Influence of operating parameters during electrocoagulation of sodium chloride and sodium bicarbonate solutions using aluminium electrodes

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ABSTRACT

Sodium salts are common in solutions used in electrocoagulation (EC) studies especially in relation to treatment of produced water. However, the influence of sodium salts upon electrocoagulation operating parameters is not well understood. Therefore, a multi-electrode electrocoagulation cell with aluminium electrodes was used to investigate the impact of polarity reversal period, electrode history, sodium chloride/sodium bicarbonate concentration, floc characteristics and starting solution pH. Effluent pH exhibited oscillating behaviour which related to electrode passivation, with cleaner electrodes raising pH and electrodes with oxide coatings decreasing pH due to variations in anode dissolution and oxidation of water. Polarity reversal could lower cell resistance by de-passivating the electrode surface with a 3 min reversal time recommended. However, electricity (2.56 kWh/kL) and electrode consumption (0.448 g/min) were enhanced. Imaging revealed that the presence of sodium chloride induced extensive pitting corrosion of the aluminium electrodes, whereas pitting was only observed with high concentrations of sodium bicarbonate. Sodium bicarbonate suppressed pH oscillation due to electrode passivation. The amount of electrode consumed was greater than predicted from Faraday's Law and as such non-electrochemical processes occurred. The wear of electrodes was uneven with those with highest load at the EC cell extremities wearing the fastest. Floc settling rates were relatively slow and not significantly impacted by salt concentration. The settled volume after 1 h was still greater than 60% of the initial volume, which may cause issues with floc separation. Residual aluminium ions in the effluent were present which may impact downstream membrane performance.

1. Introduction

Dwindling freshwater resources worldwide have promoted the need for increased focus on remediation and recycling of unconventional water sources such as produced water from the coal seam gas (coal bed methane) industry, landfill leachate and flowback water from shale oil and gas operations [1–5]. For example, coal seam (CS) water is extracted from coal seam gas (CSG) wells as a result of depressurization which allows the gas trapped in the coal cleats to flow [6]. The produced water comprises mainly of dissolved sodium chloride and sodium bicarbonate species with a total dissolved solids concentration typically in the range 1500–10000 mg/L [2,7]; although this latter range can be higher depending upon the location of the coal seam gas operation [8]. Typically, the CS water properties are not compliant with regulations regarding direct beneficial reuse for applications such as irrigation, stock watering, dust suppression and coal washing. For example, the sodium absorption ratio may be such that when used for crop watering,

issues with soil compaction occur [9]. Similarly, Kausley et al. [5] described shale gas wastewater which comprised of 5000–50000 mg/L sodium chloride and 50–500 mg/L sodium bicarbonate, along with 500–5000 mg/L calcium chloride. Again, this shale gas wastewater was not amenable to beneficial reuse without further treatment.

Consequently, various technologies may be used to desalinate or treat the produced water to achieve compliance. Ion exchange using synthetic, cationic resins is potentially viable for removal of sodium [10–12] and potassium ions [13] for example, and resins have been reported to be operational in several sites in the USA [14]. Zeolites also represent a potential means of removing cations from produced water [15,16]. In Australia, reverse osmosis (RO) has been implemented as the core desalination process [17]. RO is a robust and well-proven technique, however the nature of the produced water means that membranes may suffer from fouling or scaling due to the presence of alkaline earth ions, organic material and silicate species [18]. Therefore, various approaches have been tested to protect the RO membranes

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such as water softening with resins [19–21], removal of silicate species using activated alumina [22], use of anti-scalants [23] and forward osmosis [24].

Recently, electrocoagulation has been demonstrated to remove significant quantities (> 85%) of the major species in coal seam water which can cause scaling of the membranes and equipment, namely alkaline earth ions and dissolved silicate species [25]. Electrocoagulation (EC) involves the application of a voltage to suitable electrodes, usually aluminium or mild steel, whereupon the electrode material dissolves into solution and creates $Al(OH)_3$ and $Fe(OH)_3$ species [26,27]. Sardari et al. [28] also coupled electrocoagulation with a forward osmosis (FO) membrane and found that this system could reduce the rate of fouling of the FO membranes.

In terms of produced water treatment the issue of the impact of variable salinity upon electrocoagulation performance needs to be addressed. Notably, often sodium chloride is added to solutions which have been treated by EC in order to improve conductivity [29], yet the holistic effect this action had upon EC is often not reported. Increasing sodium chloride concentrations may accelerate the electrode consumption in excess of values predicted from Faradaic considerations [30]. Mechelhoff et al. [30] reported that addition of sodium chloride above a concentration of $8.8\,g/m^3$ resulted in up to 70% extra aluminium dissolution due to electrode interaction with chloride ions. Modelling studies by Guseva et al. [31] revealed that the electrochemical dissolution of aluminium in sodium chloride solutions can result in the production of several species including $AlOH^{2+}$, $Al(OH)_2{}^{+}$, $Al(OH)_3$, $Al(OH)_4{}^{-}$, $Al_2(OH)_2{}^{4+}$, $Al_3(OH)_4{}^{5+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $AlCl_2{}^{+}$, $Al(OH)Cl^{+}$, and $Al(OH)_2Cl$. The distribution and abundance of the latter species depended upon factors such as pH, current density and solution concentration. Canizares et al. [32] also discovered that alkaline pH values could promote chemical dissolution of aluminium species during EC of sodium chloride solutions. Moreno et al. [33] elegantly demonstrated that pH was in fact variable depending upon the location in an EC cell. Importantly, the pH was noted to be oscillatory in character and the pH values were not constant with EC test time. Hence, the question arises as to what this latter effect has upon EC efficiency.

