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## Chapter

# The Use of Biochar of High Growth Rate Plants to Agriculturally Remediate Heavy Metal Polluted Acidic Mine Wastes

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## Abstract

The chapter is meant to expose how a sound methodology can be instrumented to both, remediate acidic metal polluted mine wastes, taking advantage of the neutralizing power and high metal sorption affinity of biochar, and to utilize pyrolyzed material derived from high-rate growth plants (water hyacinth, *Eichhornia crassipes* Mart, and Eucalyptus, *Eucalyptus globulus* Labill), which have become of ecological relevance due to their unwanted proliferation over specific terrestrial, lacustrine or riverine environments. In addition, the proposal considers not only neutralizing the mine tailings and abating the toxic levels of specific heavy metals like Pb, Cd, Cu, Zn, etc., to fulfill the international and national standards and norms, but to conveniently combine biochar with widely used soil amendments to pass widely recognized biological tests of growth using heavy metal-sensitive plants. The approach addresses firstly: a) characterizing physiochemically mine tailings and biochar, in terms of their properties (metal speciation and contents, potential acidity and neutralization potential, chemical oxygen demand, heavy metal-biochar sorption-complexing affinities, among others), and secondly; b) creating a "fertile environment" by reconditioning, agriculturally, the heavy metal-polluted acidic mine waste to allow native vegetation, or other reforestation species, to regrow on the reclaimed site, based on the bioassay tests performances.

**Keywords:** biochar, mine tailings remediation, soil amendments, heavy metal phytotoxicity, heavy metal availability and speciation

## 1. Introduction

Multi-metallic mine wastes from mining activities have been produced in large quantities and disposed on soils for centuries all over the world, most of the times in a non-environmentally safe way. When exposed to environmental factors like rain and air mine tails undergo continuous chemical changes involving acid-base, redox, sorption-dissolution, and complexation equilibria increasing both, the (bio)-availability levels of specific metals to local biota, and the metal mobility, increasing the risk of extending the polluting effects to ground water and adjacent soils, affecting all forms of life. Biochar additions to soils and mine wastes have proved to be useful for mitigating the

negative effects of metal phytotoxicity by augmenting the active surface and number of new sorption sites for metal retention and increasing pH of the once acidic metal-sulfidic mine wastes that would otherwise hamper the growth of vegetation. Among other beneficial effects of biochar additions, the increase of residence time of C in soils should be mentioned. The methodologic approach presented here shows a sound proposal of how a remediation strategy can be instrumented to agriculturally stabilize and reclaim acidic metal mine wastes and polluted soils. By taking advantage of many of the relevant biochar characteristics and properties that have proved to be instrumental when used, alone or in combination with fertilizers and other soil amendments (e.g., lime, gypsum, compost, etc.), to lower metal toxic levels, and modify the relevant physico-chemical waste and soil characteristics and properties. Firstly, we focus on mitigating the phytotoxic effects of the bioavailable essential and toxic heavy metal (Cu, Zn, Pb, Cd, etc.) deposited on the acid mine tailing dams, and secondly, on creating a "fertile environment" by reconditioning agriculturally, the HM-polluted acidic mine waste, to allow metal sensitive higher plant species to grow, so that the more resistant native vegetation, or other reforesting species, can regrow on the reclaimed site, based on the successful bioassay tests performed. Pyrolyzed material derived from high-rate growth plants (water hyacinth, *E. crassipes* Mart); Eucalyptus, (*E. globulus* Labill), among others, have become of ecological relevance due to their unwanted proliferation in many terrestrial, lacustrine or riverine environments all over the planet, so that the proposal considers not only neutralizing the mine tailings and abating the toxic levels of specific heavy metals (HM) like Pb, Cd, Cu, Zn, etc., to fulfill the international and national standards and norms, but to conveniently combine biochar based on these type of plant materials, with widely used soil amendments to pass any of the widely recognized biological tests of growth using HM-sensitive plants, earthworms (*Eisenia fetida*/*Eisenia andrei* by dermal and alimentary uptake), acute toxicity test, etc., among others. The approach addresses firstly: a) characterizing physiochemically mine tailings, in terms of their relevant physical and chemical parameters and properties, i.e., metal speciation and contents, potential acidity, chemical oxygen demand, metal-biochar sorption-complexing affinities, neutralization kinetics, etc., to compare and establish definitive results of doses, etc., and secondly; b) establishing conditions for biochar production and pyrolysis so that optimal neutralization potential and surface for HM-sorption interactions can optimally be obtained.

## 2. Mine waste and metalliferous acid mine drainage

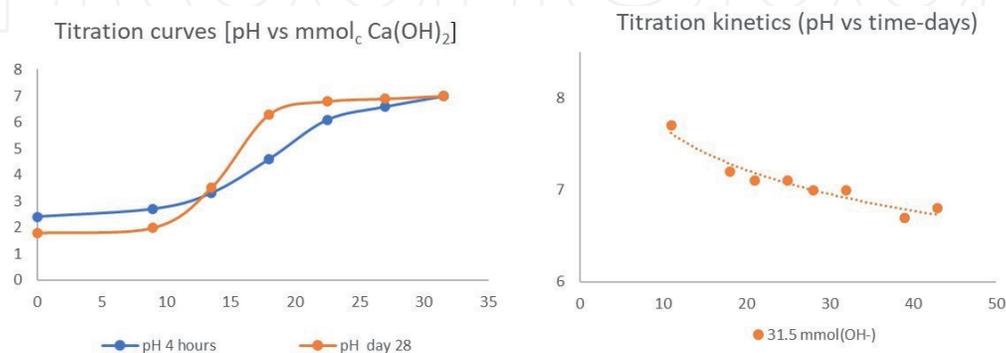
Mining extraction of metals from sulfidic materials produce considerable levels of potential acidity which eventually, if not prevented and neutralized, will generate the so-called metalliferous acid mine drainage resulting in the production of acidic water and mobilization of heavy metals [1, 2]. The quantity of acid-forming minerals found in many mines of central Mexico around the neo-volcanic mountainous axis [3, 4] and around the world, include dominantly pyrite ( $\text{FeS}_2$ ), galena ( $\text{PbS}$ ), sphalerite ( $\text{ZnS}$ ), pyrrhotites ( $\text{Fe}_{1-x}\text{S}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), arsenopyrite ( $\text{AsFeS}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), and many other metallic sulfosalts. After oxidation, these minerals generate the  $\text{H}^+$ -producing redox and hydrolytic processes of the components (e.g., S, Fe, Mn, Zn, Cu, Pb, etc.), left behind in the mine tailings. Mine wastes and tailings, polluted sites and pristine-soils (for reference and comparison) must then be chemically characterized in their metal speciation and contents, besides other relevant physicochemical properties and parameters, i.e., pH, Electrical Conductivity (EC), Cation Exchange Capacity (CEC), Acid Neutralizing Capacity (ANC), Chemical Oxygen Demand (COD)-value, etc. before any remediation technique is planned or executed. Metal speciation and fractionation must also be carefully

considered so that the so-called bioavailable, labile-toxic metal fractions and pools (soluble, exchangeable, DTPA-, acid-extractable, total metal content, etc.) must correlate well with the requirements of clean up and agrostabilization of sites.

## 2.1 Chemical characterization of mine wastes for remediation

Routinely acid–base account (ABA) is determined to specify the total quantity of acid-forming sulfur compounds in a sample relative to the neutralizing potential [1, 2]. Acid–base account methods are applied routinely to mine waste analysis of materials to assess the potential of generating acid upon redox weathering processes. Acid–base account is evaluated by determining the neutralization potential (NP) and potential acidity (PA) of a sample:  $ABA = NP - PA$  [5]. However, when common sulfide and sulfate minerals are subjected to ABA extraction methods, the ABA method fails to accurately distinguish the acid-forming from nonacid-forming minerals, resulting in errors in the determination of potential acidity mainly because the lack of consideration of all possible acid-producing species that very slowly oxidize. These errors can be subsequently visualized not only in the discrepancies between NP- and COD-values measured in a sample, but in the inaccurate liming requirements predicted to be applied, resulting not only in insufficient neutralizing amounts required and an excessive cost to cover the slowly released and underestimated potential acidity, but in the potential reclamation failure when the ABA measurement is underestimated. In this respect, the methods regularly used to determine the acidity potential, involve the acid–base treatment of a mine waste and polluted and pristine soil samples, without considering, on one hand, the kinetics or slow neutralization reactions that with time might occur, and the slow oxidation of other components which contribute to waste acidification [6]. In our proposal we measure and determine the neutralization-kinetic curve of the acidic mine waste with lime and biochar, or other amendments applied, so that the time of reaction under laboratory conditions can be considered and extrapolated to green house and field experiments. **Figure 1** shows such a neutralization curve for an acidic mine waste from Zimapan, Hidalgo State, Mexico, which showed initially very low pH values.

