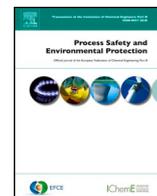




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# Process Safety and Environmental Protection

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## A review of treatment technologies for the mitigation of the toxic environmental effects of acid mine drainage (AMD)



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### ABSTRACT

Acid mine drainage (AMD) is a multi-factor pollution formed from complex chemical, physical, and biological interactions that takes place under ambient conditions in abandoned and active mines. Over the years, researchers have been investigating ways to mitigate its potential impact on the environment through various treatment technologies. The aim of this review was to critically analyze the broad spectrum of treatment methods that have been engaged in published literature on the remediation of AMDs. Adsorption treatment using zeolites, fly ash, biochar activated carbon, clay-based minerals and biomass-based adsorbents was discussed. Given an appropriate choice of adsorbent, ions in AMD can be reduced between 50% and 99%. Membrane separation processes like nanofiltration, reverse osmosis and hybrid systems were discovered to be more effective than adsorption and can effect over 90% rejection at optimized conditions. Biological processes showed a far wider range of performance amongst all treatment types due to the selectivity in performance of the different micro-organisms used although Advanced Oxidation Process (AOPs) have been shown to achieve >80% ions removal. In all biological processes studied ranging from wetlands to bioreactors, algal bioreactors seemed the most effective in this domain. Most of these treatment technologies are corrective while preventive techniques can be explored to prevent the production of AMD. Despite the positive outcomes of the different types of treatment, they have associated technical issues. It is recommended that more preventive techniques be explored to reduce the production of AMD. The review discussed how AMD treatment would affect environmental protection and water resource management.

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**1. Introduction**

The process of mining and milling metallic ores to extract metals have resulted in an imbalance of the environmental ecosystem. Processes such as grinding, blasting and crushing of these ores increase their surface area and expose the wastes to weathering where it readily combines with oxygen and the surrounding water bodies (Jamieson et al., 2015; Jonnsson et al., 2005). From this process, acids and high concentrations of metal(loid)s originates and have caused and is still causing detrimental environmental impacts to water bodies, soils and other living organisms (Ferreira et al., 2021; Havig et al., 2017). These leachates from active and abandoned mines continuously release harmful substances into the environment for decades and millennia (Hakkou et al., 2008; Ighalo and Adeniyi, 2020).

Acid mine drainage (AMD) also known as acid rock drainage (ARD) is a complex multi-factor pollution formed from complex chemical, physical, and biological interactions that takes place under ambient conditions in abandoned and active mines (Arnold et al., 2011; Gao et al., 2019; Viers et al., 2018). It is known to have a very low pH of less than 4, contains high concentrations of sulfate ions and metals such as Iron and Zn dissolved in very high concentrations (España et al., 2007; Gao et al., 2019; Xin et al., 2020). The environmental impacts of AMD can be divided into four categories; chemical (e.g. increase in acidity and metals in the environment), physical (e.g. decrease in light penetration in surrounding water bodies), biological (e.g. behavioral, respiratory, reproduction defects and death of organisms) and ecological (e.g. food chain and habitat modification, loss of food source/prey) impacts (Gray, 1997). A detailed breakdown is given in Fig. 1 adapted from John et al. (2017). One of the chief environmental implications of AMD is its very low pH which aids the growth of certain microbes referred to as

acidophilic microorganisms which are known to catalyze the production of acidic waters (España et al., 2005; Gao et al., 2019). Another issue is the abundance of metal(loid)s contained in AMD. These metal(loid)s easily find their way to surrounding soil and gets them contaminated (Gao et al., 2019). Its toxicological effects inhibit the activities of enzymes and microbes in the soil and in turn causes a reduction in soil biochemical properties and quality (Auld et al., 2013; Ferreira et al., 2021). Due to the interconnectivity of water systems, these potential heavy metals contaminate not just water bodies within the immediate environment of the drainage location but also water bodies far from it (Kefeni et al., 2018; Moreira et al., 2020).

The toxicity of AMD can cause permanent damage to an ecosystem and so the demand for effective remediation strategies for AMD as well as its impacted ecosystem has risen in the past decades (V. Gupta and Sar, 2020; A. Gupta and Sar, 2020). Untreated AMD discharged into the environment are known to have various negative impacts on living organisms (Amanda and Moersidik, 2019). AMD can contaminate groundwater and make it unfit for humans for both agricultural and other purposes. The runoff of AMD can contaminate water bodies, reducing their pH and killing fishes and other aquatic organisms present in nearby water bodies (Kaur et al., 2018). To mitigate this contaminant, researchers have dedicated time and other resources towards preventive and curative treatments of AMDs to seek remediation solutions that are sustainable and cost-effective. Based on the requirements for monitoring, chemical addition, maintenance and infrastructure, the methods utilized in the remediation of AMD can be divided into two; the active systems technique and passive systems technique (Kaur et al., 2018).

Within the last decades, researchers have reviewed the methods and techniques utilized in the treatment of AMD taking different

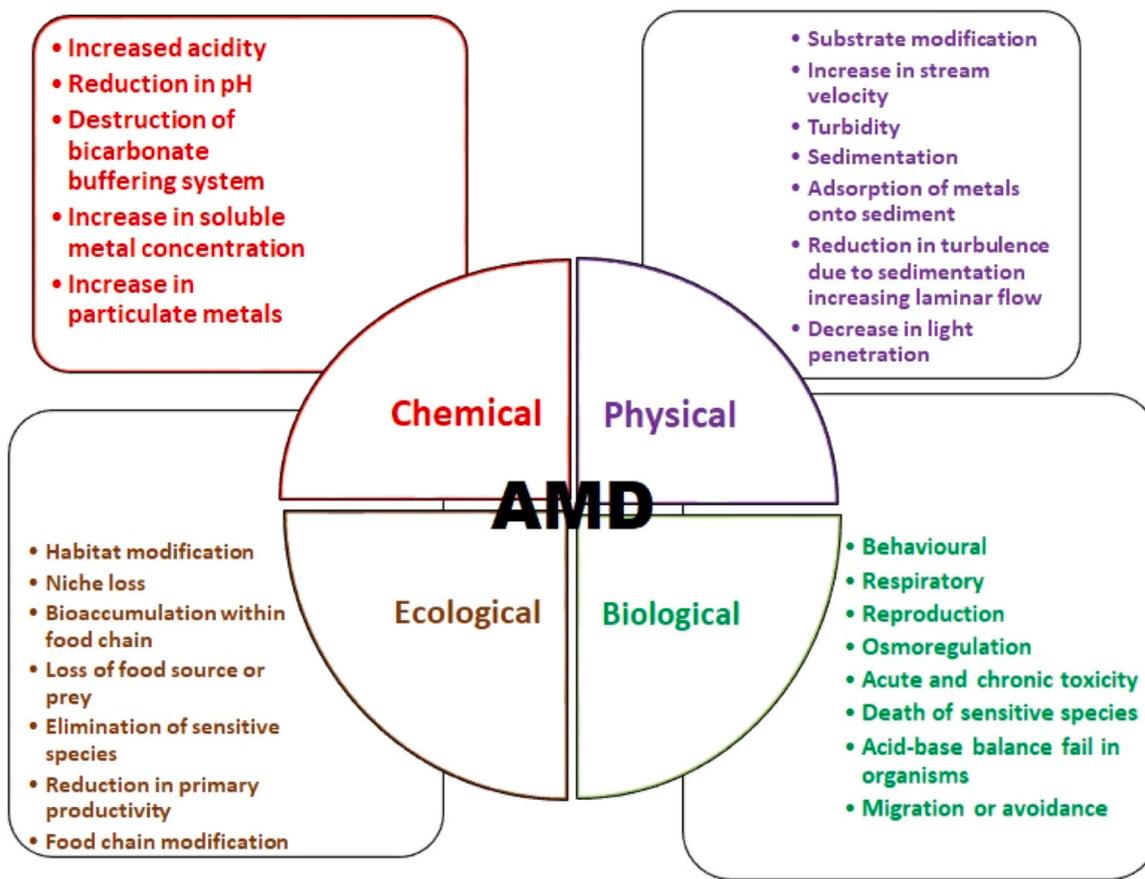


Fig. 1. Environmental effects of AMD.

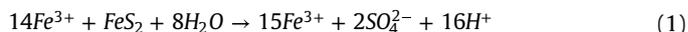
approaches. The first important review that has been carried out in this field was conducted by Gazea et al. (1996). The review was not comprehensive as it was restricted to passive treatment method systems only and was published over two decades ago. Another study by Akcil and Koldas (2006) conducted over a decade ago analyzed only the neutralization process as an effective technique for mitigating AMD. Skousen et al. (2018) reviewed the various methods utilized in the control and treatment of AMDs. Though comprehensive, much work has been done since then. In another study, Wei et al. (2018) reviewed treatment strategies for AMD. This review was centered only on researches carried out in the year 2017 and also did not critically analyze the strengths and shortcomings of each treatment method. Rodríguez-Galán et al. (2019) reviewed remediation techniques for the treatment of AMDs with a focus only on chemical methods of treatment. More recently, Rambabu et al. (2020) reviewed techniques used for treating AMD. The focus was on Biological methods only and so did not cover the entire spectrum of treatment methods.

In lieu of this, the aim of this review is to critically analyze the broad-spectrum treatment methods that have been engaged in published literature on the remediation of AMDs. A review such as this will help researchers understand the progress in research, identify the strengths and weaknesses of each treatment strategy and to document knowledge gaps that could help shape the direction of future researches in this area.

## 2. Formation and composition of AMD

AMD is formed when minerals containing sulfide from coal or metal ores such as pyrite are exposed to air and precipitation or oxygen-rich water which results in sulfide mineral oxidation (Havig

et al., 2017; Xin et al., 2020). The redox reaction that takes place is shown in Eq. 1. This oxidation reaction can be accelerated under optimal conditions by neutrophilic sulpho-oxidans and acidophilic bacteria (Demersa et al., 2015; Kadnikov et al., 2019). Metal ions, sulfate ions, and sulfuric acids are the major products of this oxidation process. The resulting acidic water dissolves alumina-silicates, oxides, and carbonates of various minerals aggressively to birth the high concentrations of metals and other solutes present in AMD (Kim et al., 2002). Apart from the introduction of high concentrations of metal ions into the environment, discharge of AMD also results in the formation of white precipitates composed majorly of sulfate, iron and aluminum ions (Kim et al., 2002). Aluminum and iron ions dominate the cations while sulfate ion dominates the anions present in AMD as seen in Table 1 (Skousen et al., 2018).



With respect to the concentration of constituents in AMD, every mine is unique just as the associated risks are also unique (Akciil and Koldas, 2006), but irrespective of the type of mine, there exist two major factors that affect the composition of AMD. The first factor deals with the characteristics of the source which could involve the composition, abundance, porosity, particle size and distribution, and type of the minerals involved. The second factor is connected to the state of the environment which consists of temperature, rainfall, climate, etc. (Paktunc, 1999). Xin et al. (2020) painted a clear picture of how changes in seasons from spring to summer to winter caused a change in the concentration of the constituents present in AMD. The pathway for the generation and environmental contamination of AMD is shown in Fig. 2 (Naidu et al., 2019) and explained in further detail by Kalin et al. (2006) and Taylor et al. (2005).

