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Electrochemical Abatement of Hydrogen Sulfide from Waste Streams

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Hydrogen sulfide is ubiquitously present in many waste streams originating from industrial activities as well as in sewage. It needs to be removed as it is toxic, corrosive, and odorous. Conventional abatement strategies involve physicochemical methods, which require significant amounts of chemicals and/or high energy input. Considering the limitations of physicochemical methods, there is a need for more cost-effective and sustainable abatement strategies. Recent advances in electrode materials and operation have stimulated interest in electrochemical methods for pollutant remediation. Several electrochemical approaches for sulfide abatement have been proposed over the last few years. Electrochemical techniques offer several advantages including the avoidance of dosage, handling, transport and storage of potentially hazardous chemicals, and the possibility of recovering sulfide or sulfur from wastewater as a product. This paper reviews electrochemical strategies that have been proposed for removal of dissolved and gaseous hydrogen sulfide. The advantages and disadvantages as well as the economic potential of each of the proposed methods are discussed. The technical aspects and key challenges to enable full-scale implementation are highlighted. Finally, opportunities for expanding electrochemical methods for sulfide abatement are presented.

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1. INTRODUCTION

Hydrogen sulfide is ubiquitously present in sewage as well as in many industrial waste streams. Dissolved sulfide is present in sewage[1] and industrial wastewater streams originating from tanneries, paper mills, oil refineries, petroleum plants, viscose rayon manufacturers, abattoirs as well as in geothermal brines.[2–4] Gaseous hydrogen sulfide is present in large quantities in natural gas, biogas from digesters, and the headspace of sewer networks (e.g., gravity sewers, pumping stations, wet wells, and manholes).[5,6] Furthermore, large amounts of gas phase hydrogen sulfide are formed in waste gas originating from different industries including the desulfurization of crude oil carried out by refineries. Hydrogen sulfide in both liquid and gas phases needs to be removed from an economic, environmental, and safety point of view as it is a toxic, corrosive, and odorous compound. For example, the emission of hydrogen sulfide from sewer networks is a notoriously costly problem for water utilities worldwide as it causes widespread corrosion of sewer networks and other wastewater infrastructures.[7,8] The annual loss of sewer asset is estimated to be in the order of one hundred million dollars in Australia (personal communication with Water Services Association of Australia), and several billion dollars in the US.[7] The widespread occurrence of emission of hydrogen sulfide (and volatile organic compounds) also results in the release of obnoxious odors. Even more importantly, the emission of hydrogen sulfide causes serious safety concerns as it is a toxic compound. For example, hydrogen sulfide present at lethal concentrations in, e.g., wet wells, manholes, and the headspace of gravity sections has caused several fatal accidents.[9]

A variety of physicochemical methods like chemical oxidation (using, e.g., hydrogen peroxide, oxygen, and chlorine) or catalytic conversion (e.g., Claus process), and precipitation (e.g., iron salts) have been proposed. An extensive overview of commonly used physicochemical methods is presented in several review papers.[1,10,11] Although their effectiveness for the removal of sulfide from both liquid and gas phases has been shown, they do pose several disadvantages. All of these methods require significant amounts of chemicals and/or energy input, which incurs large operational costs. In addition, the frequent transport, handling, and storage of chemicals come with occupational health and safety concerns.

In addition to physicochemical methods, microbiological processes have also been proposed. For example, the Thiopaq® process, which uses chemolithotrophic bacteria to oxidize sulfide to elemental sulfur under oxygen limited conditions,[12] has been successfully implemented at full scale for desulfurization of hydrogen sulfide containing gas (Paques, The Netherlands). This method is regarded as an economically attractive and sustainable solution. A disadvantage is that the efficiency is significantly reduced in the presence of organics that can be used by anaerobic sulfate and sulfur reducing bacteria to form hydrogen sulfide, which is something that cannot be avoided in most wastewaters.[13] Hence, its application is mainly restricted to gas desulfurization.

In view of the practical limitations of the existing strategies, there is general interest in alternative sulfide abatement technologies. Recent advances in electrode material research have introduced a number of highly active and economical carbon-based materials, such as carbon nanotube coated reticulated vitreous carbon (RVC)[14] and electrospun carbon nanofiber mats,[15] which would be suitable for sulfide service and would contribute to the reduction of electrochemical cell footprint, thanks to the high current densities they can support (60 A m^{-2} in microbial electrochemical anodes). Electrochemical techniques offer several advantages over the existing technologies. They do not require dosing, transport, and storage of potentially hazardous chemicals.[16] Also, the electricity required for such processes may come from a renewable source such as sun. Here, we review electrochemical techniques for sulfide abatement. We address the technological aspects and key challenges for practical implementation, and also discuss the possibility of expanding the use of electrochemical techniques by analyzing potential applications.

2. ANODIC SULFIDE OXIDATION

2.1. Concept of Anodic Sulfide Oxidation

Electrochemical oxidation reactions can be divided into direct and indirect oxidation reactions.[17] Direct oxidation at the electrode surface can take place if a compound is electrochemically active. Indirect oxidation involves the generation of oxidants or mediators such as “chemisorbed and physisorbed active oxygen,” oxygen, chlorine, Ag^{2+}, and Ce^{4+} at the electrode surface, which subsequently diffuse away from the electrode into the bulk liquid, where the actual oxidation reaction occurs.[18–21] An overview of the reactions involved in the generation of oxidants and their standard potential for formation is presented in Table 1. As sulfide is an electrochemically active compound, it can be oxidized by both reaction mechanisms.

