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Review

Review of Sulfate Removal in Low Concentration Brine Solutions

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Abstract: Sulfate is a common ion present in natural water bodies at low concentrations and as an effluent in different metallurgical processes. The discharge of sulfate into rivers and water bodies can cause direct and indirect environmental damage. Regulatory agencies have been increasing restrictions on sulfate content limits for discharge, focusing on human equity and environmental protection. A common practice is the precipitation of sulfate with lime, but the remaining solution still contains approximately 1,500 mg L^{-1} of sulfate, which is not acceptable for disposal or reuse. This work describes the main routes for sulfate removal, such as chemical precipitation, biological degradation, ion exchange, and membrane separation, and discusses the main advantages and issues of each approach. One of the main challenges is scaling up the tests and demonstrating their performance at the industrial level. The subject must be the focus of ongoing research to obtain relevant results, so that conventional technologies can be replaced by more innovative, cost-effective, and efficient methods.

***Keywords*:** biological degradation, electrocoagulation, ion exchange, membrane separation processes, precipitation, sulfate removal

1. Introduction

Sustainability concepts are widely disseminated in the society, especially in the academy. The demand for circularity in economic activities has led to research of technological advancement to improve the maintenance of natural resources, and quality of life and guarantee the survival of future generations.[1] In this context, the treatment of wastewater is a challenge to be faced. Among the common species present in natural waterbodies and wastewater is sulfate (SO_4^{2-}), an anion that impacts negatively the environment.[2]

Sulfate is a common bivalent ion present in natural waters. This anion comes naturally from volcanic activities, combustion and decomposition of organic matter, mineral weathering, oxidation of sulfides and marine emissions. It participates in natural processes such as carbon, nitrogen and phosphorus cycles, but when it is present in higher concentration, causes disturbances in these mechanisms.[2]

Anthropic actions such as the burning of fossil fuels, fertilizers for agricultural purposes, industrial waste and acid mining drainage are the biggest contributors to the increase in sulfate concentration in the natural environment.[3] High concentrations of sulfate in natural waters also affect the metabolism of aquatic organisms and can precipitate into low-solubility salts. This causes damage to the entire local biosystem, altering the chemical oxygen demand and the intrinsic

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characteristics of the water body.[2] Furthermore, harm to human health is notable when high levels of sulfate are found in drinking water, which can alter the taste of the water and cause laxative effects in consumers.[4] In the industry scenario, sulfate is also a problem, as it can cause damage to equipment or structures, interference in processes, product quality and complexity in waste handling.[5]

The growth of concentrations of salts in natural waters creates environmental problems, so government agencies have developed regulations limiting emissions in natural waters.[6] According to most countries in the world, the discharge recommendation limits for sulfates in water effluents are between 250 and 500 mg L^{-1}.[7] As shown in Table 1, depending on the region of a country or continent, legislation can change, which causes variability in environmental legislation.

Table 1. Recommended maximum levels of sulfate discharge in water effluents[4,5,8-11]

Regulatory agency	Maximum content (mg L^{-1})
EPA (USA)	250
WEPA (Asia)	250
CONAMA (Brazil)	250
Health Canada	500
Department of Water Affair (South Africa)	600
World Health Organization	250

Research articles on sulfate removal are widely available in the scientific literature.[12-16] This survey covers a variety of approaches and techniques to treat streams with different levels of sulfate concentration, with a particular focus on streams that have low concentrations of this ion, i.e., lower than 2,000 mg L^{-1}. These studies not only address sulfate removal to comply with environmental regulations when disposing of effluents into water bodies, but also consider the importance of water reuse in industrial processes.

