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# TREATMENT OF ACID MINE DRAINAGE BY BIOCHAR: A SUSTAINABLE APPROACH

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**ABSTRACT**

Acid mine drainage (AMD) formation is one of the major environmental problems. It is characterised by high acidity with higher metal concentration. This heavy metal-loaded drainage through rain water, and further seepage, mix to nearby water streams causes environmental risks. It is extremely harmful to the both flora and fauna, including aquatic life as well as wild life. A current clean-up technique uses active and passive treatment systems. But new research is developing to create more efficient eco-friendly and environmentally sustainable treatment technology that needs low operation and maintenance. Biochar, an alternative bio-material, is receiving considerable attention by scientists. Biochar is a low-cost adsorbent that reduces heavy metals and enhances the pH of acid mine drainage. The effective adsorption of metal ions by biochar is attributed to its high surface area and porosity. Biochar works with different mechanisms such as precipitation, complexation, ion exchange, electrostatic interaction and physical sorption, while removal of different heavy metals. Recent studies have explained that biochar is excellent adsorbent of heavy metals such as Fe, Mn, Mg, Cu, Zn, Pb, Ni etc. Engineered Biochar modifies the physical and chemical properties of biochar and improves the biochar properties and efficiency. The paper discusses the recent research work and findings of treatment of AMD by different biochar's. Mechanisms of metal removal and neutralization by biochar are also briefly discussed. Finally, a few recommendations for further research have been made for the efficient treatment of AMD by Biochar.

**Keywords: Acid Mine Drainage, Adsorption, Biochar, Mining**

## 1. INTRODUCTION

Acid mine drainage (AMD) is one the most important environmental problem arises from the mining industry, mainly associated with drainage from metal mines, surface or deep coal and coal refuse piles. During mining activities, when pyrite (iron sulphide) minerals is exposed to air and water, oxidation and hydrolysis takes place, and form sulphuric acid and dissolved iron and this is called acid mine drainage **[1-2]**. Some or all of this iron can precipitate to form red, orange or yellow sediments in the bottom of streams containing mine drainage. It is characterised by the high concentration of dissolved heavy metals, high acidity, sulphates, and extremely low pH **[3]**. The AMD is highly toxic and causes harmful threats to the human being, flora and fauna when mixed with groundwater, surface water and soil biota **[4-5]**.

It is therefore very important to solve out this world-wide problem. The one of the primary stages toward this are the treatment of mine water in active mines as well as closed abandoned mines. There are many treatment and preventive techniques to avoid the generation and treatment of AMD. The main two treatment methodologies for acid mine drainage are active treatment and passive treatment **[6-7]**. Active treatment of AMD is the addition of chemical compounds to precipitate the present metal ions and to enhance the pH of the fluid. This is performed by precipitation, oxidation, alkali dosing, sedimentation, reverse osmosis, sulfurization and ion exchange. Limestone drains to increase pH and remove dissolved metals from acidic mine drainage **[8-10]**. This treatment is very useful, but its success is limited by its continuous and long-term treatment, failure of used equipment and also interrupted by different weather conditions. Passive treatment of AMD includes naturally occurring chemical and biological medium without any mechanical assistance **[11]**. These are aerobic wetlands, compost/anaerobic wetlands, open limestone channels, diversion wells; anoxic limestone drains (ALD), successive alkalinity-producing systems (SAPS) vertical flow reactors (VFR), and pyrolusite process **[6, 12-13]**. It is very efficient technology, which requires minimum input of energy, chemical and manpower **[14-15]**.

However, recent water treatment technology favours for these long-term passive treatments that needs low operation and maintenance. For such a vision, biochar, an alternative bio-material, is receiving considerable attention as a natural bioadsorbent **[16-18]**. It is eco-friendly human-made bio-system and environmentally sustainable treatment technology. Biochar is a carbon-rich solid formed from the organic residue (biomass) by pyrolysis to typically temperature between 300°C and 700°C under oxygen-deprived conditions **[19-21]**. Various types of biomass have been used on a commercial scale for biochar production successfully, including agricultural and forestry by-products (straw, rice hulls, wood chips, tree bark etc.), industrial by-products (bagasse from the sugarcane industry, paper sludge, and pulp), animal wastes (chicken litter, dairy and swine manure), and sewage sludge **(Figure 1)** **[22-23]**. As per Motasemi and Afzal **[24]** biomass resources are grouped into three major forms. These are virgin resources, residues and municipal solid waste. The virgin resources include forest resources and oilseed or cereal crops. The residues composed of wood residues, agricultural residues and wastes as well as livestock residues. Municipal solid waste includes residential or non-residential wastes **[25]**.

