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Chapter

Performance Evaluation of Waste Materials for the Treatment of Acid Mine Drainage to Remove Heavy Metals and Sulfate

Satish Chandra Bhuyan, Subrat Kumar Bhuyan and Himanshu Bhushan Sahu

Abstract

Acid Mine Drainage (AMD) is the most severe environmental problem facing the mining sector in the current scenario because of low pH and high pollutants concentration. AMD contains a high amount of sulphate viz. pyrite, FeS₂, and to a lesser extent pyrrhotite and heavy metal ions, contaminate both surface water and groundwater. To treat AMD, extensive research projects have been initiated by governments, the mining industry, universities, and research establishments. The environmental impact of AMD can be minimized at these basic levels; prevention should be taken to control the infiltration of groundwater to the pollution site and control the acid-generating process. There are some conventional active methods to treat AMD, such as compost reactor and packed bed iron-oxidation bioreactors; however, these methods have associated with costly material and high maintenance cost, which increases the cost of the entire treatment. In an alternative, the use of low-cost materials such as fly ash, metallurgical slag, zero-valent iron (ZVI), cement kiln dust (CKD), and organic waste such as peat humic agent (PHA), rice husk, and eggshell can be a valuable measure for economic viability to treat the metal-rich wastewater.

Keywords: Acid Mine Drainage, Fly Ash, Metallurgical Slag, Zero Valent Iron, Organic waste

1. Introduction

The extensive mining throughout the globe leads to generate a huge quantity of sulfides caused by weathering process (O₂, moisture, and microbes), which promotes an acidic environment. The static/stream water in contact with mines and mines waste becomes a reaction site where it also acts as a reagent for deferent chemical reactions, i.e., metal/metalloid solubilization. Moreover, in-stream water, it also turns out to be a transport media for reaction products [1]. Such water constituents are called "acid mine drainage" or "acid and metalliferous drainage" (AMD) as shown in **Figure 1**. This water is generally characterized as lower pH value as well as a high heavy metals concentration such as iron, manganese, lead, chromium, mercury, cadmium, and arsenic and sulfate content [2]. AMD has a severe impact on the environment, including neighboring surfaces, groundwater,

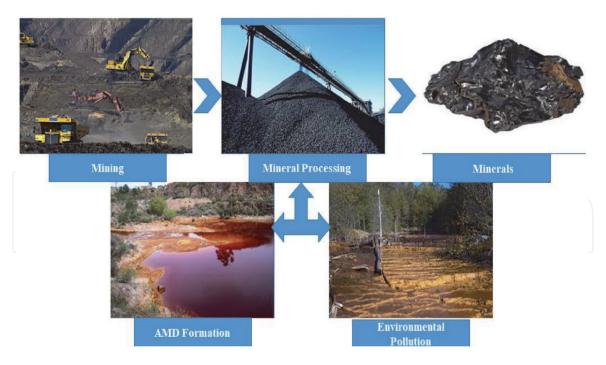


Figure 1. Formation of AMD.

and soil properties. Various reports suggest that heavy metals transmit to the human body cause severe illness and death in AMD-contaminated areas. Therefore, to ensure human health safety and to control the environmental risk, AMD must be treated.

Various alkaline materials such as CaO, NaOH, CaCO₃ have been appropriately examined in this chapter. The use of CaCO₃ is more than other neutralizing material due to its cost-effectiveness. It produces less amount of sludge but the reaction period is comparably high than other chemical reagents. The major drawback of these alkaline reagents are high in cost and effectiveness in long-term periods is low. To avoid these major drawbacks, there is always a need for a better reagent, which is cheaper, eco-friendly, easy to handle, and the effectiveness in mitigating AMD wastewater. So various industrial by-products are examined by researchers. For example, the by-products generated from the Calcium oxide production process are used to treat sulfate and metals like cobalt, nickel, zing copper cadmium with better efficiency. Some other industrial outcomes like fly ash, steel slag, cement kiln dust, and bayer residue have possible calcium oxide and calcium hydroxide alternatives to treat AMD. The availability of these materials is generally high, which offers cost-effective neutralizing materials for the treatment process.

