

Novel Cosolvent Regeneration for Organic-loaded Anion Exchange Resin

by

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## ABSTRACT

Hydrophobic ionizable organic compounds (HIOCs) like per- and polyfluoroalkyl substances (PFAS), certain pharmaceuticals, and surfactants have been detected in groundwater, wastewater, and drinking water. Anion exchange resin treatment is an effective process for removal of anionic contaminants from water. Spent anion exchange resins are conventionally regenerated with high alcohol by volume (ABV) methanol in solution with brine. While effective for regeneration of resins saturated with inorganic anions such as sulfate, nitrate, and perchlorate, HIOCs prove more resistant to regeneration. This research investigated the efficacy of using novel cosolvent solutions with brine to regenerate resins saturated with organic carboxylate and sulfonate anions to understand the effects cosolvent properties have on regenerative ability. Experiments were conducted on six PFAS compounds to evaluate trends in regeneration for three alcohols. For all PFAS species, equivalent ABV and brine solutions showed greatest regeneration with 1-propanol over ethanol and methanol. Experiments with the pharmaceutical sodium diclofenac were conducted showing similar regeneration of 75% methanol and 25% 1-propanol for equivalent salt concentrations and higher regeneration with 1-propanol than ethanol and methanol for equivalent ABV. A series of experiments with surfactant dodecylbenzene sulfonate determined that the key parameters to determine regeneration of the resin for an alcohol cosolvent solution were cosolvent volume fraction, molar mass,  $K_{ow}$  value, solution ionic strength, and dielectric constant. Individual assessments on the cost-effectiveness, flammability, and sustainability of cosolvent solutions point to possible future experiments and opportunities for recycled distillery waste streams as regenerative solutions for anion exchange resin.

## DEDICATION

To my wife Ellen, for her support of my endeavors and her interminable patience thereof.

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## CHAPTER 1

### INTRODUCTION

Anthropogenic organic chemicals are being detected in surface waters, groundwater, and drinking water. A subclass of these contaminants are hydrophobic ionizable organic compounds (HIOCs), notable for their polar, ionizable head groups and nonpolar tails (Li & SenGupta, 2004; Rao et al., 1990). Included in the HIOC chemical class are many pharmaceuticals, surfactants, and emerging contaminants like per- and polyfluoroalkyl substances (PFAS) (Gabarrón et al., 2016; Lau et al., 2007; Meegoda et al., 2020). Anion exchange resins (AERs) have been widely used for the removal of contaminants in water and have been effective for removal of HIOCs (del Moral et al., 2020; Landry & Boyer, 2013; Li & SenGupta, 1998, 2001). Once a resin has been saturated with contaminants, breakthrough occurs, and the resin must be regenerated or disposed of (Boyer, Ellis, et al., 2021). While inorganic anionic contaminants like sulfate, nitrate, perchlorate, and chromate can be readily desorbed from resins with brine to regenerate them, literature has shown resins saturated with HIOCs prove to be more resistant to regeneration due to the combination of electrostatic and non-electrostatic interactions between the saturant and resin (Gu et al., 2001; Li & SenGupta, 1998). Due to different factors controlling desorption such as cosolvent dielectric constant, cosolvent octanol-water partitioning, and solution ionic strength, novel cosolvent solutions deserve attention for regeneration of resins saturated with HIOCs. Greater understanding of solvent effects on regeneration will enable more refined techniques for regeneration considering practical engineering considerations like safety, cost, and sustainability.

Anion exchange resins have been implemented in water treatment for a variety of inorganic and organic contaminants. Target contaminants include common inorganic anions, natural organic matter NOM, hydrophobic ionizable organic compounds, and emerging contaminants like PFAS (Boyer, Ellis, et al., 2021; Cheng & Sabatini, 2002; del Moral et al., 2020; Deng et al., 2010; Gu et al., 2001; Hu et al., 2016; Landry et al., 2015; Padungthon et al., 2015). AERs are supplied with a pre-loaded counterion, conventionally being chloride ion ( $\text{Cl}^-$ ) but other ions such as hydroxide ( $\text{OH}^-$ ) or bicarbonate ( $\text{HCO}_3^-$ ) are possible (del Moral et al., 2020; Hu et al., 2016). During treatment of contaminated water, the pre-loaded counterion is displaced from the resin and is replaced by a competing anion, either inorganic or organic. The most widely used AERs are polystyrene (PS) and polyacrylic (PA), and resins can be classed as strong-base (SB) or weak-base (WB) depending on the molecular structure of the active site (Boyer, Fang, et al., 2021; Landry et al., 2015; Li & SenGupta, 2004). SB-AERs contain a quaternary ammonium ion, i.e. a nitrogen bound to a PS or PA resin backbone with three additional branched alkyl chains (Boyer, Fang, et al., 2021; Kassir, 2022). The effect is a permanently positively charged site that is bound to a counterion. WB-AERs contain a tertiary amine, i.e. a nitrogen bound to a resin backbone with two additional alkyl chains. The effect is a neutral amine site that protonates at low pH where electrostatic interactions can then occur, whereas SB-AERs are largely unaffected by pH (Kassar, 2022).

The possible regeneration of anion exchange resins is one of the attractive attributes of the treatment technology. Past studies have analyzed regeneration of PS SB-

AERs over several cycles of use, and the resin class has been shown to be overall effective at regeneration for both inorganic and organic anions (Chularueangaksorn et al., 2013; Dietz et al., 2021; Gao et al., 2017; Kassir, 2022; Landry & Boyer, 2013; Li & SenGupta, 1998; Liu & Sun, 2021; Meegoda et al., 2020; Padungthon et al., 2015; Zhang et al., 2015). The regeneration ability of the resin is affected by the composition of the resin structure, the spacing of functional groups, and the counterion loaded on the resin (Deng et al., 2010). Conventionally, regenerant solutions have been comprised of approximately 70% methanol with water and a dissolved salt, often sodium chloride (Boyer, Fang, et al., 2021; Gu et al., 2001; Li & SenGupta, 1998; Liu & Sun, 2021; Woodard et al., 2017). Incineration and pyrolysis of ion exchange resins releases hazardous byproducts including toxic and carcinogenic compounds, so regeneration of resins is both more environmentally sustainable as well as cost-effective (Boyer, Ellis, et al., 2021). Regeneration solutions have also been examined in part, with most studies utilizing methanol as the cosolvent with brine which is the dominant field implementation. A few studies have looked at alternative cosolvents such as ethanol dioxane, and acetone, but the methanol studies far exceed alternative cosolvent analyses (Li & SenGupta, 2001; Woodard et al., 2017; Zaggia et al., 2016).

Hydrophobic ionizable organic compounds are a class of chemical that lend themselves to being difficult to treat due to their dual nature of possessing both hydrophilic and hydrophobic atoms in their molecular structure (Li & SenGupta, 2004). Many pharmaceuticals fall into the HIOC class, the more ubiquitous of which are being found in the environment. Diclofenac sodium is one such drug that is prescribed routinely

(Todd & Sorokin, 1998). Diclofenac has been detected in natural water bodies and wastewater treatment plants (Zhang et al., 2008). Like many pharmaceuticals, excess diclofenac is excreted from the body through urine, and the use of anion exchange resins is a viable method to remove the excess pharmaceutical in wastewater treatment processes (Landry & Boyer, 2013; Landry et al., 2015).

Surfactants are another class of chemical that are of concern for their prevalence in water sources. In particular, linear alkyl sulfonates (LASs) are of concern due to their increase in production and their ecotoxicity (Scott & Jones, 2000). Some surfactants like sodium dodecylbenzene sulfonate classify as HIOCs and so are treatable by the same techniques mentioned previously. Environmentally, surfactants like dodecylbenzene sulfonate disrupt natural ecological systems (Alemdar et al., 2003).

An emerging class of contaminants are per- and polyfluoroalkyl substances which have been used in a variety of industries since their inception in the 1950s, including surface coatings, firefighting foams, adhesives, cookware, and others (Meegoda et al., 2020). The compounds are unique for their notable resistance to degradation in the environment (Boyer, Ellis, et al., 2021). These PFAS compounds, colloquially named part of the “forever chemicals,” have been detected in increasing concentrations in wildlife as well as in the blood of humans (Lewis et al., 2015). Their deleterious effects on mammalian life have helped spur along efforts to find novel ways to remediate and remove them from water sources (Dietz et al., 2021; Gagliano et al., 2020; Hauptert et al., 2021; Kassar, 2022; Park et al., 2020; Zaggia et al., 2016).

When considering the safety of handling cosolvents for resin regeneration, one factor is the flashpoint of the mixture. Flashpoint is the temperature at which the vapor from the mixture is ignitable, and several studies have analyzed the flashpoints of binary alcohol mixtures with water (Astbury et al., 2005; Martínez et al., 2005). As water becomes a greater fraction of the total mixture, the flashpoint temperature increases which ultimately leads to safer operating conditions. Although the risk of fire and explosion due to flashpoint vary depending on the ambient temperature of operation, flashpoints above room temperature ( $\sim 20$  °C) are preferred for inherent safety reasons (Curzons et al., 1999). Methanol with an ABV at 75% has a flashpoint at 19 °C and is therefore a flammability concern under many ambient operating conditions. A regenerant cosolvent solution that achieves the same regeneration as another but with a higher flashpoint would be the safer solution in practice.

The cost of cosolvent solutions is another consideration factor for regeneration of anion exchange resins. Requiring a higher volume fraction of cosolvent will inherently necessitate more total cosolvent required. Similarly, greater concentrations of salt in the regenerant solution will increase total cost and scaling foulant at a water treatment plant (Maul et al., 2014). Although the ultimate goal is achieving high regeneration efficiency of spent resin by reloading counter anions, if an adequate cosolvent solution requires less alcohol and less salt than another to achieve the same regeneration, then this regenerant solution should be the one implemented to avoid redundancy. This consideration has implications for cost as well as sustainability.

Regeneration of resins not only saves an operator on the total cost of materials, it also decreases the total amount of resins needed. Incineration is the terminus of resins that are no longer capable of effective regeneration, and the incineration of resins loaded with certain organics can create harmful byproducts in emissions (Dubois et al., 1995). Furthermore, balancing the carbon budget through decreased carbon dioxide (CO<sub>2</sub>) emissions has become a greater concern for sustainability measures, and incineration of polymerized resins ultimately oxidizes their carbon chains to carbon dioxide. Alcohol and polyol cosolvents are also hydrocarbons, and after a resin has been regenerated, the waste regenerant solution is normally incinerated which has significant impacts on fossil fuel depletion, carcinogen generation, ecotoxicity, and global warming potential (Boyer, Ellis, et al., 2021). This is due to combustion of alcohols also resulting in more carbon dioxide emissions. Increasing the regeneration ability of resins with a lower alcohol fraction cosolvent solution would therefore have a two-fold impact on greenhouse emissions by AER utilization.

The lack of data on alternative cosolvents to methanol, particularly for the regeneration of resins saturated with organic compounds, calls for additional inquiries into alternative cosolvents that could be used more efficiently to regenerate resin, incorporating factors like cost, safety, and sustainability. The literature on the use of methanol as cosolvent is extensive and generally shows strong regeneration as methanol volume fraction and salt concentration are increased (Boyer, Fang, et al., 2021). Past studies have analyzed ethanol in addition to methanol but not in a comprehensive manner

incorporating different salt concentrations and several different volume fractionations (Gu et al., 2001; Zaggia et al., 2016). Similarly, there has been some work focused on organic cosolvents like acetone and dioxane for resin selectivity, but a full scope that analyzes other alcohols and polyols has not been conducted (Li & SenGupta, 2001; Woodard et al., 2017). Therefore, there is a great need for research that expands the scope of possible regenerative cosolvents for organic-loaded resin.