During direct sulfide oxidation, sulfide is oxidized at the electrode surface to sulfur (S^0), thiosulfate ($S_2O_3{}^{2-}$), sulfite ($SO_3{}^{2-}$), or sulfate ($SO_4{}^{2-}$), depending on the anode material used and anode potential applied. At very high potentials, sulfate can be further oxidized to persulfate ($S_2O_8{}^{2-}$), which is a strong oxidant. Table 1 shows that direct oxidation of sulfide can already take place at low potentials, which was indeed realized by Dutta

TABLE 1. Standard electrode potentials (E^0) at pH = 7 for several sulfur and other chemical half cell reactions

Redox reaction	$E^{0'}$ (V) (at pH = 7)
$S(s)\,2e^- + 2H^+ \rightarrow H_2S(aq)$	−0.270
$S(s)\,2e^- + H^+ \rightarrow HS^-$	−0.476
$S_2O_3^{2-} + 8e^- + 8H^+ \rightarrow 2HS^- + 3H_2O$	−0.213
$SO_4^{2-} + 8e^- + 9H^+ \rightarrow HS^- + 4H_2O$	−0.213
$SO_4^{2-} + 8e^- + 10H^+ \rightarrow H_2S(aq) + 4H_2O$	−0.214
$SO_4^{2-} + 6e^- + 8H^+ \rightarrow S^0 + 4H_2O$	−0.194
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0.817
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-$	0.945
$OH^+H^+ + e^- \rightarrow H_2O$	1.967
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.720
$Ag^{2+} + e^- \rightarrow Ag^+$	1.980

The redox reactions presented in the table are written as reduction potentials (although the reverse reaction occurs), according to the International Union of Pure and Applied Chemistry convention.

et al.[22] This is a major advantage as it allows for the selective oxidation of sulfide from a liquid without any parasitic side reactions taking place. Oxidation of sulfide to elemental sulfur is preferred from an economical point of view as it requires the least number of electrons and thus energy input (i.e., 2-electron oxidation compared to, for example, an 8-electron oxidation for oxidation to sulfate). In addition, elemental sulfur is a solid, which would allow for its easier separation and recovery from the liquid phase. The key disadvantages of this approach are the passivation of the electrode by the elemental sulfur[3] and the low rate of oxidation at lower sulfide concentrations as sulfide needs to diffuse to the electrode surface to be oxidized.[23]

Contrary to the direct oxidation, the indirect oxidation of sulfide is often a non-selective process as the oxidants formed can also oxidize a wide range of oxidizable organic compounds, which results in a decrease in current utilizing efficiency for sulfide oxidation. Therefore, the coulombic efficiency (CE) of the process is lower compared to that of direct sulfide oxidation. In addition, it is important to realize that the formation of these oxidants takes place at much higher potentials (see Table 1) and thus requires more energy input. The type and amount of oxidant(s) generated and the relative importance of direct and indirect sulfide oxidations depend on the water matrix, the anode potential, presence and concentration of mediators (e.g., oxygen, chlorine, Ag^{2+}, and Ce^{4+}), and the electrode material used. The most suitable electrode materials and optimum operational conditions of the electrochemical system greatly depend on the characteristics of sulfide containing waste streams. An advantage of this approach is that sulfide does not need to diffuse to the electrode surface, allowing higher current densities.

Normally, the preferred cathodic reaction is the reduction of water to hydroxide ions and hydrogen gas:

$$H_2O + e^- \rightarrow H_2 + OH^- \qquad E^{0\prime}\left(\mathrm{pH} = 7\right) = -0.414\mathrm{V} \tag{1}$$

In most cases, the hydrogen gas produced is vented, whereas the hydroxide ions are used to neutralize the protons generated during the anodic reaction.

2.2. Applications

So far, anodic sulfide oxidation (both direct and indirect processes) has been proposed for the removal of both liquid phase sulfide from several industrial waste streams and sewage, and gaseous sulfide from sulfide contaminated gas streams such as natural gas, biogas, and headspace of sewers.

2.2.1. Anodic Sulfide Oxidation From Geothermal Brines

Geothermal brines are produced in large volumes in the petrochemical industry during oil and gas extraction.[24] Hydrogen sulfide can be present in geothermal brines up to concentrations of ~60 mM.[25] This is of major concern as it is toxic to workers, causes metal corrosion, forms sulfide scales, reduces the quality of produced gas and oil, and it can also create problems during drilling operations, as outlined by Ateya and Al-Kharafi.[3] Currently, geothermal brines are often reinjected without treatment. However, this incurs large costs as the brine needs to be injected under pressure to avoid hydrogen sulfide volatilization.[26] This can be avoided if sulfide is removed prior to reinjection.

Ateya and coworkers performed several studies that investigated the anodic oxidation of sulfide from geothermal brines using carbon based electrodes and different reactor configurations operating in both batch and continuous modes using synthetic brine solutions.[3,27–30] These studies revealed that it is possible to selectively oxidize sulfide to elemental sulfur at low anode potentials (e.g., −0.180 V vs. Ag/AgCl). The authors concluded that while anodic sulfide oxidation is a promising approach, the anode passivation by electrodeposition of elemental sulfur was the main obstacle for its practical implementation.