2. Characteristics of AMD wastewater

AMD is generally characterized by several physio-chemical properties. The chief physical properties are temperature, electrical conductivity, suspended and or dissolved solids whereas the chemical properties are mostly indicated by pH, alkalinity, acidity hardness, the concentration of metal ions, silica, salt, ammonium, and hydrocarbon contents, and radioactivity.

The physical and chemical properties depend on many factors which generally influence the oxidation process of sulfide minerals as well as promotes the migration and dilution of AMD. Hence, every mine has a different material property and should be studied carefully. In the mining sector for metal production, the most crucial factors are pH, the heavy metals concentration, and dissolved anion

concentration, i.e., sulfate, chlorides, arsenates, nitrates, etc., and hardness as well as suspended solids. For a better characterization of AMD as well as the properties of waste which are affected by AMD is summarized into five common features listed as follows [3].

- i. Acidity, and alkalinity property (pH)
- ii. The concentration of different heavy metals
- iii. Fe and Al concentration
- iv. Sulfate and Arsenate concentration
- v. Transparency loss (turbidity and suspended solids)

2.1 Acidity/alkalinity property

The pH is the measure of H⁺ concentration; in the case of pure water, H⁺ and OH⁻ are in the same concentration. If the H⁺ concentration is higher, it is acidic and if OH⁻ is higher it becomes alkaline. The pH value of water decreases when it comes in contact with oxidized sulfides. For heavy metals, the lower pH value improves the solubility of the solution and is converted to a toxic solution.

The alkalinity is a measure of the base concentration of a solution and measured by the ability of the solution to absorb protons or the capacity to neutralize a strong acid. It also depends on the $\rm CO_2$ content and mineralization process. Thus total alkalinity is also known as the sum of $\rm OH^-$, $\rm CO_3^{2-}$, $\rm HCO^{3-}$, $\rm NH_3$, $\rm HS^-$, $\rm PO_4^{-3}$, $\rm H_2BO_3^-$, and organic anions. The measurement of acidity indicates the total acid in the solution; also known as the capacity to neutralize the base.

The solution of a lower pH may contain different abundant acids. For pH higher than 7.0, total acidity rarely exists due to the lower value of sulfuric acid (H_2SO_4). The carbonate/bicarbonates convert into carbonic acid for pH less than 4.2, which then leads to the rapid dissociation into water and CO_2 [4].

2.2 Concentration of different heavy metals

Different heavy metals of high concentrations are the common feature of AMD. Some metals in the metal deposits often incorporate into the AMD at specific geochemical conditions. The toxicity level is a greater problem to aquatic life as well as human health. The control mechanism of heavy metals is quite complex and highly precise to metal and site. In the initial stage where AMD forms, the type of metallic minerals and their solubilities and or dissolution rate control the concentrations of heavy metal. In the second development stage, effluent evolves in contact with regional rocks, atmospheric conditions, and water, changes occur in the complex of metal which favor adsorption and precipitation, so control and mitigate AMD flow [5].

2.3 Iron and aluminum concentration

Iron and aluminum have different geochemical conditions than other heavy metals present in AMD. These two elements are considered seriously due to their higher concentration and effects over other metals. They form a coating along the water stream known as yellow-orange Fe oxy-hydroxides and white-yellow Al oxy-hydroxides as shown in **Figure 2**. For low solubility in nature, these two metals under natural conditions form coloration over the water stream for a long time [6].



Figure 2.
Coloration of AMD water.