The goal of this research was to provide an improved understanding of the regeneration of SB PS AERs saturated with HIOCs by alcohol and polyol cosolvents in brine solutions with an emphasis on identifying novel solutions with higher regeneration efficiency, lower flammability, and lower relative cost with the aim of identifying sustainable solutions in the future. The specific research objectives were to (1) investigate regeneration efficiency of two resins saturated with six PFAS and different alcohol compositions at equivalent alcohol by volume fractions, (2) four resins saturated with a common pharmaceutical carboxylate considering different resin properties, alcohol and polyol compositions, (3) evaluate regeneration efficiency of three resins saturated with a common surfactant using different alcohol and polyol cosolvents at varying fractions and at different salt concentrations, (4) develop a model to describe the regeneration results of the surfactant via multivariate analysis based on important variables for the solution. (5) evaluate regeneration efficiency of the surfactant as it relates to practical field concerns of flammability, cost, and sustainability. The HIOCs analyzed were diclofenac, dodecylbenzene sulfonate, and six PFAS; all compounds contained either sulfonates or carboxylates as ionizable head groups. The cosolvents analyzed were aliphatic alcohols

methanol, ethanol, 1-propanol, and 1-butanol as well as polyols propylene glycol and glycerol. All experiments were conducted in triplicate batch protocol.



## CHAPTER 2

### MATERIALS AND METHODS

#### 2.1 Materials

##### 2.1.1 Anion Exchange Resins

The resins used in this experiment were PS SB-AERs, Purolite A502P, A520E, A532E, and A592E. These resins were chosen based ability to remove organic anions, including HIOCs and PFAAs, as well as possible reversibility (Boyer, Fang, et al., 2021; Dietz et al., 2021; Landry et al., 2015; Li & SenGupta, 2004; Liu & Sun, 2021; Zaggia et al., 2016). All resins were obtained in their chloride (Cl<sup>-</sup>) mobile counterion form. Table 2-1 provides the properties of the resins chosen.

Table 2-1

*Strong base polystyrene anion exchange resin characteristics from manufacturer*

<b>Resin</b>	<b>Functional Group</b>	<b>Structure</b>	<b>Moisture Retention</b>	<b>Total Capacity (wet, eq/L)</b>	<b>Specific Gravity (g/mL)</b>
Purolite A502P	Quaternary Ammonium <sup>a</sup>	Macroporous	66 – 72%	0.85	1.04
Purolite A520E	Triethyl ammonium	Macroporous	50 – 56%	0.9	1.07
Purolite A532E	Bifunctional triethyl, trihexyl ammonium	Gel	40 – 48%	0.6	1.04
Purolite A592E	Tributyl ammonium	Macroporous	NA	0.9	NA

<sup>a</sup> Specific alkyl functional group(s) unknown

Resin A502P was chosen for its role as an organic scavenger and its high reversible adsorptive capacity as described by the manufacturer as well as a previous

study showing its ability to remove DOC (Jamil et al., 2019). Past work on A520E has shown its ability to adsorb organic compounds in addition to its primary manufacturing purpose to adsorb nitrate (del Moral et al., 2020; Zaggia et al., 2016). Resin A532E was chosen for its principal application of removing hydrophobic anions and high operating capacity, as well as being the only gel-type resin for comparison against macroporous resins (Zaggia et al., 2016). Resin A592E was chosen for its ability to remove perfluoroalkyl substances (PFAS) with the hydrophobic ionizable organic compounds in the procedure serving as surrogates for different PFAS (Liu et al., 2021).

### 2.1.2 Hydrophobic Ionizable Organic Compounds

The two HIOCs probed for saturation onto resin and then regeneration were diclofenac sodium (CAS 15307-79-6, Spectrum Chemical) and sodium dodecylbenzene sulfonate (CAS 25155-30-0, Sigma Aldrich). A summary of their properties is included in Table 2-2. The molecular structures of diclofenac anion and dodecylbenzene sulfonate can be found in Appendix A as Figure S1 and Figure S2, respectively.

Table 2-2

***HIOC solutes for adsorbance and regeneration with characteristics provided by manufacturer***

<b>Solute Name</b>	<b>Chemical Formula</b>	<b>Molecular Weight (g/mol)</b>	<b>Functional Group</b>	<b>Class</b>	<b>pK<sub>a</sub></b>
Diclofenac Sodium	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> NNaO <sub>2</sub>	318.13	Carboxylate	Pharmaceutical NSAID	~ -6
Sodium Dodecylbenzene Sulfonate	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na	348.48	Sulfonate	Surfactant	3.99

<sup>a</sup> Data sourced from suppliers and PubChem database

The compounds were chosen for two primary reasons. Firstly, each compound represents a contaminant class present in wastewater and ground water; diclofenac sodium is a common pharmaceutical non-steroidal anti-inflammatory drug that has been detected in groundwater and drinking water. Sodium dodecylbenzene sulfonate is a long-chain surfactant used as a detergent and used generally in cleaning products and has been detected in groundwater and drinking water (Alemdar et al., 2003; Ni et al., 2018; Scott & Jones, 2000). Secondly, each analyte serves as an ionizable organic compound surrogate to certain perfluoroalkyl acids (PFAAs). Diclofenac sodium contains a carboxylate group as do perfluorocarboxylic acids (PFCAs), and sodium dodecylbenzene sulfonate contains a sulfonate group as do perfluorosulfonic acids (PFSAs).

For the regeneration experiment of two resins saturated with PFAS, six different perfluoroalkyl substances were used, three carboxylate-group compounds and three sulfonate-group compounds: perfluorobutanoic acid (C4, PFBA, aqueous, CAS# 375-22-4), perfluorohexanoic acid (C6, PFHxA, aqueous, CAS# 307-24-4), perfluorooctanoic acid (C8, PFOA, solid, CAS# 335-67-1), perfluorobutane sulfonate (C4, PFBS, sodium salt, CAS# 29420-49-3), perfluorohexane sulfonate (C6, PFHxS, sodium salt, CAS# 3871-99-6), and perfluorooctane sulfonate (C8, PFOS, aqueous, CAS# 1763-23-1). All six PFAS were purchased from Sigma-Aldrich at ACS grade. These PFCAs and PFSAs were chosen for their variability in aliphatic chain length and the two functional groups of carboxylate and sulfonate which correlate with diclofenac and dodecylbenzene sulfonate. The six PFAS and their properties are listed in Table 2-3, and their deprotonated molecular structures can be seen in Figure S3.

Table 2-3

*Perfluoroalkyl acids with sulfonate and carboxylate functional groups*

<b>Perfluoroalkyl substance (PFAS)</b>	<b>Molecular Weight (g/mol)</b>	<b>Functional Group</b>	<b>Fluoroalkyl Chain Length</b>	<b>Dissociation Constant pK<sub>a</sub><sup>a</sup></b>	<b>Log K<sub>ow</sub><sup>a</sup></b>
Perfluorobutanoic acid (PFBA)	214.04	Carboxylate	C <sub>4</sub>	-0.20	2.82
Perfluorohexanoic acid (PFHxA)	314.05	Carboxylate	C <sub>6</sub>	-0.13	4.06
Perfluorooctanoic acid (PFOA)	414.07	Carboxylate	C <sub>8</sub>	-0.16	5.30
Perfluorobutane sulfonate (PFBS)	300.10	Sulfonate	C <sub>4</sub>	-6.0	3.90
Perfluorohexane sulfonate (PFHxS)	400.11	Sulfonate	C <sub>6</sub>	-6.0	5.17
Perfluorooctane sulfonate (PFOS)	450.12	Sulfonate	C <sub>8</sub>	-6.0	6.43

<sup>a</sup> Values from (Smith et al., 2016)

## 2.1.3 Cosolvents for Regeneration

The cosolvents in solution with brine to test regeneration efficiency were methanol (CAS 67-56-1, Sigma-Aldrich), ethanol (CAS 64-17-5, Acros Organics), 1-propanol (CAS 71-23-8, Acros Organics), 1-butanol (CAS 71-36-3, Sigma-Aldrich), propylene glycol (CAS 57-55-6, MP Biomedicals), and glycerol (CAS 56-81-5, Sigma-Aldrich). The cosolvents were chosen for their variability in aliphatic chain length when compared to methanol or for their variability in hydroxyl group count when compared to 1-propanol. The effect of lengthening the alkyl chain length is greater hydrophobicity of the solvent as well as a higher boiling point which alludes to greater London dispersion forces in the monoalcohols as alkyl chain length increases (Burgess, 1978). A summary of characteristics of cosolvents is provided in Table 2-4.

Table 2-4

*Cosolvent characteristics*

<b>Cosolvent Name</b>	<b>Chemical Formula</b>	<b>Molecular Weight (g/mol)</b>	<b>Relative Density at 20°C (g/mL)</b>	<b>LogK<sub>ow</sub><sup>a</sup></b>	<b>Boiling Point (°C)<sup>a</sup></b>	<b>Alkyl Chain Length</b>	<b>Hydroxyl Group Count</b>
Methanol	CH <sub>3</sub> OH	32.04	0.79	-0.77	64.7	1	1
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	46.07	0.79	-0.31	78.2	2	1
1-Propanol	C <sub>3</sub> H <sub>7</sub> OH	60.10	0.81	0.25	97.2	3	1
1-Butanol	C <sub>4</sub> H <sub>9</sub> OH	74.12	0.81	0.88	117.7	4	1
Propylene Glycol	CH <sub>3</sub> CH(OH)CH <sub>2</sub> OH	76.09	1.04	-0.92	187.6	3	2
Glycerol	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> OH	92.09	1.26	-1.76	290.0	3	3

<sup>a</sup> Values sourced from PubChem

As salt content increased in the solution, the miscibility of salt water and cosolvent decreased, making certain mixtures fractionate and preventing them from being used in experiments. The miscibility profiles of the solutions were found empirically and can be found in the Appendix Table S1.

## 2.2 Experimental Methods

### 2.2.1 Resin Pretreatment

Resins were pretreated with excess  $\text{Cl}^-$  before use. 20 mL of each resin was determined by displacement in a 100 mL graduated cylinder initially filled with 50 mL water. The water was then decanted off, and the wet resins were desiccated for 24 h at 50°C.

The 20 mL of each dried resin was submerged in 1 L volumetric flasks containing NaCl solution at a concentration of ten times equivalency of the resins. A stir bar was submerged in each, and the resins were stirred at 250 rpm for 1 h to allow for complete saturation. The brine was decanted off, and the resins were washed continuously with DI water while the conductivity was measured. Once the conductivity dropped below 20  $\mu\text{S}/\text{cm}$ , little to no aqueous  $\text{Cl}^-$  remained. The resins were again desiccated at 50°C for 24 h, then weighed. The resin working density was then calculated as the dry mass of the resin divided by the wet volume to be used for all experiments.

### 2.2.2 PFAS on Resin Regeneration

One combined solution of the six PFAS compounds (PFBA, PFHxA, PFOA, PFBS, PFHxS, PFOS) was prepared with each concentration at 120  $\mu\text{M}$  in 2.1 L for a total of 720  $\mu\text{M}$  PFAS solution. The mixture was sonicated to ensure complete dissolution of all PFAS. A 100 mL aliquot in a volumetric flask was taken for pre-saturation analysis. The remaining 2 L of master mix were dispensed into two 1 L volumetric flasks. In each flask, 240  $\mu\text{eq}$  of A520E and A592E resin were added for a

total of three-times equivalency, and a stir bar was added; each was stirred at 250 rpm for 48 hours. The resins were then isolated from the saturation solution and partially dried via vacuum filtration with a MilliporeSigma WP6211560 115V 60Hz pump. The total damp resins were vacuum dried and were weighed and transferred into 50 mL conical tubes for storage. The resins were then parceled into ten approximately equal masses and placed into 125 mL amber vials. A 100 mL aliquot of each post-saturation solution was recovered in a 100 mL volumetric flask from each filtrate.

