Bio-Based Processes for Material and Energy Production from Waste Streams under Acidic Conditions

Zeynep Cetecioglu [1,*], **Merve Atasoy** [1,2], **Adam Cenian** [3], **Gaweł Sołowski** [3], **Janja Trček** [4,5], **Aysenur Ugurlu** [6] and **Jana Sedlakova-Kadukova** [7]

1   Department of Industrial Biotechnology, KTH Royal Institute of Technology, AlbaNova University Center, 11421 Stockholm, Sweden; merve.atasoy@wur.nl
2   UNLOCK, Wageningen University and Research, 6708 PB Wageningen, The Netherlands
3   Polish Academy of Sciences, Institute of Fluid Flow Machinery, 80-231 Gdansk, Poland; cenian@imp.gda.pl (A.C.); g.solowski@wp.pl (G.S.)
4   Department of Biology, Faculty of Natural Sciences and Mathematics, University of Maribor, SI-2000 Maribor, Slovenia; janja.trcek@um.si
5   Faculty of Chemistry and Chemical Engineering, University of Maribor, SI-2000 Maribor, Slovenia
6   Department of Environmental Engineering, Hacettepe University, Ankara 06800, Turkey; ugurlu@hacettepe.edu.tr
7   Department of Ecochemistry and Radioecology, University of Ss. Cyril and Methodius in Trnava, 91701 Trnava, Slovakia; sedlakova.uni@gmail.com
*   Correspondence: zeynepcg@kth.se

Abstract: The revolutionary transformation from petrol-based production to bio-based production is becoming urgent in line with the rapid industrialization, depleting resources, and deterioration of the ecosystem. Bio-based production from waste-streams is offering a sustainable and environmentally friendly solution. It offers several advantages, such as a longer operation period, less competition for microorganisms, higher efficiency, and finally, lower process costs. In the current study, several bio-based products (organic acids, biomethane, biohydrogen, and metal leachates) produced under acidic conditions are reviewed regarding their microbial pathways, processes, and operational conditions. Furthermore, the limitations both in the production process and in the scale-up are evaluated with future recommendations.

Keywords: bio-based production; acidogenic conditions; fermentation; organic acids; biohydrogen; biomethane; bioleaching

1. Introduction

The attention towards bio-based products is constantly increasing in recent years [1,2] because of the rapid depletion of the resources and the adverse environmental effects of conventional methods, either petrol-based production methods or methods used for critical materials recovery. Traditional methods are very often energy-intensive, sensitive to initial resources quality and environmentally unfriendly. The transformation from petrol-based to bio-based production is not only resulting in green industrial production but also in resource recovery from waste-streams to reach a potentially sustainable and environmentally friendly production. Acidity is one of the major factors that must be considered during processing as it affects operational conditions, process efficiency, and finally the price of the processes used on the pilot as well as laboratory scale. Bioprocesses that run under acidic conditions can provide several advantages in comparison with processes that run under neutral pH. In the field of organic acid production, lower process pH increases the final yield of the product, provides a longer operation period in continual systems, and it also reduces cost in the pH titrant and downstream processing. Low pH in the anaerobic digestion results in direct crystallization of some acids and causes a significant increase in soluble phosphorus concentration that affects product profile [3]. Protons are engaged in the

hydrolysis of biopolymers, such as lignocellulose, starch, lignin, hemicellulose, proteins, as well as fats. Most of these products, such as simple sugars, amino acids and fatty acids, are used by microorganisms as substrates in their metabolism, producing required fatty acids, hydrogen, or methane depending on adjusted biotechnology parameters. By controlling pH, one may stimulate required bioprocesses, e.g., methanogens hardly work below pH 6, thus other microorganisms work more efficiently when pH declines. Very low pH in metal recovery by bioleaching is fundamental for bacterial life resulting in the high efficiency of metal extractions from various resources [4]. Besides application in metal recovery, bioleaching represents an interesting tool in the environmental clean-up technology aiming to produce metal free materials (e.g., removal of metals from sewage sludge or pig manure prior to their re-use) [5,6]. Metal bioleaching from waste is considered a significant research area to secure critical metals for the European market and developing processes adopting circular economy principles, especially in combination with other biological processes for metal extraction from solutions such as bioaccumulation or biosorption [4,7].

Here, we focused on microbial processes which are biotechnologically explored at low pH and are a focus of discussions in active working group, Biotechnological Applications of COST-action CA18113: Understanding and exploiting the impacts of low pH on micro-organisms. We divided them into two main groups: processes running under moderately low pH (4–6), such as organic acids, biomethane and biohydrogen production, and processes running under very low pH (1–3), such as inorganic acid production for bioleaching. In line with the United Nations 2030 Sustainable Development Goals (SDGs)—particularly SDGs 9, 11, 12, and 13—climate objectives of the Paris Agreement and targets of A European Green Deal [8], this review paper aims to bring a comprehensive perspective for biobased production from waste streams highlighting the advantages of low pH.

Nevertheless, the effects of low pH vary on the product and process type. This review aims to evaluate various bio-based products (organic and inorganic acids, minerals, biomethane and biohydrogen) produced under acidic conditions taking into account production processes and their mechanisms, operational conditions and the limitations both for operation and scaling-up. These products are chosen based on high transferability potential for biobased products, technology readiness level (TRL) of biobased production processes, and market demand for the products. The production of several organic acids, by both mixed culture and mono-culture fermentation and challenges set by lower pH, are reviewed. Main obstacles originating from low pH at biomethane production by anaerobic digestion and biohydrogen production within dark fermentation are described. Processes running under extremely low pH, such as bioleaching resulting in metal dissolution from various resources involving waste materials are also documented.

2. Moderate Acidic pH Bioprocesses (pH 4–6)

Organic acids production (specifically of short chain fatty acids), which is a typical example of the first group, may be recovered by bio-based methods, which fully produce some organic acids, such as lactic, itaconic, citric, and gluconic acids. However, more than 90% of other acids are still produced by petrol-based methods [8]. These processes cannot run under pH 4.5 by mixed culture. The pH affects both acid composition and microbial community profile during mixed culture fermentation. However, several organic acids, such as acetic acid, can be produced with monoculture (certain species of *Komagataeibacter* and *Acetobacter*) at very low pH [9]. The exploitation of heterotrophic organic acid producing microorganisms in metal recovery is a promising way, however, it is still only studied at a laboratory scale [10]. Among processes related to moderately low pH is also the production of biomethane or biohydrogen by anaerobic digestion. In this case, low pH represents an unwanted and sometimes even limiting factor. However, acclimated methanogens can withstand low pH levels and increase the system stability, in some cases even at higher biomethane yield [11]. On the other hand, in the case of biohydrogen production, low pH (4.5–6.4) during inoculum stressing as well as process operation stimulates biohydrogen production. Inoculum stress under low pH conditions suppresses methanogens and later

hydrogen consumption during the hydrogen production process. The low pH control during process operation increases hydrogen yield even more than 350% if compared to uncontrolled pH conditions [12,13].

2.1. Anaerobic Volatile Fatty Acids Production by Mixed Culture Fermentation

Volatile fatty acids (VFAs) are one of the ready-to-market bio-based products. These are extensively used in several industries [14,15]. Nevertheless, their main production route depends on chemical synthesis [16]. Only around 1–10% of VFA is produced by fermentation [17].

Recent studies showed that pH is one of the most critical factors in fermentative VFA production by mixed culture [18–21]. During VFA production, the formation of a great amount of hydrogen causes a pH drop in the medium [22]. Despite that the hydrogen is consumed by either formation of organic acids, the production of methane during the anaerobic digestion, or both—the pH drop has several consequences in the system [23,24]. The pH has direct and indirect effects on VFA production by means of affecting the growth rate of the biomass, microbial community dynamics, metabolic network, hydrogenase activity and cell morphology and structure, etc. [25].

Although the neutral pH (around 6.5–7.5) is the most suitable pH for hydrolysis and acidogenesis steps because it is the optimum pH environment for fermentative bacteria [26], the main limitation is that VFA is converted into methane under neutral pH (product loss). Therefore, inhibitor usage is required to prevent methanogenic activity. Furthermore, alkali pH (up to pH 10) improved hydrolysis rate in the complex waste streams, accordingly increasing VFA production efficiency [27]. Nevertheless, Feng et al. (2020) showed that the positive effects of alkali pH on VFA production are not sustainable for long term reactor operation because of alkalinity inhibition [28]. Moreover, Lee et al. (2014) reviewed the different types of waste-streams and operational/environmental factors for VFA production by acidogenic fermentation. According to their results, acidic pH was beneficial to increase hydrolysis rate, therefore, improving the VFA production efficiency [16]. This statement is supported by Van Aarle et al. (2015); they optimized the acidogenic fermentation by different combinations of substrate and inoculum type for VFA production under pH 6.5. Their results showed that in the highest retention time, the pH decreased to 4.6, which resulted in the highest hydrolysis rate and high production of VFA [29]. On the other hand, Liu et al. (2012) evaluated the effects of different pH (pH 3, 5, 7, 9, 11, and 12) on VFA production from acidogenic fermentation of proteinaceous sewage sludge. Their results showed that pH has not only a major impact on VFA production yield and acid distribution, but also significantly influenced the biodiversity and bacterial community in the system. The relative abundance of the bacterial community under alkaline or acidic pH conditions was less than that under neutral pH conditions, suggesting that most anaerobic fermentative microorganisms could not tolerate the hostile environment [30].

In other respects, several studies suggested that different methods/strategies enhance VFA production by fermentation. Fang et al. (2020) reviewed several pretreatment methods (physical, chemical, and biological) on VFA production from waste activated sludge fermentation. According to their review, the highest VFA production efficiency was obtained with alkaline and thermal pretreatments of waste activated sludge [31]. In addition, the same study showed that co-fermentation is one of the most effective methods to improve VFA production efficiency besides pretreatments. Furthermore, Owusu-Agyeman et al. (2020) showed that co-fermentation of sewage sludge and organic waste produced a significant amount of caproic acid (9334 mg COD/L) under acidic pH (pH 5) conditions [32]. Another promising waste stream for VFA production is lignocellulosic biomass wastes due to their valuable composition and enormous production amount [33]. According to Sun et al. (2021), pH is a critical operational parameter in VFA production from lignocellulosic biomass wastes. They stated that depending on the fermentation pathway, pH directly affects the acid profile [34].

