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Challenges and opportunities in the removal of sulphate ions in contaminated mine water: A review

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ABSTRACT

Metal sulphates are one of the major contributors to acid mine drainage (AMD) or acid rock drainage (ARD). AMD occurs by the oxidation of metal sulphides. Sulphides produce sulphates and eventually acidify the medium by converting to sulphuric acid. As AMD contaminates the water sources downstream, the set limit of sulphates for human consumption gets compromised. Stringent standards are imposed on, to comply with limitations set by the regulatory bodies. World Health Organization (WHO) emphasises on a 250 mg/L sulphate concentration in water for human consumption. Therefore, curing AMD of sulphates has become one of the prominent issues in water research. Unregulated disposal of such drainage may cause the increase in salinity and increase in the pH, which can be detrimental to the utility of the water downstream. Corrosion, scaling and health implications are definite results of AMD. Numerous approaches are available to treat sulphates from AMD. Suitability of a specific method depends on the level of removal expected, environmental legislations, available resources, space required, economy and volume of the contaminated water. Several approaches which have demonstrated promising results in the laboratory scale, but their viability at the industrial scale is yet to be established.

This paper reviews the remediation methods which are currently in practice. It discusses the approaches in two main topics, both conventional and recent developments. While the conventional methods include lime, limestone and wetlands, the recent developments include filtration, electrocoagulation, adsorption, ion exchange and precipitation with the introduction of a certain level of novelty throughout the last few years. It is well established that lime and limestone treatment of AMD are well suited for pre-treatment processes whereas the rest of the methods can be selected upon the site specific requirements. Even though the novel methods show their potential to reduce sulphate ions greatly, these need to be tested at industrial scale in order to identify the overall effectiveness.

1. Introduction

Water has been one of the fundamental requirements of human civilisations. Although, water covers more than 70% of the earth's surface, only less than 1% is available for human consumption (National Geographic Society, 2017). Despite the shortage of potable and good quality water around the world, numerous anthropogenic activities have surged the contamination of the available water resources. Acid mine drainage (acid rock drainage or acid and metalliferous drainage) is one such source of water pollution mainly associated with mining and minerals processing activities. This phenomenon naturally occurs due to pyrite oxidation when supported by air and water, where the products are sulphuric acid and dissolved iron. The acidic streams generate consequent to AMD will dissolve heavy metals and pollute both surface and ground water resources. Countries inheriting a legacy of historical mining, face a serious water pollution threat due to AMD. Even though the contaminated water contains species of heavy metals in addition to high sulphate levels, this work will focus on a specific aspect of AMD namely, the sulphate removal mechanisms and techniques.

Oxidation of metal sulphides is the main contributing factor for the introduction of the sulphates into the water streams. As most of the metals naturally occur as sulphides, those have become common minerals responsible for water pollution especially during mining activities. According to the World Health Organization (WHO) and US Environmental Protection Agency (EPA), water for human consumption should ideally contain less than 250 ppm of sulphates (Balintova et al., 2015; US EPA, 2017) albeit most of the mining effluents exceed the set limit. When the sulphate concentrations for human consumption are compromised, the human health concerns would naturally arise (Backer, 2000). Scaling of pipes and corrosion are major concerns in the

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industrial level once sulphate concentrations are higher and therefore the removal of sulphate from water has become a concern worth addressing (Del Ángel et al., 2014; Gomelya et al., 2014; Hong et al., 2014; Iakovleva et al., 2015; Amaral Filho et al., 2016; Ntui et al., 2016).

Remediation methods are available in different forms namely, physical, chemical and biological (Swanepoel, 2011), which are further divided into active and passive techniques, where the words merely imply the amount of maintenance required. Active methods require high maintenance and the passive methods are not completely independent of maintenance, but require a certain level of maintenance (Johnson and Hallberg, 2005). The traditional sulphate removal techniques include precipitation, but the latest research and technological advancements have helped us understand the intricacies of reactions. Several novel processes have been introduced to treat the sulphate in contaminated water and suitability of the option may depend on the requirement and the economy. For example, AMD treatment with granular activated carbon (GAC) and phytoremediation have recently captured greater attention of the scientific community. In addition, a number of hybrid methodologies have been implemented to catapult the effectiveness of the sulphate removal from AMD (Geldenhuys et al., 2003; Maree et al., 2004). Innovative processes and compounds have been recently developed in laboratory conditions capable of eliminating the sulphate contamination effectively (eg. activated carbon, Amberlyst A21 resins for ion exchange, dissolved air floatation, desilicated fly ash, unactivated attapulgite) but scaling up of those for industrial purposes has been extremely challenging (McCarthy, 2011). Therefore, it is observed that seeking for a perfect remediation method is merely impossible, however, most productive technique is acceptable to be adopted.

This paper will present a critical and a comprehensive review of the various methods in the area of sulphate removal from AMD. Both the traditional and the novel technologies will be discussed in this paper, along with their applications, effectiveness and economic suitability. This will not only present a mere description of the sulphate treatment methods but will also output comprehension of the positives and the negatives of the respective techniques to treat AMD.

2. Sulphate ions by mining activities

Formation of AMD can take place either naturally or by anthropogenic activities. Naturally, AMD is a part of the rock weathering process, whereas industrial effluents, gas scrubbers and mining activities artificially introduce the sulphates into the eco-systems.

Some of the metals are currently extracted from their respective sulphide ores, for example, iron (pyrite), zinc (sphalerite), copper (chalcopyrite) and nickel (pendanlite) (Keith and Vaughan, 2000; Johnson and Hallberg, 2005). Oxidation of these metal sulphides thus results in the production of AMD (Evangelou, 1995; Bowell, 2004).

The ores are chemically stable under in-situ or saturated environments without the contact of oxygen and water, but once exposed to water and atmospheric oxygen, the sulphide oxidation will commence to form AMD (Blodau, 2006). Sulphide oxidation is a natural phenomenon, where the causes are identified to transcend the beliefs of oxygen and water being the usual culprits. Additional sulphide oxidizers are identified as hydroxyl ions and CO_2 in different environmental conditions (Evangelou and Zhang, 1995).

Sulphide oxidation occurs due to both abiotic and biotic reasons. Abiotic oxidation refers to the involvement of an inorganic chemical compound whereas biotic reactions occur due to microorganism involvement (Evangelou and Zhang, 1995; Van der Zee et al., 2003; Johnson and Hallberg, 2003, 2005). Firstly, emphasising on the abiotic oxidation, mining of sulphide ore introduces the stable ore to both air and moisture (Eq. (1)).

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 4SO^{2-}_{4(aq)} + 4H^{+}_{(aq)} \tag{1}$$

Both direct and indirect oxidations are possible in the abiotic process. Eq. (1) presents the direct oxidation reaction where oxygen, along with moisture, is responsible for the production of sulphates. Oxygen dominates further in oxidizing the dissolved ferrous and results in ferric (Eq. (2)).

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \tag{2}$$

Ferric typically precipitates as $Fe(OH)_3$ at pH values between 2.3 and 3.5 (Akcil and Koldas, 2006, Eq. (3)). Afterwards, the oxidation takes place indirectly and the resulting ferric oxidizes the pyrite (Eq. (4)).

$$Fe^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 3H^{+}_{(aq)} \tag{3}$$

$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 16H^{+}_{(aq)} \tag{4}$$

Banks et al. (1997) presented that pyrite oxidation leads to the production of more acid, than it consumes as illustrated in above reactions (Eqs. (1) and (4)) and the medium thus remains acidic. Consequently, the ferric initially precipitates as $Fe(OH)_3$ and the leftover ferric reacts with pyrite and generates an additional sulphate concentration (Johnson and Hallberg, 2003; Akcil and Koldas, 2006).

The overall reaction of sulphate generation (when additional ferrous is available to oxidize pyrite) is given in Eq. (5) (Akcil and Koldas, 2006):

$$8FeS_{2(s)} + 52Fe^{3+}_{(aq)} + 15O_{2(g)} + 34H_2O_{(l)} \rightarrow 60Fe^{2+}_{(aq)} + 16SO^{2-}_{4(aq)} + 68H^{+}_{(aq)} \tag{5}$$

Eqs. (1)–(5) are related to iron based sulphide minerals and the same equations can be inferred for any other mineral inclusive of sulphides as well. The inference can be justified as most of the ores exist in association with pyrite (Spears et al., 1994; Banks et al., 1997). In addition, AMD occurs if 1–5% of sulphur content is available in the form of pyrite in the substance (Tiwary, 2001).

In open-pit mining, water draining from stockpiles of ore, washers, processing areas and waste, augments sulphate concentration of the eco systems (Kuyucak, 1999). However, in underground mining operations water is a major distraction (Rapantova et al., 2007; Mudd, 2008; Altun et al., 2010). Therefore, water is constantly pumped out in order to maintain the water table at a lower level. The process is carried out to hinder the reaction between the minerals and moisture. As the mining activities cease, free access is granted to complete the reaction between water and the ore along with the air. The contaminated water eventually reaches the groundwater sources and contaminates the complete water body.

In addition to the chemical reactions, microorganisms are also capable of oxidizing the sulphide minerals (biotic processes). Prokaryotic microorganisms are well documented as both iron oxidizers/reducers and sulphur oxidizers (Norris et al., 1996; Cha et al., 1999; Johnson and Hallberg, 2003; Rawlings, 2005; Johnson, 2006; Akcil and Koldas, 2006; Vidyalakshmi et al., 2009). The energy released from the sulphide oxidation process is utilized by the microorganisms to remain metabolically active at difficult conditions (Vishniac and Santer, 1957; Johnson and Hallberg, 2003). The main microorganism families are explained thoroughly by Bosecker (1997) as thiobacillus, leptospirillum and thermophilic bacteria. Sub divisions of the above families carry the prefixes T-, L- and Th-respectively. Microorganisms such as Leptospirillum ferrooxidans, Acidithiobacillus ("At.") ferrooxidans, Acidimicrobium ("Am.") ferrooxidans and Sulfolobus metallicus are well known for the ability to oxidize the metal sulphides (Johnson and Hallberg, 2003). While the oxidation takes place, sulphuric acid is extensively produced, which lowers the pH and eventually leads to the dissolution of the solid sulphides (Bosecker, 1997) increasing the overall sulphate concentration. However, this characteristic behaviour of microorganisms is utilized and targeted in the area of bio-mining (bio-leaching) for the extraction of gold and base metals (eg. copper) from their low grade ores (Johnson and Hallberg, 2003; Rawlings, 2005).

Correspondingly, polysulphide mechanism along with microbes also gives rise to sulphate generation (Rawlings, 2005). The chemical equations are detailed in Eqs. (6) and (7), where metal sulphide is denoted as MS:

$$2MS_{(s)} + 2Fe^{3+}_{(aq)} + 2H^{+}_{(aq)} \rightarrow 2M^{2+}_{(aq)} + H_2S_{n(aq)} + 2Fe^{2+}_{(aq)} \quad (n \geqslant 2) \tag{6}$$

$$4H_2S_{n(aq)} + 8Fe^{3+}_{(aq)} \rightarrow S_{8(s)} + 8Fe^{2+}_{(aq)} + 8H^{+}_{(aq)} \tag{7}$$

Evidently, protons and the ferric ions convert the sulphide mineral to a polysulphide, and eventually to elemental sulphur (Eq. (7)). The microbes act upon the elemental sulphur and results in additional sulphate production (Eq. (8), Friedrich, 1997; Cha et al., 1999; Rawlings, 2005).

$$S_{8(s)} + 12O_{2(g)} + 8H_2O_{(l)} \xrightarrow{microbes} 8SO^{2-}_{4(aq)} + 16H^{+}_{(aq)} \tag{8}$$

With the increasing population, as the requirement for mineral resources grows, mining activities around the world will also grow simultaneously (Mudd, 2009). Some of these mining activities will give rise to AMD and resultant sulphate concentration in water resources. Therefore, necessary management responses are mandatory to control the sulphate concentration of the effluents released to the environment. Table 1 presents a variety of mining activities that contributed to the sulphate concentrations in the water around the world. It demonstrates the critical information on how far mining activities have contributed to the elevated sulphate concentrations around the world. The reported values are well above the concentrations prescribed by the WHO or US EPA standards (i.e. 250 ppm of sulphate in consumable water – Balintova et al., 2015; US EPA, 2017). Mining companies find it extremely challenging to cope with AMD abatement, as the costs for remediation of the effluents run into millions of dollars. The tailing dams and wetlands are the most economically viable retention method of the mining by-products as a temporary solution without releasing the sulphate rich water to nearby water streams. However, a failure of a tailing dam brings catastrophic results to both the environment and human lives. In one such accident in the USA approximately 8,40,000 m^3 of contaminated liquid reached a Floridan drinking water aquifer and in China, a village was completely submerged by 2 million cubic meters of red mud (Wise Uranium Project, 2017).