2.4 Sulphate and arsenate concentration

Sulphate concentration is the most consistent feature of AMD as its origin comes from sulphate oxidation. Various studies show that the effectiveness of sulphide oxidation depends on sulphate concentration and flow of effluent from the zone of

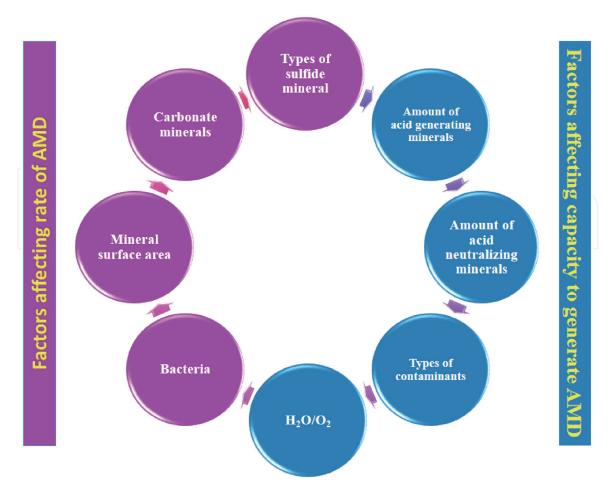


Figure 3.Various factors for the formation of AMD.

oxidation and any subsequent dilution. Arsenate does not form in such a higher concentration as that of sulphate but this metal has a different area of concern due to its toxic nature [7].

2.5 Turbidity and suspended solids

Turbidity refers to the light absorbance capacity of water preventing its transmission into depth. It is affected by the suspended solids, dissolved solids, and also plankton present in the solution. The measurement of total suspended solids in the laboratory studies indicated various disadvantages related to turbidity; during the storage of these samples, precipitation and flocculation occur. Particles can constitute suspended solid (SS) corresponding to AMD, and macromolecular colloidal particles of aluminum/iron-oxyhydroxides, macroscopic particles, and compounds such as silt and clay. Both the total suspended solids (TSS) and turbidity are of great importance corresponding to the transport phenomena of arsenic and heavy metals in the absorption process, to adverse the water quality and lower down the negative gradient on aquatic life. Also some other factors which is responsible for AMD are shown in **Figure 3** [8].

3. Occurrence of acid mine drainage

AMD normally has a lower value of pH, higher specific conductivity, high concentration of heavy metals such as iron, aluminum, and manganese, and low concentration of heavy metals viz. chromium, nickel, cobalt, arsenic, and so on. The pyrite mineral which is responsible for occurrence of AMD is shown in **Figure 4**. In the current scenario, AMD is left untreated due to inadequate, underdeveloped technologies and or infeasible processes (expensive) in various parts of the globe. The acid generation reaction due to pyrite oxidation, which is widely known as one of the sulphide minerals is given in Eq. (1). The oxidation reaction results in dissolved Fe, sulphate, and hydrogen as reaction products [9, 10].

$$FeS_2 + \frac{7}{2}.O_2 + H_2O \rightarrow Fe^{2+} + 2.SO_4^{2-} + 2.H^+$$
 (1)

As the reaction indicated in Eq. (1) moves in the forward direction, the reaction products ferrous iron, sulphate, and hydrogen cataion increase the total dissolved solids (TDS) and hence acidity by lowering pH of solution [11]. If the adjacent surroundings get sufficiently oxidized (depending on oxygen concentration, pH, and microbial activity), much of the Fe²⁺ will be oxidized into Fe³⁺ as expressed in Eq. (2).

Pyrite water + Air = low pH + Metals



Figure 4. *Pyrite mineral.*

$$Fe^{2+} + \frac{1}{4}.O_2 + H^+ \to Fe^{3+} + \frac{1}{2}.H_2O$$
 (2)

For pH equals 2.3 and 3.5, the ferric iron (Fe³⁺) precipitates as Fe(OH)₃ and $[KFe_3(SO_4)_2(OH)_6]$, respectively, a low Fe³⁺ retains in solution which lowers the pH.

$$Fe^{3+} + 3.H_2O \rightarrow Fe(OH)_3 \ solid + 3H^+$$
 (3)

The leftover Fe³⁺ in Eq. (2) which remains unreacted in Eq. (3) might promote oxidation of additional pyrite as per Eq. (4).

$$FeS_2 + 14Fe^{3+} + 8.H_2O \rightarrow 15.Fe^{2+} + 2.SO_4^{2-} + 16H^+$$
 (4)

