Combine Optimization of Surfactant Enhanced Recovery and ISCO Alkaline Activation to Treat a Brazilian Latosol Soil Contaminated with DRO Diesel

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Brazilian Context and Challenges

- Trapped contamination in soil has been the main cause of unsuccessful remediation processes in Brazil:
  - Lack of soil characterization;
  - Granulometry and organic matter.

Effective for extraction?

Best flushing conditions/concentration?

Behavior in soil?

- Soil flushing with surfactants → good alternative to mobilize contaminants from soil to GW:
  - Enhance extraction;
  - Better chemical in situ treatment in GW.

Objectives

- What we were expecting in the beginning:
  - Evaluate the behavior of surfactants in a Brazilian soil rarely studied, impacted with one of the most common contaminants (Diesel DRO);
  - Evaluate the extraction performance for 2 different surfactants;
    - Rates of contaminants' extraction (BTEX, PAH, TPH);
    - Relations with soil.
  - Test with Design of the Experiment (DOE) three main factors:
    - Surfactant concentration;
    - Flushing time;
    - Flow rate.
  - To test if the solubilized and mobilized NAPL (Diesel) can be oxidized in liquid phase and still allows the re-use of remaining surfactant in GW.

The Experiment

- Latosol → most common kind of soil formed under tropical conditions
  - 750 mi ha (World) → 300 mi ha (Brazil);
  - Rich in clays and iron oxide;
  - Our latosol: 61% clay, 23% silt / dystrophic red latosol (LV56)

- Contaminant: Brazilian Diesel (DRO)

5 kg of dried and sieved latosol (6 hours in 70ºC)

5 g of Diesel → contaminant

84 experiment runs in glass columns (172g soil in each column)

Surfactant V10
0, 1, 2, 3 and 4 g/L
+ duplicate

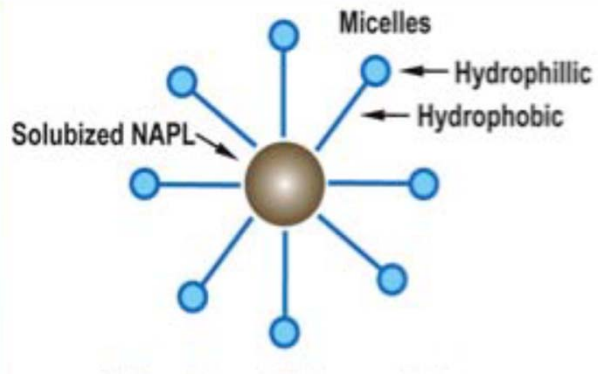
Surfactant V3
0, 1, 2, 3, 4, 5 and 10 g/L
+ duplicate

4 soil samples for analysis representative results (few variation)

Surfactants

- Surfactants are Surface Active Agents that Lower the Surface Tension of a Liquid and Decrease the Interfacial Tension between Two Liquids;

- Can act as: Detergent / Wetting agent / Emulsifier / Foaming agent / Dispersant



Surfactant V10

- Plant-derived
- Non-ionic
- Fatty odor
- Specific gravity:
  1.030 – 1.038
- Chlorinated solvent, petroleum fuel oils (diesel, gasoline, …)

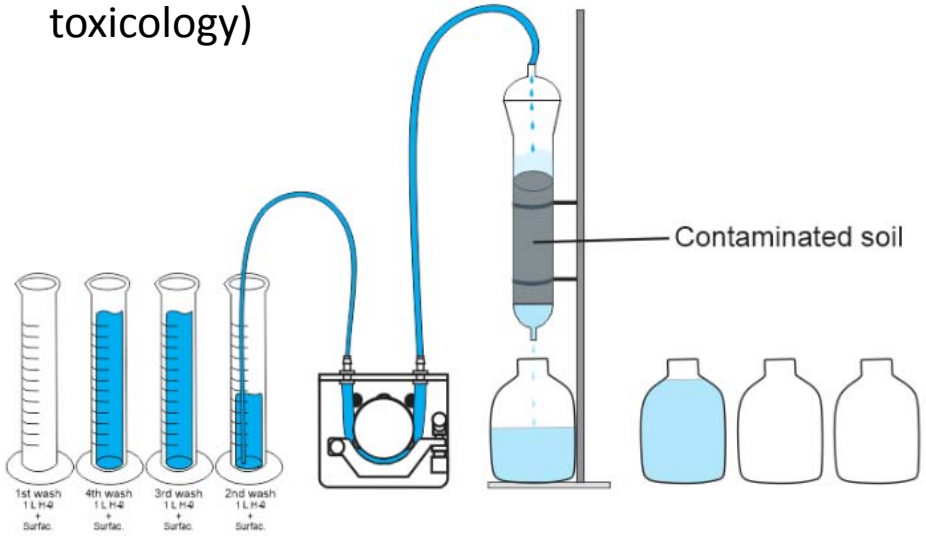
Surfactant V3

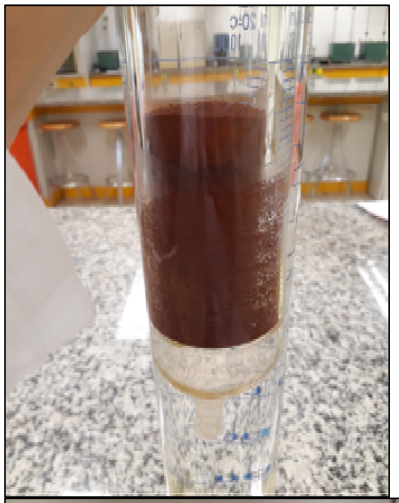
- Plant-based citrus solvent
- Non-ionic
- Specific gravity:
  0.972 – 0.984
- Heavier HCs

