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A novel electrochemical process for the recovery and recycling of ferric chloride from precipitation sludge

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ABSTRACT

During wastewater treatment and drinking water production, significant amounts of ferric sludge (comprising ferric oxy-hydroxides and $FePO_4$) are generated that require disposal. This practice has a major impact on the overall treatment cost as a result of both chemical addition and the disposal of the generated chemical sludge. Iron sulfide (FeS) precipitation via sulfide addition to ferric phosphate ($FePO_4$) sludge has been proven as an effective process for phosphate recovery. In turn, iron and sulfide could potentially be recovered from the FeS sludge, and recycled back to the process. In this work, a novel process was investigated at lab scale for the recovery of soluble iron and sulfide from FeS sludge. Soluble iron is regenerated electrochemically at a graphite anode, while sulfide is recovered at the cathode of the same electrochemical cell. Up to 60 ± 18% soluble Fe and 46 ± 11% sulfide were recovered on graphite granules for up-stream reuse. Peak current densities of 9.5 ± 4.2 A m^{-2} and minimum power requirements of 2.4 ± 0.5 kWh kg Fe^{-1} were reached with real full strength FeS suspensions. Multiple consecutive runs of the electrochemical process were performed, leading to the successful demonstration of an integrated process, comprising FeS formation/separation and ferric/sulfide electrochemical regeneration.

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1. Introduction

During conventional wastewater treatment, ferric salts (either as $Fe_2(SO_4)_3$ or $FeCl_3$) are typically dosed into primary influent (pre-precipitation), into the aerobic tank (co-precipitation) or into secondary effluent (post-precipitation), to achieve phosphorus precipitation and coagulation of organic solids. The precipitate thus obtained consists mostly of $FePO_4$, ferric (oxy) hydroxides and organic solids. This process entails significant costs associated mostly with the addition of the ferric salts and disposal of the chemical sludge thus generated. This ferric sludge can be used as a source of phosphorus and ferric iron. The latter, if recovered, can be re-utilized in the process, potentially creating significant savings for the water industry. The effectiveness of sulfide addition to ferric sludge (as phosphate or oxy-hydroxide) to achieve FeS precipitation and phosphorus recovery has been already proven (Ripl et al., 1988; Kato et al., 2006; Mejia Likosova et al., 2013b). In such a method, the addition of sulfide to the ferric sludge reduces ferric iron (Fe(III)) to ferrous iron (Fe(II)) leading to the precipitation of FeS particles, thus separating iron from any

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Table 1 – Anode and Cathode reactions and their redox potential.

Oxidation reaction (anode)		Redox potential [V]
$FeS \rightarrow Fe^{2+} + S^0 + 2e^-$	(1)	$+0.06$[a]
$FeS_{(s)} + 4H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 8H^+ + 8e^-$	(2)	-0.09[b]
$Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + e^-$ (at pH > 3)	(3)	0.51[c] (at pH 3.0)
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (at pH < 3)	(4)	$+0.771$[d]
Reduction reaction (cathode)		Redox potential [V]
$S^0 + 2e^- \rightarrow S^{2-}$	(5)	-0.476[a]

[a] Standard redox potential calculated based on a FeS solubility constant of $K_{sp} = 8 \times 10^{-19}$ (Perry and Green, 2008) and a standard redox potential of −0.476 V for the reaction $S^0 + 2e^- \rightarrow S^{2-}$ (Dutta et al., 2008).

[b] Standard redox potential calculated based on a standard redox potential of $E^0 = -0.22$ V for the reaction $S^{2-} + 4H_2O \rightarrow SO_4^{2-} + SO_4^{2-} + 8H^+ + 8e^-$ (Drake et al., 2006).

[c] Redox potential at pH 3 calculated with the Nernst equation after calculating a standard redox potential (pH 0) of $E^\circ = -0.612$ V based on a $Fe(OH)_3$ solubility constant of $K_s = 4 \times 10^{-38}$ at 25 °C and a water self-ionization constant of $K_w = 1 \times 10^{-14}$ at 25 °C (Perry and Green, 2008).

[d] (Bard and Faulkner, 2001).

phosphate and opening to a potential route for iron recovery. After the recovery of phosphorus, iron and sulfur can potentially be separated and recycled within the process, i.e. iron can be recycled as Fe(II/III) to the phosphate precipitation and coagulation process while sulfide can be reused to generate more FeS from ferric sludge.