The most common route in metallurgical processes is neutralization with lime, as shown in Equation 1. The formation of calcium sulfate is widely used due to the low cost of operation and the safety of residual calcium, offering no risk to human health and the environment.[17,18] Hence, the use of synthetic or recycled seeds, at neutral pH (5-9) during 2-5 h tests, may cause the precipitation of gypsum.[19] The limit of solubility of gypsum is high, so the final effluent will have concentrations close to 1,500 mg L^{-1}, which is too high for natural water disposal.[20]

$$Ca(OH)_2 + H_2SO_{4(aq)} \rightarrow CaSO_4 \cdot 2H_2O \tag{1}$$

This review shows the current technologies available for removing sulfate from streams with low concentrations (1,500 mg L^{-1}) from industrial effluents or acid mine drainage and assesses the challenges and highlights of each of the proposed techniques aiming to attain the discharge limit of 250 mg L^{-1}. This research explores diverse strategies, including chemical precipitation, ion exchange, biological processes, electrocoagulation and emerging technologies such as membrane separation processes. Choosing the most appropriate approach depends on the initial sulfate concentration, the specific characteristics of the effluent and the treatment objectives. Thus, the specific topic investigated in this review is the problem related to the removal of sulfate from aqueous solutions from 2,000 mg L^{-1} to 250 mg L^{-1} upon comparing the following processes: chemical precipitation, biological degradation, ion exchange, membrane separation processes, electrocoagulation and process combination. We aim to analyze the pros and cons of each route, focusing on the sulfate range concentration and the effect of physicochemical properties of the feed, such as pH and cations content.

2. Chemical precipitation

Precipitation is the process of transforming a dissolved substance into an insoluble solid from a supersaturated solution. The main sulfate removal reactions by means of chemical precipitation are shown in Equations 2, 3 and 4.

$$3Fe_2(SO_4)_3 + Na_2SO_{4(aq)} + 12H_2O \rightarrow 2NaFe_3(SO_4)_2(OH)_{6(s)} + 6H_2SO_{4(aq)} \tag{2}$$

$$6Ca(OH)_{2(s)} + 3H_2SO_{4(aq)} + 2Al(OH)_{3(s)} + 20H_2O_{(l)} \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O_{(s)} \tag{3}$$

$$Ba(OH)_{2(s)} + H_2SO_{4(s)} \rightarrow BaSO_{4(s)} + 2H_2O_{(l)} \tag{4}$$

Low solubility minerals such as jarosite ($NaFe_3(SO_4)_2(OH)_6$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) for sulfate removal are interesting options with higher sulfate removal yield. Ferreira et al. evaluated the precipitation of jarosite and ettringite in a synthetic effluent under specific conditions.[21] Jarosite was precipitated at acidic pH (1-3) while ettringite was prepared in a basic medium (pH 7-10), in a system with stirring and controlled temperature (22 ± 1 °C) for 24 h. The results showed that the yield of sulfate removal is highly dependent on pH. In acid media, jarosite precipitation leads to 40% removal of sulfate, however, with unfavorable kinetics in temperature conditions. Jarosite has favorable kinetics at temperatures above 100 °C. Ettringite, on the other hand, showed satisfactory removal values, generating final concentrations close to 100 mg L^{-1}, corresponding to a removal of 90%.[21]

The effectiveness of ettringite precipitation is supported by the literature,[22] which reported that increasing the temperature markedly increased the yield of the process, reaching a sulfate removal efficiency of up to 99%. In all the cases mentioned, impurities in the feed, such as excess ions such as Mg^{2+}, can develop a significant inhibitory effect on sulfate removal, requiring pre-treatment for relevant results.[23] In another approach, the precipitation of ettringite followed by aluminum recovery for reuse and formation of gypsum was investigated.[24] It was reported the need for aluminum recovery, taking into account the high cost of its sources and temperature for ettringite formation.