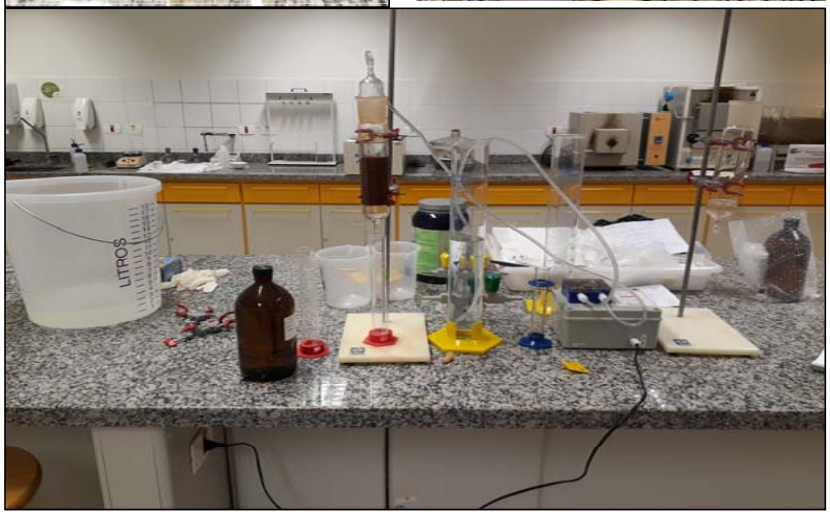
Biodegradability test – 90% in 13 days

The Experiment

- Columns:
  - 172 g of contaminated soil in each column;
  - Saturation with distilled water from base to top;
  - 4 L surfactant solution flush (4 flushes/washes of 1L);
  - Measurement of flow rates and residence time → important factors for extraction rates;
  - TPH and BTEX are compounds of interest (amount and toxicology)