Several studies were conducted by the University of Guelph, which aimed to determine the feasibility of different anode materials such as boron doped diamond (BDD),[31] IrO_2–Ta_2O_5 coated titanium,[24] carbon based electrodes[26,32], and Ebonex (Ti_4O_7)[25] using synthetic brine solutions. In addition, these studies also investigated the impact of chloride and naphthenic acids, which are often present in high concentrations in geothermal brines. Waterston et al.[31] achieved near-quantitative oxidation of sulfide to sulfate both in the presence and in the absence of chloride using BDD electrodes. Although this study clearly showed the feasibility of BDD, their high costs severely limit full-scale implementation. IrO_2–Ta_2O_5 coated titanium and carbon based electrodes were unsuitable as poisoning of the catalytic layer of the titanium electrode surface with sulfide occurred,[24] whereas the carbon materials acted as sacrificial electrodes.[26,32] It should be emphasized that the latter can be avoided if the anode potentials are kept below a certain critical potential, at which the carbon material is being oxidized itself. A CE of ~50% was achieved using Ebonex electrodes, with sulfate being the predominant product of oxidation.[25] The reduction in CE was caused by oxygen formation as well as electrode passivation by sulfide poisoning. Importantly, it was found that periodic polarity reversal was successful to overcome this electrode passivation. However, at this stage, Ebonex is available only to a limited extent on the market,[33] which limits its practical implementation.

While the studies above show the feasibility of anodic sulfide oxidation from geothermal brines, all of these manuscripts lack important information about the energy requirements of the system, which is crucial to determine its economical attractiveness. In the authors' opinion, carbon materials are the most promising anodes considering their low costs, and the possibility of selectively oxidizing sulfide to elemental sulfur at low anode potentials, and the subsequent recovery at the cathode as elemental sulfur[34] (see Section 2.3). Further laboratory-scale studies as well as pilot testing are needed to accurately assess the economic potential by determining the energy requirements, sulfur recovery, and long-term stability of the process.

2.2.2. ANODIC SULFIDE OXIDATION FROM INDUSTRIAL WASTEWATERS

Several studies reported on the removal of sulfide from industrial wastewater such as tannery wastewater,[35–40] paper mill effluents[4,41], and oil wastewater.[42] It is important to realize that for tannery wastewater the aim also includes the removal of organics (i.e., chemical oxygen demand (COD)), total Kjeldahl nitrogen (TKN), and suspended solids, in addition to sulfide removal. To achieve anodic oxidation, dimensionally stable materials such as Ti–Ru/Ir, Ti–Ta/Ir, Ti–Pt/Ir coated titanium, and platinum were used as they are capable of in situ generation of oxidants.[35–40] Studies revealed that while high removal efficiencies for COD, TKN, and sulfide can be achieved (i.e., >90%), the high energy requirements due to organics and ammonium removal (>10 kWh up to 300 kWh/m^3,[36] depending on wastewater characteristics) most likely limit its practical implementation as a main stream treatment process aiming at sulfide removal. Dutta et al. reported the continuous removal of sulfide from digester effluents at an average CE of ~80% using carbon electrodes.[4] More importantly, periodic switching of the polarity allowed for the recovery of sulfide as a concentrated polysulfide/sulfur solution in the cathode compartment. Biofilm formation was avoided due to the elevated pH levels observed in the cathode. This will be further discussed in Section 2.3.

The costs were estimated to be \$0.67/kg S removed,[43] which is well below the conventional chemical dosing.[1]

A few studies reported on the anodic oxidation of thiosulfate to sulfate from wastewater origination from photographic film processing industries using different electrode materials including PbO_2, IrO_2, and RuO_2, and glassy carbon.[44–47] Thiosulfate needs to be removed as its disposal onto receiving surface waters may lead to depletion of dissolved oxygen, and a decrease in pH due to its subsequent oxidation to sulfuric acid. These studies show that very high removal efficiencies can be obtained (i.e., >95%). Considering that thiosulfate can be readily oxidized by oxygen to sulfate, the use of aeration may be a better, less complex, and cheaper option. So far, the economic potential of electrochemical thiosulfate oxidation is yet to be evaluated.

2.2.3. ANODIC SULFIDE OXIDATION FROM SEWAGE

Oxygen is often injected to sewers to prevent sulfide generation.[48] Recently, it was found by Pikaar et al. that sulfide can be removed from sewage at high current densities using mixed metal oxide (MMO) coated titanium electrodes during laboratory scale experiments[23,49] as well as during long-term field trials[50] by electrochemically generated oxygen. The authors found that at the low sulfide concentrations normally found in sewage (i.e., <10 mg/L), direct selective oxidation on the electrode surface is negligible, whereas sulfide is predominantly removed by in situ generated oxygen, independent of the type of MMO catalytic layer used. The CE for dissolved oxygen generation was ~60%,[50] which is significantly higher than that for conventional oxygen injection (typically below 40%,[51]). The oxidation was non-selective as organics are also removed besides sulfide, with ~50% of the total electrons used for organics oxidation.[49] The final products of oxidation were a mixture of sulfur, thiosulfate, and sulfate. Elevated chloride concentrations (i.e., 1.1 g/L) often observed in coastal areas, and the type of catalytic MMO layer used (i.e., Ta/Ir, Ru/Ir, Pt/Ir, SnO_2, and PbO_2), did not significantly affect the kinetics of sulfide oxidation.[49] During long-term field trials, sulfide control with average removal efficiencies around 90% was successfully achieved at the end of a simulated rising main sewer.[50] The field trials revealed that membrane fouling caused by precipitation of inorganics resulted in increasing energy requirements and the need for membrane cleaning. This membrane fouling cannot be avoided due to the presence of calcium and magnesium in sewage. Periodic polarity switching was successful to overcome membrane fouling within the experimental time period.[52] The abovementioned studies clearly showed the feasibility of sulfide removal from sewage using anodic sulfide oxidation. In addition, in conjunction with the anodic in situ generation of oxygen, caustic can be produced cathodically.[52,53] This further increases the economic potential of electrochemical sulfide abatement in sewers, as caustic is one of the commonly used chemicals for sulfide control in sewers.[48] The costs for simultaneous in situ generation of oxygen and caustic from sewage were estimated to be \$0.83–1.17 (kg S^{-1})[52] compared to \$1.7–7.2 (kg S^{-1})[1] for conventional sulfide abatement strategies. The working principle of this method is discussed further in Section 4.2.