**Table 1**  
Composition of AMD in various locations across the world.

Country	South-Africa	South-Africa	Japan	USA	USA	USA	Germany	Romania	Sweden	Spain	South-Africa	China	Portugal	South-Africa
Temp (°C)	3.100	2.400	-	2.810	14.00	11.06	22.47	20.10	23.00	23.00	-	-	14.50	25.00
pH	2135	835.0	2.100	38.20	2.900	4.680	3.125	3.200	3.290	3.290	3.090	3.240	2.530	2.430
Fe (mg/L)	245.0	0.900	583.5	167.0	167.0	20.65	542.9	6.300	2040	2040	1350	106.9	2143	6120
Al (mg/L)	84.00	192.0	45.50	56.00	56.00	68.51	9.082	1.086	-	-	50.00	-	3735	506
Na (mg/L)	498.0	561.0	115.8	-	-	21.26	16.75	21.45	-	-	1000	-	2.850	149.7
Ca (mg/L)	428.0	385.0	34.85	-	-	399.2	294.7	397.0	-	-	-	-	257.0	606.0
SO <sub>4</sub> <sup>2-</sup> (mg/L)	-	-	2809	1439	2200	6719	80.00	57.30	5990	5990	120.0	1323	43.20	648.0
Cu (mg/L)	6.900	0.900	12.55	149.7	-	0.744	0.228	0.003	-	-	3500	13,710	5880	28,980
Zn (mg/L)	-	-	15.35	16.80	-	4.374	84.55	0.068	-	-	-	26.24	17.40	-
PO <sub>4</sub> <sup>3-</sup> (mg/L)	-	-	-	-	-	-	-	0.068	-	-	-	19.66	8.710	-
Mn (mg/L)	30.00	30.00	-	8.300	9.800	210.7	154.3	5.200	-	-	100.0	-	204.0	75.00
Pb (mg/L)	-	-	-	-	-	0.001	45.00	1.450	-	-	-	-	-	155.0
Ni (mg/L)	3.700	1.800	-	-	-	21.63	312.0	69.00	-	-	4.000	-	-	-
Co (mg/L)	1.400	0.800	-	-	-	4.546	163.0	20.00	-	-	2.000	-	-	-
Cd (mg/L)	-	-	-	-	-	0.101	163.8	0.450	-	-	-	-	-	-
NO <sub>3</sub> <sup>-</sup> (mg/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	13,700
Ref.	(Kefeni et al., 2018)	(Kefeni et al., 2018)	(S. et al., 2007)	(Kuehl and Hithel, 2020)	(Hammarstroma et al., 2003)	(Grawunder et al., 2014)	(Grawunder et al., 2014)	(Grawunder et al., 2014)	(Carrero et al., 2015)	(Agboola et al., 2017)	(Wang et al., 2020b)	(Valente and Gomes, 2009)	(Muliwaa et al., 2018)	

AMD is deficient in carbon sources and electron donors (Costa et al., 2009), contains a high concentration of sulfates, dissolved Fe (II), and mineral acids with some amounts of potentially toxic trace elements such as cadmium, arsenic, nickel, cobalt, lead, and copper as seen in Table 1 (Cheng et al., 2011; Silva et al., 2011). The iron present in AMD is majorly present as ferrous iron with a little amount of ferric iron. As the pH is increased above 4, hydrolysis and precipitation convert most of the ferric iron into ferrous iron. On exposure to the atmosphere, oxidation and then hydrolysis occurs converting the ferrous iron formed into ferric iron and iron oxyhydroxide present as a precipitate (Dold, 2014; Kim et al., 2002).

### 3. Ecotoxicology of AMD

AMD has caused pollution in the ecosystem due to the natural availability of sulfide minerals in the earth's crust, which when exposed to oxygen or water oxidize to form poisonous sulfuric acid, metal ions, and sulfate. Many researchers have conducted studies on the ecotoxicology of AMD. Some of these studies reported that AMD is toxic (summarized in Fig. 3). It was observed that when acute lethal toxicity of AMD was applied on *Daphnia magna* and *Daniorerio* embryos (Chamorro et al., 2018), the LC<sub>50</sub> was <1% and <0.08% for *Daphnia magna* and *Daniorerio* embryos respectively. The development of zebra fish embryos is also affected as the yolks are enlarged and pigmentation is absent when exposed to dilutions of AMD. The mobilization and solubility of heavy metals often increase as water becomes acidic. Based on this, further studies were using Cu and Zn solutions (Chamorro et al., 2018). When exposed to Cu and Zn at 48 and 72 hpf, there was no mortality recorded. Exposure to a Cu concentration of 67 mg/l resulted in a two-fold increase in the yolk volume of the embryos and caused embryo deformation. Cu can have a strong influence on *Daphnia magna*, which has been explained as nominal when the concentration is around 0.2 mg/l during acute exposure (Kim et al., 2018; Yim et al., 2006).

According to various works of literature, AMD of various sources is extremely toxic when exposed to daphnids due to the presence of many dissolved metals such as Cu, Cd, and Zn, among others (García-Valero et al., 2020). Cu is one of the most common heavy metals that are harmful to aquatic organisms (Ighalo et al., 2021d). Although it is needed for their growth and reproduction, any small accumulation beyond the required amount can cause irreversible harm to some of these organisms (Tierney et al., 2010). Physico-chemical characteristics of AMD was also considered in water (Olenici et al., 2017). It was observed that there are a large variation of heavy metals and high concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>. Due to the presence of heavy metals, AMD flow into the river contributed to serious environmental impairment (Luo et al., 2020). Large quantities of suspended matter that displayed orange-brownish color is usually observed which can be attributed to the concentration of SO<sub>4</sub><sup>2-</sup>, and Cu in the AMD.

Qualitatively, a study on the number of diatom species was observed (Olenici et al., 2017). It was revealed that there are notable variations among the sampling sites. Some taxa in the Abrud River suggested that there are essential saprobic levels in the river, indicating a high concentration of organic matter with NO<sub>3</sub><sup>-</sup> levels, but only during the summer of 2013. During spring 2014, there was maximum availability of *Achnanthyidium sp.*, pooling normal and abnormal due to low heavy metals and ionic concentrations compared to other sampling points, but no abnormal *A. macrocephalum*. Changes in taxonomic and morphological features of diatom assemblages, there may be an excellent indicator of the presence of heavy metal contamination. Low pH, heavy metals in combination with sulfur, sodium, and calcium are all linked to the structure of the diatom population in AMD-affected areas (Consani et al., 2019).

Considering the effect of AMD at the molecular level, it was revealed that the estimation of two genes activation in fish embryos

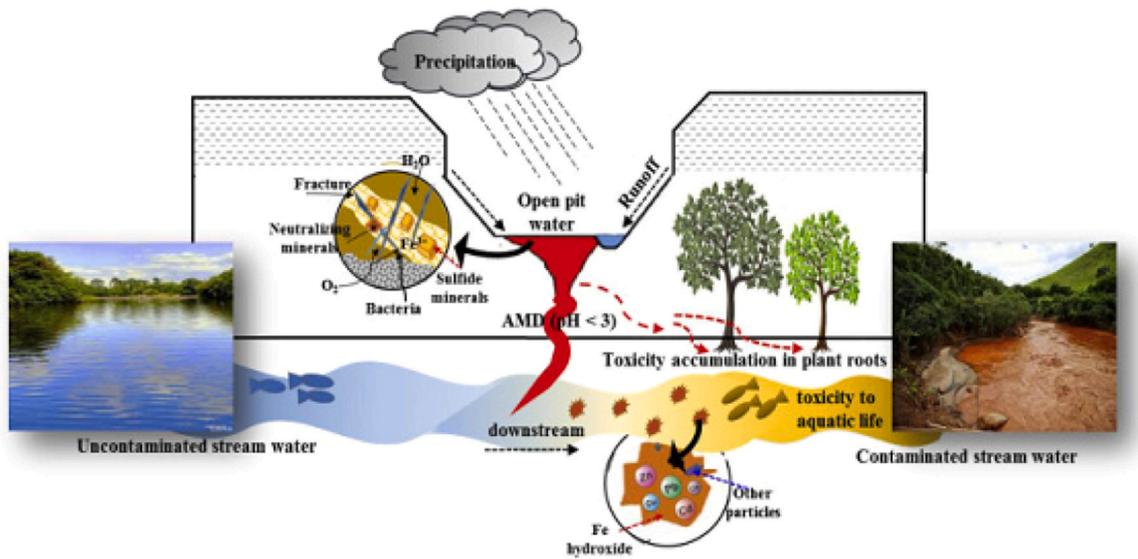


Fig. 2. The pathway for the generation environmental contamination of AMD (Naidu et al., 2019).

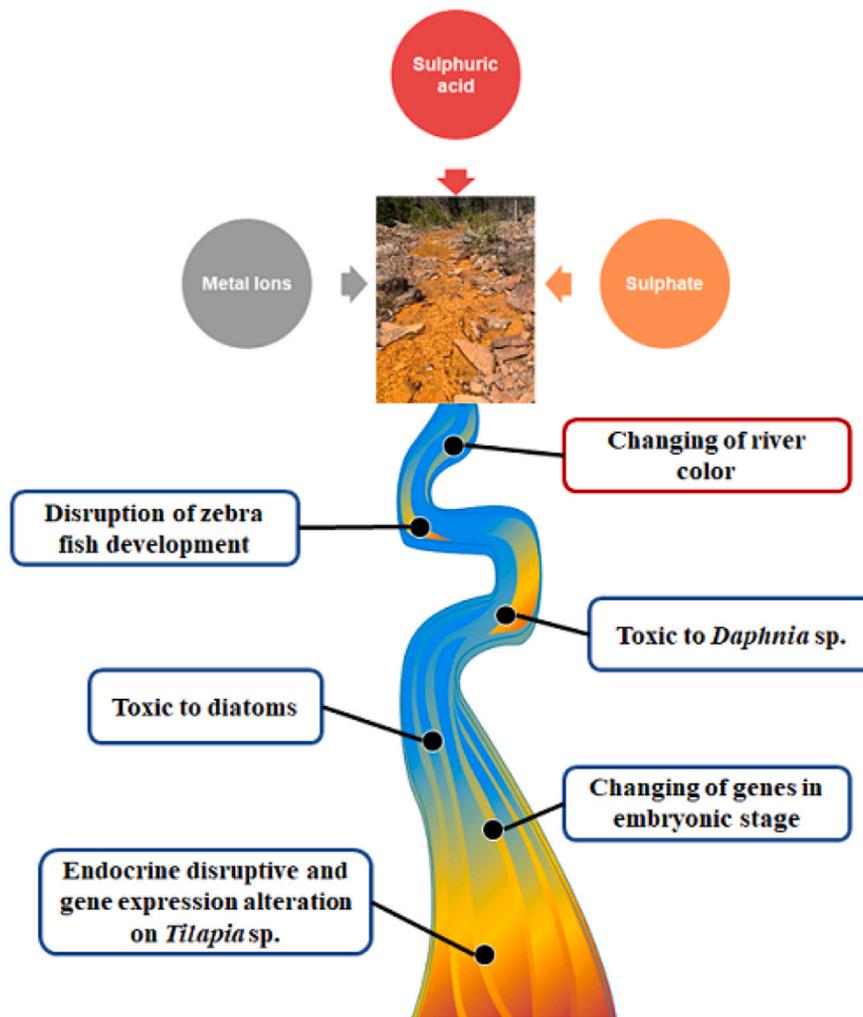


Fig. 3. Summary of environmental effects of AMD.

was examined (Chamorro et al., 2018). The genes were *cyp19a1b* (brain aromatase, responsive to estrogens) and *cyp1a* (the genetic counterpart of the EROD test). From the results, there was no activation of either gene which further established that the toxic effects of AMD were mainly based on metals. Furthermore, there was an examination on the effect of treated AMD with 95% purity using *Tilapia oreochromis* over the expression of thyroid receptor (*tr $\alpha$* ), *tr $\beta$* , androgen receptor (*ar1*), *ar2*, glucocorticoid receptor (*gr1*), *gr2*, mineralocorticoid receptor (*mr*) and aromatase (*cyp19a1b*) upon exposure for 48 h (Truter et al., 2014). There was an alterations pronunciation in the expression of the gene (*tr $\alpha$* , *tr $\beta$* , *gr1*, *gr2*, *ar1*, and *mr*) which were identified with the high concentration of some certain metals which is evidence to cause activity of endocrine disruption and also indicated that heavy metals are the main toxic agents. From these, it can be surmised that AMD has significant ecotoxicology on the environment (Fig. 3) and remediation strategies need to be implemented for efficient AMD removal.

