



# Statistical Design of Experiments Enables Rapid Exploration of Perfluorobutane Sulfonate Degradation

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The phase-out of long-chain PFAS has led to the proliferation of highly recalcitrant short-chain analogs, and mineralization technologies for these short-chain PFAS are needed to mitigate their deleterious effects on environmental and human health. In this study, we utilize a statistical design of experiments, specifically, response surface methodology, to rapidly evaluate the electrochemical degradation of the short-chain PFAS, perfluorobutane sulfonate (PFBS). We evaluate the impacts of the three primary electrochemical parameters (concentration of PFBS, concentration of supporting electrolyte, and applied current) over multiple orders of magnitude on the three primary reaction outcomes of electrochemical PFBS degradation (incomplete PFBS decomposition, complete PFBS mineralization as fluorine, and anodic energy consumption). Our results correspond with literature and clearly identify the well-known tradeoff between energy consumption and complete mineralization. Intriguingly, partial PFBS decomposition and energy consumption demonstrate nonlinear dependencies in the current/supporting electrolyte concentration space, respectively. These findings highlight the utility of the response surface methodology model to efficiently interrogate a large parameter space, identifying both common results and less-obvious interactions between electrochemical parameters and their influences on reaction outcomes.

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Manuscript submitted November 6, 2024; revised manuscript received January 21, 2025. Published February 28, 2025.

Supplementary material for this article is available online

Per- and polyfluoroalkyl substances (PFAS) are ubiquitous chemicals used in consumer, industrial, and military applications.<sup>1</sup> However, the molecules' recalcitrant, bioaccumulative, and toxic nature is damaging to the environment and human health.<sup>2</sup> Historically, research has focused on two legacy PFAS: perfluorooctane sulfonate (PFOS) and perflurorooctanoic acid (PFOA), and consequently degradation of PFOS and PFOA have been optimized across multiple fields and conditions.<sup>3</sup> Starting in the early 21st century, PFOS and PFOA were replaced with shorter-chain analogs,<sup>4</sup> for which degradation conditions, particularly in promising electrochemical systems, remain slow and energy-intensive.<sup>2</sup>, Furthermore, it is nearly impossible to fully study and optimize the degradation conditions for the thousands of short-chain PFAS molecules in existence<sup>8,9</sup> using standard experimentation techniques. As such, it is critical to identify an efficient way to gain insights into optimal degradation conditions, particularly for short-chain PFAS molecules.

In this work, we leverage a Response Surface Methodology statistical design of experiments (RSM) to efficiently investigate the electrochemical degradation of a representative short-chain PFAS: the four-carbon perfluorobutane sulfonate (PFBS). Using 26 onehour experiments, we evaluate the impacts of the three primary electrochemical reaction parameters: current density, PFBS concentration, and supporting electrolyte concentration over 2, 2, and 4 orders of magnitude (respectively). We identify the influences of these three parameters on three reaction outcomes: PFBS decomposition (i.e., decrease in PFBS over the course of the experiment), fluorine mineralization (i.e., increase in free fluorine over the course of the experiment), and anodic energy consumption in Watt-hours. We show that the results of the RSM model agree with many reported trends in electrochemical degradation of PFBS, along with new insights generated through our experiments. Since a primary benefit of utilizing RSM is the generation of optimal conditions in the outcome space, we identify optimal conditions in our parameter space for maximizing incomplete PFBS decomposition and complete PFBS degradation to fluorine while minimizing energy consumption. Our work demonstrates the utility of the RSM statistical design of experiments in rapidly interrogating a large, complex parameter space (e.g., the degradation of PFBS) and provides a framework by which this methodology can be extended to other electrochemical systems.

#### Experimental

**Electrochemical degradation procedure.**—Pre-characterization of the electrodes was performed by running 3 cycles of cyclic voltammetry from +3.0 V to -1.5 V vs Ag/AgCl. All experiments showed similar electrochemical behavior during the voltametric sweep, indicating comparable electrode behavior across our experiments and to other work (Fig. S6a). Chronopotentiometry was then performed for 60 min (Fig. S6b). Post-characterization of the electrodes was performed using an identical voltammetric procedure. Solutions were stirred constantly at 350 rpm and prepared with analytical-grade PFBS and Na<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich) and deionized water (18.2 M $\Omega$ ).