These discrepancies have been recorded [5–7] between the acidity potential (AP) and the COD-values. In a freshly sample taken from the site at Zimapan mine in Mexico, whose initial pH, AP (ABA) and neutralization potential (NP) values were 6.9,  $348 \text{ kg}_{\text{CaCO}_3} \text{ ton}^{-1}$  and  $201 \text{ kg}_{\text{CaCO}_3} \text{ ton}^{-1}$ , respectively, calculation of the acid–base balance produced a ratio of  $NP/AP < 1.2$  ( $=0.58$ ), revealing a potential for acid mine drainage generation resulting from the eventual oxidation of sulfides to sulfates

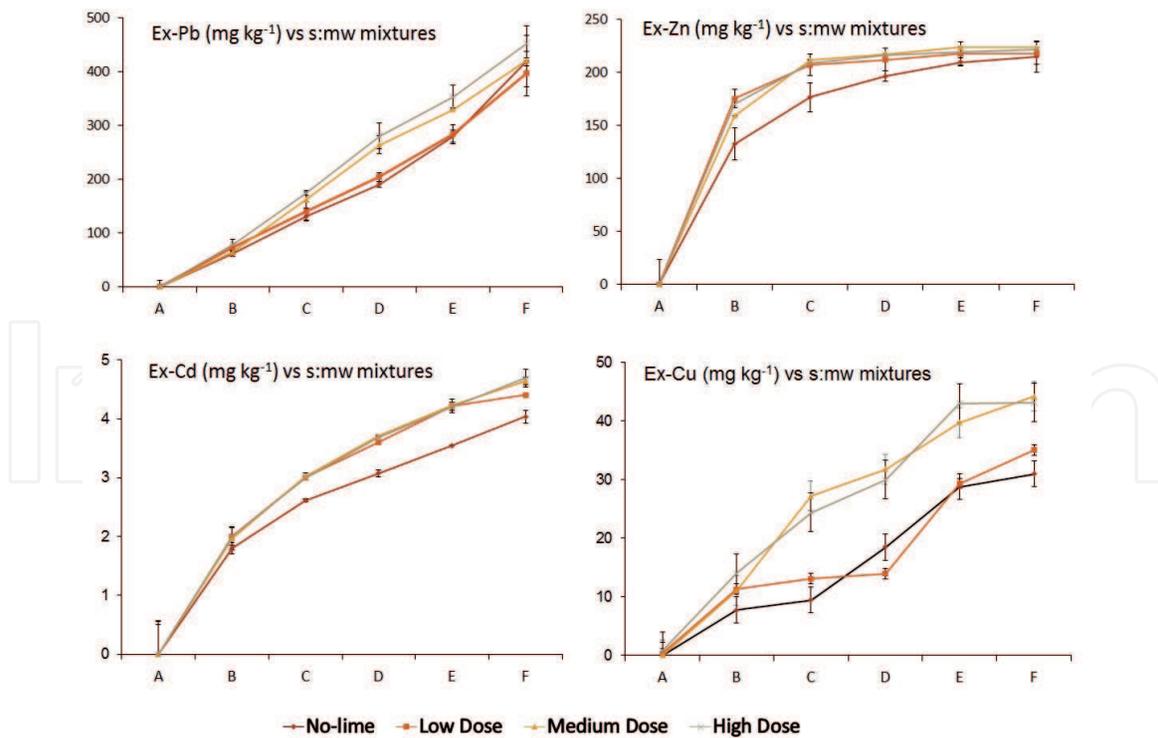


**Figure 1.**

Graphs show neutralization (pH–mmol<sub>c</sub> of OH<sup>-</sup>) and kinetic (pH–time, in days) curves of an acid mine waste from Zimapan, Hidalgo State, Mexico with lime, Ca(OH)<sub>2</sub> whose initial pH value was 2.4. Solid:liquid mixture ratios were 1:3, in small polyethylene reactor flasks with cap. Ten flasks were prepared to which various dose of liming material was added at variable levels of 0–67.5 mmol<sub>c</sub> of Ca(OH)<sub>2</sub>, which were kept incubated for the time period described. pH was monitored over time. As an example (see [6]) of curves, some flask-systems results were plotted [6].

according to reactions of the type e.g.,  $S^{-II} + \frac{3}{2}O_2 + H_2O \rightleftharpoons SO_4^{2-} + 2H^+$ , and the hydrolysis of the ferric ions,  $Fe^{3+}$ , ( $Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$ ). These values were found to be within the range of reported levels for mine tailings deposited in mining areas of central Mexico, whose acid–base balance usually lays between 0.1 and 0.9, and already present acid drainage production [8], as well as with values reported specifically for the mining area that are at 0.3 being considered as eventually acidic waste [9]. As a complement, the chemical oxygen demand, COD, corroborated an extra potential risk of acid drainage generation due to the slow oxidation processes of the mine residues. The COD-value of this sample was of  $17 \text{ kg } K_2Cr_2O_7 \text{ ton}^{-1}$ , equivalent to 12% of S(-II) content (unpublished results), assuming that all the oxidable material was pyrite, and therefore to  $376 \text{ kg}_{CaCO_3} \text{ ton}^{-1}$  waste is calculated leading to an extra amount of liming material of  $28 \text{ kg}_{CaCO_3} \text{ ton}^{-1}$  (= COD-AP), expressed as potential acidity. Thus, despite being a recently neutralized the fresh waste, in the medium or long term, the deficit in the acid–base balance and the high COD value must be considered as indicators of the potential oxidation of metal sulfides. Besides, the kinetic factor would lead to a  $\Delta pH/43$  days of 0.9 units, which would correspond to an extra amount of an extra  $4.5 \text{ mmol}_c$  (=  $5.5 \text{ kg}_{CaCO_3} \text{ ton}^{-1}$  waste) to compensate for a kinetic period of 60 days under laboratory conditions, resulting in total an extra amount of 22.8% more liming material. In close comparison with an acidified sample of the same site at Zimapan mine, calculations showed (see [6, 7]) original values of pH, AP, NP and COD-values, to be 2.2,  $38.1 \text{ kg}_{CaCO_3} \text{ ton}^{-1}$ ,  $109 \text{ kg}_{CaCO_3} \text{ ton}^{-1}$ , and  $146 \text{ kg}_{K_2Cr_2O_7} \text{ ton}^{-1}$ , equivalent to still 1.2%  $S^{-II}$  content to be yet oxidable, if all materials were pyrite. Following similar calculations as above, the amount liming material required to neutralize this naturally oxidized mine waste would be estimated to be in the order of  $37.5 \text{ kg}_{K_2Cr_2O_7} \text{ ton}^{-1}$  (plus the kinetic dose of  $5.5 \text{ kg}_{K_2Cr_2O_7} \text{ ton}^{-1}$ ), giving a total of  $43 \text{ kg}_{K_2Cr_2O_7} \text{ ton}^{-1}$  [6, 7]. The eventual production of acid drainage conditions and the consequent availability and potential mobilization of the toxic metals contained in the waste material can only be prevented when the three aspects of analysis are considered: the ABA- and COD-value, and the kinetics of neutralization factor. From that it results clear that precise and full characterization of these determinations must be considered if a successful remediation of acidic mine tailings is planned. Besides the natural tendency of field researchers to apply lime on mine tailing dams, several studies have shown that some metal can be re-specified causing some redissolution, as lime is a more soluble material than other precipitates, adsorbing or complexing amendments as phosphates, biosolids, compost, clays or biochar, alone or in combination, which has conducted many researchers to look for alternative ways of immobilizing metals in mine wastes [10–13]. We have carried out studies to prove this [7]. After applying lime, gypsum, phosphates and organic matter (compost) it was corroborated that lime and gypsum (results not shown) caused some redistribution and redissolution of metals. **Figure 2** shows for lime, when applied to local pristine soil-mine waste mixtures, ranging from 100:0% to 0:100% soil (s): mine waste (mw) mixtures. Adsorption experiments carried out on these soil-wastes emulate the various grades of pollution caused by the dispersion of the mine waste over clean unpolluted soil.

Graphs shows the effect that lime had over the desorption of the four studied metals. Curves show that as mixtures were limed at low, medium and high doses (where low, medium and high doses were chosen to suppress the summation of water-soluble, acid-extractable and DTPA-extractable heavy metals respectively), metals were, in all cases extracted in higher amounts as compared with the no-limed treatment, suggesting this amendment material serves well to neutralize the acidic mine waste, but fails to suppress the extractability of metals with respect to the non-limed fresh mine waste treatments. Results (not shown) for systems containing phosphates and organic matter (compost) effectively lowered the availability of these four metals, as other researchers have reported too [10–13]. Further experiments were planned



**Figure 2.** Comparison of the relative effect of low, medium and high doses of lime versus the non-limed treatment, on the 0.2 N acetic acid (AcO)-extractable (Ex-) Pb, Zn, Cd and Cu levels for six experimental mixtures (mx) of soil (s)/mine waste (mw): A: 100% soil, B: 80:20 s:mw, C: 60:40 s:mw, D: 40:60 s:mw, E: 20:80 s:mw, F: 100% mw. Freshly deposited mine waste was sampled, showing a pH value of 7.37 (see [7]).

to continue with this research to test the effectiveness of biochar in combination with lime and phosphate [14, 15]. Results have been published elsewhere but conclusions are presented in our case of study included in Section 4 of this chapter.

