Electrochemical sulfide removal and caustic recovery from real spent caustic streams

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INTRODUCTION

- Spent caustic streams (SCS) are generated in petrochemical refineries at thousands of cubic meters per industry annually.
- SCS contain high concentrations of reactive sulfide (0.1 – 4 wt.%) and caustic soda (5 – 12 wt.%) [1, 2].
- Common treatment methods are expensive, with no resource recovery.
- **Electrochemical treatment: HS^- removal with recovery of elemental sulfur (S^0), NaOH and hydrogen gas (H_2) [3 – 5].**

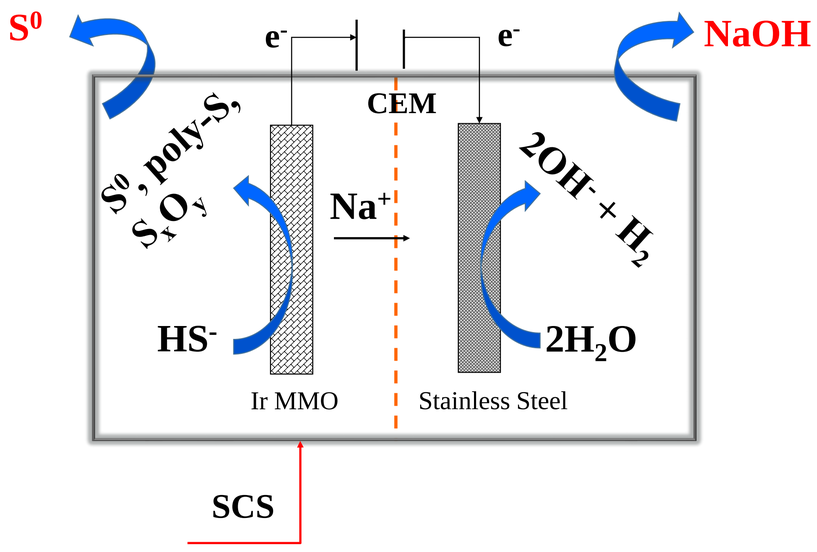
METHODS

Industrial sulfidic SCS characteristics

Parameter	Average ± SD
pH	>13
Sulfide	1.5 ± 0.4 M
Organic solvents	0.5 ± 0.1 M

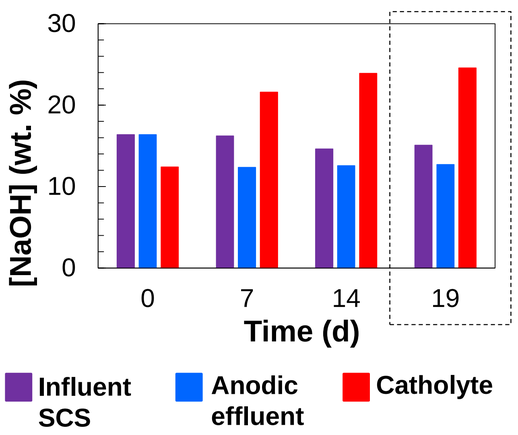
Operational parameters

Experimental	
Current density	300 A m^{-2}
Anolyte	200 gS L^{-1} d^{-1}
Catholyte	12 wt.%



Schematic layout of the electrochemical cell.

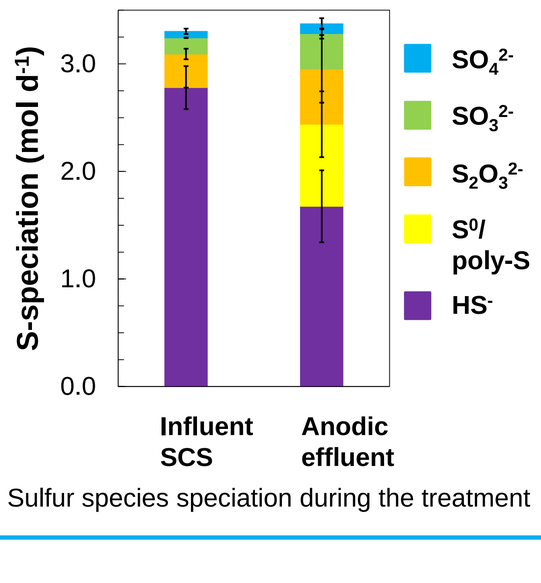
RESULTS



NaOH concentration (wt. %) in the different streams

Performance parameters

Parameter	Average ± SD
Cell voltage	1.75 ± 0.12 V
Anode potential	1.09 ± 0.02 V vs SHE
$E_{sulfide\ removal}$	38.0 ± 7.7 %

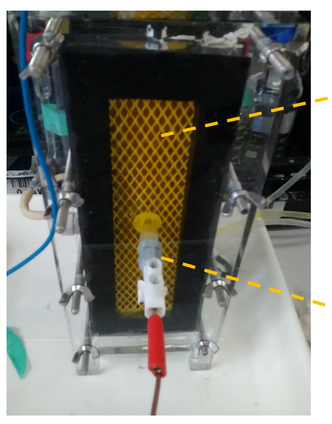


Sulfur species speciation during the treatment

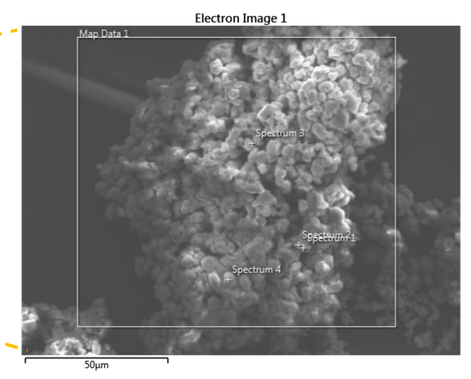
- **Oxidation product: ~ 69% S^0/poly-S**
- **80 ± 31% coulombic efficiency**
- **12.3 wt.% NaOH increase** in the cathodic compartment

DISCUSSION

- **High coulombic efficiency** and **low anode potential** indicated production of S^0.
- The S^0 particles collected from the anodic chamber were hydrophobic (θ > 70°), orthorhombic sulfur (α-S_8).



S^0 recovery on the anode surface of the electrochemical cell.



SEM-EDX image of S^0 recovered. Magnification 400 X using 20 keV.

Energy consumption at 300 A m^{-2}

Energy consumption	Average ± SD
For wastewater treatment	75.3 ± 5.0 kWh m^{-3} SCS treated
For pollutant removal	3.7 ± 0.6 kWh kg^{-1} S removed
For NaOH recovery	6.3 ± 0.4 kWh kg^{-1} NaOH recovered

CONCLUSIONS

Electrolysis as an energy efficient and potentially sustainable SCS treatment approach:

- **> 10 wt.% onsite NaOH recovery**
- **Sulfide removed with limited energy input**
- **> 20% alkalinity decrease and ~15% conductivity decrease in the treated SCS**
- **Limited NaOH production at 14-19 d, to be tackled with catholyte dilution**

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References:. [1] R. Alnaizy, Environ. Prog. 27 (2008) 295–301, [2] I. Ben Hariz et al., Sep. Purif. Technol. 107 (2013) 150–157, [3] P.K. Dutta et al., Water Res. 42 (2008) 4965–4975, [4] K. Rabaey et al. Environ. Sci. Technol. 40 (2006) 5218–5224, [5] E. Vaiopoulou et al. Water Res. 92 (2016) 38–43.

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