Aiming for the decrease operational costs, Tolonen et al. removed sulfate from an initial concentration of 1,400 mg L^{-1}, so that the yield was between 85-90% decrease in sulfate, higher than the modeled condition (71%). However, they also investigated the use of ettringite as an adsorbent of arsenate, with a capacity of 11 mg g^{-1} in adsorption capacity.[25]

Barium salts are also used for the precipitation process aiming at sulfate removal due to the low solubility of its salt (360-410 mg L^{-1}). Navamani et al. studied the removal of sulfate from the wastewater of a pigment manufacturing company by means of precipitation with barium chloride.[26] Optimizations of precipitant dosage, temperature and mixing speed were done and the maximum yield of 99.58% was obtained. Despite the good results of barium sulfate, this method is rarely used compared to gypsum because barium salts are expensive and toxic.[27] Recycling barium sulfate would be a good alternative to reduce costs. This method is generally recommended for processes where most metals were already removed.[6,20]

On the other hand, Larraguibel et al. studied the use of the dispersive alkaline substrate, DAS, treatment with $BaCO_3$, witherite, to treat acid mine drainage samples.[28] The technology is known as a passive treatment in the neutralization and removal both of metals and sulfate from the acid mine drainage. In the case of witherite, the reaction is shown in Equation 5. The sulfate initial concentration was varied from 1,234 to 2,468 mg L^{-1}. Sulfate concentration was decreased under 500 mg L^{-1}.

$$Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + BaCO_{3(s)} \rightarrow BaSO_{4(s)} + CaCO_{3(s)} \tag{5}$$

The precipitation of sulfate with the formation of barium sulfate or ettringite is well-known alternatives to decrease sulfate content. Despite the high yield, these routes are highly dependent on the pH of the medium, very expensive and the production of toxic precipitates is of main concern. Thus, the investigation of possible resuspension of the ions to reuse in the process is the main tendency in this approach. In addition to it, the presence of other cations may act as the common ion, decreasing sulfate removal, or promoting an inhibitory effect in the precipitation.

Table 2 shows the main results for sulfate removal by means of chemical precipitation, the advantages and disadvantages.

Table 2. Advantages and disadvantages of chemical precipitation for sulfate removal

Chemical precipitation	Gypsum	Jarosite	Ettringite	Barite
Pretreatment	Remove of organic acids, centrifuged and filtered	No (synthetic effluent)	Mg^{2+} removal (synthetic effluent)	No (pigment manufacturing)
Feed water sulfate limits (mg L^{-1})	1,800.0	1,480.0	1,480.0	103,555.0
Sulfate removal (%)	16.6	40.0	90.0-99.0	99.58
Maximum content (mg L^{-1})	1,500.0	888.0	14.8	434.9
Costs/maintenance	Low	Low	Low	High
Advantages	Using recycled seeded crystals is more advantageous than synthetic crystals.	Low solubility salt.	Ettringite could be used for calcium sulfoaluminate-belite cement production; Low solubility salt; Residual calcium in the treated effluent poses no risk to both humans and the environment.	Low solubility salt.
Disadvantages	Impurities in residual wastewater inhibit nucleation and increase the solubility of gypsum; High solubility compared to other salts; Generation of large amounts of waste.	Great demand for reagents for pH adjustment and precipitation reaction; Generation of large amounts of waste.	Great demand for reagents for pH adjustment and precipitation reaction; Generation of large amounts of waste.	Barium salts are expensive; Generation of large amounts of waste; Residual barium in treated effluent poses risks to both humans and the environment.
Reference	19	6, 21	21, 22	6, 20, 26

3. Biological degradation

Biological degradation uses sulfate-reducing bacteria to remove sulfate from wastewater. They are anaerobic beings that obtain energy for their growth by oxidizing organic substrates.[29] The mechanism is shown in Equation 6.

$$SO_4^{2-} + \text{organic matter} \xrightarrow{\text{bacteria}} HS^- + H_2O + HCO_3^- \qquad (6)$$

Sarti developed a pilot-scale anaerobic biofilm reactor containing coal for biomass fixation, which was fed with sulfate-rich wastewater with increasing concentration.[30] Ethanol was used as the main organic source. The results showed that the yield of sulfate removal was around 99% for the initial sulfate concentration of 500 mg L^{-1}. The authors reported the ability of the bacteria to survive in different sulfate range concentrations, which is not used for sulfate concentrations above 2,000 mg L^{-1}. Another small-scale bioreactor was studied using real wastewater (2,100 mg L^{-1} of sulfate) by means of a group of sulfate-reducing bacteria.[31] The carbon sources (lactate, glucose, sucrose and fructose) and the temperature (30-40 °C) were varied in the article, obtaining a final concentration of 212 mg L^{-1} of sulfate on the effluent studied.

