

## Phytoremediation and Nanoremediation : Emerging Techniques for Treatment of Acid Mine Drainage Water

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### ABSTRACT

Drainage from mining sites rich in sulfur bearing rocks is known as acid mine drainage (AMD). Acid mine drainage water is a serious environmental pollutant that has its ill effects on plants, animals and microflora of a region. Mine water drainage mainly results due to anthropogenic activities like mining that leave the sulfur bearing rocks exposed. This drainage water poses as a potent soil, surface water and ground water pollutant. Although a lot of remediation measures have been implemented in the past but, none of them have been able to solve the problem completely. This review intends to focus on new emerging and better techniques in the form of phytoremediation and nanoremediation for treatment of acid mine drainage water. Besides, the review also gives more importance to the phytoremediation technique over nanoremediation because of the cost effectiveness and eco-friendly nature of the first as compared to the latter. A hypothetical model discussing the use of hyperaccumulator plants in remediation of acid mine water has been proposed. The model also proposes natural induction of the phytoremedial ability of the plants involved in the remediation process. The proposed model assisted by inputs with further research, may be helpful in proper treatment of acid mine drainage water in the near future.

**Keywords:** Acid mine drainage; Phytoremediation; Nanoremediation; Hyperaccumulator; Heavy metals; Pollutant; Environment

### 1. INTRODUCTION

Pollution of the environment especially the water bodies by drainage water coming from sites containing sulfur bearing rocks is termed as acid mine drainage (AMD), and is of major concern these days. Although AMD can occur naturally, but still, anthropogenic activities like mining and processing of metal ores and coals can contribute significantly on a large scale to the generation of the same<sup>1</sup>. The sulfide minerals get exposed to the environment during the process of mining, resulting in generation of excess amount of acid which can have both immediate as well as long lasting hazardous effects on the environment. Acid mine drainage has continued to pose as a serious environmental threat. It is one of the major environmental issues being faced by the metal mining industry<sup>2</sup>. The negative impacts of AMD include adverse effects on aquatic ecosystems of the drainage water receiving streams, corrosion of mining equipment and machineries<sup>3</sup>, degradation in the quality of soil and contamination of the groundwater by leaching of heavy metals present in the acid mine water<sup>4</sup>. Focus has been put on the serious hazards imposed by acid mine drainage water on the environment and the related health risks. Furthermore, efforts have been made to highlight new emerging techniques – phytoremediation and nanoremediation and their application for proper treatment of the same. A hypothetical model has been devised where in hyperaccumulator plants could be induced to increase their phytoremedial ability for efficient treatment of polluted water generated from mines.

### 2. THE INDIAN SCENARIO

Acid mine drainage affected areas in India mainly falls under the region of Damodar valley coalfields and the north-east coalfields. The Damodar valley coalfields include the Jharia and West Bokaro coalfields in Jharkhand and Raniganj coalfield in the West Bengal. Among the north eastern coalfields, the Jaintia coalfield of Meghalaya and Makum coalfield of Assam are one of the most polluted ones. Some of the heavy metals that are generally present in the mine drainage water are Iron, Copper, Manganese, Arsenic, Zinc, Lead, Chromium and Cadmium. The mine water from the Jaintia coalfield and Makum coalfield showed higher concentration of these metals as compared to other mining sites in India. The mine water from Jaintia coalfield, Jharkhand, has the highest concentration of iron, copper, zinc and lead as compared to the others<sup>5</sup>. The coal mines of Raniganj, West Bengal is known to have the highest arsenic content in its mine water. Similarly, the mine water released by West Bokaro coalfield in Jharkhand has the highest concentration of chromium<sup>6</sup>. Mine water generated from the Makum coalfield of Assam has the highest concentration of Manganese, Nickel and Cadmium and also consist the second highest concentration of Iron, Copper, Zinc and lead<sup>7</sup>. Details about the concentration of metals present in the discharged water of all these mines have been presented in Table 1.