## 2.2 Toxic heavy metals in mine tailings

To lessen HM toxicity hazards several studies involving physical temporary solutions [16, 17]; a wide variety of chemical treatments [18, 19]; and the not always feasible biological techniques [20, 21] have been conducted and published. Physical treatments include not only confining, solidification and vitrification procedures [16, 17] but S/S technologies which in many cases are considered not to be a permanent environmental solution as metals are not removed from contaminated media; always require future monitoring and; there is a questionable longevity of the effect of the ameliorating materials added plus requiring long-term management of resulting materials based on landfilling and soil caps to prevent erosion [16, 17]. On the other hand, chemical procedures used specially for polluted sites are generally based on precipitation [22], adsorption [23] or complexation processes [24]; this last to either mobilize and bioremove HM effectively. These physical and chemical procedures, if integrally and congruently used, should have an important impact on the abiotic and biotic factors, so that the toxicity of metals left after the treatments is reduced and an attractive growing media for phytoremediation can then be promoted and established. For soils most procedures used to diminish the mobility and leaching potential of HM have used chemical remediation techniques. Several studies report an effective immobilization of HM in polluted soils when applying lime, phosphate and/or organic matter amendments were applied, resulting in a reduced bioavailability of HM [25–28]. Addition of phosphate materials for instance was effective in immobilizing Pb [29]; whereas composts, biosolids, manure and peat materials [8–10, 30] were instrumental to reduce mobility of Cd, Pb and Zn, among other HM [31].

### 3. Agrostabilization of mine waste and polluted soils

Among the most promising remediation techniques to treat heavy metal polluted wastes and soil used are the application of lime [32], phosphates [29, 33], biosolids [34, 35], composts [36] and the application of amendments with biochar [12, 15, 37]. Although the application of biosolids and composts decreases the bioavailability of metals, their effect is variable depending on the metal, soil type, dose, type, and degree of humification of organic matter [38, 39]. Most of these techniques require constant applications to ensure their success. Other studies [40] have demonstrated that fresh composts increased the solubility of metals, except perhaps for Cu [7], so that pretreatments are required to stabilize organic manufacturing, which increase application costs [36]. These above studies considered the addition of ameliorating materials to reduce chemically the HM bioavailability, however if the addition of carefully selected agro-chemical materials and doses is premeditated the remediation strategy should warrant in an initial step: 1) a stable and slow mobilization of bio-available HM; 2) the abatement and control of their toxic levels at least based on the threshold allowable levels dictated by the national and international standards and norms and; 3) a fertile media to sustain a consistent phytoremediation or phytomining activities, for instance through the use of HM sensitive indicator plant species according to standardized biological test methods [41, 42], or through the use of hyperaccumulator plants, respectively. Once this strategy works, and a well-nourished growing media is assured, a further important step should be funded in a studied introduction of perennial domesticated, native and/or undomesticated plant species whether HM hyperaccumulators or not. For acidic polluted mine wastes, studies should focus mainly on lowering the mobility of Cd, Cu, Pb, and Zn below official environmentally safe values to warrant a biologically clean and sustainable ecosystem. To reach this goal, at least two schemes must be visualized; First the addition of widely used agronomic materials consisting of lime ( $\text{Ca}(\text{OH})_2$ ); gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ); P-fertilizer ( $\text{KH}_2\text{PO}_4$ ) and/or compost, and more recently with much success biochar, to “treat” a gradient of soil-fresh mine tailings mixtures in order to assess the treatment effectiveness to lower both the most toxic metal species in solution, the free-metal ion chemical activity, ( $\text{M}^{2+}$ ), of metals like  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  [43] and the so called bio-available (acid-extractable) HM fraction imposed by international standards and norms. Second, a bioassay should be carried out to find the conditions to pass sensitive indicator plant response tests in these “fertile” ameliorated media. These studies should prove to be useful in deriving soil-substrate quality criteria to establish specific cleanup strategies and/or verify the success of remediation processes. In order to evaluate metal toxicity/abatement effectively both, the bioavailable (acid-extractable) HM fraction and the chemical activity of the free metal ion, ( $\text{M}^{\text{m}+}$ ) should be measured after incubation with the chemical-agronomic treatments mentioned above. Green house experiments and field trials are the next important steps to establish a well-founded remediation strategy.

#### 3.1 Lime

The application of lime as ameliorating material alone or in combination with compost, initially increases pH values, lowers metal solubilities and buffers the changes of the acid–base equilibria. In addition, their low-cost and easily accessible and application aspects [10] favors at first instance their use, however, due to the transient nature of organic matter, its effectiveness might decrease afterwards [11]. Although excess liming may also lead to P-deficiency in plants, an excess of mineralization of labile carbon is also possible when lime is mixed with biosolids promoting the availability of P [12]. Several authors have tested this material in combination with-red mud (a by-product of aluminum manufacturing) [10], compost from water

hyacinth [11], biochar and biosolids [12]. These studies coincide that the addition of lime is effective, but it is enhanced with mixed with other amendments. For example, Trippe, et al. (2021) (see [12]), showed that the above and belowground biomass of plants grown in mine tailings amended with lime, biochar and biosolids, was 3–4 times larger than the biomass of plants grown in tailings amended only with lime.

### 3.2 Phosphate fertilizers

The application of phosphates to metalliferous polluted wastes and soils is intended to form stable precipitates with metals, at the time of providing essential nutritional elements for the growth of the plant cover. For instance (see [44–46]). Compared to the control, they found that all P amendments significantly decreased relatively Pb phytoavailability up to 86%. The Pb immobilization was attributed to sorption and precipitates of Pb phosphate on calcite and phosphate phases and minerals. Water solubility of Cu and Zn was also lowered up to 80% and 69%, respectively. On the other hand, it has been put into discussion whether metals should be immobilized or not. Other studies have also addressed the remediation of heavy metals and metalloids of contaminated soils, to mobilize or to immobilize them by adding amendments or complexing substances, respectively. Of course, the final fate of metals becomes critical, whether they will be immobilized to mitigate the potential toxic effects on biota, or to increase their phytoavailability so that metals can be phytoextracted or leached them out from the system. In terms of adding phosphates to Pb-polluted environments, certainly it promotes Pb-immobilization, although the availability of other metals, still need to be addressed specifically, especially Cu.

### 3.3 Compost and biosolids

Some studies [38] have shown that the application of biosolids and compost decreases the bioavailability of some metals, but their effect is variable depending on the metal, soil type, dose, and degree of organic matter humification. However, some contrasting effects of manure and compost on soil pH, heavy metal availability and growth have also been recorded in soils contaminated by pyritic mine waste [39], so that in terms of specific metals, there are accounts signaling that some metals certainly are complexed and retain on organic material (e.g., Cu), but others not. The problem related to sewage sludge application arises when it contains high concentrations of potentially toxic heavy metals. The release of heavy metals associated with sewage sludge is strongly influenced by soil pH, cation exchange capacity, organic matter, and mobility and speciation of specific metals. Excessive application of sewage sludge to soil has been found to increase the bioavailability of heavy metals, but the low doses of sewage sludge did not cause a significant increase in heavy metal concentrations [47]. Although application of biosolids provides essential nutrients for plant growth, a careful assessment of the characteristics of sewage sludge, however, is required prior to land application. When sludge contains high concentrations of toxic elements, amendments may have a potential toxic impact. Co-application of organic matter, liming, phosphates, biochar, etc. may minimize the potential negative impact of land application of biosolids too. This last study [47] also showed that sewage sludge pyrolysis decreased the plant-availability, the mobile forms and the risk of leaching of Cu, Ni, Zn and Cd. Important to notice that the leaching of Cu, Ni and Zn were lower in the soil treated with biochar than in sewage sludge treatment. When mixed biosolids and biochar amendments increased soil respiration with respect to the control soil, being lower in the case of biochar than when biosolid was added alone. On the contrary, biochar amended samples reduced Ni, Zn, Cd and Pb plant availability, when compared to sewage sludge amended samples. It results clear