The use of sugarcane vinasse as an electron donor for sulfate-reducing bacteria was investigated.[32] It was used as a downflow structured bed bioreactor with *Geobacter* and *Desulfovibrio*. Sulfate content in the feed solution ranged from 1,200 to 2,700 mg L^{-1}. Specifically, for feed solution sulfate content of 1,200 mg L^{-1}, the removal was 91%, with precipitation of sulfide and pH reduction to 6.7 to 7.5.[32]

In another approach, Gandy et al. investigated the use of propionic acid as a carbon source in the reduction of sulfate and zinc removal from an acid mine synthetic solution. Residence time was 19 hours, with operation though almost 800 days. The initial zinc and sulfate concentrations were 45 and 156 mg L^{-1}, respectively. It was shown that sulfate-reducing bacteria were highly dependable on a good carbon source to decrease zinc concentration.[33]

Paques created SULFATEQ™, which is a technology to reduce sulfate to dissolved sulfide in bioreactors. The energy source in this case is alcohol or hydrogen gas. In the second step of the process, the sulfide is oxidized to elemental sulfur using air. The product guarantees sulfate reduction below 300 mg L^{-1}, generating good quality water for reuse, but the feasibility of releasing this effluent into natural water bodies must be evaluated.[34]

Artificial neural networks were investigated as the tool to describe sulfate removal from anaerobic biological systems.[35] *Desulfomicrobium*, *Desulforhabdus*, *unclassified-f-Desulfosarcinaceae* and *Syntrophus* were some sulfate-reducing bacteria used in the model, with an initial sulfate concentration of 1,200 mg L^{-1}. The results showed that the chemical oxygen demand (COD) to sulfate ratio, which was varied from 0.1 to 0.5, showed an important effect in sulfate removal. Reducing the COD/sulfate ratio caused a decline in the removal of sulfate rate. The final sulfate content after 24 h in the reactor varied from 0 to 300 mg L^{-1}.

The use of constructed wetlands for treating saline wastewater was investigated as a function of microbial community.[36] The authors used a feed solution with sulfate content ranging from 120 to 480 mg L^{-1}. It was shown that the community with *Phragmites australis* showed up to 60.1% of sulfate reduction. However, authors reported that high sulfate content favored COD removal due to the competition of bacteria for electron donation. Table 3 shows the main results for sulfate removal by means of biological degradation, advantages and disadvantages.

Table 3. Advantages and disadvantages of biological degradation for sulfate removal

Biological degradation	ASBBR reactor	Sulfate-reducing bacterial	Paques
Pretreatment	No (sulfate-rich wastewater)	Aluminum precipitation (mining-impacted waters, synthetic mine waters and acid mine drainage)	No (metals industry, salt water, acid mine drainage and viscose industry)
Feed water sulfate limits (mg L^{-1})	500.0	1,580.0	1,000.0-25,000.0
Sulfate removal (%)	38.5-99.0	51	70.0-98.8
Maximum content (mg L^{-1})	5.0	774.2	< 300.0
Costs/maintenance	High	High	High
Advantages	No generation of large amounts of waste; No great demand for reagents.		Intermediate product: metals or elemental sulfur, reduction of hardness to low levels, neutralization of acidity without agents such as caustic, safe processing under ambient conditions and without notable emissions of odor.
Disadvantages	Some species cannot survive in wastewater with a high concentration, sulfite and metals, pH, dissolved oxygen, competitive beings, viable carbon sources and temperature.		
Reference	30	15	34

Despite the good results of biological routes, the inhibitors of this process must be considered as a barrier to this application because dealing with microorganisms is a challenge. For instance, the sulfate initial concentration treated is usually low. In addition, the contents of sulfite, metals, pH, dissolved oxygen, competitive beings, viable carbon sources and temperature must be very well controlled to make their application on a large scale viable. These parameters should be monitored and controlled, which usually increases the operational costs of such processes.