**Response surface methodology model.**—In this work, we utilized a Central Composite Inscribed design of Response Surface Methodology (CCI-RSM; JMP statistical software), as has been employed in other works.<sup>10–13</sup> Below, we endeavor to describe the model in sufficient detail such that it can be understood and repeated in other systems. We refer the reader to the NIST-Sematech Engineering Statistics Handbook for additional details.<sup>11,14</sup>

Introduction to response surface methodology.—Response Surface Methodology (RSM), as a statistical design of experiments

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(DOE), is utilized to identify curvature present across a given parameter space. This differs from classical screenings such as fractional factorial or Plackett-Burman designs, which only consider whether a result increases or decreases over a given parameter space.<sup>14</sup> Both fractional factorial and Plackett-Burman designs are useful for identifying the most important results ("main effects") from a suite of possible effects. RSM designs such as Central Composite or Box-Behnken designs, on the other hand, are used to give the *shape* of those important results within a given parameter space, such that the experimenter can identify optimal process conditions. Mathematically, classical screening designs are firstorder designs, whereas RSM designs are second-order designs (quadratic & interaction effects). Third-order designs exist, but tertiary interactions are statistically rare and can result in overfitting; as such, they are seldom used.

Despite their differences, these statistical models all have one commonality: *they significantly reduce the number of experiments required to identify results across a given parameter space*. Instead of using nine experiments to explore the effects of changing one variable at a time, we can run nine experiments to understand both linear and second-order interactions of the parameters on the desired outcome(s) (Fig. S1). This significantly increases experimental throughput without requiring automation or other technological advancements.

For our purposes, we utilize an Inscribed version of a Central Composite RSM. Inscribing the Central Composite RSM allows us to cover the full parameter space without creating impossible conditions, such as negative concentrations. RSM, as described above, identifies curvature and interaction terms within the parameter space, and identifies optimal operating conditions. This model is also inherently interpretable, giving numerical evaluations of each parameter's influence on the results, akin to a sensitivity plot (*vide infra*).

*CCI-RSM model components.*—In a CCI-RSM, a set of experiments is generated based on the total number of factors and range of each factor added. This set of experiments includes replicates, called "center points," which measure the variation across the data set, and divisions of experimentation, called "blocks," which allow the model to evaluate whether the results were influenced by the sequence of experiments (e.g., blocking can identify changes in results stemming from electrode passivation over time or other systemic biases.) In this work, we ran 20 total experiments in 3 blocks, with 2 center point experiments per block (6 total; voltage-time curves for these center point experiments can be found in Fig. S6).

These experiments are used to train a second-order polynomial model using JMP software. We confirm the model accuracy by testing at two or more unique conditions and comparing the experimental results to model predictions, as shown in Fig. 1. We then evaluate the parameter space based on (i) response surface coefficients (RSCs), which demonstrate the relative influence of each factor in the model, akin to a sensitivity analysis; (ii) simulated runs, which give insight into the patterns in the full parameter space; (iii) optimal operating conditions, which identify parameter combinations that give an optimal response. RSCs are scaled, modelspecific parameters. This means that each model term is comparable to other model terms; however, model terms cannot be compared across models (e.g., "current" can be compared to "[PFBS]" within the PFBS decomposition model, but "current" in the PFBS decomposition model cannot be compared to "current" in the fluorine mineralization model.) It is of note that we do not utilize p-values as a metric in our evaluation of the models, although we have included them in the supplementary information for the interested reader (Table S2). A detailed description of reasoning can be found in previous work and work from the American Statistical Association.<sup>10,15</sup>

**Parameter and parameter range determination.**—In this work, we utilize  $Na_2SO_4$  as our supporting electrolyte, following previous works indicating that it represents a model electrolyte in PFBS degradation.<sup>16</sup> We also utilize chronopotentiometry instead of chronoamperometry to ensure the reaction is performed at a constant rate and thereby generate a proportional amount of hydroxyl radicals to perform the oxidation.

For this study, we endeavored to identify broad patterns in electrodegradation of PFBS using RSM. Because of this, we utilized relatively high concentrations of both  $Na_2SO_4$  and PFBS, but targeted a wide range (ranges 5–50,000 ppm and 0.05–500 ppm, respectively). We used a current range of 1–750 mA to fit within the maximum operating conditions of our potentiostat.