Resin regeneration was conducted for each parcel of resin saturated with PFAS. Regeneration solutions were synthesized in stock solutions in 1000 mL volumetric flasks. A 250 mL volumetric flask was used to measure the volume of solvent and volume of water needed for each regeneration solution. Solutions contained 0.5% NaCl on a m/m basis of the total regenerant solution. Table 2-5 contains the cosolvent conditions used for regeneration.

Table 2-5.

***Regeneration cosolvent mixture conditions prepared in 1 L volumetric flasks for 6 PFAS***

<b>Solvent</b>	<b>Volume % Solvent</b>	<b>Volume % Water</b>	<b>0.5% m/m NaCl (g)<sup>a</sup></b>
Methanol	25	75	4.7275
Ethanol	25	75	4.7250
1-Propanol	25	75	4.7388

<sup>a</sup> Mass per mass of total solution

The mass of sodium chloride on a total solution mass per mass basis was calculated based off the following equation:

$$\text{Mass NaCl} = (V_S\rho_S + V_W\rho_W) * (\text{Mass Fraction Salt})$$

$V_s$  is the volume of solvent (mL),  $\rho_s$  is the density of the solvent at 20°C (g/mL),  $V_w$  is the volume of water (mL),  $\rho_w$  is the density of water (g/mL).

To perform regeneration, 100 mL of each cosolvent, measured via graduated cylinder, was inserted into each amber bottle. The bottles were placed on a Thermo Scientific SHKE2000 MaxQ Shaker table and agitated at 250 rpm for 1 h which is consistent with past experiments (Dixit et al., 2020). After regeneration, each solution was passed through a 0.45  $\mu\text{m}$  cellulose acetate syringe filter into a 50 mL conical tube. For the regenerant solutions and the saved pre-saturation and post-saturation solutions, 0.5 mL was pipetted into 9.5 mL of DI water for an initial twenty-times dilution. From the initial dilutions, 1 mL was pipetted into 50 mL volumetric flasks which were then filled to 50 mL for a second fifty-times dilution for a total of a thousand-times dilution. Before analysis, samples were diluted further by an additional factor of one hundred for a total of 100,000 $\times$  dilution.

### 2.2.3 Diclofenac on Resin Regeneration

A total of four 9.0 mM solutions of diclofenac sodium, one for each of four resins (A502P, A520E, A532E, A592E), were prepared by dissolving 3.4538 g in 1.2 L which was distributed to a 1 L volumetric flask for the experiment and a 200 mL volumetric flask for pre-saturation analysis. A 0.5 mL aliquot was taken from the 200 mL volumetric



flask and diluted with DI water into a 100 mL volumetric flask for analysis. Then, 3.0 meq of each resin was added to each 1 L volumetric flask for a three times equivalency of diclofenac sodium to resin. A stir bar was added to each flask, and the mixtures were stirred at 250 rpm for 24 h to allow full saturation of the diclofenac anion onto each resin. The resins were then isolated from the saturation solution and partially dried via vacuum filtration with the same pump used for diclofenac. The total damp resins were allowed to dry and were weighed and transferred into 50 mL conical tubes for storage. The resin was separated into 50 equivalent parcels in 20 mL scintillation vials. A 100 mL aliquot of each post-saturation solution was recovered in a 100 mL volumetric flask from each filtrate. These post-saturation solutions had 1 mL aliquot taken from each and diluted with DI water into 100 mL volumetric flasks for analysis.

Resin regeneration was conducted for each parcel of resin saturated with diclofenac anion. Regeneration solutions were synthesized in stock solutions in 250 mL volumetric flasks. A 200 mL graduated cylinder was used to measure the volume of solvent and volume of water needed for each regeneration solution. Solutions always contained 5% NaCl on a mass per mass basis of the cosolvent mixture. Table 2-6 contains the the conditions of the cosolvent solutions used to regenerate diclofenac-loaded resin.

Table 2-6

***Regeneration cosolvent mixture conditions prepared in 250 mL volumetric flasks for diclofenac anion***

<b>Cosolvent</b>	<b>Volume % Solvent</b>	<b>Volume % Water</b>	<b>5% m/m NaCl (g)<sup>a</sup></b>
None	0	100	12.463
Methanol	25	75	11.822
Methanol	50	50	11.181
Methanol	75	25	10.541
Ethanol	25	75	11.813
1-Propanol	25	75	11.856
Propylene Glycol	25	75	12.566
Propylene Glycol	50	50	12.669
Propylene Glycol	75	25	12.772

<sup>a</sup> Mass per mass basis of total regenerant solution

To perform regeneration, 20 mL of cosolvent solution was pipetted into the 20 mL scintillation vials containing resin. The vials were placed on a Thermo Scientific SHKE2000 MaxQ Shaker table and agitated at 250 rpm for 1 hour, based off prior research (Dixit et al., 2020). A 1 mL aliquot was pipetted from the regeneration solution and diluted to 100 mL in a 100 mL volumetric flask. These dilutions were saved for analysis. The remaining resin and regeneration solution were disposed of in appropriate waste containers.

#### 2.2.4 Dodecylbenzene Sulfonate on Resin Regeneration

Resin saturation for the dodecylbenzene sulfonate procedures was performed twice for the entire procedure. One batch of resin was used for all of the 5% NaCl m/m solution regenerations. A second resin batch was used for the 0.5 and 0.05% NaCl m/m solution regenerations.

For the resins saturated with dodecylbenzene and regenerated with 5% NaCl m/m cosolvent solutions, total of three 9.0 mM solutions of sodium dodecylbenzene sulfonate, one for each resin (A502P, A520E, A592E), were prepared by dissolving 3.4499 g in 1.1 L which was distributed to a 1L volumetric flask for the experiment and a 100 mL volumetric flask for pre-saturation analysis. A 1.0 mL aliquot was taken from the 200 mL volumetric flask and diluted with DI water into a 100 mL volumetric flask for analysis. Then, 3.0 meq of each resin was added to each 1L volumetric flask for three-times equivalency of sodium dodecylbenzene sulfonate to resin. A stir bar was added to each flask, and the mixtures were stirred at 250 rpm for 24 hours to allow full saturation of the dodecylbenzene sulfonate anion onto each resin. The resins were then isolated from the saturation solution and dried via vacuum filtration with a MilliporeSigma WP6211560 115V 60Hz pump. The total resins were weighed and transferred into 50 mL conical tubes for storage. The resin was separated into fifty roughly equivalent parcels in 20 mL scintillation vials. A 100 mL aliquot of each post-saturation solution was recovered in a 100 mL volumetric flask from each filtrate. These post-saturation solutions had 1 mL aliquot taken from each and diluted with DI water into 100 mL volumetric flasks for analysis. Loaded mass and saturation percent were calculated via the same method used for diclofenac and PFAS anions. The conditions for regenerant solutions are listed in Table 2-7.

Table 2-7

***Regeneration cosolvent mixture conditions prepared in 200 mL volumetric flasks for dodecylbenzene sulfonate anion, 5% NaCl***

<b>Solvent</b>	<b>Volume % Solvent</b>	<b>Volume % Water</b>	<b>0.5% m/m NaCl (g)<sup>a</sup></b>	<b>0.05% m/m NaCl (mg)<sup>a</sup></b>
None	0	100	0.9970	99.7
Methanol	5	95	0.9867	98.7
Methanol	25	75	0.9455	94.6
Methanol	50	50	0.8940	89.4
Methanol	75	25	0.8425	84.3
Ethanol	5	95	0.9866	98.7
Ethanol	25	75	0.9450	94.5
Ethanol	50	50	0.8930	89.3
Ethanol	75	25	0.8410	84.1
1-Propanol	5	95	0.9872	98.7
1-Propanol	25	75	0.9478	94.8
1-Propanol	50	50	0.8985	89.9
1-Propanol	75	25	0.8493	84.9
1-Butanol	5	95	0.9877	98.8

<sup>a</sup> Mass per mass basis of total solution

For the resins saturated with dodecylbenzene and regenerated with both 0.5% NaCl and 0.05% NaCl m/m cosolvent solutions, a similar method was followed with a few slight deviations. Firstly, although a three-times equivalency of dodecyl benzene sulfonate to resin was still maintained, the solution concentrations were lowered to 3.0 mM dodecylbenzene sulfonate, and the resin was 1.0 meq/L. The parcel sizes were smaller in mass, but this allowed for 10× dilutions rather than 100× dilutions for analysis.

For resin regenerations at 5% m/m NaCl was conducted for each parcel of resin saturated with dodecylbenzene sulfonate anion. Regeneration solutions were synthesized in stock solutions in 200 mL volumetric flasks. A 200 mL graduated cylinder was used to

measure the volume of solvent and volume of water needed for each regeneration solution. Solutions always contained 5% NaCl on a mass per mass basis of the cosolvent mixture. The method for calculating the amount of NaCl needed for each regenerant solution followed the diclofenac procedure.

Regenerating with 0.5 and 0.05% NaCl followed the same procedure as above, but additional trials were performed so that each monoalcohol cosolvent solution would be analyzed for regeneration at 5, 25, 50, and 75% ABV excluding 1-butanol, and no further regeneration procedures were attempted for propylene glycol and glycerol. The regenerant cosolvent mixture parameters are listed below in Table 2-8.

Table 2-8

*Regeneration cosolvent mixture conditions prepared in 200 mL volumetric flasks for dodecylbenzene sulfonate anion, 0.5 and 0.5% NaCl values*

<b>Solvent</b>	<b>Volume % Solvent</b>	<b>Volume % Water</b>	<b>5% m/m NaCl (g)</b>
None	0	100	9.970
Methanol	25	75	9.455
Methanol	50	50	8.940
Methanol	75	25	8.425
Ethanol	25	75	9.450
1-Propanol	25	75	9.478
1-Butanol	5	95	9.877
Propylene Glycol	25	75	10.053
Propylene Glycol	75	25	10.218
Glycerol	25	75	10.603
Glycerol	75	25	11.868

Regeneration was carried out via the same method used for diclofenac and PFAS anions. Regeneration efficiency was calculated via the same method as well.

### 2.3 Analytical Methods

The pH and conductivity measurements were completed using an Orion Dual Star Multiparameter meter, Orion 9156BNWP Combination pH probe, and an Orion Star A212 conductivity probe. Precision of regeneration of resin and reuptake of Cl<sup>-</sup> was checked by running regenerations in triplicate, and triplicate results were averaged to determine values. The concentrations of both diclofenac anion and dodecylbenzene sulfonate anion were determined by UV absorbance using a UV-Visible Spectrophotometer (UV-Vis 2700, Shimadzu) operating in photometric mode at a single wavelength. Previous work has found diclofenac anion has a maximum peak absorbance around 275 nm (da Silva et al., 2015; Landry & Boyer, 2013). A 5-point calibration curve was created using serially diluted standard concentrations of 0.0 mmol/L, 0.01 mmol/L, 0.02 mmol/L, 0.05 mmol/L, and 0.075 mmol/L ( $R^2 = 0.99998$ ). Measurements of experimental samples were checked by comparing standards with the calibration curve beforehand.

A previous study has found dodecylbenzene sulfonate has a maximum peak absorbance at 223 nm (Ni et al., 2018). A 7-point calibration curve was created using serially diluted standard concentrations of 0.0 mmol/L, 0.001 mmol/L, 0.01 mmol/L, 0.02 mmol/L, 0.05 mmol/L, 0.08 mmol/L, and 0.095 mmol/L ( $R^2 = 0.99983$ ). Each measurement of experimental samples was preceded by checking at least three standards with the calibration curve to maintain accuracy.

