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Review article

How to tackle the stringent sulfate removal requirements in mine water treatment—A review of potential methods

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ABSTRACT

Sulfate (SO_4^{2-}) is a ubiquitous anion in natural waters. It is not considered toxic, but it may be detrimental to freshwater species at elevated concentrations. Mining activities are one significant source of anthropogenic sulfate into natural waters, mainly due to the exposure of sulfide mineral ores to weathering. There are several strategies for mitigating sulfate release, starting from preventing sulfate formation in the first place and ending at several end-of-pipe treatment options. Currently, the most widely used sulfate-removal process is precipitation as gypsum ($CaSO_4 \cdot 2H_2O$). However, the lowest reachable concentration is theoretically 1500 mg L^{-1} SO_4^{2-} due to gypsum's solubility. At the same time, several mines worldwide have significantly more stringent sulfate discharge limits. The purpose of this review is to examine the process options to reach low sulfate levels (< 1500 mg L^{-1}) in mine effluents. Examples of such processes include alternative chemical precipitation methods, membrane technology, biological treatment, ion exchange, and adsorption. In addition, aqueous chemistry and current effluent standards concerning sulfate together with concentrate treatment and sulfur recovery are discussed.

1. Introduction and background

The main sources of sulfur to natural waters are solubilization from minerals, fertilizers, atmospheric precipitation, and dry deposition (Wetzel, 2001). Mining activities are significant point-sources of anthropogenic aqueous sulfur as sulfate (SO_4^{2-}) concentrations in mine waters can explicitly exceed 10,000 mg L^{-1} (de la Torre et al., 2011). However, sulfate is also a naturally occurring ubiquitous major anion: its concentration varies typically from 0 to 630 mg L^{-1} in rivers, 2 to 250 mg L^{-1} in lakes, and 0 to 230 mg L^{-1} in ground water (UNEP, 1990). The typical level of sulfate in seawater is approximately 2700 mg L^{-1} (Hitchcock, 1975). In rainwater, sulfate concentration is approximately 1–6 mg L^{-1} (Franklin et al., 1985; WHO/UNEP, 1989), but it has been declining as a result of atmospheric sulfur emission reduction policies (Vet et al., 2014).

Sulfate is not considered toxic as such, but it can cause diarrhea, dehydration, catharsis, and changes in methaemoglobin and sulfhemoglobin levels in humans and animals when ingested in large amounts (Cocchetto and Levy, 1981; Digesti and Weeth, 1976; Gomez et al., 1995; Paterson et al., 1979). In freshwater species, sulfate can be directly lethal at elevated concentrations due to osmoregulatory stress (Soucek and Kennedy, 2005). However, as an example, sulfate has been found to be less toxic to freshwater daphnids than other major ions such as K^+, Mg^{2+}, HCO_3^-, or Cl^- (Mount et al., 1997). Nevertheless, sulfate is a contributor to the salinization of freshwater bodies and is therefore seen as an urgent environmental issue (Cañedo-Argüelles et al., 2013). In addition to the environmental and health effects, sulfate causes the deterioration of concrete (i.e., sulfate attack) (Glasser et al., 2008; Monteiro, 2005) and increases the chloride-induced corrosion rate of concrete reinforcements (Al-Tayyib and Shamim Khan, 1991; Dehwah et al., 2002). Sulfate also enhances metal release from corrosion scales in water pipes (Sun et al., 2017). However, sulfate can also act as a pitting corrosion inhibitor by providing a supporting electrolyte that reduces the migration of, for instance, chloride into pits (Frankel, 1998). Under anaerobic conditions, sulfate can be bacterially reduced to hydrogen sulfide (H_2S), which is significantly more toxic (Doujaiji and Al-Tawfiq, 2010; Reiffenstein et al., 1992) and causes microbiologically influenced corrosion (Enning and Garrelfs, 2014).

The speciation of sulfur is presented in Fig. 1. Sulfate is present as either deprotonated SO_4^{2-} (pH > approx. 2) or in the protonated form, HSO_4^{2-} (pH < approx. 2). As an interesting note, the existence of aqueous sulfide (S^{2-}) species has been seriously questioned based on recent

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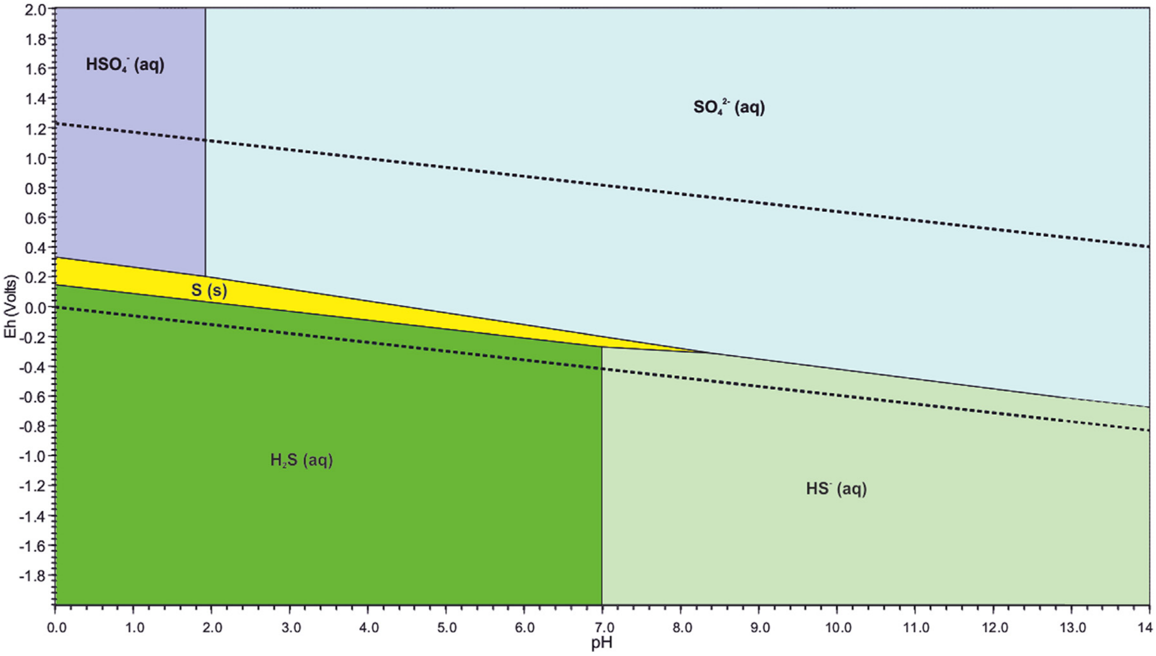

Fig. 1. Eh-pH diagram of sulfur illustrated with the HSC Chemistry software. The deprotonated sulfide (S^{2-} (aq)) has been excluded from the diagram as its existence is unlikely (May et al., 2018).

Raman spectroscopy measurements even in extremely alkaline conditions (May et al., 2018) and thus it has been excluded from Fig. 1. The reduction of sulfate requires a very strong reducing agent, such as Cr(II) (Stone and Forstner, 1957), and thus does not occur in natural aqueous environments by chemical means. However, sulfate can be reduced by hydrocarbons at elevated temperatures (approx. 100–180 °C), which is referred to as thermochemical sulfate reduction and causes the high concentrations of hydrogen sulfide in oil reservoirs (Goldstein and Aizenshtat, 1994; Machel, 2001). However, in practice, the most common pathway to sulfate reduction is via the action of sulfate reducing bacteria (SRB), such as *Desulfovibrio vulgaris*.