The aforementioned basic reactions suggest that the acid generation produces ferric iron which gradually precipitates into $Fe(OH)_3$ and may be represented as Eq. (5) which is a combined reaction of Eqs. (1) and (3).

$$FeS_2 + \frac{15}{4}.O_2 + \frac{7}{2}.H_2O \rightarrow Fe(OH)_3 + 2.SO_4^{2-} + 4H^+$$
 (5)

In another way, Eq. (6) represents the overall reaction for stable Fe^{3+} used to oxidize additional pyrite.

$$FeS_2 + \frac{15}{8}.O_2 + \frac{13}{2}.Fe^{3+} + \frac{17}{4}.H_2O \rightarrow \frac{15}{2}.Fe^{2+} + 2.SO_4^{2-} + \frac{17}{2}.H^+$$
 (6)

In all of the above equations except Eqs. (2) and (3), the oxidant and oxidized mineral are presumed as oxygen and pyrite, respectively. However, pyrrhotite and chalcocite minerals contain altered proportions of metal sulfide and also metals excluding iron [12].

When the water is adequately acidic, acidophilic microbes that flourish at low pH can build up themselves. The microorganism "Thiobacillus Ferroxidans" is assumed to take a huge part in accelerating the synthetic response occurring in mine water circumstances, i.e., these microbes catalyze the oxidation of Fe²⁺. Another microorganism "Ferroplasma Acidarmanus" has recently been found to play an important role in acid generation in the source water.

Although the formation of H⁺ as a result of certain metals precipitations expressed in Eqs. (7) and (8) are not the major acidity sources, these also are considered as treatment alternatives [13].

$$Fe^{+3}/Al^{+3} + 3.H_2O \rightarrow Fe(OH)_3/Al(OH)_3 + 3.H^+$$
 (7)

$$Fe^{+2}/Mn + +0.25O_2 (aq.) + 2.5H_2O \rightarrow Fe(OH)_3/Mn(OH)_3 + 2H^+$$
 (8)

Different metals are normally found in AMD because they are available in rocks, like pyrite. There are different metal sulphides viz. ZnS, PbS, NiS, CdS, CuS, etc. which may deliver metal particles into solution but may not produce acidity. The key factors determining the acid generation rate are as follows.

- i. Water pH and environment temperature
- ii. Oxygen concentration aqueous solution
- iii. Saturation degree (in water)

- iv. Chemical activity of ferric iron
- v. Exposed surface area
- vi. Chemical energy (activation) to initiate acid generation
- vii. Presence of bacteria that promote oxidation

In the special case where microbial acceleration is significant, some other factors such as activation energy (biological), population density (microbes), and growth rate determine the activity of bacterial. The growth rate depends on pH, temperature, and the presence of various nutrients like nitrate, potassium, ammonia, phosphorous and CO₂ content.

4. Environmental impact of acid mine drainage

AMD shows unique characteristics because the formation and generation of acidic water continue even after the mining area is ceased. So this acidic nature of water is not suitable for the human, animal as well as aquatic life. This problem of the acidic nature of water is not restricted to a limited area near the source of generation but extended to a larger area if this water gets discharged to the main water stream [14]. The AMD has generally more impact on the groundwater than that of the quality of surface water [15]. If the mines which are producing acidic water are present in the permeable formation, this acidic water (low pH)

Heavy metal	Effect on human health	Effect on plant physiological	Permissible level (mg/L)	
Cu	Anemia, liver and kidney damage	Inhibits photosynthesis and reproductive process	0.10	
Cd	Renal dysfunction, lung infection, and cancer	Decreases seed germination and lipid content	0.01	
Zn	Damage to the nervous system	Reduces Ni toxicity, promotes plant development	5.0	
Ni	Allergic contact dermatitis, chronic bronchitis, lung, and nasal cancer		0.05	
As	Bronchitis, Skin and bladder disease, kidney damage, bone marrow depression	Growth inhibition, Loss of yield and fruit production, Food chain harming	0.05	
Mn	Affect the central nervous system	Decreases seed germination, protein, and enzyme	0.1	
Hg	Impaired neurodevelopment, decrease in memory	Decreases photosynthetic activity, water uptake, and antioxidant	0.001	
Pb	Mental retardation in children, developmental delay	Reduces chlorophyll production and development of plant	0.10	
Cr	Affect the nervous system, fatigue, and irritability	Decreases enzyme activity, development of plant; Causes membrane damage, chlorosis, and root damage	0.05	

Table 1.Influence of heavy metals on animals and plants.