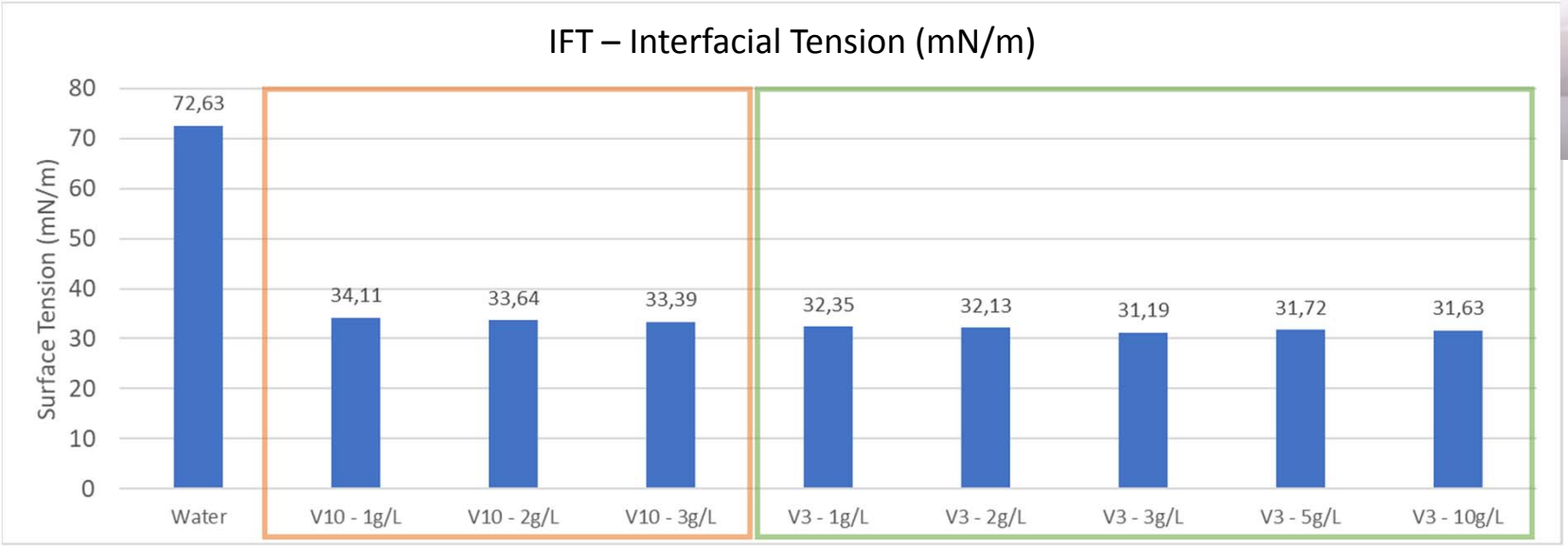




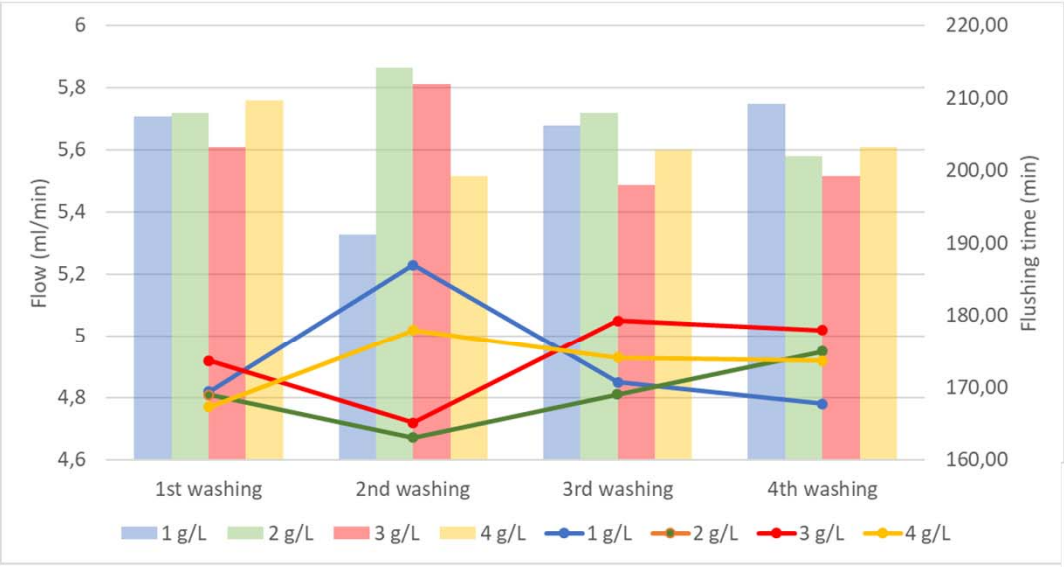


Results

- Surface tension of water: reduced from 72.63 to 31.19 mN/m;
- Both surfactants were able to remove contaminants, in different levels;
- No results were observed in washing with water only (control) → no extraction;
- Surfactant concentration, flow rate and flushing time were key factors observed.