Sulfate in mine water originates mainly from the geochemical weathering of rocks and to a lesser extent from sulfur-containing process chemicals. When elemental sulfur (S^0) or sulfides (such as pyrite, FeS_2) are oxidized in the presence of water, and frequently catalyzed by micro-organisms, sulfuric acid is generated according to the frequently used overall reactions (1) and (2) (Silva et al., 2012). The water stream in which reactions occur is referred to as acid mine drainage (AMD) (Heikkinen et al., 2009). AMD formation also continues after mine closure if appropriate management is not practiced (Ríos et al., 2008).

$$FeS_2\ (s) + 3\tfrac{1}{2}\ O_2\ (aq) + H_2O \rightarrow FeSO_4\ (aq) + H_2SO_4\ (aq) \tag{1}$$

$$2S\ (s) + 3O_2\ (aq) + H_2O \rightarrow 2H_2SO_4\ (aq) \tag{2}$$

It should be noted, though, that pyrite oxidation is a multistep process (Johnson and Hallberg, 2005) and that the main oxidant is usually ferric iron (Fe^{3+}) instead of dissolved oxygen (Evangelou, 1995). A more thorough set of reactions occurring during pyrite, arsenopyrite (FeAsS), or chalcopyrite (CuFeS) oxidation can be represented by reactions (3)–(7), (8)–(10), and (11)–(12), respectively (Parviainen, 2012). The oxidation reactions can also result in the formation of metastable anions, such as sulfite (SO_3^-), thiosulfate ($S_2O_3^{2-}$), and polythionates ($S_nO_6^{2-}$), which will eventually be oxidized into sulfate (Descostes et al., 2004; Moses et al., 1987).

$$FeS_2\ (s) + 7/2O_2\ (aq) + H_2O \rightarrow Fe^{2+}\ (aq) + 2SO_4^{2-}\ (aq) + 2H^+\ (aq) \tag{3}$$

$$Fe^{2+}\ (aq) + 1/4O_2\ (aq) + H_2O \rightarrow Fe^{3+}\ (aq) + 1/2H_2O \tag{4}$$

$$FeS_2\ (s) + 14Fe^{3+}\ (aq) + 8H_2O \rightarrow 15Fe^{2+}\ (aq) + 2SO_4^{2-}\ (aq) + 16H^+\ (aq) \tag{5}$$

$$FeS_2\ (s) + 15/4O_2\ (aq) + 7/2H_2O \rightarrow Fe(OH)_3\ (s) + 2SO_4^{2-}\ (aq) + 4H^+\ (aq) \tag{6}$$

$$Fe_{(1\text{-}x)}S\ (s) + (2\text{-}x/2)O_2\ (aq) + xH_2O \rightarrow (1\text{-}x)Fe^{2+}\ (aq) + SO_4^{2-} + 2xH^+\ (aq) \tag{7}$$

$$FeAsS\ (s) + 11/4O_2\ (aq) + 3/2H_2O \rightarrow Fe^{2+}\ (aq) + H_3AsO_3\ (aq) + SO_4^{2-}\ (aq) \tag{8}$$

$$H_3AsO_3\ (aq) + 1/2O_2\ (aq) \rightarrow HAsO_4^{2-}\ (aq) + 2H^+\ (aq) \tag{9}$$

$$FeAsS\ (s) + 7/2O_2\ (aq) + 6H_2O \rightarrow Fe(OH)_3\ (s) + SO_4^{2-}\ (aq) + H_2AsO_4^-\ (aq) + 3H^+\ (aq) \tag{10}$$

$$2CuFeS_2\ (s) + 4O_2\ (aq) \rightarrow 2Cu^{2+}\ (aq) + Fe^{2+}\ (aq) + SO_4^{2-}\ (aq) \tag{11}$$

$$2CuFeS_2\ (s) + 17/2\ O_2\ (aq) + 5H_2O \rightarrow 2Cu^{2+}\ (aq) + 2Fe(OH)_3\ (s) + 4SO_4^{2-}\ (aq) + 4H^+\ (aq) \tag{12}$$

Only few natural processes, such as precipitation of gypsum ($CaSO_4{\cdot}2H_2O$), epsomite ($MgSO_4{\cdot}7H_2O$), jarosite ($(K,Na,H)Fe_3(SO_4)_2(OH)_6$), or other secondary minerals, remove sulfate from ground and surface waters (Lottermoser, 2010). Therefore, sulfate has a relatively long residence time in the aqueous environment once it is released. The direct and indirect environmental concerns of sulfate release have led to continuously more stringent sulfate removal requirements for mines worldwide, which cannot be attained via the conventionally used gypsum precipitation. The theoretically reachable minimum concentration with gypsum precipitation is 1500 mg L^{-1} SO_4^{2-} (at 20 °C) due to the solubility of gypsum (Geldenhuys et al., 2003). Consequently, the aim of this review paper is to present an up-to-date overview of recent research results of the available sulfate removal methods with a special emphasis on single or combined technologies capable of reducing sulfate to levels lower than with conventional gypsum precipitation. The possibility to recover sulfur chemicals from mine effluents is also briefly discussed.

2. Sulfate guideline levels and discharge limits

In drinking water, the recommended sulfate level is 250 mg L^{-1} (WHO, 2011), but some countries have set stricter sulfate recommendations to prevent the corrosion of pipes (e.g., less than 150 mg L^{-1} in Finland (Ministery of social affairs and health, 461/2000). The sulfate discharge limits for mine drainage and other industrial effluents vary typically from 250 to 1000 mg L^{-1} (Liang, 2014; Namasivayam and Sureshkumar, 2007; Silva et al., 2012). For example, in Chile, the sulfate limits for groundwater and surface water discharge are 250–500 mg L^{-1} and 1000–2000 mg L^{-1}, respectively (Jarvie-Eggart, 2015). There is considerable variation in sulfate discharge limits among countries and mines within a country depending on the characteristics of the receiving water body. In an extreme case, the sulfate limit can be as low as 10 mg L^{-1}, as in the U.S. state of Minnesota to protect wild rice (Minnesota Pollution Control Agency, 2017). In Finland, as another example, authorities have just in recent decades started to set limits for sulfate in mine water discharge: the limits range between 1000 and 4000 mg L^{-1}, but there are still active sulfide ore mines without sulfate discharge limits.

Another means of measuring sulfate (and other dissolved ions) is as total dissolved solids (TDS, mg L^{-1}). Theoretically, 1 mg L^{-1} of dissolved ions contributes 1 mg L^{-1} to the TDS value. In practice, TDS is measured based on electrical conductivity (Eq. (13)):

$$TDS = EC \times f, \tag{13}$$

where EC is electrical conductivity (μS cm^{-1}) and f is the conversion factor (dimensionless). For 45 different South African mine waters, the average f was determined to be 0.85, while 0.67 is frequently used as an approximation if the factor is not known (Hubert and Wolkersdorfer, 2015). On the other hand, each mg L^{-1} of sulfate contributes 1.54 μS cm^{-1} (at 25 °C) to conductivity (Clescerl et al., 1999).

3. Sulfate removal technologies

Preventing the formation of AMD and sulfate-containing process wastewaters should be the first means in preserving the environment from aqueous sulfate emissions. This can be done by the management of rock waste and tailings (Kefeni et al., 2017) and by optimizing the process conditions. Once AMD or sulfate-containing process wastewater is formed, it should be managed and treated properly (Kefeni et al., 2017). In recent years, not only sulfate removal but also the recovery and recycling of sulfate have become goals in the treatment of sulfate effluents. The recovery of the sulfur chemicals can take place from concentrates or solids formed in various treatment processes.

There are several techniques available for sulfate removal from effluents, as discussed in the below sections. Mine effluent treatment options can be fundamentally divided into active and passive, of which the first refers to a process requiring pumping, mechanical devices, and a continuous supply of chemicals, electricity, and maintenance, whereas the latter utilizes gravitational water flow and natural chemical and biological processes (Lottermoser, 2010).

3.1. Precipitation

In the gypsum precipitation of sulfate, an alkaline chemical, such as lime (Reaction (14)), is used to raise the mine water pH typically to 9.5. Limestone (Reaction (15)) can also be used, but it can only raise the mine water pH up to approximately 7 (Maree et al., 2004a). The use of industrial by-products as alternative calcium sources have also been investigated (Alakangas et al., 2013; Mackie et al., 2010a, 2010b; Mackie and Walsh, 2012; Tolonen et al., 2014). Gypsum precipitation is a well-known method that has been used for decades due to its effectiveness for the treatment of highly acidic mine waters, the relative simplicity of the process, and its tolerance toward temperature fluctuations (Brown et al., 2002). However, the use of gypsum precipitation as the sole process is not frequently effective enough to meet environmental limits when easily soluble metal sulfates, such as sodium sulfate, are present in water (Geldenhuys et al., 2003). Other shortcomings of the process include the formation of large amounts of high-water-content sludge with limited options for usage, difficulties in the dewatering of the sludge, high sludge disposal costs, and the scaling of equipment and pipelines (Chen et al., 2009; Matlock et al., 2002). Polymers, such as polyacrylamides and polyamines, can be used to enhance dewatering and improve the floc strength of the gypsum precipitate. Part of the sludge can also be recycled within the gypsum precipitation process, which is called the high-density sludge (HDS) process (Aubé and Lee, 2015). In the HDS process, the precipitates are formed onto recycled particles, creating larger and denser precipitates that can be more easily settled and dewatered (Aubé and Lee, 2015). Gypsum solubility limits the minimum reachable sulfate concentration to 1500 mg L^{-1} (at 20 °C) when no sodium or magnesium ions are present (Geldenhuys et al., 2003). However, with the high pH lime treatment (pH > 11), magnesium no longer inhibits sulfate removal as it precipitates as hydroxide, enhancing the gypsum precipitation (Tolonen et al., 2015).

$$Ca(OH)_2\ (s) + H_2SO_4\ (aq) \rightarrow CaSO_4{\cdot}2H_2O\ (s) \tag{14}$$

$$Ca(CO_3)\ (s) + H_2SO_4\ (aq) + H_2O \rightarrow CaSO_4{\cdot}2H_2O\ (s) + CO_2\ (g) \tag{15}$$

Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$) precipitation has been shown to be capable of reducing sulfate concentration down to 200 mg L^{-1} (Madzivire et al., 2010; Tolonen et al., 2016a, 2016b). However, the presence of magnesium in the treated water has been found to inhibit sulfate removal with ettringite precipitation (Dou et al., 2017). In ettringite precipitation, the pH of the effluent is increased to approximately 12 with lime, and aluminum salt is added, leading to the precipitation of ettringite (Reaction (16)). The most commonly used aluminum salts are sodium aluminate and aluminum hydroxide, but the use of industrial aluminum-containing wastewaters has also been studied (Álvarez-Ayuso and Nugteren, 2005). Electrocoagulation can be used to provide aluminum ions to the ettringite precipitation process. Similarly as with gypsum precipitation, polymers can be used to improve precipitate quality. When ettringite precipitation is used for waters with a high sulfate concentration (> 3000 mg L^{-1}), it may be economical to use the conventional lime precipitation as a pre-treatment. This decreases the consumption of the more expensive aluminum chemicals. The pH after ettringite precipitation can be decreased to meet the discharge limits by treating it with CO_2, which results in the precipitation of calcite ($CaCO_3$). The operational costs of ettringite precipitation can be lowered by regenerating the aluminum salt by decomposing the precipitated ettringite (Smit, 1999) or by further using the precipitated ettringite, for example, as an adsorbent for arsenate removal (Tolonen et al., 2016a, 2016b). HDS process can be used to obtain denser sludge (Sapsford and Tufvesson, 2017).

$$6Ca(OH)_2 + 3H_2SO_4 + 2Al(OH)_3\ (s) + 20H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O\ (s) \tag{16}$$

Jarosite ($XFe_3(SO_4)_2(OH)_6$, where X is usually a mixture of Na^+ and K^+) precipitation (Reaction (17)) is used in hydrometallurgical processes for dissolved iron removal from acid leach solutions before, for instance, zinc recovery (Dutrizac, 1999). Jarosite is also a commonly encountered natural secondary mineral precipitate in AMD (Valentene and Gomes, 2009). Efficient jarosite precipitation requires low pH (0–4), high temperature (130–140 °C), high pressure (5–7 bar), and a reaction time of 1–3 h (Nilsson and Jokinen, 1997). Although jarosite precipitation could theoretically be applied for mine effluents and other wastewaters (Shengfeng et al., 2007) the reported results have been poor, and the required harsh reaction conditions further decrease its feasibility (Tait et al., 2009). Also, the management of jarosite precipitates would introduce problems as decreased acidity promotes the dissolution of jarosite. Consequently, jarosite precipitation is likely not a practical method for sulfate removal from mine effluents. However, biological or combined chemical and biological jarosite precipitation could have potential for sulfate removal from AMD (Nurmi et al., 2010).

$$3Fe_2(SO_4)_3\ (aq) + Na_2SO_4\ (aq) + 12H_2O \rightarrow 2NaFe_3(SO_4)_2(OH)_6\ (s) + 6H_2SO_4\ (aq) \quad (17)$$

The precipitation of sulfate via barite can be implemented with barium salts, such as barium hydroxide, sulfide, or carbonate (Reactions (18)–(20), respectively) (Bologo et al., 2012; Bosman et al., 1990; Hlabela et al., 2007; INAP, 2003; Kefeni et al., 2015). Barium hydroxide and sulfide can be used to treat highly acidic mine waters directly, but in the case of barium carbonate, pre-treatment with, for example, lime is needed (Adlem et al., 1991). When using barium sulfide, hydrogen sulfide stripping is required (Kefeni et al., 2015; Maree et al., 2004b). Sulfate removal from mine water with barite precipitation results sulfate concentration lower than 200 mg L^{-1} (Adlem et al., 1991; Hlabela et al., 2007; Maree et al., 2004b). The solubility of barite is very low (Benatti et al., 2009). However, the barite precipitants are expensive and toxic. The process also generates barium-containing waste that needs to be disposed (Benatti et al., 2009) or, preferably, recycled. For instance, $BaSO_4$ can be thermally reduced to BaS and further converted to $BaCO_3$ and H_2S by passing CO_2 through BaS solution (Hlabela et al., 2007). $BaCO_3$ can be thermally decomposed to BaO and further hydrolyzed to $Ba(OH)_2$ (Adlem et al., 1991). Also, the produced effluent requires the monitoring of barium traces and possibly post-treatment (Benatti et al., 2009).

$$Ba(OH)_2\ (s) + H_2SO_4\ (aq) \rightleftharpoons BaSO_4\ (s) + 2H_2O \quad (18)$$

$$BaS\ (s) + H_2SO_4\ (aq) \rightleftharpoons BaSO_4\ (s) + H_2S\ (g) \quad (19)$$

$$BaCO_3\ (s) + H_2SO_4\ (aq) \rightleftharpoons BaSO_4\ (s) + H_2CO_3\ (aq) \quad (20)$$

In addition, iron anodes have been reported to work successfully in sulfate removal from synthetic effluent by electrocoagulation although the exact removal mechanism remained unexplained: the formation of species such as $Fe_2(SO_4)_3$ among other coagulation mechanisms was speculated (Mamelkina et al., 2017). Sulfate removal from beamhouse and tannery wastewater and also synthetic samples by adsorption on metal oxides/hydroxides formed in electrocoagulation treatment has also been speculated (Murugananthan et al., 2004). When comparing iron and aluminum anodes, the latter was found to result in a better removal of sulfate (Nariyan et al., 2017). One additional possible removal mechanism is the adsorption of sulfate on the formed aluminum flocs (Sandoval et al., 2017).

3.2. Adsorption

Sulfate removal with adsorption has been studied with a wide range of materials: activated carbon (Hong et al., 2014, 2017; Hou et al., 2014; Salman, 2009), fly ash (Koshy and Singh, 2016), modified geopolymers (Runtti et al., 2016a), modified zeolites (Oliveira and Rubio, 2007; Runtti et al., 2017; Vujaković et al., 2000), limestone (Iakovleva et al., 2015; Silva et al., 2012), modified coir pith (Namasivayam and Sureshkumar, 2007), modified rice straw (Cao et al., 2011), nano-alumina (Katal et al., 2012), soils (Bazer-Bachi et al., 2007; Delfosse et al., 2006; Gustafsson et al., 2015), iron sand, and pulp and paper waste (Iakovleva et al., 2015). Chemical modification has been performed, for instance, with polypyrrole (Hong et al., 2014, 2017; Hou et al., 2014), $BaCl_2$ (Runtti et al., 2016a, 2017), $ZnCl_2$, (Namasivayam and Sangeetha, 2008), NaOH (Moret and Rubio, 2003), $(NH_4)_2S_2O_8$ (Sang et al., 2013) and $ZrOCl_2{\cdot}8H_2O$ (Mulinari and da Silva, 2008), and cationic surfactants (Rui et al., 2011). The modification has frequently aimed to convert surface charge into positive or introduce sulfate-precipitating elements (such as Ba) in the adsorbent structure.

Adsorption mechanisms of sulfate has been in dispute, but the suggested mechanism is the formation of an oxi-hydroxide layer on the surface and a change of the surface charge into positive (i.e., Coulomb interaction between surface and sulfate anion) as summarized by Runtti et al. (2016a) and the references therein. Furthermore, the ligand exchange with the formation of surface outer- and inner-sphere complexes have a role in the mechanism (Rahnemaie et al., 2006). In addition, surface precipitation onto the adsorbent contributes to the removal on some cases (Ishiguro et al., 2006; Sokolova and Alekseeva, 2008).

Adsorption, in general, has potential to be an effective and economic method (Fu and Wang, 2011; Gupta et al., 2013; Yavuz et al., 2003). However, there are many factors in industrial applications that affect the technical and economic feasibility. First, the adsorbent should have high adsorption capacity and selectivity for sulfate. Currently, there is a lack of commercially available adsorbents specifically for sulfate removal from mine effluents. However, a recent patent application describes an adsorbent for the removal of sulfur substances (Aalto et al., 2017). The raw materials and the preparation of the adsorbent (including possible chemical modification) should be as inexpensive, simple, and environmentally friendly as possible. Finally, the adsorbent should be regenerable, otherwise the operational costs arising from the continuous consumption of the adsorbent will likely be too high for large-scale use. In industrial applications, adsorption is generally performed with continuous flow reactors. The treatment efficiency is determined by pH, temperature, concentration, flow rate, dose of adsorbent (or bed volume), and ionic strength, for instance. Most likely the most economical use for adsorption would be after other sulfate removal methods in cases where extremely low sulfate concentrations are required. The existing literature on sulfate adsorbents is summarized in Table 1.