4. Ion exchange

Ion exchange resins are widely used for the removal of ions from wastewater. Regarding sulfate removal, an anionic resin can be used to remove sulfate and add hydroxyl groups to the medium.[12] The mechanism occurs in two steps, the first being the protonation of the resin, shown in Equation 7, which is favored by the pH reduction, followed by the ion exchange of sulfate in the active sites of the resin, Equation 8.

$$\text{R-NH}_{3(\text{resin})} + \text{H}_2\text{O} \rightleftharpoons \text{R-NH}_4{}^{+}{}_{(\text{resin})} + \text{OH}^{-}{}_{(\text{aq})} \tag{7}$$

$$2\text{R-NH}_4{}^{+}{}_{(\text{resin})} + \text{SO}_4{}^{2-}{}_{(\text{aq})} \rightleftharpoons (\text{R-NH}_4{}^{+})_2(\text{SO}_4{}^{2-})_{(\text{resin})} \tag{8}$$

Rahman et al. investigated the behavior of two types of synthetic layer double hydroxide (LDH) of Mg-Al in sulfate ion exchange. Tests were carried out with sodium sulfate with a concentration of 96 mg L^{-1}. The observed mechanism was the anion exchange of the SO_4^{2-} in the aqueous medium and the NO_3^- in the adsorbent. The best results obtained for sulfate removal were 135.14 and 92.59 mg g^{-1} for LDH with Mg^{2+}/Al^{3+} molar ratios of 2:1 and 4:1, respectively.[37] Even presenting relevant results, the process of ion exchange is limited in terms of selectivity and ability to remove sulfate ions, making it difficult to implement as a primary method of treatment.[38]

Aminated peat was investigated as anion exchanger both in batch and column applications.[39] Sulfate initial content was 1,950 mg L^{-1}. The modified bio-based material showed higher sulfate uptake capacity was higher for column application (154.2 mg g^{-1}) compared to the batch test (125.7 mg g^{-1}). The evaluation of the pH effect on anion exchange showed that a low pH (2.0) increases sulfate removal, while a higher pH (5.8) favors resin regeneration. Table 4 shows the main results for sulfate removal by means of ion exchange, advantages and disadvantages.

Table 4. Advantages and disadvantages of ion exchange for sulfate removal

Ion exchange	Amberlyst A21	LDH of Mg-Al	Aminated peat
Pretreatment	No (metallurgical industrial effluent)	No (synthetic solution)	No (real acid mine drainage)
Feed water sulfate limits (mg L^{-1})	9,841.0	96.0	1,950
Sulfate removal (%)	1.7	35	75
Maximum content (mg L^{-1})	9,670.0	62.4	487.5
Costs/maintenance	Low	Low	Low
Advantages	Elution for sulfate recovery declared almost total efficiency.	High specific surface, excellent anion exchange capacity, high temperature resistance and reduced treatment cost.	Highest adsorption capacity at pH 2.0 and desorption at pH 5.8. Highest adsorption in column mode (154.2 mg g^{-1}) compared to batch mode (125.7 mg g^{-1}).
Disadvantages	High selectivity and limited ability to remove sulfate ions makes its application as a main treatment method challenging.		High adsorbent content (4-20 g L^{-1}).
Reference	12	37	39

Despite of the high efficiency of sulfate removal upon using ion exchange resins and high exchange capacity, the number of cycles of work should be considered in order to demonstrate the viability of such routes. Besides, the presence of cations the pH of the initial sulfate solution can cause a high effect in the removal of sulfate. For instance, if the ion exchange resin is in hydroxyl form, it can change both pH and surpass the cations solubility, precipitating some hydroxides in the column and reducing the efficiency of sulfate removal.