For the analysis of the six PFAS saturated onto resins then regenerated, an Agilent high pressure liquid chromatograph (HPLC, 1100) utilizing gradient elution and a Phenomenex Gemini C18 column (110 Å, 100×3 mm, 5µm) was used in accordance with past experiments (Dietz et al., 2021). The HPLC was outfitted with two additional guard columns, a C18 guard column and a Zorbax Diol guard column (12.5×4.6 mm, 6 µm). The total apparatus was paired with a Sciex 3200 triple quadruple mass spectrometer in multiple reaction monitoring and negative electrospray ionization mode. Between the pump and the autosampler was a Luna C18 delay column (100 Å, 30×3 mm, 5 µm), and injections were performed at 20 µL volume. The delay column and Optima Grade LC/MS water and methanol were used to eliminate possible background contamination of PFAS contamination. The flow rate was maintained at 0.8 mL/min, and the gradient mobile phase was comprised of 20 mM ammonium acetate in water and methanol, beginning with 5% methanol raised to 60% methanol in 45 seconds, further raised to 100% methanol over 4 minutes, and maintained for 3 additional minutes. The methanol concentration was then lowered to 5% over 1 minute and then maintained at 5% for an additional 2 minutes. PFAS standard compounds were attained from Wellington Laboratories.

## 2.4 Data Analysis

Regeneration efficiency was calculated on a mass basis. The amount of saturant on the resin was calculated by mass balance in the pre- and post-solutions. After the saturated resins were weighed, the mass of saturant on each parcel was determined by the mass fraction of the parcel to the total mass of saturated resin. All batch protocols were

conducted in triplicate. Error was represented as standard deviation for regeneration experiments, and error bars on graphs represent one standard deviation from the mean in all cases. Comparing the concentrations of the initial pre-saturation solution and the post-saturation solution allows for the formulation of how much mass was loaded onto the resin, displacing Cl<sup>-</sup> ion.

$$M_L = (C_i - C_f)V$$

$M_L$  is the mass of saturant anion loaded onto the resin (mmol),  $C_i$  is the initial concentration of the saturant anion pre-saturation (mmol/L),  $C_f$  is the final concentration of the saturant anion post-saturation,  $V$  is the volume of solution used to saturate (L). Resin saturation percent was also calculated based off the reported capacity of the resin compared to the capacity found experimentally.

$$\text{Saturation \%} = (M_L/M_P) * 100$$

Saturation % is the ratio of the capacity of the resin determined experimentally to the capacities published by the manufacturer,  $M_L$  is the amount of saturant anion loaded onto the resin (mmol),  $M_P$  is mass of resin used based off its published equivalency (meq).

Regeneration efficiency was calculated using the new concentration of diclofenac anion in the regeneration solution after the resin had been regenerated with Cl<sup>-</sup>.

$$\text{Regeneration \% Efficiency} = \frac{C_R V_R}{(R_P/R_T) * M_L} * 100\%$$



$C_R$  is the concentration of saturant anion in the regeneration solution (mmol/L),  $V_R$  is the volume of the regeneration solution (L),  $R_P$  is the resin parcel mass,  $R_T$  is the total mass of the saturated resin (mg).  $M_L$  is the mass of contaminant or saturant loaded onto the resin during saturation (mmol).

## 2.5 Modeling Regeneration of dodecylbenzene sulfonate

Multivariable linear regression analyses were conducted using Microsoft Excel extension Analysis Toolpak and the LINEST function. For the three resins used for regeneration with dodecylbenzene sulfonate saturated, backwards step-wise regressions were performed with ten starting parameters of pure monoalcohol solvent characteristics ultimately being chosen to create models to predict regeneration efficiency based off cosolvent and solution characteristics. These parameter values are found in Table SWWW. The null hypothesis stated that there was no significant correlation ( $p > 0.05$ ) between cosolvent characteristics and regeneration efficiency. The alternative hypothesis stated that there was a significant correlation between cosolvent characteristics and regeneration efficiency ( $p < 0.05$ ) and that a model could be generated to predict regeneration efficiency from an alcohol solvent solution.

## 2.6 Economic, Safety, and Sustainability Considerations

Economic analysis was performed by sourcing normalized prices of solvents and salts from two large laboratory suppliers and then averaging the costs to form a baseline operating cost. Solvent costs were normalized to 1L of ACS grade 99+% purity of

solvent. Salt was normalized to 1 kg of sodium chloride. Table 2-9 shows the cost of these solvents for the month of June 2022 and their averages.

Table 2-9

***Regenerant solution chemical costs for the month of June 2022, normalized to 1L and 1kg of ACS grade products***

<b>Cosolvent</b>	<b>Methanol</b>	<b>Ethanol</b>	<b>1-Propanol</b>	<b>1-Butanol</b>	<b>Propylene Glycol</b>	<b>Glycerol</b>	<b>Sodium Chloride</b>
<b>Amount</b>	<b>1 L</b>	<b>1 L</b>	<b>1 L</b>	<b>1 L</b>	<b>1 L</b>	<b>1 L</b>	<b>1 kg</b>
Chemical Supplier #1	\$61.10	\$146.00	\$92.30	\$92.30	\$97.00	\$188.00	\$73.10
Chemical Supplier #2	\$46.70	\$204.50	\$79.00	\$124.70	\$81.80	\$107.10	\$115.50
Average	\$53.90	\$175.25	\$85.65	\$108.50	\$89.40	\$147.55	\$94.30

As can be seen from Table 2-9, the solvents were similarly priced for the same quality of product, but the discrepancies are accounted for in the average. The normalized cost of a total cosolvent solution disregarded the cost of water needed to be added to the solution.

$$Solution\ Cost\ (\$/L) = \left( \frac{1\ L}{Cosolvent\ Price} \right) * \left( \frac{Cosolvent\ Volume}{Fraction} \right) + \left( \frac{NaCl\ mass}{1000g} \right) * \left( \frac{1\ kg}{NaCl\ Price} \right)$$

The analysis of effective cost was then determined by dividing solution cost by regeneration efficiency to determine a cost per regeneration percent for each parameter. As the total value decreased, the cost-effectiveness of the regeneration solution increased.

Considering safety of regenerant solutions, a flashpoint above 20° C was operationally considered to be safe. As water volume fraction increases, flashpoint

temperature increases, but literature has shown that high water volume fraction inhibits resin regeneration. The purpose of this consideration, therefore, is to find an optimal point where flashpoint temperature is above expected operating temperatures, but regeneration is still able to achieve 90+ %. Table 2-10, below, shows the flashpoints of various alcohol and water mixtures. Note that 1-butanol is not miscible with water past 9% ABV, so no values were recorded after 5% ABV.

Table 2-10

***Flashpoints of alcohol and cosolvent solutions determined through direct citation and interpolation***

<b>Alcohol</b>	<b>Cosolvent Volume Fraction with Water</b>			
	<b>0.05</b>	<b>0.25</b>	<b>0.5</b>	<b>0.75</b>
Methanol <sup>a</sup>	77 °C	41 °C	27 °C	19 °C
Ethanol <sup>b</sup>	58 °C	29 °C	23 °C	19 °C
1-Propanol <sup>a</sup>	52 °C	33 °C	31 °C	30
1-Butanol <sup>a</sup>	50 °C	NA	NA	NA

<sup>a</sup> Direct values from (Astbury et al., 2005)

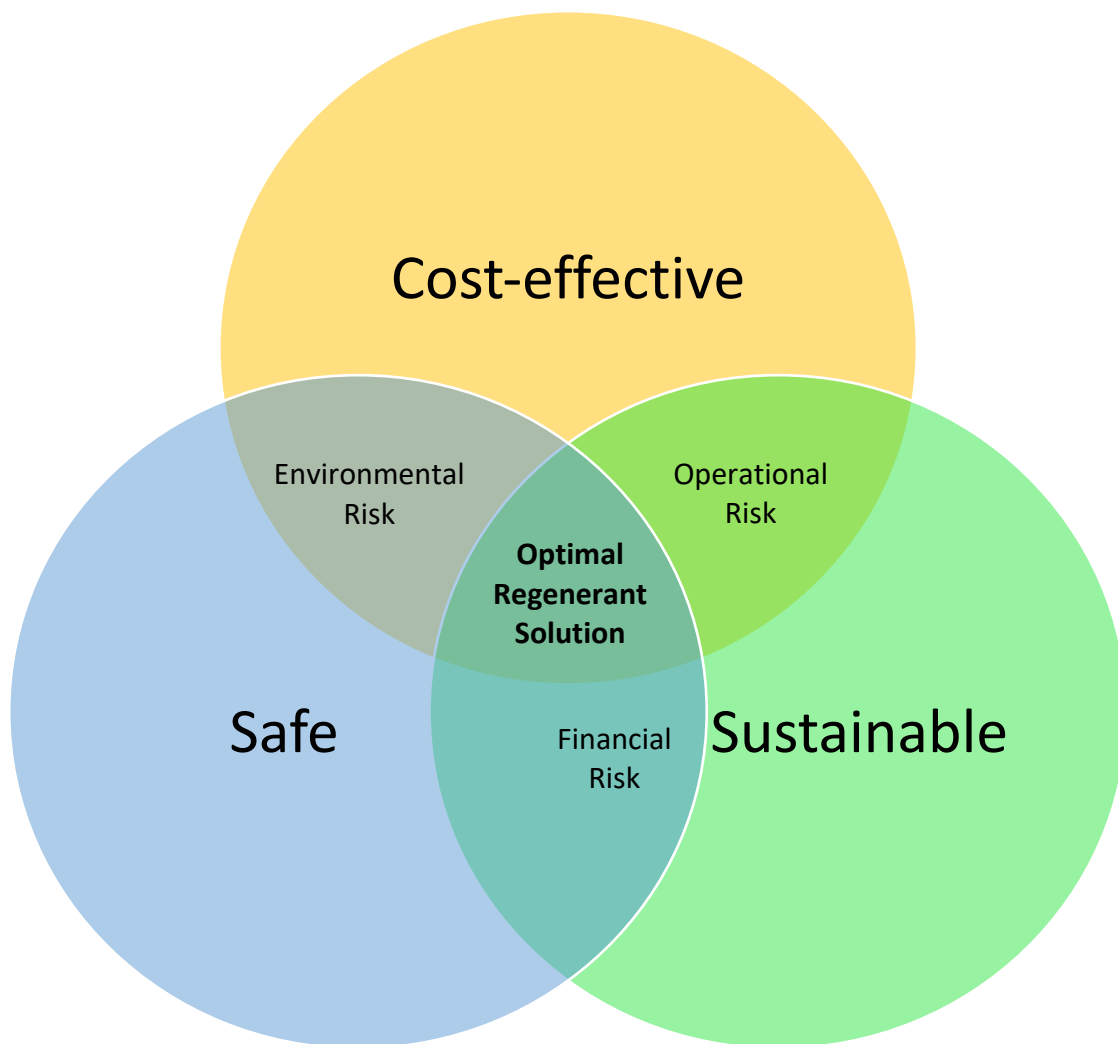
<sup>b</sup> Interpolated values from (Martínez et al., 2005)

The final practical engineering consideration is sustainability. Both the production of alcohol from sugars and the final oxidation of alcohols release carbon dioxide emissions. Although it has already been established there are a variety of factors that go into the sustainability of a resin regenerant solution, such as carcinogen release, ecotoxicity, etc., this study will focus on potential for global warming as a function of carbon dioxide emissions from incineration of waste regenerant solution (Boyer, Ellis, et al., 2021; Dubois et al., 1995). Similar to the previous cost analysis, resin regeneration is

compared against 1 L of normalized solution and the carbon dioxide emission potential therein. The equation is listed below.

$$CO_2 \text{ Emission Potential} \left( \frac{gCO_2}{L \text{ Regen.Sol.}} \right) = \left( \frac{1 L}{\text{Regen.}} \right) * \left( \frac{\text{Cosolvent}}{\text{Volume Fraction}} \right) * \rho_{\text{Cosolvent}} * \frac{1}{MW_{\text{Cosolvent}}} * \left( \frac{\text{Mol } CO_2}{\text{Mol Cosolvent}} \right) * 44 \frac{g}{\text{mol}} CO_2$$

When considering alternatives to high ABV methanol as regenerant solution, the initial focus needs to be regeneration strength. If the alternative cannot approach the same level of regeneration as the standard, then there is no reason to proceed with further consideration, but if other cosolvent solutions rival or even surpass the standard, then the next steps are to consider cost, safety, and sustainability. Figure 2-1, below, shows the breakdown of these considerations.