3.3. Ion exchange

Ion exchange is the displacement of counter ions on the exchanger surface by impurity ions from the solution (Haghsheno et al., 2009; Sincero and Sincero, 2003). Selective ion exchange media are available, and sulfate ions can typically be removed by weak base anion resins (Guimarães and Leão, 2014; Sincero and Sincero, 2003). Basic ion exchange resins consist of polymers (such as poly(styrene-divinylbenzene)) to which positively charged functional groups (such as tertiary amine) are attached, which act as exchange sites (Sincero and Sincero, 2003). The number of these groups determines the exchange capacity, and the type of the groups determines the ion selectivity (Sincero and Sincero, 2003). The affinity of most common anions for the ion exchange resin follows the sequence citrate > SO_4^{2-} > NO_3^- > I^- > Br^- > Cl^- > formate > acetate > F^- (Sincero and Sincero, 2003). The patented GYP-CIX process consists of weak base anion and strong acid cation resins and is suitable for the effective removal of sulfate at concentration levels near the saturation stage of gypsum (INAP, 2003). The GYP-CIX process was tested, for example, by Robertson et al. (1993) who found that the initial sulfate concentration (8000 mg L^{-1}) was decreased to 1980 mg L^{-1} after gypsum precipitation and further to 200 mg L^{-1} by using the GYP-CIX process. Another process, called Sulf-IX, has been developed based on the GYP-CIX process (Doughty and Littlejohn, 2015).

After the ion exchanger is saturated, it can be regenerated with, for instance, NaOH (suitable for strong base and weak base anion resins) (Valverde et al., 2006). In the GYP-CIX process, 2% lime and 10% sulfuric acid solutions are used for the regeneration of the weak base anion and the strong acid cation resins, respectively. Furthermore, in the GYP-CIX process, the regeneration solutions are seeded with gypsum crystals, which promotes the precipitation of calcium as calcium sulfate (Schoeman and Steyn, 2001). However, due to limited capacities and selectivities, ion exchange may not be suitable as primary technique, but rather after chemical precipitation (Feng et al., 2000).

Table 1
Different adsorbents for sulfate removal.

Adsorbent	Effluent type	Adsorption capacity q_e [mg/g]	Initial pH	C0 [mg/L]	Sorbent dose [g/L]	Contact time [h]	T [°C]	Ref.
Chitosan-*graft*-Polyacrylamide copolymer	Synthetic	277.78[a]	< 4	500–3000	3	–	–	Fosso-Kankeu et al. (2015)
Chitin-based shrimp shells	Synthetic	156.0[a]	4.3	0–2350	10	1	25	Moret and Rubio (2003)
Desilicated fly ash	AMD	147.06[b]	10–12	–	20	1	35	Ntuli et al. (2016)
Barium-modified blast-furnace slag geopolymer (Ba-BFS-GP)	AMD	119.0[c]	7–8	865	1.3–15	24	22–23	Runtti et al. (2016a)
poly(m-phenylenediamine)	Synthetic	108.5[a]	< 3	500–4000	13.3	1	30	Sang et al. (2013)
Barium-modified blast-furnace slag geopolymer (Ba-BFS-GP)	Synthetic	91.1[c]	7–8	100–1800	5	24	22–23	Runtti et al. (2016a)
Epichlorohydrin and trimethylamine modified rice straw	Synthetic	74.76[a]	6.4	50–500	2	2	25	Cao et al. (2011)
Ba-modified zeolite	Synthetic	64.10[a] (1.33 meq g^{-1})	6.0	< 1000	10	2	25	Oliveira and Rubio (2007)
Polypyrrole-grafted granular activated carbon	Synthetic	48.0[c]	–	10–400	2.5	24	20	Hong et al. (2014)
Polypyrrole modified hardwood-based activated carbon	Synthetic	44.7[c]	7–7.2	250	2.5	24	20	Hong et al. (2017)
Alkali-treated fly ash	Groundwater	43.0[c]	7	200	0–2	2.5	–	Geethamani et al. (2014)
Metasomatite	Synthetic	31.1[d]	2	1770	4	0.18	–	Sadeghalvad et al. (2016)
Andisols	Synthetic	28.2[a] (300 mmol/kg)	4–7	0.14–81,660 (0.0015–850 mmol/L)	8.3	3	–	Ishiguro et al. (2006)
Quartz-albitophire	Synthetic	26.2[d]	2	1950	4	2.17	–	Sadeghalvad et al. (2016)
Filter sand	Synthetic	25.07[c] (261 mmol g^{-1})	–	20–2000	40	480	22	Iakovleva et al. (2015)
Limestone	Synthetic	23.7[a]	6.5	50–3000	25	9	23	Silva et al. (2012)
Flotation fines	Synthetic	21.23[c] (221 mmol g^{-1})	–	20–2000	40	480	22	Iakovleva et al. (2015)
FeCl3 modified carbon residue (MCR)	Synthetic	19.6[c]	4	50–1000	5	24	20–23	Runtti et al. (2016b)
Electrochemically polymerized.activated carbon	Synthetic	18.0[c]	7–7.2	250	2.5	24	20	Hou et al. (2014)
Barium-modified acid washed analcime (Ba-Ac-ANA)	Synthetic	13.7[c]	3–6	10–500	5	3	23	Runtti et al. (2017)
Raw rice straw	Synthetic	11.68[a]	6.4	50–500	2	2	25	Cao et al. (2011)
Nano alumina	Synthetic	10.86[b]	5.0	50	0.5–40	0.6	20	Katal et al. (2012)
Surfactant modified coir pith	Synthetic	8.76[a]	2	10–50	4	–	32	Namasivayam and Sureshkumar (2007)
Pristine hardwood-based activated carbon	Synthetic	4.0[c]	7–7.2	250	2.5	24	20	Hong et al. (2017)
γ-Al_2O_3	Synthetic	7.7[a]	5.7	20–40	–	24	25	Wu et al. (2002)
Activated carbon	Synthetic	7.6[c]	2	50–1000	5	24	20–23	Runtti et al. (2016b)
Surfactant-modified clinoptilolite	Synthetic	~7.5[a] (~78 mmol/kg)	4.0–5.1	96–500 mg/l (1–5.2 mmol/l)	5%(w/w)	24	25	Vujaković et al. (2000)
$ZnCl_2$ activated coir pith carbon	Synthetic	4.9[a]	4.0	20–80	10	0.75	35	Namasivayam and Sangeetha (2008)
Barium-modified zeolite (ZSM5-Na-Ba)	Synthetic	3.8[c]	4–7	10–1000	5	3	23	Runtti et al. (2017)
Surfactant-modified palygorskite	Synthetic	3.24[a]	4	20–130	10	4	35	Rui et al. (2011)
Raw date palm seeds	Synthetic	3.2[c]	3.5	100	10	–	25	Koumaiti et al. (2011)
Barium-modified analcime (Ba-ANA)	Synthetic	2.3[c]	6–7	10–1000	5	3	23	Runtti et al. (2017)
Pulp and paper waste	Synthetic	2.786[c] (29 mmol g^{-1})	–	20–2000	40	480	22	Iakovleva et al. (2015)
Soils of Sao Paulo State, Brazil	Synthetic	0.18–1.420[c]	–	0–0.156	100	24	–	Alves and Lavorenti (2004)
Kaolinite	Synthetic	1.2[c]	6	–	100	24	30	Rao and Sridharan (1984)
Iron sand	Synthetic	1.153[c] (12 mmol g^{-1})	–	20–2000	40	480	22	Iakovleva et al. (2015)
Feldspar	Synthetic	0.275[a]	5.5	1–5	100	3	25	Priyantha and Perera (2000)
Coir pith carbon	Synthetic	0.06[a]	4.0	20–80	10	0.75	35	Namasivayam and Sangeetha (2008)

[a] Langmuir isotherm maximum adsorption capacity.
[b] Dubinin-Raduschkevich isotherm maximum adsorption capacity.
[c] Experimental maximum adsorption capacity.
[d] Experimentally optimized conditions.

3.4. Biological treatment

Microbial sulfate removal from AMD has been studied for over 50 years (Tuttle et al., 1969), and the number of publications on this topic is immense. The technology and related science has also been reviewed numerous times (Barton and Fauque, 2009; Hansen, 1994; Johnson and Hallberg, 2005; Klein et al., 2014; Lens et al., 2002; Sánchez-Andrea et al., 2014; Sheoran et al., 2010; Wu et al., 2013). Therefore, the aim of this section is to provide a brief overview of the technical principles and focus summarizing recent publications.