2.2.4. HYDROGEN SULFIDE REMOVAL FROM GAS STREAMS

Several million tons of hydrogen sulfide are recovered annually from natural gas plants, refineries as well as from various metallurgical processes. The most commonly used method involves a wet absorption process, followed by the Claus process.[54] This is a well-established physicochemical technique, in which part of the sulfide is burned to SO_2 that subsequently reacts with the remainder of the hydrogen sulfide to form elemental sulfur. In this way, very high sulfur recovery efficiency (i.e., >95%) is obtained. The size of these plants can differ significantly, ranging from less than 0.2 tons of H_2S per day to more than 50 tons of H_2S per day.[55] Major disadvantages are the high energy demand and relatively high investment costs.[56] Therefore, several studies have investigated electrochemical approaches for the removal of hydrogen sulfide from gas streams.[57–65] The gas stream is directed through an alkaline scrubber to dissolve the sulfide. This alkaline scrubber solution is subsequently fed to an electrochemical reactor for sulfide oxidation. These studies showed that it is feasible to oxidize sulfide to elemental sulfur, although these manuscripts did not present important information about the economic potential. Also, most of these studies could not overcome issues with anode passivation due to sulfur deposition. Periodic switching of the polarity of the electrodes should avoid this problem[34] and would allow for the recovery of sulfide as concentrated polysulfide solution (see the next section). Considering the large electrode surface areas required at high sulfide loading rates, the approach seems to be more suitable for smaller size plants. Further research at both laboratory and pilot scales is warranted to determine the feasibility and long-term performance of this concept, and its comparison with the existing and other emerging technologies.

More recently, the use of redox mediators such as Ce (IV),[20] Ag (II),[21] Fe (II),[66] and VO_2^{+}[54] has been proposed. The advantage of the use of redox mediators is that the system operates at ambient pressure and temperatures, whereas the catalyst is continuously being regenerated, which minimizes the chemical consumption. The abovementioned studies achieved very high efficiencies up to complete removal of hydrogen sulfide. Some of these studies claim this method to be more economical than the existing techniques.[20,21] However, these studies do not provide data to support these claims nor compare with for example the Thiopaq® process, a patented biological method, which is regarded as an economically attractive and sustainable solution.

Nonetheless, these studies clearly show the technical potential of the technique for removal of hydrogen sulfide from gas streams. Though, in order to accurately assess the practical and economic potential long-term pilot testing, further research is necessary.

2.3. Future Opportunities for Anodic Sulfide Oxidation

Sodium sulfide has a considerable market value of ~\$800 per ton, the key users of this chemical are tanneries and gelatine producers. The extensive use of sulfide in their processes not only leads to considerable chemical cost, but also causes the production of wastewaters with high sulfide content. Treatment typically requires pH correction as well as iron dosage for precipitation. One can use the reversibility of the anode reaction to harvest sulfide from wastewater.[34] This could be done via sending the wastewater through an anode and allowing sulfide oxidation until the anode is substantially covered with sulfur. Subsequently, the flow through the anode can be stopped, and via polarity reversal the anode can become a cathode from which the sulfur is reduced. In a first phase this generates polysulfide, upon prolonged reduction a concentrate of sulfide is obtained. This concentrate may be useful for reuse on sites. Indeed, a recent cost analysis, based on the outcome of extensive laboratory-scale studies, showed the economic potential of this novel approach with estimated costs of \$0.67/kg S removed, without taking into account the potential revenue for the recovered sulfur/polysulfide.[43] The shortage of sulfur is not expected in the short term as the reserves of sulfur in crude oil, natural gas, and ores are still large. However, in the long term, alternative sources for sulfur are required as crude oil, natural gas, and ores are non-renewable sources. In this perspective, electrochemical sulfur recovery from sewage and industrial waste streams may become an important alternative resource in the long term. In this perspective, while electrochemical sulfur recovery from sewage and industrial waste streams may become an important alternative resource in the long term, the current main drivers for the development of anodic sulfide oxidation (and the subsequent recovery as sulfur/polysulfide) should be the economic and environmental benefits this method offers. The recently obtained experimental results and assessment of the economic potential[43] certainly warrant further research.

