

Electrochemical removal of sulfate from petroleum produced water

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ABSTRACT

Petroleum produced water (PPW) is a waste-stream that entails huge cost on the petroleum industry. Along with other suspended and dissolved solids, it contains sulfate, which is a major hurdle for its alternative use intended toward enhanced oil recovery. This study proposes a two-step process for sulfate removal from PPW. A synthetic PPW was designed for the study using response surface methodology. During the first step, sulfate present in PPW was reduced to sulfide by anaerobic fermentation with 80% efficiency. In the second step, more than 70% of the accumulated sulfide was electrochemically oxidized. This integrated approach successfully removed sulfate from the synthetic wastewater indicating its applicability in the treatment of PPW and its subsequent applications in other oil field operations.

Key words | petroleum produced water, response surface methodology, sulfate removal, sulfate-reducing bacteria

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INTRODUCTION

In the current industrial era, petroleum is a major source of energy and its dominance in the energy sector is expected to continue (International Energy Outlook 2014). Despite, the interminable demand for petroleum demand, adverse effects on the environment during production, distribution and consumption cannot be overlooked. Crude petroleum is produced with large volumes of wastewater accounting for more than 80% of liquid waste, which can go up to as high as 95% in ageing oilfields (Igunnu & Chen 2012). This water known as petroleum produced water (PPW), is the largest volume waste stream in the exploration and production processes, with worldwide production of about 250 million barrels per day in 2007 (SPE 2011). With the increasing number of mature oil reservoirs, the treatment and management of PPW requires urgent attention.

PPW usually contains high concentrations of sulfate, dissolved sodium chloride, dissolved hardness (calcium and magnesium carbonates), suspended solids, and emulsified oils (Fakhru'l-Razi *et al.* 2009). Thus, disposal/treatment

of such large volumes of contaminated wastewater is a major issue considering the stringent environmental regulations. Borole & Tsouris (2013) patented a method for treating fuel-processing effluent containing carbonaceous compounds and inorganic salts using microbial fuel cells and electrosorption units. They have used an elaborate set of apparatuses for the wastewater treatment. A pilot-scale catalytic electrochemical system was used by Ma & Wang (2006) for produced water treatment using M/C/Fe electrodes. However, the use of noble metal as catalyst in this study makes its commercial use challenging.

As an alternative use, PPW can be pumped under pressure into the reservoir to increase the yield of the crude oil from the production wells and to maintain reservoir pressure (water flooding). But the anaerobic condition in the oil field along with the sulfate salts present in this water is conducive for the growth of sulfate-reducing bacteria (SRB), which can lead to numerous problems like souring of the oil and gas reservoir, production reduction,

corrosion of equipment and reservoir plugging. However, SRB can use sulfate as the terminal electron acceptor in their energy metabolism, i.e. they are capable of dissimilatory sulfate reduction (Thauer *et al.* 2007). This inherent property of SRB can be utilized to reduce the sulfate levels in the waste stream and convert them to sulfides. Subsequently, the sulfides generated by SRB can be electrochemically oxidized to other valuable forms like sulfur. There are previous studies reported by Pikaar *et al.* (2011a, b) dealing with electrochemical oxidation of sulfide in domestic wastewater. Similarly, sewer wastewater was also electrochemically treated (Pikaar *et al.* 2012) using mixed metal coated titanium electrode. Wang *et al.* (2012) reported oil wastewater oxidation for sulfides using Ti/IrO₂ electrodes at various current densities. Dutta *et al.* (2010) treated paper mill effluent for sulfides; however, it also contained organics which were shown to interfere with sulfide removal. Polluted geothermal brines were also electrochemically oxidized for sulfide removal by Ateya *et al.* (2003).

Thus, in this study sulfate reduction to sulfide was carried out by a selected consortium of SRB in a synthetically designed PPW. The synthetic PPW was initially formulated using response surface methodology (RSM). In the second step, the sulfides were electrochemically oxidized to easily recoverable forms like sulfur.

METHODS

Optimization of synthetic feed for sulfate reduction using RSM

Natural PPW contains varying concentrations of various constituents, which depends upon the location, geography, age, etc. of the reservoir (Fakhru'l-Razi *et al.* 2009). Therefore, to maintain uniformity in the experiments, a synthetic feed was designed containing MgSO₄·7H₂O, NaCl, (NH₄)₂FeSO₄, and sodium lactate, maintaining their concentrations similar to that in natural PPW (Fakhru'l-Razi *et al.* 2009).