Microbial sulfate removal from wastewater is based on the activity of sulfate reducing bacteria (SRB) and other prokaryotes capable of reducing sulfate (i.e., using it as a terminal electron acceptor) while oxidizing organic compounds or hydrogen (i.e., using them as electron donors) (Barton and Hamilton, 2007). The formed sulfide can precipitate with metals or volatilize as hydrogen sulfide gas (Isosaari and Sillanpää, 2017). Sulfate reduction by SRB typically takes place in anaerobic conditions (no free dissolved oxygen present) with a pH of 5–8 and an oxidation-reduction potential less than − 100 mV (Postgate, 1984). However, acidophilic and acid-tolerant SRB can survive at a lower pH; for instance, a pH of 4.0 was found to be optimum in one study (Santos and Johnson, 2017). A high sulfate concentration (3500 mg L^{-1}) was found to be initially inhibiting (i.e., the reactor became fully operational more slowly) for sulfate conversion in comparison to a lower concentration (1000 mg L^{-1}) (Bernardez et al., 2012). SRB can tolerate cold temperatures, as documented for instance by Baldwin et al. (2016): a full-scale bioreactor had successfully operated for approximately 10 years at a temperature of 0–17 °C in Canada. In addition, several other studies (Auvinen et al., 2009; Sahinkaya et al., 2015; Tsukamoto et al., 2004) have indicated that microbial sulfate removal has potential for low temperature conditions but with a relatively lower sulfate reduction rate. Finally, it should be noted that SRB can use many other electron acceptors in addition to sulfate (e.g., nitrate is more preferable than sulfate), and they have to compete with other anaerobes for the available substrates (Muyzer and Stams, 2008). The coexistence of different microbes can be, however, beneficial since SRB are unable to utilize complex organic compounds without fermentation (Muyzer and Stams, 2008).

The generalized overall reaction occurring during microbial sulfate removal can be presented as follows (Reaction (21)):

$$8H^{+}\ (aq) + 8e^{-}\ (aq) + SO_4^{2-}\ (aq) \rightarrow S^{2-}\ (aq) + 4H_2O\ (aq) \tag{21}$$

In the above reaction, the electrons can be supplied from hydrogen gas, acetate, propionate, butyrate, or lactate, for instance, as presented by reactions (22)–(26), respectively (Muyzer and Stams, 2008):

$$4H_2\ (aq) + SO_4^{2-}\ (aq) + H^{+}\ (aq) \rightarrow HS^{-}\ (aq) + 4H_2O\ (aq) \tag{22}$$

$$CH_3COO^{-}\ (aq) + SO_4^{2-}\ (aq) \rightarrow 2HCO_3^{-}\ (aq) + HS^{-}\ (aq) \tag{23}$$

$$CH_3CH_2COO^{-}\ (aq) + 0.75\ SO_4^{2-}\ (aq) \rightarrow CH_3COO^{-}\ (aq) + HCO_3^{-}\ (aq) + 0.75HS^{-}\ (aq) + 0.25H^{+}\ (aq) \tag{24}$$

$$CH_3CH_2CH_2COO^{-}\ (aq) + 0.5\ SO_4^{2-}\ (aq) \rightarrow 2CH_3COO^{-}\ (aq) + 0.5HS^{-}\ (aq) + 0.5H^{+}\ (aq) \tag{25}$$

$$CH_3CHOHCOO^{-}\ (aq)\ 0.5\ SO_4^{2-}\ (aq) \rightarrow CH_3COO^{-}\ (aq) + HCO_3^{-}\ (aq) + 0.5HS^{-}\ (aq) \tag{26}$$

As with other AMD treatment processes, those involving SRB can be classified as passive or active. Active systems require the continuous management of chemicals and/or energy, while passive systems can operate several years without maintenance (Gusek and Schueck, 2004; Rose et al., 2004, 2007). According to Skousen et al. (2017), passive biological systems capable of sulfate reduction are anaerobic constructed wetlands, vertical flow wetlands, and bioreactors. Similar systems are also sometimes called infiltration beds, alkalinity-producing systems, or successive alkalinity-producing systems (Isosaari and Sillanpää, 2017; Skousen et al., 2017). When treating effluent from a closed mine, perhaps the simplest passive system is to add a suitable substrate directly to the flooded shafts (Bomberg et al., 2015). Active systems involving SRB, on the other hand, are referred to as sulfidogenic bioreactors.

Anaerobic constructed wetlands consist of vegetation on a permeable substrate (e.g., soil mixes, peat moss, spent mushroom compost, sawdust, manure) frequently mixed with limestone (Skousen et al., 2017). The substrate and vegetation act as electron donors and carbon and nutrient sources. The effluent flow direction is horizontal, and it typically occurs at the surface. The system generates alkalinity from sulfate reduction and from calcium carbonate dissolution. It is important to keep the conditions continuously anaerobic to prevent sulfate removal perturbations, ferric hydroxide formation, and subsequent clogging. Lefèvre et al. (2013) found that ethanol injection was an efficient means to recover an SRB process from oxygen exposure in comparison to several other methods. In vertical flow wetlands, effluent flows from an elevated (1–2 m) pond through a substrate and limestone bed (0.2–0.6 m) in which oxygen is depleted and sulfate reduction occurs (Skousen et al., 2017). In terms of efficiency, an average 31% of 900 mg L^{-1} sulfate was removed during a two-year pilot using surface-flow wetland to treat AMD (O'Sullivan et al., 2004). Bioreactors (also known as compost bioreactors, sulfate-reducing bioreactors, or infiltration beds) are constructed of a covered bed of organic material and fine particle size limestone or other calcareous material through which AMD is allowed to flow vertically (Skousen et al., 2017). The design of passive systems for sulfate removal is discussed in numerous publications (Gusek, 2004; Neculita and Zagury, 2008; URS Corporation, 2003). A typical feature of all such systems is a relatively long hydraulic retention time, as can be seen from Table 3. In addition, before the start-up of the treatment, the process needs a maturation period for suitable conditions and microbe strains to develop. The addition of bacteria inoculum (such as manure) can aid the start-up phase. Passive treatment systems perform relatively well for the first few months after start-up, but issues faced in the long-term performance include, leakage, a too-low pH level, seasonal variation, substrate limitations, and clogging problems (Neculita et al., 2007).

Sulfidogenic bioreactors are constructed and operated for the optimized production of hydrogen sulfide. They can be implemented in several set-ups, such as a continuously stirred tank reactor, an up-flow anaerobic sludge bed reactor, an expanded granular bed reactor, a fluidized bed reactor, a gas-lift bioreactor, or a membrane bioreactor (Bijmans, 2008; Kousi et al., 2015). One interesting approach is to use modular low pH (influent pH ≈ 1.5–4) sulfidogenic bioreactors which utilize acidophilic/acid-tolerant SRB, non-acid substrates (e.g., glycerol), and Zn^{2+} to buffer pH and remove H_2S for biosulfidogenesis (i.e., end-products of sulfate reduction are H_2S and H_2CO_3 instead of HS^{-} and HCO_3^{-}) (Kimura et al., 2006; Ňancucheo et al., 2016). In addition, low pH sulfidogenic bioreactors can be used for selective recovery of metals (Ňancucheo and Johnson, 2011). The advantage of active systems compared to passive ones is that they are more predictable and their performance is more controllable, which improves the potential for the selective metal recovery in addition to effective sulfate removal. However, since the electron donors and other chemicals are continuously fed, the operational costs can be higher than with passive systems. Similar to passive systems, sulfidogenic bioreactors require a long hydraulic retention time (Table 3).

One of the most important aspects in the microbiological sulfate removal design is the selection of the substrate, which supplies electrons, carbon, and nutrients. For passive systems, solid and usually waste-based substrates are used, while active systems employ liquid or gaseous materials. Suitable substrates have been reviewed by, for instance, Liamleam and Annachhatre (2007) and Dev et al. (2015). The selection should be based on the treatment efficiency (the reduction of sulfate and minimizing the occurrence of other pollutants) and the cost per unit sulfate converted into sulfide (Liamleam and Annachhatre,

Table 2
Examples of recent microbial sulfate removal studies from AMD.