Further complicating the situation is the fact that passivation of electrodes during EC studies is well known [34,35], wherein the electrodes are covered with oxide species which results in inhibition of anode dissolution. One suggested solution to this latter problem was the addition of chloride ions to destroy the passive layer [34]. Alternatively, polarity reversal has been employed in an attempt to minimize passivation of electrodes during electrocoagulation processes. Timmes et al. [36] used a pilot plant electrocoagulation unit as part of a pre-treatment system prior to an ultrafiltration/reverse osmosis module for seawater desalination; and indicated that a polarity reversal period between 30 and 250 s was required to reduce scale formation and maintain stability of coagulant delivery. As an outcome, the EC unit was operated for a period in excess of 200 h. Cesar Lopes et al. [37] examined the change in EC electrodes in a 6 iron electrode system, after operation to treat dairy milk production effluent. The electrode consumption was reduced when polarity reversal was not employed due to formation of a passivated layer. Interestingly, inspection of the mass loss data for each anode revealed significant variation in the value recorded.

The history of the electrodes used in electrocoagulation has been illustrated to be important in terms of the subsequent electrochemical performance. Mechelhoff et al. [38] found that roughened electrodes de-passivated whereas smooth electrodes did not. The behaviour of electrodes also depended upon whether they were employed in simple batch EC units with only 2 electrodes (anode and cathode) or in EC systems which had multiple electrodes (> 2). Batch EC units have been widely reported due their simplicity and ease of construction [39]. However, continuous EC systems are probably more relevant to practical use as they can potentially treat larger volumes of water in a shorter time [25,36]. For example, Lu et al. [40] found that fluoride

removal from solution was improved by the use of a continuous EC process compared to a batch EC system. Nevertheless, studies of such continuous EC units are considerably less abundant compared to batch systems and more information about their operational characteristics is necessary.

The aforementioned evaluation of the EC literature has revealed several research needs which require addressing in order to develop an effective continuous electrocoagulation process comprising of multiple electrodes for treating solutions containing sodium chloride and sodium bicarbonate (such as coal seam water or water from shale oil and gas operations). The hypothesis was that EC performance and viability for produced water treatment is highly dependent upon the salinity of the sample and that operational conditions need to be tailored to minimize electrode and electrical consumption. Consequently, the aim of this study was to develop an improved understanding of the impact of sodium chloride and sodium bicarbonate in solution upon the performance of a continuous EC system. Specific research questions included: (1) what is the impact of sodium chloride and sodium bicarbonate concentration upon process electrochemistry and floc characteristics; (2) how do operating conditions such as pH, hydraulic retention time, current density and test time influence EC performance with salt solutions; (3) when does the EC system attain steady state conditions; (4) what is the benefit of polarity reversal and how does this factor impact EC parameters; (5) do the electrodes corrode evenly in a multi-electrode EC unit; and, (6) how does the initial solution pH influence the electrochemistry occurring. A bench top EC unit was designed to answer the aforementioned research questions and used to treat a range of solutions comprising of dissolved sodium chloride and sodium bicarbonate under a variety of operating conditions.

2. Material and methods

2.1. Chemicals

Solutions were prepared using deionized water to which appropriate amounts of salt were added. Analytical reagent grade sodium chloride (95.7%, Chem-Supply), sodium bicarbonate (99.7%, Chem-Supply), sodium hydroxide (40 wt/v%, Chem-Supply), and hydrochloric acid (32 wt/V%, Chem-Supply) were used.

2.2. Electrocoagulation cell

The cell used was designed in-house and consisted of 13 electrode plates in a bipolar arrangement with the current applied *via* the external electrodes (Fig. 1). The bipolar arrangement wherein only the outermost electrodes are connected to the power supply unit has been suggested to be preferable in terms of electrocoagulation cell effectiveness [41].

The EC cell allowed for vertical flow of the solution *via* an inlet (0.625 cm inner diameter) located at the lower region of the unit. The solution was then dispersed by means of a diffuser system to facilitate even distribution of the flow over the electrodes which were of 10 cm length, 15 cm height and 0.3 cm width, spaced 0.3 cm from one another. Aluminum plates were laser cut from 5005 grade aluminium sheets. These aluminium sheets typically contained between 0.5 and 1.1% iron content. When placed in a bipolar configuration the 13 electrodes provided $1800\,cm^2$ of active anodic surface area. The aluminium electrodes were initially scrubbed clean of any residual oils using acetone and soft scourers then rinsed with deionized water. The plates were placed in an oven at 125 °C for one hour to dry and allowed to cool. The cooled plates were weighed before and after any experimentation to assist in determining a total mass balance of the system.

The effluent stream of the EC cell was equipped with in-line pH probe (TPS Aqua) which was electrically isolated to prevent interference from the electrocoagulation process. The potential was applied to the cell using an AC-DC converter to which the current supplied was