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In-situ caustic generation from sewage: The impact of caustic strength and sewage composition

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ABSTRACT

Periodic caustic dosage is a commonly used method by the water industry to elevate pH levels and deactivate sewer biofilms responsible for hydrogen sulfide generation. Caustic (NaOH) can be generated in-situ from sewage using a divided electrochemical cell, which avoids the need for transport, handling and storage of concentrated caustic solutions. In this study, we investigated the impact of caustic strength in the cathode compartment and the impact of sodium concentration in sewage on the Coulombic efficiency (CE) for caustic generation. The CE was found to be independent of the caustic strength produced in the range of up to ~3 wt%. Results showed that a caustic solution of ~3 wt% could be produced directly from sewage at a CE of up to 75 ± 0.5%. The sodium concentration in sewage had a significant impact on the CE for caustic generation as well as on the energy requirements of the system, with a higher sodium concentration leading to a higher CE and lower energy consumption. The proton, calcium, magnesium and ammonium concentrations in sewage affected the CE for caustic generation, especially at low sodium concentrations. Economical assessment based on the experimental results indicated that sulfide control in sewers using electrochemically-generated caustic from sewage is an economically attractive strategy.

1. Introduction

Hydrogen sulfide is generated in sewer networks by sulphate reducing bacteria (SRB) under anaerobic conditions. It causes sewer corrosion, which has an enormous economic impact on sewer management (Brongers, 2001; Sydney et al., 1996; Zhang et al., 2008). Emission of hydrogen sulfide to the atmosphere, along with other volatile organic compounds also produced under anaerobic conditions, results in the release of obnoxious odours and poses a threat for sewer workers. Traditionally, methods to prevent sewer corrosion include chemical sulfide oxidation by addition of oxygen, hydrogen peroxide and chlorine (Tanaka and Takenaka, 1995; WERF, 2007; Zhang et al., 2008), prevention of anaerobic conditions using oxidants such as oxygen and nitrate (Gutierrez et al., 2008; Mohanakrishnan et al., 2008), precipitation of sulfide using iron salts (Nielsen et al., 2005; Padival et al., 1995; Zhang et al., 2009, 2010) and prevention of the emission of hydrogen sulfide to the gas phase by pH elevation (8.5–9.0) through the addition of NaOH or $Mg(OH)_2$ (Gutierrez et al., 2009). These methods incur large operational costs as they require continuous (24 h a day and 7 days a week) dosing of significant amounts of chemicals (Zhang et al., 2008).

A recent industry survey showed that in addition to these traditional methods, pH shock is also commonly used by the Australian Water Industry (Ganigue et al., 2011). This method

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involves the addition of NaOH to increase pH to levels above 10.5 for a short period (e.g. several hours) to deactivate microorganisms present in sewer biofilm including SRB. In this way, hydrogen sulfide generation can be significantly reduced for several days or even up to several weeks (WERF, 2007). This is a cost-effective method as only intermittent dosing is required (Ganigue et al., 2011). Despite this strong advantage, transport, handling and storage of concentrated caustic (normally purchased as 50% w/w) poses a serious occupational health and safety (OH&S) concern.

In a previous study we investigated the feasibility of in-situ caustic generation directly from sewage using a divided electrochemical cell (Pikaar et al., 2011c). The anode was continuously fed with sewage with a short hydraulic retention time (HRT) (i.e. $<$ 1 min), while the cathode was initially filled with clean water, which was constantly recirculated (i.e. long HRT). By applying a current, cations migrate from the anode to the cathode compartment to maintain electroneutrality of the solution. As the concentration of cations, such as Na^+ in wastewater, is much higher than the proton concentration ($[H^+]$ at pH 7 is 10^{-7} M), the migration of protons is several orders of magnitude lower than Na^+. Consequently, a concentrated caustic solution is produced in the cathode compartment (Pikaar et al., 2011c; Rabaey et al., 2010). Due to the very short hydraulic retention time of sewage in the anode, the pH decrease in the anode (i.e. sewage) is negligible. The produced caustic can be discharged to sewers periodically (e.g. once every few days), thus achieving caustic shock of sewer biofilms without the transportation of large volumes of caustic to the dosing site. Further advantages, in comparison to external caustic addition, include the chemical-free nature of the technology as Na^+ in the caustic solution comes from sewage, and that oxygen is continuously being generated in the anode resulting in continuous oxygenation of sewage (Pikaar et al., 2011a, 2011b). This method is expected to be economically favourable compared to existing methods for sulfide abatement in sewers.