### 3. FORMATION OF ACID MINE DRAINAGE

Acid mine drainage is produced by natural oxidation of sulfide containing minerals like Iron pyrite or Iron disulfide, when exposed to air or water. Beside natural processes, man-

**Table 1. Presence of heavy metals in drainage water of various mines in India<sup>8</sup>**

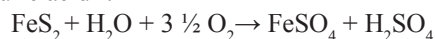
Mines	Concentration of heavy metals (in µg/L) present in mine drainage water								
	Fe	Cu	Mn	As	Cr	Cd	Pb	Ni	Zn
Jharia Coalfield (Jharkhand)	423	32.3	136	3.4	8.1	-	14.9	17.6	106.1
West Bokaro Coalfield (Jharkhand)	652	46	1431	7.21	81.2	-	34.3	154	194
Raniganj Coalfield (West Bengal)	329	18.8	39.4	10.06	44.6	-	22.6	45.6	60
Jaintia Coalfield (Meghalaya)	118400	320	4070	-	60	30	430	1080	4220
Makum Coalfield (Assam)	105300	310	10200	-	56	35	270	3120	1530

made activities such as mining and other construction activities expose the earth surface leading to acidic drainage. The reaction of metal sulfides with oxygen and water leads to formation of metal sulfates and sulphuric acid. The acidity can increase by further oxidation of the metals<sup>9</sup>.

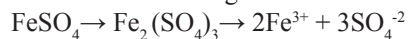
Water enters the mines as fresh water either in the form of rain water or also in the form of water used in the mines to control dust, for drilling purposes and other mining operations. In case of underground mines, there is always a chance of seepage of ground water into the mines through fissures and cracks. Water serves as a mode of transport for the oxidized products of sulfide minerals into the surrounding aqueous environment, which then may be further carried away to nearby rivers and other water bodies<sup>10</sup>. Water and oxygen reacts mainly with pyritic sulfur leading to formation of sulfuric acid and iron sulfate. This type of scenario is common in case of coal mines and the acidic environment thus created promotes the growth and activity of certain acidophilic bacteria such as *Thiobacillus ferroxidans*. The bacterium catalyses the acid production reaction and makes it much faster than that of the chemical oxidation process, in turn making the water more acidic<sup>11</sup>. The acidity of the mine drainage water is mainly governed by the formation of sulfuric acid along with the hydrolysis of oxidized products of pyrite. On the other hand the sulfur content helps in estimating the amount of reactive pyrite present in a particular stream<sup>10</sup>.

The complete mechanism behind AMD (Fig. 1) can be explained by a series of chemical reactions.

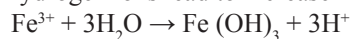
In the first step ferrous sulfide (pyrite) reacts with water and oxygen from the environment to form ferrous sulfate and sulfuric acid<sup>12</sup>.



Ferrous sulfate is formed as a result of oxidation of pyrite and may be oxidized even further in an accelerated manner to ferric sulfate in the presence of bacteria like *Thiobacillus*<sup>13</sup>. Further the ferric sulfate gets dissolved in the acidic water.



$\text{Fe}^{3+}$  upon contact with water can undergo hydrolysis reaction to form ferric hydroxide with release of hydrogen ions. The hydrogen ions lead to increase in the acidity of water.



The ferric hydroxide formed during this reaction further reacts with pyrite to produce more amount of acid along with ferrous and sulfate ions. The increase in acidity is directly proportional to the oxidation of iron. At high pH, the oxidized iron due to less solubility gets precipitated at the base of the

drainage, leaving behind the sulfate content constant. This sulfate content can be used to estimate the acidity of the drainage water. But, with the accumulation of acid, the solubility of iron increases as the pH falls below 3.