Prior work has shown that fully defluorinated intermediates, such as formate and acetate, make up over 93% of products during the degradation of PFBS.<sup>2,5</sup> This indicates that PFBS, once adsorbed onto the electrode surface, will completely degrade into fluorine and carbon dioxide. As such, we focused on evaluating the influence of starting PFBS concentration, starting Na<sub>2</sub>SO<sub>4</sub> concentration, and applied current on total PFBS decomposed (incomplete PFBS degradation), total fluorine generated (complete PFBS degradation), and energy consumed.

*Electrochemical reactor design and operation.*—In this work, 125 ml high-density polyethylene bottles (Thermo Scientific) were used as electrochemical reactors. A separate reactor was used for each experiment to minimize contamination. One custom-fabricated lid was used and transferred between reactors to ensure electrode distances were always identical (Fig. S2).

A single semicylindrical stir bar (dimensions  $2.5 \text{ cm} \times 0.5 \text{ cm} \times 0.5 \text{ cm} \times 0.5 \text{ cm}$ ) was used in all experiments, with cleaning between each experiment, to ensure comparable mass transfer. Each reaction used 95 ml of electrolyte and was stirred on a stir plate (Thermolyne MIRAK) at a constant rate of 350 rpm.

Both the working and counter electrodes were double-sided 5 µm thick boron-doped diamond (BDD) deposited on 2 mm thick niobium substrates (Fraunhofer USA), which were sealed with epoxy on all sides to ensure no niobium was exposed. Boron-doped diamond, used broadly as an electrode in electrochemical PFAS degradation, was selected for (i) its resistance to (electro)chemical degradation, (ii) high overpotential for the oxygen evolution reaction  $(\sim 1.9 \text{ V vs RHE})$ , and (iii) generation of hydroxyl radicals, which can effectively degrade PFBS.<sup>2,5,17</sup> Each electrode was immersed in electrolyte such that 3 cm<sup>2</sup> on each side was exposed, for a total of 6 cm<sup>2</sup> of working geometric area. All voltages are half-cell anodic voltages, referenced to 3 M Ag/AgCl (BASi). Electrochemical tests were performed using an Interface 1010E potentiostat (Gamry). Minimal changes to the electrodes were observed over the course of the 26 experiments, which was confirmed by the model blocks having no influence on the results.

**Product analysis.**— Sample preparation.—An aliquot of sample volume was transferred to a 15 ml tube and diluted by a factor of 1,000 with deionized water (10  $\mu$ l sample volume and 9.99 ml deionized water), which was then used for tandem liquid chromatography-mass spectrometry analysis to determine PFBS concentrations. Another aliquot of sample volume was transferred to a 15 ml tube and diluted by a factor of 10 with deionized water (1 ml sample volume and 9 ml deionized water), which was then used for ion chromatography analysis to determine fluorine concentrations.

Liquid chromatography-mass spectrometry (LC-MS) method.— Samples for analysis were prepared in glass 2 ml auto sampler vials in water with 100  $\mu$ l of isotopically labeled PFBS at a concentration of 125 ppb to a final sample volume of 1 ml. Samples were prepared in triplicate to assess analytical variation. All volumes were pipetted and measured by mass to calculate exact concentrations.



**Figure 1.** Model validation under (a) 600 mA applied current, 350 ppm PFBS, and 35000 ppm  $Na_2SO_4$  and (b) 450 mA applied current, 400 ppm PFBS, and 347000 ppm  $Na_2SO_4$ . The x-axis indicates each optimization criteria used in the model: amount of PFBS decomposed, amount of fluorine mineralized, and amount of energy consumed. The left-hand y-axis indicates the amount of either PFBS decomposed, which is represented by the leftmost bar in (a) and (b), or fluorine mineralized, which is represented by the central bar in both (a) and (b). The right-hand y-axis indicates the amount of energy consumed, which is represented by the central bar in both (a) and (b). The right-hand y-axis indicates the amount of energy consumed, which is represented by the rightmost bar in both (a) and (b). The corresponding axis is also indicated by arrows above each bar pointing to the left or right. The model is accurate for PFBS decomposition, fluorine mineralization, and energy consumption predictions. It is of note that PFBS decomposition predictions vary widely. This results from the combination of variation in experimental results and the wide range of analytical error currently accepted within the community. As analytical methods improve, model prediction values will become more accurate.