Although there are several AMD treatment methods exist at the laboratory scale that promise high contaminant removal, a considerable attention has now been given to the applicability to larger scale applications in the field. The field application is challenged by the host of issues, such as the volume of effluents to be treated, contaminants present and method of which affect the eventual remediation bill. Therefore, effective processes are in demand to address the issues posed by AMD.

3. Conventional sulphate removal methods

3.1. Lime treatment

The application of lime to treat AMD is a cost-effective technique that has been used to precipitate the sulphates from the contaminated water. The process is continuous in order to both neutralize the acidic water and precipitate metals, hence enlisted in the active treatment family (Johnson and Hallberg, 2005). Applicability of this method mainly depends on the low solubility of metal hydroxides in the contaminated water, therefore, pH plays a major role in evaluating the effectiveness of the process (Aube et al., 2003). Although other active systems incur more capital and operational costs, lime treatment is preferred due to the ability to remove dissolved heavy metals and the offered numbness to temperature changes (Khorasanipour et al., 2011).

Dissolution of lime promotes the alkalinity of the media by which metal hydroxide precipitation is encouraged. Eqs. (9) and (10) (where M^{2+}/M^{3+} is a metal ion) illustrate the effectiveness of lime in precipitating metals as hydroxides in sulphate contaminated water along with the formation of gypsum ($CaSO_4$) where the mixture is well known as “sludge” in this particular treatment method (Aube et al., 2003).

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)} \tag{9}$$

$$Ca(OH)_{2(s)} + M^{2+}/M^{3+}_{(aq)} + H_2SO_{4(aq)} \rightarrow M(OH)_2/M(OH)_{3(s)} + CaSO_{4(s)} + H_2O_{(l)} \tag{10}$$

Lime exhibits hydrophobic characteristics, hence require intense mechanical mixing in order to disperse in water (Skousen et al., 2000). The typical utility of lime treatment is, to raise the pH of the solution and precipitate the heavy metals. Indeed, a partial removal of sulphate is much expected to leave a gypsum saturated solution to be further treated. Hence, lime is mainly considered as a pre-treatment process (Robertson and Rohrs, 1995; Akcil and Koldas, 2006). It is expected that more lime will lead to more metal precipitation, conversely, more lime creates more unreacted lime and decreases overall sulphate removal efficiency.

Geldenhuys et al. (2003) investigated a contaminated sample with an initial sulphate concentration of 3000 mg/L. In this study, the sample was mixed with both lime and limestone. Limestone treatment brought down the sulphate concentration to 1900 mg/L and further treatment with lime, the sulphate levels were reduced to 300 mg/L, beyond the anticipated level of 1200 mg/L of sulphate. The system was independent of scaling as the medium was well below the gypsum saturation level, which is 1500–1800 mg/L (Geldenhuys et al., 2003; Bowell, 2004).

Khorasanipour et al. (2011) presented lime treatment efficiencies using contaminated water at Sarcheshmeh porphyry copper mine in Iran, where the initial sulphate concentration was recorded as

Table 1
Sulphate concentrations of AMD at different mining operations.

Location	Type of mine	Sulphate concentration (mg/L)	Reference
Witwatersrand Basin, South Africa	Gold	4800	Bologo et al. (2017)
Harmony mine, South Africa	Gold	4800	Motaung et al. (2008)
Abandoned mine Guanajuato, Mexico	Silver	3567	Del Ángel et al. (2014)
Mine site in Pennsyvania, USA (after lime treatment)	Coal	773	Hong et al. (2014)
Copper Mine, China	Copper	20800	Bai et al. (2013)
Carnoule’s mine, France (inactive)	Lead-Zinc	2000–7500	Giloteaux et al. (2013)
Sarcheshmeh Mine, Iran	Copper	3000	Ardejani et al. (2008)
Landau Colliery, South Africa	Coal	2650	Maree et al. (2004)
Brown Mine, Czech Republic	Coal	500–3500	Vidlář et al. (2002)
Chessy Mines, France	Copper	5000	Foucher et al. (2001)
Nickel Rim Mine Site, Canada	Nickel	2400–4600	Benner et al. (1997)
Avoca Mines, Ireland	Copper	10579	Gray (1996)
Gauteng Western basin region, South Africa	N/A	3500	Agboola et al. (2017)

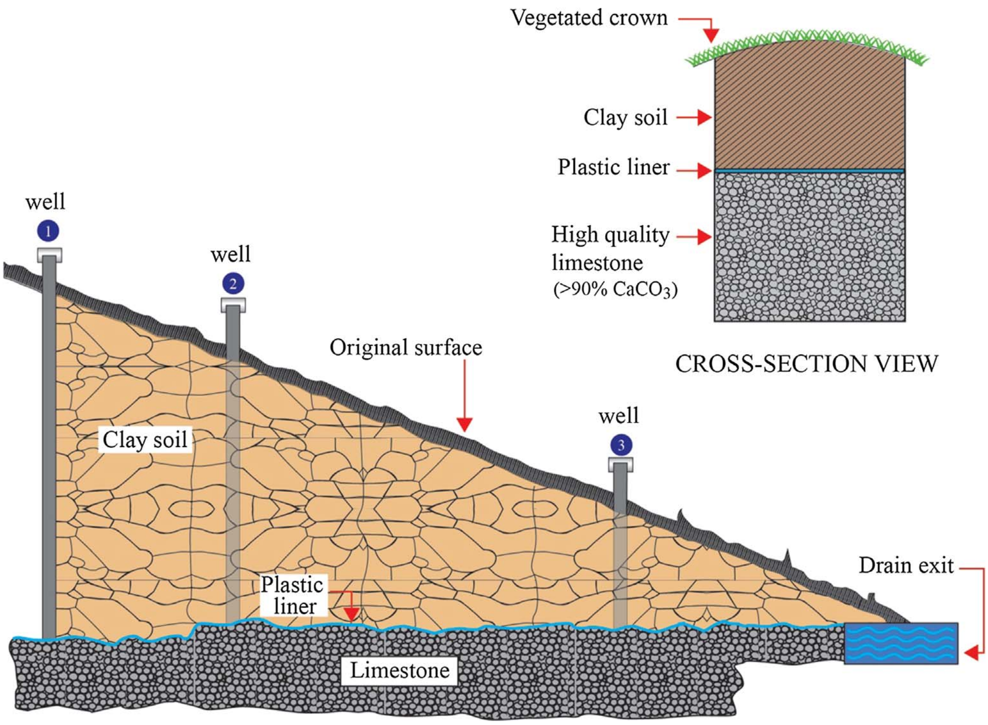

Fig. 1. Layout of a Limestone bed/ALD for AMD treatment. Reproduced from Gazea et al. (1996) with permission from Minerals Engineering.

2000–3000 mg/L. With the lime treatment a drop in the sulphate value to 800–900 mg/L was reported eventually, which is far better than a partial removal (Ardejani et al., 2008; Khorasanipour et al., 2011).

3.2. Limestone treatment

The use of limestone is considered to be a step forward from the conventional lime treatment. Limestone beds are often constructed as anoxic limestone drains (ALD) which have no contact with the atmosphere (Fig. 1). The primary objective of adding limestone is to introduce alkalinity to the solution thereby neutralizes the AMD (Dvorak et al., 1992; Gazea et al., 1996; Johnson and Hallberg, 2005). Subsequently, the dissolved iron in the solution remains in its reduced form ferrous and no precipitation will occur below pH 5.5 (Gazea et al., 1996). The lime treatment holds additional management of the sludge generated by the precipitation of calcium salts. On the contrary, the use of limestone, promotes sulphate sorption on the limestone's surface, which leaves very little maintenance (Ziemkiewicz et al., 1997; Johnson and Hallberg, 2005; Akcil and Koldas, 2006).

A plastic liner is placed over the limestone bed to inhibit oxygen supply into the solution. If oxygen is allowed to the system an oxidizing environment is created. Subsequently, ferrous is converted to ferric. Afterwards, $Fe(OH)_3$ precipitates on the limestone which covers the surface. Further passivation may occur by precipitation of gypsum, silica, clay minerals and $Al(OH)_3$ (Hammack et al., 1994). The chemical reactions of the limestone process are as follows (Gazea et al., 1996):

$$CaCO_{3(s)} + 2H^{+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2CO^{*}_{3(aq)} \tag{11}$$

$$CaCO_{3(s)} + H_2CO_{3(aq)} \rightarrow Ca^{2+}_{(aq)} + 2HCO^{-}_{3(aq)} \tag{12}$$

$H_2CO_3^*$ in Eq. (11) is conventional for dissolved CO_2. Alkalinity is provided to the system by the bicarbonate ion, hence to promote the bicarbonate production most systems increase the partial pressure of CO_2 (Hedin et al., 1994; Johnson and Hallberg, 2005) as limestone's solubility generally depends on temperature, pH and CO_2 concentration (Gazea et al., 1996). Additionally, the cost saving from chemicals adopting a limestone fluidised bed is 29–38% of lime, although the capital costs remain the same as lime treatment (Maree et al., 1992; Potgieter-Vermaak et al., 2006).

A recent study carried out by Silva et al. (2012) on the sulphate removal from AMD with calcite (limestone assaying above 50% calcium), using two different particle sizes in the experiments. The first one was in the range of 0.42–0.59 mm and the other being less than 0.045 µm. The samples tested contained initial sulphate concentrations of 588, 800 and 1100 mg/L with a pH value of 6.5. To study the sulphate sorption on limestone the coarser particles were used in fixed bed column experiments while the finer particles were employed in stirred tank (rpm 1200) experiments. The study resulted in a sulphate loading of 8.3 mg-sulphate/g-limestone for finer particles in the initial concentrations of 588 mg/L. Considering the other sulphate loading values reported by Namasivayam and Sangeetha (2008), limestone can be considered to be an economical alternative for sulphate removal. The coarser particle's sulphate sorption on limestone fitted the Langmuir isotherm, which predicted a maximum loading of 23.7 mg-sulphate/g-limestone. The analysis was made with variable flow rates (i.e. 1, 2, 3 and 10 mL/min) and variable bed heights (i.e. 10, 15, 20 and 25 cm). The study revealed that the sulphate loading capacity increased with the increasing flow rates and with the increasing bed heights. Higher the initial sulphate concentration (1100 mg/L), higher the sulphate loading recorded on limestone, which corresponded to a 19.34 mg-sulphate/g-limestone at 25 cm bed depth and 10 mL/min. At low flow rates a lower sulphate loading was recorded, conversely, an increased flow rate ascribing to a decreased film resistance affected positively to the mass transfer (Silva et al., 2012).