The effective adsorption of metal ions by biochar is attributed to its high surface area and porosity **[26-28]**. Biochar provides alkalinity thus increases the pH and reduces the acidity of the industrial waste-water **[29]**. Biochar is alkaline because of presence of solid Ca and Mg carbonates, which is formed during pyrolysis **[30]**. Also, biochar is characterised by high surface area and exchange capacity which provide it a novel structure to remove cations and anions from the acid mine drainage **[31-33]**. The mechanism of metal removal by biochar is attributed to surface adsorption, binding of oxygen-containing functional groups (carboxylic and phenolic functional groups) and to the co-precipitation of aluminium with silicate particles **[34-35, 18]**. Biochar's have increased porosity therefore biochar considered as a potential absorbent to reduce metals ion in acid mine drainage **[36-37]**. These characteristics of biochar are receiving increasing attention from scientists and policy makers worldwide.

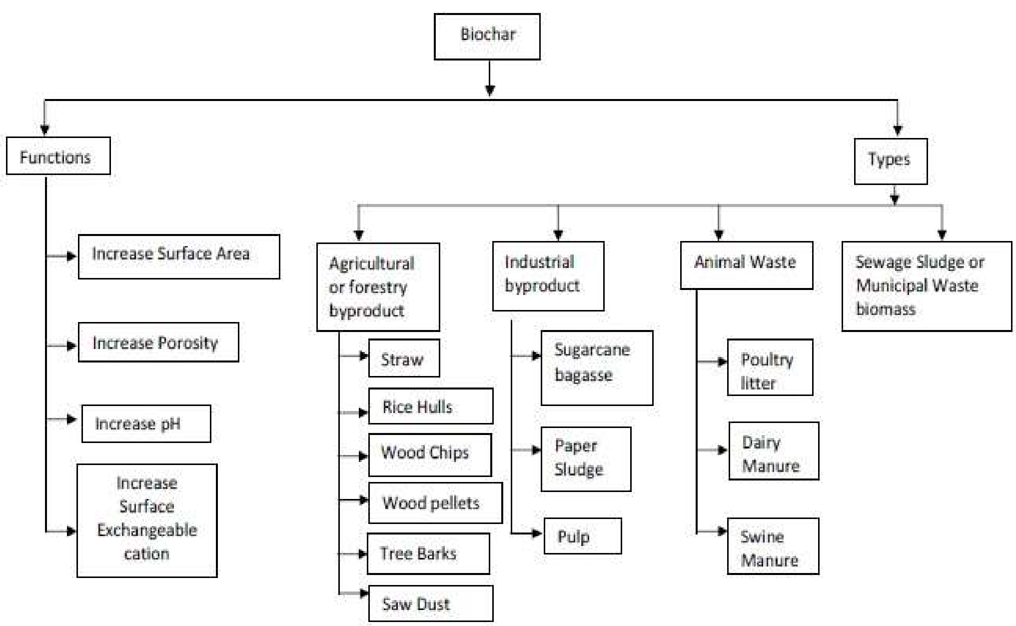


**Figure 1: Types and functions of Biochar**

Biochar's can also be engineered to have specific physical and chemical properties by selecting appropriate feedstock and pyrolysis conditions **[38]**. Recently vast work has been performed for the preparation of modified biochar as per the target of the particular metal **[39]**. Modified or engineered biochar are to prepare to get the more micro pores (pores smaller than 2 nm in diameter) or meso pores (pores larger than 50 nm in diameter) on biochar so to improve the novel properties of biochar that is surface properties, functional group, surface area and also porosity **(Figure 2) [40]**.