3. ELECTRO-PRECIPITATION

3.1. Concept of Electro-Precipitation

Electro-precipitation (also often referred to as electro-coagulation and electro-flotation) involves the in situ generation of dissolved iron ions (i.e., Fe^{2+}/Fe^{3+}) by means of the use of sacrificial iron anodes.[67] For this purpose, iron either in plate form or packed form of scarps (e.g., steel turnings and milling) is normally used. In situ electrolytic oxidation of the metallic plate leads to the anodic dissolution of the iron ions:

$$\mathrm{Fe}^{(0)} \rightarrow \mathrm{Fe}^{2+} + 2e^- \qquad E^0 = -0.440\mathrm{V} \tag{2}$$

$$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + e^- \qquad E^0 = +0.771\mathrm{V} \tag{3}$$

Sulfide ions exist in solution mostly as H_2S or HS^-, depending on the pH (acidic or neutral/basic, respectively). Ferrous iron reacts with sulfide forming an insoluble metal sulfide precipitate as follows:

$$\mathrm{Fe}^{2+} + \mathrm{HS}^- \rightarrow \mathrm{FeS} + \mathrm{H}^+ \tag{4}$$

However, at neutral/alkaline pH, iron sulfides turn into more stable hydroxides, which are quickly oxidized to ferric form in the presence of oxygen at circumneutral pH. The reaction then proceeds to give metal oxo-hydroxide:

$$\mathrm{Fe\,(OH)_3} \rightarrow \mathrm{FeO\,(OH)} + \mathrm{H_2O} \tag{5}$$

In the cathode, the evolution of hydrogen will typically take place (see Eq. (1)). This hydrogen production will favor the electro-flotation process, in which the formed hydrogen bubbles will rise up to the surface of the tank. As these bubbles adhere to the surface of suspended particles, these particles will also float to the surface.[68]

Electro-precipitation offers several advantages including the simple process configuration (i.e., a simple electrochemical system is used), the ease of automation, and the fine-tuning of the process (i.e., the dosing is directly related to the current supplied).[18] It also avoids the addition of anions (i.e., sulfate or chloride) required in conventional precipitation, thus does not lead to an increase in the salt content of the treated water.

Electro-precipitation is not a selective process. Besides sulfide, suspended solids, COD and oil, and grease, if present in the wastewater, are also removed.[68] Hence, the energy input (which determines the amount of iron ions added to the wastewater) required to achieve high sulfide removal efficiencies predominantly depends on the wastewater composition. Also, given the low selectivity of the electrocoagulation process, the large volume of the iron sludge produced by this technology is considered a drawback, i.e., there is an increase in the operational costs as a consequence of the sludge transportation and disposal to landfill, plus the associated environmental footprint due to heavy metal leaching.

In addition to sulfide, often sulfite and sulfate also need to be removed. Contrary to sulfide, sulfite and sulfate cannot be removed by precipitation. The removal of these compounds involves a physical process in which both ions are enmeshed in the metal (Fe/Al) oxide/hydroxide precipitates formed during the process.[69]

Another important parameter is the wastewater conductivity as this can have a significant impact on the ohmic losses and therefore the energy requirements of the system.[18] Depending on the origin, wastewaters can have a wide range of conductivities. Domestic wastewater normally has low ranges ($\sim$1 mS·cm^{-1}),[70] while some industrial wastewaters have higher conductivities ($>$5 mS·cm^{-1}).[71] Although electrical technologies can be successfully applied to wastewater with low conductivity as shown in, e.g., Ref.50, special care should be taken in the design of the electrochemical cell with a focus on minimizing the anode and cathode distance in order to minimize ohmic losses.

3.2. Applications

Electro-precipitation has been tested in the removal of dissolved sulfide (and sulfite and sulfate) in pulp and paper mill wastewater,[72] petroleum refinery wastewater,[73] and tannery wastewater.[69,74] Electro-precipitation was proven to be highly efficient in the removal of dissolved sulfide from pulp and paper mill wastewater with sulfide removal efficiencies up to 88% at an effluent sulfide concentration of only 1.05 mg/L.[72] The charge required was only $\sim$8 C/mg sulfide-S removed. Assuming a cell voltage in the range of 2–5 V, the energy requirements are only 0.19–0.46 kW/kg S removed.[72] In this study, 500 mL of wastewater was treated in an electro-precipitation cell constructed from four monopolar iron cells, reaching sulfide removal efficiencies up to 88% at an effluent sulfide concentration of 1.05 mg/L and an electric charge per volume of 7.99 C/mg S^{2-}. Murugananthan and coworkers investigated the removal of sulfide from tannery wastewater and observed maximum sulfide removal efficiencies of 73%, 68%, and 48%, using iron, aluminum, and titanium as electrode materials, respectively.[69] Feng et al. achieved sulfide removal efficiencies above 90% using mild steel as the electrode, while only 12% sulfide removal efficiency was observed when using aluminum.[74] These studies also investigated the removal of sulfate and found that the sulfate removal was not significantly affected by the electrode material used (Fe or Al), but was affected significantly by the pH and the zeta potential of the iron and aluminum oxide/hydroxides. In accordance to previously reported values,[75] the isoelectric point (iep), i.e., point of charge zero, of iron and aluminum oxides/hydroxides was observed at a pH of 7.7 and 8.8, respectively. As the pH became more acidic, the zeta potential of iron and aluminum oxides/hydroxides increased in magnitude. However, in the presence of sulfite and sulfate, the zeta potential magnitude decreased without any shift in the isoelectric point. This phenomenon suggests a physicoelectrical interaction, instead of a chemical one. As a result, the obtained sulfate removal efficiency decreased from 72% under slightly acidic conditions (pH = 5.5) to $\sim$20% at a pH of 10.5.[69] It should be noted that in a practical situation, such high pH levels are not expected.