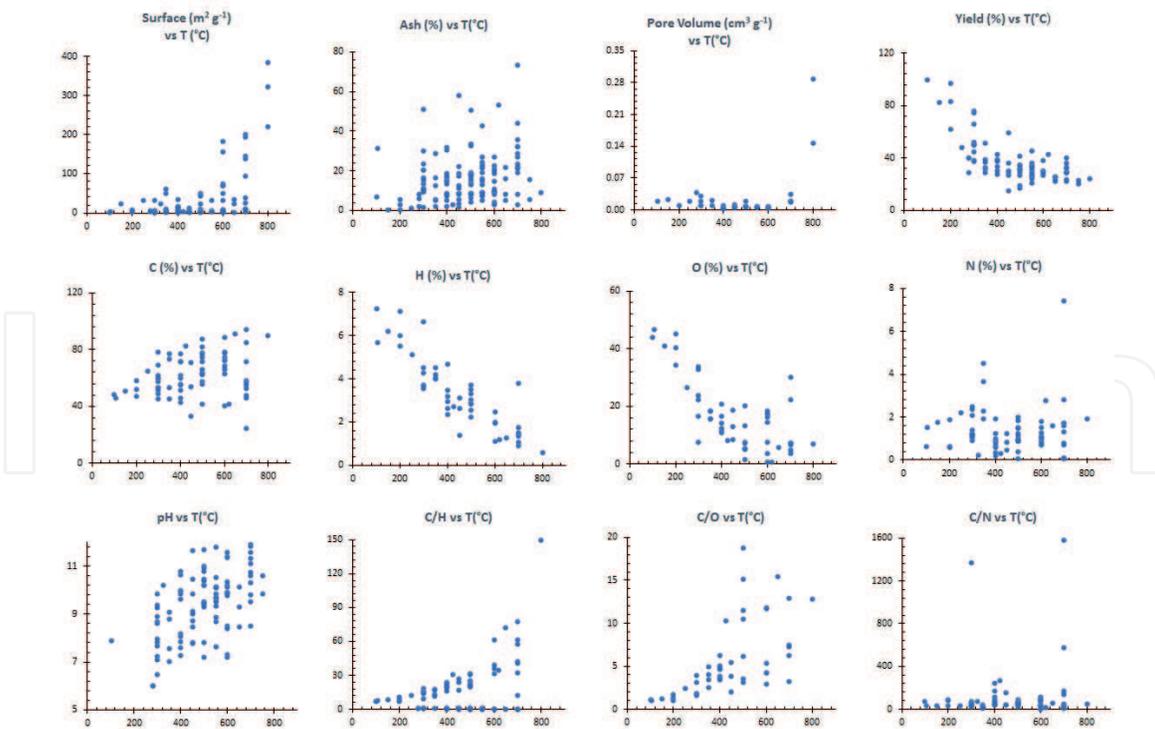
then, that biosolids, at low dose have a good influence in soil than biochar alone, in that particular case, however, it also results clear that sewage sludge when mixed with biochar can have better results to lower metal availability for plants. Beneficial effects can be obtained when biochar is incorporated to the application of amendments.

### **3.4 Clays**

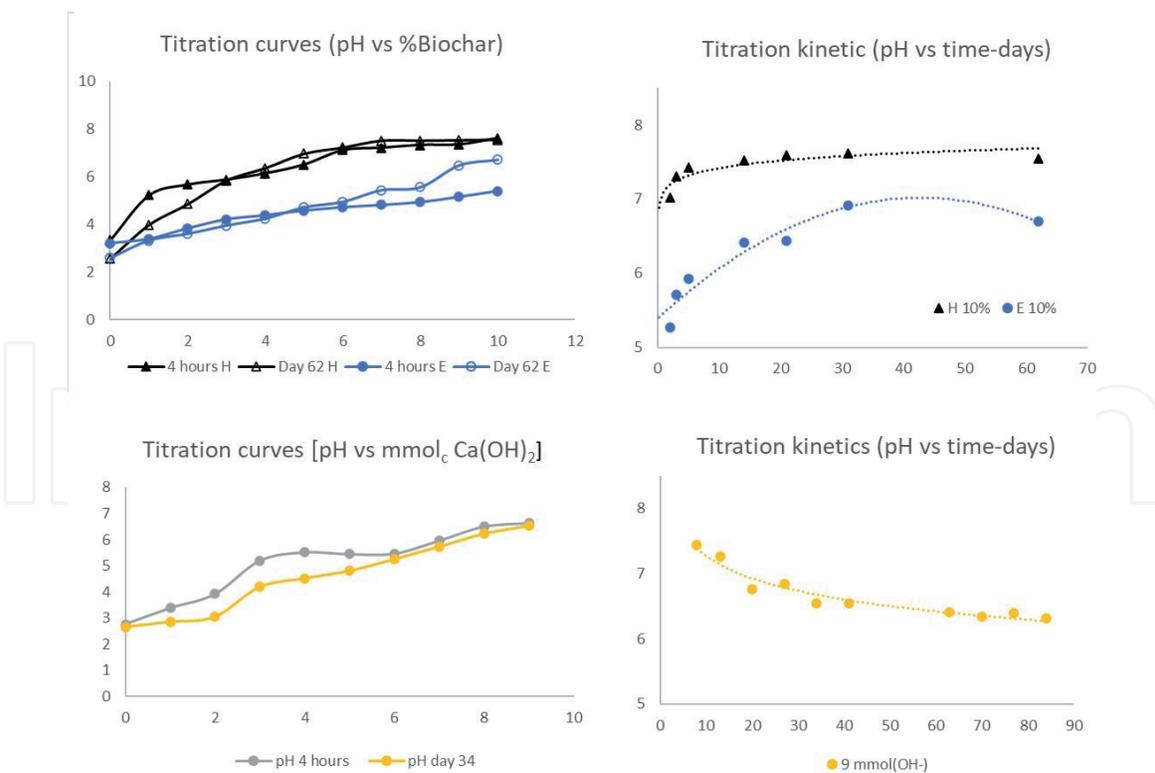
Clays have been tested to remediate heavy metals contaminated soils too. Their use has been recommended because of the low cost, clay materials can easily be obtained, and result innocuous to the environment. Among these, bentonite, montmorillonite, attapulgite [48], palygorskite, sepiolite [49], illites and kaolinites [50] can also be mentioned. It has been observed that sepiolite can increase the pH of systems due to its alkaline nature, it is rich in oxides and carbonates of Ca, Mg, Al and Si, and it improves microbial activity in soils contaminated with mining residues [51]. Nevertheless, the main characteristic clays impose on treatments are related to those factors that influence the adsorption of heavy metals on clays. According to Otunola and Ololade, 2020 [50] these are: a) increase of cation exchange capacity (CEC) and the specific surface area of the clay, which are the determining properties of sorption; b) longer contact times between the clay and the contaminated site, both related to the type of metal and the pH value of the site; c) moderate dose of clay, being 4 to 8% to remove more than 70% of heavy metals [52]; d) increase of pH of the system or the site, as it influences the leaching of cationic metals. The best absorption they mentioned was between pH values of 6 to 8 [53]. The increase of pH generates negatively charged sorption sites on soil colloids and on the surface of organic matter which favors adsorption of the HM's [54]; and e) the temperature that influences the amount of adsorbed metal, being lower when temperature is greater than 36°C [49]. Nowadays, methods have been designed to modify the adsorption capacity, although it is not yet known which is the best modification method for each type of clay and the required dose [50]. These are the following modification methods: a) Forming organic complexes with clay, where the clay is mixed with compost or residual sludge, which can rise the sorption of metals up to six times more due to the upturn in CEC [55], this is an environmentally friendly method, however the presence of organic matter can affect the immobilization of metals [56]; b) Modification with nano-zero valent iron (nZVI), small particles are used as binders that increase the active adsorption sites on the clay surfaces by impregnation, followed by filtering, washing and drying [48]. This can also be done by chemical synthesis, with H<sub>2</sub> or Fe<sup>2+</sup>, which are reduced at high temperatures [57]; c) Thermal modification that consists of heating the clay to temperatures of 200–1000°C for a time of 3–12 hours, the process dehydrates and dehydroxylates clays. The procedure reduces the mass, increases the porosity and the cation exchange surface but the disadvantage is that the time and temperature must be determined for each type of clay [58]; d) Modification with acids to remove impurities as Ca, Mg K and metal oxides present in the clay, and modify the adsorption surface [59]. Although the method increases the cost of the amendment, and it can release new agents into the environment [60]. However, the application of pristine or modified clays as remediation methods, require more field studies to determine the ecotoxicity and biocompatibility. Since the change in pH, redox potential, temperature and CEC of the soil strongly influences the mobility of metals. In addition, clays are not selective and have partial binding capacities [61].

### **3.5 Biochar**

Biochar as a solid product of biomass pyrolysis has shown to present large specific surfaces for sorption [62] and remotion of heavy metals from mine tailing



**Figure 3.** Biochar characteristics and properties as affected by temperature of charring. Tendencies and general behavior of relevant parameters usually measured and reported are shown vs. temperature ( $^{\circ}\text{C}$ ). Data plotted show Specific surface ( $\text{m}^2 \text{g}^{-1}$ ); Ash contents (%); Pore Volume ( $\text{cm}^3 \text{g}^{-1}$ ); Yield (%); C-content (%); H-content (%); O-content (%); N-content (%); pH; and C/H; C/O; and C/N ratios. Data compiled from [75–103].