Hedin et al. (1994) reported that according to the study's test conditions, 17% of the initial sulphate concentration was retained in the limestone bed. The study also revealed that the lifetime of the facility to be in excess of 20 years, which makes the investment worthwhile. Geldenhuys et al. (2003) suggested the limestone process integrated with lime yields better results. The objective of Geldenhuys et al. (2003) study was to reduce the sulphate concentration from 3000 to 1200 mg/L, which was successful with initial limestone neutralization (reduction of sulphates from 3000 to 1900 mg/L). Maree et al. (1998) documented a sulphate reduction from 15,000 to 2000 mg/L with limestone neutralization. However, the gypsum saturation level must be carefully observed as limestone dissolution ceases once the solution is saturated to gypsum (Geldenhuys et al., 2003). Therefore, pre-treatment is in order and the effluent from the limestone treatment may be routed to a wetland or integrated with another treatment process to achieve better results (Gazea et al., 1996; Johnson and Hallberg, 2005). Conversely, if the sulphate loading exceeds the gypsum precipitation limits considerably, lime treatment is still preferred over limestone as a cost-effective and a highly efficient approach (Silva et al., 2012).

3.3. Wetlands

Employment of wetlands to treat contaminated water is becoming very attractive, which coincides with the sustainable environmental concept. The technique was extensively studied in the lab scale and initially used for acidic water with low metal content (Gazea et al., 1996). The main contributors in wetland treatment system are the microbes and the method is less labour intensive, hence enlisted in the passive biological remediation type (Gazea et al., 1996; Johnson and Hallberg, 2005). The microbial activity plays a vital role in wetland treatment method (Webb et al., 1998; Kosolapov et al., 2004; Whitmire and Hamilton, 2005; Sheoran and Sheoran, 2006). Microbes can perturb the mobility, toxicity and bioavailability of metals as a whole. They are also capable of biosorption, metal sulphide precipitation by sulphate reducers, redox transformations and micro species-plant interactions (Kosolapov et al., 2004; Johnson and Hallberg, 2005).

The wetlands are constructed (constructed wetlands) to emulate the natural counterparts by understanding the scientific phenomena and the contributing factors in purification. Constructed wetlands are mainly of two types, namely, aerobic and anaerobic (Johnson and Hallberg, 2005; Sheoran and Sheoran, 2006). Aerobic is the type where oxygen is freely available and anaerobic is the exact opposite.

As ferric and sulphates are main attributes of AMD (Johnson and Hallberg, 2005), the role of wetlands would be to produce alkalinity (Eq. (13)) and reduce the already oxidized ferric and sulphate (Gazea et al., 1996). The first step of producing alkalinity is thoroughly influenced by the photosynthetic microorganisms, which feed on the weak bases (i.e. bicarbonate).

$$HCO^{-}_{3(aq)} + 6H_2O_{(l)} \rightarrow C_6H_{12}O_{6(s)} + 6O_{2(g)} + 6OH^{-}_{(aq)} \tag{13}$$

The microorganisms produce strong base, where the system becomes net alkaline (Eq. (13)). As the alkalinity increases in the system, the solid phase ferric ions convert to aqueous ferrous ions (Eq. (14)).

$$Fe(OH)_{3(s)} + 3H^{+}_{(aq)} + e^{-} \rightarrow Fe^{2+}_{(aq)} + 3H_2O_{(l)} \tag{14}$$

The electron is provided by an organic substrate (Johnson and Hallberg, 2005). By the reduction of ferric to ferrous, indirect oxidation of pyrite is avoided (Eq. (4)). Consequently, the organic matter available in the substrate reacts with the sulphates (Eq. (15), CH_2O represents an organic substrate) (Gazea et al., 1996; Johnson and Hallberg, 2005; Sheoran and Sheoran, 2006).

$$2CH_2O_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow H_2S_{(aq)} + 2HCO^{-}_{3\,(aq)} \tag{15}$$

Additionally, the generated bicarbonates involve again in increasing the alkalinity of the media (Eq. (13)). The release of hydrogen sulphide facilitates the metal sulphide precipitation eventually. Eq. (16) presents (M^{2+} is a metal) the chemical reaction responsible for metal sulphide precipitation (Gazea et al., 1996; Johnson and Hallberg, 2005; Sheoran and Sheoran, 2006).

$$M^{2+}_{(aq)} + H_2S_{(aq)} + 2HCO^{-}_{3(aq)} \rightarrow MS_{(s)} + 2H_2O_{(l)} + 2CO_3^{2-}{}_{(aq)} \tag{16}$$

3.3.1. Aerobic wetlands

Aerobic wetland systems (Fig. 2a) are employed to remediate neutral or alkaline water, where the main processes responsible are highlighted as ion exchange and adsorption (Eger, 1994; Johnson and Hallberg, 2005). Whilst oxygen is freely available in aerobic systems Eqs. (2) and (3) become dominant and precipitation takes place along with a lowered pH. Macrophytes are observed in aerobic wetlands to provide both aesthetic beauty and to enhance the microbial activities below ground (Ledin and Pedersen, 1996; Collins et al., 2004; Gangon et al., 2007; Yang et al., 2007; Lizama et al., 2011). As plants are involved in remediation, this methodology is widely known as phytoremediation (Salt et al., 1995; Terry and Benuelos, 1999; Weis and Weis, 2004; Horne and Fleming-Singer, 2005; Pilon-Smits, 2005). Aerobic wetlands naturally deal with surface flow and the plant roots readily create an oxygenated atmosphere in the soil layer to stimulate the oxidation of contaminants (i.e. ferrous) (Stottmeister et al., 2003; Johnson and Hallberg, 2005; Maine et al., 2006; Johnson and Younger, 2006; Gangon et al., 2007). However, if the system does not inherit sufficient alkalinity, a tendency exists to output rich iron effluents. To counter this, the system is induced alkalinity by introducing the influent to an anoxic limestone drain (ALD) (Collins et al., 2004; Johnson and Hallberg, 2005).

Aerobic wetlands have witnessed a novel counterpart in the recent years, which are floating wetlands. As implied by the word, floating wetlands are inclusive of macrophytes, which require no connection to the bottom sediments and are visible as a mat floating on the water surface (Headley and Tanner, 2008). Principles affecting the floating wetland remediation remain the same with the typical wetlands, but these have the ability to withstand different climate conditions (Kadlec and Wallace, 2008; Headley and Tanner, 2008; Tanner and Headley, 2011).

Maine et al. (2006) used a constructed wetland at the Bahco Argentina metallurgic plant in Argentina to evaluate the metal and nutrient removal efficiency whilst observing the sulphate concentration in the process. The chemical analysis of the inlet water is listed in Table 2. The constructed wetland in this particular study included three major locally available macrophytes namely, *Eichhornia crassipes* (water hyacinth), *Typha domingensis* (cattail) and *Panicum elephantipes* (elephant panicgrass) from which water hyacinth was noted as the dominant species with a surface cover of almost 80%. The inlet water was alkaline (Table 2), hence the treatment method was via an aerobic wetland. Oxygen concentration and the pH are important parameters in ferrous oxidizing kinetics (Eq. (17)) (Johnson and Hallberg, 2005).

$$\frac{d\,[Fe^{2+}]}{dt} = k\cdot\frac{[O_2]\cdot[Fe^{2+}]}{[H^{+}]^2} \tag{17}$$

The reduced value of oxygen (Table 2) reveals the oxygen involvement for the underlying ferrous oxidation. Sulphates are also tamed in the effluent recording 44% removal, which implies sulphide formation. Overall retention of Fe in the wetland was 95%, which accounts for the formation of both $Fe(OH)_3$ and FeS. It is worth highlighting the iron content because Eq. (4) suggests a relationship between ferric and ferrous in a solution to the formation of sulphates.

3.3.2. Anaerobic wetlands

On the other hand, anaerobic wetlands (Fig. 2b) are characteristically able to treat acidic water as alkalinity is generated through the reduction of sulphate and ferric (Eqs. (14) and (15)) (Eger, 1994). Inhibited root propagation towards the organic substrate is a mandatory requirement for an effective operation of an anaerobic wetland as the treatment of AMD is resulted by sub-surface flow. Root propagation promotes the oxygen ingress into the organic substrate, which in turn discourages the reductive actions (Hedin and Nairn, 1993; Johnson and Hallberg, 2005). The low cost substances and wastes, such as horse and cow manure, peat, hay bales, spent mushroom compost, sawdust and wood chips are well recognized organic substrates used in remediating AMD (Vile and Weider, 1993; Gazea et al., 1996). As the ecosystems get richer in organic matter, an optimal background is provided for sulphate reducing bacteria (SRB) to react (Taketani et al., 2010). These use sulphates/ferric ions as electron acceptors (eg. Eq. (15), Alphenaar et al., 1993) under anoxic conditions particularly in organic substrates

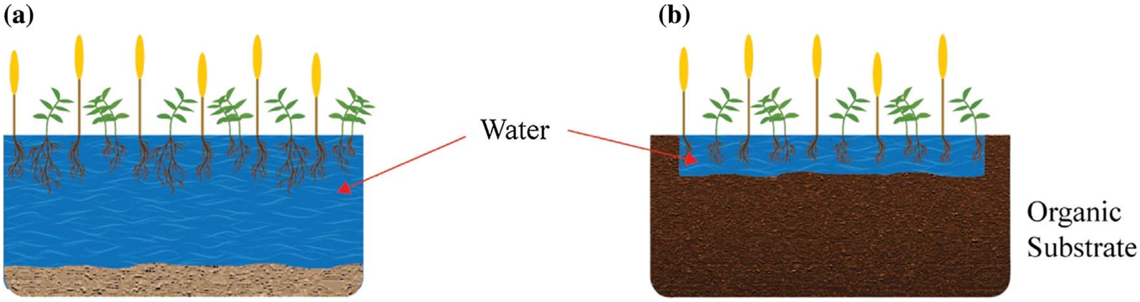

Fig. 2. Schematic diagrams of (a) aerobic wetland and (b) anaerobic wetland. Reproduced from Nebel (2005).

and play a key role in cycling sulphur along with generating alkalinity (Faulwetter et al., 2009). In the anaerobic interface firstly nitrate reduction takes place, subsequently ferric ions and finally, sulphates due to the thermodynamic sequence followed by microorganisms (Whitmire and Hamilton, 2005; Otte and Jacob, 2006).

A study carried out by Lloyd et al. (2004) on sulphate contaminated water in Ranger uranium mine (Australia) with a sulphate concentration of 384 mg/L, employed an anaerobic constructed wetland. The initial results on the removal of sulphates were not very promising, therefore, sucrose and NH_4Cl were added to the test environment expecting stimulated results. After being supplemented, the removal of sulphates reached above 90% and the importance of such supplements is researched in several studies (eg. Terrados et al., 1999; Nielsen et al., 2001; Weissner et al., 2005; Johnson and Younger, 2006). The study also revealed that a carbon source is a necessary requirement for SRB to establish an effective pathway for the sulphate removal (Weissner et al., 2005; Neculita et al., 2007; Faulwetter et al., 2009), while no removal was observed without the added incentives. Fig. 3 depicts the overall process of the sulphate reduction.

An anaerobic wetland was utilized in Collins et al. (2004)'s experiments to treat coal pile run-off immediately followed by a couple of aerobic wetlands to investigate the sulphate removal efficiency. Acidic water with pH 2.4 was introduced to the anaerobic wetland, which eventually recorded a pH value of 6.4 and an improved removal of iron by 93–99%, where the iron removal is likely to be resulted by sulphide formation.

In a different study, Mitsch and Wise (1998) employed a wetland system to treat a low order AMD stream in south-eastern Ohio (USA) including 9 cells with 2 being anaerobic (Fig. 4). The inflow to the wetland had a sulphate concentration of 1672 mg/L. The aerobic wetlands (from A-G) brought down the sulphate concentration level to 1216 mg/L by 27%. In anaerobic wetlands (from H-I), the system maintained a subsurface fluid flow, which increased the sulphate concentrations to 1256 and to 1286 mg/L respectively. The release of the reduced sulphides from the substrate to the water and the subsequent re-oxidation to sulphates, insufficient contact time, inability to maintain the redox conditions and the competition between the ions are highlighted as the possible reasons for this phenomenon. Hence it was concluded by Willow and Cohen (2003) that the quality of the organic substrate and the residence time of the water also have a sway on the overall sulphate removal from the contaminated water.