#### 4. ENVIRONMENTAL EFFECTS OF ACID MINE DRAINAGE

Acid mine drainage water may have possibility of being contaminated with trace (heavy) metals. At low pH, the heavy metals present in the nearby environment become soluble in drainage water. This solubility is generally governed by the reaction of the heavy metals with iron sulfate and sulfuric acid. The acidity and presence of toxic heavy metals in the drainage water exceeds the drinking water standards, making it unfit for consumption<sup>14</sup>. Beside this high amount of hardness, deposition or sedimentation of ore particles along with bacterial contamination further render the water unfit for drinking<sup>15</sup>. Moreover contact with such type of water either directly or indirectly may lead to many diseases both in plants and animals and as well as in humans<sup>16</sup>. The acid mine drainage water not only contaminate the local areas near the source but can also affect distance places if the water gets discharged into main streams like rivers<sup>17</sup>. The acid mine drainage has been found to have severe impacts in the ground water more than that of the surface water. The acidic water generally percolates deep into the soil and through permeable rocks to the ground water. This polluted water gets spread out further over a wide area through ground water movement. The polluted ground water is ultimately consumed by humans either from wells or bore wells<sup>18</sup>. The acidic mine water also corrodes equipment of mine plants and leads to pollution of the mine surface environment<sup>19</sup>. The high acidity of acid mine drainage water may also have negative impacts on growth rates and reproduction of fishes<sup>20</sup>. The acidic water causes loss of sodium ions from the blood of fishes. It also adversely affects the functioning of gills, ultimately leading to death<sup>21</sup>. Furthermore, the ferric hydroxide present in the drainage water may form precipitate, completely layering the bottom of the streams, thus making it unfit for growth of benthic organisms<sup>22</sup>.

#### 5. TECHNIQUES FOR REMEDIATION OF ACID MINE DRAINAGE

Wide ranges of technologies are available for remediation of acid mine drainage, but, sustainability of these techniques still remains questionable. Many processes that are being widely used to treat acid mine drainage water generally lead to

formation of other secondary waste products. These secondary wastes may require further treatment and proper disposal<sup>23</sup>, thus increasing the cost of remediation. As such, there is an utmost need of designing and implementation of new emerging techniques for proper remediation of acid mine drainage. The two most emerging techniques that can be followed for the remediation of acid mine drainage water are phytoremediation and nanoremediation. The first makes use of plants that can remediate mine drainage water contaminated with various pollutants and toxic metals. While the latter makes use of nano particles having size less than 100 nm to reduce the pollutant load in such water. The current study although proposes both of the strategies but still it puts more emphasis on the phytoremediation technique after thorough analysis and thus proposes a model in favour of the technique.

### 5.1 Phytoremediation

Phytoremediation is one of the emerging technology for the remediation of acid mine drainage which can be applied to both water and soil impacted by acid mine drainage. It is defined

as ‘the use of green plants and their associated microbiota, soil amendments and use of agronomic techniques to remove, contain or render harmless environmental contaminants’<sup>24</sup>. Acid mine drainage impacted soil may erode away to the surrounding water bodies causing pollution. As such, remediation of both soil and water near the mining sites is quite essential. Mainly two phytoremediation techniques- phytoextraction and phytostabilisation out of the others are taken into consideration in this study. The phytoextraction process involves extraction of heavy metals by the plants and their storage in different parts such as roots, stems and leaves. While, phytostabilisation works to provide a vegetative cover that binds acid sulfate contaminated soils that are highly prone to erosion<sup>25</sup>. Plants tolerant to certain metals are generally used in the process of phytoremediation of mining sites. Moreover plants known as hyperaccumulators that have an ability to accumulate metals 100 times more than that of a normal plant can be used for the purpose<sup>26</sup>. Hyperaccumulator plants are characterized by high accumulation and high translocation factor<sup>27</sup>. High accumulation factor also known as bioaccumulation factor