Sulfide is an electrochemically active compound and the anodic oxidation of aqueous sulfide has been studied and demonstrated by different authors (Lalvani and Shami, 1986; Kelsall et al., 1999; Ateya et al., 2003, 2005; Dutta et al., 2008, Dutta et al. 2010; Pikaar et al., 2011). The range of oxidation products is affected by anode materials and imposed potentials (Kelsall et al., 1999), and include elemental sulfur (S^0), polysulfide (S_n^{2-}), sulfate (SO_4^{2-}), sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$).

Efficient removal of sulfide from dilute aqueous solutions at circum-neutral pH via oxidation to S^0 has been demonstrated on graphite anodes (Dutta et al., 2008), whereby elemental sulfur was deposited onto the anode surface. Sulfur was effectively removed because it adsorbed onto the anode surface. Dutta and co-workers demonstrated a method for in-situ recovery of the electrodeposited S^0 on the electrode. This method consists of switching the polarity of the electrodes, i.e. periodic switching between anodic sulfide oxidation to S^0 and cathodic sulfur reduction to sulfide. During cathodic operation, the previously deposited S^0 is reduced to sulfide. As a result, a concentrated sulfide solution can be recovered from the same electrochemical cell used for the sulfide oxidation to sulfur. However, a big fraction of the elemental sulfur was reduced to polysulfides when batch experiments were performed without pH control, during which the pH varied between 7.3 and 11.4 (Dutta et al., 2008).

In a previous study, we found that freshly generated FeS_x particles are reactive towards anodic oxidation to elemental sulfur on graphite electrodes (Mejia Likosova et al., 2013a).

In this work, we demonstrate the feasibility of an electrochemical process for the resource-efficient recovery of soluble iron and sulfide from FeS sludge. The process is based on the electrochemical oxidation of sulfide (in the form of particulate FeS) to S^0 (Reaction 1), and partially sulfate (Reaction 2) (Mejia Likosova et al., 2013a), with consequent release of soluble ferrous ions in solution. Soluble Fe^{2+} is then oxidised to ferric hydroxide, and subsequently to free ferric ions (Reaction 4) as the pH drops to <3 due to the acidity generated by the ferric hydroxide (Reaction 3) and sulfate (Reaction 2) formation. As the formed S^0 is bound to the anode surface, it can be subsequently reduced back to sulfide upon polarity switching of the electrode, the only net input being electricity. In the system described above, the reactions occurring at the anode and their redox potentials vs. SHE are listed in Table 1.

In this study, the recovery of soluble iron and sulfide according to the proposed process has been demonstrated. Additionally, the feasibility of the full phosphorus and ferric recovery process with real sludge was established. For this work, carbon-based electrode materials were chosen, based on their proven reactivity with FeS, low cost and wide availability.

2. Materials and methods

2.1. *Preparation of synthetic FeS precipitate and dilute synthetic, dilute real and full-strength real FeS suspensions for electrochemical anodic oxidation experiments*

Synthetic FeS precipitate was prepared by reaction of synthetic 0.1 M ferric phosphate ($FePO_4$*$4H_2O$, 24% Fe) with continuing dosing of a 0.8 M sodium sulfide solution (Na_2S*$9H_2O$, reagent grade), up to 1.75 S:Fe molar ratio at pH 4 (these conditions were found to be optimal for FeS formation and separation) within 30 min as described elsewhere (Mejia Likosova et al., 2013b). The pH was controlled using a 3 M HCl solution. The reaction of ferric phosphate and sulfide, at an S:Fe molar ratio of 1.75 and slightly acidic conditions, can be represented by the following stoichiometry (Kato et al., 2006; Firer et al., 2008):

$$FePO_{4(s)} + 1.75H_2S \rightarrow FeS_{(s)} + 0.5S^0_{(s)} + 0.25H_2S + H_2PO_4^- + H^+ \tag{6}$$

The resulting synthetic precipitate is a combination of nanoparticulate mackinawite (FeS) and elemental sulfur (S^0) (Mejia Likosova et al., 2013a). The suspension was divided into two 50-mL Falcon tubes without leaving any air headspace and centrifuged at 2100 *g* for 5 min to enhance separation of the gravity-settled FeS particles. The supernatant with residual soluble sulfide and phosphate in solution was removed. A dilute synthetic FeS suspension (103 ± 46 mg Fe L^{-1}) was

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