LC-MS analysis for PFBS quantitation was performed using a liquid chromatography instrument (Acquity SM-F and Acquity BSM, Waters) connected to a triple quadrupole mass spectrometer (Xevo TQ-SM, Waters). The LC column (Acquity UPLC BEH C18 1.7  $\mu$ m) was eluted using a two-solvent gradient protocol (Section S1.1). The MS collected sample data using a MS scan method for the duration of the LC run (Section S1.2). Quality control for the LC-MS data was also employed (Section S1.3).

Ion chromatography (IC).—Samples were analyzed for fluorine using a ion chromatograph (Dionex Aquion, ThermoScientific) with IonPac AS22 guard and analytical column and a sodium bicarbonate/ carbonate eluent. Samples were measured along with fluorine standard elemental reference solutions (Fluka Analytical) for calibration and check standards. Fluorine peaks were observable at a retention time of 2.960 (+/-.20) min.

Sample analysis and data processing.—After analysis by LC/MS, final concentrations of PFBS were determined by subtracting the LC/MS-determined average concentration of PFBS in the post-electrolysis solution from the LC/MS-determined average concentration of PFBS in the pre-electrolysis solution (Table S1). This change represented the amount of PFBS decomposed during the electrolysis process. Any solutions that appeared to have *increases* in PFBS concentration were set to 0, as there was no PFBS decomposition occurring during electrolysis. These results were input to the model.

After analysis by IC, final concentrations of fluorine were determined by subtracting the IC-determined concentration of fluorine in the *pre*-electrolysis solution from the IC-determined concentration of fluorine in the *post*-electrolysis solution (Table S1). This change represented the amount of fluorine mineralized during the electrolysis process, and the results were input to the model.

To analyze the amount of (anodic) energy consumed during the electrolysis process, the measured voltage (referenced to Ag/AgCl, *vide supra*) was averaged over the hour-long run. This average voltage was then multiplied by the applied current to obtain the total wattage used for the anodic reaction, and then multiplied by the hours ran (in this case, 1) to determine the watt-hours of energy consumed at the anode. This value represents the average anodic

energy consumed during the electrolysis process, and the results were input to the model.

# **Results and Discussion**

*Model validation.*—We first validated the model by testing two sets of model predictions against triplicate experimental results (Fig. 1). At both tested conditions, the model predictions and experimental results were within error of each other, indicating that the model works well and can be used for further analysis. Note that the large error bars on the PFBS decomposition predictions include both analytical measurement error (a documented phenomenon in quantifying PFAS molecules<sup>8</sup>) and the variability inherent in the electrocatalytic system (Table S1).

*Individual response evaluation.*—After validating the model, we explored the influence of each parameter ([PFBS], [Na<sub>2</sub>SO<sub>4</sub>], and current) on each response (incomplete PFBS decomposition, complete PFBS degradation as fluorine mineralization, and energy consumption). Model fit results can be found in Table I.

PFBS decomposition (incomplete PFBS degradation).—PFBS decomposition (i.e., the incomplete degradation of PFBS) shows high sensitivity to [PFBS] and applied current (Fig. 2a). [PFBS] and current both have positive response surface coefficients (RSCs), indicating that increasing either of them independently (i.e., while holding the rest of the parameters constant) will increase PFBS decomposition. However, both show strong negative curvature in their squared terms. This indicates that increasing [PFBS] (or current) independently will increase PFBS (or current) decomposition, until a plateau is reached. This logarithmic growth-like curve indicates a limiting [PFBS] (or current) beyond which there are minimal increases to PFBS decomposition. This behavior is stronger for [PFBS], due to its weaker linearity and stronger curvature. Furthermore, the interaction of [PFBS] and current is weakly positive, indicating that increasing both [PFBS] and current simultaneously will also increase PFBS decomposition. Highest PFBS decomposition is seen to occur at moderately high [PFBS] and high currents (Fig. 2b).

Table I.	Details of each	individual r	nodel (PFBS	decomposition,	fluorine mi	neralization,	energy	consumption),	including	model	significanc	e/fit/
balance,	RSC values, an	nd maximiza	tion of desira	bility. All conc	entrations a	e in ppm, a	ll curre	nts are in mA.				