#### 4. Separation processes for AMD treatment

##### 4.1. Adsorption treatment

Several techniques for AMD treatment have been discussed in this article, it should be noted that the applicability and suitability of a given treatment approach is a function of the nature (the major constituent) of the AMD and their initial concentration, as well as the cost and environmental impact of the operation (Igberase et al., 2018; Motsi et al., 2009). The adsorption technique which involves the transfer of solutes particles from the aqueous phase onto the adsorbents solid surfaces (active sites) is both a promising and preferred technique for AMD treatment (Hashem et al., 2021a, 2021b). Its preference is related to its environmental, operational and economic efficiency (Aniagor et al., 2021; Ighalo et al., 2020e). Its near zero-waste drive achievable through adsorbent reuse is a desirable feature (Dlamini et al., 2019a). In the present review, heavy metal pollutants were majorly targeted by adsorptive treatment, as the majority of the other AMD pollutants (such as sulfate, phosphate ions, etc.) are readily remediated through biological treatment approaches. The application of different synthetic and natural adsorbents was summarized in Table 2. For a holistic and concise analysis, the adsorbents were generally classified, (based on their primary constituent) as organic, clay/earth-based material, activated carbon/biochar, zeolites, fly ash and others (Ighalo et al., 2020d, 2021b). Furthermore, the link between each adsorbent type and their metal sorption ability (in the light of the present review) will be elucidated in the subsequent subsections.

##### 4.1.1. Organic/biomass-based adsorbents

Organic-based adsorbents are mostly derived from abundant natural precursors. Despite the acidic nature of the AMD, which Feng et al. (2004) believe may degrade the organic adsorbents, several studies successfully applied them for AMD metal ion uptake at batch and column mode. During the batch adsorption processes, high adsorptive capacities were recorded by these adsorbents. According to Chockalingam and Subramanian (2009), the metal-binding surface functional groups (such as carboxyl, phenolic acid, amino, hydroxyl groups, etc.) on these adsorbents were generally responsible for reported high metal ion uptake. The adsorbents' inherent intrinsic porosity which is useful for pollutant entrapment is considered as a strong contributing factor to the high sorption capacity (Masukume et al., 2014). Besides from the presence of relevant metal-binding functional groups and surface porosity, the metallic ion sorption capacity of these adsorbents was also a function of the initial pH and adsorbent mass. In a single solute system, an increase in the respective adsorbent masses significantly improved the metal ion % removal and also lowered the acidity of the AMD (Zhang, 2011). The

optimal adsorbent loading must be carefully chosen to minimize or avoid the precipitation of the target metal. The adsorptive uptake of metal ions was reported to occur mainly by ion exchange and chemical interaction mechanism, hence, the dependence of the adsorbent-adsorbate affinity on the hydrated ionic radius and electronegativity of the respective metal ions (Masukume et al., 2014; Zhang, 2011). The higher the electronegativity and the lower the hydrated radius of a given metal ion, the better their affinity to an electrostatically compatible adsorbent. Meanwhile, in the presence of varied ions, the ionic competitive effect was only significant at high initial concentrations. For instance, at 0.04 mmol/L initial  $\text{Cu}^{2+}$  concentration, Zhang (2011) reported an adsorption capacity of 0.002 mmol/g for  $\text{Cu}^{2+}$  in both the single and multi-solute systems. Upon an increase in the initial concentration up to 4.75 mmol/L, adsorption capacities of 0.245 mmol/g (for  $\text{Cu}^{2+}$  single system), 0.205 mmol/g (for  $\text{Cu}^{2+}/\text{Zn}^{2+}$  system), 0.157 mmol/g (for  $\text{Cu}^{2+}/\text{Pb}^{2+}$  system) and 0.139 mmol/g (for the  $\text{Cu}^{2+}/\text{Pb}^{2+}/\text{Zn}^{2+}$  system) were recorded. For the column adsorption, the number of available active sites, as well as the breakthrough time and capacity are strongly dependent on the adsorbent bed height and the initial concentration of adsorbate. Masukume et al. (2014) noted that the initial concentration sustains the most significant effect on the metal ion uptake from AMD. Higher adsorbent bed height implies the availability of more active sites (due to increased mass transfer zone), extended breakthrough time and improved breakthrough capacity. Similarly, high initial concentration shortens the breakthrough time and facilitates the exit of the mass transfer zone, thus lowering the breakthrough capacity (Bhaumik et al., 2013). The reusability studies of rice husk (Chockalingam and Subramanian, 2006) and diary compost manure (Zhang, 2011) were reported. It was observed that both studies used dilute HCl for the elution of the metal ion and a high desorption efficiency (>94.0%) was sustained over a two to three adsorption-desorption cycle. The thermodynamics consideration elucidated the feasibility, exothermicity and spontaneity of the metal ion uptake (Chockalingam and Subramanian, 2006).

##### 4.1.2. Clay/earth-based minerals

The successful application of clay/earth-based adsorbents is predicated on their demonstrable high specific surface area, structural stability, excellent cation exchange and water absorption capacity (CEC) (Masindi et al., 2015). Furthermore, the high adsorption capacity of clay material (Table 2) is believed to be due to their Brønsted and Lewis acidity (Bhattacharyya and Gupta, 2006). Generally, the metal uptake performance of this adsorbent type was studied under the influence of varying initial contaminant concentrations and solution pH. Findings showed that the optimal metal ion uptake was attained at low initial contaminant concentration, mostly due to the availability of more unsaturated active sites, which gets depleted at higher initial concentrations (Masindi et al., 2015). Similarly, the pH of the treated AMD often increases when compared to that of the untreated stream due to the likely dissolution of trace amounts of the alkaline clay minerals (such as calcite and silicates). Hence, ion exchange remains the predominant adsorption mechanism as opposed to precipitation (Iakovleva et al., 2015), although there exist isolated cases where metal precipitation and co-precipitation towards hydro complex/oxyhydroxides formation is the chief mechanism. Both physisorption and chemisorption interaction was reported in the studies, with the chemisorption occurring via monodentate or multidentate linkage with the surface -OH groups (Feng et al., 2019). In the presence of competing ions, Fe and Cu ions with one of the lowest  $\text{pK}_h$  and  $\text{K}_{sp}$  values depict the strongest affinity for the attapulgite clay mineral and their uptake is rarely subject to ionic competing effects even at higher initial concentrations (Falayi and Ntuli, 2014). The ionic radius of the metal ions also influenced their preferential uptake, at both batch and fixed-bed column studies, as those with smaller radii tends to adsorb

**Table 2**  
Summary of studies on AMD adsorption focusing on various pollutant species.

Adsorbent	Adsorbate	Adsorption capacity	RE (%)	Adsorption mode	Initial pH	Ref.
<b>Organic-based</b>						
Saw dust	Cu <sup>2+</sup>	29.93 × 10 <sup>3</sup> mmol/g	80.00	Batch	5.01	(Stanković et al., 2009)
	Fe <sup>3+</sup>	6.26 × 10 <sup>3</sup> mmol/g	10.00			
	Mn <sup>2+</sup>	18.20 × 10 <sup>3</sup> mmol/g	–			
	Zn <sup>2+</sup>	21.80 × 10 <sup>3</sup> mmol/g	–			
Compost manure	Cu <sup>2+</sup>	0.428 mmol/g	77.15	Batch	4.0	(Zhang, 2011)
	Zn <sup>2+</sup>	0.237 mmol/g	47.53			
	Pb <sup>2+</sup>	0.460 mmol/g	93.13			
Shrimp shell	Fe <sup>3+</sup>	–	≈96.00	Batch	3.04	(Núñez-Gómez et al., 2020)
	Mn <sup>2+</sup>	–	≈78.00			
Mussel byssus	Fe <sup>3+</sup>	–	≈96.00	Batch	3.04	(Núñez-Gómez et al., 2020)
Sea shells	Mn <sup>2+</sup>	–	≈78.00	Batch	5.5–7.3	(Masukume et al., 2014)
	Al <sup>3+</sup>	–	≈100.0			
Rice husk	Fe <sup>2+</sup> /Fe <sup>3+</sup>	–	≈100.0	Batch	4.0	(Chockalingam and Subramanian, 2006)
	Fe <sup>3+</sup>	–	≈99.0			
	Fe <sup>2+</sup>	–	≈98.0			
	Zn <sup>2+</sup>	–	≈98.0			
<i>Eucalyptus tereticornis</i> bark	Cu <sup>2+</sup>	–	≈95.0	Batch	3.2	(Chockalingam and Subramanian, 2009)
	Fe <sup>3+</sup>	–	≈96.0			
	Zn <sup>2+</sup>	–	≈75.0			
	Cu <sup>2+</sup>	–	≈92.0			
SO <sub>4</sub> <sup>2-</sup>	–	≈41.0				
<b>Clay/earth-based material</b>						
Bentonite	SO <sub>4</sub> <sup>2-</sup>	221.8 mg/g	>50.00	Batch	3.0	(Masindi et al., 2015)
	Mn <sup>2+</sup>	30.70 mg/g	–			
	Al <sup>3+</sup>	30.50 mg/g	–			
	Fe <sup>2+</sup> /Fe <sup>3+</sup>	30.20 mg/g	–			
Modified diatomaceous earth particles	Fe <sup>2+</sup> /Fe <sup>3+</sup>	–	97.20	Batch	5.0	(Larsson et al., 2018)
	Cu <sup>2+</sup>	–	99.00			
	Pb <sup>2+</sup>	–	38.00			
	Zn <sup>2+</sup>	–	38.00			
	Al <sup>3+</sup>	–	51.00			
Modified limestone	Cd <sup>2+</sup>	–	56.00	Batch	6.0–7.0	(Iakovleva et al., 2015)
	Cu <sup>2+</sup>	–	98.32			
	Fe <sup>3+</sup>	–	≈ 100.0			
	Ni <sup>2+</sup>	–	92.76			
Hydrotalcite	Zn <sup>2+</sup>	–	94.65	Batch	4.0	(Goldani et al., 2012)
	Fe <sup>2+</sup>	≈90.0 mg/g	63.7			
	Mn <sup>2+</sup>	≈90.0 mg/g	666.7			
Fe <sub>3</sub> O <sub>4</sub> -chitosan@bentonite	Cu <sup>3+</sup>	62.10 mg/g	–	Batch	5.0	(Feng et al., 2019)
Bentonite	Cu <sup>2+</sup>	–	99.90	Batch	4.6	(Esmaeili et al., 2019)
	Zn <sup>2+</sup>	–	89.20			
	Ni <sup>2+</sup>	–	99.90			
	Co <sup>2+</sup>	–	100.0			
	Fe <sup>2+</sup>	–	100.0			
Attapulgit	Co <sup>2+</sup>	–	93.00	Batch	2.84	(Falayi and Ntuli, 2014)
	Ni <sup>2+</sup>	–	95.00			
	Mn <sup>2+</sup>	–	66.00			
	SO <sub>4</sub> <sup>2-</sup>	123.86 mg/g	61.38			
	Fe <sup>2+</sup>	–	100.0			
<b>Malan loess</b>						
<b>Activated carbon/biochar</b>						
Bone Char	Mn <sup>2+</sup>	22.00 mg/g	–	Batch	5.7	(Sicupira et al., 2014)
Polypyrrole-tailored AC	SO <sub>4</sub> <sup>2-</sup>	48.00 mg/g	–	Batch	NS	(Hong et al., 2014)
Polypyrrole-modified AC	SO <sub>4</sub> <sup>2-</sup>	44.70 mg/g	–	Batch	NS	(Hong et al., 2017)
<b>Zeolites</b>						
Natural Zeolite	Fe <sup>3+</sup>	–	99.11	Batch	2.8	(Varvara et al., 2013)
	Zn <sup>2+</sup>	–	71.94			
	Mn <sup>2+</sup>	–	45.00			
Synthetic Zeolite	Cu <sup>2+</sup>	30.03 mg/g	98.16	Batch	3.0	(Wulandari et al., 2020)
Natural Zeolite	Cu <sup>2+</sup>	23.80 mg/g	93.98	Batch	3.0	(Wulandari et al., 2020)
Natural zeolite	Fe <sup>3+</sup>	6.40 mg/g	59.90	Batch	2.5–3.5	(Motsi et al., 2009)
	Cu <sup>2+</sup>	0.54 mg/g	56.80			
	Mn <sup>2+</sup>	0.52 mg/g	18.90			
	Zn <sup>2+</sup>	2.21 mg/g	67.80			
	As <sup>3+</sup>	0.175 mg/g	–			
Iron oxide modified zeolite	As <sup>3+</sup>	0.175 mg/g	–	Batch	3.0–8.0	(Nekhunguni et al., 2017)
	Zn <sup>2+</sup>	94.50 mg/g	–	Batch	3.0	(Hidayat et al., 2021)
Modified fly ash	Cu <sup>2+</sup>	91.90 mg/g	–	Batch	5.0	(Ileri and Sanliyüksel Yucel, 2020)
	Fe <sup>3+</sup>	–	99.00			
	Al <sup>3+</sup>	–	99.00			
	Zn <sup>2+</sup>	–	97.00			
	Co <sup>2+</sup>	–	95.00			
	Ni <sup>2+</sup>	–	94.00			
	Cu <sup>2+</sup>	–	92.00			
	Mn <sup>2+</sup>	–	92.00			