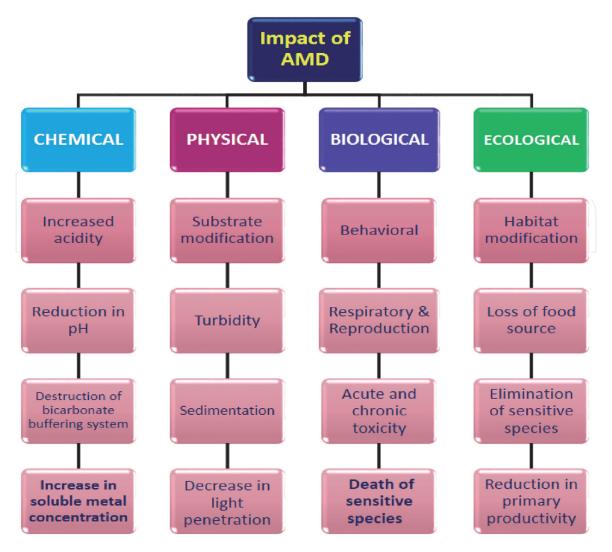


Figure 5.
Several impacts of AMD.

penetrates the aquifer and spreads into and over a larger area with the movement of groundwater which is used by human beings in different ways like wells and bore wells. This acidic and Fe-contaminated water is not only the key reason for corrosion in mine plant equipment by forming scales on the delivery pipe but also pollute the mining atmosphere and surrounding ecosystem [16].

AMD has a serious impact on human heal as well as the ecosystem due to the presence of heavy metals which are not degradable and causes various diseases and disorders in living organisms as well as the plant physiology which is given in the **Table 1**. Various impact of AMD has been shown in **Figure 5**. The pH of this water is very low so the heavy metals present in this water are insoluble and its high concentration causes a toxicological effect on aquatic life. This high presence of metals in water can kill the organisms directly and in the long term effect, lowers the growth and reproduction rates.

5. Treatment technology for AMD

Treatment of AMD is broadly classified into active and passive treatments which is clearly shown in **Figure 6** [17]. The active method is more complicated and required more unit measures and the operational cost is high than other treatment

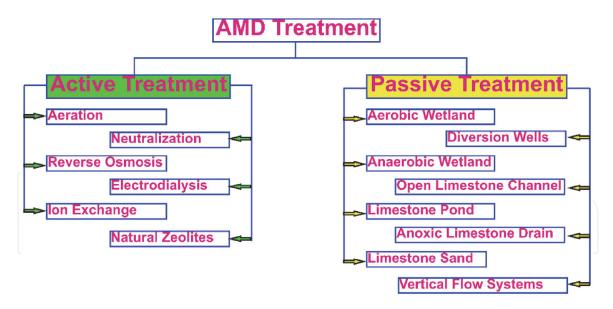


Figure 6. *AMD treatment methods.*

methods like passive treatment. The various strategy applied by the various nations for the AMD treatment comprising precipitation, neutralization, ion exchange, electrochemical remediation, adsorption oxidation, etc. All these methods are used for wastewater treatment among which the adsorption technique is the most suitable method for being comparatively economically viable and eco-friendly [18].

5.1 Active technologies for the treatment of AMD

The appropriate strategy used to mitigate wastewater (acidic) that includes the expansion of a chemically neutralizing agent is known as active treatment. The addition of various basic materials will improve the pH and accelerate the oxidation process (chemical) of (Fe²⁺) and precipitation of different metals into hydroxide and carbonates. The different neutralizing agents viz. lime, slaked lime,



Figure 7.