Results



Surfactant V10

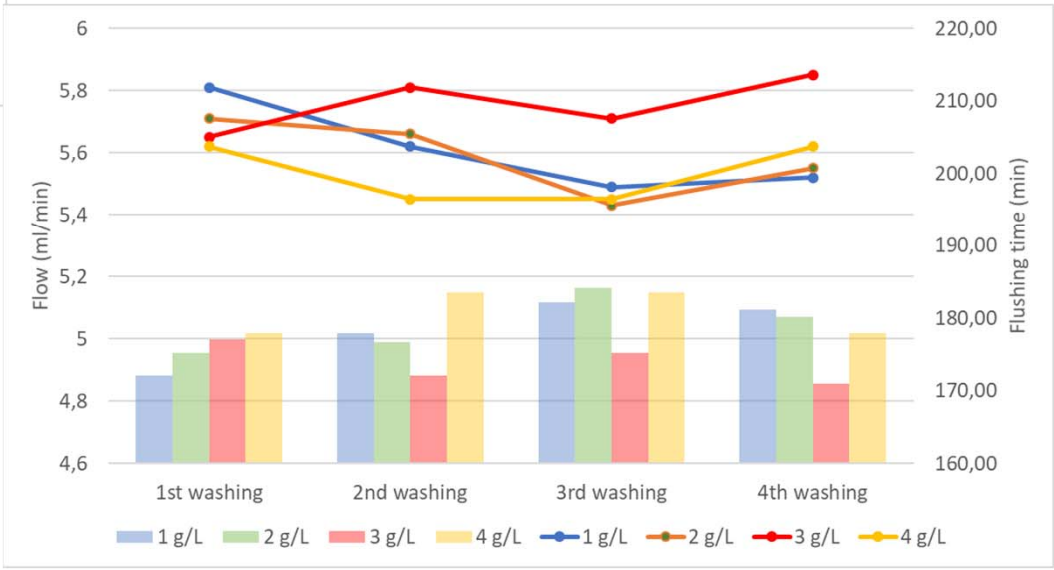
Average Flow Rate: 4,89 ml/min

Average Flushing time: 204,58 min

Surfactant V3

Average Flow Rate: 5,62 ml/min

Average Flushing time: 177,97 min



TPH Extraction by Wash - Surfactants V10 and V3

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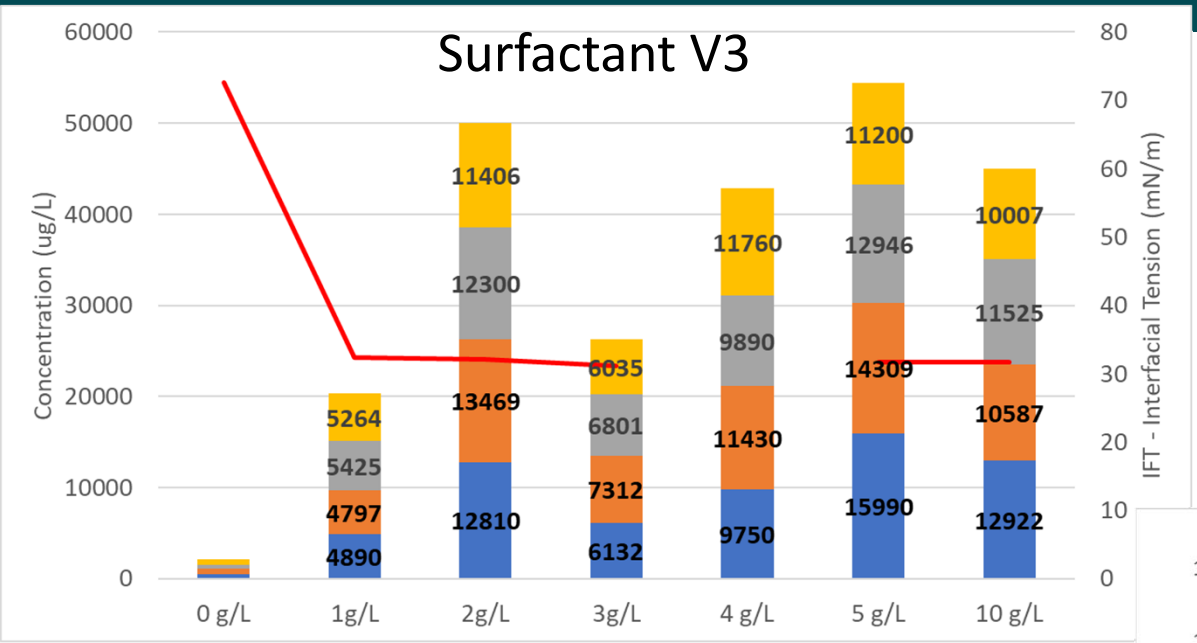
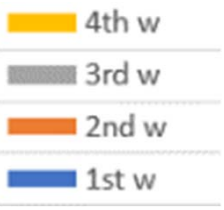
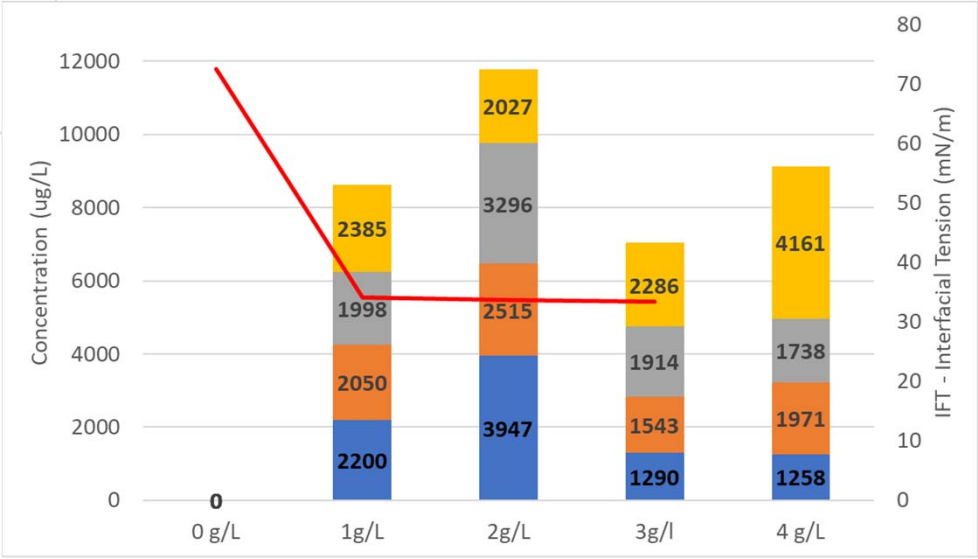
Surfactant V3