(continued on next page)

Table 2 (continued)

Adsorbent	Adsorbate	Adsorption capacity	RE (%)	Adsorption mode	Initial pH	Ref.
Modified fly ash	Al <sup>3+</sup>	–	99.00	Batch	2.8	(Sahoo et al., 2013)
	Fe <sup>3+</sup>	–	96.00			
	Pb <sup>2+</sup>	–	94.00			
	Ni <sup>2+</sup>	–	89.00			
	Zn <sup>2+</sup>	–	92.00			
	Mn <sup>2+</sup>	–	60.00			
Fly ash	Mg <sup>2+</sup>	–	≈100.0	Batch	10.5–11.0	(Gitari et al., 2006)
	Cu <sup>2+</sup>	–	≈100.0		6.0	
	Pb <sup>2+</sup>	–	≈100.0		6–7	
<b>Others</b>						
Fe <sup>3+</sup> modified calcium silicate	Cu <sup>2+</sup>	13.51 mg/g	99.94	Batch	2.0	(Barrera et al., 2017)
	Zn <sup>2+</sup>	7.47 mg/g	99.99			
	Cd <sup>2+</sup>	3.41 mg/g	99.98			
	As <sup>3+</sup>	6.01 mg/g	99.96			
	PO <sub>4</sub> <sup>3-</sup>	38.75 mg/g	99.65			
Polymeric ion exchange resin/Fe-O ion-exchange/HZrO <sub>2</sub> nanocomposite	Al <sup>3+</sup>	–	61.93	Batch	6.81	(Dlamini et al., 2019b)
	Al <sup>3+</sup>	–	99.67	Batch	1.8	(Dlamini et al., 2019a)
	Fe <sup>2+</sup>	–	98.99			
	Mn <sup>2+</sup>	–	97.48			
maghemite nanoparticles	Hg <sup>2+</sup>	–	75.00	Batch	3.0	(Etale et al., 2014)
Silica nanoparticles	Hg <sup>2+</sup>	–	56.00	Batch	3.0	(Etale et al., 2014)
Iron slags	Cu <sup>2+</sup>	88.50 mg/g	–	Batch	5.5	(Feng et al., 2004)
	Pb <sup>2+</sup>	95.24 mg/g	–			
Steel slags	Cu <sup>2+</sup>	16.21 mg/g	–	Batch	5.5	(Feng et al., 2004)
	Pb <sup>2+</sup>	32.26 mg/g	–			
Ferrihydrite	Pb <sup>2+</sup>	–	>90.00	Batch	8.0	(Karapinar, 2016)
	Cu <sup>2+</sup>	–				
	Zn <sup>2+</sup>	–				
Double-oxidize MWCNTs	Cu <sup>2+</sup>	14.00 mg/g	79.00	Batch	5.5	(Rodriguez and Leiva, 2019)
	Mn <sup>2+</sup>	6.60 mg/g	78.00			
	Zn <sup>2+</sup>	4.00 mg/g	48.00			
Cobalt-methylimidazolate framework	Pb <sup>2+</sup>	105.0 mg/g	–	Batch	9.0	(Nqombolo et al., 2019)
Non-viable activated sludge	Zn <sup>2+</sup>	3.4 mg/g	–	Batch	3.8	(Utgarikar et al., 2000)
	Cu <sup>2+</sup>	5.9 mg/g	–			

faster (Esmaeili et al., 2019; Larsson et al., 2018). Due to the observed chemisorption, the metal ion adsorption capacity of most clay minerals decreased over an extended adsorption-desorption cycle. Feng et al. (2019) reported a 3% reduction in the adsorption capacity of magnetic bentonite (Fe<sub>3</sub>O<sub>4</sub>-CS@BT) after five cycles using 0.01 M NaOH eluent. In contrast with the exothermic adsorption reported for organic-based adsorbents, the metal uptake process by clay/earth-based minerals was endothermic (Falayi and Ntuli, 2014; Zheng et al., 2019).

#### 4.1.3. Biochar/activated carbon-based adsorbents

The effectiveness and versatility of activated carbon and biochar in metal ion adsorption application due to their large surface area and pore volume have been highlighted (Hashem et al., 2021b). Sicupira et al. (2014) applied bone char for the adsorptive uptake of Mn<sup>2+</sup> from AMD and the experimental finding shows the dependence of uptake capacity on the solid/liquid ratio, initial solution pH and adsorbents particle sizes. The Mn<sup>2+</sup> uptake efficiency was found to increase with the increase in the solid/liquid ratio, although with an extended adsorption duration. Meanwhile, the Mn<sup>2+</sup> uptake efficiency was negatively impacted in the presence of other ionic species, even at a high solid/liquid ratio, when compared to a single solute system. This finding called for efficient modulation of the initial solution pH for achieving optimal metal uptake. Asides from its effect on the Mn<sup>2+</sup> loading kinetics, the adsorbent particle size variation generally had negligible effects on the metal uptake efficiency, even at extended adsorption duration (Sicupira et al., 2014). Based on reports, the application of smaller particle-sized adsorbents results in a shorter equilibration time for both single and multiple ionic conditions. Similarly, Hong et al., (2014, 2017) used polypyrrole modified activated carbon of positively charged functionality in sulfate adsorption from AMD. The study reported the sulfate uptake dependence on the activated carbon precursor.

Accordingly, hardwood based activated carbon offered better adsorptive functionality than bituminous, oak wood and pristine activated carbon. The significant effect of the nature of the solvent used during the synthesis of the polypyrrole modified activated carbon was highlighted. Among the three solvents tested (methanol, ethanol and DI water), DI water prepared activated carbon (with the largest nitrogen content) recorded the most adsorptive uptake. This high adsorptive performance is linked to the varying conjugation chains on the polypyrrole structure (Hong et al., 2017). The breakthrough behavior of the sulfate ion was studied via a rapid small scale column test. The nature of the synthesis solvent reportedly had a significant effect on the breakthrough point, due to physical and chemical characteristic variations (Hong et al., 2014).

#### 4.1.4. Zeolites

Zeolites are mainly tetrahedral aluminosilicates (SiO<sub>4</sub> and AlO<sub>4</sub>) assemblage of three-dimensional structure. Their high metal ion adsorptive capacity is due to their net surface negative charge due to the isomorphous cationic substitution within their structural lattice (Varvara et al., 2013). In addition to their ease of functionalization, zeolites possess combined ion exchange and molecular sieve properties, hence their strong affinity for heavy metal ions (Varvara et al., 2013). The efficient adsorptive application of zeolite was subject to variations in experimental conditions. It was generally noted that the increase in adsorption duration and zeolite dosage significantly favored the heavy metal uptake (Nekhunguni et al., 2017). The significance of initial pH variation was mostly negligible because of the predominance of surface complexation mechanism (which is pH-independent) during metal uptake (Nekhunguni et al., 2017). In the presence of other oxyanions anion (SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup>), Nekhunguni et al. (2017) reported an insignificant interference in the adsorption of As<sup>3+</sup>. Meanwhile, aside from the Fe<sup>3+</sup>, whose main uptake mechanism was precipitation, the selective adsorption of

other studied heavy metals ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) was significantly hampered in the multicomponent adsorption system (Motsi et al., 2009). The observed variation in metal sorption selectivity was a function of the radius of ionic hydration, hydration enthalpy, and cation solubility (Hidayat et al., 2021). The reusability assessment of zeolite-based adsorbent using varying NaCl concentrations (3 M and 0.34 M), 10%  $\text{HNO}_3$ , and 2%  $\text{H}_2\text{SO}_4$  proved unsuccessful. A reasonable degree of desorption of  $\text{As}^{3+}$  from zeolite was achieved using 0.1 M  $\text{HNO}_3$  as the eluent (Nekhunguni et al., 2017).

#### 4.1.5. Fly ash

The oxide forms of Si, Al, Ca, and Fe present in fly ash is responsible for their high metal ion sorption capacity. Their negative surface charge which predominates as it (fly ash) is in contact with water explains their strong affinity for cations (Ileri and Sanliyuksel Yucel, 2020). Considering its huge volume of generation from thermal power stations, fly ash constitutes serious environmental problems that are extensively upon successful application as a low-cost and easily available adsorbent (Ileri and Sanliyuksel Yucel, 2020). Generally, the adsorptive performance of fly ash was positively impacted at increased adsorbent dosage, extended contact time and acidic pH (Gitari et al., 2006; Sahoo et al., 2013). As earlier observed with the zeolite adsorbents, Fe and Al uptake were not affected in the multicomponent adsorption system, since precipitation accounts for their main uptake mechanism. The fly ash reusability study showed that cation desorption from the fly ash was favorable in acidic media (Ileri and Sanliyuksel Yucel, 2020).