		Individual model						
	Parameter	PFBS decomposition	Fluorine mineralization	Energy consumption				
Model Significance	P-value	0.083	0.0001	< 0.0001				
	R-sq	0.82	0.98	0.9972				
Model Fit	RMSE	18.944	1.6496	0.116				
	P-value	0.248	0.0002	0.1750				
Model Balance	Max VIF	1.6746655	1.6746655	1.6746655				
	Max COE	0.5498	0.5498	0.5498				
Response Surface Coefficients	[PFBS]	17.939678	10.39498394	-6.74E-06				
-	$[Na_2SO_4]$	4.2706851	-0.542114071	-0.000808152				
	Current	37.231085	9.612298454	0.002619502				
	$[PFBS] \cdot [Na_2SO_4]$	-2.215761	3.23733809	-0.000082863				
	[PFBS] · Current	18.612341	9.310561937	-0.000070331				
	[Na <sub>2</sub> SO <sub>4</sub> ] · Current	19.68755	-0.125962747	-0.001100067				
	[PFBS] · [PFBS]	-34.83075	0.290322005	-0.000231035				
	$[Na_2SO_4]$ · $[Na_2SO_4]$	2.4900983	-0.50146627	0.00053272				
	Current · Current	-16.45884	-0.040268422	0.00048105				
Desirability Maximization	Desirability	0.626393	0.99844	0.99782				
	[PFBS]	287.81258	383.23949	168.92815				
	$[Na_2SO_4]$	39973.885	19755.174	20257.497				
	Current	663.86011	670.48456	1				
	Target estimated value	78.62155	26.38039	-0.21961				
	Target low value	35.98059	22.66727	-0.48075				
	Target high value	121.2625	30.09351	0.04154				

This complexity likely originates in the shift in the reaction from diffusion- to kinetic limitations. Higher [PFBS] increases diffusive flux, increasing PFBS adsorbed onto the electrode surface. Because the first step in PFBS decomposition requires a direct electron transfer from PFBS to electrode,<sup>2</sup> more available PFBS increases decomposition. Similarly, increased current increases the reaction rate. However, PFBS decomposition is limited by the availability of active sites,<sup>2,5</sup> and so once every active site is saturated, the reaction becomes kinetically-limited, where PFBS decomposition is only dependent on the rate of electron transfer between the electrode and PFBS. Increasing current can improve this rate, but it becomes less impactful as current increases.<sup>2</sup> Some of this behavior could also be attributed to increased rates of water oxidation as current increases, where additional amperage only serves to perform the oxygen evolution reaction. While prior work using lower concentrations of PFBS (µg/l or less) in similar systems showed that higher concentrations of PFBS were more facile to decompose.<sup>6,17,18</sup> our work demonstrates that this is only true until kinetic limitations are reached (in our system, ~200-300 ppm), after which higher concentrations of PFBS do not affect results.

*Fluorine mineralization (complete PFBS degradation).*— Fluorine mineralization (i.e., the complete degradation of PFBS to carbon dioxide and fluoride), like PFBS decomposition, shows high sensitivity to [PFBS] and applied current; however, there is almost no curvature inherent in the system (Fig. 2c). [PFBS] and current both have positive RSCs, indicating that increasing either of them independently will increase fluorine mineralization. Furthermore, the interaction of [PFBS] and current is also strong and positive, indicating that increasing both [PFBS] and current *simultaneously* will also increase fluorine mineralization. Highest fluorine mineralization is predicted to occur at the highest [PFBS] and highest currents (Fig. 2d).

Interestingly, fluorine mineralization does not plateau at increased currents, nor increased [PFBS], unlike PFBS decomposition. After the initial electron transfer, the  $CF_2$  "unzipping" mechanism reported in prior work indicates that PFBS can mineralize either at the surface of the electrode *or* from mediated reactions with

hydroxyl or sulfate radicals in solution.<sup>2,5</sup> While the heterogeneity in this mechanism obscures precise current efficiency calculations, it also reduces dependence on flux to the electrode and reaction rate and thus increases total mineralization. The variations between conditions optimal for fluorine mineralization and PFBS decomposition are likely the influence of seemingly conflicting results in prior work.<sup>7,19</sup> The kinetics and mass transfer of the reaction can also be influenced by electrode area/roughness, temperature, stir rate, and pH, among others.<sup>20</sup> Enhancing both PFBS decomposition and fluorine mineralization requires careful selection of reaction conditions to meet optimum conditions.