During 4-hour long experiments, caustic at a strength of 0.61 $\pm$ 0.10 wt% NaOH was produced from sewage at a Coulombic efficiency of 53 $\pm$ 8% (Pikaar et al., 2011c). The results indicated that proton cross-over and/or hydroxide back-transport had a significant impact on the process efficiency, although their relative importance could not be discerned. For practical applications, caustic concentrations higher than that achieved in the previous study (Pikaar et al., 2011c) are needed to minimise the footprint of the caustic storage tank, as the electrochemical system would be installed at pumping stations which often have limited space available. However, at a higher caustic strength, the cathode-to-anode diffusion of hydroxide ions may become important due to the higher concentration gradient between the cathode and anode compartments, lowering the CE and consequently the cost-effectiveness of the method.

Caustic production depends on the amount of sodium (and potassium) transported to the cathode from the anode. The transport of other cations does not contribute to caustic production and most of them would lead to hydroxide consumption. For example, the transport of ammonium would result in the formation of ammonia under high pH thus consuming hydroxide, while the transport of bivalent cations would lead to precipitation reactions with hydroxide forming e.g. $Ca(OH)_2$ or $Mg(OH)_2$. The transport of calcium and magnesium also causes membrane scaling, which would result in increased energy requirements of the system (Pikaar et al., 2011c). Hence, the membrane transport of the relevant cation species (i.e. Na^+, Ca^{2+}, Mg^{2+}, K^+, protons and NH_4^+) may have a significant impact on the process efficiency. The relative amount of each cation transported through the membrane is expected to depend on the sewage composition. The sodium concentration in sewage can vary significantly, depending on local conditions. For example, the infiltration of seawater in coastal areas, the addition of trade waste discharges, and even water consumption restrictions would all affect sodium concentration. In Queensland (Australia), the sodium concentration in 19 sewage treatment plants surveyed ranged between 100 and 700 mg/L, with a mean value of $\sim$230 mg/L (Taylor and Gardner, 2007).

This study aims to experimentally investigate the impact of the sodium concentration in sewage on caustic production and energy requirements of the system. Another aim is to determine the impact of the caustic concentration in the cathode, which could affect the back diffusion of hydroxide ions to the anode, on the CE for caustic production. The study further aims to determine the economic potential of electrochemical caustic generation from sewage for sulfide control in sewer networks.

2. Materials and methods

2.1. *Electrochemical cell and operation*

Experiments were performed using a two-chambered electrochemical cell (anode and cathode each having a liquid volume of 90 mL) as previously described (Pikaar et al., 2011c). Ru/Ir (RuO_2/IrO_2: 0.70/0.30) coated titanium electrodes (diameter: 240 mm; thickness: 1 mm; specific surface area: 1.0 cm^2/cm^2, Magneto Special Anodes BV, The Netherlands) with a projected surface area of 24 cm^2 were used in both the anode and cathode compartments. The rationale for using mixed metal coated titanium electrodes instead of low cost carbon electrodes has been described elsewhere (Pikaar et al., 2011a, 2011b). The electrodes were placed directly at the membrane surface in order to minimise ohmic losses. The anode and cathode compartments were separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA). The membrane surface area exposed to the liquid was equal to the dimensions of the electrode used (i.e. 24 cm^2). A new cation exchange membrane was used for each experimental run.

Fresh sewage was collected every 4 days from a local pumping station in Brisbane and immediately stored at 4 °C in a cold room. The characteristics of the sewage used is presented in Table 1. The anode compartment was fed with sewage at a flow rate of 9 L/hr using a peristaltic pump (Watson Marlow, UK), resulting in a hydraulic retention time of 0.6 min. Prior to being pumped into the anode, the sewage was heated to the ambient temperature (24.0 $\pm$ 0.5 °C) using a water bath. A recirculation flow of 60 L/h was applied in the anode chamber to create mixing using a peristaltic pump (Watson Marlow, UK).