Common neutralizing reagents.

sodium-carbonate/hydroxide, calcium/magnesium-carbonate/hydroxide can be utilized which is shown in **Figure** 7; differ in cost and efficiency. Although active chemical treatment has better efficiency for mitigation of AMD water, it has a disadvantage of high operational cost and produces more amount of sludge as an effluent. In this treatment process a variety of refinements to improve its efficiency and minimizes the sludge-related problems. The different flocculating reagent is added to increase precipitation. The iron-rich sludge created by the expansion of basic material is highly voluminous and rich in water. This sludge is used as a recycling process by dewatering the sludge in a lime-holding tank [19].

The cost for AMD treatment depends on the location and different scenarios like requirements of manpower, mechanical equipment, and dispensing facilities, and also cost. Soda ash, caustic soda, and ammonia have the lowest cost due to the less expensive equipment needed for the operation. Calcium oxide has the highest cost of installation because of the construction of a lime treatment plant and an aerator. The calcium hydroxide cost is low but the operation cost is high which is used for a long period of treatment for high loading and high acidic condition. Different active technology method which are generally followed for the treatment of AMD is given in **Table 2**.

Sl. No.	Methodology	Membrane used	Feed solutions	Experimental condition	Percentage removal
1.	Reverse osmosis	Cellulose acetate membrane	Fe, Cu, Zn, Ca, Mg, Mn, Ni, and A1	Product rate 26.2 g/hr. for an effective surface area of 13.4 cm ²	95–99% metal separation efficiency [20]
2.	Reverse osmosis	Polyamide ultra-low- pressure reverse osmosis		Feed rate at 1200 L/hr. 0.9–1.0 MPa	Removal percentage of Ni ²⁺ , Cu ²⁺ , Zn ²⁺ and Pb ²⁺ was 97.41%, 97.73%, 97.89% and 98.06% respectively [21]
3.	Filtration	Nano- filtration membrane		Feed rate at 1200 L/hr. 0.9–1.0 MPa	Removal percentage of Ni ²⁺ , Cu ²⁺ , Zn ²⁺ and Pb ²⁺ was 92.45%, 93.24%, 94.37% and 95.19% respectively [21]
4.7	Ion exchange			Gel type strong acidic cation exchange resin of the sulphonated polystyrene, porous medium base anion exchange resin with an acrylic matrix	100% Metal removal and 98% of water recovery [22]
5.	Electro- dialysis	HDX 200 anion- exchange and cation exchange membrane		_	The metal removal efficiency was 97% [23]
6.	Natural zeolites	_		6 hrs. of reaction time with a dose of 37 g/L.	Removal efficiency of Fe ³⁺ , Mn ²⁺ , Zn ²⁺ , and Cu ⁻ was 80%, 95%, 90%, and 99% respectively [24]

Table 2.Different active treatment technology.

5.2 Passive technologies for the treatment of AMD

The passive treatments of AMD rely upon biological, physical, and geochemical cycles to improve the nature of water. Primary passive methods can be compressively separated into biological and geochemical systems/reactors that use inorganic substances such as carbonates. The biological systems contain anaerobic and vertical flow wetlands, bioreactors. The geochemical systems include limestone drains, open limestone channels, limestone/steel slag leach beds, limestone sand. The selection of an effective passive treatment method relies on the water chemistry, flow rate, local topography, and characteristics of the site [25].

5.3 Treatment using various waste materials

Active treatment methods are adopted in a wide range but they cause high establishment and absorbent expense. Also, some treatment methods associated with the active process like reverse osmosis, ion exchange requires pre-treatment of influent which is mentioned in the **Table 2**. Waste materials are generally economical than any other treatment method also reduces the environmental load. Various waste material which are generally used for the Treatment process of AMD are given in **Table 3**. They have the capacity and effectiveness to improve the pH of the AMD water and also to remove various pollutants from the wastewater. These waste materials provide a larger surface area, increasing the pH and adsorption rate to remove various pollutants at different concentrations [34, 35].