**Figure 4.** Graphs show neutralization (pH-% biochar) and kinetic (pH-time in days) curves of an acid mine waste from Zimapan, Hidalgo State, Mexico with biochar of water hyacinth, *Eichhornia crassipes* Mart, (H) and Eucaliptus, *Eucalyptus globulus* Labill, (E) whose initial pH was ca. 2.9. Solid:liquid ratio was 1:3, processed in small polyethylene reactor flasks with cap. Ten flasks were prepared to which various dose of liming material was added at variable levels of 0–10% biochar, which were kept incubated for the time period described. pH-values were monitored over time. As an example of curves, some flask-systems results are plotted [14, 15].

sites and polluted soils [12].; being a porous material [63], it has been reported to improve soil physical properties [64]; to provide nutrients, allowing the development of microorganisms [62] too, and last but not least, increasing both, pH values which normally range between 5 to 12, depending on the material and the pyrolysis temperature (see **Figure 3**), and the alkaline neutralization potential (**Figure 4**).

### 3.5.1 Effects on the acidic mine waste remediation

Biochar can be used to modify soil structure, improve physicochemical properties and enhance nutrient intake by plants, modify habitat for microorganisms, adsorb pollutants and mitigate climate change by changing the availability of elements in soils, especially C [62]. Yuan et al., 2019 [62] also propose the use of biochar in alkaline-saline soils, in cultivation areas and industrialized regions. However, more long-term experiments are required to assess the environmental risk, in addition to considering more mechanisms to make progress in biochar production, when modifying biomass type, pyrolysis temperature, gas flow, retention times, all to increase the efficiency of using biochar as an amendment (see Section 4.1). The fissure intensity factor has also been evaluated [64, 65], with positive conclusions towards the reduction of cracks in this respect, because these affect permeability and water retention and balance in soils. Here water hyacinth (*Eichhornia crassipes*) and soil biochar were studied to know their effect on water content and soil suction in doses of 0 to 10% (w:w) for 3 months. More suction was observed when higher doses of biochar were added, when compared to unamended treatments, finding best doses close to 10% values for most soils, to increase permeability and water retention in soils. Zimmerman, 2010 [66] carried out laboratory experiments to model C-longevity in soils, for controlling pollution migration, increasing fertility and sequestering carbon. The author mixed pyrogenic or “black” carbon-lime-biosolids and biochar-lime-biosolids-inoculum in soils contaminated with mine tailings, the results were that even in the absence of inoculum, microorganisms made progress under the two systems studied. However, both systems generally decreased with increasing charring temperature. Recalcitrant organic carbon content of soil increased in the long run, showing a slow natural mineralization of up to 26% losses in 100 years, projecting half-lives of  $10^2$  to  $10^7$  years in the environment [66]. Unfortunately, there was found evidence to suggest that its stability was less than previously thought, being that biochar-carbon was considered to be extremely refractory. Biochar lability was found to be strongly controlled by the relative amount of a more aliphatic and volatile component, which later an inferred though came up to suggest that their losses could be utilized as an indicator of biochar C longevity. Final conclusions were made in terms of its practical value for considering biochar as a tool for soil remediation, amelioration, or atmospheric C sequestration. The stability of two biochar materials of rye grass and pine wood has also been evaluated at 350°C under oxic conditions. Markers of lipid extracts [67], and the composition of n-alkanes and n-fatty acids was used as indicators of stability to microorganisms. Pyrolysis breaks down these molecules and reduces them to shorter chains. Lignin seems to “survive” the process, it is also mentioned that the first day’s microorganisms were more predisposed to degrade the biochar of grass than that of wood. Among some of the disadvantages of this amendment it can be found that: it can cause health problems when inhaling the dust [68]; requires high temperatures to be used as a remediation method for liming and adsorbing various metals [69]. The potential risk of using biochar and establishing vegetation creates these and some extra problems, since these may also acidify the soil due to the release of acids that again might solubilize the metals in the biochar, what has called for the attention to make a review of

several cases in China where after a while some metals are released. Recent studies indicate that biochar applications could pose ecological and health risks by releasing toxic substances into soils or by inhalation of biochar dust during production or its application on the fields [67]. In China, biochar is commonly used for remediating agricultural soils. Processes for metal interactions with biochar-soil materials may involve adsorption-precipitation and/or complexation reactions, as affected by pH, CEC, organic matter contents, and other modified soil properties. Most field trials showed HM uptake by plants and concentrations of mobility-bioavailability HMs in soil that biochar addition reduced. However, there can also be adverse effects of applying biochar to contaminated soils. Toxic substances contained in biochar may be released to the environment, resulting in increased pollution, and impacting soil organisms and soil functioning, as there are no application standards of regulatory frameworks for biochar application, safety precautions, food safety and human health effects upon exposure, and long-term effects of biochar applications to HM contaminated soils on soil ecosystems. Biochar has been used mixed with mud at 300–900°C, with pyrolysis temperature affecting pH, specific surface, and functional groups, as well as the composition and content of the dissolved organic matter. The higher the temperature, the metal content decreased more (from 91.7% to 9.4% for Cu, 92–63% for Zn, 55.9% to 4.9% for Pb, and 78.2% to 12.5% for Cd, among other metal(oids)). The length of the shoots and roots, and the activity of microbes, in sandy and silty soils, were also increased. In general, biochar prepared at high temperatures was safe for their production or application. High doses of 3–9% (equivalent to more than 60 to 200 Mg ha<sup>-1</sup>) were estimated to be required to remedy heavy metal contaminated soils [70]. Due to this it has been proposed to mix small amounts of biochar with lime or with compost to increase the pH of acid residues so that other properties in the soil can be improved [12, 71]. Miscanthus biochar (*Miscanthus giganteus*) was utilized in acid residues with low pH values (pH < 3), applying doses of 0 to 5% (w/w) with and without lime and fertilizers. To evaluate its effect, a bioassay carried out with Blue Wildrye (*Elymus glaucus* cv. 'Elkton'), showed that lime mixed with biochar greatly decreased the extractable metal levels. Higher doses of biochar also reduced the extractable concentration of metals and improved the microbial activity [71]. Currently, there are studies too, where biochar has also been modified by the addition of alkalis, oxidants (as O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>MnO<sub>4</sub> and air), microwaves, CO<sub>2</sub> and steam, to improve its sorption capacity [72]. Biochar activation methods have been studied [73], utilizing water hyacinth to remove metals from polluted waters, which subsequently was pyrolyzed and applied to the soil with phosphates. According to authors [74] positive and negative effects on biochar activation were observed, depending on the method of activation, kind of bioassay and kind of soil too, however, the increase of biochar specific surface area caused a significant reduction of toxicity of water leachates due probably to the presence dissolved organic carbon in soils.

As noticed, biochar is widely recommended for remediation of heavy metals polluted environments due to its excellent immobilization effect, which may last for many years [67]. There is a general agreement, then, that the increase–decrease of biochar effectiveness with time, depends on the abiotic and biotic factors [56, 66–74].

### *3.5.2 Relevant characteristics of biochar as affected by temperature*

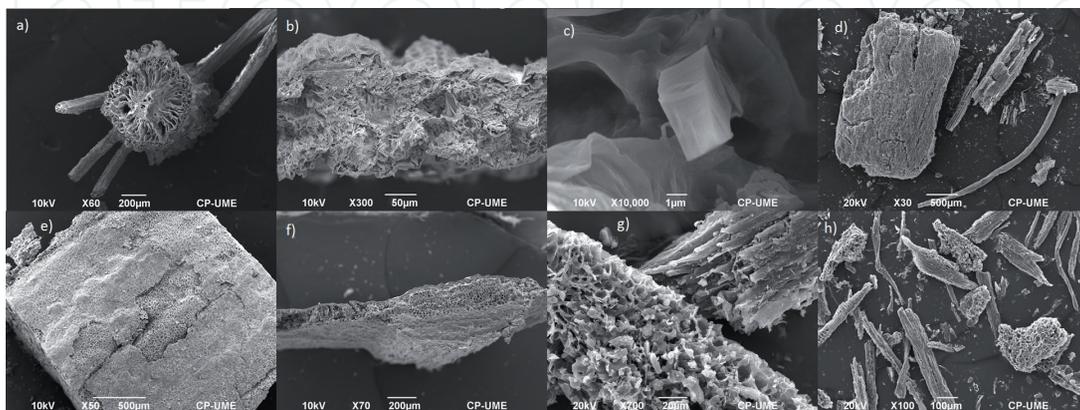
According to all researchers and papers reviewed and mentioned above, many of the characteristics of biochar vary and depend mainly on temperature of charring, and type of initial material too, among other characteristics and conditions of biochar production. However, most of their important characteristics tend to be congruent with this. Nevertheless, some parameters and analyses reported in literature show