She et al. (2020) evaluated the effects of freezing/thawing (F/T) pretreatment on VFA production from waste activated sludge. The F/T pretreatment improved VFA production from 3603 to 4852 mg COD/L [35]. Atasoy and Cetecioglu (2020) aimed to produce a butyric acid dominant VFA mixture via bioaugmented mixed culture with *Clostridium butyricum* (butyric acid producer). According to their results, bioaugmentation changed the dominant acid type from propionic acid to butyric acid by increasing butyric acid production by 12-fold and total VFA production by 3.5 folds, compared with the control reactor [36].

Although VFAs are one of the closest products for biobased production on an industrial scale, some challenges limit large-scale production. In mixed culture fermentation, low production efficiency (the self-inhibitory effects from end products), a slow growth rate of microbial strains, degeneration of fermentative bacteria, limited hydrolysis rate with lower conversion rate [37], and high substrate cost [38] are challenges for VFA production. Furthermore, the unstable production process and the purification and separation of VFA from the effluent mixture are significant challenges for scaling-up VFA production via fermentation from laboratory and pilot-scale to full-scale applications [15,16]. Despite that there are several technologies and methods for VFA separation and purification (such as absorption, adsorption, solvent extraction, distillation, membrane processes, e.g., nanofiltration, electrodialysis, microfiltration, ultrafiltration, membrane contactor and reverse osmosis and in-line recovery), the recovery of each acid type is required to commercialize biobased VFA production. On the other hand, another point to reach efficient and cost-effective bio-based VFA production is to increase production yield in the process. The process efficiency is closely connected with operational conditions (pH, retention time, organic loading rate, etc.), type of inoculum and substrate, and pretreatment/post-treatment methods.

2.2. Aerobic Volatile Fatty Acid Production by Pure Culture Fermentation

Besides mixed microbial culture, pure cultures can also be used for organic acids production. Among the organic acids, acetic acid is one of the most largely commercially available types of organic acid [39]. The global acetic acid market size was valued at USD 8.92 billion in 2019 and is expected to grow at a compound annual growth rate of 5.2% from 2020 to 2027. Acetic acid is aerobically produced by acetic acid bacteria, especially of the *Acetobacter* and *Komagataeibacter* genera [40]. In these processes, organic components are transformed into acetic acid during two sequential biochemical steps: at the beginning, the sugars are fermented into ethanol by native or commercially available yeasts, then the ethanol is oxidized to acetic acid by acetic acid bacteria. Although the produced acetic acid decreases pH-value very quickly, at 3% of acetic acid the pH value is already 3.5, these conditions are not detrimental for acetic acid bacteria. In line with this are also the results of Li et al. (2015) who reported an optimal pH for acetic acid production from food wastes using yeast and acetic acid bacteria to be in the range of 3.0–3.5 [41]. It is also important to note that certain strains of acetic acid bacteria exhibit a higher acetic acid production rate at higher concentrations of acetic acid [41]. Utilization of pure starter cultures for aerobic acetic acid production strongly relies on acid tolerant mechanisms that have acetic acid bacteria evolved to withstand low pH caused by acetic acid accumulation during fermentation. The tolerance is a result of the physical barrier surrounding the bacterial cells in the form of capsular polysaccharides that hinder the diffusion of undissociated acetic acid into the cells. Besides the physical barrier, the intracellular mechanisms are buffering the acetate and hydrogen ions produced after acetic acid enters the cells and dissociates at neutral intracellular pH [42]. Since the species of both genera possess different mechanisms for acetic acid/acetate tolerance and thus also to low pH [43,44], the strains of *Acetobacter* spp. are mainly used to produce maximal 6% of acetic acid and strains of *Komagataeibacter* spp. for higher concentrations of acetic acid. Besides this acid-tolerant phenotype, acetic acid bacteria have another, technologically very important characteristic: the enzymatic reaction for the production of acetic acid is catalyzed by membrane-bounded alcohol- and aldehyde dehydrogenase. Since both enzymes are attached to the outer surface of the

cytoplasmic membrane, the acetic acid is directly released out of the cell, which results in the high efficiency of the bioprocess [42,45]. Altogether this means that these acid tolerant bacteria are very suitable for aerobic acetic acid production from various organic materials.

This kind of process became attractive during the last years to valorize different types of agricultural and food wastes. Recently, acetic acid has been successfully produced from food waste collected at a student cafeteria in China. Before the process initiation, the animal bones were removed from the food waste and the rest of the material was crushed and selected for particles smaller than 2 mm. The food waste mainly contained cooked rice, vegetables, meat, and eggs. *Saccharomyces cerevisiae* and acetic acid bacteria Brand HuNiang No. 1.01 were added to proceed with bench-scale fermentation experiments in bottles with a working volume of 0.5 L without caps to prevent anaerobic conditions. At the beginning of the process, the pH was 5.9 but decreased to below 2 by the end of fermentation. The process yielded a maximal 25.9 g/L of acetic acid. Other volatile fatty acids were also produced, such as isovaleric, propionic, and butyric acid, but acetic acid predominated with almost 80% by the end of the process. The ratio of VFA varied during the process since butyric and isovaleric acids were transformed into propionic acid [41].

Vashisht et al. (2019) used *Acetobacter pasteurianus* SKYAA25, which tolerates 42 °C, for the acetic acid production from apple pomace. In this process, a moderately acidic pH (pH 5.5) was necessary to achieve maximal acetic acid production with a final yield of 54.4 g/L per 100 g dry matter of apple pomace. pH-values above 5.5 rapidly decreased acetic acid production. Besides, by using a thermotolerant strain of acetic acid bacterium, the process contributes to energy savings otherwise necessary to cool down exothermic acetic acid-producing bioprocess [46].

The food waste materials can be fermented directly by acetic acid bacteria to acetic acid containing useful products, such as vinegar. Different agricultural waste materials, such as banana peels, pineapple waste, apple waste, worthless onion, and coconut water have been successfully used for acetic acid production [41,47,48]. The acids, with acetic acid as the predominant one, are removed from the rest of the organic material by filtration. For this purpose, microfiltration with a large pore size (50 nm–5 mm) and a low-pressure pump with 1–4 bar is used. Furthermore, ultrafiltration proceeds with membrane pore size between 2 and 50 nm and a pump able to reach 5–9 bar, which is required to separate cells, proteins, and fats. The separation is based on size exclusion or sieving mechanism [49].

Since acetic acid bacteria are strictly aerobic microorganisms, the presence of oxygen is mandatory for the successful growth of these bacteria. During acetic acid production with acetic acid bacteria, oxygen is a terminal acceptor of electrons from enzymes oxidizing ethanol to acetic acid. Additionally, oxygen is necessary for the formation of proton motive force, which is directly connected to acetic acid-efflux [50]. Supplying enough oxygen for an optimal metabolism of acetic acid bacteria might be a limiting factor in process scale-up. An efficient aeration strategy is also necessary for not depriving the process of ethanol and acetic acid due to evaporation. Recently, a novel two-stage oxygen supply has been proposed to achieve efficient aeration in the aerobic acetic acid production process [51]. In this process, the aeration rate 0.1 vvm was for 9 hours and then raised to 0.15 vvm. In this way, a 20.78% higher production rate was achieved than at the 0.1 vvm one-stage aeration process.

Using pure culture of acetic acid bacteria for acetic acid production has an advantage compared to mixed microbial culture since the acetic acid is the only or a predominant product of the fermentation with ethanol to the acetic acid yield of about 98% [49]. However, the acetic acid still has to be separated from water which needs further processing by methods such as fractional distillation, azeotropic dehydration, distillation, solvent extraction, and adsorption [52,53].

2.3. Biomethane

Production of biomethane via anaerobic digestion can be regarded as a renewable energy source by using a wide range of biomasses (e.g., waste sewage sludge, industrial wastewaters, animal manure, agricultural residues, organic solid waste, microalgae). The

anaerobic biochemical conversion of organic material proceeds in four main steps including hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Process pH is one of the most important factors affecting system stability. For optimum growth of the methanogens, pH control of the reactors is essential. The optimum pH range for methanogens and acidogens are reported as between 6.4 and 7.6 [52] and as 5.5 and 6.5, respectively. The pH in the anaerobic digester may drop to as low as 4.5–5.0 during instabilities and varies depending on microbial species, substrate characteristics, organic loading, configuration of reactors, temperature, etc. Although the optimum pH for growth of *Methanosarcina* sp. is near neutrality, it was shown that some of its strains withstand pH as low as 4.5 [53]. Taconi et al. (2008) observed that methane production at low pH is possible after adequate acclimation of the methanogens [54]. Thus, the maintenance of the equilibrium between acetogenesis and methanogenesis is a crucial factor for continuous methane production.

The system pH is often affected by various stress conditions related to change in organic loading, environmental conditions, substrate characteristics, presence of toxic compounds, etc. [55]. VFA accumulated during start-up resulting in system imbalances is usually due to the insufficient methanogenic population to convert these acids into methane at the same rate that they are produced. The main factors that may help to improve the performance of the anaerobic digestion system and methane production are shown in Figure 1.

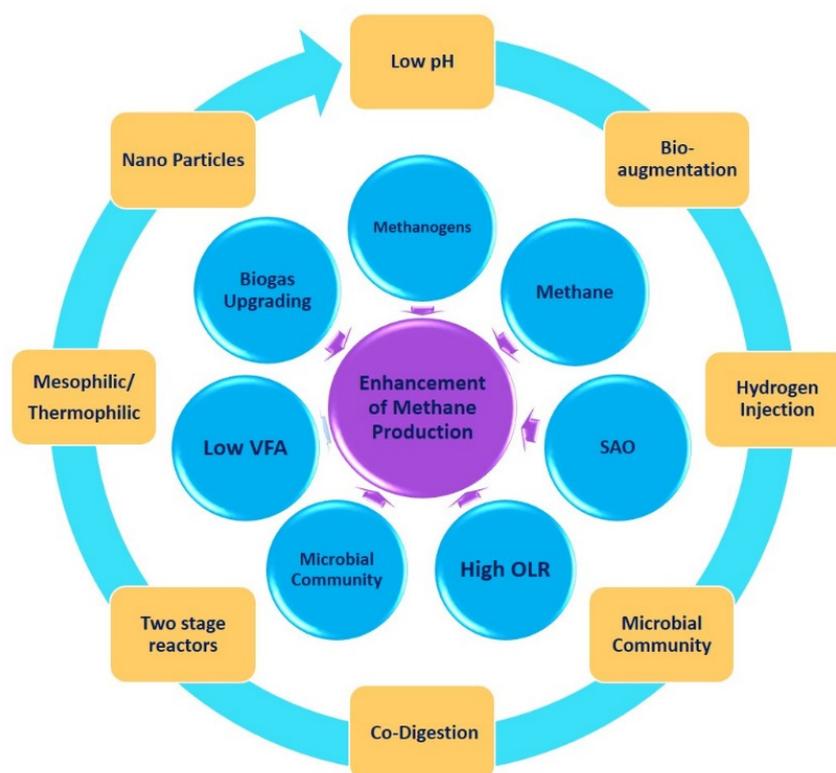



Figure 1. Main factors affecting methane production and used for enhancement of methane production.