To optimize concentrations of MgSO₄·7H₂O, NaCl and pH of the feed, RSM was used (Table 1). Since the main focus of this study is on sulfate removal, sulfate reduction was used as the parameter for optimizing the feed. To see the efficacy of the system with the varying concentrations of sulfate, MgSO₄ was used as a component of the RSM study. Also, PPW usually has varying salinity, which makes it important to understand the performance of the

Table 1 | Different experimental runs according to the Box-Behnken model

Run Order	MgSO ₄	NaCl	pH
1	1.6	25	5
2	0.9	25	5.5
3	0.9	25	5.5
4	1.6	10	5.5
5	0.2	10	5.5
6	0.9	10	6
7	1.6	40	5.5
8	0.9	25	5.5
9	0.2	25	6
10	0.9	40	6
11	0.2	40	5.5
12	0.9	40	5
13	0.2	25	5
14	0.9	10	5
15	1.6	25	6

proposed system with different NaCl concentrations. The concentrations of (NH₄)₂FeSO₄ and sodium lactate were kept constant at 0.2 g/L and 4.8 ml/L, respectively. Iron is an essential element for cytochrome and hydrogenase activity by SRB and in this media it is supplemented in the form of (NH₄)₂FeSO₄ (Mohr's salt). This salt of ferrous is preferred because it does not get readily oxidized to ferric and thus is available to microbial use. Sodium lactate was used as the limiting carbon source for the growth of SRB (Sharma 2014).

The three variables were designated as A (MgSO₄·7H₂O), B (NaCl), and C (pH). A total of 15 runs were formulated by the RSM software to test the various combinations of these variables (Table 1). The feed thus optimized was used for sulfate reduction by an SRB consortium, TERI-MS-003, anaerobically, which was later used as anolyte for the reactor described in section 'Reactor set-up for sulfide oxidation'. This consortium has been previously studied extensively for its sulfate-reducing properties and was isolated from oil refineries across India (Sharma *et al.* 2014). Although TERI-MS-003 was used by Sharma *et al.* (2013b) for acetate and butyrate reduction, SRB are also known to reduce sulfate to sulfide.

Thus, conversion of sulfate to sulfide by TERI-MS-003 constituted the first step of the removal process. For this conversion, TERI-MS-003 was inoculated in anaerobically prepared synthetic PPW and incubated at room temperature for 72 h prior to analysis.

Reactor set-up for sulfide oxidation

Conventional dual-chambered reactors as described by Sharma *et al.* (2013a) were used for experiments. The anolyte was purged with nitrogen gas (Sigma Gases, India) before sealing the anode chamber with butyl rubbers. Since electrolysis of water is expected to take place at the cathode, open air conditions were maintained in the cathode chamber. These conditions would help in venting out the hydrogen produced during electrolysis of water (Pikaar *et al.* 2015). Both the cathode and anode compartment consisted of activated carbon fabric ($5 \times 3 \text{ cm}^2$; HEG Pvt. Ltd, India) wrapped around a carbon rod ($10 \times 0.25 \text{ cm}^2$).

Electrochemical analysis

Four reactor set-ups were used with different anolytes in this study (Table 2). In the first reactor (RI), the optimized synthetic feed, after treatment with TERI-MS-003 was used as anolyte. Reactor II (RII) had the same feed, but $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was replaced with an equivalent amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and prior treatment with the bacterial consortium was not carried out.

The feed composition that gave the least sulfate reduction in the RSM studies was used as the third reactor's (RIII) anolyte, after treating it with TERI-MS-003. The fourth reactor (RIV) also had $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ replaced with an equivalent amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in RIII's anolyte composition.