Initial SO_4^{2-} [mg L^{-1}]	pH	T [°C]	HRT [h]	Electron donor/substrate	Experimental set-up	SO_4^{2-} reduction rate [(g m^{-3}) d^{-1}]	SO_4^{2-} removal	Final SO_4^{2-} [mg L^{-1}]	Ref.
315	3.02 or 6.25	≈ 2–15	5–25	Rice bran	Continuous 50 L vertical flow bioreactor	n.r.	≈ 30–60% (pH 6.25, HRT 12 h)	≈ 80–230	Aoyagi et al. (2017)
1986	≈ 5–7	n.r.	100	Chitinous substrate	Continuous 1.15 L up-flow column	239 (HRT 100 h), 415 (HRT 50 h)	81% (HRT 100 h), 62% (HRT 50 h)	361 (HRT 100 h), 759 (HRT 50 h)	Aoyagi et al. (2017)
1600[a]	2.62–3.06	Room temp.	0.08–120	Spent mushroom compost, activated sludge, woodchips	Batch test in 2 L bioreactor	n.r.	95% (HRT 120 h)	80 (HRT 120 h)	Muhammad et al. (2017)
172	3.2–3.5	Average 8 °C	9–53	Mussel shell	Full-scale vertical flow bioreactor at mine site, dimensions: top: 32 m × 20 m, height: 1.2 m, bottom: 24 m × 12 m), 200 mm water cover	≈ 25	8%	158	DiLoreto et al. (2016)
1750 or 2570	3.99 or 2.81	Room temp.	8–168	Straw, chicken manure, mushroom compost	Continuous 3.1 or 6.2 L up-flow column	200–600	6–24%	1200–2300	Jeen and Mattson (2016)
171[a]	4.6	16–22	115	Hydrogen gas	Laboratory-scale constructed wetland (a floating hydroponic root mat on a 1 m × 0.15 m × 0.2 m water layer) with continuous flow of AMD	n.r.	Up to 87%	22	Richter et al. (2016)
1000	2.6	Room temp.	120	Marine waste extract	0.9 L up-flow column packed with polyurethane beads	122–132	62–66%	380–340	Dev et al. (2016)
702	7.5	17–25	720	Synthetic domestic wastewater sludge	1 L plastic bags as batch reactors	Up to 120 (at 25 °C)	96% (at 25 °C)	28 (at 25 °C)	Van Den Berg et al. (2016)
2500[a]	3.0–3.7	Room temp.	24–96	Cow manure, mushroom compost, sajo sawdust, wetland sediment	Continuous 5 L up-flow column	n.r.	> 60%	1000–2000 (HRT 48 h)	Vasquez et al. (2016)
900–1800	2.75–5	30	32–48	Glycerol or H_2/CO_2	Continuous 0.3 L up-flow column packed with pozzolana	72–600 (using H_2/CO_2)	n.r.	0–1200 (using H_2/CO_2)	Battaglia-Brunet et al. (2012)
3538	3.09	n.r.	n.r.	Wood chips, straw, seasoned municipal yard waste	Full-scale (3000 m^2 area) bioreactor packed with 5887 m^3 of limestone-amended compost	n.r.	67.4%	1153	Burns et al. (2012)
128	7.9	8	19	Compost, wood chips, activated sludge	Continuous flow column (4.3 L) or pilot-scale reactor (3.75 m^3) under identical field conditions	n.r.	4–7%	119–123	Gandy and Jarvis (2012)
1000–4750	4.2–4.6	Room temp.	94–96	Peat, H_2 (produced from water with zero valent iron)	Continuous up-flow column (1.86 L) packed with peat and zero valent iron	55	200–500 mg L^{-1}	n.r.	Jeen et al. (2014)
6000[a]	3	Room temp.	Up to 1680	Indigenous South African grass cuttings	1.8 L batch experiments	n.r.	80%	1240	Ramla and Sheridan (2015)
590–1100	≈ 3–9	Average 20	n.r.	Mushroom compost	Full-scale bioreactors packed with substrate (0.5 m), limestone (1 m), and 1–1.5 m overlaying water.	Up to 10.8	n.r.	n.r.	Jung et al. (2015)
2000–6700[a]	1.3–3	30	≈ 10–140	Glycerol	Laboratory-scale (2.3 L) sulfidogenic bioreactor	≈ 120–180	Up to 98%	48	Ňancucheo and Barrie Johnson (2014)
4000	7.1–7.5	35	Up to 336	Marine waste extract	Batch experiments (1 L reactor)	8.8–11.10	68–97%	119–1251	Dev and Bhattacharya (2014)
680–2655[a]	2.7	30	18 or 24	Maize straw/sodium lactate	Up-flow anaerobic column (0.79 L) packed with beads containing immobilized SRB	Up to 3.2	61–99%	≈ 0–1000	Zhang and Wang (2016)
5050	2.5	5–28	n.r.	Herbaceous or woody substrates with livestock manure and whey	Field experiment in mine site using 0.21 m^3 flow-through reactors	n.r.	26–35 mol-%	≈ 1500–5500	Lefticariu et al. (2015)
109–1090	6.2–7.9	20	Up to 360	Municipal wastewater and sludge	Batch experiments (1 L reactor)	n.r.	n.r.	0–900	Deng et al. (2016)

HRT = hydraulic retention time, n.r. = not reported.

[a] Synthetic AMD.

Table 3
General feed water pre-treatment requirements for NF and RO membranes (Flynn, 2009; Sutzkover-Gutman and Hasson, 2010).

Feed water pre-treatment requirements for NF and RO	
Silt density index	< 5
Turbidity [NTU]	< 1
TOC [$mg\,L^{-1}$]	< 3
Color [APHA color units]	< 3
Metals: Fe, Mn, Al [$mg\,L^{-1}$]	< 0.05
Hydrogen sulfide [$mg\,L^{-1}$]	< 0.1
Oil and grease [$mg\,L^{-1}$]	< 0.1–0.5
Bacterial count [$CFU\,mL^{-1}$]	< 1000

2007). Complex electron donors, such as molasses or hydrocarbons, tend to remain incompletely oxidized and thus increase the COD content in treated effluent (Liamleam and Annachhatre, 2007). Ethanol has been deemed the most cost-effective when treating < 200 kg SO_4^{2-}/h, while hydrogen gas becomes competitive at higher loadings (Liamleam and Annachhatre, 2007). Hay was found to provide more dissolved organic carbon (and thus achieve a higher sulfate reduction rate) than wood, whereas manure addition was deemed to be unnecessary (Mirjafari and Baldwin, 2016).

Table 2 summarizes recent studies in which SRB are used for sulfate and usually coexisting metal removal from AMD. As can be seen, microbial sulfate removal has potential to reach very low sulfate levels ($< 100\,mg\,L^{-1}$). However, a disadvantage is the required long hydraulic retention time, which can prevent treating large flow rates, or, alternatively, several parallel units are required. Microbial sulfate removal by SRB is utilized in some commercialized processes, for instance, Rhodes BioSURE (capacity 10,000 m^3/d, wastewater sludge as substrate, HRT 12 h, sulfate after treatment $< 100\,mg\,L^{-1}$) (Rose, 2013) or THIOPAQ (synthesis gas as substrate, several different size full-scale installations exist for sulfate/metal removal) (Buisman et al., 1999). An interesting alternative approach was taken by Li et al. (2017), who utilized SRB and other microbes to remove metals and COD, respectively, from landfill leachate using AMD as a sulfate source. They were also able to produce methane due to coexisting methane producing bacteria and SRB (COD/SO_4^{2-} weight ratio was optimally 3.0) (Li et al., 2017).

Microbial fuel cells (MFCs) are a novel method for removing sulfate from AMD. A review of their operational principles and design is provided, for instance, by Du et al. (2007). In short, in a conventional two-chamber MFC, bacteria catalyze the oxidation of organic or inorganic electron donors at the anode, the electrons are transferred to the cathode via an external circuit, and at the cathode other bacteria species utilize the electrons for reduction reactions, such as sulfate reduction (Logan et al., 2006; Rabaey and Rozendal, 2010; Rosenbaum et al., 2011; Su et al., 2012). When used for sulfate removal, both one- and two-chamber MFC set-ups have been studied. MFCs could be designed to contain an autotrophic biocathode in which the SRB use CO_2 as the carbon source and the SRB consist of an acidophilic strain, which potentially removes the need to adjust the pH before treatment (Coma et al., 2013; Teng et al., 2016). MFCs also have potential to produce electricity directly from chemical energy, but the power generation is still inefficient (Du et al., 2007).

Tang et al. (2016) reported that their MFCs were able to remove 51.2%, 39.8%, and 33.1% of sulfate from 1000, 2000, and 3000 $mg\,L^{-1}$ SO_4^{2-} concentrations, respectively, using a 48-h hydraulic retention time and activated sludge as a substrate. They were also able to generate up to approximately 230 mV voltage, which decreased to approximately 50 mV after 15 days of operation (Tang et al., 2016). Teng et al. (2016) reported up to approximately 40% sulfate removal from a 200 $mg\,L^{-1}$ SO_4^{2-} initial concentration with a two-chamber MFC. The current density produced by their MFC was up to 50 $A\,m^{-3}$, from which it gradually decreased during operation (Teng et al., 2016). Peng et al. (2017) were able to remove up to 71% of the sulfate (from 3000 $mg\,L^{-1}$ in synthetic AMD) and generate 51.3 $mW\,m^{-2}$ power density from their MFC using wastewater sludge as a substrate. Lee et al. (2012, 2014) used a combination of SRB and sulfide-oxidizing bacteria biofilms on an MFC anode, and the generated sulfide was converted irreversibly to elemental sulfur. Finally, Zhao et al. (2008) used activated carbon cloth as anode material in their MFC and achieved up to 99% sulfate removal (from approx. 3000 $mg\,L^{-1}$ SO_4^{2-}). However, the technology readiness level of MFCs is still rather low.