Bioaugmentation of the propionate degrading consortia with high resistance to low pH can also help restore the reactor performance [56] and can accelerate the conversion of propionate and acetate to methane under acidic conditions [56]. It has been shown that hydrogenotrophic methanogens also dominate under a short hydraulic retention time (HRT). In order to improve the performance of anaerobic digesters operated under the short HRT and low pH, introducing hydrogenotrophic methanogens might help.

The substrate type also affects either the metabolism, metabolites, or both, of AD, which results in the dominancy of specific methanogens [57]. Acclimatization of the microorganisms to the substrate, by enhancing the enzymatic activities, may increase methane

production as well as system stability. Some of the substrates with high carbohydrate contents acidify quickly and may result in VFA formation and accumulation, leading to a decrease in pH and inhibition of methanogenesis. Kurade et al. (2019) investigated the co-digestion of fats/oil/grease (FOG) and observed that the methane production was mainly by acetoclastic pathway whereas syntrophic acetate oxidizers and hydrogenotrophic methanogens were almost absent [58].

The lignocellulosic material, such as agricultural residues and microalgae, containing polymers, such as cellulose, hemicellulose, and lignin, has great biogas production potential. Since the cellulose is strongly cross-linked and shielded by lignin, the accessibility of enzymes and microorganisms to the cellulose is hindered [59]. This recalcitrant characteristic of the lignocellulosic biomass makes it resistant to physical, chemical, or biological degradation. Therefore, its breakdown is usually the major limiting factor for biogas yield and requires an affective pretreatment to improve the performance of anaerobic digestion. Application of physical, chemical, or biological pretreatment methods or their combinations can help disruption of this rigid cell wall to improve biogas production. The high energy cost and residence time and the production of inhibitory products during processing make pretreatment a challenging task. Biological pretreatment methods are considered as a more sustainable alternative to energy-intensive physicochemical pretreatments.

Wang et al. (2020) demonstrated that acetoclastic *Methanothrix* and hydrogenotrophic *Methanolinea* were the dominant methanogens when a gradual stepwise decrease in pH was evident. Whereas, a sharp decrease in pH resulted in inhibition of the acetoclastic methanogens and a stop in methane production [60]. Therefore, hydrogenotrophic methanogens demonstrated high acid tolerance and bioaugmentation by hydrogenotrophic methanogens is beneficial for a more efficient reactor recovery.

In order to overcome the negative effects of pH drops on methanogens during acid production, and to provide optimum growth conditions for the acidogens and methanogens, two-phase anaerobic systems are proposed. However, it is difficult to separate acidogenesis from methanogenesis completely, and some methanogenic activities in the acidogenic phase are still present. The presences of hydrogenotrophic methanogens in the acidogenic phase of a two-phase anaerobic digestion system have been identified [61,62]. The methanogens in the acidogenic reactor could withstand pH level as low as 5.6 with high organic acid concentrations and produced more than 15% of the total biogas yield [63]. Xiao et al. (2013) observed that high acetic acid concentrations (565.29–2781.19 mg HAc/L) were not inhibitory for the acidogenic phase methanogens at pH 5.5, 6.0, and 6.5, whereas it was inhibitory at lower concentrations (at pH 6 and 1619.47 mg HAc/L) in the methanogenic reactor [62].

2.4. Biohydrogen

Biohydrogen is produced during dark fermentation, a type of anaerobic digestion process (Figure 2), which converts various substrates (including lignocellulosic, municipal solid, agricultural and food industry waste, sewage sludge, etc.) into hydrogen, carbon dioxide, and low organic acids, e.g., butyric, acetic, propionic, caproic, or lactic [13]. In the case of lignocellulosic waste, a proper pretreatment method is needed, as discussed below. In order to achieve significant amounts of hydrogen, the final stage of anaerobic digestion, i.e., methanogenesis, must be inhibited by inoculum stressing and process operation under low pH.

The anaerobic digestion and dark fermentation usually proceed under a stable mesophilic temperature, in the range 38–42 °C, but recent reports on higher methane production and possibly more valuable by-products (such as lactic acid) turned interests toward the thermophilic temperature range (55–60 °C) [64]. The optimal pH for hydrogen production during dark fermentation seems to be from 5 to 6 [65,66] while for methane production in anaerobic digestion tends toward 7 to 9 [66,67]. However, quite surprisingly, high hydrogen yields are also reported during dark fermentation of wheat straw at pH 2.4 [68] and 9 [69]. In contrast, Giovannini et al. (2016) reported that during fermentation of substrates with higher content

of lignin (above 10%), due to growing pH, methanogens are stimulated to higher methane production (and net hydrogen production decreases) [70].

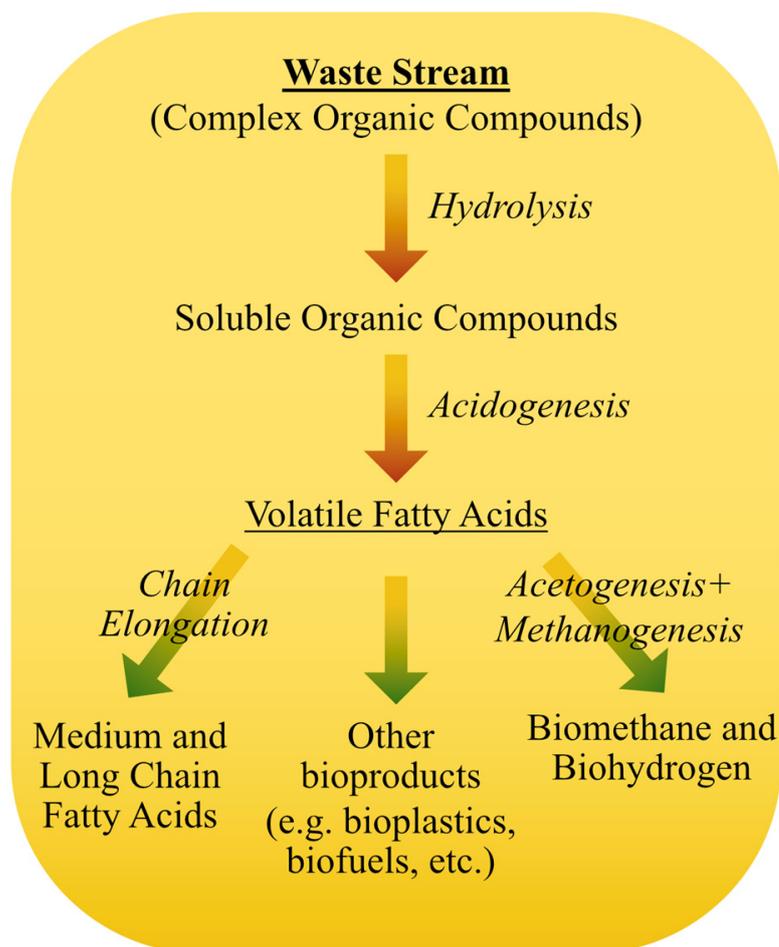



Figure 2. Summarization of anaerobic digestion processes with the emphasis on product type.

The role of low pH control during dark fermentation of chosen biowastes is demonstrated in Supplementary Figure S1. It is clearly seen that control of acidic conditions may significantly increase hydrogen production—without pH control condition, pH value soon rises above 7, the favorite pH for methanogenesis. Moreover, methanogenic archaea adaptation to acidic conditions (pH value below 6—a favorite for dark fermentation) can be observed 13 or 17 days after dark fermentation process initiation (Supplementary Figure S2). Comparing the data, a time lag of 5–7 days separate initiation of hydrogen and methane generation (Supplementary Figures S1 and S2).

The first limitation is the choice of inoculum and its pretreatment (stressing), although Lakaniemi et al. [71] and Li et al. [72] found that hydrogen production may proceed without pretreatment in the case of some substrates. A special case of hydrogen production that proceeds without bacteria stressing is gangrene infection (bacterial community including *Clostridium perfringens*), wherein very little methane was found in up to 40% of hydrogen [73]. Sometimes, to start hydrogen production from complex substrates, an addition of a simple sugar such as glucose might be required [74].

Another limiting factor is a choice of substrate and proper pretreatment methods, acidic, alkali, thermal, etc. There is a series of review papers published in the last decade [75–78] relating to lignocellulose pretreatment methods as a limiting step in biorefinery technologies. Nissilä et al. (2012) concentrate on the issue of dark fermentation hydrogen production from lignocellulosic hydrolysates obtained from pretreatment processes. The authors consider various lignocellulose pretreatment methods, including physical

(using grinder or comminution, e.g., by waterjets, etc.), chemical, e.g., acid, alkaline or ionic liquid, and physicochemical (hydrothermal and steam explosion). They have shown that the highest hydrogen yield on hexose was 3 mol·mol^{-1} from corn stover pretreated simultaneously with steam explosion and diluted sulfuric acid. The diluted acid or hydrothermal pretreatments of wheat straw also lead to high yields of 2.8 and 2.6 mol·mol^{-1}, respectively. The authors pointed to the need for continuous studies on H$_2$ fermentation from hydrolysates in order to utilize online pH control, optimize hydrolysate concentration, and minimize inhibitory effects [79].