5. Membrane separation processes

The membrane separation process consists of a barrier that separates two phases and totally or partially restricts the transport of one or more chemical species present in the phases.[40] In this context, a membrane can be a solution for sulfate removal. Furthermore, membrane processes should stand out for their low maintenance, high selectivity, low energy cost and design simplicity.[41] The use of nanofiltration for the removal of bivalent ions has shown good results, depending upon the chemical composition of the membranes, so polyamide over polysulfone showed better results than sulfonated polyethersulfone.[42]

Pino et al. investigated the operational condition of sulfate and metals removal from acid mine drainage using commercial nanofiltration membranes (NF90 and NF270). The feed concentration of sulfate was 2,443 mg L^{-1}. The best result was found for NF 270 operating with 700 L h^{-1} of feed solution for 10 days, with rejection of 84% and flux decline of 12%, at 25 °C. The authors also used a pretreatment with a ceramic membrane with a pore diameter of 0.45 µm.[43]

Hosseini et al. prepared a nanofiltration membrane by using a mixed matrix membrane based on activated carbon nanoparticles dispersed in polyethersulfone. The membrane was used in the removal of 1,000 mg L^{-1} of Na_2SO_4 and showed 95% rejection, with only a 5% flux decline during 60 minutes.[44]

The use of ZnO as top layer coating over NF 270 membrane was investigated in the literature aiming to increase antifouling properties of the membrane.[45] Membranes were prepared by atomic layer deposition. Wastewater samples with sulfate content ranging from 9,600 to 2,300 mg L^{-1}, in the presence of other ions. The flux recovery rate of the modified membranes was higher (83 to 93%) than the commercial membrane (73 to 85%). No differences in membrane rejection to sulfate were reported for the four different wastewater samples. The authors showed that the superficial treatment of the membranes was improved, but the changes should be improved for larger-scale applications.

In another attempt to improve the antifouling properties of nanofiltration membranes, Yu et al. prepared a polyamide membrane with modified capsaicin. The use of bidirectional interfacial polymerization was used in membrane preparation. The abundant hydroxyl and negatively charged groups of modified capsaicin were responsible for the antipollution and separation performance of the membranes. Authors reported an increase in membrane flux from 67 to 129 L m^{-2} h^{-1} with rejection to Na_2SO_4 aqueous solution of 98.43%, using a feed concentration of 2,000 mg L^{-1} of sodium sulfate.[46]

Carbon dots were used in the preparation of nanofiltration membranes with charged voids aiming for an increase in membrane antifouling properties.[47] Cationic and anionic membranes were prepared upon using carbon dots with polyetherimide and polysulfone membranes. The water permeability was increased to 30.9 L m^{-2} h^{-1} bar^{-1} and Na_2SO_4 rejection of 99.4%.

Grossi et al. investigated the use of different membrane processes for the removal of sulfate and other contaminants from mining wastewater, upon combining ultrafiltration and reverse osmosis. The feed solution showed 314 mg L^{-1} of sulfate and the rejection was varied from 84 to 95% as a function of the recovery rate of reverse osmosis stage.[48] Table 5 shows the main results for sulfate removal by means of membranes, the advantages and disadvantages.

Table 5. Advantages and disadvantages of membranes for sulfate removal

Membranes	Nanofiltration	Reverse osmosis
Pretreatment	Ettringite precipitation (electronics factory)	Microfiltration and nanofiltration (gold mining effluent)
Feed water sulfate limits (mg L^{-1})	900	21,400
Sulfate removal (%)	98.2	98.7
Maximum content (mg L^{-1})	16	278.2
Costs/maintenance	Low	Low
Advantages	High selectivity, low energy cost, design simplicity, reaches effluent concentrations below those proposed by legislation	
Disadvantages	Pre-treatment prior to use of the membrane, with risk of fouling, requiring adjustments and frequent maintenance of the membranes.	
Reference	49	13