Permeable reactive barriers (PRBs) are a variant of wetlands wherein the key role is played by SRB (Benner et al., 2002; Gibert et al., 2002). PRBs are simply barriers which disturb the flow of contaminated water through a permeable material or a series of materials (i.e. modified zeolites, limestone, zero valent iron and organic material) (Johnson and Hallberg, 2005; Golab et al., 2006). The materials present in the barrier should allow safe passage through, while simultaneously purifying it. If not, clogging might occur and preferential flow paths are created avoiding the barrier. In addition, the material should be environmentally compatible and should allow good stability over a long period of time (Bartzas and Komnitsas, 2010). Although extensive studies have been carried out on PRBs only five full scale PRBs are active around the world until 2011 and the characteristics are listed in Table 3 (Gibert et al., 2011).

All techniques under the wetland criterion are of no doubt-environmentally friendly. The only downfall of the techniques can be highlighted as the amount of time that is consumed. Wetlands are expected to perform in longer periods (typically in years). In addition, the large space requirement is also a concern in implementing this remediation method. Consequently, in a larger area the maintenance becomes problematic and the discharge quality must be monitored time to time. Therefore, modifications in the wetlands are mandatory, in order to counter the negatives.

4. Recent developments in sulphate removal methods

4.1. Nanofiltration

The separation method of nanofiltration is influenced by molecular sieving and dissolve-diffusion mechanisms, which are unique characteristic methods of separation in microfiltration and reverse osmosis (RO), respectively (Preuβ et al., 2012). Typically, membranes are negatively charged to reject anions, although some positively charged membranes also exist (Peeters et al., 1998). The Donnan effect (i.e. inducing preferential ion flow) governs the ion distribution through the membranes when different valences exist in the solution, therefore, selectivity takes place. (Rautenbach and Gröschl, 1990; Peeters et al., 1998; Preuβ et al., 2012).

Nanofiltration and RO are compatible with removing dissolved ions

Table 2
Chemical analysis of the water from Bahco Argentina metallurgic plant (After Maine et al., 2006).

Parameter	Inlet		Outlet surface		Outlet bottom		
	Mean	Range	Mean	Range	Mean	Range	Mean removal (%)
pH	8.7	7.2–10.8	7.2	6.9–8.1	7.5	7.0–8.3	–
SO_4^{2-} (mg/L)	957	98.1–2506	395	159–855	538	158–950	44
Fe (mg/L)	13.7	0.16–74	0.38	0.05–1.2	0.67	0.11–3.2	95
Cr (mg/L)	22	3.3–150	3.6	2.8–5.3	3.0	1.0–3.5	86
O_2 (mg/L)	2.4	0–7.1	1.5	0–5.6	0.5	0–7.5	–

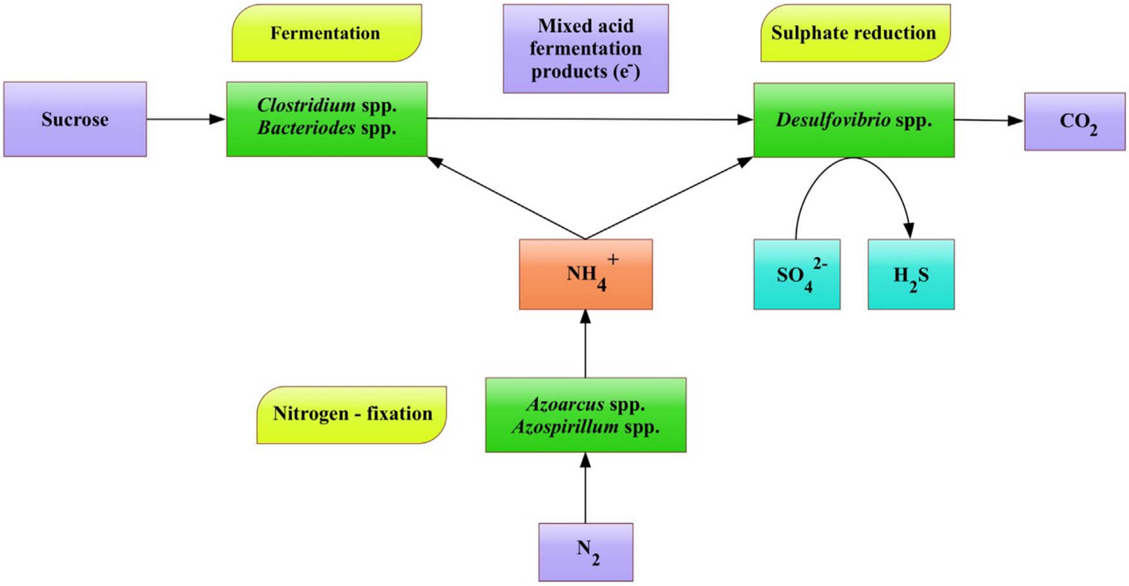

Fig. 3. Sulphate reduction mechanism of an anaerobic constructed wetland. Reproduced from Lloyd et al. (2004) with permission from Water Research.

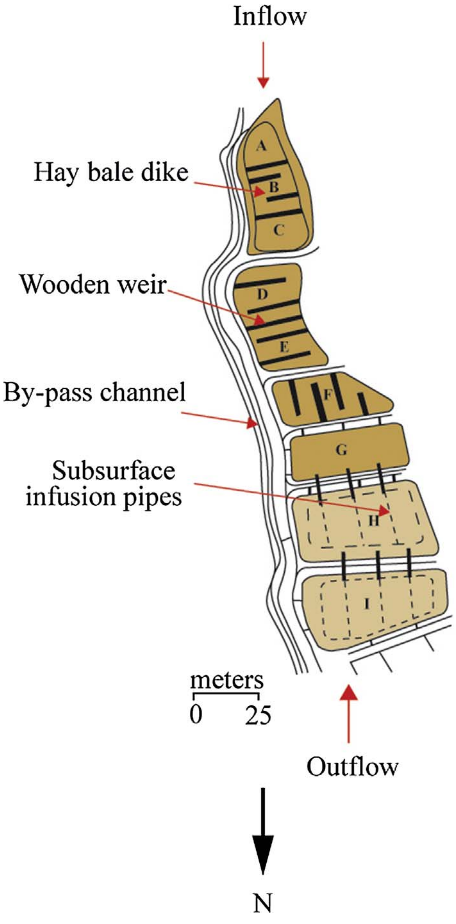

Fig. 4. Lick Run wetland layout. A-G are aerobic wetlands and H, I are anaerobic wetlands. Reproduced from Mitsch and Wise (1998) with permission from Water Research.

Table 3
Characteristics of the PRBs around the world as of 2011 (After Gibert et al., 2011).

Location	Filling components	Inflow SO_4^{2-} (mg/L)	Removal of SO_4^{2-} within the PRB (%)
Sudbury, Ontario, Canada	Municipal compost (20%) Leaf mulch (20%) Wood chips (9%) Pea gravel (50%) Limestone (1%)	2500–5200	25–78
Vancouver, British Columbia, Canada	Leaf compost (15%) Pea gravel (84%) Limestone (1%)	Not reported	Not reported
Charleston, South Carolina, USA	Leaf compost (30%) Zero-valent iron (20%) Pea gravel (45%) Limestone (5%)	1800–49500	83–99
Shilbottle, UK	Compost horse manure and straw (25%) Green compost (25%) Limestone (50%)	8700	40
Azanalcollar, Spain	Vegetal compost (35–40%) Sewage sludge (0–5%) Iron (0–5%)	1000	0–43

and salts, but not particulate matter. Therefore, a pre-treatment process is a requirement as AMD typically attributes particulate matter. Membranes used for nanofiltration triumphs over RO membranes in required pressure for operation, therefore, leading to a substantial saving on energy (Agboola et al., 2017). Despite the resemblance of operation and concept between nanofiltration and RO, the significant difference lies in the ability to remove monovalent ions, where RO leads.

Negatively charged membranes repulse the multivalent anions such as sulphates and carbonates where the consistency is recorded almost close to 90% and above but monovalent anion rejection ranged around 50% (Eriksson, 1988; Barr, 2001; Visser et al., 2001; Tanninen et al., 2006). Although nanofiltration has been witnessed with great success in water quality improvement, extreme challenges still prevail such as membrane fouling issues, remediating measures, improving separation and lifetime, improving the selective rejection of pollutants where

Table 4
The water treatment plant parameters before and after nanofiltration (After Preuβ et al., 2012).

Parameter	Before nanofiltration	After nanofiltration
pH	7.67	6.80
Electrical conductivity (μS/cm)	2760	350
Temperature (°C)	21	23
Alkalinity (mmol/L)	2.57	1.5
Silicate (mg/L)	6.3	6.2
Chloride (mg/L)	10.4	26.0
Sulphate (mg/L)	1850	65
Calcium (mg/L)	605	95
Iron (mg/L)	0.3	< 0.1

further studies are required (Van der Bruggen et al., 2008).

Eriksson (1988) clearly pointed out in his experiments that irrespective of the NaCl concentration, $MgSO_4$ rejection remained as high as 95–99% owing to the fact that sodium ions bind with the negatively charged membrane and allow the low charge density substance (i.e. chloride ions) to pass through.

Preuβ et al. (2012) performed an experiment to evaluate the performance of the nanofiltration membranes in removing sulphates from mine drainage. The experiment used water that was traditionally treated by lime and the initial parameters were tabulated in Table 4. A smooth flow was witnessed with the absence of magnesium. Had magnesium been present in the system, the gypsum saturation limit would be elevated thereby permeate has a tendency to experience higher sulphate levels. Therefore, pre-treatment tanks were employed to avoid the magnesium interference.

The conventional lime treatment of the tested water had reduced the sulphate concentration to 1850 mg/L. However, after nanofiltration the sulphate concentration was recorded as 65 mg/L (Table 4), which results in an impressive 96% rejection of sulphates. The nanofiltration process also reduced the overall ion content, which was reflected by the electrical conductivity measurements (350 μS/cm compared to 2760 μS/cm by conventional lime treatment). By further understandings of the process, alkaline sludge was decided to be an alternative for the conventional lime treatment plants. The sludge of the desalting process can be used for conventional mine water treatment to improve the economics of the process. In addition, the crystallised gypsum has the potential to be used as a building material. The process thus has the potential to reduce the waste by allowing the sludge to be used for as an alternative for lime treatment (Preuβ et al., 2012).

Agboola et al. (2017) investigated different types of nanofiltration membranes (i.e. Nano-Pro-3012 and NF90) for contaminant removal. In both the membranes, a higher cation removal was observed at a higher pH value because the fouling effect is possible at lower pH values. Conversely, for anions the study reflected a higher removal at a lower pH value. Finding the correct compromise of the operating pH value is thus important. The rougher membrane, NF90, demonstrated a higher removal of sulphate compared to the Nano-Pro-3012 membrane. The investigated water sample, Gauteng Western basin region, South Africa was composed of 3500 mg/L of sulphate and the sulphate removals were recorded as 97.6% and 86.3% for NF90 and Nano-Pro-3012, respectively, at pH 2.2.

However, the costs associated with the filtration/membrane processes are markedly higher than the conventional treatments. For the process to be effective, softening of the influent and the neutralization of the effluent is also required.