**2. Treatment of acid mine drainage by biochar**

Poultry litter is one of the most potential organic biomass that are extensively studied and recognized as potential raw material for preparation of low-cost adsorbent. Poultry Litter is a mixture of poultry excreta, feathers, spilled feed and material used as bedding to absorb liquid fractions of excreta, which typically include wood chips, sawdust, wheat straw, peanut hulls, and rice hulls, in poultry operations at large scales **[41]**.Oh and Yoon **[42]** reported efficiency of poultry litter-derived biochar to treat acid mine drainage (AMD) at Ilkwang copper mine in South Korea. They removed Fe, Al, Cu, and As by 100%, and Zn, Mn and $SO_4^{2-}$ by 99%, 61% and 31% respectively. The reason for which was due to the neutralization provided by carbonate minerals and finally adsorption to the large surface of biochar. Admir *et al*. **[43]** also tested poultry litter-derived biochar (400°C) enriched with three sources of sulphate reducing bacteria (SRB) (sediments from AMD, cattle manure and domestic activated sewage sludge) to reduce the toxic metal concentration in AMD. Cow manure SRB-enriched biochar reduces the sulphate to 41% and 39% compared to original AMD and other treatments (control, AMD sediment, sludge) respectively. SRB efficiently reduces sulphate ($SO_4^{2-}$) to sulphide ($S^{2-}$) by using the electrons from the organic matter. Further, formed sulphides precipitate the heavy metals ions **[44]**. SRB also neutralizes the acidity of AMD by generating the alkalinity. Efficiency of SRB basically depends upon the type of organic matter used in biochar **[5, 45]**.

Biochar produced through thermal decomposition of lignocellulosic biomass (sawdust, wood chips etc.) in the limited oxygen conditions are very well known for their efficiency of metal adsorption **[46, 39]**. Janin and Harrington **[47]** studied three biochar's (mixed spruce, pine, and fir) BCD, (spruce, pine, fir, willow and poplar) BCZ and (Willow and fish bone meal) BCT and three wood residues (poplar chips, spruce chips and spruce needles). All biochar's were found alkaline with the pH between the ranges of 9-10. They found 35 to 69% removal of arsenic and more than 90% removal of Cd, Cu and Zn from the acidic effluent. The BCT material was found for maximum removal of higher concentrations of metals Cd (11mg/kg), Zn (164.2mg/kg), Fe (3755.8mg/kg), and Na (15814.5mg/kg). Kim *et al*. **[48]** increased the pH of AMD from approximately 4 to 7 by using spent coffee ground biochar (waste products through the production of instant coffee and coffee brewing). Biochar from common reed species was prepared by Mosley *et al*. **[49]** at 450°C to neutralize the pH and remove the metals Fe, Al, Ni, Zn, Mn. They reported that in a column leaching experiment alkalinity was produced up-to 5 pH and in a batch experiments the pH was above 6.5. Concentration of Fe, Al, Ni, Zn, and Mn were reduced by 89 to 98% in the leachate. Biomass of roots of rose (*Rosa damascena*) and stem of eucalyptus (*Eucalyptus citriodora*) were converted into biochar by Khare *et al*. **[50]**. They reported maximum 60 mg/g removal of each metal from multi-metal contaminated acidic solution.

Yang *et al*. **[51-52]** worked to inhibit the source of origin of the AMD. Chalcopyrite has been reported as the most abundant copper-containing sulfide mineral in the source for copper extraction, which when dissolved by biological or chemical oxidation forms a source of AMD **[51, 53]**. Yang *et al.* **[52]** experimented the inhibition of chalcopyrite bio-dissolution by the corn straw biochar to inhibit the formation of AMD. They reported that corn straw biochar (3g/L) formed at 300°C gives the best inhibition results by reducing the bio-dissolution rate of chalcopyrite from 57.1% to 39.4%. The reason for inhibiting the bio-dissolution of chalcopyrite is attributed to the formation of passive layer and absorbance by bacteria, thus releasing fewer copper and iron ions and less acid.

There are several approaches to modify the biochar which can be divided into four main categories, i.e., chemical modifications, physical modifications, magnetic modifications and impregnation with mineral oxides **(Figure 2) [25]**.