good agreement and tendencies with temperature of charring, but some others not as can be seen from the curves plotted from a compiled data collected from references [75–103] (see **Figure 3**). Among the strategies that have been receiving greater attention, the use of biochar has been outstanding in this respect. The coal produced from the pyrolysis of biomass, compiled data with temperatures ranging from 250 to 750°C [104]. It is known that the material used for the preparation of the biochar, the pyrolysis temperature, the size of the waste to be pyrolyzed, the speed of pyrolysis, among others, influenced the physical, chemical and biological characteristics of the material obtained, such as ash content, specific surface, and pH-values, among others [104]. Biochar materials used in the retention of polar contaminants are obtained at high temperatures, because in this condition the specific surface area and sites for adsorption are increased [105]. Pyrolysis temperatures of 400 to 750°C caused the biochar produced to get values of pH > 7, higher values of ash contents and lower specific surfaces, than those generated at temperatures below 400°C [106]. However, biochar produced with straw, at high temperatures (>500°C), usually present high concentrations of the potentially toxic polycyclic aromatic hydrocarbons (PAHs) due to incomplete combustion. Therefore, it is necessary to carefully define the conditions of pyrolysis, to generate a non-toxic biochar suitable for the intended plants and soil microorganisms [67, 107]. There is information explaining the retention mechanisms that occur when biochar is used for the purpose of sequestering organic and inorganic pollutants. Metals interact with biochar through electrostatic interactions, by cation exchange, adsorption by proton exchange and specific bindings [67, 108]. It is known that the adsorption of Pb by biochar is attributed to phosphate and carbonate in the aqueous phase of the pores of the material, whereas for Cu, pyrolysis temperature and increased pH, correlate well with metal adsorption. Uchimiya et al., 2012 [109] reported that biochar can adsorb up to 42,000 mg of Cu per kg<sup>-1</sup> in aqueous solution at acidic pH values. If the pH value increases, the retention is due to the organic binders on the surface of the material and to the sorption-precipitation with carbonates and oxides which are also found in the pores.

**Figure 3** shows that specific surface, pore volume, yield, C-, H-, O-content, pH and C/H, and perhaps C/O ratios show some tendencies as charring-burning temperature of materials increases. It must be mentioned that a variety of materials and burning conditions, besides temperature, vary, however, some very clear tendency behavior can be observed. Most interesting for the purposes of this chapter are the tendencies observed for pH, specific surface, yield and C-content and C/O ratios, as these variables will correspondingly stand for the acid–base account, sites for exchange capacity, and functional groups (represented by C and O-contents) which should favor removal via sorption of HM present in the mine wastes. The production and application of biochar from plants with high growth rates and weeds, for instance, present areas of opportunity to remediate acid residues generated by mining activities, at the time of contributing to solve some of the unwanted proliferation of these plants on terrestrial and lacustrine, riverine, or irrigation and wastewater channels around urban areas all over the world. Water hyacinth plants present growth rates ranging from of 100 to 208 Mg ha<sup>-1</sup> year<sup>-1</sup> [110, 111], which besides its high biomass yields, possesses strong adsorption capacities, due to its high cellulose content and carboxyl and hydroxyl functional groups [112]. These properties give to this material an extreme potential for use for remediating activities in metalliferous acidic mining wastes. For this reason, is that it has been used in wetlands, in solid dry form (as biochar), to remove toxic metals from aqueous solutions, wastewater and effluent treatments [113], and soil [114]. Eucalyptus trees on the other hand, also present high growth rates of the order of 25.5–40.2 Mg ha<sup>-1</sup> year<sup>-1</sup> dry matter equivalent with cutting periods of 7 to 10 years [115]. Although not many studies can be found on this plant, it might easily be considered of special interest in this respect.

#### 4. Biochar as a remediation amendment for acid mining wastes: A case of study

Zimapan mining district in Hidalgo State, Mexico generates mine wastes with high Cu, Pb and Zn contents. Water hyacinth (*Eichhornia crassipes*) and Eucalyptus (*Eucalyptus globulus* Labill) trees require attention as they have been proliferating excessively in lacustrine, riverine, irrigation- and wastewater-channels and in streets and parks of cities and urban areas of Mexico, and other parts of the world, creating enormous residues of plant material, branches and wood. Remediation treatments to solve both problems seem to converge into the single strategy presented here. The objectives of the research were: a) to evaluate biochar derived from water hyacinth, *E. crassipes* Mart (H) and Eucalyptus, *E. globulus* Labill (E) to treat acidic metal-liferous mining wastes; and b) to compare biochar performances vs. lime (L), both alone and in combination with phosphate (F) fertilizers. Combined biochar and lime amendments with phosphates included were (FH), (EH) or with lime (FL), via running a root length growth bioassay using barley plants (*Hordeum vulgare* L), to correlate them with total, DTPA-extractable and water-soluble metal contents and pH as published in [14]. In this investigation four substrates were used to emulate pollution gradients, ranging from pristine soil to pure acidic mining waste. Treatments were: 100%-neutral pristine soil (M1) from the mine surroundings; 100%-acid mine residues (M4); and two mixtures of soil:residues (w/w) of 65:35 (M2) and 35:65 (M3). Substrates were treated with the amendment gradient doses (w/w) of up to 10% (H) or (E), lime, L (3.4%), and phosphate F (0.06%). Blanks (non-amended mixtures) were included. The study showed that water hyacinth (H) and eucalyptus (E) could be utilized as an acid mine residue treatment by converting them firstly into biochar. Biochar materials were produced from water hyacinth (H), *E. crassipes* Mart, and eucalyptus (E), *E. globulus* Labill (branches and leaves) collected from Lake Patzcuaro, Michoacan State, and from Texcoco, State of Mexico, respectively, both in Mexico. Briefly, plants were air dried and milled to pass a 3.5 mm mesh. Both plant materials were slowly pyrolyzed following conditions of temperature of 600°C, speed of 10°C min<sup>-1</sup> and resilience time of 30 min, as described in Refs. [14, 15, 108]. The surface morphology of the both uncharred plant- and biochar-materials were examined using a scanning electron microscope and Jeol Scanning Electron Software for elemental analysis [14]. Images shown in **Figure 5** were taken with an



**Figure 5.** Images of root (a) and leaf (b) cross-section of water hyacinth cut;  $\text{CaCO}_3$  crystals in water hyacinth leaf (c); biochar particles of the bulb and root of the water hyacinth less than 2 mm (d); eucalyptus bark (e); cross-section of eucalyptus leaf (f); pyrolytic eucalyptus bark with crystals (g); and eucalyptus biochar particles greater than 2 mm (h). Scan images were taken with a JEOL Model JSM-6390 scanning electron microscope, at the electron microscopy unit (UME) of Postgraduate College, Montecillos-Campus (COLPOS), at Texcoco, Mexico State, Mexico [14].

EDX Oxford Instruments Model INCA-X-ACT probe. **Figure 5** includes the images of root- and leaf-cross-section of water hyacinth cut;  $\text{CaCO}_3$  crystals in water hyacinth leaf; biochar particles of the bulb and root of the water hyacinth less than 2 mm; eucalyptus bark; cross-section of eucalyptus leaf; pyrolytic eucalyptus bark with crystals and eucalyptus biochar particles greater than 2 mm, respectively.

Alkalinity (ABA) determinations were carried out for biochar and lime treatments as reported by other works [1, 2, 5, 14, 15]. Results produced liming potentials for H and E equivalent to  $16.4 \text{ g kg}^{-1}$  ( $\text{kg ton}^{-1}$ ) and  $8.02 \text{ g kg}^{-1}$  ( $\text{kg ton}^{-1}$ ) of  $\text{CaCO}_3$ , respectively. The equivalent doses necessary to correct the acidity of the mine residues to bring them to pH 6.5 were 5% for H, and 9% for E as shown in the neutralization curves of biochar depicted in **Figure 4**. Lime dose to correct the acidity of M4 to reach pH of 6.5, was  $9.2 \text{ mmol}_{(\text{OH}^-)}$  for 10 g of M4, equivalent to  $34 \text{ kg of Ca(OH)}_2 \text{ ton}^{-1}$  of the residues, amount that was found to be in the order of magnitude of other author's quantifications [5]. Worth to mention is that the pH stabilization time for lime was 34 days, a longer time in comparison to that required when biochar was used as a neutralizing agent. Extra details on the experiment and results can be found in Ref. [14, 15]. **Figure 4** shows the neutralization (titration) curves and kinetics of the acid mine waste for both studied biochar materials, as well as with lime. From curves it results clear that neutralization reactions under ideal (laboratory conditions) take several months to stabilize, which consequently will project to take even years for these materials to complete the neutralization reactions, depending of course on particle size (specific surface for reaction) and water content of substrate materials in the field, among others. We have discussed in the introduction section, some of the ABA method details to determine the balance between the acidity potential of the mine tailing material and the neutralization potential of bases naturally present in the soil. An extended discussion of the detail characterization of the acidity of mine materials, including the use of COD-determination and kinetics should be considered if a successful strategy to avoid the so-called acid mine drainage must be stopped. Calculations for neutralizing the mine waste with lime, were included in Section 2.1, and herein we present those of biochar as a liming material (see [14, 15]).