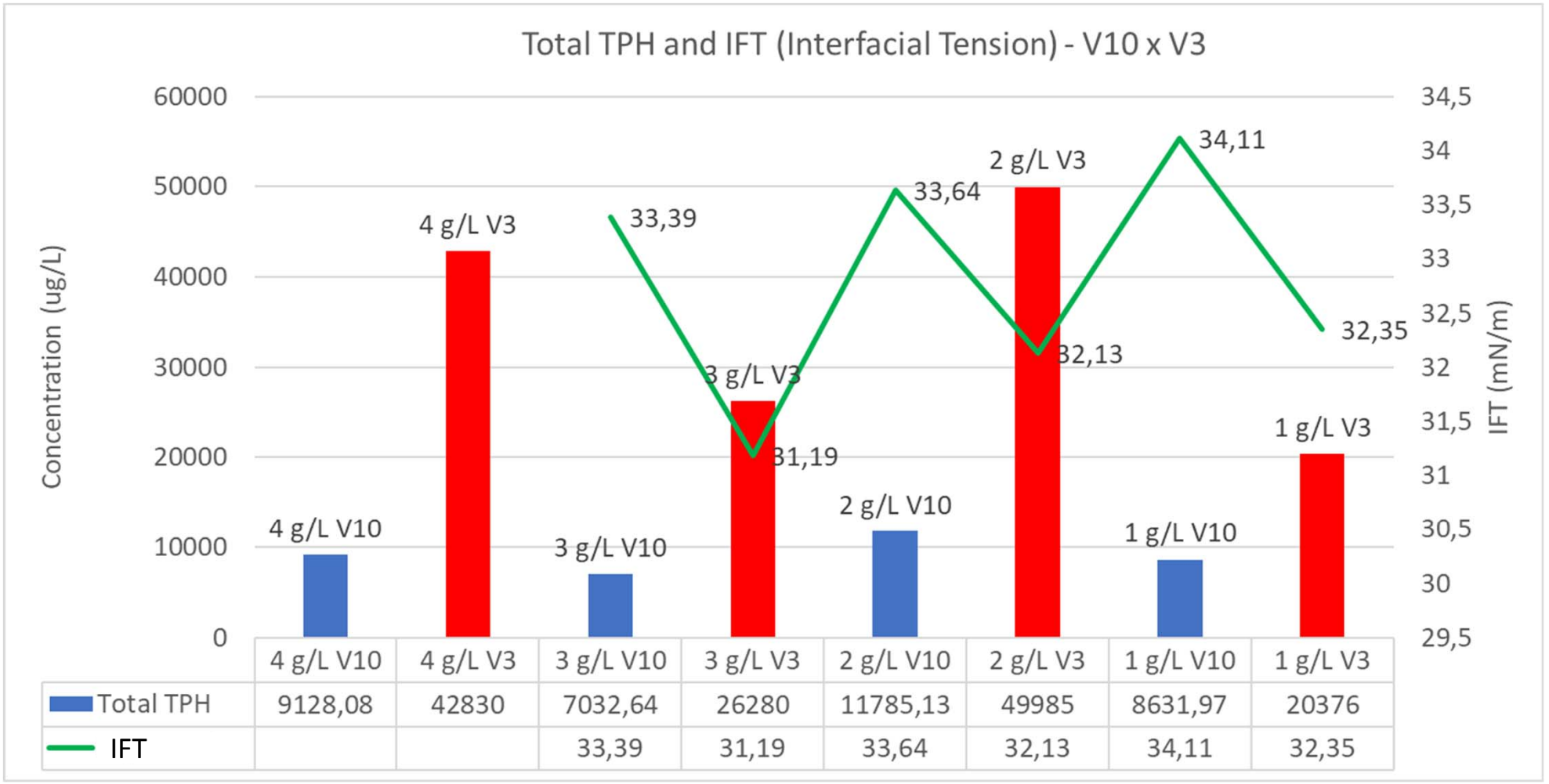




Surfactant V10

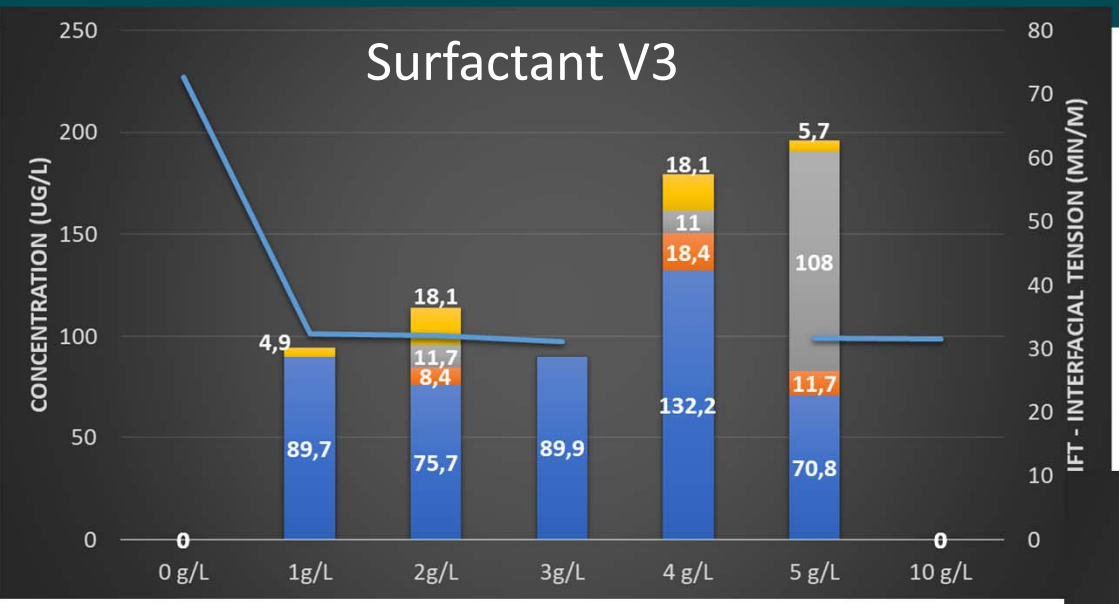


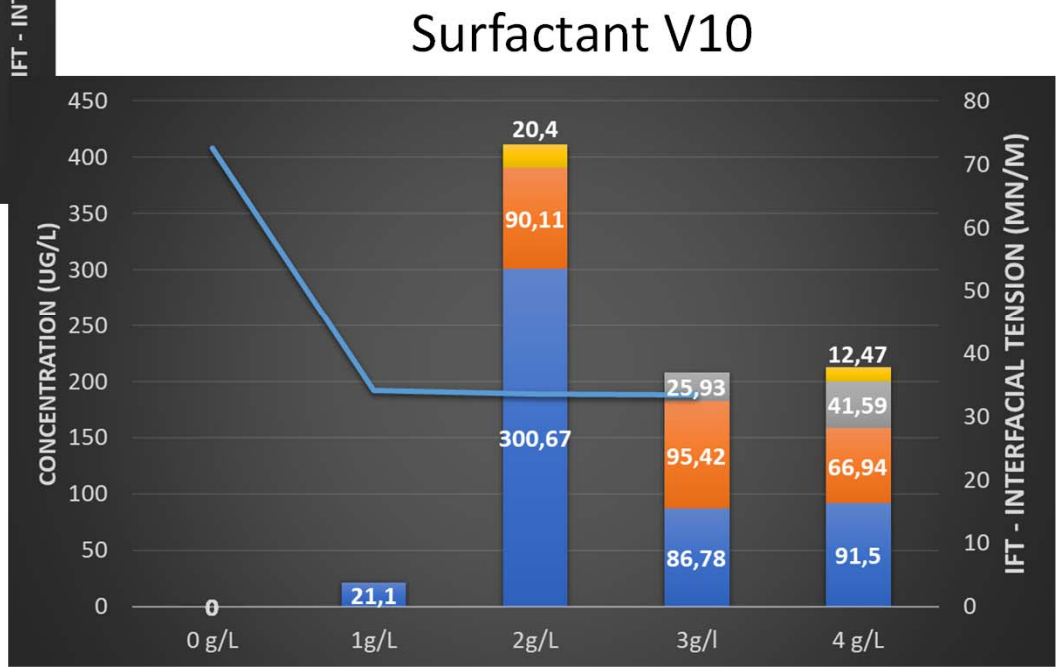
Results for Surfactants V10 and V3 for TPH