*Energy consumption.*—Finally, energy consumption shows high sensitivity to  $[Na_2SO_4]$  and applied current, while effects of [PFBS] were limited (Fig. 2e).  $[Na_2SO_4]$  has a negative RSC, indicating that increasing  $[Na_2SO_4]$  independently will *decrease* energy consumption, with its positive squared RSC showing a less pronounced effect at high  $[Na_2SO_4]$  (mimicking exponential decay-like behavior). Current, however, has a positive RSC, indicating that increasing current independently will *increase* energy consumption, with its positive squared RSC showing a less pronounced effect at low currents (exponential growth-like behavior). The interaction of  $[Na_2SO_4]$  and current is negative, indicating that increasing both  $[Na_2SO_4]$  and current *simultaneously* will *decrease* overall energy consumption. Increasing the concentration of  $[Na_2SO_4]$  at a constant current decreases the energy consumption in the system, which becomes more pronounced at higher currents (Fig. 2f).

Increased current applied in an electrochemical system increases the energy the system consumes. However, increased supporting electrolyte enhances the solution conductivity, which decreases system resistance and thus energy consumption (Fig. S3). Interestingly, the relationship between  $[Na_2SO_4]$  and energy consumption is nonlinear, implying that degradation of PFBS can be less energy-intensive by the addition of supporting electrolyte, beyond what is currently present in water streams.

System optimizations.—Finally, we sought optimal solutions from our model. To do so, we generated 1,000 simulated



**Figure 2.** Evaluating the individual responses of (a)–(b) incomplete PFBS decomposition, which depends primarily on [PFBS] and current; (c)–(d) complete PFBS degradation as fluorine mineralization, which depends primarily on [PFBS] and current; and (e)–(f) energy consumption, which depends primarily on [Na<sub>2</sub>SO<sub>4</sub>] and current. These responses are evaluated through (a), (c), (e) response surface coefficients and (b), (d), (f) simulated runs. Larger absolute values of response surface coefficients (which are scaled to the size of the response value, and as such are not comparable across different responses), indicate a greater influence on the response. For simplicity, the two most influential responses are shown in the simulated runs. The simulated runs indicate that, while all responses depend on current, energy consumption is not dependent on the same set of parameters as PFBS decomposition or fluorine mineralization. Thus, by modulating the concentration of supporting electrolyte, it is possible to decrease overall energy consumption while still maintain high PFBS degradation rates.

experiments and mapped a desirability factor (Table S3) onto the outcomes. We first sought to maximize PFBS decomposition and fluorine mineralization while minimizing energy consumption, a three-objective optimization (Fig. 3d). Optimum conditions fell in the moderate ranges of all three responses (PFBS decomposition, fluorine mineralization, energy consumption), indicating optimization for all three desired responses are not fully compatible. We then explored two-objective optimizations using each combination of parameters (Figs. 3a–3c). PFBS decomposition and fluorine mineralization optima trend together linearly, with high desirabilities at optimal conditions (Fig. 3a). This corresponds with our evaluation of

individual responses, as increasing the PFBS decomposed increases the amount of fluorine available to mineralize.

Optimizing either PFBS decomposition or fluorine mineralization alongside energy consumption show different, nonlinear trends. PFBS decomposition and energy consumption shows the least desirable "optimal" results. At minimum energy consumption, 50% less PFBS is decomposed than at maximum PFBS decomposition; however, maximum decomposition consumes triple the energy (Fig. 3b). Fluorine mineralization and energy consumption reach marginally more desirable "optimal" results (Fig. 3c). The trends in energy consumption *versus* fluorine mineralization are nearly



**Figure 3.** Two- and three-objective optimizations for each desired response. (a) Optimization of PFBS decomposition and fluorine mineralization trends linearly, with higher PFBS decomposition corresponding to higher fluorine mineralization. "Desirability" is a parameter that assesses how close an optimization is to achieving the user-defined optimal solution for each response under consideration (e.g., a desirability value of 1 signifies that the optimization goals for all responses have been reached.) Each 2D plot ((a)-(c)) contains dashed lines indicating the optimal desirability criterion for each response, as described in Table S3. (b) Optimization of PFBS decomposition and energy consumption the nonlinearly, with higher PFBS decomposition requiring, at minimum, intermediate energy consumption. (c) Optimization of fluorine mineralization and energy consumption also trend nonlinearly, corresponding to behavior seen in (b). (d) Three-objective optimization of PFBS decomposition, fluorine mineralization, and energy consumption. Most optimal conditions are found at intermediate to high fluorine mineralization, intermediate energy consumption, and intermediate PFBS decomposition. These are only moderately desirable conditions, between 0.5 and 0.6.

identical to those seen in PFBS/energy (Fig. 3b). Corresponding to similar results seen in literature (*vide supra*), any optimization attempting to maximize PFBS decomposition *or* fluorine mineralization will require meaningful tradeoffs in energy consumption.