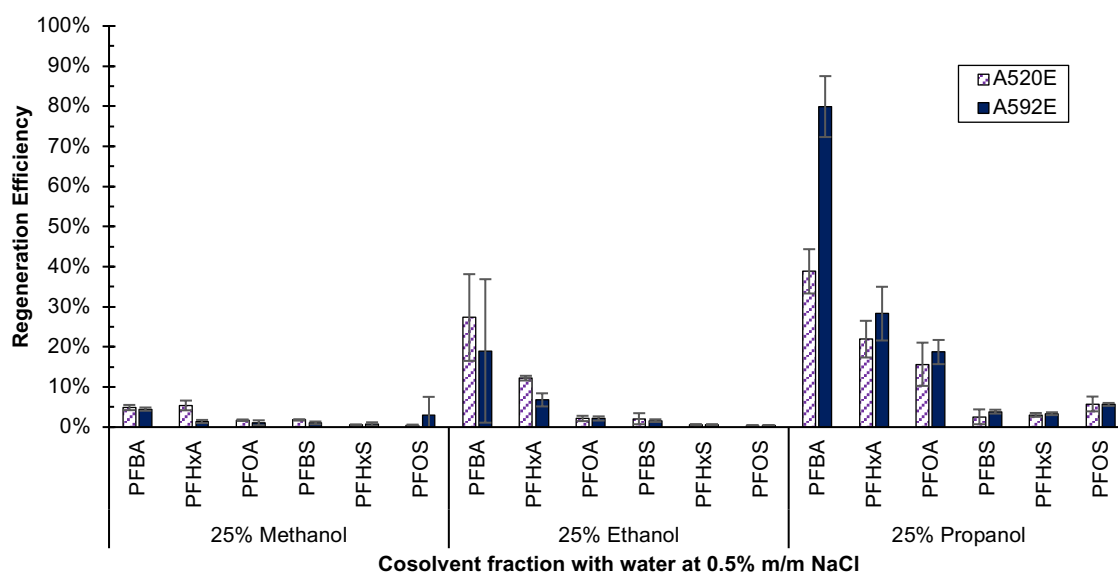
*Figure 2-1.* Venn diagram of cosolvent optimization for regeneration when regeneration efficiency is high, highlighting the specific issue if any factor is ignored.

## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 Evaluation of PFAS saturant regeneration

Two polystyrene macroporous anion exchange resins (A520E, A592E) were saturated with six PFAS anions, three carboxylates and three sulfonates, and then regenerated with three different alcohols (methanol, ethanol, 1-propanol) all at 25% ABV with 75% water and 0.5% NaCl m/m of total solution. The results of this experiment can be found below in Figure 3-1.



**Figure 3-1.** Regeneration efficiency of two Purolite strong-base polystyrene anion exchange resins saturated with three perfluoroalkyl carboxylates: perfluorobutanoate (PFBA), perfluorohexanoate (PFHxA), and perfluorooctanoate (PFOA), as well as three perfluoroalkyl sulfonates: perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS) and regenerated with 0.5% NaCl on a mass per mass basis for each given cosolvent parameter. Legend: Purolite Resin A520E (diagonal striped purple), Purolite Resin A592E (solid navy). All data are measured

values. All measured data are mean values of duplicate samples with error bars showing one standard deviation.

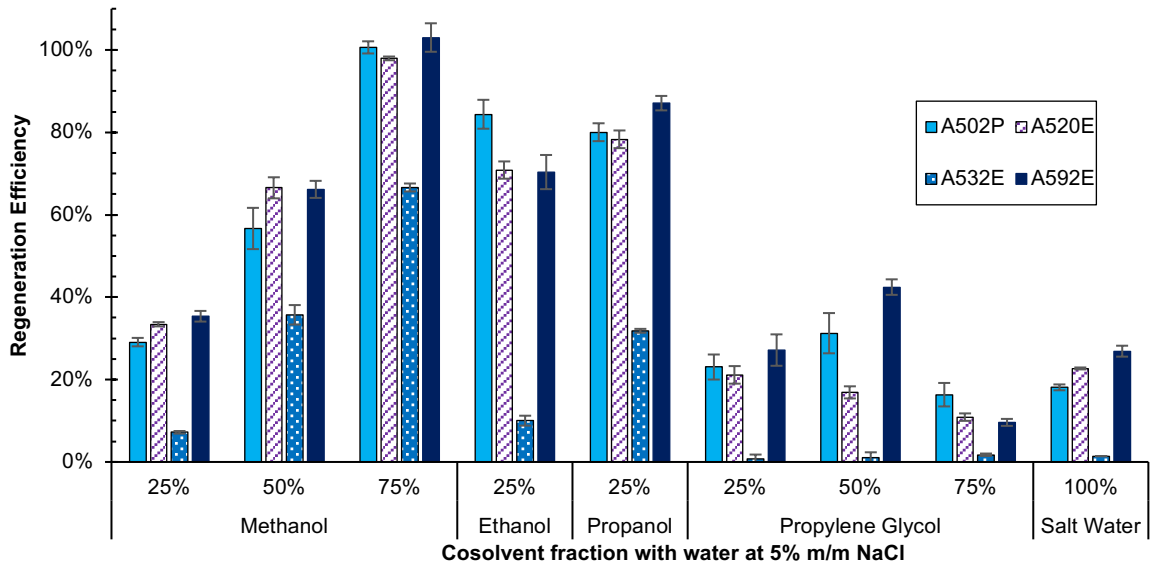
Across all three regenerant solutions, desorption of perfluoroalkyl carboxylate compounds from the resin was greater than perfluoroalkyl sulfonate compounds. Furthermore, removal of short-chain PFAS from the resins was higher than long-chain PFAS. These results reflect the combination of electrostatic and non-electrostatic interactions between the PFAS and the resin. Carboxylate has weaker electrostatic interactions with the resin than sulfonate, and the shorter perfluoroalkyl chains have weaker non-electrostatic interactions than the longer perfluoroalkyl chains. Although overall regeneration was < 90% for all PFAS experiments, the expected trend was observed that for equivalent ABV and 0.5% NaCl regenerant solutions, 1-propanol outperformed ethanol which outperformed methanol. As the alkyl chain on the alcohol lengthened, the solution became more nonpolar, and the dielectric constant of the solution decreased allowing for more desorption of the hydrophobic PFAAs from the resin (Li & SenGupta, 1998). For typical hydrogenated alkyl chains, the Van der Waals forces and London dispersion forces between the organic anion and the cosolvent would contribute to the desorption from the resin, but the presence of fluoroalkyl chains diminishes the polarizability of the compound that would allow these weak intermolecular forces (Adam et al., 2015). Although Van der Waals dispersion forces may still exist, they are certainly less than those exhibited by conventional alkyl chain interactions. Furthermore, the steric hindrance of PFAAs increases with fluoroalkyl chain length, making it more difficult for a counterion to displace them from the resin which also matched results. Despite the

overall low regenerations, the superiority of equivalent ABV and NaCl concentration 1-propanol compared to ethanol and methanol observation served as the proof of concept for further experiments into desorbing organic compounds from saturated resins using novel alcohol cosolvents of longer alkyl chains.

### 3.2 Evaluation of diclofenac saturant regeneration

Four polystyrene anion exchange resins were probed for regeneration after being saturated with diclofenac which features a carboxylate head group. Three of the resins were macroporous (A502P, A520E, A592E), and one resin was gel-type (A532E). Past work has shown that resin uptake of diclofenac anion is characterized by electrostatic interaction between the deprotonated carboxylate head group on diclofenac and the quaternary ammonium complex on the resin as well as by Van der Waals forces and the  $\pi$  -  $\pi$  interactions between the resin divinyl benzene group and the aromatic rings on diclofenac. (Kassar, 2022; Landry & Boyer, 2013; Landry et al., 2015). This suggests that regenerating the resin requires a cosolvent solution that promotes these same or similar interactions but between the cosolvent and the HIOC. Figure 3-2 shows the results of the regeneration experiment comparing mono-alcohols and diol at different ABV.





**Figure 3-2.** Regeneration efficiency of four Purolite strong-base polystyrene anion exchange resins saturated with diclofenac anion and regenerated with 5% NaCl on a mass per mass basis for each given cosolvent parameter. Legend: Purolite Resin A502P (solid sky blue), Purolite Resin A520E (diagonal striped purple), Purolite Resin A532E (dotted blue), Purolite Resin A592E (solid navy). All data are measured values. All measured data are mean values of duplicate samples with error bars showing one standard deviation.

As can be seen in Figure 3-2, increasing the volume fraction of methanol led to greater regeneration for all four resins. At 75% methanol by volume, all three macroporous resins achieved 90+ % regeneration. This result was to be expected as this is the common volume ratio of methanol that is conventionally used for optimal regeneration of organic-loaded resin. When comparing volume ratios that were the same, i.e. 25% methanol versus ethanol versus 1-propanol, all resins achieved greater regeneration with 1-propanol than with ethanol than with methanol. This shows that for

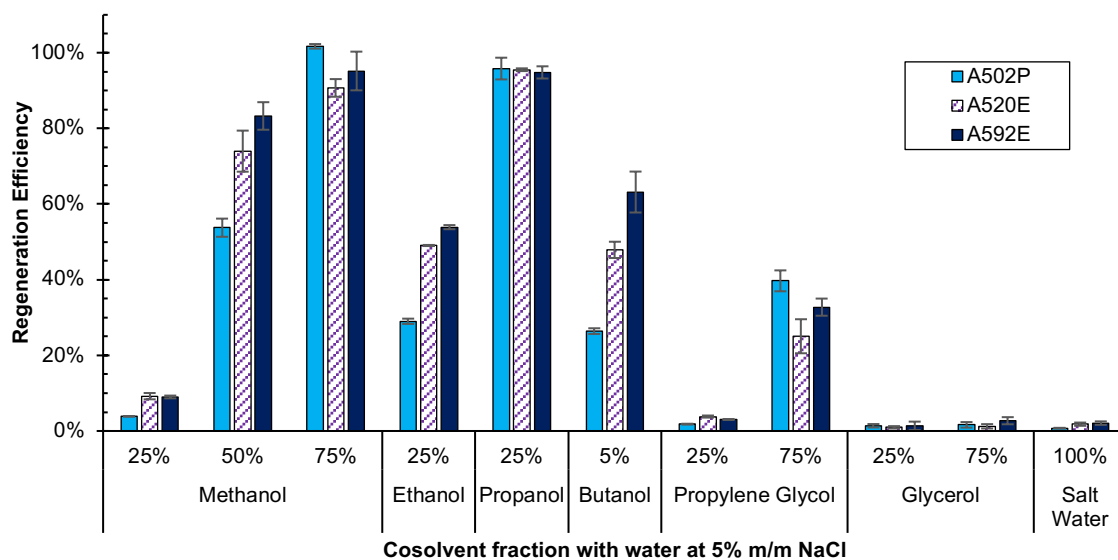
equivalent alcohol concentrations, the HIOCs will more readily desorb when the alkyl chain of the cosolvent alcohol is longer. This is in part due to the non-electrostatic Van der Waals intermolecular interactions between the nonpolar tail of the alcohol and the nonpolar body of the HIOC, promoted by the decreased dielectric constant of the overall solution (Adam et al., 2015; Burgess, 1978). Because salt concentrations were held equal, and regeneration at 25% ABV varied across alcohols, electrostatic forces between the resin quaternary ammonium and the carboxylate in competition with chloride counterion were not the determination of regeneration efficiency. Propylene glycol was probed as a polyol alternative due to its nontoxicity, ready availability, nonflammability, and similar structure to 1-propanol. However, propylene glycol did not achieve even 50% with any of the resins or at 25% or 75% volume fraction. The single gel-type resin A532E showed the lowest regeneration across all experiments which matched prior literature on the difficulty of regenerating gel type PS SB-AERs (Zaggia et al., 2016). Although resin A532E has been shown to be effective for removal of HIOCs, regeneration of the resin is higher with macroporous PS SB-AERs.