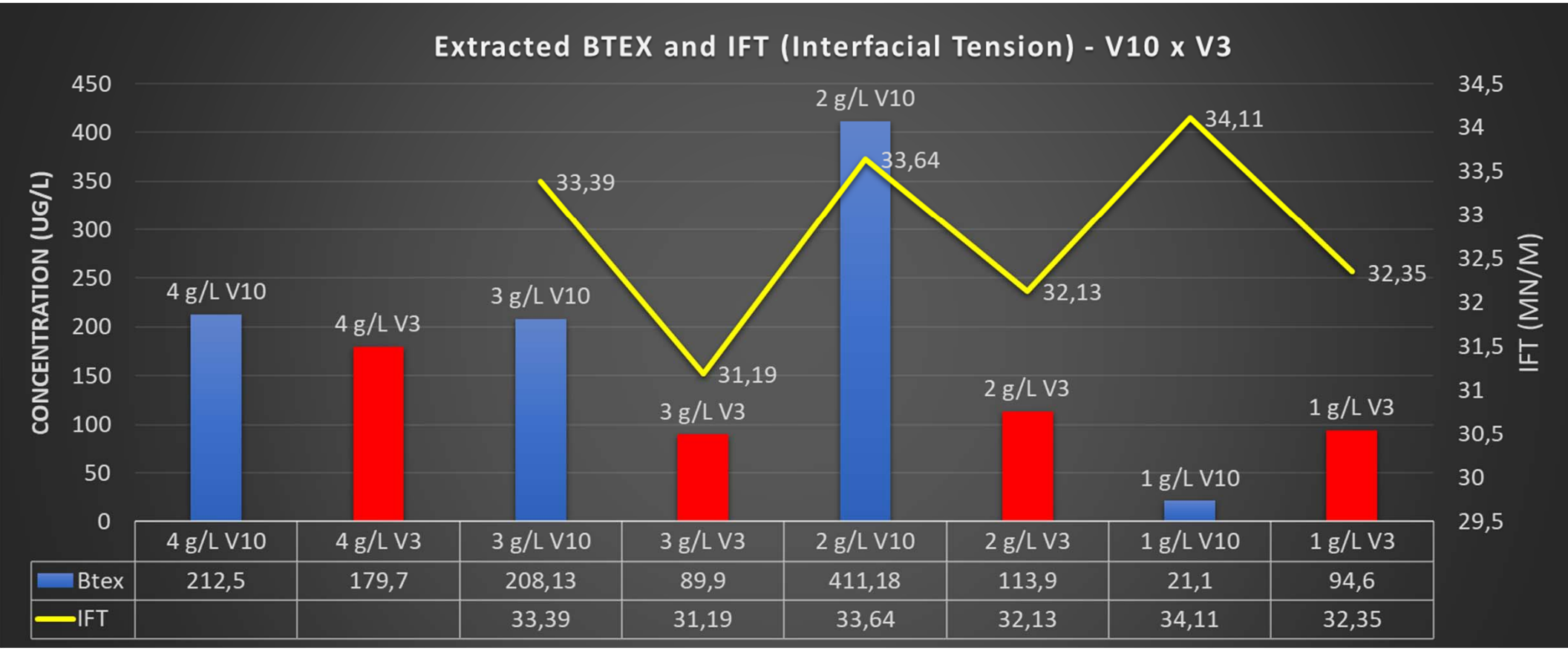
	4 g/L V10	4 g/L V3	3 g/L V10	3 g/L V3	2 g/L V10	2 g/L V3	1 g/L V10	1 g/L V3
Total TPH	9128,08	42830	7032,64	26280	11785,13	49985	8631,97	20376
IFT			33,39	31,19	33,64	32,13	34,11	32,35

BTEX Extraction by Wash for Surfactants V10 and V3





Results for Surfactants V10 and V3 for BTEX



Summary of Removed Mass for BTEX and TPH

V10 conc.	Wash	Mass/L TPH (mg)	Total mass TPH (mg)	Mass/L BTEX (mg)	Total mass BTEX (mg)
1 g/L	1st w	2,2	8,61	0,0211	0,0211
	2nd w	2,04		0	
	3rd w	1,99		0	
	4th w	2,38		0	
2 g/L	1st w	3,95	11,78	0,3	0,4104
	2nd w	2,51		0,09	
	3rd w	3,29		0	
	4th w	2,03		0,0204	
3 g/L	1st w	1,29	7,02	0,08678	0,20813
	2nd w	1,54		0,09542	
	3rd w	1,91		0,02593	
	4th w	2,28		0	
4 g/L	1st w	1,26	9,13	0,0915	0,2125
	2nd w	1,97		0,06694	
	3rd w	1,74		0,04159	
	4th w	4,16		0,01247	

V3 conc.	Wash	Mass/L TPH (mg)	Total mass TPH (mg)	Mass/L BTEX (mg)	Total mass BTEX (mg)
1 g/L	1st w	4,89	20,376	0,09	0,0946
	2nd w	4,80		0,00	
	3rd w	5,43		0,00	
	4th w	5,26		0,00	
2 g/L	1st w	12,81	88,56	0,0757	0,1139
	2nd w	13,47		0,0084	
	3rd w	12,3		0,0117	
	4th w	49,98		0,0181	
3 g/L	1st w	6,13	26,28	0,09	0,0899
	2nd w	7,31		0,00	
	3rd w	6,80		0,00	
	4th w	6,04		0,00	
4 g/L	1st w	9,75	42,83	0,1322	0,1797
	2nd w	11,43		0,0184	
	3rd w	9,89		0,011	
	4th w	11,76		0,0181	
5 g/L	1st w	15,99	54,45	0,0708	0,1962
	2nd w	14,31		0,0117	
	3rd w	12,95		0,108	
	4th w	11,2		0,0057	
10 g/L	1st w	12,922	45,041	0	0
	2nd w	10,587		0	
	3rd w	11,525		0	
	4th w	10,007		0	

Statistics ANOVA and Surface Response Model

- Factors: Surfactant concentration (g/L) / Flush time (min) / Flow Rate (mL/min);
- Response: Contaminant Extraction (ug/L).
- Duplicates were all considered and showed good relations.