#### 4.1.6. Other adsorbents

Nanomaterials and ferric based adsorbents fall within this group. The successful application of nanomaterials in metal uptake is due to their higher reactivities and large surface area to volume ratios (Balarak et al., 2021; Eletta et al., 2019). Their negative surface charge is apt for efficient cation adsorption (Iwuozor et al., 2021). Etale et al. (2014) adsorbed mercury unto silica and maghemite nanoparticles. The study reported a successful mercury uptake even in the presence of equimolar sulfate and manganese ions. Similarly, the application of ion-exchange/hydrated  $\text{ZrO}_2$  nanoparticles in the uptake of several heavy metal ions from AMD was reported as successful (Dlamini et al., 2019b). The hydrated nanoparticle was efficiently regenerated with a binary solution of NaCl–NaOH at pH > 12. Ferrihydrite, an acid mine formation product was successfully adopted for the sequestration of heavy metal from AMD. The author reported above 90% removal efficiencies for all the target cations (Karapinar, 2016).

#### 4.1.7. Technical issues associated with adsorption

Though adsorption is considered a very important process in the treatment of AMD, there are some issues associated with its use. AMD can have a high pollutant load making it difficult to treat large volumes of the water before the adsorption capacity gets used up. It would be observed that adsorption studies utilized the removal of the ionic species as their indices which is in itself quite simplistic. Considerations of total dissolved solids, turbidity or chemical oxygen will paint a truer picture of this limitation. Hence, for practical purposes, we do not believe that the advantage of low cost and ease of technical application of adsorptive systems can offset the drawbacks presented by its inability to handle water with a high pollutant load.

### 4.2. Membrane separation processes

The performance of a membrane in physical separation is defined in terms of two simple factors, flux and selectivity. Flux, also known as permeation rate, refers to the flowrate of liquid passing through the membrane per unit area of membrane per unit time. Selectivity,

on the other hand, is the fraction of solute in the feed retained by the membrane. This section reviews the performance of membrane processes for AMD treatment using standalone membranes—nanofiltration (NF), reverse osmosis (RO) and hybrids (FO+NF, mixed matrix membranes).

#### 4.2.1. Nanofiltration (NF)

Nanofiltration entails a pressure-driven technique that combines unique separation capabilities with lower operating pressures when compared to traditional membrane processes such as reverse osmosis (RO). Some typical features of NF membranes include low rejection of monovalent ions, high rejection of divalent ions and tiny organic molecules (up to 2 nm) and higher flux compared to RO membranes (Junker et al., 2021; Mohammad et al., 2015). Studies by Al-Zoubi et al. (2010a) using NF membranes resulted in the total removal of metals and sulfates. This could be attributed to the steric hindrance mechanism characteristic of NF membranes; thus, aids size exclusion as large sizes of cations and metals are effectively rejected by the small pores of the membranes. In another development, high removal of metals and sulfates (>85%) was obtained by NF membrane (Aguilar et al., 2015, 2016; Al-Zoubi et al., 2010b; Ambiado et al., 2017; Lopez et al., 2018; Sierra et al., 2013; Siew et al., 2020; Wadekar and Vidic, 2018) and this could be attributed to concentration polarization wherein there exists a concentration gradient of ions found across the membrane in the permeate and retentate. Thus, divalent ions and heavy metals are preferentially rejected over monovalent ions since they have lower diffusion coefficients, higher Stokes' radii and larger sizes which would be excluded by the membrane (Wadekar and Vidic, 2018).

#### 4.2.2. Reverse osmosis (RO)

The attractiveness of RO membranes for AMD treatment stems from the fact that it offers advantages such as selectivity, operating cost and modest energy savings when compared with other types of membranes (Ambiado et al., 2017; Bodalo-Santoyo et al., 2003). Research findings showed that the use of RO membranes resulted in a high rejection of divalent metal species and sulfates corresponding to >92% (Aguilar et al., 2015, 2016; Al-Zoubi et al., 2010b; Ambiado et al., 2017). This could be associated with high electrical conductivity and diffusion which varies with relative amounts of water and ion fluxes across the membrane, thus, increases as pressure build up in the system (Al-Zoubi et al., 2010b; Ricci et al., 2015). From Table 3, it was observed that lower permeate fluxes were obtained using RO membranes (50 L/h.m<sup>2</sup>; 39 L/h.m<sup>2</sup>; 10.2 L/h.m<sup>2</sup>; 10.2 L/h.m<sup>2</sup>) when compared to NF membranes (220 L/h.m<sup>2</sup>; 67 L/h.m<sup>2</sup>; 88.6 L/h.m<sup>2</sup>; 88 L/h.m<sup>2</sup>) respectively. This could be attributed to the structure of the membranes as their densely polymeric nature increases membrane resistance and significantly decreases permeate flux (Aguilar et al., 2015, 2016). As a remedy, it has been suggested that surface modification by plasma polymerization (Zou et al., 2011) and functionalization using protic acids (Kulkarni et al., 1996) increases the hydrophilic properties and enhances permeate flux by as much as a factor of two in RO membranes.

#### 4.2.3. Hybrid systems

Hybrids such as mixed matrix membrane (MMM) (Daramola et al., 2015) and volume retarded osmosis–low pressure membrane (VRO-LPM) (Choi et al., 2019) have been applied in AMD treatment due to the balance between microporosity and compatibility which they offer in separations technology (van Essen et al., 2021). Furthermore, it has been identified that specific advantages such as high ductility, malleability and very fine thickness (<10 μm) are derived from these types of membranes (Davey et al., 2016). The findings of Choi et al. (2019) showed that the utilization of chelating agents as draw solutions created a difference in rejection efficiencies for seven



Table 3 (continued)

Type of membrane	AMD contaminant ions/ molecules	Influent mode	Operating conditions	Permeate flux (L/h.m <sup>2</sup> )	Membrane rejection (%)	Ref.
FO + NF	Mn	Dead-end	Pressure = 7.5 bar; feed flow rate = 250 mL/min	0.4	100%	(Choi et al., 2019)
	As				100%	
	Cd				100%	
	Pb				100%	
	Fe				>80%	
	Cu				>80%	
NF	Zn	Cross flow	Pressure = 10 bar; temperature = 25 °C; feed flowrate = 4.0 L/min	Not determined	>80%	(Siew et al., 2020)
	Mg <sup>2+</sup>				>97%	
	Cu				>97%	
	Mn				>97%	
Mixed matrix membranes	SO <sub>4</sub> <sup>2-</sup>	Cross flow	Temperature = 25 °C; pressure = 1.1 bar;	Not determined	>84%	(Daramola et al., 2015)
	Pb <sup>2+</sup>				57.44%	
	Mg <sup>2+</sup>				50%	
	Cu <sup>2+</sup>				17.6%	
	Mn <sup>2+</sup>				6%	
	Al <sup>3+</sup>				Not specified	
FO	Al	Not specified	Temperature = 25 °C	12	99.8%	(Vital et al., 2018)
	Si				97.1%	
	Ca				99.3%	
	Mn				99.6%	
	Fe				100%	
	Co				99.4%	
	Cu				98.9%	
	Zn				99.5%	
	Mg				98.9%	
	Al				99%	
	As				99%	
NF	Fe	Not specified	Pressure = 20 bar; feed flowrate = 1000 L/h	23.67	99%	(Sierra et al., 2013)
	SO <sub>4</sub> <sup>2-</sup>				97%	
	Cu				97%	
MD	Cu	Cross flow	Flow rate = 1.0 L/min; temperature = 55 °C	14.5	232.9 mg/L	(Ryu et al., 2020)
	Al					
NF	Zn	Not specified	Temperature = 24 °C;	9.05	100%	(Pino et al., 2018)
	Cu				97%	
	SO <sub>4</sub> <sup>2-</sup>				95%	
	As(V)				98%	
PIM	As(V)	Not specified	Temperature = 25 °C;	Not determined	95.8%	(Zawierucha et al., 2020)
NF	Mg <sup>2+</sup>	Not specified	Pressure = 4 bar; temperature = 25 °C	2.3	67.4%	(Ntshangase et al., 2021)
	Mn <sup>2+</sup>				70%	
	Na <sup>2+</sup>				51.5%	
	Al <sup>3+</sup>				71.1%	
	Fe <sup>3+</sup>				74.2%	
	Ca <sup>2+</sup>				73.6%	
MF	Fe	Cross flow	Pressure = 1.2 bar; temperature = 25 °C; feed flowrate = 82 L/h	590	>99.9%	(Meschke et al., 2015)
		Dead-end	Pressure = 1.9 bar; temperature = 25 °C; flow rate = 7.3 L/h	220		
NF	Na	Cross flow	Feed flow rate = 5.68 L/min; pressure = 35 bar; temperature = 25 °C	Not determined	80%	(Wadekar and Vidic, 2018)
	K				>80%	
	Cl				44%	
	SO <sub>4</sub> <sup>2-</sup>				>97%	
	Ba				>97%	
	Ca				>97%	
	Mg				>97%	
	Mn				>97%	
	Ni				>97%	
	Sr				>97%	
	Se				96.1%	
	Al				>80%	
	As				33%	
MF	Fe <sup>2+</sup>	Cross flow	Pressure = 1 bar; temperature = 26 °C	93	88.3%	(Machodi and Daramola, 2019)
	Mn <sup>2+</sup>				90.4%	
	Mg <sup>2+</sup>				89.3%	
	Ca <sup>2+</sup>				75.7%	
	SO <sub>4</sub> <sup>2-</sup>				56.33%	

(continued on next page)

Table 3 (continued)

Type of membrane	AMD contaminant ions/ molecules	Influent mode	Operating conditions	Permeate flux (L/h.m <sup>2</sup> )	Membrane rejection (%)	Ref.
NF	Zn Cu Al Fe Ca La Pr Nd Sm Dy Yb Cl <sup>-</sup> SO <sub>4</sub> <sup>2-</sup>	Cross flow	Temperature = 25 °C	Not determined	>98% >98% >98% >98% >98% >98% >98% >98% >98% >98% >98% 18% 52–64%	(López et al., 2019)
NF	SO <sub>4</sub> <sup>2-</sup> Total solids	Not specified	Temperature = 25 °C; feed flow rate = 2 L/min; pressure = 10 bar	88	99.5% 87.8%	(Aguiar et al., 2015)
RO	SO <sub>4</sub> <sup>2-</sup> Total solids			10.2	92% 85%	
ED	SO <sub>4</sub> <sup>2-</sup>	Not specified	Flow rate = 50 L/h	Not determined	60% (current efficiency)	(Martí-Calatayud et al., 2014)
NF	SO <sub>4</sub> <sup>2-</sup> Fe <sup>2+</sup> Cu <sup>2+</sup> Zn <sup>2+</sup>	Cross flow	Temperature = 25 °C; feed flow rate = 14.3 L/min; pressure = 10 bar	Not determined	>90% >90% >90% >90%	(Lopez et al., 2018)

heavy metals. Consequently, perfect rejection (100%) was recorded for Mn, As, Cd, Pb while relatively high rejection (>80%) was recorded for Cu, Fe, Zn. This difference could further be explained in terms of differences in ionization energies resulting in metals with larger atomic radii (Mn, As, Cd, Pb) being efficiently rejected via the size exclusion principle of membrane separation than metals (Cu, Fe, Zn) with small atomic radii. From Table 3, very low permeate flux were recorded whilst using hybrid membrane (0.4 L/h.m<sup>2</sup>) in the treatment of AMD. This could be explained in the light higher osmotic pressures as a result of concentration gradient acts against transmembrane pressure, thereby, driving the solutes to the permeate across membrane pores.