### 3.3 Dodecylbenzene sulfonate

#### 3.3.1 Evaluation of regeneration

Three PS SB-AERs were saturated with surfactant dodecylbenzene sulfonate ion then regenerated under different cosolvent conditions. Whereas diclofenac contains a carboxylate functional group, dodecylbenzene sulfonate contains a sulfonate functional group. The regenerant solutions were made of different alcohols and polyols at varying

ABV with brine at different NaCl concentrations. For the 5% NaCl m/m regeneration experiments, high salt concentration prevented miscibility with high ABV ethanol and methanol. The diol propylene glycol and triol glycerol were examined in addition with the monoalcohols. The results of this experiment are seen in Figure 3-3.

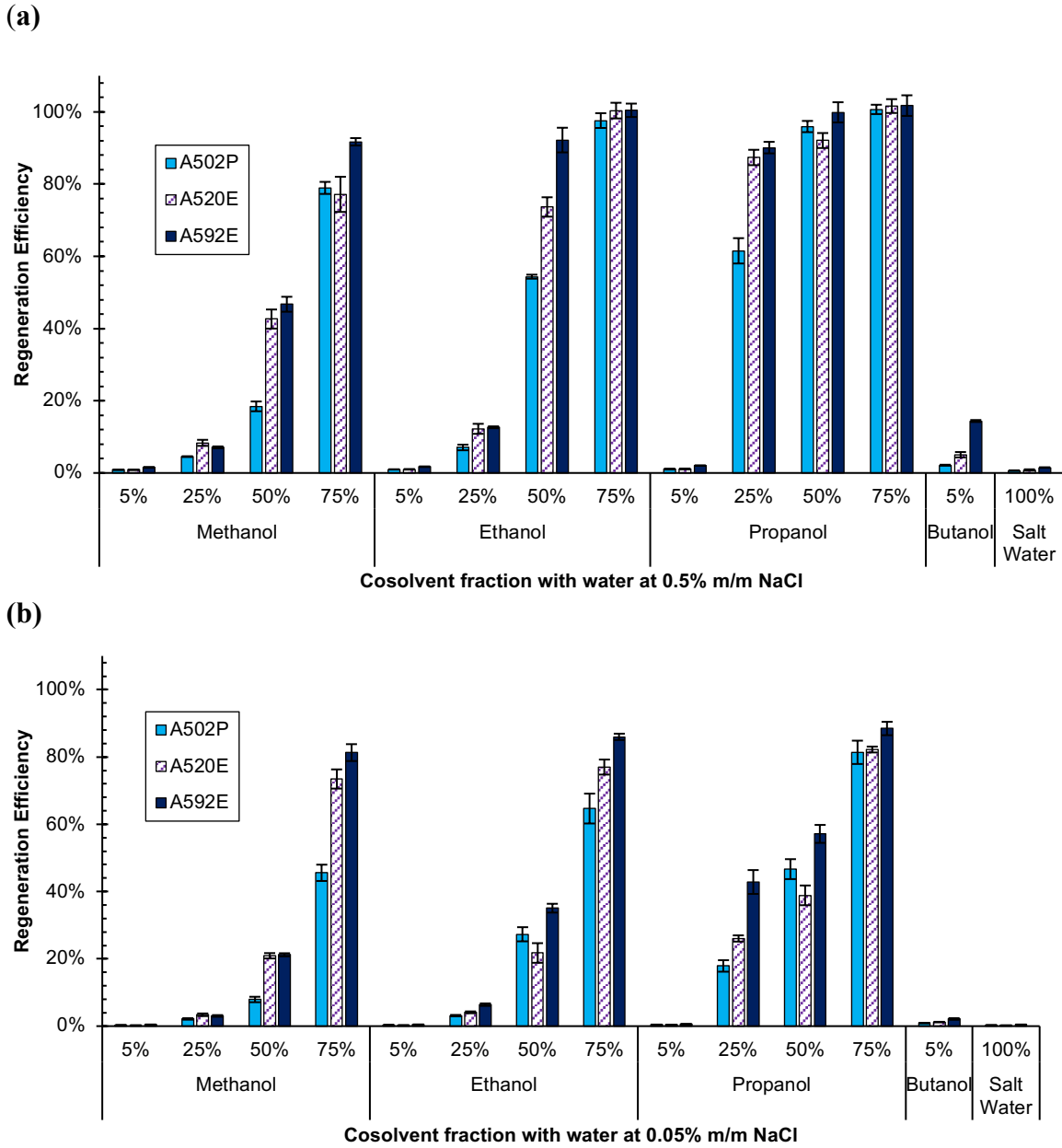


**Figure 3-3.** Regeneration efficiency of three Purolite strong-base polystyrene anion exchange resins saturated with dodecylbenzene sulfonate anion and regenerated with 5% NaCl on a mass per mass basis for each given cosolvent parameter. Legend: Purolite Resin A502P (solid sky blue), Purolite Resin A520E (diagonal striped purple), Purolite Resin A592E (solid navy). All data are measured values. All measured data are mean values of duplicate samples with error bars showing one standard deviation.

Similar to the results seen with the diclofenac procedure at 5% m/m NaCl, increasing the volume fraction of methanol led to greater regeneration and desorption of dodecylbenzene sulfonate across all resins. When comparing 25% ABV across alcohols, i.e. methanol versus ethanol versus 1-propanol, all resins achieved greater regeneration

with 1-propanol than with ethanol than with methanol. In addition, even though the 1-butanol regenerant solution was only 5% ABV, it achieved  $63.2 \pm 5.4\%$ . Again, these results highlight the effect that the decrease in polarity of the regenerant solution has on the ability of the HIOC to desorb from the resin and dissolve in solution. Similar to the diclofenac procedure, propylene glycol was not an effective regenerant, and glycerol proved to be worse, achieving approximately the same regeneration as the brine solution without cosolvent.

For the 0.5 and 0.05% m/m NaCl regenerant solutions, the decreased salt concentration allowed greater miscibility for high ABV solutions with methanol, ethanol, and 1-propanol. Propylene glycol and glycerol, given their poor results with 5% m/m NaCl regenerant solutions were not continued. The results of these procedures are found in Figure 3-4, below.



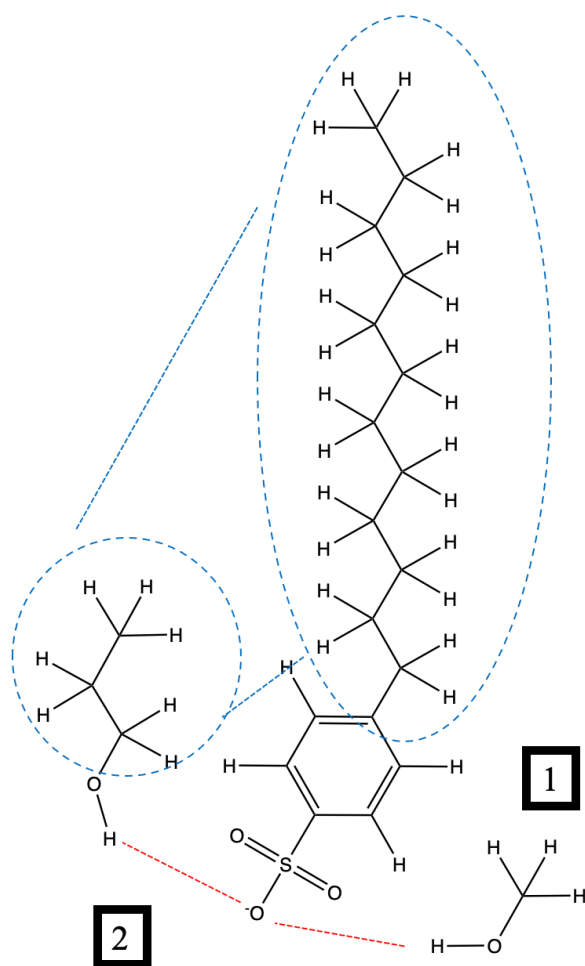
**Figure 3-4.** Regeneration efficiency of three Purolite strong-base polystyrene anion exchange resins saturated with dodecylbenzene sulfonate anion and regenerated with 0.5% NaCl (a) and 0.05% NaCl (b) on a mass per mass basis for each given cosolvent parameter. Legend: Purolite Resin A502P (solid sky blue), Purolite Resin A520E (diagonal striped purple), Purolite Resin A592E (solid navy). All data are measured

values. All measured data are mean values of duplicate samples with error bars showing one standard deviation.

The key takeaways from interpreting the results of the 0.5% and 0.05% NaCl regenerations are again the cosolvent solution parameters. For 0.5% NaCl regenerative cosolvent solutions, 75% ethanol and 75% 1-propanol achieved greater than 90% regeneration for all resins, and 75% methanol did not. In addition, 50% 1-propanol achieved greater than 90% regeneration while 50% ethanol did not. These results show the favorability of the HIOCs to desorb off the resin back into a more nonpolar solution where nonpolar interactions dominate. That said, electrostatic effects still play a large role as regeneration decreased for all cosolvent solutions when the salt concentration dropped from 0.5% to 0.05%. Because no cosolvent matrix with 0.05% NaCl achieved at least 90% regeneration, this salt concentration was determined to be too low for adequate regeneration. The correlative relationship between salt concentration and regeneration is further evidenced by comparing the regeneration experiments at 5% m/m NaCl for equivalent ABV. For 25% ABV ethanol and 25% 1-propanol, decreasing the salt concentration from 5% to 0.5% saw a loss in regeneration efficiency which further decreased when the salt concentration dropped to 0.05%. This demonstrates that regeneration of the resin and desorption of the HIOC is both dependent on the polarity of the cosolvent as well as the concentration of the counterion.

During desorption, the strong electrostatic bond between the HIOC sulfonate group and the quaternary ammonium is disrupted by the introduction of an alcohol

cosolvent. The oxygen in the hydroxyl group on the alcohol draws electrons towards itself and away from the hydrogen due to its electronegativity, and the hydrogen atom maintains a slight positive charge for ionic hydrogen bonding with the sulfonate group (Meot-Ner, 2005). This electrostatic force is weaker than the cation/anion electrostatic force exhibited by the quaternary ammonium and sulfonate, so additional forces are needed to desorb dodecylbenzene sulfonate from the resin. Increasing cosolvent ABV and salt concentration decreases the dielectric constant which allows for greater solubility of dodecylbenzene sulfonate. Finally, longer chain alcohols, and the London dispersion forces between the HIOC alkyl tail and the alcohol alkyl tail assist in desorption from the resin. These interactions are only possible for the longer chain alcohols and do not occur with methanol. A qualitative figure displaying this phenomenon is found below in Figure 3-5.