Chen et al. (2017) focused on lignocellulosic-biomass transformation to high-value chemicals. They stated that there is a need for the development of an efficient, eco-friendly, low cost, and operationally simple pretreatment process [76]. The existing methods should be optimized by combining saccharification and respective fermentation processes. An important objective should be not only the production of biogas but the extraction of complex high-value chemicals through highly efficient separation and economically feasible follow-up processes.

However, even an efficient preliminary pretreatment does not guarantee high dark fermentation hydrogen production when trace elements, especially iron and nickel, essential for hydrogenases (including (Fe), (NiFe)- and (NiFeSe)-hydrogenase) being built, are lacking. The experiments by Cieciura-Włoch et al. (2020) revealed that Fe$_2$O$_3$ addition greatly enhanced hydrogen production from sugar beet pulp, whereas iron salts (FeSO$_4$, FeCl$_3$) are not effective [80]. However, it was later pointed out that microbial communities of low diversity (typical for dark fermentation) are less stable [80] and have limited rebuilding capabilities [81], which influence hydrogen production stability. Although, it was confirmed that some biogas plants (with acidic pretreatment) might be easily transformed [82] for efficient production of cheap hydrogen [83].

Another limiting factor is hydrogen partial pressure; its higher value results in the reduction of oxidized ferredoxin, thus hindering hydrogen production [84]. Thus, continuous release of H$_2$ pressure is essential for high dark fermentation process efficiency.

Finally, it was confirmed that in order to stabilize the hydrogen production in industrial installations, low pH control during process operation and an efficient hydrogen release system are necessary. Further research on optimal fermentation conditions for various available biowastes is also recommended.

2.5. Metal Solution Produced by Organic Acids

An emerging way of biologically produced organic acids exploitation is in metal recovery. Many organic acids, such as citric, oxalic, and gluconic acids, have been proven very good lixiviants transforming insoluble metallic forms into soluble ones resulting in metal recovery from ores or waste materials [85]. Acidic pH in the range of 4–6 is the most favorable for a highly efficient process. However, the majority of these processes are still studied at laboratory-scale and need more research to be applied widely in the industry. They are very promising from the view of circular economy as they can be combined with the degradation of organic waste since heterotrophic bacteria and microscopic fungi producing organic acids require organic carbon sources for their growth, which could be derived from municipal or agriculture waste combining several waste-treatment processes [86]. Low pH is required for acidolysis as one of the main mechanisms responsible for metal dissolution. The process is enhanced by the mechanical deterioration of solid material by biomechanical action such as hyphae penetration or mucus production [87]. This great advantage offers the recently understood possibility of metal bioaccumulation into the fungal biomass immediately after its dissolution reducing the necessity of metal extraction from acidic solutions [88,89]. Among the most exploited organic acid producers in biometallurgy are microscopic fungi from genera *Aspergillus* and *Penicillium*, however, heterotrophic bacteria (e.g., *Gluconobacter oxydans*, *Sphingomonas* sp., *Streptomyces albidoflavus*) have been studied, as well. The application of these microorganisms in metal recovery from various waste streams is very promising. For example, it was applied to recover metals from different

spent catalysts [90], red mud [91], LCD monitors [92], Li-ion batteries [93], or spent printed circuit boards from computers and mobile phones [94–96] with efficiency from 31 to 99% depending on metal recovered and waste treated (Supplementary Table S1).

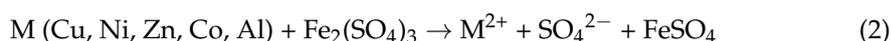
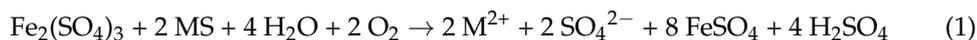
3. Extreme Acidic pH Bioprocess (pH 1–3)

Biological processes with industrial implications running under extreme pH (below 3) are very often related to metal recovery. They are gaining attraction as an alternative to conventional metallurgical processes [97]. The global bioleaching market has reached 15 million in 2020 and is expected to grow to 23 million in the period 2021–2027 and reach CAGR at 4.9% during this period. Its main advantages present low energy, labor and capital requirements, environmentally friendly operations, and mild reaction conditions. Due to its simplicity, flexibility, low sensitivity to changes in feedstock, and ability to process a low amount of materials, bioleaching is increasingly being studied for the processing of various metal-bearing solid wastes [98]. A great advantage in comparison with traditional metallurgical processes is the possibility to develop a more selective process able to also recover minor and inexpensive metals [99].

The term bioleaching is used for metal dissolution from metal-bearing ores or waste materials by various microorganisms. Extremely low pH, usually in the range of 1–3, sometimes even lower, is typical for metal bioleaching by chemolithotrophic bacteria. In natural ecosystems, the process of Fe(II) to Fe(III) oxidation is the main step in their energy gaining within aerobic respiration. Maintaining pH below 3 is crucial to keep Fe^{3+} ions in soluble form. Ferric iron serves as a very strong oxidizing agent for sulfidic minerals resulting in Fe^{2+} ions as well as H_2SO_4 production [4]. At higher pH (above 5) iron oxidation can take place by both abiotic and microbial processes, however, below 4 bacterial actions are dominant [100]. These processes are very typical in natural ecosystems rich in metals, such as ore deposits, however, in the last decades, they serve as a basis of biotechnological/biometallurgical technologies, as well.

Up to now, there have been two main known mechanisms responsible for bioleaching by S- and Fe-oxidizing bacteria (Figure 3). The direct mechanism is carried out by direct contact of bacteria and metal-bearing material using bacterial enzymes as bioleaching agents [101]. This mechanism was demonstrated for sulfidic ores; however, it was not recorded for waste material. The most common is the indirect mechanism where microorganisms mobilize metals through the oxidation of ferrous to ferric iron and the oxidation of elemental or sulfidic sulfur to sulfuric acid. Sulfuric acid production improves overall process efficiency. For example, Dorado et al. (2012) pointed out the fact that the H^+ ions concentration decreased at the beginning of the chalcopyrite bioleaching process, due to the acid consumption during the protonic attack enabling acidic dissolution of the chalcopyrite [102]. They reported, e.g., 50% of total copper recovery under most acid conditions (pH 1.5), 15% in the slightly acid conditions (pH 4), and practically negligible at close to neutral conditions (pH 6). Ferric iron is a strong oxidizing agent oxidizing elemental or sulfidic sulfur to sulfuric acid and forming water soluble metal sulfates—Equation (1)—or in the case of waste, oxidizing metallic form into soluble metal ions—Equation (2):

$$Fe_2(SO_4)_3 + 2\ MS + 4\ H_2O + 2\ O_2 \rightarrow 2\ M^{2+} + 2\ SO_4^{2-} + 8\ FeSO_4 + 4\ H_2SO_4 \qquad (1)$$

$$M\ (Cu,\ Ni,\ Zn,\ Co,\ Al) + Fe_2(SO_4)_3 \rightarrow M^{2+} + SO_4^{2-} + FeSO_4 \qquad (2)$$

where MS represents metal sulfide, M represents metal, and M^{2+} represents dissolved metal ion.

Bacteria in indirect mechanisms do not leach minerals directly but regenerate the leaching agent, and thus, oxidize Fe^{2+} to Fe^{3+} ions:

$$2\ FeSO_4 + 0.5\ O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (3)$$

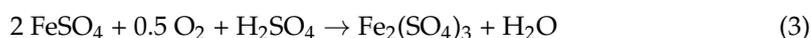
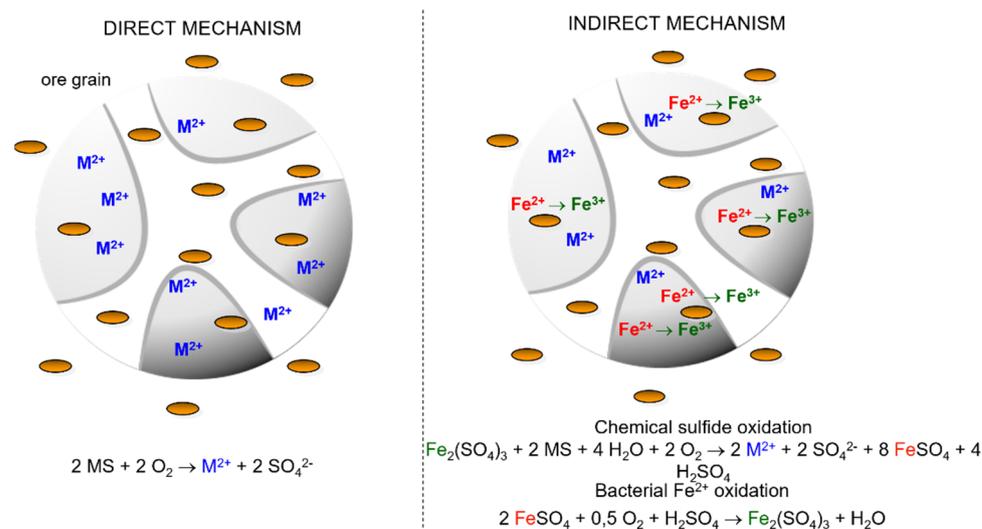



Figure 3. Differences between direct and indirect bioleaching mechanisms (M-metal).

The most often used bacteria producing sulfuric acid as one of the leaching agents belong to the genus *Acidithiobacillus*. Among them, mesophilic *A. ferrooxidans* and *A. thiooxidans* as well as moderately thermophilic *A. caldus* is the most widely applied. From other genera, members of the genus *Leptospirillum*, such as *L. ferriphilum* and *L. ferrooxidans*, are often studied [103,104]. At the present time, thermophiles (such as *Sulfobacillus thermosulfidooxidans*, *S. acidophilus*, *Ferroplasma thermophilum*, *Thermoplasma acidophilum*) have also attracted more attention [105,106]. The application of sulfuric acid producing bacteria in metal recovery from low-grade ores is well-established biotechnology in the industry. However, in recent years due to the growing market of consumer goods resulting in increasing amounts of various wastes, metal bioleaching applied in metal-containing waste materials spread into this area as well. The growing interest in Fe- and S-oxidizing bacteria utilization in metal recovery from waste is also visible from an increasing amount of waste materials successfully treated with acidophilic bacteria. Over 90% of Cu, Zn, and Ni was recovered from spent printed circuit boards from computers [107–109], in some studies reaching almost 100% efficiency [4,6]. The process was successfully applied to various battery treatment, such as Ni-Cd batteries [110], spent coin cells, Zn-Mn batteries [111], or Li-batteries [112]. Furthermore, other kinds of waste, such as electroplating sludge, sewage sludge [5] or incineration sludge [113], LED and LCD [114,115], and waste magnets [103] were treated with acid producing bacteria with high efficiency not only for non-ferrous metals recovery but also for rare earth elements (Supplementary Table S2).