4.2. Electrocoagulation

Electrocoagulation (EC) employs an electric circuit made of an anode and a cathode to generate coagulants through the application of direct current (Ciardelli and Ranieri, 2001; Holt et al., 2002; Oncel et al., 2013; Del Ángel et al., 2014). Several factors are influential in the effectiveness of the EC process namely, potential difference, nature of the electrodes, competition among ions and pH (Ciardelli and Ranieri, 2001; Del Ángel et al., 2014). Zeta potential of the hydrated cations is yet another critical factor in order to determine the perfect pH for the effective removal of the contaminants.

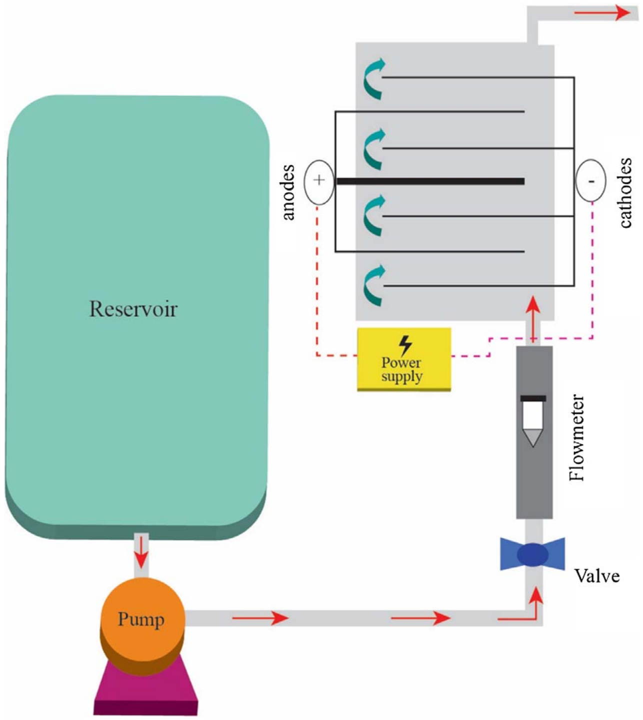

Fig. 5. The process layout presenting a serpentine flow path. Reproduced from Del Ángel et al. (2014).

Del Ángel et al. (2014) investigated the feasibility of the EC process to remove arsenic and sulphates from the AMD collected from Guanajuato city in Mexico. Initial concentrations of total arsenic and sulphates were recorded as 24 μg/L and 3567 mg/L, respectively. Aluminium electrodes were employed in the experiment and the layout was as depicted in Fig. 5. The process adopted a serpentine flow path to allow proper mass transport within the system (Mollah et al., 2004). The hydrated aluminium ions absorbed both $HAsO_4^{2-}$ and sulphate ions. The experiment was conducted at pH 7 due to the observed anode passivation at high pH solutions, hence pre-treatment was a requirement. The variables of the experiment were flow rate of the solution (from 1.82 to 9.11 cm/s) and the current density (4 and 6 mA/cm^2) applied to the EC cell. The lowest flow rate (i.e. 1.82 cm/s) along with 4 mA/cm^2 yielded the best arsenic (92.5%) and sulphates (52.7%). However, in the context of sulphate removal, increase of current density did not improve the removal as expected. The reason was deduced as the competition between ions. Priority is given to the more kinetically favourable ion through the system, in this instance, it was $HAsO_4^{2-}$.

Murugananthan et al. (2004) explored the variability of electrodes, the initial concentration of the solution, current density and pH for sulphur anions (i.e. sulphide, sulphate and sulphite) removal. The experiment was conducted on three types of electrodes namely aluminium, iron and titanium from which titanium was ruled out due to the backward generation of sulphates from the oxidation of the removed sulphide. Both aluminium and iron electrodes were found to be very favourable from the results obtained with aluminium yielding better results once compared between. As the initial ion concentration increased, removal percentage was observed to decrease (Fig. 6a). The experimental conditions were anode: iron, time: 600 s, pH: 7, current density: 32 (sulphide) and 62 (sulphate and sulphite) mA/cm^2. Owing

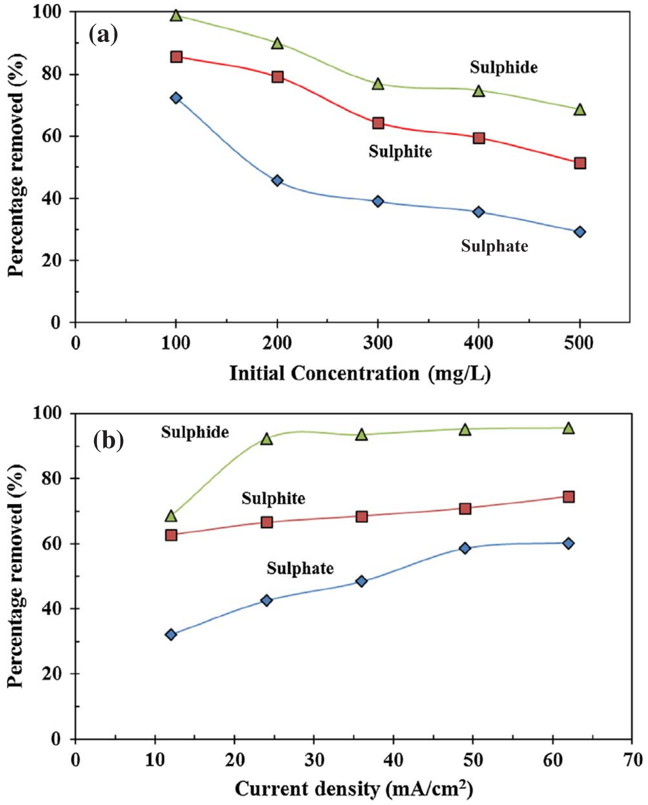

Fig. 6. Sulphur anions removal percentages with (a) varying initial concentration of the solution and (b) current density. Reproduced from Muruganathan et al. (2004) with permission from the Journal of hazardous materials.

to the results, the lowest concentration (i.e. 100 mg/L) was selected as the concentration to proceed the experiments. Consequently, the current density was investigated keeping the rest of the parameters as mentioned earlier. The results (Fig. 6b) proved that more the current density, better the removal was.

Considering process economics, Oncel et al. (2013) conducted a study to compare the cost of the EC process with the conventional chemical precipitation in treating AMD from a coal mine. Chemical precipitation at pH 8 resulted removal efficiencies ranging from 28.4 to 99.96% at EUR 4.53/m^3 (USD 6.02/m^3 in 2013). On the contrary, the EC process recorded over 99.9% removal efficiencies under pH 2.5, with a current density 500 A/m^2 for 40 min at EUR 1.98/m^3 (USD 2.63/m^3 in 2013). Thereby, present day EC process is proved to be both effective and economical, however, industrial application of this technique pertaining to AMD has not been recently reported in the literature.

4.3. Precipitation methods

Precipitation methods have been the most used technologies in the area of waste water treatment due to simplicity and inexpensive nature. Although lime treatment is at the forefront of all precipitation methods (Section 3.1), the extensive literature review has revealed a number of better performing precipitating technologies. Current typical technologies include precipitation by calcium salts, barium salts and aluminium coagulants (Gomelya et al., 2014). In addition, further developments such as SAVMIN and fly ash (FA) treatments are also popular in the industry. The resultant precipitates are removed by either sedimentation or filtration (Fu and Wang, 2011).

Flocculating agents come in handy in order to counter the long retention times to create the precipitate (Vidlář et al., 2002). Other metal constituents are most troublesome for the efficiency of the process although sometimes prove to improve the sulphate removal as in the FA application (Madzivire et al., 2011). Recovering the metals from the precipitates is a common approach to minimise the costs of the initial chemical compounds (Bowell, 2004; Bologo et al., 2012).

Smit (1999) introduced a sulphate removal methodology named SAVMIN. The technology was developed in collaboration with Mintek, Savannah mining and the Wren group, South Africa. The process entails the precipitation of metal hydroxides, calcium sulphate, ettringite (Eq. (18)) and calcium carbonate with the use of conventional reactors at ambient temperatures and pressures with inexpensive reagents. In the SAVMIN process, the pH of the feed water is raised by the addition of lime whereby the metals precipitate as hydroxides. Subsequently, the solution enters an environment where gypsum is precipitated. Afterwards, aluminium hydroxide is added and eventually an insoluble salt, ettringite forms (Eq. (18)).

$$6Ca^{2+}_{(aq)} + 3SO_4^{2-}{}_{(aq)} + 2Al(OH)_{3(s)} + 37H_2O_{(l)} \rightarrow 3CaO\cdot 3CaSO_4\cdot Al_2O_3\cdot 31H_2O_{(s)} + 6H_3O^+_{(aq)} \tag{18}$$

The tests carried out using a pilot plant assured an extraction of over 90% sulphate proving the viability of the process. At the South African Stillfontein plant, SAVMIN reduced the sulphate concentration from 800 mg/L to 200 mg/L (Bowell, 2004). A removal efficiency of 100–150% was observed when lime was used with aluminium coagulants (Gomelya et al., 2014).

Barium salts such as sulphides, carbonates and hydroxides are the typical compounds in terms of treatment methodologies. Maree et al. (2004) studied the possibility of using BaS for sulphate removal. The four staged process is inclusive of a lime pretreatment, the addition of BaS to the solution, stripping of H_2S by using CO_2 and $CaCO_3$ precipitation. The process map is depicted in Fig. 7.

Lime treatment provides a metal removal along with a partial sulphate removal (Section 3.1). As per the investigation carried out by Maree et al. (2004) the feed contained 2650 mg/L of sulphate which was partially reduced to 1250 mg/L by lime treatment. The subsequent solution, once analysed, was almost free from metal ions. The BaS addition then yielded a solution with 250 mg/L sulphate. The final sulphate concentration remained the same albeit sulphide was added to the system uninvited, the concentration was controlled to less than 20 mg/L through stripping of H_2S. The cost factor was largely dependent on the recovery of BaS from $BaSO_4$ precipitates (Eq. (19)). The cost analysis of the BaS process predicted a total running cost of ZAR 2.28/m^3 (USD 0.35/m^3 in 2004, ZAR – South African Rand) and a product value of ZAR 5.63/m^3 (USD 0.87/m^3 in 2004) in 2004 (i.e. products are water, sulphur and calcium carbonate).

$$BaSO_{4(s)} + 2C_{(s)} \rightarrow BaS_{(s)} + 2CO_{2(g)} \tag{19}$$

Barium carbonate ($BaCO_3$) is another alternative for sulphate removal. Hlabela et al. (2007) presented that barium carbonate only has the capability to remove the sulphates associated with calcium. The authors were also successful in finding a solution (adding a lime treatment step) to the difficulties pointed out by Kun (1972) related to $BaCO_3$ usage, which were long retention times, high residual concentrations of barium in the treated solution and high costs involved in $BaCO_3$ (Bologo et al., 2012). The study resulted in a sulphate removal from 2274 mg/L to 200 mg/L. $BaSO_4$, the resulting precipitate, is recycled by thermally reducing with coal to barium sulphide, which is considered as the starting point of all barium salts (Eqs. (19) and (20)).

$$BaS_{(s)} + 2CO_{2(g)} + H_2O_{(l)} \rightarrow BaCO_{3(s)} + H_2S_{(g)} \tag{20}$$

Barium carbonate was used with lime in order to nullify the effects from other cations, for example magnesium. Additionally, the recovery of BaS provides an extra comfort to manage the economy of the process. The cost analysis performed by Hlabela et al. (2007) expressed a total running cost of ZAR 1.28/m^3 (USD 0.18/m^3 in 2007) along with a product value of ZAR 2.76/m^3 (USD 0.39/m^3 in 2007) (products: sulphur and water). It implies lower running costs compared to BaS