- Considerations for V3:
  - As flow rate explains relations as equal as flush time, this factor was not considered in the model;
  - Statistical model has shown to be valid, with R2 adjusted higher than 0.73 and all p-values less than 0.01 (1% error as maximum, for flushing time);
  - Flush time and surfactant concentration explains at least 73% of the contaminant extraction.

- Considerations for V10:
  - In all experiments, better extractions related to 4th wash → no relation with higher retention time → considered as not impacting for this correlation;
  - Statistical model has shown to be valid, with R2 adjusted higher than 0.8 and all p-values less than 0.06 (6% error as maximum);
  - All factors have interactions, so 3D surface graphic is not possible to be designed (must be 4D);
  - Variables explain more than 80% of extraction results.

Statistics and Surface Response Model

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Fit Statistics | Model Comparison Statistics

Fit Statistics

Std. Dev.	14,75		R^2	0,7522
Mean	92,73		Adjusted R^2	0,7316
C.V. %	15,90		Predicted R^2	0,6961
			Adeq Precision	19,3061

The **Predicted R^2** of 0,6961 is in reasonable agreement with the **Adjusted R^2** of 0,7316; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 19,306 indicates an

β Coefficients | = Coded Equation | = Actual Equation

Analysis of Variance

ANOVA for Reduced Quadratic model

Response 1: TPH Extrac
Transform: Square Root
Constant: 0

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	23776,05	3	7925,35	36,43	< 0.0001	significant
A-Flashing	1549,89	1	1549,89	7,13	0,0113	
B-Surfac	10874,53	1	10874,53	49,99	< 0.0001	
B^2	11170,36	1	11170,36	51,35	< 0.0001	
Residual	7831,01	36	217,53			
Lack of Fit	7421,94	29	255,93	4,38	0,0248	significant
Pure Error	409,07	7	58,44			
Cor Total	31607,05	39				

Perturbation | One Factor | All Factors | Interaction | Contour | Pred. vs. Actual

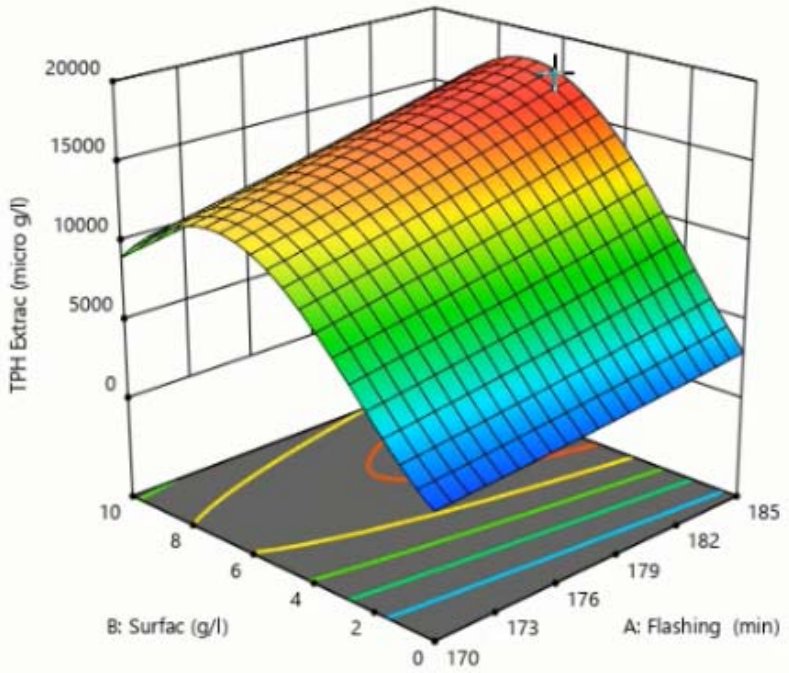
Transform | Fit Summary | Model | ANOVA | Diagnostics | Model Graphs