Despite various advantages mentioned above, bioleaching as an emerging technology in waste treatment suffers from various limitations. Among them, the most challenging is the slow leaching rate and metal ion toxicity for bacteria often leading to low efficiency. Leaching times are often longer, with lower pulp densities and leach yields [116]. Adaptation of bacteria to waste material is the simplest way to increase the bioleaching efficiency [101]. The exploitation of thermophilic bacteria seems to be another way how to overcome time and efficiency limitations. Zhou et al. (2019) reached over 99% recovery of Cu, Zn, Ni, and Cr from electroplating sludge within 5 hours after application of the consortium of moderately thermophilic bacteria [105]. Total Mn dissolution was reached after the application of a consortium of thermophilic S-oxidizing bacteria to bioleaching of sewage sludge. A promising approach to reducing the toxicity of metals resulting in higher yields in a shorter time is the application of indirect, non-contact bioleaching, also called two-step bioleaching [117]. Bioleaching agents are generated by microbial cultures in a separate reactor without the addition of waste. Then, the spent media containing ferric iron and sulfuric acid or secondary metabolites (cyanide, organic acids) are used in a consequent leaching step without direct contact of waste with bacteria. It allows increasing the pulp

density by over 10% [118] which significantly affects the reactor design and operating cost. The increase of the pulp density from 1 to 10% leads to a sharp decrease (by 90%) of the liquid phase volume and the reactor size, significantly reducing the treatment costs [119]. Recently the application of a voltage in a bioleaching reactor demonstrated a significant reduction of bioleaching time [120]. Metals, such as Cu, Zn, Cr, and Ni, have been extracted from electroplating sludge with an efficiency ranging from 66 to 84% within 9 hours. The voltage of 0.2 V has been shown to be the most effective for maximizing metal extraction. The authors suggested using a bio-electrochemical reactor for the metabolic stimulation of microbially-influenced processes [120]. Wei et al. (2020a) found that direct current electric field application in bioleaching significantly enhanced bioactivity, facilitated Fe^{2+} ions oxidation, and shortened the time of total Cu bioleaching from 5 to 3 days [121].

4. Future Perspectives and Conclusions

Industrial scale bio-based chemical production is compulsory for a sustainable and environmentally friendly chemical industry. Furthermore, waste streams offer a valuable feedstock for biobased chemical production to sustain circular economy objectives. Nevertheless, the bioproduction process must be optimized for efficient and economical production and acidic conditions have several advantages for biobased chemical production depending on the product type: In biohydrogen production and bioleaching, acidic conditions are the force majeure. In organic acid production, acidic pH provides easier operation and less chemical consumption for pH regulations. This review paper aimed to provide a comprehensive perspective for acidic conditions on the production of the most promising bio-based chemicals.

Organic acids, specifically VFA, have gained worldwide attention as promising bio-based products for resource recovery approaches from waste streams. It is expected to increase considerably in the next decade due to the objectives of both the Horizon Europe 2030 and the EU Green Deal—as well as national programs and agreements. From the view of VFA production from waste streams, acidogenic conditions have importance regarding process efficiency and product profile. Despite that VFA cannot be produced under pH 4.5 by mixed culture, pH 5 enhances VFA production for long term reactor operation and it provides chain elongation conditions. Nevertheless, further studies are required for process optimization to increase production efficiency and to produce target products by tailor-made process design.

Aerobic production of acetic acid by pure cultures is a promising alternative to mixed cultures, due to acido-tolerant mechanisms present in certain bacterial species of the genera *Komagataeibacter* and *Acetobacter*. Moreover, some strains even increase acetic acid production rate at lower pH. However, further technological improvements are needed for this microbial process, especially due to the necessity for constant oxygen supply to bacteria producing acetic acid.

Inoculating certain microorganisms for bioaugmentation will improve the process efficiency of anaerobic digestion by either increasing the resistance of microorganisms to organic or hydraulic overloading conditions, improving methane production and decreasing the start-up period of a bioreactor, or in combination. Application of pretreatment and bioaugmentation in combination with lignocellulosic substrates can enhance methane yields significantly. Besides, injecting hydrogen gas into the reactor for biogas upgrading can also enrich hydrogenotrophic methanogens which also prevents reactor failure during instabilities.

Biohydrogen could play important role in future green energetics as well as the basic substrate for the chemical industry; first, one should solve the problem of stable operation of the dark fermentation process. However, it was already confirmed that some biogas plants (with acidic pretreatment) might be easily transformed for the efficient production of cheap hydrogen. In order to stabilize the hydrogen production in industrial installations, low pH control during process operation and an efficient hydrogen release system are

necessary. Furthermore, further research on optimal fermentation conditions for various available biowastes is recommended.

The exploitation of bacterial leaching is growing in the metal recycling sector owing to its low energy and capital input, mild reaction conditions, and environmentally friendly operations. It offers a competitive alternative for recycling complex and refractory metal-bearing solid wastes. Based on the process advantages, metal bioleaching from secondary resources is considered a significant area of research for securing critical metals for the European market and developing processes adopting circular economy principles, especially in combination with other biological processes for metal extraction from solutions, such as bioaccumulation or biosorption. However, there are still several limitations that need to be solved, such as the longer time necessary for the process compared to the conventional processes, lower efficiency due to metal toxicity to bacteria, etc. Application of thermophilic bacteria, indirect bioleaching using spent bioleaching media or application of voltage can increase the efficiency considerably and shorten the time required for the process.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/fermentation8030115/s1, Figure S1: Cumulative hydrogen production from: cotton with pH 6 ■ or without pH control □ and from sour cabbage with pH 6 (OFR = 0) ● and (OFR = 2 mL/h) ○ and without pH control ×; VSS 40 g/L; Figure S2: Cumulative methane production from sour cabbage under pH 6 control conditions (OFR = 0) ● and (OFR = 2 mL/h) ○; VSS 40 g/L; Table S1: Bioleaching by organic acid producers; Table S2: Bioleaching by inorganic acid producers.

Author Contributions: Writing—original draft preparation: all authors; writing—review and editing: Z.C., M.A. and J.S.-K.; visualization: M.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: This work was funded through the COST Action "Understanding and exploiting the impacts of low pH on microorganisms" (EuroMicropH) CA18113.

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

References

1. Mussatto, S.I. Challenges in Building a Sustainable Biobased Economy. *Ind. Crops Prod.* **2017**, *106*, 1–2. [CrossRef]
2. Van Schoubroeck, S.; Van Dael, M.; Van Passel, S.; Malina, R. A review of sustainability indicators for biobased chemicals. *Renew. Sustain. Energy Rev.* **2018**, *94*, 115–126. [CrossRef]
3. Chen, Y.; Nielsen, J. ScienceDirect Biobased organic acids production by metabolically engineered microorganisms. *Curr. Opin. Biotechnol.* **2016**, *37*, 165–172. [CrossRef]
4. Sedlakova-Kadukova, J.; Marcincakova, R.; Mrazikova, A.; Willner, J.; Fornalczyk, A. Closing the loop: Key role of iron in metal-bearing waste recycling. *Arch. Metall. Mater.* **2017**, *62*, 1459–1466. [CrossRef]
5. Chen, S.-Y.; Cheng, Y.-K. Effects of sulfur dosage and inoculum size on pilot-scale thermophilic bioleaching of heavy metals from sewage sludge. *Chemosphere* **2019**, *234*, 346–355. [CrossRef]
6. Wei, X.; Liu, D.; Huang, W.; Huang, W.; Lei, Z. Simultaneously enhanced Cu bioleaching from E-wastes and recovered Cu ions by direct current electric field in a bioelectrical reactor. *Bioresour. Technol.* **2020**, *298*, 122566. [CrossRef]
7. Yu, Z.; Han, H.; Feng, P.; Zhao, S.; Zhou, T.; Kakade, A.; Kulshrestha, S.; Majeed, S.; Li, X. Recent advances in the recovery of metals from waste through biological processes. *Bioresour. Technol.* **2020**, *297*, 122416. [CrossRef]
8. European Commission. *The European Green Deal*; European Commission: Luxembourg, 2019.
9. Vidra, A.; Németh, Á. Bio-produced acetic acid: A review. *Period. Polytech. Chem. Eng.* **2018**, *62*, 57–67. [CrossRef]
10. 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]
11. Li, Y.; Sun, Y.; Li, L.; Yuan, Z. Acclimation of acid-tolerant methanogenic propionate-utilizing culture and microbial community dissecting. *Bioresour. Technol.* **2018**, *250*, 117–123. [CrossRef]
12. Sołowski, G.; Konkol, I.; Cenian, A. Methane and hydrogen production from cotton waste by dark fermentation under anaerobic and micro-aerobic conditions. *Biomass Bioenergy* **2020**, *138*, 105576. [CrossRef]

13. Sarkar, O.; Rova, U.; Christakopoulos, P.; Matsakas, L. Influence of initial uncontrolled pH on acidogenic fermentation of brewery spent grains to biohydrogen and volatile fatty acids production: Optimization and scale-up. *Bioresour. Technol.* **2021**, *319*, 124233. [CrossRef] [PubMed]

14. Atasoy, M.; Owusu-Agyeman, I.; Plaza, E.; Cetecioglu, Z. Bio-based volatile fatty acid production and recovery from waste streams: Current status and future challenges. *Bioresour. Technol.* **2018**, *268*, 773–786. [CrossRef] [PubMed]

15. Bhatia, S.K.; Yang, Y.-H. Microbial production of volatile fatty acids: Current status and future perspectives. *Rev. Environ. Sci. Bio./Technol.* **2017**, *16*, 327–345. [CrossRef]

16. Lee, W.S.; Chua, A.S.M.; Yeoh, H.K.; Ngoh, G.C. A review of the production and applications of waste-derived volatile fatty acids. *Chem. Eng. J.* **2014**, *235*, 83–99. [CrossRef]

17. Spekreijse, J.; Lammens, T.; Parisi, C.; Ronzon, T.; Vis, M. Insights into the European Market of bio-based chemicals. In *Analysis Based on Ten Key Product Categories*; Publications Office of the European Union: Luxembourg, 2019.