3.5. Membrane technology

Pressure-driven membranes are conventionally classified as microfiltration, ultrafiltration, nanofiltration (NF), and reverse osmosis (RO), depending on their separation capacity. Of these classes, NF and RO are suitable for sulfate rejection as they can effectively separate divalent and monovalent ions, respectively. In general, both NF and RO have demonstrated high efficiency for sulfate removal, achieving over 99% rejection in ideal conditions (Ambiado et al., 2017; Aubel et al., 2017; Bódalo et al., 2004; Visser et al., 2001). Consequently, NF- or RO-based mine water treatment allows the attainment of even the most stringent sulfate discharge limits or reuse permeate in processes with high water quality requirements. In practice, however, NF is the more appropriate choice for mine water treatment due to lower energy consumption and operational costs compared to RO but still with excellent permeate quality (Al-Zoubi et al., 2010). It should be noted, though, that the energy consumption is strongly affected by the feed concentration of dissolved solids and subsequently required osmotic pressure (Ghalavand et al., 2015)

The feed water sulfate concentration for membranes can be relatively high; for instance, Bódalo et al. (2004) used a commercial cellulose acetate RO membrane (SEPA-SS1C, Osmonics) to treat sulfate concentrations up to 25,000 $mg\,L^{-1}$ and obtained 99.6% rejection. However, other water quality parameters (Table 3) need to be carefully controlled or various types of membrane fouling and/or scaling can occur. The build-up of suspended and dissolved solids on the membrane surface is caused by the concentration polarization: the hydraulic flow along the membrane surface creates a boundary layer in which the convective flow toward the membrane is faster than the back diffusion away from the membrane (Flynn, 2009). Fouling and scaling causes operational costs to increase due to a need for chemical cleaning and anti-scalant use, decreased membrane service life, and lowered water recovery (Goh et al., 2018; Jiang et al., 2017; Landaburu-Aguirre et al., 2016; Shirazi et al., 2010). In practice, the lower feed water quality also decreases the flux (amount of water passing through a given membrane area per unit of time) that can be used (Flynn, 2009). The feed water pre-treatment represents a significant fraction of a desalination plant's total capital costs: up to 20% (Sutzkover-Gutman and Hasson, 2010). As an example of the innovative pre-treatment of AMD, Masindi et al. (2017) used basic oxygen furnace (BOF) slag, lime, and soda ash before RO and were able to recover drinking quality water. In their study, the sulfate concentrations were 18,000, 4570, 200, 20, and 0.19 $mg\,L^{-1}$ as initially, after BOF slag, lime treatment, Na_2CO_3 treatment, and RO, respectively. Another recently demonstrated pre-treatment scheme involved caustic soda followed by ozone to remove especially Fe(II) and Mn(II) from coal mine drainage (Boyden et al., 2017). The use of microfiltration before NF or RO is also a feasible option (Kyllönen et al., 2017).

The water recovery (i.e., the amount of pure water or permeate) of NF or RO varies within 50–90% of the total treated water volume, and thus the concentrate (i.e., rejectate or brine) requires further treatment and management (see Section 3.6 for further details) (Flynn, 2009; Giwa et al., 2017). As can be seen from Table 4, the typical water recoveries have varied between 60% and 70% in recent studies.

The most common NF or RO membrane materials are asymmetric cellulose acetate or polyamide composites (Flynn, 2009). The latter are

Table 4
Examples of recent mine effluent treatment studies with NF or RO.

SO_4^{2-} [mg L^{-1}]	pH	Membrane (commercial name)	Pressure [bar]	Flowrate [m^3 h^{-1}]	Flux [L h^{-1} m^{-2}]	Water recovery [%]	Sulfate rejection [%]	Ref.
2000–2800	3.4–3.8	NF270[a]	10	0.14	25 (avg.)	60	87	Aguiar et al. (2018)
790	5.6	NF270[a]	10	0.79	n.r.	57	88	Wadekar et al. (2017)
6900–10,500	2.6–5.5	NF270[a]	7–20	0.200–0.225	32–34	70	≈ 87–97	Mullett et al. (2014)
2443	3.5	NF270[a]	5–30	1	20–100	n.r.	≈ 96–98	Pino et al. (2018)
9600	2.0–2.8	NF270[a]	4.5–20	0.858	n.r.	n.r.	89 (for Na_2SO_4)	Lopez et al. (2018)
790	5.6	NFHL[a]	10	0.79	n.r.	57	81	Wadekar et al. (2017)
790	5.6	XN45[a]	10	0.79	n.r.	57	88	Wadekar et al. (2017)
6900–10,500	2.6–5.5	TriSep TS80[b]	10–23	0.200–0.225	32–35	70	≈ 95–98	Mullett et al. (2014)
2443	3.5	NF90[b]	5–30	1	20–100	n.r.	> 98	Pino et al. (2018)
2620	2.1	NF90[b]	≈ 8	0.144	10–60	70	94	Andrade et al. (2017)
3500	2.2	NF90[b]	10	n.r.	15–40	n.r.	96	Agboola et al. (2017)
790	5.6	NF90[b]	10	0.79	n.r.	57	88	Wadekar et al. (2017)
3500	2.2	Nano-Pro-3012[b]	10	n.r.	10–23	n.r.	86	Agboola et al. (2017)
790	5.6	NFX[b]	10	0.79	n.r.	57	90	Wadekar et al. (2017)
790	5.6	NFW[b]	10	0.79	n.r.	57	80	Wadekar et al. (2017)
790	5.6	NFG[b]	10	0.79	n.r.	57	20	Wadekar et al. (2017)
790	5.6	NFCK[c]	10	0.79	n.r.	57	90	Wadekar et al. (2017)
9600	2.0–2.8	HydraCoRe 70pHT[d]	4.5–20	0.858	n.r.	n.r.	75 (for Na_2SO_4)	Lopez et al. (2018)

n.r. = not reported.

[a] Polypiperazide amide composite membrane.

[b] Polyamide composite membrane.

[c] Cellulose acetate.

[d] Sulfonated polyethersulfone.

also referred to as thin-film composite, and they consist of support, polysulfone backing, and a polyamide or polypiperazide layer (Flynn, 2009). The general difference is that cellulose acetate membranes are more resistant to fouling, whereas polyamide composites typically exhibit higher rejection (Flynn, 2009). Furthermore, polyamide composite membranes have a negative charge, implying higher sulfate rejection than neutral-charged cellulose acetate membranes (Flynn, 2009; Mullett et al., 2004). Membrane characteristics, such as thermal, mechanical, and chemical properties, affect the operational efficiency. Chemical modifications can be implemented to alter surface charge, hydrophilicity, roughness, or permeability to improve their properties. One attempt was made by Juholin et al. (2018), who coated a commercial NF membrane (NF270, Dow) with ZnO using atomic layer deposition for the treatment of real mine wastewaters. They observed that reversible fouling decreased (while irreversible fouling was not affected) and that relative flux possibly increased slightly when compared to membranes without coating (NF90 and NF270, Dow). However, there was Zn leaching into the permeate from the coating, and the sulfate rejection remained unchanged at $> 91\%$.

In addition to the conventional pressure-driven membrane processes described above, other membrane techniques have also been applied for mine effluents. Electrodialysis (ED) is a membrane process in which the selective transport of ions through charged membranes is caused by applying an electrical field (Mulder, 1998). Anion-exchange membranes contain positively charged groups and cation-exchange membranes negatively charged groups (Mulder, 1998). Typically a series of anion- and cation-exchange membranes are placed between an anode and a cathode to form an ED cell. Negatively charged sulfates will migrate toward the positively charged anode when an electrical field is applied (Mulder, 1998; Buzzi et al., 2013). One diluted and one concentrated effluent are formed during ED treatment (Buzzi et al., 2013). Buzzi et al. (2013) have used ED to treat AMD with 518–7399 mg L^{-1} sulfate content with 98–99% sulfate extraction efficiency.

Membrane distillation utilizes temperature difference, and subsequent vapor pressure difference, across a hydrophobic membrane as the driving force: vapor molecules are transported through the membrane while dissolved solids are retained (Alkhudhiri et al., 2012). The use of membrane distillation was demonstrated with synthetic AMD: $> 99\%$ TDS rejection was obtained with 80% water recovery, flux of $38\,\text{L/m}^2/\text{h}$, and a $34\,^\circ\text{C}$ temperature difference (Hull and Zodrow, 2017). The relatively low temperature difference suggests that membrane distillation could be utilized with geothermal energy or other low-grade heat sources (Hull and Zodrow, 2017).