All electrochemical measurements were performed using a potentiostat (IviumStat, The Netherlands). Activated carbon fabric was used for both the working electrode (anode) and the counter electrode (cathode). For reference electrode, Ag/AgCl (3.5 M KCl) was used. Phosphate buffer

(0.1 M, pH 7) was used as the catholyte in all reactors. The working electrodes of the reactors were potentiostatically poised at anodic potentials of +0.1 V, +0.2 V and +0.3 V (vs. standard hydrogen electrode (SHE)) (Rabaey *et al.*, 2006; Dutta *et al.* 2010; Pikaar *et al.* 2015) and chronoamperometric data were continuously recorded. Each voltage was tested for 24 h. Cyclic voltammograms (CV) over a range of -0.3 V to $+0.4 \text{ V}$ (vs. SHE) were recorded after 12 and 24 h of operation at a scan rate of 5 mV/s.

The ability of a cell to hold electrical charge can be depicted in the form of capacitance, which is also a measure of the amount of electrical energy stored at an applied electric potential. Capacitance is governed by the equation:

$$C = q/V \quad (1)$$

where q is the charge stored on the capacitor (in coulombs, C), E is the potential across the capacitor (in volts, V), and C is the capacitance (in farads, F) (Sharma *et al.* 2014).

Chemical analysis

For chemical analyses, 5 mL of samples was collected from the sampling port of the reactors using a sterile and N_2 -purged syringe. pH was measured using a calibrated pH meter (Mettler Toledo, India). Samples for sulfide analysis were taken with minimum aeration and were preserved with zinc acetate and sodium hydroxide solution before examination. For sulfide analysis, samples were treated with *N,N*-dimethyl-*p*-phenylenediamine sulfate and ferric chloride solution to produce methylene blue, whose intensity was spectrophotometrically determined at 664 nm (Clesceri *et al.* 1999). For sulfate measurement, the

Table 2 | Reactor set-ups

	Reactor I	Reactor II	Reactor III	Reactor IV
Anolyte (g/L)				
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.60 (0.65 SO_4^{2-})	0.00	0.30 (0.12 SO_4^{2-})	0.00
NaCl	24.00	24.00	10.00	10.00
$(\text{NH}_4)_2\text{FeSO}_4$	0.20	0.20	0.20	0.20
Na_2S	0.00	4.87 (0.65 S^{2-})	0.00	0.91 (0.12 S^{2-})
pH	6	–	5.3	–
Catholyte				
Phosphate buffer	0.1 M	0.1 M	0.1 M	0.1 M
Biological pretreatment				
With TERI-MS-003	Yes	No	Yes	No

turbidimetric method using barium chloride was followed (Clesteri *et al.* 1999).

RESULTS AND DISCUSSION

In this study, a combination of biological and electrochemical approaches was used for the removal of sulfate from PPW. In the first stage, an electroactive SRB consortium, TERI MS-003, was used to treat sulfate to sulfide, which was then electrochemically oxidized. The inoculum source has been previously characterized by fluorescence in situ hybridization and consists predominantly of SRB (Sharma *et al.* 2013a). For the initial step of bacterial conversion of sulfate to sulfide, a synthetic feed was designed based upon the composition of natural PPW. This synthetic feed was optimized for sulfate reduction using RSM.

Optimization of synthetic feed composition for sulfate reduction using RSM

RSM is an empirical statistical modeling technique that performs multiple regression analysis of quantitative data to solve multivariable equations simultaneously (He *et al.* 2009). The nature of the response surface was described by a three-level (-1, 0, +1) three-factor Box-Behnken design as also discussed by Ferreira *et al.* (2007). The center point of the corresponding composition was selected to be $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.9 g/L, NaCl 25 g/L, and pH 5.5. Fifteen runs were carried out in this experiment. The samples were analyzed for their sulfate content (data not shown). Data obtained from the experiments (Table 1) were analyzed by linear multiple regression using Minitab 14. The corresponding second-order response model formulated after

Table 3 | Estimated regression coefficients for percent sulfate reduction

Term	t-value	p-value
Constant	3.509	0.017
A	2.195	0.080
B	0.181	0.863
C	1.371	0.229
A^2	1.589	0.173
B^2	-3.740	0.013
C^2	1.192	0.287
AB	-0.013	0.990
AC	3.456	0.018
BC	-0.612	0.567