Good membrane yield is obtained since pre-treatment of the effluent is conducted before feeding the membrane module, which usually increases operating costs. Incrustation is also very likely to occur, which requires optimization of operating variables and constant cleaning or replacement of membranes. The development of membrane materials with higher quality, chemical resistance and anti-fouling properties, is the main subject of new research. Besides, the investigation of membrane regeneration and cleaning is still scarce in the literature.[50]

6. Electrocoagulation

Electrocoagulation is based on the use of electrochemistry to gain and lose electrons. The removal of sulfate is based on the enmeshment of iron oxides and hydroxides as well as charge neutralization by positively charged hydroxocomplexes.

Foudhaili et al. investigated the use of electrocoagulation for sulfate removal from acid mine drainage. The feed solution was used with 1,300 mg L^{-1} of sulfate. The use of electrocoagulation caused a removal of sulfate ranging from 6 to 31%.[51]

Mamelkina et al. used a factorial design to investigate the removal of sulfate by means of electrocoagulation. The authors reported the removal of up to 54% of sulfate for an initial sulfate solution of 1,000 mg L^{-1}, and applied current of 3 A. The results showed that iron electrodes caused higher sulfate removal rates compared to aluminum ones. Thus, the moderate removal of the sulfate indicated that the study of solution speciation is of utmost importance to the understanding of sulfate removal mechanism.[52]

Nariyan et al. investigated the removal of sulfate from acid mine water upon combining precipitation with CaO followed by electrocoagulation. The results showed a decrease in sulfate content from 13,000 mg L^{-1} to 1,600 mg L^{-1} in the first stage and to 250 mg L^{-1} in the second one. The optimal current density was 25 mA cm^{-2}, with two aluminum and two stainless steel anode-cathode configuration.[53]

Taking as a whole, the results show that electrocoagulation is a moderate sulfate removal yield and cannot be used as a unique method for sulfate removal, but can show some interesting results combined with other processes. Table 6 shows the main results for sulfate removal by means of electrocoagulation, the advantages and disadvantages.

Table 6. Advantages and disadvantages of electrocoagulation for sulfate removal

Electrocoagulation	Fe electrodes	Fe electrodes	Fe or Al monopolar and bipolar anodes
Pretreatment	None	Synthetic model solutions	Precipitation with calcium oxide
Feed water sulfate limits (mg L^{-1})	1,300	1,000	1,600
Sulfate removal (%)	6-31	54	63.8-84.4
Maximum content (mg L^{-1})	897	460	250
Costs/maintenance	High	High	High
Advantages	Combination of methods decrease the time to sulfate removal.	Sulfate removal dependent on the applied current.	High sulfate removal efficiency.
Disadvantages	Higher removal rates are associated to pretreatment with $Ca(OH)_2$ and high density sludge.	Moderate sulfate removal rates due to neutralization by iron hydroxocomplexes.	Electricity consumption should be optimized.
Reference	51	52	53

7. Process combination

The idea of process combination is based on the use of different processes, acting in their best range of sulfate removal to attain the final result, with sulfate content suitable for discharge.

Foudhaili et al. combined high-density sludge, precipitation and electrocoagulation to investigate the removal of sulfate from mine drainage solution. The combination of processes caused a reduction of sulfate content from 1,300 to 650 mg L^{-1}, so that electrocoagulation was used as a polishing step.[51]

Huang et al. investigated the use of a bioelectrochemical system for desalination of seawater, with 2,200 mg L^{-1} of sulfate. They added sodium acetate for the biofilm formed in the cathode. The sulfate removal was 98.5% while the sodium acetate was completely consumed. It was found that sulfate was reduced to sulfide, with a final concentration of 498 mg L^{-1}, for 132 h.[54]