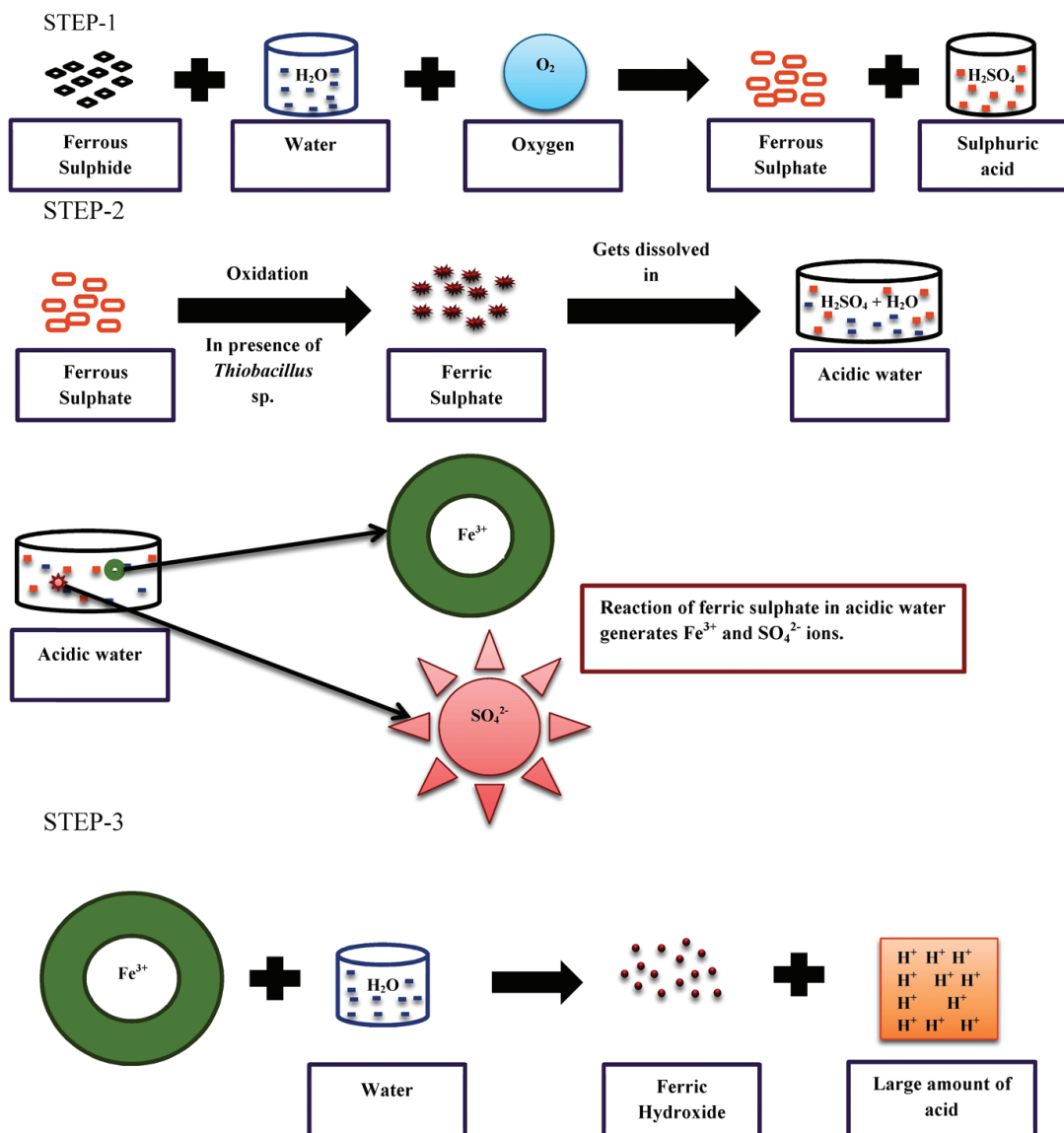


Figure 1. Mechanism of formation of acid mine drainage.

is used to determine the intake and storage capacity of pollutants in plants. The ratio of concentration of metal in the root tissues of the plants to that of concentration of metal pollutant in the environment gives the bioaccumulation factor. For a plant to be considered as hyperaccumulator, it must have a bioaccumulation factor of more than 1<sup>28</sup>. Similarly, the translocation factor is defined as the ratio of metal pollutant concentration in the shoots to that in the roots of the plants. Plants having translocation factor more than 1 are considered to have high efficiency for translocation of metals from roots to shoots<sup>29</sup>. Plants such as *Cyperus alternifolius* and *Chrysopogon zizanioides* are highly acid tolerant species and have been reported to thrive under pH as low as 2.4. These plants not only help in neutralising the acidic water from mines, but also have been found to remove significant amount of sulfate. Wide range of plant species like *Chrysopogon aciculatus*, *Sesbania rostrata*, *Cynodon dactylon*, *Melaleuca alternifolia* etc. have been successfully used for remediation of heavy metals from soil and water affected by acid mine drainage<sup>30</sup>. Species like *Acacia auriculiformis*, *Acacia confusa*, *Jatropha carcass* and *Melaleuca armillaris* can even survive at pH near about 2.0 and are a viable option for remediation of acid mine water and can act as a potential biofuel feedstock (Table 2)<sup>31</sup>.