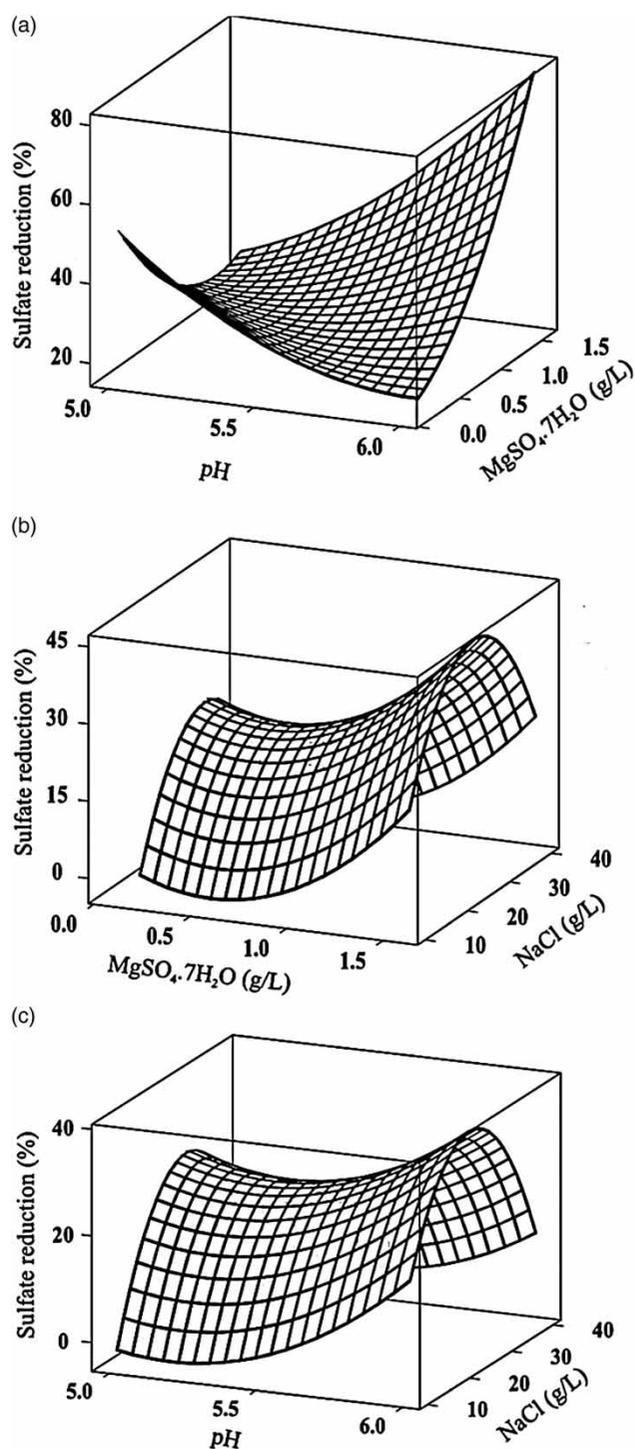


Figure 1 | Surface plots for the percent sulfate reduction with (a) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and pH; (b) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and NaCl; (c) pH and NaCl.

analysis for the regression was:

$$Y = 1046.97 - 356.19A + 8.11B - 364.59C + 20.68A^2 - 0.11B^2 + 30.41C^2 - 0.01AB + 60.50AC - 0.50BC$$

where Y is the percent sulfate reduction, and A , B and C are coded values of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (used as source of sulfate), NaCl and pH .

The adequacy of the model was indicated by the determination coefficient ($R^2 = 0.885$), which explained 88.5% of the response variability. The model coefficients calculated by regression analysis for each variable were evaluated Student's t -test and p -values (Table 3). The larger the t -test value and smaller the p -value, the higher the significance of the corresponding coefficient (He *et al.* 2009). Of the modeled terms, constants B^2 and AC were significant at the 95% probability level.

The surface plots are a graphical representation of the regression equation. Figure 1 presents the plots for the optimization of medium composition for sulfate reduction. Each figure presents the effect of two variables on the reduction of sulfate, while the other variable was held at mid-level. The combination of parameters giving the optimum results was: 1.6 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.649 g/L SO_4^{2-}), 24 g/L NaCl , 0.2 g/L $(\text{NH}_4)_2\text{FeSO}_4$ and pH 6. It has been previously observed by Cao *et al.* (2009) that a higher MgSO_4 concentration promotes SRB growth. Mg^{2+} ions help in both sulfate utilization and salinity tolerance (Cao

et al. 2009), which might be the reason for better sulfate reduction at higher MgSO_4 concentration.