3.3. Future Opportunities

Emerging technologies are creating an opportunity to turn the waste FeS_x sludge from electro-precipitation into a valuable resource. The FeS_x sludge can be separated and subsequently anodically oxidized to Fe^{3+} and elemental sulfur. Elemental sulfur deposited on the electrode surface can be recovered as sulfide or polysulfide electrochemically,[22] as discussed in a previous section, while the liberated ferric can be reused as a coagulant, with consequent savings for the water industry. Indeed, anodic FeS_x oxidation has recently been demonstrated as part of a process proposed to recover ferric and phosphorus from the ferric phosphate containing sludge.[76] After secondary treatment of the wastewater, iron salts such as iron chloride ($FeCl_3$) are often dosed to precipitate phosphate in the water, leading to the formation of a sludge containing mostly ferric phosphate. This represents an increasing problem to water utilities due to the high costs associated with both chemical consumption and sludge disposal. As a result, the development of a more cost-effective and efficient method to recover ferric iron and recycle it within the process is of concern for the water industry. The recovery of iron and phosphorus from the iron phosphate sludge via sulfide addition has been proposed.[77] After sulfide addition, an insoluble iron sulfide (FeS_x) precipitate is formed, releasing phosphate in high concentrations, which can be subsequently recovered. The FeS_x-containing sludge is then fed to the anodic compartment of an electrochemical cell, where FeS_x is oxidized to ferric and elemental sulfur (deposited on the electrode surface), respectively. Iron and sulfur can then be separated and recovered for reuse within the process, i.e., iron as Fe^{3+} is recycled in the coagulation/flocculation and phosphate removal process and sulfur as sulfide can be recycled in the phosphate recovery stage.[78] A preliminary cost analysis of the 2-stage integrated process showed the economic potential of this novel approach. At the current Fe and S recoveries of 60% and 50%, respectively, an operational cost of €8.9/kg Fe recovered was estimated compared to the current €11.4/kg Fe incurred by the water industry in Europe in terms of ferric addition and sludge incineration.[79]

4. SULFIDE ABATEMENT WITH ELECTROCHEMICALLY GENERATED CAUSTIC

4.1. Concepts of Sulfide Abatement with Electrochemically Generated Caustic

Hydrogen sulfide generation is often the result of microbial activities of sulfate reducing bacteria (SRB). By inhibiting SRB activity, hydrogen sulfide generation and the need for counteractive measures can be avoided. A commonly used method to inhibit hydrogen sulfide generation is the addition of caustic to create elevated pH levels to deactivate SRB activity.[48]

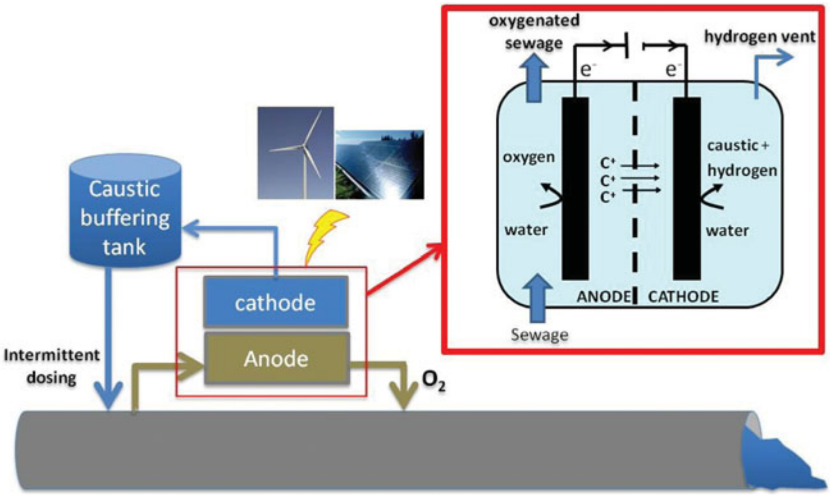

FIGURE 1. Working principle of electrochemical in situ generation of caustic and oxygen from sewage using a divided electrochemical cell.

Caustic is normally produced in the chlor-alkali industry, in which chlorine is generated from a brine solution in the anode, while water or oxygen is reduced to hydroxide ions in the cathode:

$$H_2O + e^- \rightarrow H_{2(g)} + OH^- \qquad E^0 = -0.82V \tag{6}$$

$$O_2 + 2H_2O + 4e^- \rightarrow +4OH^- \qquad E^0 = +1.23V \tag{7}$$

Recently, it was shown that caustic could also be produced at moderate strengths from anaerobic digester effluents treating brewery wastewater using a bioelectrochemical system[80] as well as from sewage by a direct electrochemical method.[52] The working principle relies on the imperfect proton transport from the anode to the cathode.[81] The latter is caused by the low proton concentration (i.e., 10^{-7} at pH 7) in wastewater compared to other cations (e.g., sodium, calcium, magnesium, and potassium), which are present in much higher concentrations. In the cathode, which is fed with a clean solution, a reduction reaction takes place that consumes protons, and consequently a caustic solution is produced. If the cathode is operated in a batch mode in which a small volume is continuously recirculated over a long period of time (i.e., several hours up to days), a concentrated caustic solution can be obtained.[52] On the other hand, as the anode is continuously fed with wastewater with a low hydraulic retention time (HRT), the drop in pH is negligible.[52] A schematic overview of electrochemical caustic generation from sewage is presented in Figure 1.