18. Khan, M.A.; Ngo, H.H.; Guo, W.; Chang, S.W.; Nguyen, D.D.; Varjani, S.; Liu, Y.; Deng, L.; Cheng, C. Selective production of volatile fatty acids at different pH in an anaerobic membrane bioreactor. *Bioresour. Technol.* **2019**, *283*, 120–128. [CrossRef]

19. Yu, X.; Yin, J.; Shen, D.; Shentu, J.; Long, Y.; Chen, T. Improvement of acidogenic fermentation for volatile fatty acid production from protein-rich substrate in food waste. *Waste Manag.* **2018**, *74*, 177–184. [CrossRef]

20. Jiang, J.; Zhang, Y.; Li, K.; Wang, Q.; Gong, C.; Li, M. Volatile fatty acids production from food waste: Effects of pH, temperature, and organic loading rate. *Bioresour. Technol.* **2013**, *143*, 525–530. [CrossRef]

21. Atasoy, M.; Eyice, O.; Schnürer, A.; Cetecioglu, Z. Volatile fatty acids production via mixed culture fermentation: Revealing the link between pH, inoculum type and bacterial composition. *Bioresour. Technol.* **2019**, *292*, 121889. [CrossRef]

22. de Lemos Chernicharo, C.A. *Anaerobic Reactors*; IWA Publishing: London, UK, 2015; Volume 6, ISBN 9781843391647.

23. Meng, Y.; Mumme, J.; Xu, H.; Wang, K. A biologically inspired variable-pH strategy for enhancing short-chain fatty acids (SCFAs) accumulation in maize straw fermentation. *Bioresour. Technol.* **2016**, *201*, 329–336. [CrossRef]

24. Joyce, A.; Ijaz, U.Z.; Nzeteu, C.; Vaughan, A.; Shirran, S.L.; Botting, C.H.; Quince, C.; O'Flaherty, V.; Abram, F. Linking microbial community structure and function during the acidified anaerobic digestion of grass. *Front. Microbiol.* **2018**, *9*, 540. [CrossRef] [PubMed]

25. Weissbrodt, D.G.; Laureni, M.; van Loosdrecht, M.C.M.; Comeau, Y.; Chen, G.; Ekama, G.A.; van Loosdrecht, M.C.M.; Brdjanovic, D. (Eds.) Basic microbiology and metabolism. In *Biological Wastewater Treatment: Principles, Modeling and Design*; IWA Publishing: London, UK, 2020; ISBN 9781789060362.

26. Zhang, B.; Zhang, L.-L.; Zhang, S.-C.; Shi, H.-Z.; Cai, W.-M. The Influence of pH on Hydrolysis and Acidogenesis of Kitchen Wastes in Two-phase Anaerobic Digestion. *Environ. Technol.* **2005**, *26*, 329–340. [CrossRef] [PubMed]

27. Jankowska, E.; Chwialkowska, J.; Stodolny, M.; Oleskowicz-Popiel, P. Volatile fatty acids production during mixed culture fermentation—The impact of substrate complexity and pH. *Chem. Eng. J.* **2017**, *326*, 901–910. [CrossRef]

28. Feng, K.; Wang, Q.; Li, H.; Zhang, Y.; Deng, Z.; Liu, J.; Du, X. Effect of fermentation type regulation using alkaline addition on two-phase anaerobic digestion of food waste at different organic load rates. *Renew. Energy* **2020**, *154*, 385–393. [CrossRef]

29. van Aarle, I.M.; Perimenis, A.; Lima-Ramos, J.; de Hults, E.; George, I.F.; Gerin, P.A. Mixed inoculum origin and lignocellulosic substrate type both influence the production of volatile fatty acids during acidogenic fermentation. *Biochem. Eng. J.* **2015**, *103*, 242–249. [CrossRef]

30. Liu, H.; Wang, J.; Liu, X.; Fu, B.; Chen, J.; Yu, H.-Q. Acidogenic fermentation of proteinaceous sewage sludge: Effect of pH. *Water Res.* **2012**, *46*, 799–807. [CrossRef]

31. Fang, W.; Zhang, X.; Zhang, P.; Wan, J.; Guo, H.; Ghasimi, D.S.M.; Morera, X.C.; Zhang, T. Overview of key operation factors and strategies for improving fermentative volatile fatty acid production and product regulation from sewage sludge. *J. Environ. Sci. (China)* **2020**, *87*, 93–111. [CrossRef]

32. Owusu-Agyeman, I.; Plaza, E.; Cetecioglu, Z. Production of volatile fatty acids through co-digestion of sewage sludge and external organic waste: Effect of substrate proportions and long-term operation. *Waste Manag.* **2020**, *112*, 30–39. [CrossRef]

33. Clauser, N.M.; González, G.; Mendieta, C.M.; Kruyeniski, J.; Area, M.C.; Vallejos, M.E. Biomass waste as sustainable raw material for energy and fuels. *Sustainability* **2021**, *13*, 794. [CrossRef]

34. Sun, J.; Zhang, L.; Loh, K.C. Review and perspectives of enhanced volatile fatty acids production from acidogenic fermentation of lignocellulosic biomass wastes. *Bioresour. Bioprocess.* **2021**, *8*, 68. [CrossRef]

35. She, Y.; Hong, J.; Zhang, Q.; Chen, B.Y.; Wei, W.; Xin, X. Revealing microbial mechanism associated with volatile fatty acids production in anaerobic acidogenesis of waste activated sludge enhanced by freezing/thawing pretreatment. *Bioresour. Technol.* **2020**, *302*, 122869. [CrossRef] [PubMed]

36. Atasoy, M.; Cetecioglu, Z. Butyric acid dominant volatile fatty acids production: Bio-Augmentation of mixed culture fermentation by Clostridium butyricum. *J. Environ. Chem. Eng.* **2020**, *8*, 104496. [CrossRef]

37. Zigová, J.; Šturdík, E. Advances in biotechnological production of butyric acid. *J. Ind. Microbiol. Biotechnol.* **2000**, *24*, 153–160. [CrossRef]

38. Khan, M.A.; Ngo, H.H.; Guo, W.S.; Liu, Y.; Nghiem, L.D.; Hai, F.I.; Deng, L.J.; Wang, J.; Wu, Y. Optimization of process parameters for production of volatile fatty acid, biohydrogen and methane from anaerobic digestion. *Bioresour. Technol.* **2016**, *219*, 738–748. [CrossRef] [PubMed]