#### 4.2.4. Technical issues associated with membrane processes

The issue associated with NF membrane on the industrial level is scaling effects due to the precipitation and deposition of insoluble mineral salts on the membrane surface. Thus, transport of metals and ions through the pores are hindered and permeate flux volume is reduced thereby resulting in an increase in operating cost and shortening of membrane service life. To reduce the amount of deposits on membrane pores, the use of an anti-scaling solution and neutralization of acidic pH levels in the mines prior to membrane filtration could in effect minimise the scaling effects associated with NF membranes. Furthermore, membrane processes are quite expensive. Hence, except there is a high premium of clean water due to limited sources, it would be financially impractical to treat AMD using it (albeit on a large scale).

### 5. Advanced oxidation processes (AOPs) for AMD treatment

Advanced oxidation processes (AOPs) have shown great performances for the removal of a wide range of organic and inorganic pollutants from aqueous solutions and industrial wastewaters (Ahmadi et al., 2020; Balarak et al., 2019; Ighalo et al., 2021c; Othmani et al., 2019). AOP has been the subject of a considerable amount of research and publication since the 1980 s (Skoumal et al., 2008). These methods have also shown considerable promise in terms of being able to oxidize organic compounds in a cost-effective and environmentally safe way (Khajouei et al., 2019; Othmani et al., 2020; Tony and Lin, 2020). They can be selected for either

transforming pollutants into less toxic compounds which can subsequently undergo biological treatment, or integrated at the end of the process to mineralize pollutants and by-products before discharge (Badawy et al., 2006). AOPs are used when conventional oxidation techniques are insufficient, when process kinetics are slow or when pollutants are refractory to chemical oxidation processes in aqueous solutions and/or their oxidation leads to the formation of stable intermediates and more toxic than the initial molecule of interest (Othmani et al., 2020). AOPs are based on the production of sulfate radicals (SO<sub>4</sub><sup>•-</sup>), and hydroxyl radicals (<sup>•</sup>OH) in sufficient quantity to oxidize pollutants; their lifetime is very short (10<sup>-9</sup> s) (Hooshi et al., 2012; Rocha et al., 2012). AOPs can be divided into four main groups (Fig. 4). The photo, sono, and electro assisted AOPs to utilize ultraviolet (UV), ultrasound (US) rays, and electric current, respectively as their sources of energy which helps in the creation of <sup>•</sup>OH and SO<sub>4</sub><sup>•-</sup> radicals which lead to pollutants degradation. The advanced chemical oxidation processes use chemicals such as ozone, hydrogen peroxide, ferrate, persulphate, Fenton-catalysts, etc for contaminants degradation (Ighalo et al., 2021c).

#### 5.1. AOPs performance

AOPs have been efficaciously applied for the degradation of toxic AMD including ozonolysis, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), photolysis, and Fe(VI) oxidation processes (Table 4). Most of the researchers (Table 4) investigated the reduction of AMD using the chemical oxidation processes. Gervais et al. (2020) studied and compared three different AOPs for thiosalts treatment (Table 4); the AOPs were promising for thiosalts degradation with ozonation showing the greatest efficiency. The H<sub>2</sub>O<sub>2</sub> process was better than Fe(VI) oxidation for thiosalts removal (96%) but required a longer treatment time. Greater than 80% Fe<sup>2+</sup> degradation was observed by Miller (2015) via the same H<sub>2</sub>O<sub>2</sub> process. Munyengabe et al. (2020) obtained remarkable results with 100%, 99.04%, 100% degradation efficiency for AMD constituents (Fe<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, respectively) using Fe(VI) oxidation. The use of photocatalytic degradation with TiO<sub>2</sub>/Si-C composite was also effective in yielding polycyclic aromatic hydrocarbons (PAHs) removal greater than 60%. Most of the researchers (Table 4) examined the reduction of AMD using the advanced chemical oxidation processes. From general observation, a

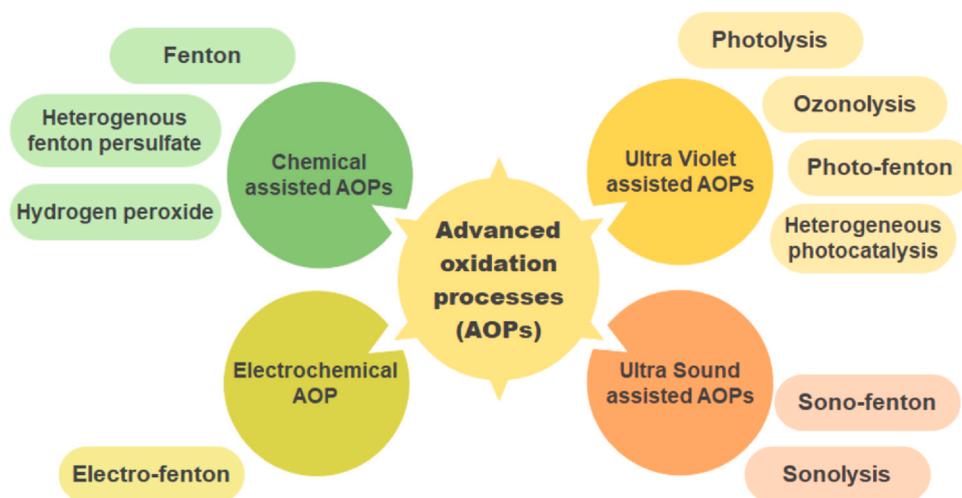


Fig. 4. Types of AOPs utilized for contaminants degradation.

considerable number of studies have not been done on AMD mitigation through the AOP. Not all the AOPs types have been investigated for AMD degradation especially the sonochemical and electrochemical AOPs. Even combinations of different AOPs categories have not been employed for this problem. Therefore, this leaves gaps to be covered by researchers in this field.

### 5.2. Technical issues associated with AOPs

AOPs as shown from the review can be quite effective for the treatment of AMD. However, two technical issues are associated with their use in this respect. Firstly, there is the generation of sludge from the processes. This sludge will need to be taken care of in a variety of ways. Secondly, there is the expensive nature of AOPs utilization. Continuous production and utilization of ozone and peroxides at industrially relevant volumes can be expensive. UV and ultrasound (for sono-processes) will also have an electrical requirement. If sunlight is used as an alternative to artificial UV light, then the technique would only be applicable to areas with high solar insolation (and for daytime only).

## 6. Biological treatment of AMD

Biological treatment of AMD can be divided into two major parts, in which to treat the AMD or to avoid leaching and to remediate the AMD-contaminated environment. Soil and water body are two environmental media mostly contaminated by AMD. For the purpose of treatment, bioreactors and wetlands of various types have been reported to be successfully treating the AMD before releasing to the environment or to avoid leaching. On the remediation side, algal-remediation, microbial-remediation, and wetland are the three most reported systems to be successfully applied to remediate AMD-contaminated aqueous environment.

### 6.1. Bioreactor

Bioreactor in for treating AMD mostly related to the sulfate reducing processes (Aoyagi et al., 2017). Although metal precipitating bacteria are considerably applicable, but most of the treatment involved the two stages processes, in which precipitating reactor connected with sulfate reducing reactor. Metal precipitating bacteria played important roles in the natural attenuation process of AMD which operated on the basis of the fate of metals in AMD (Fernandez-Rojo et al., 2017). On the other side, sulfate reducing bacteria produce  $H_2S$  gasses from the degradation of sulfate

accompanied by various carbon source. The produced  $H_2S$  gas was then injected into the precipitating reactor, reacted with metals to produce metal-sulfide that precipitated at the bottom of the reactors (Yildiz et al., 2019a), which then can be separated or recovered further (Tabak et al., 2003). Several bioreactor systems to treat AMD and its performance are summarized in Table 5.

### 6.2. Microbial bioremediation

Discussion about AMD-contaminated environment cannot be separated from algal/microbial remediation. Algal remediation can be applied in contaminated water bodies while microbial remediation can be used to remediate AMD-contaminated water or soil. Algae have the capability to perform biosorption, which can bio-concentrate the metals (mostly as concerned pollutant) in AMD (Santos et al., 2020). The bioconcentrated metals in algae cells can be separated or recovered. For microbial remediation, biostimulation is the widely used method. Biostimulation works by injecting nutrients into contaminated soil to enhance the growth of indigenous bacteria (Zhu et al., 2020). Indigenous bacteria commonly have higher resistance to the pollutants and can perform adapted enzymatic reactions to prevent toxicity to their cells (Imron et al., 2021, 2019; Kurniawan et al., 2018). The biostimulation also commonly accompanied by bioaugmentation, in which superior laboratory culture bacterium is introduced into the system to assist the remediation processes (Purwanti et al., 2020; Wang et al., 2020a). Several bioremediations of AMD contaminated environment are tabulated in Table 6.

### 6.3. Wetland

Wetland is a promising technology to be used in remediating AMD-contaminated environments (soil and water). Wetland can perform the simultaneous physical and biological treatment as the result of the used medium, plants, existed microbial community, and interaction between microbes and plants during the treatment (Abdullah et al., 2020; Al-Ajalin et al., 2020; Jehawi et al., 2020). In AMD treatment or remediation using wetland, phytoextraction and phytostabilisation become the most involved mechanisms (Ismail et al., 2020; Purwanti et al., 2020). Phytoextraction is the process of plants uptaking pollutants into their cell, while phytostabilisation is the process of metal changing from mobile phase into less mobile phase during the treatment (Li et al., 2020; Purwanti et al., 2020; Tangahu et al., 2011). The utilization of wetland to treat AMD or to remediate AMD contaminated areas should concern the plants'

**Table 4**  
The efficiency of different AOP processes for the removal of AMD.

Process type	Target pollutant	Optimum conditions	Results	Ref.
Ozonolysis	Thiosalts	Sparging rate = 75 g/h, time = 1 h, pH = not adjusted, synthetic effluent concentration = 290 mg/L $S_2O_3^{2-}$	99%	(Gervais et al., 2020)
Fe(VI) oxidation	Thiosalts	wet Fe(VI) dose = 65 mg/L, time = 2 h, synthetic effluent concentration = 100 mg/L $S_2O_3^{2-}$ , temperature = 22 °C	82%	(Gervais et al., 2020)
H <sub>2</sub> O <sub>2</sub>	Thiosalts	(H <sub>2</sub> O <sub>2</sub> :S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ) molar ratio = 2:1, Time = 7 days, temperature = 8 °C	96%	(Gervais et al., 2020)
Fe(VI) oxidation	Fe <sup>2+</sup> , Zn <sup>2+</sup> , Mn <sup>2+</sup>	Time = 30 min, pH = 3, Volume of synthetic AMD = 15 mL, ferrate (FeO <sub>4</sub> <sup>2-</sup> ) concentration = 5 × 10 <sup>-2</sup> mmol/L	100%, 99.04%, 100% respectively	(Munyengabe et al., 2020)
Photocatalysis	PAHs	TiO <sub>2</sub> /Si-C composite mass = 100 mg, UV intensity = 125 W, reaction time = 1 h, PAHs concentration = 180 µg/L	> 60%	(Lattuada et al., 2013)
H <sub>2</sub> O <sub>2</sub>	Fe <sup>2+</sup>	[Fe <sup>2+</sup> ]/[H <sub>2</sub> O <sub>2</sub> ] = 2:1, time = 1 min, pH = 2.82, total iron = 94 mg/L	> 80%	(Miller, 2015)

capability in tolerating acidic conditions and the hyperaccumulator characteristics of the plants. Several successful applications of wetland in treating or remediating AMD-contaminated environments are summarized in Table 7.