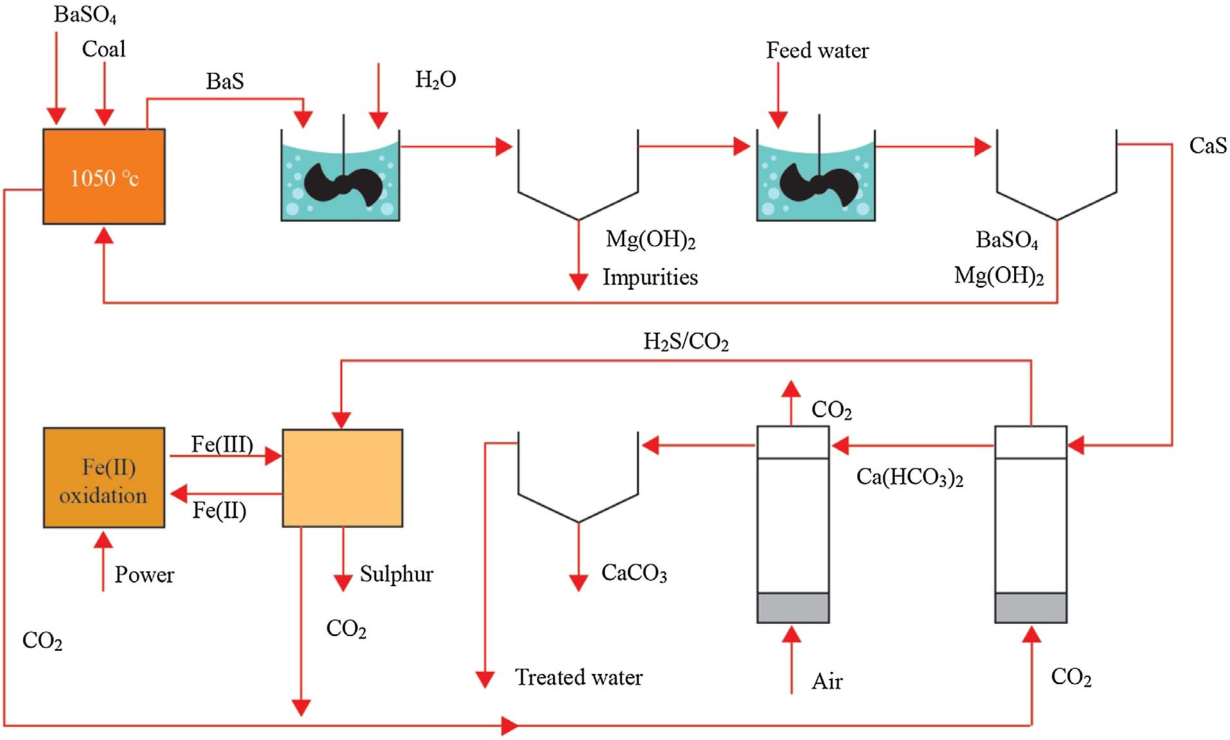

Fig. 7. BaS treatment method. Reproduced from Maree et al. (2004) with permission from Mine Water and the Environment.

addition, but the calculated product value is low in $BaCO_3$ application.

The addition of $Ba(HCO_3)_2$ has also captured attention in the lab scale experiments. Akinwekomi et al. (2017) compared the productivity of sulphate removal between the $BaCO_3$ and $Ba(HCO_3)_2$ addition approaches, where the $Ba(HCO_3)_2$ was prepared by introducing CO_2 to the $BaCO_3$ solution. The study revealed a sulphate removal from 1050 mg/L to 96 mg/L by using $Ba(HCO_3)_2$ and a removal from 1050 mg/L to 768 mg/L by $BaCO_3$ in a 15 min interval. Indeed, the higher solubility of the $Ba(HCO_3)_2$ presents the opportunity for Ba^{2+} ions to be abundant in the solution, whereby a higher number of SO_4^{2-} ions are bound and precipitated as $BaSO_4$. In addition, a better desalination is offered by adopting the $Ba(HCO_3)_2$ approach as the pH is fluctuated around 7, whereas in $BaCO_3$ the pH is recorded to be around 9–10. The requirement of a CO_2 source and the over dosage of $BaCO_3$ are highlighted as the limitations in this method (Akinwekomi et al., 2017).

Barium hydroxide is also used with magnesium hydroxide mainly for metal removal and pH adjustment. After the metals are precipitated with the addition of magnesium hydroxide, barium hydroxide is added to the subsequent solution, which causes precipitation of both magnesium hydroxide and barium sulphate. Magnesium hydroxide and barium hydroxide are recovered from the resulting sludge to improve the economy of the process. It was observed that the final sulphate concentration heavily depended on the barium hydroxide dosage. The process was carried out with two types of mine water, namely water from a coal mine and gold mine recording an initial sulphate concentration of 2487 and 4890 mg/L, respectively. The treated solution recorded sulphate values of 181 and 24 mg/L, respectively, which posited an over 90% removal of sulphates along with an impressive metal recovery. Unlike in the other processes, metal hydroxides not mixing with gypsum is considered to be a major benefit of this approach (Bologo et al., 2012). The cost analysis carried out by Bologo et al. (2012) suggested a running cost of ZAR 1.76/m^3 (USD 0.21/m^3 in 2012) and ZAR 2.71/m^3 (USD 0.33/m^3 in 2012) for coal and gold mine water treatments, respectively. The value of the products (water, sulphur, $Mg(OH)_2$ and $CaCO_3$) rounded up to over ZAR 5/m^3 (USD 0.6/m^3 in 2012) in both the cases.

Fly ash (FA) is a by-product of coal power plants and an environmental pollutant, which finds its way to sulphate removal from AMD as another innovative method to optimise the waste utilisation with being an ideal cost effective approach (Potgieter-Vermaak et al., 2006). Typical composition of FA can be listed down as SiO_2, Al_2O_3, Fe_2O_3 and CaO (Gitari et al., 2006; Ahmaruzzaman, 2010; Madzivire et al., 2011). AMD containing high concentrations of iron and aluminium buffered the solution thereby further CaO dissolution occurred, which led sulphates to precipitate as gypsum (Madzivire et al., 2011). On the other hand, the very presence of iron and aluminium encourage sulphate precipitation as oxyhydroxysulphates (Gitari et al., 2006; Madzivire et al., 2011). Madzivire et al. (2010, 2011) studied the effect of FA on circumneutral mine water (CMW). The results did not deduce a significant amount of sulphate removal when treated with pH 9–10. CMW was richly composed of calcium and magnesium instead of iron and aluminium. CMW treatment with FA accounted for a sulphate removal of 16% and 71% below and over pH 10, respectively. Therefore, the studies were carried out with a mixed ratio of CMW and AMD. The mixed solution resulted in 80% removal of sulphates when the solution pH was increased over 10. The underlying reason was understood to be an effect taking place by the provision of iron and aluminium ions from AMD.

4.4. Adsorption

Many compounds have been tested for sulphate adsorption during the last decade. Modified and unmodified compounds have been utilized to understand the adsorption mechanisms and at the same time to enhance the contaminant removal.

One of the latest developments in sulphate removal research from mine drainage is, the use of activated carbon (AC). This can be derived from coal, peat, wood, nut shells, coconut shells and some synthetic organic polymers (Marsh and Reinoso, 2006). AC offers high porosity, large surface area, and higher degree of surface reactivity (Garrido et al., 1987; Sircar et al., 1996; Biniak et al., 1997; Tancredi et al., 2004; Dias et al., 2007; Hameed et al.,2007; Tan et al., 2008), which are

Table 5
Sulphate sorption results in fixed bed experiments (After Guimarães and Leão, 2014).

Experimental condition	Breakthrough volume (mL)	Breakthrough time (min)	Saturation volume (mL)	Saturation time (min)	Bed capacity of adsorption (mg SO_4^{2-})	Maximum loading of resin (q_{max}) (mg SO_4^{2-}/mL resin)
Sulphate inlet concentration (mg SO_4^{2-})/L)						
55	600	40	1500	100	93.8	8.52
80	450	30	1200	80	105.7	9.61
160	150	10	750	50	126.7	11.5
Bed height (cm)						
6	150	10	1200	80	101.6	12.7
9	300	20	1350	90	111.6	10.1
12	450	30	1650	110	138.7	9.6
Flow rate (mL/min)						
10	400	40	1100	110	88.5	8.1
15	450	30	1200	80	95.6	8.7
20	400	20	1200	60	96.8	8.8

considered ideal for purification processes, water treatment and the utility as catalysts (Tancredi et al., 2004). Two types of AC are easily identified, namely granular activated carbon (GAC) and powdered activated carbon (PAC) and they differ each other primarily on particle size. PAC is produced from fine particles such as saw dust, whereas GAC is from rather harder materials such as coconut shells and wood (Tancredi et al., 2004).

Hong et al. (2014) recently explored the possibility of removing sulphate from AMD using GAC. The primary objective was to capture the initial sulphates and afterwards to release a concentrated sulphate output for future utility. Polypyrrole was successfully grafted into wood-based GAC (RGC – wood-based GAC) and the potential for sulphate removal was investigated. Polypyrrole is widely used in the electronics and sensors industry (Wang et al., 1989; MacDiarmid, 1997; Malhotra and Chaubey, 2003; Muthulakshmi et al., 2006) for its high conductivity, energy storage, environmental benignness and easy polymerization (Hong et al., 2014). X-ray photoelectron spectroscopy (XPS) test results showed the presence of nitrogen and chlorine after pyrrole grafting, which in turn confirmed the polymerization of pyrrole into RGC. It can change in between net charges from positive to neutral when triggered electrically. The material also showed sorbing properties when it is positively charged and released when it is neutral.

Pyrrole grafted RGC solution yielded a 44.7 mg/g sulphate sorption, whilst the initial sulphate concentration was 250 mg/L in laboratory conditions. Comparing the values with other sulphate sorption options namely, 7.7 mg/g for $\gamma{-}Al_2O_3$, 8.5 mg/g for chitin-based shrimp shells and 4.9 mg/g for $ZnCl_2$ -activated coir pith carbon, polypyrrole grafted RGC clearly showed the promise. Contaminated water samples collected from a mine site contained 773 mg/L of sulphate was treated and the polypyrrole grafted RGC recorded a sulphate sorption of 41 mg/g (Hong et al., 2014).

After noting the promise the polypyrrole-grafted RGC had offered, other variants were also developed. Polypyrrole was grafted into bituminous based activated carbon, which showed comparatively lower sulphate sorption but further research is required to identify the potential. Another medium with polypyrrole alone (without GAC) was developed and tested for sulphate sorption. Batch adsorption isotherms recorded an impressive adsorption of 80 mg/g sulphate for the polypyrrole only medium. On the contrary, rapid small-scale tests experienced a blockage of the liquid flow due to the formation of cauliflower-like structures of the spherical nanoparticles of polypyrrole (Hong et al., 2014). Even though Hong et al. (2014) was successful in loading sulphates on to RGC, the subsequent recovery of the RGC or sulphate was not mentioned.

Amberlyst A21 resin (a weak base resin) for sulphate removal from AMD was also investigated and Guimarães and Leão (2014) examined both sorption capability and the desorption capability of it. As Amberlyst A21 is a nitrogen containing compound, wherein protonation of the nitrogen is imperative to sorb sulphates. Hence, the study employed pH 4 for sulphate sorption studies. With the increasing initial sulphate concentration, the loading rate resulted in an increase. A two-staged sorption process was carried out (resin protonation and sulphate sorption). Both the processes were found to be fast as the equilibrium concentration (11.6 mg SO_4^{2-}/mL resin) was reached in 45 min. The relationship between inlet sulphate concentration, bed height and flow rate with sulphate loading were conducted by performing fixed bed experiments and the results are shown in Table 5.

It can be observed that the sulphate loading also increases as the initial sulphate concentration rises (Table 5). Saturation time and breakthrough time are reached the soonest, when the initial concentration is the highest or the bed height is the lowest.