5.3.1 Fly ash

Fly ash is an unconventional, eco-friendly, low-cost material used as an alternative absorbent for activated carbon. Various research has also suggested that it has also an alternate material to dolomite and limestone used for the pre-treatment process [36]. This waste is used for the treatment of AMD which is successfully removed various heavy metals viz. manganese calcium, iron, aluminum, cadmium, cobalt, zinc, nickel respectively; increases the pH of the solution [26]. The efficiency of fly ash depends on the fly ash characteristics viz. the concentration of CaO and MgO. Initially, the concertation of Ca and Mg increases due to the leaching effect of Ca²⁺ and Mg²⁺ from fly ash surface. But later when gypsum is formed (made of oxygen, sulfur, calcium, and water), concentration Ca and Mg decreases. As the water starts evaporation, it does not protect the sulfur and oxygen-sulfur bonding forms a sulfate (SO_4^{2-}) . The sulfate then bonds with calcium (Ca) and water (H₂O) to create gypsum and the Ca concentration decreases. Formation of gypsum occurs at pH >5.5 and absorbs sulphate with high concentration by Fe $(OH)_2$ at pH > 6. Fly ash not only treats heavy metals but also helps in the removal of radioactive material from mine water. It acts as a sink property for the degradation of heavy metals like uranium and thorium. The free CaO present in fly ash attributes to the sulphate removal rate, precipitates gypsum.

5.3.2 Biomass ashes

The synergistic solution is turning out to be exceptionally attractive for sustainability and circular economy where the waste from one industry becomes an asset for another industry, Biomass ash, which is a result of consuming biomass in a power station, can be considered as an effective material for the treatment of acidic water. This ash is a complex alkaline mixture with poly-component, heterogeneous and different variety of composition. Biomass burning is a significant part of

Sl. No.	Used material	Optimum mixing ratio/dose	Initial pH	Final pH	Reaction time	The percentage removal of metals
1.	Fly ash	1:3	2.78	9.1	1440 mins	Greater than 90% for toxic metals, 78% for sulfate [26]
2.	Coal fly ash	_	4	7.0	12 hrs.	60.4% sulfate, 53.4% chemical oxygen demand and removal of Cd ²⁺ , Cu ²⁺ and Zn ²⁺ were 42.9%, 74.8% and 26.7% [27]
3.	FA followed by seeding with gypsum crystals and the addition of amorphous Al(OH) ₃	1:2	6.6 ± 0.21	12.25		Removal of 79.57% sulfate [28]
4.	Alkaline ash leachates	_	3.3– 5.0	8.0	7 days	Removal of 99.97% of Cu, 99.78% of Zn, 90.2% of Cd, 99.94% of Pb, 62.71% of Ni, and 99.41% of Co [25]
5.	Modified fly ash	120 g/L	1.6	2.8– 6.6	180 min	89%, 92%, 94%, 96%, 60%, and 99% for Ni, Zn, Pb, Fe, Mn, and Al respectively [29]
6.	BOF/SAF slag	30 g/L	2.03	6.32	24 hrs.	Greater than 90% removal of heavy metals and anions [30]
7.	Stainless steel slag	100 gm/L	2.5	5.9	240 mins	Removal of 63.6% iron,39.8% sulfate [31]
8.	Iron slag	30 g/L	2.03	6.68	24 hrs.	Greater than 90% removal of heavy metals and anions [30]
9.	Cement kiln dust slurry	25% of CKD slurry	(2.4 ±0.1)	9.5	1 minute	98% of zinc and 97% of iron [32]
10.	Rice husk	1:10	2.3	4.0	24 hrs.	99% Fe3+, 98% Fe ²⁺ ,98% Zn ²⁺ , 95% Cu ²⁺ [33]
11.	Peat humic agent	1:500	2.7	3.1	1 hr	Removal of 36% Fe, 26% Al, 20% Zn, 35% Cu, 43% Cd, 98% Pb,40% Ni, 21% Co [34]

Table 3.Removal of metals using different waste material.

worldwide eco-friendly power which is developing very rapidly overall. Research suggested that the amount of biomass ashes created around the world is 480 Mtpa which can be compared to the coal ash, i.e., 780 Mtpa. Both coal and biomass ashes are generally alkaline and their pH ranges between 9 and 12. They are different in composition such as coal consist of oxides of silicon, aluminum, and iron and content less mount of calcium oxide also the presence of some heavy metals.