#### 6.4. Technical issues associated with biological processes

Biological treatment of AMD is usually achieved by biochemically-mediated processes taking place within living organisms. Hence, they are usually quite slow. Compared to the other major process techniques, this genre is the slowest as longer retention times are needed to achieve adequate pollutant reduction. Consequently, for such technologies to be applied in practical scenarios where a large volume of water needs to be handled, the design is usually scaled-up. Larger facilities for biological treatment is needed to achieve equivalent performance for smaller set-ups for other processes. Due to the delicate nature of biochemically-mediated degradation processes, the pH and temperature have to be carefully monitored and maintained, else performance will reduce or can stop entirely.

### 7. Significance of AMD remediation in sustainable water resource management

Sustainable water resource management centers on the availability, sustainable management of water, accessibility, quality of water resources and overall sanitation (Ighalo and Adeniyi, 2020). It emphasizes the need to consider the long term usage of water as well as the present. Water resource systems that are conserved and managed to satisfy the dynamic demands placed on them for present and future purposes without system degradation can be referred to as “sustainable” (Loucks, 2000). This resource management is of high necessity as its essential for unlocking productivity and economic growth and also provides leverage for health and education investments already in existence (Loucks and Van Beek, 2017) in light of present AMD pollution challenges.

Water is an important component of human life and it has an inextricable linkage to national development (Ighalo et al., 2021a). Making water accessible and providing a quality one is a very crucial element for horticultural and extensive financial development. Sustainability considerations recognize that ecosystems and their inhabitants are all water users and that can make or mar the quality and availability of fresh water (Harrison et al., 2016). Actions at the local medium to meet water needs may trigger environmental stress and thus create a trade-off between environmental sustainability and human water needs (Bhaduri et al., 2016). Though water is very essential to the ecosystem, the escalated pressure on the water system is evident through increased global demand and mismanagement of our water resources (Ighalo et al., 2020b). Some of the threats include; sewage discharge without treatment, inhabitation in the river basins, high use of fertilizer for production which in turn increases waste water effluent flows like nitrogen in rivers, lack of access to an improved drinking water resource, high dependence on untreated surface water and use of water with fecal contamination (Ighalo et al., 2020a). Based on these issues, the question of how sustainable water management can be ensured while safeguarding the vital support system on which the welfare of current and future generations depends arises.

During excavation and activities mining such as highway construction, percolation of water through sulfide minerals results in their oxidation and subsequently, acids are formed with or without the inhibition of acidophilic bacteria (Nordstrom and Southam, 2018). The acidified water seeped from above into underground mines are discharged into streams or holding ponds and when the mines are abandoned, accumulates in its various chambers and cavities (Naidu et al., 2019). Active defunct gold and coal mines

**Table 5**  
Various bioreactors to treat AMD.

System	Biological Agent	Pollutant (s)	Operational Condition	Removal Efficiency	Finding (s)	Ref.
Anaerobic up-flow reactor	Indigenous bacteria	Sulfate Cuprum Nickel	Contact time = 0–178 days pH = 7 Temperature = 25 °C Working volume = 500 mL	Sulfate = 100% Cuprum = 63% Nickel = 95%	Ethanol was a better electron donor and carbon source rather than acetate.	(Yildiz et al., 2019a)
Anion-exchange	Aminated Peat	Sulfate	Contact time = 30 mins pH = 2.2, 4.3, 5.8 Temperature = 2–22 °C	76%	The anion exchanger performed better under acidic pH of 2.0. Temperature did not significantly affect the removal efficiency	(Gogoi et al., 2021)
Continuous-flow natural attenuation	Indigenous bacteria	Arsenic Iron	Contact time = 20–1800 mins pH = 2.6–3.4 Temperature = 20 °C	Arsenic = 65% Iron = 65%	The wastewater height, floating biofilms, chemical composition, and wastewater feed need to be monitored in order to preserve bacterial community.	(Fernandez-Rojo et al., 2017)
Fluidized bed	Bacteria	Sulfate Iron Mangan	Contact time = 4–16 h pH 2.3	Sulfate = 90% Iron = 98% Mangan = 98%	Co-treatment with hospital wastewater improved the removal efficiencies from both pollutant's parameter	(Makhathini et al., 2021)
Fluidized bed	Bacteria	Iron Nickel	pH 3 and 7	Iron = 90% Nickel = 85%	Metal was recovered as nano powder and has potential to be used in industry	(Kumar and Pakshirajan, 2021)
Membrane bioreactor	Bacteria	Arsenic Iron	Contact time = 6–24 h pH 3.5–4	Arsenic = 99% Iron = 99%	Ceramic membrane bioreactor attained the microbial community dominated by <i>Alicyclobacillus tolerans</i> and <i>Acidiphilium cryptum</i>	(Demir et al., 2021)
Membrane bioreactor	Anaerobic bacteria	Iron Cuprum Zinc Cobalt Nickel Arsenic	Contact time = 12.5–46 h pH 3.5–4	Iron = 99% Cuprum = 99% Zinc = 99% Cobalt = 99% Nickel = 99% Arsenic = 99%	As removal was decreased by the increasing of the sulfide concentration	(Yigit et al., 2020)
Membrane bioreactor	Bacteria	Iron	Contact time = 12–48 h pH 1.5 – 2.5	Iron = 97%	Organic matter helped the startup of the bioreactor	(Demir et al., 2020)
Membrane bioreactor	Bacteria	Iron Cuprum Zinc Cobalt Nickel Mangan Arsenic	Contact time = 1.3–2 days pH 4	Iron = 99% Cuprum = 99% Zinc = 99% Cobalt = 99% Nickel = 99% Mangan = 71% Arsenic = 67%	As removal was decreasing by the increasing of sulfide concentration	(Yurtsever et al., 2019)
Membrane bioreactor	Anaerobic bacteria	Silica Iron Cuprum Natrium Magnesium	Temperature = 35 °C	–	<i>Desulfovibrio</i> sp. dominated the system	(Sahinkaya et al., 2018)
Mussel shell bioreactor	Bacteria	Aluminum Iron Nickel Thallium Zinc	pH 3.4	Aluminum = 99% Iron = 99% Nickel = 90% Thallium = 90% Zinc = 90%	The system can increase the AMD pH until 8.3	(DiLoreto et al., 2016a)
Mussel shell Matrix	Mussel shell	Iron Aluminum Nickel Zinc Thallium	Successive alkalinity producing systems with 6 days retention time	Iron = 99.7% Aluminum = 99.3% Nickel = 98.8% Zinc = 99.3% Thallium = 98.4%	The bioreactor able to simultaneously remove metals and alter the pH into neutral	(DiLoreto et al., 2016b)
Packed bed bioreactor	Bacteria	Iron Cuprum Zinc Magnesium Nickel	Contact time = 48 h pH 7	Iron = 98% Cuprum = 98% Zinc = 98% Magnesium = 98% Nickel = 98%	Results of treatment already meet the effluent quality standards for AMD	(Dev et al., 2017)
Packed bed bioreactor	Iron-oxidizing bacteria	Iron Cuprum	Contact time = 8–40 h pH 1.2–2.2	–	<i>Leptospirillum</i> sp. was detected as dominant genus in the bioreactor	(Fan et al., 2019)
Sequential bioreactor	Sulfate reducing bacteria	Sulfate Mangan Calcium Magnesium	Contact time = 172 days pH 4.5	Sulfate = 84.7% Mangan = 80% Calcium = 50% Magnesium = 38%	The addition of tailing leachate into the system improved the metal removal efficiencies. <i>Desulfovibrionaceae</i> sp. dominated the microbial community.	(Gomez et al., 2021)
Structured bed bioreactor	Sulfate reducing bacteria	Sulfate Iron Cobalt Nickel Cuprum Zinc	Contact time = 51 days pH 4.7	Sulfate = 55 – 91% Iron = 70% Cobalt = > 80% Nickel = > 80% Cuprum = 73% Mangan = 60% Zinc = 80%	<i>Geobacter</i> sp. and <i>Desulfovibrio</i> sp. were dominant genus in the bioreactor. Effluent pH was detected as normal (6.5 – 7.5)	(Nogueira et al., 2021)

(continued on next page)

Table 5 (continued)

System	Biological Agent	Pollutant (s)	Operational Condition	Removal Efficiency	Finding (s)	Ref.
Structured bed bioreactor	Anaerobic bacteria	Iron Cuprum	Contact time = 7 days pH 4.5	Iron = 25% Cuprum = 5%	The increasing of Cu concentration inhibited the sulfate reduction activity thus limiting the availability of electron donor	(Costa et al., 2021)
Sulfidogenic bioreactor	Indigenous bacteria	Zinc Iron	Contact time = 99 days pH 2.1	Zinc = 70% Iron = 70%	<i>Desulfoporosinus acididurans</i> was dominating the community over time	(González et al., 2019)
Sulfidogenic bioreactor	Bacteria	Iron Mangan	Contact time = 12 h	Iron = 87% Mangan = 47%	<i>Desulfovira</i> , <i>Desulfobulbus</i> , <i>Desulfovibrio</i> , and <i>Syntrophus</i> sp. were dominating the microbial community	(Deng et al., 2016)
Sulfidogenic bioreactor	Indigenous bacteria	Cobalt Nickel Zinc	Contact time = 462 days Temperature = 35 and 45 °C pH 4 and 5	Cobalt = 99.9% Nickel = 99.9% Zinc = 99.9%	The acid tolerant bacteria ( <i>Desulfoporosinus acididurans</i> and <i>Peptococcaceae</i> CEB3) maintain the performance of bioreactor	(Santos and Johnson, 2017)
Sulfidogenic bioreactor	Bacteria	Cuprum Nickel	Contact time = 148 days pH 2	-	Cuprum recovery was optimum in ethanol-feed bioreactor	(Yildiz et al., 2019b)
Sulfidogenic bioreactor	Bacteria	Sulfate Iron	Stirring = 150 rpm Temperature = 35 °C	Sulfate = 80% Iron = 99.7%	<i>Desulfovibrio</i> sp. was detected as the major genus in the bioreactor	(Ferraz et al., 2021)
Sulfate-reducing bioreactor	Indigenous bacteria	Sulfate	Contact time = 5–10 h pH = 3 and 7 Working volume = 50 L	Up to 71.4% in neutral pH (6 h) and 66.7% in acidic pH (20 h)	Contact time and operational pH significantly affect the bacterial community composition in the bioreactor.	(Aoyagi et al., 2017)
Sulfate-reducing bioreactor	Sulfate reducing bacteria	Sulfate	Contact time = 12.5 h pH 6.7	Sulfate = 77.9%	Transition from aerobic to anaerobic zone was important for degradation	(Sato et al., 2022)
Two stages bioreactor	Sulfate reducing bacteria	Aluminum Cadmium Cobalt Cuprum Iron Mangan Nickel Zinc	pH = 4–5 Working volume = 250 mL	Aluminum = 99.8% Cadmium = 99.8% Cobalt = 99.7% Cuprum = 99.1% Iron = 97.1% Mangan = 87.4% Nickel = 47.8% Zinc = 100%	Sulfate reducing bacteria produced adequate amount of sulfide to be recycled back in the precipitating tank to form metal-sulfide (solid).	(Tabak et al., 2003)

Table 6  
Bioremediation of AMD-contaminated area.