**Figure 3-5.** Intermolecular relationships between dodecylbenzene sulfonate ion and (1) methanol, showing only ionic hydrogen bonding (red), and (2) 1-propanol, showing both ionic hydrogen bonding (red) and London dispersion forces (blue). Note that explicit hydrogen atoms are shown.



### 3.3.2 Model Interpretation

Modeling the regenerative capabilities of three polystyrene macroporous anion exchange resins saturated with dodecylbenzene sulfonate was performed as a multivariate linear analysis with ten initial parameters in backwards step-wise function. The regeneration of resin A502P was found to be a function of four statistically significant parameters: cosolvent volume fraction, cosolvent molar mass, ionic strength, and  $K_{ow}$ . Regeneration of resin A520E was found to be a function of three statistically significant parameters: cosolvent volume fraction, cosolvent molar mass, and ionic strength. Regeneration of resin A592E was also found to be a function of three statistically significant parameters: cosolvent volume fraction, ionic strength, and  $K_{ow}$ . The empirically determined equations are found below in Figure 3-6.

(a)

$$\text{A502P Regeneration Efficiency} = -0.809 + \left( \frac{\text{Cosolvent volume}}{\text{fraction}} \right) * 1.16 + \left( \frac{\text{Cosolvent molar}}{\text{mass}} \right) * 0.0158 + \left( \frac{\text{Ionic}}{\text{Strength}} \right) * 0.391 + (K_{ow}) * 0.0570$$

(b)

$$\text{A520E Regeneration Efficiency} = -0.524 + \left( \frac{\text{Cosolvent volume}}{\text{fraction}} \right) * 1.26 + \left( \frac{\text{Cosolvent molar}}{\text{mass}} \right) * 0.00861 + \left( \frac{\text{Ionic}}{\text{Strength}} \right) * 0.411$$

(c)

$$\text{A592E Regeneration Efficiency} = -0.140 + \left( \frac{\text{Cosolvent volume}}{\text{fraction}} \right) * 1.32 + \left( \frac{\text{Ionic}}{\text{Strength}} \right) * 0.373 + (K_{ow}) * 0.0435$$

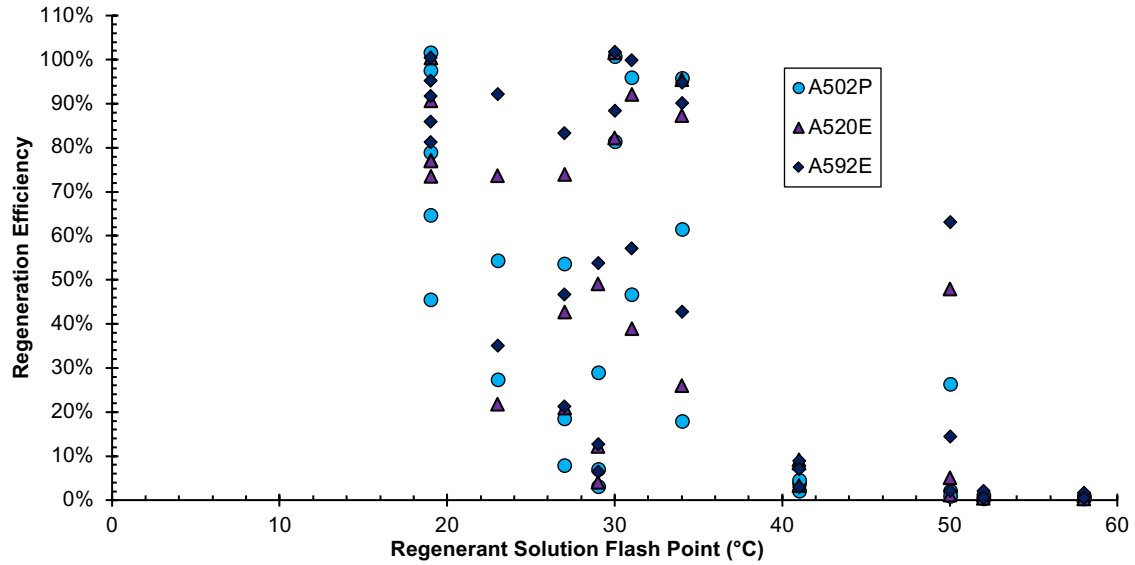
**Figure 3-6.** Three multivariate linear functions of regeneration efficiency for resins A502P (a), A520E (b), and A592E (c). Statistical significance was defined at 95% confidence interval  $p < 0.05$  for each parameter.

they primarily serve to illuminate the key parameters relevant to regeneration and how those parameters will either increase or decrease regeneration of the resin. Firstly, cosolvent volume fraction was one of two parameters that was statistically significant for all three resins used in the experiment. For all three resins, the coefficient was positive, indicating that increasing the amount of cosolvent volume fraction increased regeneration. The other parameter that was common across all three models was ionic strength. The ionic strength coefficient was also always positive, indicating that as salt concentration in the solution increased, the regeneration efficiency increased. The tradeoff here is that as more salt is dissolved in solution, the more nonpolar alcohols will no longer be miscible with the brine solution. Surprisingly, dielectric constant was not

determined to be a significant variable which does not match expectations from previous literature that cites dielectric constant of the regenerant solution as one of the most important factors for regeneration (Gu et al., 2001; Li & SenGupta, 2001). This highlights some of the limitations of the model used. As alcohol volume fraction and salt concentration increase, the dielectric constant of the overall solution will decrease. While there are both empirical datasets and various models for dielectric constant determinations of binary alcohol and water solutions as well as single solute with water solutions and single solute in alcohol solutions, there is limited data on solutions that contain water, alcohol, and salt (Akhadov, 1980; Zuber et al., 2014). Therefore, the pure solvent dielectric constant did not significantly correlate with resin regeneration per the models.

### 3.3.3 Flammability, Cost, and Sustainability

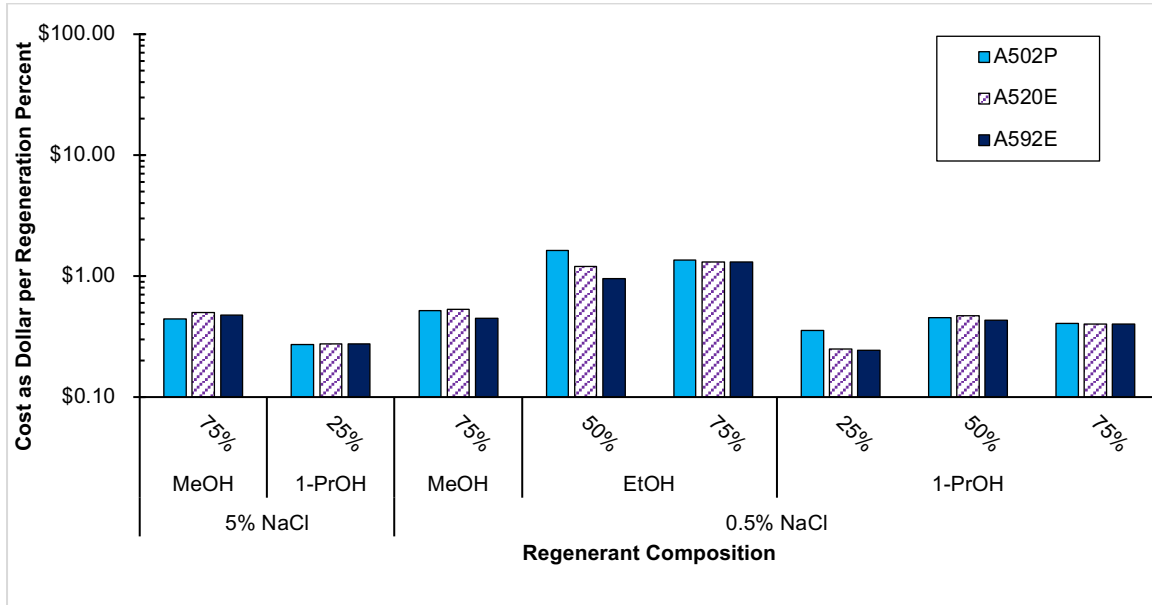
One safety consideration when handling alcohol cosolvent is the flammability of the mixture. As the volume percent of alcohol increases, the flashpoint temperature decreases. For the purposes of this study, a flashpoint above room temperature (20 °C) was operationally defined as the “safe” limit. Regeneration solutions that achieved  $\geq 90\%$  regeneration for at least one resin and had a flashpoint above 20 °C were considered to be both effective and safe for regeneration when considering flammability. A scatterplot of regeneration efficiency versus solution flashpoint is below in Figure 3-7.



**Figure 3-7.** Regeneration efficiencies for various cosolvent compositions across three resins compared to regenerant solution flashpoint for three resins

The solutions that achieved both objectives for regeneration and flashpoint for at least one resin were 25% 1-propanol with 5% NaCl; 50% and 25% ethanol with 0.5% NaCl; and 25, 50, and 75% 1-propanol with 0.5% NaCl. Most regenerant solutions fell outside the optimal range, and a general trend was observed that as flashpoint temperature increased, regeneration decreased. This is not surprising based off the data and models that showed that increasing cosolvent volume fraction increased regeneration, and increasing cosolvent fraction of an alcohol decreased flashpoint.

Cost of regenerant solution is another practical consideration for engineering. Each regenerant solution was normalized to the cost of 1 L from the average of two large chemical suppliers. The results of this analysis are shown below in Figure 3-8.

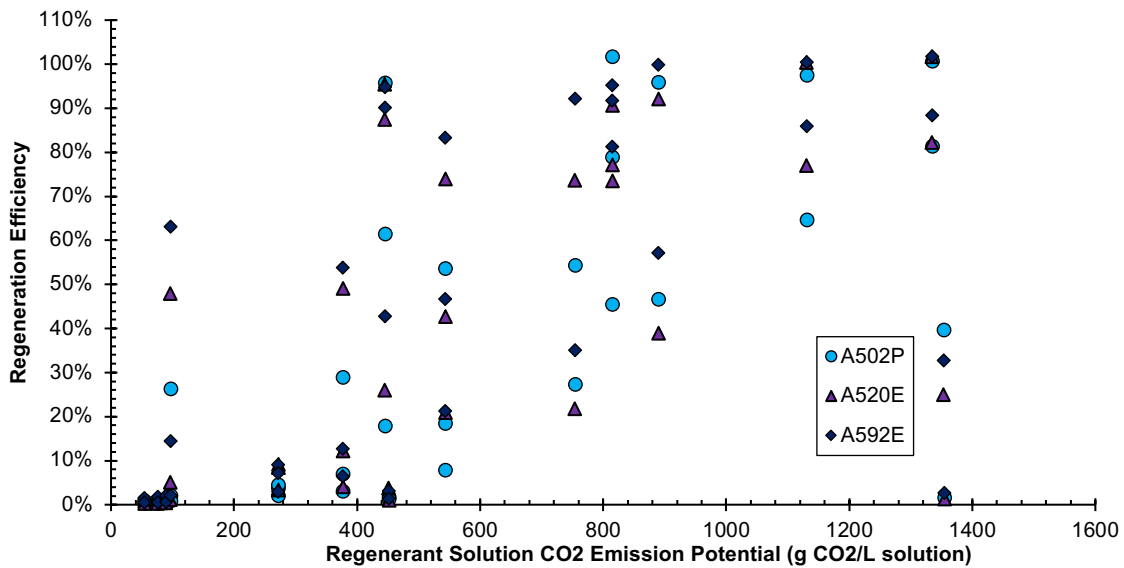


**Figure 3-8.** Cost effectiveness of regenerant solutions for dodecylbenzene sulfonate determined by normalized cost of 1L regenerant solution divided by regeneration for the given experiment for regeneration solutions that achieved at least 90%. Note the Y-axis is logarithmic. Legend: Purolite Resin A502P (sky blue circle), Purolite Resin A520E (purple triangle), Purolite Resin A592E (navy diamond).