**Table 2. Plant species responsible for remediation of acid mine drainage**

Plant species	Function
<i>Cyperus alternifolius</i>	Acid tolerant up to pH=2.4
<i>Chrysopogon zizanioides</i>	Removal of sulfate
<i>Chrysopogon aciculatus</i>	Acid tolerant
<i>Sesbania rostrata</i>	Removal of heavy metals
<i>Cynodon dactylon</i>	like Fe, Cu, Cr etc.
<i>Melaleuca alternifolia</i>	
<i>Acacia auriculiformis</i>	Acid tolerant (pH 2.5 to 2.0)
<i>Acacia confusa</i>	
<i>Jatropha carcass</i>	Potential biofuel feedstock
<i>Melaleuca armillaris</i>	

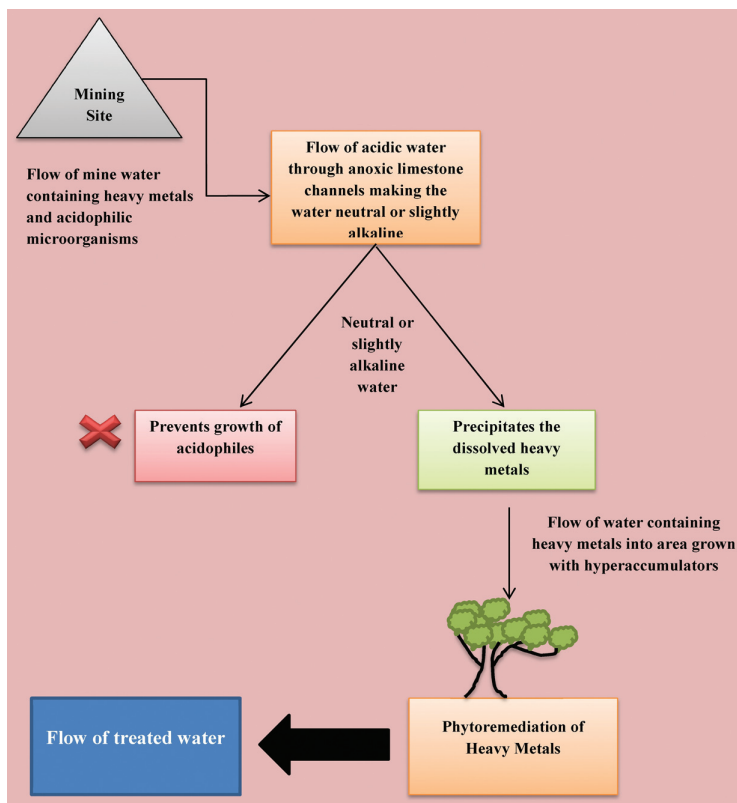
Remediation of acid mine drainage water through plants assisted with rhizospheric microbes and soil amendments still poses certain drawbacks but very less as compared to other techniques. The first drawback in the case is the selection of proper plants. Not every plant will be able to survive in the polluted acidic conditions. As such ideal plants for the purpose must be chosen which will be able to grow in low levels of nutrient concentration, various weather conditions and must be able to accumulate more amounts of contaminants than other normal plants could. These specific characteristics make it difficult for selection of ideal plants for remediation of acid mine drainage. Other drawback is that there are chances of animal consumption of the contaminated vegetation used in the remediation process<sup>27</sup>.