Jin et al. proposed a combination of nanofiltration and ettringite precipitation for sulfate removal from an electronics factory with an initial sulfate content of 900 mg L^{-1}. The nanofiltration permeate was mixed in the precipitation stage and subsequently destined for disposal or reuse. A concentrated stream with high sulfate content was destined for the precipitation of ettringite. The study showed relevant results such as insignificant fouling and a permeate with sulfate content of 16 mg L^{-1}. The resulting stream for discharge or reuse had its concentration below sulfate concentration of 250 mg L^{-1}, showing a viable and low-cost way to remove sulfate.[49]

The combination of microbial-catalyzed electrochemical systems with fuel cell membranes was investigated aiming at the removal of sulfate and other ions in produced water.[55] The authors used biotic anode and an abiotic cathode separated by a cation exchange membrane (CEM, CEMI-7000). The sulfate initial concentration was 60 mg L^{-1}, and the sulfate removal efficiency ranged from 38 to 56%. The best result was shown for a closed circuit with an applied resistance of 1 kΩ. Dominance of *Proteobacteria* and *Actinobacteria* with enrichment of sulfate-reducing bacteria (*Desulfobibrio sp*. and *Desulfobulbus sp*.) was noticed in the abiotic anode.

Almasri et al. investigated the use of two-stage sulfate precipitation of retentate stream from nanofiltration. The authors studied an initial solution with 9,600 mg L^{-1} sulfate aiming for zero-liquid discharge. The first stage was based on the precipitation of sulfate with calcium, forming gypsum. This caused the removal of 88% of the initial sulfate content. In the second stage, authors investigated the precipitation of sulfate with aluminum, forming ettringite, which was highly dependable on the pH of the solution. The final content of sulfate in the solution was 384 mg L^{-1}, which indicated total sulfate removal of 96%.[56]

Siddiqui et al. investigated the use of a laboratory-scale up-flow anaerobic sludge bed reactor integrated with cross-flow dynamic membrane modules to treat saline wastewater. The results showed the reduction of sulfate and the formation of a dynamic membrane in the reactor. The removal sulfate efficiency was 34%, with an initial sulfate content of 150 mg L^{-1}. *Trichococcus* and *Desulfovibrio* were the most abundant bacteria both in sludge samples and the dynamic membrane layer. Statistical analysis showed positive correlations between sulfate reduction, the formation of a dynamic layer over the membrane and microbial dynamics.[57]

The combination of precipitation, biological treatment and hydrogen sulfide removal was investigated by Cheng et al.[58] Authors investigated the removal of cations in neutral mine drainage, followed by microbial sulfate reduction and ferrosol reactive barrier for removing biogenic dissolved H_2S. The first step did not cause sulfate concentration change, but the combination of the second and third steps caused the reduction of sulfate content from 2,500 mg L^{-1} to less than 10 mg L^{-1}, indicating that the customized route, considering the pH and metal cations in the aqueous solution, should be considered for treating sulfate-containing effluents.

Process combination seems to be a very interesting alternative so that each stage is responsible for decreasing sulfate content to an optimum level, leading to good yield upon using different approaches. Biological, chemical and physical-based technologies have pros and cons that can be adjusted to obtain excellent performances, upon minimizing the unfavored aspects.

8. Conclusion

The variety of processes for sulfate removal is wide, so the best application for a process will depend on the characteristics of the effluent, the investments available for treatment, and the destination of the water treated. Each mechanism shown in this article has its pros and cons, so an extensive analysis is essential to avoid its negative aspects. For instance, precipitation with barium chloride and nanofiltration showed the highest sulfate removal percentages (> 99%), while the good results found for biological degradation (99%) are devoted to more diluted sulfate content. The yield of ion exchange (75%) and electrocoagulation (84.4%) were lower than the other routes, demanding a combination with other processes for sulfate removal. Innovation techniques are constantly studied to solve this problem, but in addition, current studies aim to combine these processes for better effectiveness and cost-effectiveness of these processes. One of the main challenges is to scale up the tests and show the performances at the industrial level. The subject must be the focus of constant study to obtain relevant results so that usual technologies are replaced by more innovative, cheap and efficient methods.

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Conflict of interest

Authors declare no conflicts of interest.

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