39. Allied Market Research. *World Acetic Acid Market—Opportunities and Forecasts, 2019–2026*; Allied Market Research: Portland, OR, USA, 2020.
40. Trček, J.; Barja, F. Updates on quick identification of acetic acid bacteria with a focus on the 16S-23S rRNA gene internal transcribed spacer and the analysis of cell proteins by MALDI-TOF mass spectrometry. *Int. J. Food Microbiol.* **2015**, *196*, 137–144. [CrossRef] [PubMed]
41. Li, Y.; He, D.; Niu, D.; Zhao, Y. Acetic acid production from food wastes using yeast and acetic acid bacteria micro-aerobic fermentation. *Bioprocess Biosyst. Eng.* **2015**, *38*, 863–869. [CrossRef]
42. Trček, J.; Mira, N.P.; Jarboe, L.R. Adaptation and tolerance of bacteria against acetic acid. *Appl. Microbiol. Biotechnol.* **2015**, *99*, 6215–6229. [CrossRef]
43. Trcek, J.; Toyama, H.; Czuba, J.; Misiewicz, A.; Matsushita, K. Correlation between acetic acid resistance and characteristics of PQQ-dependent ADH in acetic acid bacteria. *Appl. Microbiol. Biotechnol.* **2006**, *70*, 366–373. [CrossRef]
44. Trček, J.; Jernejc, K.; Matsushita, K. The highly tolerant acetic acid bacterium Gluconacetobacter europaeus adapts to the presence of acetic acid by changes in lipid composition, morphological properties and PQQ-dependent ADH expression. *Extremophiles* **2007**, *11*, 627–635. [CrossRef]
45. Matsushita, K.; Takaki, Y.; Shinagawa, E.; Ameyama, M.; Osao, A. Ethanol Oxidase Respiratory Chain of Acetic Acid Bacteria. Reactivity with Ubiquinone of Pyrroloquinoline Qui none-dependent Alcohol Dehydrogenases Purified from Aceto-bacter aceti and Gluconobacter suboxydans. *Biosci. Biotechnol. Biochem.* **1992**, *56*, 304–310. [CrossRef]
46. Vashisht, A.; Thakur, K.; Kauldhar, B.S.; Kumar, V.; Yadav, S.K. Waste valorization: Identification of an ethanol tolerant bacterium Acetobacter pasteurianus SKYAA25 for acetic acid production from apple pomace. *Sci. Total Environ.* **2019**, *690*, 956–964. [CrossRef] [PubMed]
47. Perumpuli, P.A.B.N.; Watanabe, T.; Toyama, H. Identification and characterization of thermotolerant acetic acid bacteria strains isolated from coconut water vinegar in Sri Lanka. *Biosci. Biotechnol. Biochem.* **2014**, *78*, 533–541. [CrossRef] [PubMed]
48. Tanamool, V.; Chantarangsee, M.; Soemphol, W. Simultaneous vinegar fermentation from a pineapple by-product using the co-inoculation of yeast and thermotolerant acetic acid bacteria and their physiochemical properties. *3 Biotech* **2020**, *10*, 115. [CrossRef] [PubMed]
49. Pal, P.; Nayak, J. Acetic Acid Production and Purification: Critical Review Towards Process Intensification. *Sep. Purif. Rev.* **2017**, *46*, 44–61. [CrossRef]
50. Matsushita, K.; Inoue, T.; Adachi, O.; Toyama, H. Acetobacter aceti possesses a proton motive force-dependent efflux system for acetic acid. *J. Bacteriol.* **2005**, *187*, 4346–4352. [CrossRef] [PubMed]
51. Zheng, Y.; Chang, Y.; Zhang, R.; Song, J.; Xu, Y.; Liu, J.; Wang, M. Two-stage oxygen supply strategy based on energy metabolism analysis for improving acetic acid production by Acetobacter pasteurianus. *J. Ind. Microbiol. Biotechnol.* **2018**, *45*, 781–788. [CrossRef] [PubMed]
52. Anderson, G.; Yang, G. pH Control in Anaerobic Treatment of Industrial Wastewater. *J. Environ. Eng.* **1992**, *118*, 551–567. [CrossRef]
53. Bräuer, S.L.; Cadillo-Quiroz, H.; Yashiro, E.; Yavitt, J.B.; Zinder, S.H. Isolation of a novel acidiphilic methanogen from an acidic peat bog. *Nature* **2006**, *442*, 192–194. [CrossRef]
54. Taconi, K.A.; Zappi, M.E.; Todd French, W.; Brown, L.R. Methanogenesis under acidic pH conditions in a semi-continuous reactor system. *Bioresour. Technol.* **2008**, *99*, 8075–8081. [CrossRef]
55. Ugurlu, A.; Forster, C.F. The impact of shock loadings on the performance of thermophilic anaerobic filters with porous and non-porous packings. *Bioresour. Technol.* **1992**, *39*, 23–30. [CrossRef]
56. Li, Y.; Zhang, Y.; Liu, Y.; Zhao, Z.; Zhao, Z.; Liu, S.; Zhao, H.; Quan, X. Enhancement of anaerobic methanogenesis at a short hydraulic retention time via bioelectrochemical enrichment of hydrogenotrophic methanogens. *Bioresour. Technol.* **2016**, *218*, 505–511. [CrossRef] [PubMed]
57. Wilkins, D.; Lu, X.-Y.; Shen, Z.; Chen, J.; Lee, P.K.H. Pyrosequencing of mcrA and archaeal 16S rRNA genes reveals diversity and substrate preferences of methanogen communities in anaerobic digesters. *Appl. Environ. Microbiol.* **2015**, *81*, 604–613. [CrossRef] [PubMed]
58. Kurade, M.B.; Xiong, J.-Q.; Govindwar, S.P.; Roh, H.-S.; Saratale, G.D.; Jeon, B.-H.; Lim, H. Uptake and biodegradation of emerging contaminant sulfamethoxazole from aqueous phase using Ipomoea aquatica. *Chemosphere* **2019**, *225*, 696–704. [CrossRef] [PubMed]
59. Khan, M.U.; Ahring, B.K. Lignin degradation under anaerobic digestion: Influence of lignin modification—A review. *Biomass Bioenergy* **2019**, *128*, 105325. [CrossRef]
60. Wang, H.; Li, J.; Zhao, Y.; Xu, C.; Zhang, K.; Li, J.; Yan, L.; Gu, J.-D.; Wei, D.; Wang, W. Establishing practical strategies to run high loading corn stover anaerobic digestion: Methane production performance and microbial responses. *Bioresour. Technol.* **2020**, *310*, 123364. [CrossRef]
61. Shimada, T.; Morgenroth, E.; Tandukar, M.; Pavlostathis, S.G.; Smith, A.; Raskin, L.; Kilian, R.E. Syntrophic acetate oxidation in two-phase (acid–methane) anaerobic digesters. *Water Sci. Technol.* **2011**, *64*, 1812–1820. [CrossRef]
62. Xiao, K.K.; Guo, C.H.; Zhou, Y.; Maspolim, Y.; Wang, J.Y.; Ng, W.J. Acetic acid inhibition on methanogens in a two-phase anaerobic process. *Biochem. Eng. J.* **2013**, *75*, 1–7. [CrossRef]
63. Dalkılıc, K.; Ugurlu, A. Biogas production from chicken manure at different organic loading rates in a mesophilic-thermopilic two stage anaerobic system. *J. Biosci. Bioeng.* **2015**, *120*, 315–322. [CrossRef]

64. Pradhan, N.; d'Ippolito, G.; Dipasquale, L.; Esposito, G.; Panico, A.; Lens, P.N.L.; Fontana, A. Simultaneous synthesis of lactic acid and hydrogen from sugars via capnophilic lactic fermentation by Thermotoga neapolitana cf capnolactica. *Biomass Bioenergy* **2019**, *125*, 17–22. [CrossRef]

65. Poggi-Varaldo, H.M.; Munoz-Paez, K.M.; Escamilla-Alvarado, C.; Robledo-Narváez, P.N.; Ponce-Noyola, M.T.; Calva-Calva, G.; Ríos-Leal, E.; Galíndez-Mayer, J.; Estrada-Vázquez, C.; Ortega-Clemente, A.; et al. Biohydrogen, biomethane and bioelectricity as crucial components of biorefinery of organic wastes: A review. *Waste Manag. Res.* **2014**, *32*, 353–365. [CrossRef]

66. Muñoz-Páez, K.M.; Alvarado-Michi, E.L.; Buitrón, G.; Valdez-Vazquez, I. Distinct effects of furfural, hydroxymethylfurfural and its mixtures on dark fermentation hydrogen production and microbial structure of a mixed culture. *Int. J. Hydrogen Energy* **2019**, *44*, 2289–2297. [CrossRef]

67. Kim, C. Potential of anaerobic digestion for material recovery and energy production in waste biomass from a poultry slaughter-house. *Waste Manag.* **2016**, *34*, 204–209. [CrossRef] [PubMed]

68. Nasirian, N.; Almassi, M.; Minaei, S.; Widmann, R. Development of a method for biohydrogen production from wheat straw by dark fermentation. *Int. J. Hydrogen Energy* **2011**, *36*, 411–420. [CrossRef]

69. Li, Y.; Yang, G.; Li, L.; Sun, Y. Bioaugmentation for overloaded anaerobic digestion recovery with acid-tolerant methanogenic enrichment. *Waste Manag.* **2018**, *79*, 744–751. [CrossRef]

70. Giovannini, G.; Donoso-Bravo, A.; Jeison, D.; Chamy, R.; Ruíz-Filippi, G.; Vande Wouwer, A. A review of the role of hydrogen in past and current modelling approaches to anaerobic digestion processes. *Int. J. Hydrogen Energy* **2016**, *41*, 17713–17722. [CrossRef]

71. Lakaniemi, A.-M.; Koskinen, P.E.P.; Nevatalo, L.M.; Kaksonen, A.H.; Puhakka, J.A. Biogenic hydrogen and methane production from reed canary grass. *Biomass Bioenergy* **2011**, *35*, 773–780. [CrossRef]

72. Li, Y.; Zhang, Q.; Deng, L.; Liu, Z.; Jiang, H.; Wang, F. Biohydrogen production from fermentation of cotton stalk hydrolysate by Klebsiella sp. WL1316 newly isolated from wild carp (*Cyprinus carpio* L.) of the Tarim River basin. *Appl. Microbiol. Biotechnol.* **2018**, *102*, 4231–4242. [CrossRef]

73. Chi, C.H.; Chen, K.W.; Huang, J.J.; Chuang, Y.C.; Wu, M.H. Gas composition in Clostridium septicum gas gangrene. *J. Formos. Med. Assoc.* **1995**, *94*, 757–759.

74. Nasirian, N.; Almassi, M. Optimization of biological hydrogen production process using stepwise regression method. *Int. J. Biosci.* **2014**, *6655*, 289–299. [CrossRef]

75. Sindhu, R.; Binod, P.; Pandey, A. Biological pretreatment of lignocellulosic biomass—An overview. *Bioresour. Technol.* **2016**, *199*, 76–82. [CrossRef]

76. Chen, X.; Xiang, X.; Dai, R.; Wang, Y.; Ma, P. Effect of low temperature of thermal pretreatment on anaerobic digestion of textile dyeing sludge. *Bioresour. Technol.* **2017**, *243*, 426–432. [CrossRef] [PubMed]

77. Kumari, D.; Singh, R. Pretreatment of lignocellulosic wastes for biofuel production: A critical review. *Renew. Sustain. Energy Rev.* **2018**, *90*, 877–891. [CrossRef]

78. Yoo, C.G.; Meng, X.; Pu, Y.; Ragauskas, A.J. The critical role of lignin in lignocellulosic biomass conversion and recent pretreatment strategies: A comprehensive review. *Bioresour. Technol.* **2020**, *301*, 122784. [CrossRef] [PubMed]

79. Nissilä, M.E.; Li, Y.-C.; Wu, S.-Y.; Puhakka, J.A. Dark Fermentative Hydrogen Production from Neutralized Acid Hydrolysates of Conifer Pulp. *Appl. Biochem. Biotechnol.* **2012**, *168*, 2160–2169. [CrossRef]

80. Cieciura-Włoch, W.; Borowski, S.; Domański, J. Dark fermentative hydrogen production from hydrolyzed sugar beet pulp improved by iron addition. *Bioresour. Technol.* **2020**, *314*, 123713. [CrossRef]

81. Detman, A.; Laubitz, D.; Chojnacka, A.; Wiktorowska-Sowa, E.; Piotrowski, J.; Salamon, A.; Kaźmierczak, W.; Błaszczyk, M.K.; Barberan, A.; Chen, Y.; et al. Dynamics and Complexity of Dark Fermentation Microbial Communities Producing Hydrogen From Sugar Beet Molasses in Continuously Operating Packed Bed Reactors. *Front. Microbiol.* **2021**, *11*, 3303. [CrossRef]

82. Cieslik, M.; Dach, J.; Lewicki, A.; Smurzyńska, A.; Janczak, D.; Pawlicka-Kaczorowska, J.; Boniecki, P.; Cyplik, P.; Czekała, W.; Jóźwiakowski, K. Methane fermentation of the maize straw silage under meso- and thermophilic conditions. *Energy* **2016**, *115*, 1495–1502. [CrossRef]

83. Kozłowski, K.; Lewicki, A.; Malińska, K.; Wei, Q. Current State, Challenges and Perspectives of Biological Production of Hydrogen in Dark Fermentation Process in Poland. *J. Ecol. Eng.* **2019**, *20*, 146–160. [CrossRef]

84. Chong, M.-L.; Sabaratnam, V.; Shirai, Y.; Hassan, M.A. Biohydrogen production from biomass and industrial wastes by dark fermentation. *Int. J. Hydrogen Energy* **2009**, *34*, 3277–3287. [CrossRef]