In this paper, a hypothetical model has been proposed (Fig. 2) which suggest ways to remediate acid mine drainage water through hyperaccumulator plants. It has been reported that soil augmented with chemicals like anoxic lime stone<sup>32</sup>helps in increasing the available metal fraction

for plants in the soil. The anoxic limestone helps in making the acid mine drainage water neutral or slightly alkaline thus preventing the growth of acidophilic bacteria. First the acidic water from the mines should be passed through compartments or beds containing limestone channels. The change in pH from acidic to neutral or alkaline conditions would prevent the growth of acidophilic microorganisms, which are responsible for increasing the acidity of the mine water. Further, it would also precipitate the dissolved toxic heavy metals present in the water. The alkalized mine water along with the precipitated heavy metals then should be allowed to flow into an area grown with hyperaccumulators. These hyperaccumulators will help uptake the heavy metals from the stream and render the polluted mine water harmless up to a great extent.

### 5.2 Nanoremediation

Nanoremediation is comparatively a new technology, currently in its nascent stage which implements nano-sized particles (having diameter less than 100 nm) for remediation of polluted water and soil. Zero-valent iron is an emerging and important tool in the field of nanoremediation and has been able to successfully treat acidic water polluted with several heavy metal pollutants<sup>33</sup>. Zero valent iron effectively and rapidly neutralizes the acid in mine water and removes dissolved heavy metals by immobilising them. Studies reveal that removal of heavy metals is mainly due to adsorption of the same onto the surface of nano sized iron particles. The corrosion products of iron, present on the unreacted metal surface also serves as a site for adsorption. Gradually the metal uptake process becomes slow and can be accelerated



**Figure 2. Hypothetical model for treatment of mine drainage water employing hyperaccumulators.**

even further by the presence of sulfate-reducing bacteria<sup>34</sup>. Sometimes the surface of the zero valent iron is coated with an oil liquid membrane to form an emulsified zero valent iron particle<sup>35</sup>. Another form of nanoparticle being used is the bi-metallic nanoparticles. This type of nanoparticle generally consists of a combination of metal and metal catalysts. These bi-metallic nanoparticles increase the kinetics of redox reactions, thus catalysing it. The most commonly used nanoparticles of such types are the combination of iron and palladium<sup>36</sup>. In the recent years, nanomaterial in the form of carbon nanotubes has been introduced for remediation of polluted water. These nano tubes are highly effective due to their unique adsorption properties and their affinity towards the molecule of target<sup>37</sup>. The carbon tubes are stable both chemically and thermally and act as a substitute to activated carbon. These are mainly used in removal of heavy metals like chromium, lead and zinc. They also help in removing various biological impurities and many types of organic and inorganic compounds<sup>38</sup>. Although nanoremediation has been successfully implemented in the remediation of mine water but still it raises many questions that remain unanswered. More work needs to be carried out, to reveal the toxicological aspects of the nanoparticles on the components of environment<sup>39</sup>. This leads to, many drawbacks and risks related to the use of nanoparticles.

### 5.2.1 Drawbacks and Risks Associated with use of Nanoparticles

The use of nanoparticles is a rapidly emerging technique with large number of benefits. Studies show it to be a very quick and efficient method for remediation of ground water<sup>36</sup> and surface water<sup>40</sup> as well as the contaminated soil<sup>41</sup>. There still exists certain drawbacks and risks associated with the use of nanoparticles such as nano zero valent iron (nZVI), which may be attributed to the lack of proper or complete knowledge on the way these nanoparticles behave in the environment and their possible ecological implications. High concentrations of nZVI can agglomerate to form clusters, thus losing the effectiveness as a nanoparticle. Further, the risk to human and ecological health still remains unknown<sup>42</sup>. Nanoparticles because of their small size and higher mobility can easily disperse in the environment and thus spread to larger distance causing ecotoxicity. The nanoparticles are also highly persistent in nature and have the risk of bio-accumulating in the living organisms<sup>43</sup>. Certain nanoparticles like nZVI have wide adverse effect on living entities. Certain bacterial pure cultures like the sulphate reducing bacteria are able to oxidize nZVI. However, oxidization of high concentration of nZVI leads to the formation of reactive oxygen species (ROS)<sup>44</sup>. Generation of ROS may cause oxidative stress, damaging the cell membrane and may ultimately lead to death. Reports suggest that higher concentration of nZVI in plants show stronger toxic effect, thus reducing the transpiration rate and translocation to the shoots<sup>45</sup>. Reduced transpiration and translocation in the plants may result in stunted growth of some plants and may lead to death of the plant after an exposure for an extended period. In case of humans, exposure of nanoparticles has been reported to cause genotoxicity, inflammation,