The latest development in engineered biochar is the magnetization of the biochar **[54]**. Adsorbent magnetization is an emerging water remediation area to overcome filtration problems of non-magnetic adsorbents. The modified biochar's have overwhelming features over unmodified biochar and are especially characterised by the increased surface area, enhanced porosity, high number of surface functional group, have increased number of surface positive charge and readily provide the co-precipitation of the metal ion **(Figure 2) [40]**. Mohan *et al*. **[55]** efficiently increased the Pb(II) and Cd(II) removal by magnetic biochar. The chitosan-modified biochar's is also low cost adsorbent effectively used for removal of heavy metal ions from wastewater. Zhou *et al*. **[56]** modified peanut hull, hickory wood, sugarcane bagasse, and bamboo with chitosan to enhance the surface area of the biochar. They observed enhanced absorption of Cd(II), Cu(II), and Pb(II) compared with the unmodified biochar's. Further chitosan-modified bamboo biochar was found with increased sorption capacity of lead (14.3 mg/g). The reason for which was attributed to the interaction of amino functional groups on the biochar surface. Biochar was modified with $HNO_3$, $H_2SO_4$, and $Na_2S_2O_4$ through nitration and reduction reactions by Yang and Jiang **[57]** to target the removal of Cu(II). They reported that integration of amino group's bounded chemically to functional groups of the surface of biochar. This modification of amino group enhanced five times the absorption of Cu(II). Ma *et al*. **[58]** prepared amino-rich biochar through polyethyleneimine to remove Cr(VI). They observed higher absorption capacity with modified biochar of 435.7 mg/g than that of the unmodified biochar of 23.1mg/g. Shi *et al*. **[59]** also prepared modified biochar from waste glue residue with various modifiers HCl, KOH, and $ZnCl_2$ to improve the adsorption capacity of biochar in chromium contaminated water's management. The maximum adsorption of Cr(VI) was 325.54 mg/g, observed with $ZnCl_2$ modified glue residue biochar. Wibowo *et al*. **[60]** worked with biochar and clamshell to treat the AMD. Clamshell has high $CaCO_3$, and considered as a potential feedstock to generate CaO by using calcination process, used to neutralize the AMD. Biochar was reported to reduce heavy metals up to 97% for Mn and 80% for Fe, respectively. The optimum mass of clamshell in 60mg was successfully increased pH from 2.7 to 7.0.