The levels of variables giving maximum and minimum sulfate reduction were taken for sulfide oxidation experiments as described in section 'Electrochemical analysis'. Hence, for the first step toward synthetic PPW treatment, sulfate was reduced to sulfide by up to 79.27% in the optimized set. Prior to optimization, the percent sulfate reduction was approximately 27%. Since sulfide is an electro-active compound, the synthetic PPW after the first step was fed into electrochemical cells for sulfide oxidation.

Sulfide monitoring

Sulfide content of all the reactors was monitored at 0, 2, 6, 12 and 24 h to understand the pattern of sulfide oxidation with time. The initial sulfide concentration varied according to the reactor set, with RIII having the least amount (RI: 0.52 g/L, RII: 0.66 g/L, RIII: 0.02 g/L, RIV: 0.13 g/L). However, percentage sulfide oxidation was found to be almost equal with (RI and RIII) or without (RII and RIV) biological pretreatment (Figure 2).

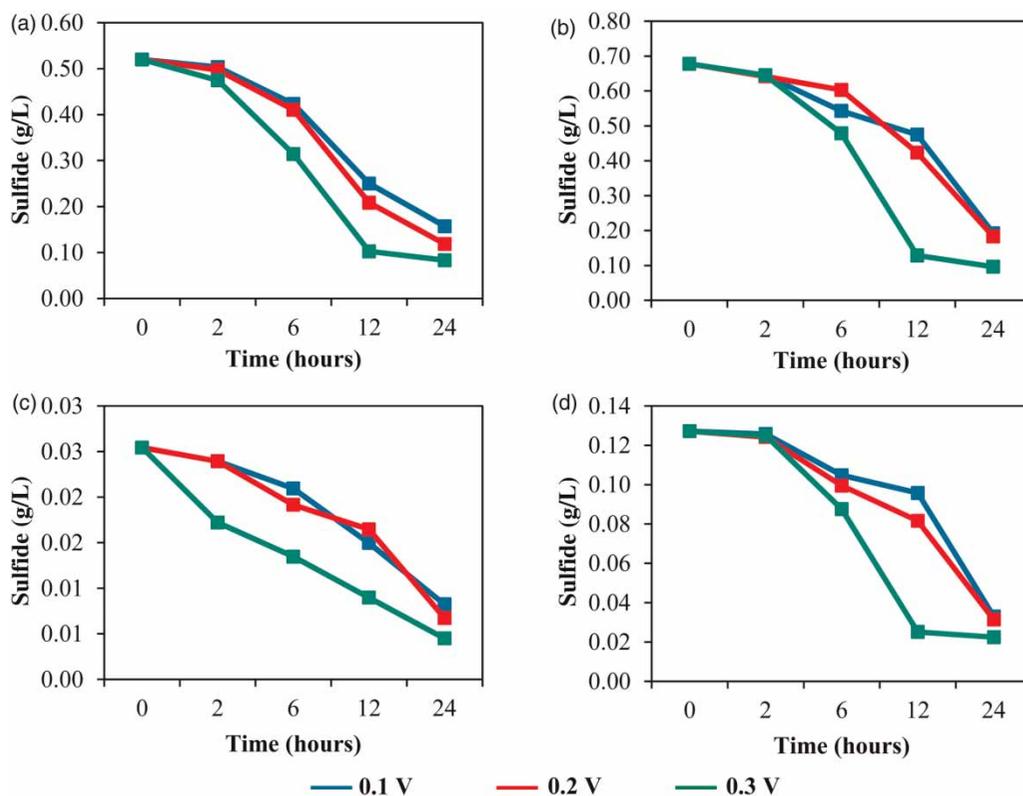


Figure 2 | Sulfide concentration with time for reactors RI (a), RII (b), RIII (c) and RIV (d).

There was more than 70% decrease in sulfide concentration with maximum taking place at +0.3 V (vs. SHE) for all the four reactors. At +0.3 V, the removal efficiency in percentage after 24 h of reactor operation was 83.96, 85.80, 81.15 and 82.35, respectively, for RI, RII, RIII and

RIV. Higher voltages were not tested since they can lead to conversion of sulfide to more oxidized forms like sulfate in wastewater, which always creates a risk for re-reduction to sulfide by micro-organisms. Also, sulfur is preferred as an end product since it requires less energy input (i.e.