Design-Expert® Software
Factor Coding: Actual
Original Scale

TPH Extrac (micro g/l)
402 — 16380

X1 = A: Flashing
X2 = B: Surfac

Actual Factor
C: Flow = 5,5

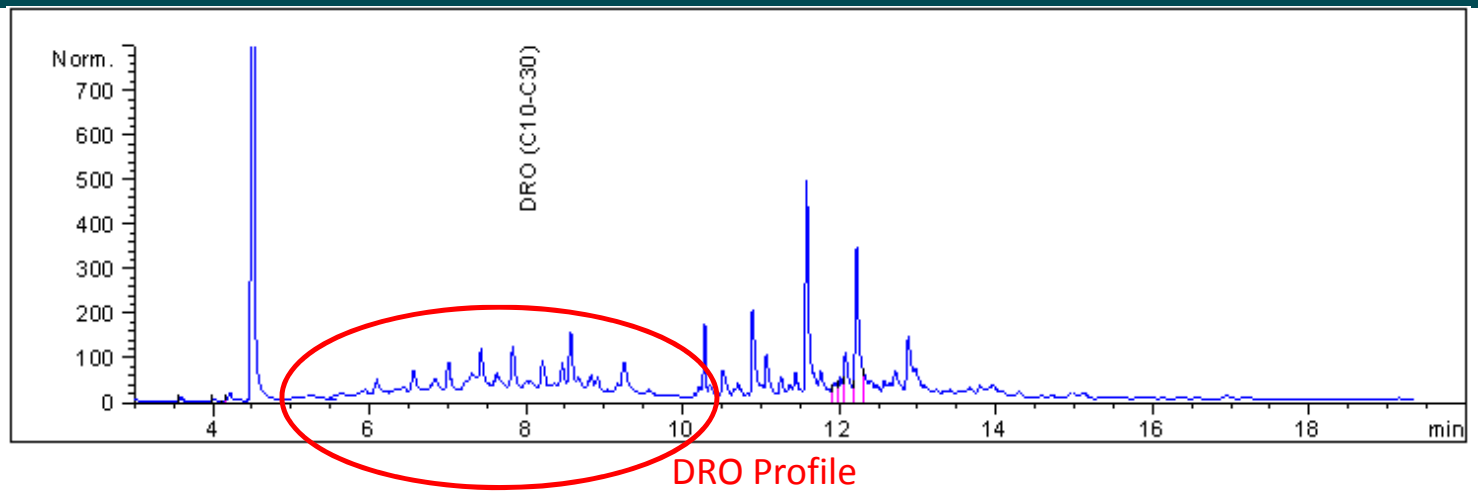


ISCO Activation and Treatment

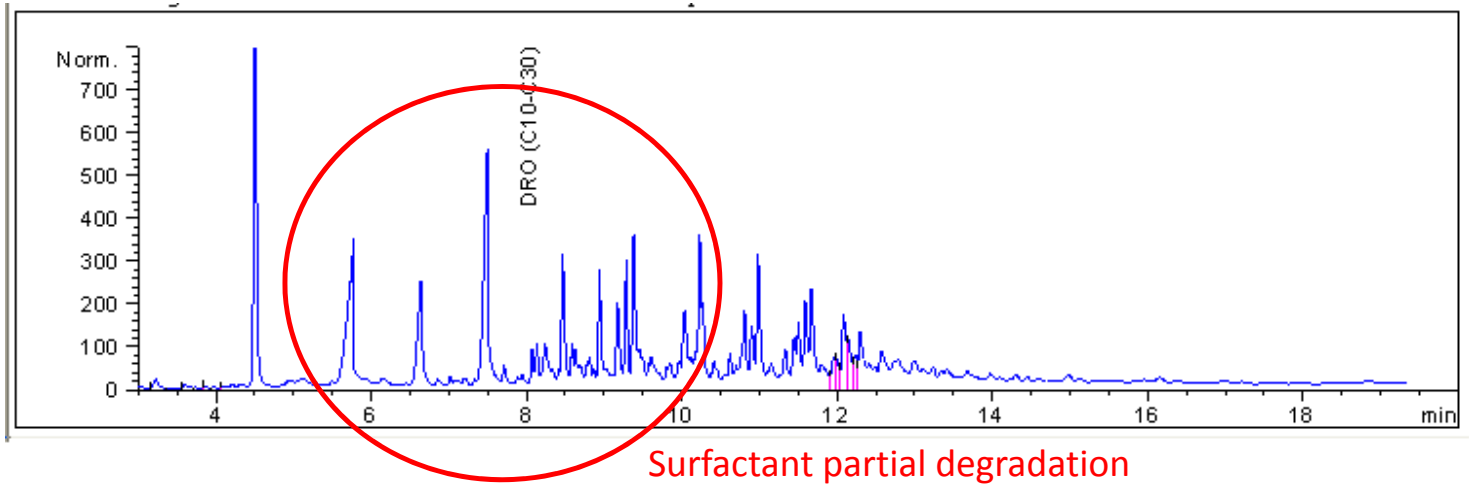
- Washing samples after extraction by surfactant, after 4 washes, were composed and sent to bench treatability test.

- Treatability test conditions:
  - Oxidant: Sodium persulfate;
  - Activation: Alkaline pH 10.5 – 11.0 (NaOH);
  - Reaction time: 0 time; 24h; 48h; 96h;
  - Initial oxidant concentration: 30 g/L;
  - Final oxidant concentration: 23.9 g/L;
  - CoC (TPH) initial concentration: 12.5 mg/L
  - After 24h no Diesel was detected. Remaining timing reactions kept the same result (no Diesel detected);
  - Initial IFT: 32.13;
  - IFT after 96h: 34.97 mN/m.

ISCO Results



DRO Profile



Surfactant partial degradation

Final Conclusions

- Surfactants were able to extract contaminants (BTEX and TPH) in all concentrations, at different rates.
- Surfactant V3 had better extractions for TPH and Surfactant V10 for BTEX;
- Specific properties of V3 showed around 15% higher flow rates.
- The 2g/L surfactant concentration had better extraction rates at both surfactants
  - Higher concentration did not lead to higher extraction rates necessarily
  - Relations were not linear and other factors may be determinant.
- DOE with statistical treatment validated experiments and the consideration of Surfactant concentration, Flushing time and Flow rate as key factors for extraction rates.
- NAPL after solubilized and mobilized to water phase could be completely oxidized. Oxidant as well as the surfactant remained after the process:
  - Surfactant and oxidant can be recycled.

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Thank you!

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