The in situ generation of caustic offers several advantages as it avoids the handling, transport, and storage of concentrated caustic (i.e., NaOH is normally purchased as 30–50 wt% NaOH), all of which come with serious workplace health and safety (WH&S) issues.

4.2. Potential Applications

Inhibition of SRB that are present in the biofilm on the wall of sewer pipes can be achieved by dosing caustic to create toxic pH levels (i.e., pH > 10). In this way, microbial activities can be inhibited over a longer period of time (i.e., several days to weeks).[48] This allows for a periodic dosing strategy, thereby reducing chemical consumption. Several studies showed the feasibility of this method for sewer application.[82,83] A recent industrial survey showed that pH shock loading to deactivate sewer biofilms, and thereby inhibiting the sulfide generation for several days, is a commonly used method by the water industry.[48]

During the laboratory experiments reported in Ref.52, caustic was successfully generated directly from sewage at a CE of ∼50% and a caustic strength of 0.61 ± 0.10 wt%. In the anode, oxygen was continuously being generated in the sewage, without significant pH changes.[52] However, this study also revealed that membrane transport of calcium, magnesium, and ammonium, all of which lead to the consumption of hydroxide ions in the cathode, as well as the back-diffusion of hydroxide ions from the cathode to the anode, had a significant impact on caustic production. In addition, membrane transport of calcium and magnesium resulted in membrane fouling. The latter caused increasing energy consumption and the need for membrane cleaning. These are issues to be addressed in future research. For example, membrane cleaning was achieved by polarity switching every four hours.[52] Continuous long-term pilot testing is needed to accurately assess the economic potential and stability of the process over a longer period of time (e.g., >1 year).

Depending on the size of the sewer, the electrochemical cell could be driven by a solar panel, making it a very sustainable solution. In addition, methane emissions caused by methanogenic activity, which can increase the carbon footprint of wastewater management by up to 30%,[84] can also be reduced. As many water utilities have set their goal of achieving greenhouse gas (GHG) neutral wastewater management in the future, the minimization of methane emission from sewers is critically important.

Hydrogen sulfide is often also a significant pollutant in biogas generated from anaerobic treatment of industrial wastewater or organic solids, including the sludge from municipal wastewater treatment processes. The biogas utilization potential can be restricted by the H_2S concentration. To remove H_2S from biogas, a caustic scrubber solution is typically used, which needs to be replaced and/or regenerated regularly. The cathodic cell of an electrochemical process would provide an alternative solution to H_2S removal as the solution is typically alkaline due to OH^- production with the generation of hydrogen at the cathode. The hydrogen formed can either be stripped into the biogas, or can be converted to methane through methanogenesis, if the conditions are suitable for biological processes. The latter process will also convert some of the CO_2 present in biogas to methane, providing a further improvement in the biogas quality. The sulfide absorbed in the catholyte can then be removed as a concentrated solution or recovered as elemental sulfur at the anode (see Section 2.3).

5. CHALLENGES

5.1. Electrode Passivation During Anodic Sulfide Oxidation

A major disadvantage associated with the formation of elemental sulfur on an electrode is that it is an insulator with an electrical resistivity of approximately $10^{17}\ \Omega\ cm^{-1}$.[85] Hence, the deposition of elemental sulfur onto the electrode surface results in electrode passivation and ultimately in a complete end of the process.[3,27,65] Several strategies have been suggested to overcome this problem including (i) the use of organic solvents, (ii) rotating a wiper blade electrode, (iii) using a high voltage pulse, or (iv) periodic polarity switching.

Shih and Lee reported on the successful oxidation of sulfide to elemental sulfur without the occurrence of electrode passivation by means of continuous dosing of toluene (an organic solvent), at an overall process efficiency of 40–80%.[86] Although, this study showed the feasibility of deactivation control through the use of an organic solvent, it has limited value for practical applications due to the need for continuous addition of toluene. Also, a posttreatment step is needed in most situations as toluene needs to be removed prior to wastewater being discharged to sewerage systems or surface waters.

Farooque and Fahidy reported on the use of a platinum rotating tripolar viper blade to avoid anode passivation.[87] This technique involves the use of a three-compartment cell in which a viper blade electrode rotates between the compartments. The first compartment is filled with piperidine, an organic solvent, where sulfur is washed off the anode surface. The second compartment is filled with deionized water to remove traces of piperidine. The actual oxidation of sulfide takes place in the third reactor. Although this configuration minimizes the use of an organic solvent, its complex reactor setup limits its practical implementation.

Shi et al., reported on the use of a temporarily increased voltage of 1.5 V (for 2 minutes) to enable the oxidation of elemental sulfur to soluble sulfur species (e.g., sulfate).[88] A disadvantage is the increase in energy requirement of the system. In addition, the use of a high voltage rules out the use of carbon-based anodic materials (carbon would be oxidized at the high voltage applied). While demonstrated through laboratory studies, the applicability of the method to practical applications is yet to be demonstrated.