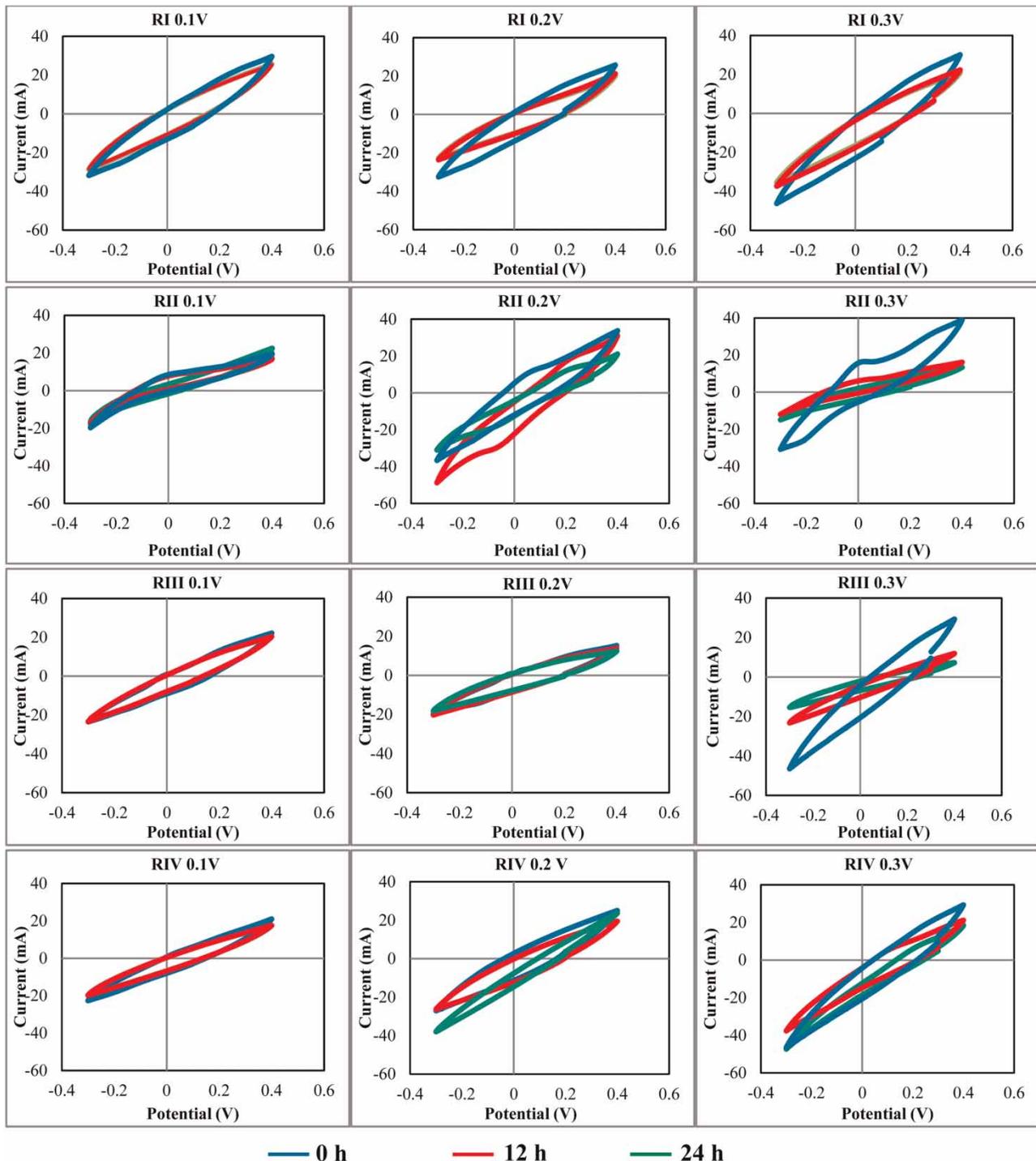


Figure 3 | CV recorded at 5 mV/s for all the four sets (RI, RII, RIII, RIV) over time.

two-electron oxidation compared to an eight-electron oxidation for oxidation to sulfate) (Pikaar *et al.* 2015).