Furthermore, the most important property behind the use of Amberlyst A21 is the resin's ability to cause significant elution (Guimarães and Leão, 2014). Mostly sulphate elutions from other substances such as Duolite 161, Duolite A375 and Amberlite IRA67 range between 90 and 95% (however, the process is pH dependent) (Feng et al., 2000; Namasivayan and Sangeetha, 2008; Guimarães and Leão, 2014). The key mechanism behind Amberlyst A21 elution is the protonation. In an acidic media the protonation takes place and encourages sulphate sorption. But in a basic media, the resin loses its ability to bind any anion since the solution is deprived of H^+ ions. Amberlyst A21 boasts an elution of 100% when pH is raised from 10 to 12 along with a maximum sulphate loading of 11.6 mg SO_4^{2-}/mL resin and also an improved sulphate loading with respect to increasing temperatures (Guimarães and Leão, 2014). Authors were also able to verify the competition caused by other ions (chloride and fluoride) disappear as the system became saturated with sulphates.

Modified rice straw, an agricultural residue, has exhibited great advances in sulphate adsorption. Cao et al. (2011) reported excellent capabilities of rice straw by chemically converting into a strong basic anion exchanger (RS-AE). Unmodified rice straw recorded a sulphate adsorption value of 11.68 mg/g and a further study was continued by modifying the rice straw characteristics. Introduction of $NaOH$ took place in order to form a sodium cellulose and modified the rice straw. Indeed, the addition of more $NaOH$ created more adsorption sites but on the other hand loss of product yield occurred. A $NaOH$ concentration of 10% along with an operating temperature of 80 °C was selected. Clearly, it was observed that RS-AE exhibited remarkable adsorption capabilities compared to raw rice straw. It reached a rapid adsorption (equilibrium adsorption of 74.76 mg/g) when the sulphate concentration was lower. Recovery of spent RS-AE was obtained by applying 0.1 M $NaOH$ solution. Sulphate adsorption efficiency of RS-AE was reduced by less than 10% after four adsorption and regeneration cycles (Cao et al., 2011). Therefore, RS-AE has the potential to serve both as an economically feasible and a very productive compound in the context of sulphate removal. However, commercial utility and process

Table 6
Properties of the adsorbents (After Iakovleva et al., 2015).

Name of adsorbent	Particle size (μm)	Specific surface area (m^2/g)	Zeta potential (mV) pH = 11
Flotation fines (FF)	599	1.35	0
Filter sands (FS)	451	1.82	−25
Iron sand (RH)	180	62.5	−7
Paper waste (DI-60)	1390	3.29	−14

economics of the treatment method is yet to be investigated.

Falayi and Ntuli (2014) investigated the productivity of the use of unactivated attapulgite ($(MgAl)_2Si_4O_{10}\cdot 4H_2O$ – magnesium aluminium phyllosilicate clay) for sulphate removal from AMD. The study was unable to yield the expected promise with a low removal of sulphates (9.7%) of the feed and the activation of the attapulgite was recommended.

Iakovleva et al. (2015) recently examined on the adsorption capability of materials on sulphate removal from alkaline solution. This approach is reviewed to validate the removal of sulphates. The knowledge of this can be applied to AMD if a pre-treatment process is carried out to make the AMD alkaline. Four compounds were studied, namely iron sand (RH), paper waste (DI-60) and two limestone types, namely, filter sands (FS) and flotation fines (FF). The properties of the compounds are tabulated in Table 6.

Although RH comprised of the highest surface area, it is the second best behind DI-60 (Fig. 8). The reason was highlighted as RH's affinity for monovalent ions (i.e. chloride) as the ion size is much smaller than a divalent ion. An adsorbent amount of 40 g/L was used throughout the study. The results show the optimum recovery at 480 h and thus it was selected as the residence time for further investigations.

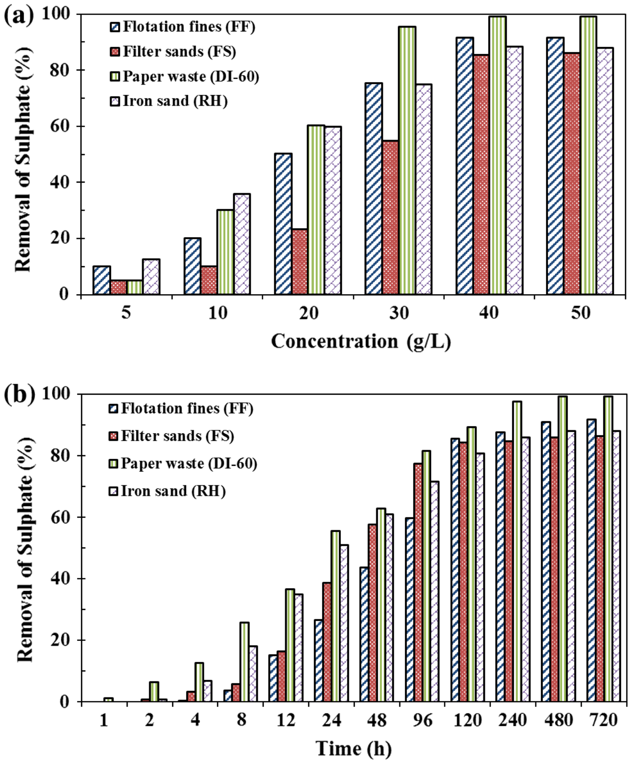

Fig. 8. Sulphate removal efficiencies of flotation fines (FF), filter sands (FS), paper waste (DI-60) and iron sand (RH) with respect to the a) adsorbent concentration and b) residence time. Reproduced from Iakovleva et al. (2015) with permission from Chemical Engineering Journal.

The tests carried out with the mine water yielded the sulphate removals 73%, 68%, 54% and 75% for FF, FS, DI-60 and RH, respectively. The results, were not as expected however, can be justified by emphasising the existence of additional anions in the mine processed water, which in return create competition. The study encourages the use of all the mentioned adsorbents for industrial purposes to utilise the solid wastes that keep piling up around the world.

Ntuli et al. (2016) reported successful sulphate removal results with the use of de-silicated fly ash (DFA). DFA originates from FA itself simply by leaching out silica. Unlike in FA used as a precipitating agent (Section 4.3), DFA is used as an adsorbent. The investigated parameters were DFA quantity, residence time and temperature on overall removal of sulphate. A 2% DFA addition resulted in a removal of above 50% of sulphate. As the time is increased, more contact is permitted on DAF and an obvious increase in the sulphate removal was observed. The tested temperatures were 25, 35 and 45 °C. The adsorption process was found to be endothermic (enthalpy ~ 125.1 J/mol), thus an increase of removal was resulted from 25 to 35 °C. Over 70% of sulphates was removed at 35 °C (2% DFA, 60–90 mins). However, a drop of the removal percentages from 35 to 45 °C was observed due to the increased solubility of sulphates in the solution with the increased temperature. The adsorption followed the Langmuir isotherm and the process recorded a maximum adsorption capacity of 147.06 mg/g. Since DFA derived from FA the main difference between the two, is the amount of compound required for sulphate removal being 2% of DFA, which is 50% of FA (Ntuli et al., 2016).

4.5. Ion exchange

Ion exchange is a reversible process where the interactions of ions between the liquid phase and the solid phase (which is also known as the resin) take place, which eventually result replacement of ions (Bowell, 2004). Both natural and synthetic materials are amongst the resin constructions, however the synthetics are more preferred. The selection of a resin material (synthetics, natural zeolites and natural silicate minerals) mainly depends on the cost and the availability (Fu and Wang, 2011). Exchangers work to remove cations as well as anions. However, resins inherit limited capacity to treat contamination by nature. Adoption of ion exchange method can be beneficial in comparison to lime precipitation as the addition of lime precipitates sulphates as gypsum and the solution may still contain soluble sulphate ions below gypsum saturation level (Vidlář et al., 2002; Lopez et al., 2009).

An ion exchange treatment plant is composed of three main processes, namely resin loading, regeneration and rinsing (Lopez et al., 2009). Ion exchangers therefore, require additional technologies to regenerate the resin subsequently to manage both sludge and the saline product (Vidlář et al., 2002). Gypsum precipitation by counter-current ion exchange (GYP-CIX) and Sulf-IX (sulphate removal by ion exchange) are industrially established processes. The latter being inspired mainly by the previous, to negate the inefficiencies.

Robertson and Rohrs (1995) studied the GYP-CIX process since the process outcomes were favourable in terms of costs incurred. Reduction of costs is mainly due to regenerant of chemicals, namely, sulphuric acid and lime in contrast to the conventional hydrochloric acid and caustic soda, which are considered to be more expensive (Miller et al., 2009). This technique is a continuous fluidized ion exchange process which uses a counter-current flow to regenerate the resin. It is a two-staged process where firstly, the cations will be exchanged and secondly, the anions. The constituting chemical reactions are represented in Eqs. (21)–(24) (Lopez et al., 2009).

$$Ca^{2+}_{(aq)} + 2R_f\cdot H_{(s)} \rightarrow (R_f)_2Ca_{(s)} + 2H^{+}_{(aq)} \tag{21}$$

$$2H^{+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2R_f\cdot OH_{(s)} \rightarrow 2R_f\cdot H_2SO_{4(s)} \tag{22}$$

$$(R_f)_2Ca_{(s)} + H_2SO_{4(aq)} + H_2O_{(l)} \rightarrow 2R_f\cdot H_{(s)} + CaSO_4\cdot 2H_2O_{(s)} \tag{23}$$

$$R_f\cdot H_2SO_{4(s)} + Ca(OH)_{2(aq)} \rightarrow R_f\cdot OH_{(s)} + CaSO_4\cdot 2H_2O_{(s)} \tag{24}$$

where R_f being the functional group in the resin. Eqs. (21) and (22) represents calcium loading and sulphate loading, respectively, along with Eqs. (23) and (24) that show the regeneration of the cationic resin and the anionic resin, respectively.

The feed is introduced to a cation exchanger irrespective of the pH and subsequently to an anion exchanger to strip off the sulphates (Miller et al., 2009). The only waste of this particular process is a gypsum slurry which can later be sold in the pure solid state to offset the operating costs. As the gypsum slurry is taken away from the system separately, recovered water can be recirculated in the system. GYP-CIX has impressed with an average water recovery of 90% albeit further improvements can be made. Feeds with 1000 mg/L calcium and 2000 mg/L sulphates can easily be treated with the technique with higher flow rates. The investigation carried out by Robertson and Rohrs (1995) on GYP-CIX, the tested water recorded concentrations of calcium and sulphate as 500 mg/L and 1200 mg/L, respectively. After the treatment the concentrations were less than 50 mg/L for calcium and less than 200 mg/L for sulphate, which was quite promising. The resin replacement recorded as low as 5–10% per annum and the process required no skilled labour.

Miller et al. (2009) have documented a GYP-CIX cost analysis of a pilot project. The project was carried out on a 50 gallons/min flow rate. To reduce the sulphate concentration from 1500 mg/L to 250 mg/L, the operation cost was USD 2–5/1000 gallons. Resin fouling, resin loss/breakage and resin capacity are common concerns in ion exchange processes. Ion exchange processes can be used as an alternative for lime precipitation method or as a post-treatment process to lime. Additionally, the technique may also serve as a pre-treatment method to already existing demineralization plants (Robertson and Rohrs, 1995).

The review by Lopez et al. (2009) points out a newer development of ion exchange procedures, which is Sulf-IX mainly inspired by GYP-CIX. The process is trademarked under BIOTEQ, Canada. Sulf-IX fundamentally uses the same theory as GYP-CIX but excels in flexibility for different feed chemistries, better gypsum capturing mechanisms and allowing feeds with magnetism to be treated.

4.6. Dissolved air flotation method (DAF)

Among the many flotation techniques (eg. column flotation, nozzle flotation, centrifugal flotation) DAF technique has reserved a compelling position as it found its wide utility in the fields of waste water and mineral processing (Rubio et al., 2002).