The two-objective optimizations give insight into the threeobjective optimization. Maximizing both PFBS decomposition and fluorine mineralization will give highly desirable results. Our analysis shows, however, that this corresponds to high applied currents, which is at odds with minimizing energy consumption. According to the RSM analysis, optimal conditions for maximization of both incomplete PFBS decomposition and complete PFBS degradation to fluorine, while minimizing energy consumption, comes at a starting [PFBS] of 347 ppm, [Na<sub>2</sub>SO<sub>4</sub>] of 37000 ppm, and applied current of 564 mA (Fig. 4a). These conditions result in 67 ppm PFBS decomposed and 19 ppm fluorine mineralized, at an energy consumption of 2.8 Wh (Fig. 4b). These numbers fall in the moderate-to-low range of PFBS decomposition, moderate-to-high range of fluorine mineralization, and moderate range of energy consumption, corresponding to our above model analyses. Optimal conditions for one- and two-objective optimizations (Fig. S4), along with the corresponding results of each optimization (Fig. S5), show that increasing the number of objectives decreases overall fluorine mineralization and increases overall energy consumption, while PFBS decomposition does not meaningfully change. However, [PFBS], [Na<sub>2</sub>SO<sub>4</sub>], and applied current all fluctuate dramatically between each optimal condition, indicating that some of the interactive effects we observe combine to result in the same outcome. These conditions could be further tailored with the expansion of the methodology to include additional solutes seen in real wastewater. Overall, our results echo those seen in prior work, while indicating new phenomena, such as the nonlinear effect of supporting electrolyte concentration on energy consumption, to be investigated in future work.



Figure 4. (a) Optimal reaction parameters corresponding to (b) optimal reaction outcomes when seeking to achieve all 3 objectives (maximize PFBS decomposition, maximize fluorine mineralization, and minimize energy consumption). (a) The left-hand y-axis indicates either the amount of PFBS in the starting solution, which is represented by the leftmost bar, or the amount of current applied, which is represented by the central bar. The right-hand y-axis indicates the amount of Na2SO4 in the starting solution, which is represented by the rightmost bar. (b) The left-hand y-axis indicates the amount of either PFBS decomposed, which is represented by the leftmost bar, or fluorine mineralized, which is represented by the central bar. The right-hand y-axis indicates the amount of energy consumed, which is represented by the rightmost bar. The corresponding axis for both (a) and (b) is also indicated by arrows above each bar pointing to the left or right.

# Conclusions

Using a high-throughput response surface methodology statistical design of experiments, we identified curvature and interactive effects present in the influences of reaction parameters of PFBS concentration, Na<sub>2</sub>SO<sub>4</sub> concentration, and applied current on reaction outcomes of PFBS decomposition (incomplete PFBS degradation), fluorine mineralization (complete PFBS degradation), and energy consumption during the electrolysis process. The results of only 26 experiments corroborate results in prior work, indicating the high currents required for both PFBS decomposition and fluorine mineralization can only partially be offset by manipulations of the reaction parameters, and thus the system optimization for the desirable conditions of low energy consumption, high PFBS decomposition, and high fluorine mineralization. The model interrogates this 3dimensional parameter space further by identifying the nonlinear effects of the interaction of starting [PFBS] and applied current on incomplete PFBS decomposition, as well as those of the interaction of starting [Na<sub>2</sub>SO<sub>4</sub>] and applied current on anodic energy consumption. These two results indicate new levers by which PFBS degradation can be further optimized, beyond existing knowledge of linear influences of each reaction parameter on different outcomes. Our work demonstrates RSM as a comprehensive alternative to traditional experimental designs that can efficiently identify common characteristics in electrochemical PFBS degradation, as well as provide new insights for future exploration.

### Acknowledgments

This work was supported by the Laboratory Directed Research and Development program (project number 233084) at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This research was also supported in part by an appointment to the Universities Research Association (URA) Summer Fellowship Program at Sandia National Laboratories, sponsored by URA and administered by the Oak Ridge Institute for Science and Education to RNG. Additionally, this material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 2140745 to JAL. The authors gratefully thank Mohammed Shohel and Zoe K. Bryant for many helpful discussions, Andrew W. Knight for his vision and support during the work, and Rvan D. Davis and James J. Griebler for their thoughtful comments on the manuscript. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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