85. Fomina, M.A.; Alexander, I.J.; Colpaert, J.V.; Gadd, G.M. Solubilization of toxic metal minerals and metal tolerance of mycorrhizal fungi. *Soil Biol. Biochem.* **2005**, *37*, 851–866. [CrossRef]

86. 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]

87. Gadd, G.M. Metals, minerals and microbes: Geomicrobiology and bioremediation. *Microbiology* **2010**, *156*, 609–643. [CrossRef] [PubMed]

88. Faraji, F.; Golmohammadzadeh, R.; Rashchi, F.; Alimardani, N. Fungal bioleaching of WPCBs using Aspergillus niger: Observation, optimization and kinetics. *J. Environ. Manag.* **2018**, *217*, 775–787. [CrossRef] [PubMed]

89. Sedlakova-Kadukova, J.; Marcincakova, R.; Luptakova, A.; Vojtko, M.; Fujda, M.; Pristas, P. Comparison of three different bioleaching systems for Li recovery from lepidolite. *Sci. Rep.* **2020**, *10*, 14594. [CrossRef]

90. Mouna, H.M.; Baral, S.S. A bio-hydrometallurgical approach towards leaching of lanthanum from the spent fluid catalytic cracking catalyst using Aspergillus niger. *Hydrometallurgy* **2019**, *184*, 175–182. [CrossRef]

91. Urík, M.; Bujdoš, M.; Milová-Žiaková, B.; Mikušová, P.; Slovák, M.; Matúš, P. Aluminium leaching from red mud by filamentous fungi. *J. Inorg. Biochem.* **2015**, *152*, 154–159. [CrossRef]

92. Cui, J.; Zhu, N.; Li, Y.; Luo, D.; Wu, P.; Dang, Z. Rapid and green process for valuable materials recovery from waste liquid crystal displays. *Resour. Conserv. Recycl.* **2020**, *153*, 104544. [CrossRef]

93. Bahaloo-Horeh, N.; Mousavi, S.M.; Baniasadi, M. Use of adapted metal tolerant Aspergillus niger to enhance bioleaching efficiency of valuable metals from spent lithium-ion mobile phone batteries. *J. Clean. Prod.* **2018**, *197*, 1546–1557. [CrossRef]

94. Arshadi, M.; Nili, S.; Yaghmaei, S. Ni and Cu recovery by bioleaching from the printed circuit boards of mobile phones in non-conventional medium. *J. Environ. Manag.* **2019**, *250*, 109502. [CrossRef]

95. Díaz-Martínez, M.E.; Argumedo-Delira, R.; Sánchez-Viveros, G.; Alarcón, A.; Mendoza-López, M.R. Microbial Bioleaching of Ag, Au and Cu from Printed Circuit Boards of Mobile Phones. *Curr. Microbiol.* **2019**, *76*, 536–544. [CrossRef]

96. Kaliyaraj, D.; Rajendran, M.; Angamuthu, V.; Antony, A.R.; Kaari, M.; Thangavel, S.; Venugopal, G.; Joseph, J.; Manikkam, R. Bioleaching of heavy metals from printed circuit board (PCB) by Streptomyces albidoflavus TN10 isolated from insect nest. *Bioresour. Bioprocess.* **2019**, *6*, 47. [CrossRef]

97. Willner, J.; Fornalczyk, A. Extraction of metals from electronic waste by bacterial leaching. *Environ. Prot. Eng.* **2013**, *39*, 197–208. [CrossRef]

98. Akbari, S.; Ahmadi, A. Recovery of copper from a mixture of printed circuit boards (PCBs) and sulphidic tailings using bioleaching and solvent extraction processes. *Chem. Eng. Process. Process Intensif.* **2019**, *142*, 107584. [CrossRef]

99. Pagnanelli, F.; Moscardini, E.; Altimari, P.; Abo Atia, T.; Toro, L. Leaching of electrodic powders from lithium ion batteries: Optimization of operating conditions and effect of physical pretreatment for waste fraction retrieval. *Waste Manag.* **2017**, *60*, 706–715. [CrossRef] [PubMed]

100. Ehrlich, H.L.; Newman, D.K. *Geomicrobiology*; CRC Press: Boca Raton, FL, USA, 2009.

101. Mražíková, A.; Marcinčáková, R.; Kaduková, J.; Velgosová, O. Influence of bacterial culture to copper bioleaching from printed circuit boards. *Inz. Miner.* **2013**, *14*, 59–62.

102. Dorado, A.D.; Solé, M.; Lao, C.; Alfonso, P.; Gamisans, X. Effect of pH and Fe(III) ions on chalcopyrite bioleaching by an adapted consortium from biogas sweetening. *Miner. Eng.* **2012**, *39*, 36–38. [CrossRef]

103. Auerbach, R.; Bokelmann, K.; Stauber, R.; Gutfleisch, O.; Schnell, S.; Ratering, S. Critical raw materials—Advanced recycling technologies and processes: Recycling of rare earth metals out of end of life magnets by bioleaching with various bacteria as an example of an intelligent recycling strategy. *Miner. Eng.* **2019**, *134*, 104–117. [CrossRef]

104. Ma, X.; Gao, M.; Yin, Z.; Zhu, W.; Liu, S.; Wang, Q. Lactic acid and animal feeds production from Sophora flavescens residues by Rhizopus oryzae fermentation. *Process Biochem.* **2020**, *92*, 401–408. [CrossRef]

105. Zhou, W.; Zhang, L.; Peng, J.; Ge, Y.; Tian, Z.; Sun, J.; Cheng, H.; Zhou, H. Cleaner utilization of electroplating sludge by bioleaching with a moderately thermophilic consortium: A pilot study. *Chemosphere* **2019**, *232*, 345–355. [CrossRef]

106. Zhang, L.; Zhou, W.; Liu, Y.; Jia, H.; Zhou, J.; Wei, P.; Zhou, H. Bioleaching of dewatered electroplating sludge for the extraction of base metals using an adapted microbial consortium: Process optimization and kinetics. *Hydrometallurgy* **2020**, *191*, 105227. [CrossRef]

107. Priya, A.; Hait, S. Extraction of metals from high grade waste printed circuit board by conventional and hybrid bioleaching using Acidithiobacillus ferrooxidans. *Hydrometallurgy* **2018**, *177*, 132–139. [CrossRef]

108. Arshadi, M.; Mousavi, S.M. Multi-objective optimization of heavy metals bioleaching from discarded mobile phone PCBs: Simultaneous Cu and Ni recovery using Acidithiobacillus ferrooxidans. *Sep. Purif. Technol.* **2015**, *147*, 210–219. [CrossRef]

109. Sodha, A.B.; Tipre, D.R.; Dave, S.R. Optimisation of biohydrometallurgical batch reactor process for copper extraction and recovery from non-pulverized waste printed circuit boards. *Hydrometallurgy* **2020**, *191*, 105170. [CrossRef]

110. Velgosová, O.; Kaduková, J.; Marcinčáková, R.; Mrážiková, A.; Fröhlich, L. The Role of Main Leaching Agents Responsible for Ni Bioleaching from spent Ni-Cd Batteries. *Sep. Sci. Technol.* **2014**, *49*, 438–444. [CrossRef]

111. Ubaldini, S.; Kadukova, J.; Mravzíková, A.; Fornari, P.; Luptáková, A.; Marcincakova, R.; Pizzichemi, P. Application of Innovative Processes for the Valorisation of Spent Alkaline Batteries. *Chem. Eng. Trans.* **2014**, *39*, 1609–1614.

112. Marcinčáková, R.; Kaduková, J.; Mražíková, A.; Velgosová, O.; Luptáková, A.; Ubaldini, S. Metal bioleaching from spent lithium-ion batteries using acidophilic bacterial strains. *Inz. Miner.* **2016**, *17*, 117–120.

113. Auerbach, R.; Ratering, S.; Bokelmann, K.; Gellermann, C.; Brämer, T.; Baumann, R.; Schnell, S. Bioleaching of valuable and hazardous metals from dry discharged incineration slag. An approach for metal recycling and pollutant elimination. *J. Environ. Manag.* **2019**, *232*, 428–437. [CrossRef]

114. Pourhossein, F.; Mousavi, S.M. Enhancement of copper, nickel, and gallium recovery from LED waste by adaptation of Acidithiobacillus ferrooxidans. *Waste Manag.* **2018**, *79*, 98–108. [CrossRef]

115. Pourhossein, F.; Mousavi, S.M. A novel step-wise indirect bioleaching using biogenic ferric agent for enhancement recovery of valuable metals from waste light emitting diode (WLED). *J. Hazard. Mater.* **2019**, *378*, 120648. [CrossRef]

116. Kaksonen, A.H.; Boxall, N.J.; Gumulya, Y.; Khaleque, H.N.; Morris, C.; Bohu, T.; Cheng, K.Y.; Usher, K.M.; Lakaniemi, A.-M. Recent progress in biohydrometallurgy and microbial characterisation. *Hydrometallurgy* **2018**, *180*, 7–25. [CrossRef]

117. Vyas, S.; Ting, Y.-P. Microbial leaching of heavy metals using Escherichia coli and evaluation of bioleaching mechanism. *Bioresour. Technol. Rep.* **2020**, *9*, 100368. [CrossRef]
118. Natarajan, G.; Ting, Y.-P. Gold biorecovery from e-waste: An improved strategy through spent medium leaching with pH modification. *Chemosphere* **2015**, *136*, 232–238. [CrossRef] [PubMed]
119. Yang, Q.; Hui, L.; Wenjie, T.; Xiaoqing, W.; Xuemeng, W.; Xiaohui, J.; Ben, S.; Song, G.; Tang, Y. Leaching of valuable metals from red mud via batch and continuous processes by using fungi. *Miner. Eng.* **2015**, *81*, 1–4.
120. Huang, T.; Wei, X.; Zhang, S. Bioleaching of copper sulfide minerals assisted by microbial fuel cells. *Bioresour. Technol.* **2019**, *288*, 121561. [CrossRef]
121. Wei, X.; Li, J.; Huang, W.; Zheng, X.; Li, S.; Chen, X.; Liu, D. Comparative Study of Iron-Oxidizing and Sulfur-Oxidizing Bioleaching Processes for Heavy Metal Removal and Nutrient Leaching from Pig Manure. *Water Air Soil Pollut.* **2020**, *231*, 34. [CrossRef]