Recently, a novel strategy was developed with which sulfur passivated graphite electrodes were reactivated by electrochemical regeneration by means of polarity switching (i.e., the anode becomes the cathode and vice versa).[34] At the anode, sulfide is being oxidized to elemental sulfur, while in the cathode, elemental sulfur previously deposited is reduced to a concentrated sulfide/polysulfide solution. Hence, sulfide can be removed from wastewater in the anode, and recovered in the cathode, with the latter also serving to regenerate the electrode. This concept was recently demonstrated using real wastewater (sludge digester effluents).[4] This is a major breakthrough as this is the first time that a sustainable method with good potential for full-scale implementation becomes available, which allows for the continuous removal (and recovery) of sulfide using a simple configuration. An additional benefit of polarity reversal is that both compartments are periodically exposed to elevated pH (above 10), as pH in the cathode increases sharply when operated in a batch mode. The elevated pH minimizes the occurrence of biofouling of the electrode and membrane surface. The long-term performance of this strategy is yet to be investigated.

5.2. Membrane and Electrode Scaling and Biofouling

In most applications, the electrochemical cell is divided by an ion exchange membrane. In case the electrochemical cell is operated at low anode potentials, biofilm formation on both the membrane and electrode surface can be expected. The formation of a biofilm containing electrochemical active bacteria would lead to removal of organics and a decrease in sulfide removal efficiency.[4] Hence, for long-term operation the biofilm formation needs to be avoided. An option is to regularly clean the anode compartment with an acid solution. However, this is not the preferred option as this results in downtime of the system as well as the need for chemical dosing. Alternatively, biofilm formation can be avoided by periodic polarity switching. By switching the polarity (i.e., the anode becomes the cathode and vice versa), bacteria are exposed to high pH regularly and thus biofilm formation is prevented.[4]

The membrane and electrode surface are also prone to inorganic fouling due to the membrane transport of the bivalent cations such as magnesium and calcium, which are present in most wastewater streams. In theory, the use of monovalent membranes should prevent transport of bivalent cations. In practice, these membranes are not strictly monovalent[89] and thus cannot completely prevent inorganic fouling. However, they do have a higher selectivity toward monovalent ions and may thus reduce the rate at which fouling occurs. Nevertheless, regular membrane cleaning appears to be needed to ensure stable operation. Polarity switching may also provide a solution to this problem due to periodic acidification of the membrane surface.

5.3. Microbial Interactions

Bacteria can play a catalytic role in anodic sulfide oxidation from wastewater. Rabaey et al. investigated the use of sulfide as an electron donor for bacteria in a so-called microbial fuel cell.[90] Using a sulfide containing wastewater as feedstock, they revealed the enrichment of a *Paracoccus* species as a dominant member of the microbial community. Relatives of this organism were previously shown to be able to link sulfide oxidation to sulfur to the reduction of, e.g., nitrate.[91] However, later studies showed that microbial sulfide conversion in wastewater did not necessarily bring advantages.[92] Indeed, further data showed that microorganisms used sulfur reduction to sulfide as a means to oxidize organic matter, thereby leading to sulfide formation in the anode, requiring further electrochemical oxidation. Overall this microbial process can decrease the efficiency of sulfide recovery as there is some sulfide loss. A second disadvantage of bacterial catalysis is the fact that bacteria can achieve complete oxidation of sulfide to sulfate at low potentials, as shown in a 2002 study on marine sediment microbial fuel cells.[93]

5.4. Scale Up

So far, the feasibility of electrochemical techniques for sulfide abatement has only been evaluated using laboratory scale systems. To transfer this technology from the bench scale to the full scale, several engineering and technological considerations have to be addressed.

The main limitation to large-scale implementation of anodic sulfide oxidation is thought to be the current densities that can be sustained with the currently available electrode materials, especially where electrochemical reactions occur between solid particles and electrodes (see, e.g., Section 3.3). In order to limit the size and thus the cost of the scaled-up systems, high current densities of 50–100 A m^{-2} are paramount. This demands preparation and testing of novel electrode materials with high surface areas and high activity. Pretreatment of carbon materials to activate their surfaces by chemical or physical functionalization, thereby increasing the maximum attainable current densities, will need to be investigated. Another problem for scale-up is the insufficient electrical conductivity of carbon electrodes, which demands the use of either suitable current collectors or bipolar plates. When bipolar plates are used to minimize electron travel distances, serially stacked systems result. The control of these is known to be problematic due to unwanted polarity reversal of the poorest performing cells in the stack, leading to unsuccessful removal of sulfur species and electrode corrosion. However, novel process control methods have been devised recently to solve this problem.[94] The membrane lifetime may also be of concern due to their limited stability, especially when exposed to continuous cycles from high to low pH levels (as during, e.g., ferrous sulfide oxidation, as described in Section 3.3).

6. CONCLUSIONS

This review gives an overview of electrochemical techniques for sulfide abatement from waste streams. Over the last few years, several electrochemical approaches have been proposed. The selective oxidation and subsequent recovery of sulfide as sulfur/sulfide from industrial wastewater, caustic generation from sewage to prevent sulfide generation, as well as the use of redox mediators for the removal of hydrogen sulfide from gas streams appear to be the most promising applications.

Economic assessments based on experimentally obtained results clearly indicated the economic potential of electrochemical caustic generation from sewage for sulfide control and anodic oxidation of sulfide (and recovery as sulfur) from 1industrial wastewater. In order to determine the long-term performance and accurately assess their economic potential, long-term pilot testing is essential.

To transfer the technology to full-scale implementation, several engineering and technological considerations have to be addressed. Future research should focus on pretreatment of carbon materials by chemical or physical functionalization to activate their surfaces, strategies to avoid or minimize membrane and electrode fouling, and obtain a more detailed understanding of microbial interactions.

In addition, several novel opportunities have been identified such as iron recovery, polysulfide recovery, and biogas cleaning, which need to be explored.

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