System	Biological agent	Contaminated Area	Pollutant (s)	Removal efficiency	Ref.
Algae bioremediation	<i>Chlorella sorokiniana</i>	Surface water	Cuprum	Up to 99.5%	(Ayala-Parra et al., 2016)
Algae bioremediation	<i>Chlamydomonas</i> sp. <i>Eumotia exigua</i>	Surface water	Iron	Up to 99.98%	(Fyson et al., 2006)
Algae bioremediation	<i>Scenedesmus</i> sp.	Surface water	Arsenic Iron Lead Mangan Zinc	Arsenic = 53% Iron = 94% Lead = 40% Mangan = 72.5% Zinc = 60%	(Santos et al., 2020)
Anaerobic packed bed	<i>Clostridium</i> sp. <i>Desulfovibrio</i> sp. <i>Desulfotobacterium</i> sp.	Surface water	Arsenic Cadmium Cobalt Chromium Cuprum Iron Lead Mercury Nickel Zinc	Average metal removal of 80% with the highest of 99%	(Martins et al., 2011)
Biostimulation	Indigenous bacteria	Ground water	Aluminum Cadmium Cobalt Cuprum Iron Nickel Zinc	Up to 99.6%	(Jeen and Mattson, 2016)
Biostimulation	<i>Acidithiobacillus ferrooxidans</i>	Soil	Iron	n.a.	(Schippers et al., 2010)
Biostimulation	Indigenous bacteria	Soil	Arsenic Iron	Ranged between 32% and 99%	(Zhu et al., 2020)
Biostimulation	Indigenous bacteria	Surface water	Iron Mangan	Iron = 73% Mangan = 19.85%	(Nurcholis et al., 2018)

**Table 7**  
The utilization of wetland for AMD treatment or remediation.

Purpose	System	Plant species	Contaminated area	Pollutant (s)	Removal efficiency	Ref.
Remediation	Free-surface flow	<i>Juncus canadensis</i> <i>Carex lacustris</i> <i>Typha latifolia</i>	Soil Surface water	Iron Sulfate	Iron = 30% Sulfate = 100%	(A. Gupta et al., 2020; V. Gupta et al., 2020)
Remediation	Surface flow	<i>Helianthus tuberosus</i>	Soil	Cadmium Cuprum Lead Mangan Nickel Zinc	Cadmium = 12% Cuprum = 30% Lead = 10% Mangan = 20% Nickel = 50% Zinc = 30%	(Willscher et al., 2017)
Remediation	Free-surface flow	<i>Salix drummondiana</i> <i>S. monticola</i> <i>S. planifolia</i> <i>Typha latifolia</i>	Surface water	Cadmium Lead	Up to 87%	(Kersten et al., 2017)
Treatment	Horizontal sub-surface flow	<i>Typha latifolia</i>	Surface water	Aluminum Cobalt Chromium Iron Mangan Nickel Sulfate	Aluminum = 59.7% Cobalt = 93.7% Chromium = 99.7% Iron = 91.6% Mangan = n.a. Nickel = 97.8% Sulfate = 44–75%	(Singh and Chakraborty, 2020)
Treatment	Sub-surface flow	<i>Iris pseudoacorus</i> L.	Surface water	Cadmium Chromium Cuprum Iron Zinc	Cadmium = 53.24% Chromium = 83.5% Cuprum = n.a. Iron = 59.6% Zinc = 42.38%	(Chen et al., 2021)
Treatment	Surface flow	<i>Carex rostrata</i> <i>Eriophorum angustifolium</i> <i>Phragmites australis</i>	Surface water	Cuprum Iron Zinc	Cuprum = 57% Iron = n.a. Zinc = n.a.	(Nyquist and Greger, 2009)
Treatment	Free-surface flow	<i>P. australis</i>	Surface water	Cuprum Iron Mangan Zinc	n.a.	(Ding and Sun, 2021)

continue to pollute ecosystems through AMD and deposits of radioactive elements (John et al., 2017). To maintain the supply of freshwater contaminated by AMD and other pollutants, water fractioning is done in many cases and also the active implementation of water resource management.

Several active and passive water treatment techniques have been developed to control AMD (Kuyucak, 2002). Active systems require the use of long term systematic addition of various alkaline chemicals such as hydrated lime, caustic soda and ammonia (Saha and Sinha, 2018). They require a long commitment and are also very expensive. Conversely, passive treatment systems are cost-effective with very little maintenance. This method relies on the dissolution of limestone to increase pH and alkalinity and precipitate metals. Various studies have recorded that blast furnace slag has a capacity of absorbing phosphorous and heavy metals. This absorption property has good potential of assisting in the development of new types of environmentally harmless, cheap and effective filters for water purification, materials stabilization, landfills covers and other purposes. Environmental harm caused by mining and construction, and other nature imposed disturbing activities were highly underplayed, hence the consequences (Ighalo et al., 2020c). One of the principles of conservation is development which states that sustainable development depends on good environmental management and in turn, good environmental management equally depends on sustainable development (López-Gamero et al., 2011). Due to the high complexity of AMD, the impact poses a difficulty in terms of quantification and prediction.

The effects of pollution caused by AMD can be categorized as metal toxicity, acidity, salinization and sedimentation processes. These effects inadvertently reduce its ecological stability. AMD is known to be a complex factor pollutant and the effect varies with

the recipient host systems. AMD impact is quite unpredictable due to the variation of its discharge. Acidic water formed by AMD dissolves metals thereby posing as threats to wildlife and humans. Hence, the environment needs to be protected from AMD. This is to ensure the safety of all organisms in the ecosystem in the long term. This is because AMD also occurs even after mining ends (Ochieng et al., 2010). This is a huge problem because AMD cannot easily be stopped once it occurs on a large scale. Environmental protection also needs to be implemented because damages caused by AMD disrupts growth and reproduction of animals and plant, causes diseases and increases corroding effects of acids on the parts of infrastructures like bridges. AMD is not only limited to ecological concerns but also linked to economic concerns due to the general decline in tourism and outdoor recreation (Mogale and Odeku, 2018). With water being one of the basic medium for transportation of contaminants, AMD can be controlled by managing the water flow, diversion of the surface water flowing towards the pollution site, prevention of groundwater infiltration and adequate management of acid generated wastes.

In efforts to reduce AMD, several treatment techniques have been birthed and tested. This has proven to be of high relevance as regards the term 'reduction'. Chemical treatments are quite expensive but not ruled out (Ighalo et al., 2021c). They can be achieved either by active treatments where chemicals are added to AMD or by passive treatment where AMD is channeled to pass through wetlands. Limestone is one of the raw materials used for active treatment but not devoid of limitations. For better treatments, low-cost materials such as fly ash and zeolite materials are used as alternatives. Corrective techniques are designed to treat acidic waters produced by mining while the objective of preventive techniques are to prevent the production of AMD. These preventive techniques attack the

essential elements in acidic water formation; oxygen, water and *Thiobacillus ferrooxidans* bacteria. For preventive treatments, surface water diversion technique tries to reduce the supply of water to potential acid-generating materials by the use of waterproofed channels and other means (Pozo-Antonio et al., 2014). This is a low-cost technique that is easy to apply but the application could be flawed. Soil compaction technique is not totally a restoration scheme but works effectively when put in practice with others. The permeability of mining wastes decreases when compacted. This works by reducing water flow and in turn, hinders the oxidation of the material and acid production rate. Dry covers aim at stabilization of mining wastes to prevent erosion, inhibition and prevention of pollutant release and esthetic appearance movement. The effectiveness of this technique increases when choosing a dry and high location for the dump. Coverings with sludge improve vegetation establishment, productivity and fertility. The yield of this treatment is relatively higher when compared to other inorganic fertilizers. Handling tailing technique is very expensive but gives excellent results. Cognizance of underground or surface mines is not taken when using the corrective technique. In line systems plants gives the most effective results both in percentage recovery aspects and in economic aspects. This is in contrast with the plants by ion exchange or reverse osmosis which is highly effective and quite expensive. These treatment techniques are all good with their limitations. A combination of blended techniques can be adopted for positive results.

## 8. Conclusion

The ecotoxicology of AMD was established in the study and various treatment methods were analyzed especially corrective treatment methods. It should be noted that the applicability and suitability of a given treatment approach is a function of nature (the major constituent) of the AMD and their initial concentration, as well as the cost and environmental impact of the operation. The adsorption technique is a popular choice by investigators due to its environmental, operational and economic efficiency. Those involving the transfer of solute particles from aqueous states to the solid surfaces of the adsorbent proves to be the preferred method because of the operational, environmentally and economic efficiency, but most significantly its zero to waste adsorbent reusable characteristics. The presence of metal-binding surface functional group on organic based adsorbent accounts for their high metal ion uptake with high adsorptive capacities being observed in the batch process. Given an appropriate choice of adsorbent, ions in AMD can be reduced between 50% and 99%. Membrane separation processes are more effective than adsorption and can effect over 90% rejection at optimized conditions. Considering, nano-filtration, reverse osmosis and hybrid systems, concentration polarization is one of the advantages of nano-filtration. Selectivity, operating cost and decent energy reservation when compared with other type of membrane makes reverse osmosis stand out. AOPs have been shown to achieve > 80% ions removal. AOPs are peculiar due to their ability to oxidize organic compounds in a cost effective manner, less toxicity, mineralization of by-products and pollutants into less harmful compounds. AOPs are adopted when oxidation is less sufficient. A considerable number of studies have not been done on AMD mitigation through the AOP especially the sonochemical and electrochemical AOPs. Even combinations of different AOPs categories have not been employed for this problem. There is also a high generation of sludge from the process and high expensive nature of utilizing AOPs that possess as a problem. Ultraviolet and ultrasound used for sono-processes has high electrical requirement. Therefore, this leaves gaps to be covered by researchers in this field.

Biological processes showed a far wider spread of performance due to the selectivity in performance of the different micro-organisms

used. Biological are of two main aspects, one targets the treatment of AMD while the other avoids leaching and remediates AMD infected environments. However, algal bioreactors seemed the most effective in this domain as they have been shown to effectively remove both sulfates and heavy metals and is used for AMD treatment whereas microbial and algae remediation are used to remediate AMD infused environments. For treatment, bioreactors and wetlands of various types have been reported to be successfully treating the AMD before release to the environment or to avoid leaching. Though biological processes are quite slow, demanding high retention time, and very sensitive to pH and temperature, scaling up is advised. It is recommended that more AOPs types be investigated including the combination of different process types and cost effective ways of ozone utilization and its continuous production. As long as there are limitations to these treatment processes, AMD remediation is not totally guaranteed so preventive techniques should be investigated so as to reduce the production of AMD. The review considered the significance of AMD remediation in sustainable water resource management. Corrective techniques are designed to treat acidic waters produced by mining while preventive techniques are to prevent the production of AMD: each approach has its technicalities. In-line systems plants give the most effective results both in percentage recovery aspects and in economic aspects though a combination of blended techniques can be adopted for positive results.

## Compliance with ethical standards

This article does not contain any studies involving human or animal subjects.

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## CRediT authorship contribution statement

**Joshua O. Ighalo:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Validation, Project administration. **Setyo Budi Kurniawan:** Writing – original draft, Writing – review & editing, Validation. **Kingsley O. Iwuozor:** Writing – original draft, Writing – review & editing, Validation. **Chukwunonso O. Aniagor:** Writing – original draft, Writing – review & editing, Validation. **Oluwaseun J. Ajala:** Writing – original draft, Writing – review & editing, Validation. **Stephen N. Oba:** Writing – original draft, Writing – review & editing, Validation. **Felicitas U. Iwuchukwu:** Writing – original draft, Writing – review & editing, Validation. **Shabnam Ahmadi:** Writing – original draft, Writing – review & editing, Validation. **Chinenye Adaobi Igwegbe:** Supervision, Writing – original draft, Writing – review & editing, Validation.

## Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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