Electrochemical evaluation

An overview of the electrochemical behavior of a system can be obtained through a series of steps at different potentials with recording of the current–time curves. CV is an electrochemical technique that involves varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current (Kounaves 1997). In the present study, the changes in current with respect to sulfide oxidation were analyzed using this technique. For the four set-ups, CVs were monitored in the potential range of -0.2 to $+0.4$ V (vs. SHE) at a scan rate of 5 mV/s. The voltammetric profiles showed higher charge when the systems were poised at $+0.3$ V (Figures 3 and 4), which suggests that the availability of electrons on the electrode was higher at this potential. The availability of more electrons facilitated faster sulfide oxidation, as also seen in Figure 2. Moreover, with time there was a reduction in anodic peak currents along with a decrease in sulfide content (Figure 2) of the system, as also observed by Baldo *et al.* (2002). In all the

reactors, $+0.3$ V showed lowest peak current after 24 h of operation, followed by $+0.2$ V and $+0.1$ V, respectively (Figure 4). Also, as compared to RIII and RIV, RI and RII showed better performance in terms of peak currents, which could be due to the higher initial sulfide content in RI (0.52 g/L) and RII (0.66 g/L) at $+0.3$ V. Pikaar *et al.* (2011a) also observed that the rate of sulfide oxidation decreases at lower sulfide concentrations. Moreover, since no biological component was involved, secondary biological conversions and associated reactions could not take place in RII, leading to a drastic change in anodic peak current with time (Figure 4).

The redox activity in voltammograms is represented in the form of oxidation/reduction peaks. Presence of peaks at around $+0.17$ V in the CV (Figure 3) also suggests the presence of sulfide sulfur redox reactions in the system (Kabil & Banerjee 2010). In some of the CV curves, the peaks may not be clearly visible; however, their absence does not necessarily mean that no redox activity is taking place in the system. As described by Bard & Faulkner (2001), the redox peaks might not appear at high scan rates. Moreover, the capacitance of the electrode or the non-faradic currents in the system can also overpower and reduce the visibility of peaks in the voltammograms (Harnisch & Freguia 2012).

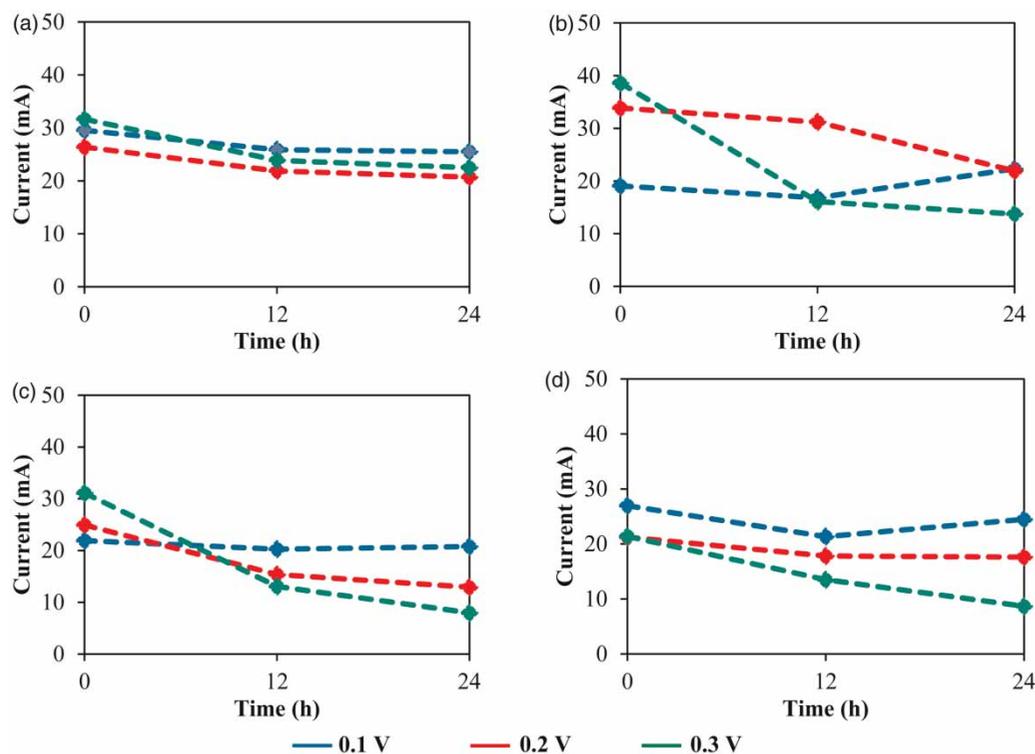


Figure 4 | Variation in anodic peak currents with time for reactors RI (a), RII (b), RIII (c) and RIV (d).