3.6. Concentrate treatment and recovery of sulfur chemicals

Several of the discussed processes (ion exchange, adsorption, and membrane technologies) result in the formation of concentrated effluent (i.e., concentrate or reject water). In the case of membrane separation, the reject water sulfate concentration can be calculated with Eq. (27) (Flynn, 2009):

$$Reject\ SO_4^{2-}\left(\frac{mg}{L}\right) = \frac{Feed\ flow\ rate\left(\frac{m^3}{h}\right)}{Reject\ flow\ rate\left(\frac{m^3}{h}\right)} \times Feed\ SO_4^{2-}\left(\frac{mg}{L}\right) \tag{27}$$

Concentrate treatment is an essential issue when considering the feasibility of the discussed processes. For instance, membrane processes result typically approximately 40% concentrate of the feed water volume (Banerjee et al., 2015). To increase utilization possibilities of concentrates, they need to be further concentrated. One method is through multiple membrane filtration stages: for instance, a two-stage RO process has been used for years (Morillo et al., 2014).

One still research-level method is the use of forward osmosis (FO), in which the concentration difference across a semipermeable membrane is the driving force. In short, water passes from the concentrate through the membrane to the draw solution (which has a higher concentration than the concentrate). Due to the very low hydraulic pressure required, FO is expected to deliver many potential advantages, such as less energy input, lower fouling tendency, easier fouling removal, and higher water recoveries over pressure-driven processes (Akther et al., 2015).

ED is currently being studied as a another option to concentrate RO rejects and to obtain solid salts that can be further reused (Casas et al., 2012). Sulfuric acid can be produced from AMD with ED (Mulder, 1998; Martí-Calatayud et al., 2014). Nleya et al. (2016) have reviewed technologies for the recovery of acid from wastewaters.

Freeze crystallization (FC) is a possible method for the concentration of concentrated effluents produced in the membrane processes (Randall and Nathoo, 2015). In FC, effluent is cooled below the freezing point of water, and water crystallizes into ice concentrating the effluent (Naidu et al., 2018; Randall and Nathoo, 2015). Eutectic freeze crystallization (EFC) is an extended FC process that enables the recovery of salt and pure water from effluents. When effluent is cooled down to its eutectic point, ice and salt crystallize simultaneously, and, by utilising their density difference, separation is possible (Hasan et al., 2017). Furthermore, if the system contains multiple salts, each is formed at its characteristic crystallization temperature and no problematic mixture of salts is obtained. EFC is also advantageous in regard to energy consumption: the heat of fusion ($6.01\,\text{kJ mol}^{-1}$) is lower than the heat of the vaporization ($40.65\,\text{kJ mol}^{-1}$) of water (Pérez-González et al., 2012). EFC has been tested for the full-scale process, for instance, for the treatment of RO brine (Randall et al., 2011).

The chemically-enhanced seeded precipitation (CESP) of RO concentrate has also been studied (McCool et al., 2013). In CESP, gypsum seeds are added to supersaturated lime pre-treated RO concentrate to induce gypsum precipitation (McCool et al., 2013). McCool et al. (2013) have stated that a 93% desalting recovery of RO concentrate with CESP could be possible. Aubé and Lee (2015) have suggested the use of the high-density-sludge process for NF and RO concentrate treatment. Evaporation is used for RO concentrate treatment (Khan et al., 2009). The simplest evaporation method is solar evaporation, in which the brine is left in an evaporation pond, where the water evaporates and salt is left (Morillo et al., 2014). However, evaporation ponds need large land areas, hot and dry conditions, and need to be constructed properly to avoid seepage (Khan et al., 2009). Also, water recovery is not possible with solar evaporation (Vane, 2017). With other evaporation techniques water is vaporized from the concentrate and can be subsequently recovered with condensation (Kim, 2011). Evaporation technologies are energy intensive, and enhanced evaporation techniques, such as thermal vapor compression and mechanical vapor compression for minimizing energy consumption, have been developed (Khan et al., 2009; Subramani and Jacangelo, 2014; Vane, 2017,).

The treatment of concentrate using membrane distillation (MD) has also been proposed (Naidu et al., 2018). Water vapor is transported through a hydrophobic membrane in the thermal-based MD process (Naidu et al., 2018). However, scaling caused by inorganic ion precipitation on the membrane surface has been reported (Naidu et al., 2018).

Mulopo (2016) has studied elemental sulfur recovery from AMD through thermal reduction of $BaSO_4/CaCO_3$ and $CaSO_4/Mg(OH)_2$ sludges to barium and calcium sulfide and the stripping of the sulfide with CO_2 gas to produce sulfur.

4. Conclusions

Sulfate is a commonly occurring major anion that is not considered toxic as such. Nevertheless, it can possess threads, especially to freshwater biota, when present in excessive amounts. One important point source of sulfate release in aquatic environments are mines. The currently practiced gypsum precipitation is capable of reducing sulfate down to approximately 2000 mg L^{-1} as the theoretical minimum. However, this is not enough for the most stringent environmental requirements and therefore more efficient treatment means are needed. The discussed alternatives in this review were alternative precipitation methods, adsorption, ion exchange, biological treatment, and membrane technologies. In addition, the further treatment of concentrate, which is formed in many of the aforementioned processes, was overviewed.

Ettringite and barite are alternative low-solubility minerals that sulfate can be precipitated into to reach sulfate levels down to 200 mg L^{-1} or less. Both processes use more expensive chemicals compared to gypsum precipitation, but the formed precipitates can be recycled to decrease operational costs. In the case of barite precipitation, however, the barium salts are also significantly toxic. Sludge as the secondary waste from these processes needs to be properly managed and ideally reclaimed. The third alternative precipitation process involves the formation of jarosite, but the harsh reaction conditions (pH 0–4, temperature 130–140 °C, pressure 5–7 bar, and reaction time 1–3 h) required make this option unfeasible.

Adsorption has been performed with a number of experimental materials with or without chemical modifications. However, no fully commercialized processes exist yet. The most likely application area would be as a polishing method after pre-treatment in the case where a very low sulfate level is required. In the process, sulfate is bound to a solid adsorbent, which needs to be regenerable, for several times, to be economically feasibility. The secondary waste is therefore a concentrate from regeneration containing sulfate and regenerant. Other key issues are the capacity and selectivity of the adsorbent for sulfate. Thus far, the highest reported theoretical adsorption capacities are approximately 280 mg g^{-1}. This means that, even in this ideal case, the removal of, for instance, 500 mg L^{-1} of sulfate would require an adsorbent dose of 1.8 g L^{-1}; that is 180 kg of adsorbent per hour for 100 m^3 h^{-1} flow rate, as an example. This clearly demonstrates the need for regeneration.

Weak base anion resins are typically used in sulfate removal. Ion exchange may not be suitable as a primary technology, but it has potential to be used in combination with other processes. The CYP-CIX process is effective for sulfate removal at the concentration near the gypsum saturation level.

Biological treatment involves SRB, which convert sulfate into sulfide. Sulfide can be further precipitated with metals, and ideally the product can be reclaimed. The process can be implemented as passive or active, which indicates whether the substrate (electron, nutrient, and carbon source) is supplied as a batch lasting for several years or continuously, respectively. The active treatment results in a more predictable performance, but the operational costs are higher than with passive systems. Biological treatment systems have been demonstrated to be operational even in cold conditions, and the reachable sulfate concentration is down to approximately 100 mg L^{-1}. However, the downside is the required long contact time of several or even tens of hours. One interesting application of biological treatment are the microbial fuel cells (MCFs) that have the potential of generating electricity during treatment. MFCs, though, are not yet commercially available.

Membrane technologies capable of rejecting sulfate from mine water sufficiently to reach even the most stringent sulfate discharge are NF, RO, and ED. The quality of the permeate enables its reuse in process. Even 25,000 mg L^{-1} concentrations can be treated by using a commercial RO membrane, and over 99% rejections can be achieved in ideal conditions. Water quality needs to be controlled to prevent membrane fouling and/or scaling, to ensure sufficient water flux, and to lower energy consumption. Feed water pre-treatment causes up to 20% of capital costs.

Ion exchange, adsorption, and membrane technologies form concentrates whose treatment has to be taken into account to consider the feasibility of these processes. The volume of concentrate can be reduced through multiple membrane filtration stages, for instance, with the two-stage RO process. Concentrate treatment can be done with membrane technologies, crystallization, or thermal processes.

As a final remark, it can be concluded that reaching concentrations clearly lower than those with gypsum precipitation ($\approx$ 1500 mg L^{-1}) is definitely possible with commercially available technology. However, all the methods still have unresolved issues, at least in terms of cost-efficiency, compared to gypsum precipitation. Nevertheless, gypsum precipitation will still have an important role as the first process step in mine effluent treatment, and more advanced methods can be used as polishing steps.

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