The results of this analysis show a wide discrepancy to the point where a logarithmic scale was needed to display the results together. The most cost-effective regenerant solution for any resin loaded with dodecylbenzene sulfonate ion was found to be A592E with 5% ABV 1-butanol at 5% NaCl. The cost per regeneration percent was \$0.16/Regen%. However, this solution only achieved  $63.2 \pm 5.4\%$ . If the results are truncated to only include regeneration efficiencies of 90+ %, the best performing regenerant solution for the three resins is 25% ABV 1-propanol with 5% NaCl at an

average of \$0.27/Regen%. Similar to the flashpoint determination, the 25% ABV 1-propanol with 5% NaCl solution is the optimal solution.

Sustainability considerations were determined by the CO<sub>2</sub> emission potential of 1 L of normalized solvent. The results of this analysis are shown below in Figure 3-9.



**Figure 3-9.** Regeneration efficiencies for various cosolvent compositions across resins compared to g CO<sub>2</sub> emission potential per L regenerant solution. Legend: Purolite Resin A502P (sky blue circle), Purolite Resin A520E (purple triangle), Purolite Resin A592E (navy diamond).

An overall trend positive is seen for regeneration efficiency vs. carbon dioxide emission potential. The regeneration experiments established that increasing the CO<sub>2</sub> emission potential generally increased with regeneration efficiency. If an arbitrary designation is made to consider only regeneration that achieved 90+ % and had a CO<sub>2</sub>

emission potential of 500 g CO<sub>2</sub>/Lsol., only 25% ABV 1-propanol accomplishes that goal at 445 g CO<sub>2</sub>/Lsol. Based off the above assessments for safety, cost-effectiveness, and sustainability, 25% ABV 1-propanol with 5% NaCl is determined to be the optimal regenerant, being the only one to meet all three criteria.

Considering future sustainability practices when using regenerative cosolvents for spent anion exchange resin, particularly when regenerating resins saturated with organic compounds, distillation byproducts from ethanol fermentation could play a role in resin regeneration. Distilleries make three cuts during the distillation process to separate the desired consumable product from which are the head, heart, and tail for spirit production (Botelho et al., 2020; Caldeira et al., 2019). The cuts are designed to separate the ethanolic spirit from unpleasantly flavored and even toxic compounds like methanol, propanol, butanol, and fusel oils which are also included in the initial mash (Christoph & Bauer-Christoph, 2007). If longer chain alcohols are successful in regenerating saturated resins, then these distillation byproducts could be considered for recycled use as regenerant solutions for AERs. Efforts have been made to decrease the concentration of methanol in the heart which would allow for greater concentrations of methanol as byproduct to be recycled for use in anion exchange resin (Lucca et al., 2013). Furthermore, carbon dioxide is generated during fermentation, and the process is a significant contributor to the global carbon budget, so recycling the distillation byproducts would reduce the overall carbon budget on two fronts (Becker et al., 2020). The limitation to implementation of distillation byproducts as novel regenerant hinges on a few factors. An analysis of the heads, hearts, and tails cuts of distillate from fermented

*Arbutus unedo* found that the concentration of ethanol in the heads cut was 64.77% v/v with far lower concentrations of other alcohols at 3.87 g/L methanol, 0.10 g/L 1-propanol, and 0.45 g/L isobutanol (Caldeira et al., 2019). If combined with salt, this solution could act as a regenerant, provided the other organic anions in the head cut distillate do not exchange onto the resin. This could be mitigated with acid addition to protonate any organic anions.



## CHAPTER 4

### CONCLUSION

This study examined the regeneration capabilities of anion exchange resins after they had been saturated with hydrophobic ionizable organic compounds. The following are the key conclusions from the research.

First, regeneration of resins with monoalcohol cosolvents other than methanol shows efficacy with HIOC saturants. The conventional use of ~70% methanol with dissolved salt is adequate at higher salt concentrations of 5% m/m NaCl, but dropping salt concentration to 0.5% m/m NaCl prevented resin regeneration with methanol from achieving 90% with dodecylbenzene sulfonate, whereas 50 and 75% 1-propanol solution with 0.5% were able to accomplish 90+% regeneration for all resins. Longer alkyl chains on monocalcohols and high salt concentration promoted a lower overall solution dielectric constant which prevented miscibility of alkyl chain alcohols with the brine. Dodecylbenzene sulfonate ion shares structural similarities with perfluoroalkyl sulfonic acids and general regeneration trends can be extrapolated, but whereas the twelve-carbon alkyl chain of dodecylbenzene sulfonate can interact with Van der Waals and London dispersion forces, the electron density of perfluoroalkyl chains limits polarizability and provides steric hindrance for counterions to access the quaternary ammonium (Adam et al., 2015)

Second, this research further supported existing literature that regeneration efficiency of resins loaded with organics depends on competition from both electrostatic

and non-electrostatic forces between the loaded organic anion and the resin as well as the organic anion and the cosolvent solution. Electrostatic ionic hydrogen bonding between alcohols and the functional group are assisted by non-electrostatic Van der Waals and London dispersion forces to promote desorption from the resin (Boyer, Fang, et al., 2021; Dietz et al., 2021; Gu et al., 2001; Kassir, 2022; Landry & Boyer, 2013; Li & SenGupta, 1998).

Third, this research revealed the experimental gaps in anion exchange resin regeneration for organic-loaded resins concerning cosolvents. In addition to the standard methanol cosolvent, ethanol, 1-propanol, and 1-butanol prove to be not only viable alternatives but even more efficient for HIOC desorption when other variables are kept consistent. As these experiments were conducted in batch protocol, column experiments demand attention to confirm these preliminary results, and alternative salts besides NaCl should be tested in addition to a wider range of cosolvents.

Fourth, considerations for engineering of a larger scope and scale point to novel cosolvent regenerants beyond methanol as preferable for concerns of cost, safety, and sustainability. Furthermore, recycled waste streams from other industries like commercial distillation could serve as regenerant solutions in certain settings. Future experiments should analyze the viability of amending and adapting these recycled byproducts for sustainable regeneration.

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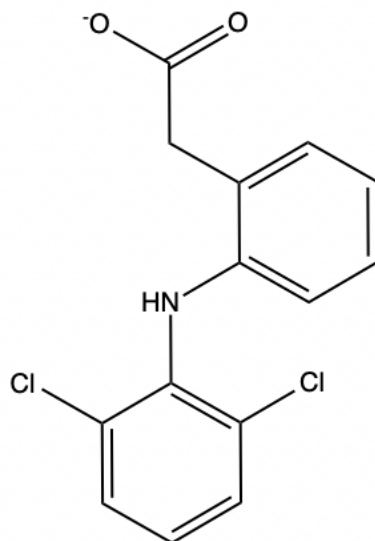
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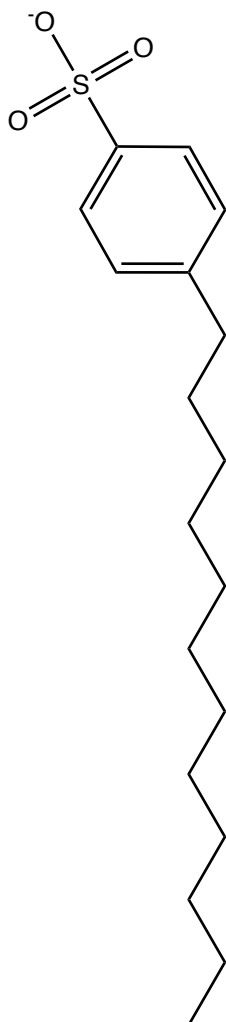
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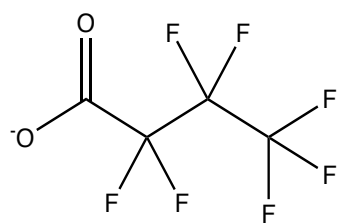
APPENDIX A  
SUPPLEMENTARY FIGURES



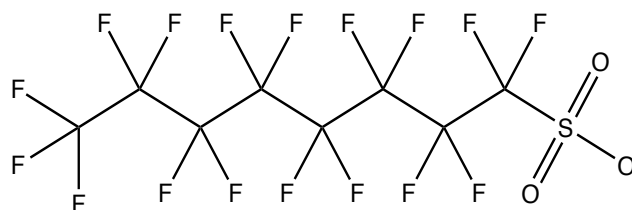
**Figure S1.** Diclofenac anion molecular structure



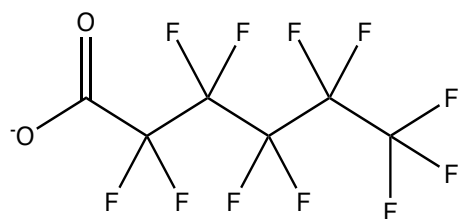
*Figure S2.* Dodecylbenzene sulfonate anion molecular structure



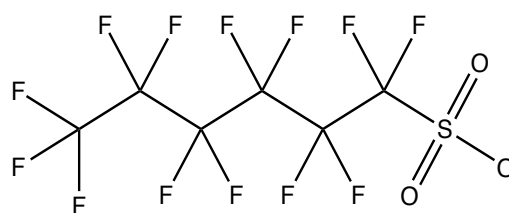
Perfluorooctanoic Acid (PFOA)



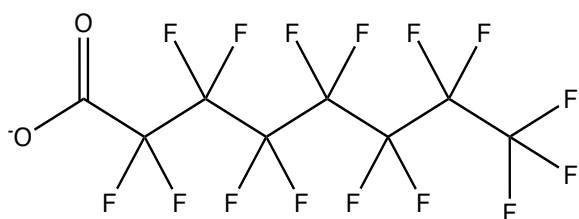
Perfluorooctanesulfonic Acid (PFOS)



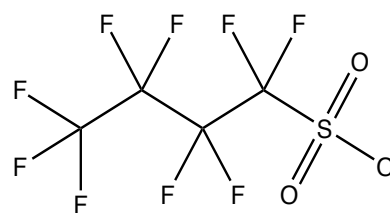
Perfluorohexanoic (PFHxA)



Perfluorohexanesulfonic Acid (PFHxS)



Perfluorobutanoate (PFBA)



Perfluorobutanesulfonic Acid (PFBS)

**Figure S3.** Six deprotonated perfluoroalkyl acid anions

APPENDIX B  
SUPPLEMENTARY TABLES

Table S1

*Solubility of NaCl in pure alcohol solvent conditions at 25 °C*

<b>Solvent</b>	<b>Solubility of NaCl <sup>a</sup> (g NaCl / kg solvent)</b>
Water	360
Methanol	14
Ethanol	0.65
1-Propanol	0.12
1-Butanol	0.050
Propylene glycol	71
Glycerol	83

<sup>a</sup> Sourced from (Burgess, 1978)

Table S2

*Empirically determined miscibility of monoalcohol cosolvent and brine solutions*

Alcohol	Salt Content (m/m)	Cosolvent Volume Fraction			
		0.05	0.25	0.5	0.75
Methanol	0.05	Miscible	Miscible	Miscible	Miscible
	0.5	Miscible	Miscible	Miscible	Miscible
	5	Miscible	Miscible	Miscible	Miscible
Ethanol	0.05	Miscible	Miscible	Miscible	Miscible
	0.5	Miscible	Miscible	Miscible	Miscible
	5	Miscible	Miscible	Immiscible	Immiscible
1-Propanol	0.05	Miscible	Miscible	Miscible	Miscible
	0.5	Miscible	Miscible	Miscible	Miscible
	5	Miscible	Miscible	Immiscible	Immiscible
1-Butanol	0.05	Miscible	Immiscible	Immiscible	Immiscible
	0.5	Miscible	Immiscible	Immiscible	Immiscible
	5	Miscible	Immiscible	Immiscible	Immiscible