5.3.3 BOF and SAF slags

Basic oxygen furnace (BOF) and submerged arc furnace (SAF) slags have complex physical and chemical characteristics [30]. These materials are composed of oxides of calcium, silicon, phosphorus, sulfur, and manganese produced in steel refining processes. Depending upon the sufficiency of the cleaning cycle, inadequately Fe and entrapped metal droplets during the tapping also incorporate into

BOF/SAF slags. Because of the popularity of steel, which is linked to the increase in population results during the production cycle of steel produces more amount of BOF and SAF slags from the production process. Various studies suggested that every year steel industry produced is about 100–200 kg of slag as by-products. After the production, the slags are partially reprocessed but a major part of the slag is used as a landfill material and holds pond and lagoon due to the less demand in the market. This slag raises the pH of AMD and reduces the chemical elements (pollutants) to the desired amount. However, it partially removes the sulphate and also various metals such as Mn, Ni, Co, Zn, Mg. This slag is an ideal candidate for the treatment of AMD and also minimizes the environmental impact with the disposal process of these slags [37].

5.3.4 Eggshell waste

Now a day's egg production rates are higher in various countries so that the waste shell produces from eggs are increasing rapidly [38]. According to the study, the global egg production rate is approaching 86.8 Mtpa globally per year soon. This material is used as alternative treatment material to treat AMD. The primary constituent of ES is CaCO₃ is an alkaline material that reacts with acidic water to neutralize it by the process of adsorption and precipitation of metals and also used for the complex, binding, and ion exchange material for various metals ions in the wastewater (Equation 9). This eggshell waste is a very cheap and biodegradable material which are collected, characterized, prepared, and evaluated for the degradation of various anions like aluminum, iron, manganese, and anions like sulphate present in AMD. Due to similar properties like limestone, it can be a good neutralizing agent [39].

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$
 (9)

6. Discussion

In the above, various discussions have been made for remediation of AMD wastewater, emphasizing waste materials used for the treatment process. Prevention measures play an essential role in controlling AMD formation, but the plan should be made for proper treatment if it can exceed a dangerous level. It is often not wholly possible, requiring corrective techniques to reduce or remove contamination from water. Active and passive treatment methods are mainly utilized to mitigate AMD and improve the quality of the water. Still, their maintenance cost is high, slow treatment process, and requires a large area for operation. But the waste materials play an essential role in mitigating AMD. Different factors like surface area, pH increasing ability, leachability of the material, retention time, cost factor, and environmental impact must be considered when choosing a waste material. The finding results of these waste materials are described below:

- Fly ash and cement kiln dust rich in lime content have better efficiency in removing heavy metals than any other waste material with different pH values.
- Iron and steel slag have ion exchange and sorption properties to degrade metals from the liquid solution.
- BOF and SOF slag are given the same results to increase the pH value above 8
 of the aqueous solution; as a result, precipitation of metals occurs.

- The surface area and pH of modified fly ash have more than the fly ash. It requires more reaction time and dose for the absorption process.
- Rice husk was found to be a better reagent and can grow the D. nigrificans, also known as sulfate-reducing bacteria.
- The peat humic agent is also used as an alternative to treat wastewater and can modify kaolinite clay to increase the sorption property of the clay, which can absorb the heavy metals within a pH range of 5 to 8.5.
- Eggshell waste can remove the aluminum and iron content at low temperatures but required a high temperature to remove manganese.

7. Conclusions

This chapter concluded that the demand of various waste materials to be tasted due to their characteristics to determine the suitable condition and amount of dose required to remove metals by absorption process from the AMD. This process also generates some new waste streams and some waste materials that cannot completely remove heavy metals from mine wastewater. So further research and innovation are required to address this issue associated with AMD.

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Conflict of interest

The authors declare no conflict of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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