [CrossRef]
101. Wall, D.; Krumholz, L.R. Uranium reduction. *Annu. Rev. Microbiol.* **2006**, *60*, 149–166. [CrossRef] [PubMed]
102. Lee, J.U.; Kim, S.M.; Kim, K.W.; Kim, I.S. Microbial removal of uranium in uranium-bearing black shale. *Chemosphere* **2005**, *59*, 147–154. [CrossRef] [PubMed]
103. Srivastava, R.R.; Kim, M.-S.; Lee, J.-C. Novel aqueous processing of the reverted turbine-blade superalloy for rhenium recovery. *Ind. Eng. Chem. Res.* **2016**, *55*, 8191–8199. [CrossRef]
104. Motaghed, M.; Mousavi, S.M.; Rastegar, S.O.; Shojaosadati, S.A. Platinum and rhenium extraction from a spent refinery catalyst using *Bacillus megaterium* as a cyanogenic bacterium: Statistical modeling and process optimization. *Bioresour. Technol.* **2014**, *171*, 401–409. [CrossRef] [PubMed]
105. Faramarzi, M.A.; Brandl, H. Formation of water-soluble metal cyanide complexes from solid minerals by *Pseudomonas plecoglossicida*. *FEMS Microbiol. Lett.* **2006**, *259*, 47–52. [CrossRef] [PubMed]
106. Xiong, Y.; Xu, J.; Shan, W.; Lou, Z.; Fang, D.; Zang, S.; Han, G. A new approach for rhenium(VII) recovery by using modified brown algae *Laminaria japonica* adsorbent. *Bioresour. Technol.* **2013**, *127*, 464–472. [CrossRef] [PubMed]
107. Xiong, Y.; Wang, H.T.; Lou, Z.N.; Shan, W.J.; Xing, Z.Q.; Deng, G.C.; Wu, D.B.; Fang, D.W.; Biswas, B.K. Selective adsorption of molybdenum(VI) from Mo–Re bearing effluent by chemically modified astringent persimmon. *J. Hazard Mater.* **2011**, *186*, 1855–1861. [CrossRef] [PubMed]
108. Shan, W.J.; Fang, D.W.; Zhao, Z.Y.; Yue, S.; Lou, Z.N.; Xing, Z.Q.; Xiong, Y. Application of orange peel for adsorption separation of molybdenum(VI) from Re-containing industrial effluent. *Biomass Bioenergy* **2012**, *37*, 289–297. [CrossRef]