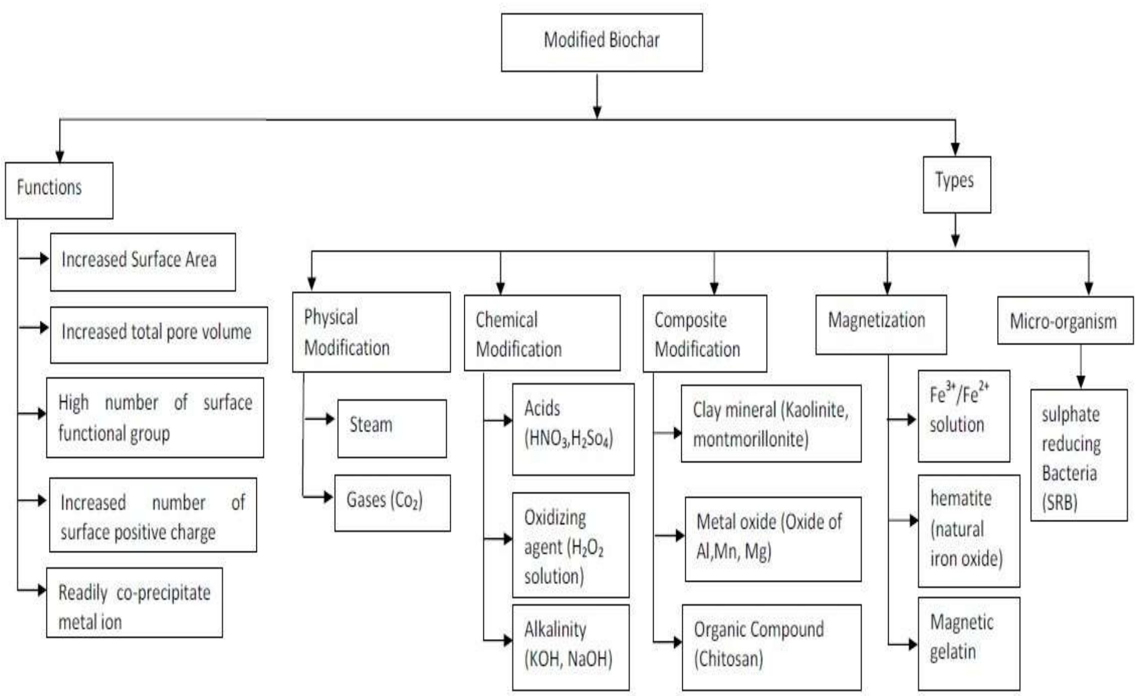


**Figure 2: Types and functions of modified Biochar**

It is suggested that anaerobic digestion could be used as new activation method (i.e. 'biological activation') to create high-efficiency carbon-based sorbents for heavy metals **[61-63]**. Inyang *et al*. **[62]** prepared biochar by the anaerobically digested sugarcane bagasses and revealed that it is a far more effective sorbent of lead than biochar from undigested bagasses and even more effective than commercial activated carbon. By the anaerobic digestion of dairy waste and whole sugar beets through slow pyrolysis two biochar's were prepared by Inyang *et al*. **[64]**. The removal efficiency of the four metals (Cu, Pb, Zn, Cd) by DWSBC (digested whole sugar beet char) was higher than 97%, indicating this biochar has a strong affinity for all the tested heavy metals. DAWC (digested animal waste char) also showed high removal efficiency for Pb(II) (99%) and Cu(II) (98%), but relatively low removal efficiency for Cd(II) (57%) and Ni(II) (26%).

Biochar based composites are produced by impregnating biochar with metal oxides, clays, organic compounds or carbonaceous materials, such as graphene oxide or carbon nanotubes, or by inoculation with microorganisms, to alter the surface properties of the biochar **[40,65]**. Wang *et al*. **[66]** suggested that the engineered biochar-based composite is an efficient adsorbent for the removal of Cr(VI) from AMD. In the experiment they synthesized biochar-montmorillonite composite (B@M)by heating peanut shell B@M to remove Cr(VI) from AMD. They reported that biochar surface was covered with montmorillonite successfully. They found maximum adsorption capacity of Cr(VI) of biochar and B@M was 9.18 and 12.18 mg/g, respectively.

Biochar obtained from sewage sludge, final products in a wastewater-based circular economy, has attracted increasing attention for metal pollutant removal from wastewater and soils. Sewage sludge or biosolids is an enriched organic matter waste that is produced in the water and waste water treatment plants. Sludge derived biochar (SDBC) efficiently immobilize various metal ions such as Pb(II), Cu(II), Ni(II), and Cd(II), and the oxoanionic such as Cr(VI) and As(III) as it provides **[67]** . Lu *et al*. **[31]** investigated the feasibility of sludge-derived biochar for the lead sorption in acid mine drainage. The observed that SDBC effectively removed Pb(II) with the capacities of 16.11, 20.11, 24.80, and 30.88mg/g at the pH values 2, 3, 4 and 5 respectively. They reported that adsorption of Pb is due to the chemical coordination of metal ion with organic hydroxyl and carboxyl functional groups (38.2-42.3%), as well as the co-precipitation or complex on mineral surfaces (57.7-61.8%) and led to a bulk of Ca(II) and Mg(II) release during sorption process. To enhance the adsorption capacity of sewage sludge-derived biochar Chen *et al*. **[68]** modified it by co-pyrolysis of sewage sludge and transition metal oxides ($Fe_2O_3$, $MnO_2$, and

ZnO). They found that Fe-modified biochar showed better Cd(II) adsorption performance in compare to unmodified, $MnO_2$ and ZnO modified biochar.

**3. Recommendations and Conclusions**

Acid mine drainage (AMD) is one of the largest environmental problem in the mining industry. AMD is highly acidic, possess extremely low pH, and contain high concentrations of sulphates and metal pollutants such as Cu, Zn, Pb, Cd, Ni, Hg etc. Biochar is a natural cheap resource that successfully addresses the management of AMD by increasing the pH and immobilizing the metal contaminants, decreasing the toxicity, and bioavailability. The affinity of biochar for adsorption of metal pollutants is due to its large surface area, high porosity, charged surface and functional group. Further various studies have revealed that engineered biochar enriched the active site and functional group of biochar's and thus enhances its efficiency. Metal sorption by biochar's largely depends on the characteristics of biochar such as resource of feedstock (biomass), temperature during pyrolysis and oxygen content while production of biochar, modifiers, and modification methods etc.

Biochar is not yet widely applied for industrial waste water management and still in the infancy stage. Further research, development and demonstrations of different biochar for acid mine drainage is need to be addressed for efficient working for long period of time. Climate change abatement option of biochar is also an important issue need to be worked out for the viability of the treatment. Further explorations are warranted in the directions of sustainable biochar development, continuous adsorption process, industry scale applications and spent biochar management. Inter-disciplinary and arduous location-specific research and investigations has to be performed for studying the long-term effect of biochar on acidity, pH and metal concentration of the acid mine drainage.

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