#### 4.1 Biological tests

Biological methods to run biotoxicity assays have been widely used to test the ecological risk assessment of soils [41] and other ameliorated polluted substrate materials (wastes, biosolids, sludge, composts, etc.) [116–121]. These include measuring the inhibition of root growth [41, 42, 116, 118, 119–121]; the effects of chemicals on emergence and growth of higher plants [117, 119]; root length responses, germination viability; green house and field tests [122], using metal sensitive higher plants [41, 116–121] or mesofauna [123, 124] or on the emergence and growth of higher plants when evaluating the effects of pollutants on soil flora [117, 119]. However, it must be stated clearly, what the authors declare about the application and scope of these biological methods. As stated by the authors in many of the presented references, these bioassays are applicable to the comparison of soils of known and unknown quality and to the measurement of effects of materials (compost, sludge, waste) or chemicals deliberately added to the soil [41], and that as stated in references [116–120], that methods are not intended to be used as a measure of the ability of the soil [and other soil materials, wastes, biosolids, etc. to support sustained plant growth. Nevertheless, the importance and relevance of testing remediated environments should always rely on the fact that recovering native or reforesting vegetation, should be one, and not the unique target of the final goals of remediation strategies, to remediate sites and recover plant growth. Having said that, we present herein some of the more relevant results of the bioassays carried out with the neutralized and amended acidic mine tailings with water hyacinth (H) and Eucalyptus

(E) biochar materials as compared with lime (L), alone or mixed with mono-potassium phosphate (F). The biological test was applied according to the described methods in Ref.s [41, 42, 116–121]. The experiment and results are presented in Section 4.4.

## 4.2 Physicochemical characterization of soil and biochar materials

For the application of the bioassay, barley seeds (*Hordeum vulgare* L. var. Hope) were used and the applied procedure was carried out according to the methodology described by ISO-references [116, 117]. Physicochemical characterization values for pristine soil, mining waste and mixtures [M1 is 100% soil; M2 is 35:65% (M1:M4); M3 is 65:35% (M1:M4); and M4 is 100% acidic mining residue], and biochar materials (H) and (E) are shown in **Table 1**. Determined parameters included pH, Electrical Conductivity (EC), Saturation Percentage (SP), Cation Exchange Capacity (CEC), total-metal levels for  $\text{Cu}_T$ ,  $\text{Pb}_T$  and  $\text{Zn}_T$ , and water soluble-Cu, Pb and Zn. Determinations were carried out according to procedures followed in reference [15].

Texture of the control soil (M1) was clayey, and its pH (=6.8) is considered neutral, while the M4 sieved at 2 mm presented an acidic pH of 3.3 (see **Table 1**). The mixtures of soil with the acidic mining residue (M4) raised the pH of both M2 and M3 substrates in greater proportion than in M4. The concentration of water soluble-Zn and -Pb in M2 and M3 samples were lower than the phytotoxic value reported by other authors [125, 126]. The pH value of each substrate decreased as the mine residue increased correspondingly. EC-values, the soluble Cu content, the extracted bases and the CEC increased from M2 to M4 (see **Table 1**), due to the dissolution of the carbonates present in the pristine soil [3] as promoted by the acidity of the mining residue. The pH values of the (H) and (E) biochar materials used in this study were, on an average, about 10 (**Table 1**), like those found by other authors [127–131] who reported that pH of biochar materials reached high alkaline values due to the pyrolysis temperatures used (> 500°C), contents greater than 2% of alkaline elements (Ca, Mg, K and Na), and losses of the functional groups of the source material (carboxyl, phenolics, lactone, etc.). Both the pH and neutralization potential values found in this study (equivalent to 16.4 and 8.02 g  $\text{CaCO}_3 \text{ kg}^{-1}$  of biochar materials H and E, respectively), are directly related to the contents of exchangeable bases. These values are comparable too with those reported by other works [127]. The EC of the biochar were 0.3 and 0.6  $\text{dS m}^{-1}$ , for E and H respectively. These results are similar to those obtained in wood and paper biochar produced at a temperature of 550 and 700°C [129], whose values ranged between 0.09 to 0.44  $\text{dS m}^{-1}$  (ratio of 1:5 s:v). Other researchers [106, 132] have reported that some properties of biochar differ according to the pyrolysis method employed, and temperature, the source material, the amount applied and the climatic conditions, so that the variability in these conditions makes the results not entirely comparable and conclusive. The different and contrasting values of pH, neutralization potential, number of bases, EC, etc., might also vary depending on the analytical methods used, as well as the way in which these are processed, as demonstrated by Singh et al., 2010 [129]. **Table 1** also show the CEC-values measured by silver thiourea method (AgTU) [15], without removal of carbonates and soluble salts, which for E was 16.1  $\text{mmol}(-) \text{ kg}^{-1}$ , while for H it was 41.3  $\text{mmol}(-) \text{ kg}^{-1}$ . These authors [129] also recommend measuring CEC and base saturation, with the above method, but with prior removal of salts, since these can increase the pH of the extracting solution (pH > 8) promoting the precipitation of Ag with sulfides, which occurs at basic pH-values, leading to a possible overestimation of both parameters. The authors also determined CEC of an eucalyptus biochar, measured with AgTU without removal of carbonates and soluble salts and obtained values of 91  $\text{mmol}(-) \text{ kg}^{-1}$ , however, when these carbonates and salts were removed, the CEC decreased by 60% (to 36.4  $\text{mmol}(-) \text{ kg}^{-1}$ ). According to them, the actual CEC, if the effect

pH	EC	SP	CEC	BS	(mg kg <sup>-1</sup> )						
					Cu <sub>T</sub>	Pb <sub>T</sub>	Zn <sub>T</sub>	Cu-soluble	Pb-soluble	Zn-soluble	
Mixture substrates											
M1	6.8 ± 0.2	334 ± 25	62 ± 0.1	27 ± 3	39 ± 1	76 ± 11	173 ± 3	379 ± 11	<DL	39 ± 5	<DL
M2	6.6 ± 0.2	415 ± 21	50 ± 0.4	46 ± 1	50 ± 1	210 ± 20	2384 ± 3	1090 ± 18	0.3 ± 0.04	64 ± 2	<DL
M3	4.7 ± 0.1	468 ± 70	38 ± 0.2	24 ± 6	21 ± 1	324 ± 29	4279 ± 3	1699 ± 24	1 ± 0.04	29 ± 2	5 ± 0.002
M4	3.3 ± 0.1	481 ± 43	35 ± 0.2	22 ± 5	18 ± 1	457 ± 38	6490 ± 3	2409 ± 31	11 ± 0.03	48 ± 6	29 ± 2
Biochar											
H	10.2 ± 0.1	604 ± 32	346 ± 7.0	42 ± 2	424 ± 3	199 ± 33	<DL	115 ± 20	1.2 ± 0.04	< DL	< DL
E	9.9 ± 0.1	277 ± 20	222 ± 0.1	16 ± 1	17 ± 1	213 ± 20	<DL	192 ± 9	1.5 ± 0.04	< DL	4 ± 2

*Metal Detection Limit (DL): Cu<sub>T</sub> = 10 mg kg<sup>-1</sup>; Pb<sub>T</sub> = 5 mg kg<sup>-1</sup>; Zn<sub>T</sub> = 8 mg kg<sup>-1</sup>; and water-soluble Pb = 1 mg kg<sup>-1</sup>; Zn = 0.1 mg kg<sup>-1</sup> and Cu = 0.1 mg kg<sup>-1</sup>. Where: EC<sub>1:20</sub> is the Electrical Conductivity (1:20 ratio, μS cm<sup>-1</sup>); SP (%); Saturation Percentage; CEC is the Cation Exchange Capacity (mmol<sub>c</sub> kg<sup>-1</sup>); BS is the Base Saturation mmol<sub>c</sub> kg<sup>-1</sup>; Cu<sub>B</sub> Pb<sub>T</sub> and Zn<sub>T</sub> are the total metal levels.*

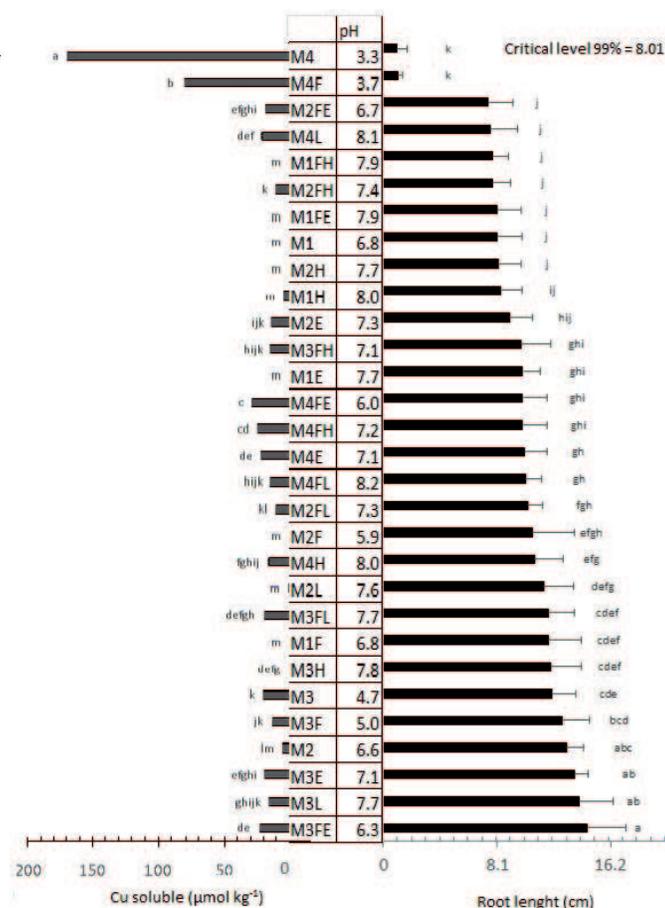
**Table 1.**

*Physicochemical characterization values and standard deviations of chemical properties determined on pristine soil (M1), mixture substrates (M2) and (M3), mine waste (M4) and biochar materials from water hyacinth (H) and eucalyptus (E). Parameters included are pH, Electrical Conductivity (EC) in dS m<sup>-1</sup>, Saturation Percentage (%SP), Cation Exchange Capacity (CEC) mmol<sub>c</sub> kg<sup>-1</sup>, Base saturation, BS [mmol<sub>c</sub> kg<sup>-1</sup>], total-metal levels for Cu<sub>B</sub> Pb<sub>T</sub> and Zn<sub>T</sub> (mg kg<sup>-1</sup>) and water soluble-Cu, Pb and Zn (mg kg<sup>-1</sup>). Determinations were carried out according to [15].*