oxidative stress, lipid peroxidation, pulmonary disease<sup>46</sup> and may ultimately lead to death.

## 6. SOLUTIONS TOWARDS EFFECTIVE MANAGEMENT OF PROPOSED TECHNIQUES

The two techniques proposed for the treatment of mine drainage water have their own pros and cons as depicted (Table 3).

The technique of nanoremediation although being very quick and efficient has numerous drawbacks and ecological risks associated as discussed in the previous section. The problems related, can be sorted out by providing better solutions for effective management of the same. Use of green nanoparticles synthesized from plant and plant parts<sup>47</sup> reduces release of toxic by-products into the environment<sup>48</sup>, thus reducing ecological toxicity. Similarly, employing nanoparticles derived from microbes also known as bio-nanoparticles can be a quick and efficient method for biodegradation of heavy metals present in acid mine water. Fungi also referred to as 'Nanofactories' are extremely suitable for synthesising metal nanoparticles<sup>49</sup>. The drawbacks related to zero valent iron can be overcome by use of emulsified zero valent iron (E-ZVI) which are prepared by encapsulating iron nano particles in biodegradable oil membrane. This is because the surface coating protects the zero valent iron nano particle from other constituents or inorganic pollutants, which may react with the iron, reducing its capacity<sup>50</sup>. These few solutions can be effectively used against the drawbacks and risks posed by the use of nanoparticles in remediation of acid mine drainage water.

As a solution to the problems the activity of plants before selection for the remediation process must be well studied and its effectiveness should be confirmed. Use of ideal plants along with suitable soil amendments and rhizospheric microorganisms, all together as a system (as proposed in Fig. 2) can prove to be an effective remedial strategy. Consumption of the plants involved in the remediation process can be prevented by fencing the area earmarked for phytoremediation.

**Table 3. Pros and Cons related to the proposed techniques – Phytoremediation and Nanoremediation**

Techniques	Pros	Cons
Phytoremediation	Remediation of huge amount of metals is possible, can be employed on a large scale basis, Eco-friendly, cost-effective.	Proper selection of plants needed, chances of animal consumption of the vegetative parts of the plant, remediation is slower.
Nanoremediation	Rapid, effective due to small size and high surface area.	High cost, chances of accumulation in living organisms, chances of causing eco-toxicity, large scale implementation is not feasible.

## 7. CONCLUSION

Acid mine drainage water is a serious threat to the environment and its remediation is utmost necessary. Although there are many chemical processes for the treatment of the polluted water but still, none of them have been able to solve the problem completely. Besides, these methods are very costly and may form by-products that may be harmful for the living organisms. Taking the current scenario into consideration, new emerging and eco-friendly techniques like phytoremediation and nanoremediation needs to be adopted. Phytoremediation process though takes a longer time but still may be considered as a better alternative due to its low cost and environment friendly approach. The nanoremediation process involves the use of nano particles that are although quite effective but at the same time very costly. This indicates that further research needs to be carried out to devise cheap methodologies for the synthesis of nanoparticles, thus making their use possible on a large scale basis. The hypothetical model discussed in the current review may assist in increasing the phytoremedial ability of the hyperaccumulator plants, thus effectively treating acid mine water and the constituent pollutants in it. The emerging fields of phytoremediation as well as nanoremediation need to be considered by researchers for further in depth study. These techniques have all the potentiality to emerge as a better alternative to other treatment methods in the years to come.

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## CONFLICT OF INTEREST

The author declares there is no conflict of interest.

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## CONTRIBUTOR

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