Amaral Filho et al. (2016) recently discussed dissolved air flotation method (DAF) method to treat sulphates in AMD as one of the novel treatment techniques. The strategy was based on precipitating sulphates with polyaluminum chloride (PAC) and was eventually separated by the use of flotation techniques. Precipitates required to be flocculated by introducing a cationic polyacrylamide in order to achieve a successful removal via flotation. The initial aluminium ratio was tested to yield an efficient sulphate removal. An enhanced removal was observed as the aluminium and sulphate ratio is increased (i.e. 5:1). However, for experimental purposes a ratio of 4:1 was selected to limit the reagent consumption. A flocculent concentration of 20 mg/L was used for inducing enough hydrophobicity to the precipitates to attach to the bubbles, the precipitates were observed to be hydrophilic otherwise. Subsequently, the above-defined parameters were tested on a natural AMD sample from the coal region of Santa Catarina State, South Brazil, which contained 1753 mg/L of sulphates. The sulphate content was reduced quite drastically to 350–400 mg/L. Both micro and nanobubbles assisted in the removal of the generated sulphate-bearing flocs and a first order kinetics model was obtained (rate constant of 4.1 min^{-1}) (Amaral Filho et al., 2016). Three main mechanisms were identified in this approach and these were the connections between bubbles and flocs, the capturing the flocs and rapid movement of the formed aerated flocs. However, the process required the testing media to be free from metal ions. Thus, the testing media was pre-treated with lime at pH 8.5. In addition, approximately 80% of sulphate removal would result due to the process inefficiencies and equilibrium of the precipitates with the solution, and the method was endorsed for high superficial rates in flotation circuits (Amaral Filho et al., 2016).

4.7. Modified approaches of constructed wetlands

Though wetlands have been in use for quite some time, in this section a few modern modified approaches to promote sulphate removal will be discussed. SRB systems (Section 3.3) received an upgrade through Bai et al. (2013) study. Typical SRB systems employ the sole utility of SRB to remediate sulphates in the wastewater. But in Bai et al. (2013) study additional zero valent iron was added to the system. It is a reducing agent (Sohn et al., 2006; Zhang et al., 2011), which enhances SRB activity (Lindsay et al., 2008). The microorganisms for the study were collected from an active wastewater plant and the dissolved oxygen was purged. 90% pure iron and an up-flow anaerobic multi-flow bed reactor were used in this work. The initial mine water was rich in sulphates (20800 mg/L). A lower hydraulic residence time (HRT) was found to be decreasing the performance of this method. An elevated HRT (48 h) was thus employed and a final sulphate concentration of 8600 mg/L at a loading rate of 217 mg/L h was resulted (61% of overall sulphate reduction). The treatment procedure increased the pH from 2.75 (feed) to 6.20 in the effluent. The treatment via zero valent iron thus provides an elevated level of sulphate reduction with respect to the natural wetland treatment. However, long residence times still stand out as the main drawback of the wetland treatment (Bai et al., 2013).

Rakotonimaro et al. (2017) recently carried out an investigation for the removal of both iron and sulphates from artificial AMD. This entailed a pre-treatment process to remove iron initially, via the adoption of wood ash or calcite based dispersed alkaline substrate (DAS) and a mixture of organic and inorganic materials (i.e. woodchips, chicken manure, leaf compost, sand and calcium carbonate) in a passive biochemical reactor (PBR) for the sulphate removal. In the wood ash based pre-treatment phase, the process manifested a sulphate removal of between 7.5 and 37% and an enhanced efficiency was attained at higher HRT (i.e. 5 days). However, for the calcite based DAS yield a 47% removal and was reported to be efficient only in short HRT. However, in the PBR run, the sulphate removal was recorded below 14%. The reason was highlighted to be, when ferric ions are sufficiently high, iron reducing bacteria takes over SRB, retarding the sulphate removal efficiency (Deng et al., 2016).

5. Comparison of sulphate removal techniques

In summary, different approaches may yield different results. Selection of a particular technique also includes several decisive parameters, which are time constraints, space, costs associated and types of contaminants present. Table 7 presents a summarised insight on the remediation techniques discussed in this work, which summarises both the mertis and demerits of each treatment method.

The conventional lime and limestone treatments are well known for their inexpensiveness. These two methods do extremely well in raising the pH and precipitation the trace metals in the solution as hydroxides. In fact, these methods perform rather poorly as far as sulphate removal is concerned. Lime and limestone treatments are capable of producing a solution which is in the vicinity of gypsum saturation and therefore virtually 1200 mg/L of sulphates will be left out in the solution. The generated sludge by lime/limestone requires further processing. Wetlands are environmentally benign systems in treating contaminated water but the kinetics of the system is very slow typically in the scale of years. Sulphate removal can thus be highlighted as very low, therefore,

Table 7
Merits and demerits of AMD sulphate treatment methods.

Method	Merits	Demerits	References
Lime	Inexpensive Metal precipitation as hydroxides	Produces high amount of sludge hence the increased capital costs on sludge ponds Leaves high gypsum saturated solution High maintenance	Skousen et al. (2000), Aube et al. (2003) Geldenhuys et al. (2003), Bowell (2004) Johnson and Hallberg (2005), Potgieter-Vermaak et al. (2006) Ardejani et al. (2008), Khorasanipour et al. (2011)
Limestone	Inexpensive compared to lime treatment Produces lower amount of sludge compared to lime treatment Efficient pH control Higher removal by adsorption (ex: 23.7 mg/g) Longer lifetime	High maintenance Passivation of limestone Gypsum saturation concentration is a decisive factor for the process, above which no dissolution of limestone will occur Complex than the application of lime	Dvorak et al. (1992), Hammack et al. (1994) Hedin et al. (1994), Ziemkiewicz et al. (1997) Maree et al. (1998), Geldenhuys et al. (2003) Akcil and Koldas (2006), Potgieter-Vermaak et al. (2006) Silva et al. (2012)
Electrocoagulation	High removal efficiency Amount of sludge is lesser More economical than chemical treatment	Power consumption can be an issue pH needs to be managed Anode passivation Pre-treatment required Competition of ions is higher	Ciardelli and Ranieri (2001), Holt et al. (2002) Mollah et al. (2004), Muruganathan et al. (2004) Oncel et al. (2013), Del Ángel et al. (2014)
Wetlands	Less maintenance since a passive method No chemical costs involved Environmentally friendly	Long residence time Slow reaction rates Low removal efficiency	Collins et al. (2004), Kosolapov et al. (2004),Horne and Fleming-Singer (2005), Johnson and Hallberg (2005) Whitmire and Hamilton (2005), Johnson and Younger (2006) Maine et al. (2006), Sheoran and Sheoran (2006) Gangon et al. (2007), Yang et al. (2007),Headley and Tanner (2008), Kadlec and Wallace (2008) Faulwetter et al. (2009), Taketani et al. (2010), Lizama et al. (2011)
Filtration	Very high removal efficiency Produced sludge can be used as an alternative for lime pre-treatment	Membrane fouling Limited lifetime Insufficient rejection of pollutants (magnesium ions) pH should be managed	Eriksson (1988), Rautenbach and Gröschl (1990) Peeters et al. (1998), Visser et al. (2001) Tanninen et al. (2006), Van der Bruggen et al. (2008) Barr (2001), Preuβ et al. (2012)
Adsorption	Wastes become useful High removal efficiency Can be modelled through established isotherms (Langmuir and Freundlich) Novel approach Less expensive Regeneration is easier	Still a growing area of research	Sircar et al. (1996), Kadirvelu et al. (2003) Malhotra and Chaubey (2003), Tancredi et al. (2004) Marsh and Reinoso (2006), Muthulakshmi et al. (2006) Dias et al. (2007), Hameed et al. (2007), Tan et al. (2008) Cao et al. (2011), Hong et al. (2014), Hou et al. (2014)
Ion exchange	Reversible process High removal efficiency Fast kinetics Able to treat residual sulphate concentrations	Regeneration must take place Capacity is limited Economy depends on the resin	Vidlář et al. (2002), Lopez et al. (2009), Miller et al. (2009) Fu and Wang (2011)
Precipitation (excluding lime)	Inexpensive (except the use of barium salts) Ability to recover the main components of the sludge created	Forms a sludge Residual sulphate concentration is left in the solution	Smit (1999), Vidlář et al. (2002), Bowell (2004),Maree et al. (2004), Gitari et al. (2006), Hlabela et al. (2007) Hlabela (2009), Ahmaruzzaman (2010), Fu and Wang (2011) Madzivire et al. (2011), Bologo et al. (2012),Gomelya et al. (2014)

special design improvements are required. The quality of the substrate, oxygen availability and residence time are key parameters to be addressed when designing wetland systems.

The recent developments have introduced a certain level of novelty to some of the established methods in treating AMD. Especially, the filtration methods are capable of producing drinking water quality with a higher capital and operating costs. Inability to cope with scaling issues and short membrane life are major drawbacks of this method. However, the sulphate removal from filtration is second to no other method. Electrocoagulation is considered to be in par with filtration although the industrial use is yet to be established. Adsorption is the most recent trend in contaminant removal, which takes place by simply modifying the chemical structure of the surfaces of certain substances. The method proves to be very effective as sometimes the waste materials are utilized as adsorbents. Healthy sulphate removal is thus experienced, however the method only remains effective in laboratory conditions since dealing with a higher inflow might be challenging.

Ion exchange, of course is one of the best methods in treating sulphates since it gives larger sulphate reduction rates. Additionally, ion exchange method is able to produce a drinking water quality output, leaves brine and sludge to be dealt with in the downstream. Regeneration of the resin requires monitoring, as the resin is the key to this method's performance. The capital cost of GYP-CIX (ion exchange) can be considerably lower compared to filtration and electrocoagulation. Precipitation methods require careful monitoring as sludge is produced. Barium salts are well established in reducing sulphates to a low level, however, results are expected to be unfavourable when other metal constituents are available in the solution. Therefore, the usage of barium salts alone will not be ideal in order to treat AMD. SAVMIN technique excels in both reducing the sulphate concentration and trace metal removal. The produced ettringite (Eq. (18)) is capable of being recycled, thereby operating costs will be reduced.

6. Conclusions and recommendations for future work

The paper reviewed all the remediation technologies pertaining to sulphate removal from AMD to date and presented a comprehensive list of methods that are available to tackle the sulphate problem from AMD. Researchers have proposed a number of promising techniques to address the issue under controlled laboratory trials but their industrial level applications still need to be tested. The utility of respective methods is determined by the economies of scale of operation, climates in which they operated and capability offered by the individual method or technique. AMD consists of many contaminants apart from sulphates, which pose an additional threat by introducing competition among the ions.

Sulphate removal from AMD was discussed under conventional methods as well as the recent developments. Conventional sulphate removal methods mainly consist of lime, limestone and wetlands. Although these methods have been extensively investigated, the sulphate removal is not up to the expected level. The recent developments, which entail filtration, electrocoagulation, adsorption, ion exchange and precipitation discussed in this work show high sulphate removal results compared to conventional methods.

In summary, lime or limestone is a potential pre-treatment approach to treat the solution from metal constituents. Solution pH will be raised and a gypsum saturated solution will be resulted. The subsequent selection of the treatment process is decided according to the plant requirements. For high water volume SAVMIN would be a better option as recycling permits cost reductions. Filtration methods pave the way to a drinking water quality with high process costs. Maintenance costs are substantially reduced if a passive treatment method is opted, but these lag behind in time taken for sulphate reductions. Adsorption methods are a definite area of research interest. They are considered environmentally friendly, as the waste materials can be modified into adsorbing agents. However, large-scale trials are required to acquire conclusive evidence if the adsorption methods excel in the ability to remove sulphates as promised in the laboratory scale.

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