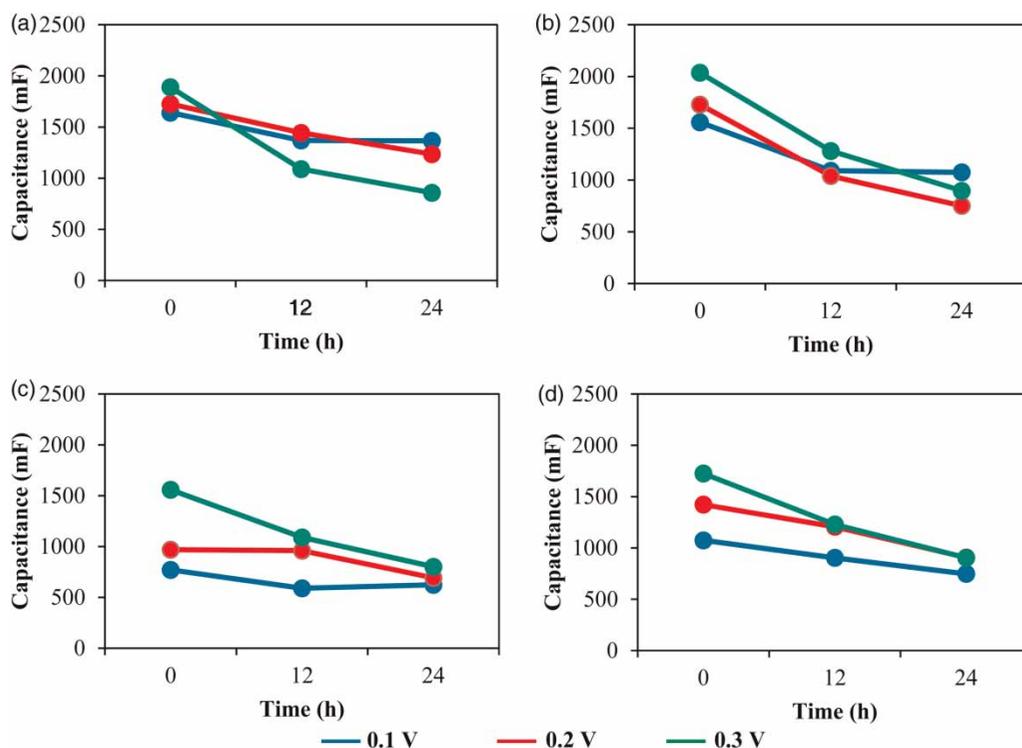


Figure 5 | Variation in capacitance with time for reactors RI (a), RII (b), RIII (c) and RIV (d).

The electrode–solution interface is analogous to that of a capacitor, which helps to determine the ability of a cell to store ions. For all the four reactors, higher capacitance was observed at +0.3 V (RI: 1,889.30 mF, RII: 2,036.23 mF, RIII: 1,557.83 mF, RIV: 1,725.13 mF), thus indicating efficient ion-holding capacity at higher voltage (Figure 5). This also shows that this capacitance is a function of the applied potential as also mentioned by Bard & Faulkner (2001).

CONCLUSIONS

The harmful effects of produced water and the depletion of usable water resources act as the driving force for treatment of PPW. Moreover, disposal of such large volumes of contaminated wastewater is a major issue because of the stringent environmental regulations. Treatment of PPW in terms of sulfate can be a major advantage for the petroleum industry, facilitating its reinjection into the oil wells. Sulfate removal was tested in a synthetically designed PPW in a two-step process. The composition of synthetic PPW was optimized using Box–Behnken design for sulfate reduction by TERI-MS-003. Sulfides generated by TERI-MS-003 after sulfate reduction were successfully oxidized electrochemically. Poise potential

of +0.3 V was found to be most effective for sulfide oxidation in terms of sulfide removal efficiency. Since the poise potential is so low, it may also come from a renewable source such as solar.

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