of salts on the biochar of the study were eliminated, it would lead to CEC-values of 9.7 mmol(−) kg<sup>-1</sup> for E and 24.8 mmol(−) kg<sup>-1</sup> for H biochar.

### 4.3 Results of the root length bioassay

**Figure 6** shows the results of the root length bioassay only for Cu, carried out with barley plants under the conditions mentioned at the start of the section. For more details of the experiments for other metals (like Pb and Zn) refer to [15]. Results show the effect of treatments on barley root length (*Hordeum vulgare* L. var. Hope), pH and soluble copper in the soil-acid mining residue gradient. The lowercase letters on each bar indicate statistical differences (Fisher's test,  $P < 0.01$ ). Where the first letter and subscript indicate the mixture type [M1 is 100% soil; M2 is 35:65% (M1:M4); M3 is 65:35% (M1:M4); and M4 is 100% acidic mining residue] and the last letter(s) indicates the treatment. To be able to define a critical reference level ( $P < 0.01$ ) of root growth length and using it as an indicator of phytotoxicity and efficacy of treatments, the average value of the root length of the pristine soil (M1) was used. This was the minimum mitigation value to be achieved. The M4 and M4F treatments had a growth below the critical level of the reference value (**Figure 6**), mainly due to the low pH of these substrates (3.2 and 3.7, respectively), that is, due to the phytotoxicity caused by the high chemical activities of the H<sup>+</sup> ions. The high activity of H<sup>+</sup> ions, caused by the hydrolytic oxidation of minerals such as pyrite (FeS<sub>2</sub>), causes the release of free sulfuric acid [133]. In contrast, the response of the remaining treatments was equal to or greater than that



**Figure 6.** Effect of treatments on barley root length (*Hordeum vulgare* L. var. Hope), pH and soluble copper in the soil gradient substrates-acid mining residue. The lowercase letters on each bar indicate statistical differences (Fisher's test,  $P < 0.01$ ). Where the first letter and subscript indicate the mixture [M1 is 100% soil; M2 is 35:65% (M1:M4); M3 is 65:35% (M1:M4); and M4 is 100% acidic mining residue] and the last letter(s) indicates the treatment where F corresponds to phosphates, L to liming, H and E to biochar of water hyacinth and eucalyptus, respectively.

of M1, due, on the one hand, to the increase in pH, which favors the decrease of the chemical activity of H<sup>+</sup> ions and the phytotoxicity caused by the sorption of metals onto the solid phase [134]. In M1 the response was: M1F > M1E > M1H = M1 = M1FE = M1FH, where treatments with F and E were the ones with the greatest response. The rest of the treatments showed no significant differences. The effect of F treatment, in combination with biochar, was not significant with respect to M1. Karami et al. [135] showed that wood-derived biochar applied at doses of 20% (v:v), reduced phosphorus availability. In our case the bioassay showed this type of antagonism when phosphates were applied with H and E in M1. For the M2 substrate (pH = 6.6, 65% soil and 35% acid residue), the control treatment, i.e., the mixture without any additional treatment, promoted the highest root growth. The order of response was: M2 > M2L = M2F = M2FL = M2E = M2H > M1 = M2FH = M2FE. It is evident that the presence of M1 soil in 2/3 parts of the substrate was sufficient to mitigate the phytotoxic effect of 1/3 of the acid residue. The addition of L, F, FL, E and H generated less root growth each time, respectively, with respect to the blank treatment. Treatment pH-values of those with neutralizing potential (L, H and E and mixtures of these with F) were greater than 7, while for phosphates pH was 5.9, having, as expected, no effect on pH. However, FH and FE treatments in this system decreased the response even more than the combination of lime-phosphate (FL) and that of lime (L). For the M3 (1/3 of M1 and 2/3 M4) the response order to the application of E and L, was: M3FE = M3L = M3E = M3F = M3 = M3H = M3FL > M3FH > M1. All these treatments showed better responses than the reference level shown by the pristine soil (M1). According to **Figure 6**, soluble-Cu was not detected in the pristine soil, but for the treatments of the same substrate (M3), this metal contributed evidently to the positive response. The pH values of the treatments ranged from 4.7 (M3) to 7.7 in M3L and M3FL. The correlation between the pH and the concentration of the soluble metal, and that between the soluble metal and the root length are related to the increased extractability of the soluble metal at low pH values (<4), while reducing root growth. The inferred relationship is indicative of the level of the phytoavailability of Cu, more than to the reduced phytotoxicity in the treatment. The increase in root length in the M2 and M3 substrates, compared to the reference materials (M1 and M4), was as expected, because soils naturally tend to reduce the mobility and mitigate the phytotoxicity of metals such as Pb, Zn and Cu, especially when metals are in high concentrations [134]. This seems to occur because there are sites where metals can be adsorbed and complexed with free organic and inorganic functional groups. However, the process can be accelerated if some amendments are used to agrostabilize the environment, such as phosphoric fertilizers, composts, biochar or biosolids, and/or liming materials, among others [136]. Also, the positive effect on root growth in M2 and M3 compared to M1 treatment is satisfactorily explained by the fertility contribution of phosphate (and potassium) from the F treatments and the micronutrients Cu and Zn coming from the mining residue. The addition to M4 to H, FL, E, FH and FE treatments enlarged the length of roots with respect to the blank. The order: M4H = M4FL = M4E = M4FH = M4FE > M1 = M4L > M4F = M4. Treatment response in this case showed equal or greater response in growth than M1, fact that can be explained by the pH increase caused by the basic materials added, and the increased phytoavailability of Cu, as compared with the other substrates.

## 5. Conclusions

The chapter presents in its introduction, a general view of the sound methodology that is proposed through the rest of the sections, to both, remediate acidic metal polluted mine wastes, taking advantage of the neutralizing alkalinity and high metal sorption affinity of pyrolyzed materials, and to utilize biochar derived from high-rate

growth plants (water hyacinth, and eucalyptus, which have become of ecological relevance due to their unwanted proliferation over specific terrestrial, lacustrine or riverine environments. Relevant calculations are presented in the section two to analyze the discrepancies reported in literature among ABA methods, COD-redox measurements and kinetic factors, that may affect the determination of the right doses to neutralize with lime or pyrolyzed materials of alkaline reaction, the acidity of metalliferous mining wastes. In this section too, the status of the heavy metal problematic provoked by the sulfidic mine tailings deposits on dams is also considered, that in terms of dimensioning the relevant physicochemical characteristics to overcome when a remediation strategy is planned or put on action, when trying to mitigate and abate the toxic effects of HM on the biota. The section also addresses the importance of not only neutralizing the mine tailings but abating the toxic levels of heavy metals (HM) like Pb, Cd, Cu, and Zn, to fulfill the international and national standards and norms. Section three includes a review of the main amendment materials used, alone or in combination with biochar, to remediate heavy metal polluted sites. These references reviewed include lime, phosphates, compost, biosolids, clays and more precisely the role of biochar on these reclamation activities. A comprehensive compilation of characteristics of biochar as affected by temperature, is presented in **Figure 3**. Data plotted against charring temperature show behavior of specific surface; ash contents, pore volume, yield, C-, H-, O- and N-contents, pH; and C/H, C/O and C/N ratios. In Section 4 a case of study is presented to congruently exhibit how the strategy proposed was tested through following the methodology described herein. An experiment where biochar was combined with phosphate, and compared against the performance of lime, alone and combined with phosphate too, is exposed. Results of the root length bioassay only for Cu, carried out with barley plants under the conditions mentioned at the start of the section. For more details of the experiments for other metals (like Pb and Zn) refer to [15]. Results of the effect of soil-acid mining residue gradient were tested applying a bioassay on barley (*H. vulgare* L. var. Hope) plants and correlated with pH and soluble copper levels.

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