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Removal of *n*-hexane extractable material from synthetic oil produced water using Desmopan®5377A thermoplastic polyurethane packed bed reactor

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Abstract

Background: Water extracted during oil and gas exploration and production is known as produced water (PW). It contains dissolved and dispersed hydrocarbons and harmful chemical additives used in drilling or fracturing, rendering it highly polluted. This research investigates the efficiency of Desmopan® 5377A thermoplastic polyurethane beads in a packed bed sorption column to remove n-hexane extractable material (HEM) from synthetic PW. To our knowledge, the use of Desmopan® 5377A for removing HEM from produced water has not been documented.

Methods: Experiments were designed using the D-optimal method within the response surface methodology (RSM) framework. Analysis of variance (ANOVA) was used to evaluate the effects of salinity, surfactant, and initial pH.

Results: Under optimal conditions, a maximum HEM removal efficiency of 70.25% was achieved at high salinity, a surfactant (Tween 80) concentration of 482 mg/L, and an initial pH of 9. Salting-out was identified as the primary mechanism enhancing HEM removal. The lowest removal efficiency was observed at pH 7. The interaction between surfactant concentration and pH showed that increasing Tween 80 concentration improved removal efficiency at pH 4, 6, and 9 up to an optimal point, beyond which efficiency declined.

Conclusion: A polymeric sorbent is recommended as a pre-treatment method to reduce HEM content in PW for treating complex contaminated media.

Keywords: Environmental pollutants, Hydrocarbons, n-hexane, Polyurethanes, Salinity

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Introduction

In the oil and gas industry, produced water (PW) refers to the water that is extracted during the exploration and production of oil and gas. This by-product, often referred to as a waste stream, is the largest volume of material generated during oil and gas production (1). Globally, approximately 250 million barrels of PW are generated daily, three times as much as the approximately 80 million barrels of oil produced daily, resulting in a water-to-oil ratio of 3:1 (2). The increasing age of oil wells has led to an average water-to-oil ratio of 12:1 (v/v) for global crude oil production in 2025. As a result, there is expected to be further growth in the market for managing and reusing PW (3). Studies on the quality of PW show that total oil varies from 40 mg/L to 2000 mg/L (4). PW contains naturally occurring radioactive elements (^{226}Ra and ^{228}Ra), and heavy metals (Ba, Cd, Cu, Cr, Li, Pb, Zn, Sr, Ti, B, and Al).

Cations and anions significantly influence PW chemistry. Chlorine (Cl^-) and sodium (Na^+) ions, primarily responsible for PW salinity, range in concentration from 1 mg/L to 300,000 mg/L. Ions such as Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, Na^+, K^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Fe^{2+}, and Sr^{2+}influence conductivity and scale formation potential (5). PW is heavily contaminated with dissolved and dispersed hydrocarbons and harmful chemical additives introduced during drilling or fracturing, including corrosion inhibitors, scale inhibitors, demulsifiers, polyelectrolytes, methanol, and glycol (6). Surfactants can be present in PW due to their use in production processes. Surfactants primarily contribute to oil droplet stability, reduced oil-water interfacial tension, and the zeta potential of oil droplet surfaces (7). The physical and chemical properties of PW vary widely depending on the geologic age, depth,

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and geochemistry of the hydrocarbon-bearing formation, the chemical composition of the oil and gas phases in the reservoir, and any chemicals added during production (8).

Operators treating PW aim to achieve objectives such as the removal of dispersed oil and grease (deoiling), desalination, elimination of suspended particles and sand, removal of soluble organics and dissolved gases, reduction of naturally occurring radioactive elements, disinfection, and water softening (5). Given the global scarcity of water, PW is recognized as a valuable resource. The management of PW primarily involves reinjection or discharge, with the choice of method determined by factors such as quality and quantity, location, and infrastructure availability (9). In the United States, the Environmental Protection Agency (EPA) regulates the maximum allowable concentration of oil and grease in PW for offshore discharge in the Gulf of Mexico, setting a daily maximum limit of 42 mg/L and a monthly average limit of 29 mg/L (10). In Europe, a regulatory standard of 30 mg/L has been established by the OSPAR Commission as the regulatory threshold for the concentration of oil in PW discharged into the ocean (11). Various methods are available for treating PW, including membrane filtration, thermal treatment, biological treatment, flotation, evaporation, adsorption, media filtration, ion exchange, chemical oxidation, electrodialysis, advanced oxidation processes, and polymer extraction (12-23). These methods can be applied independently or in combination, depending on the physicochemical properties of the water and the desired treatment level (24). Different types of hydrocarbons exhibit varying degrees of susceptibility to microbial degradation. Linear alkanes are the most readily degraded, followed by branched alkanes, small aromatics, and cyclic alkanes in decreasing order of susceptibility. However, high molecular weight polycyclic aromatic hydrocarbons (PAHs) are often highly resistant to microbial degradation (25).

A high COD/BOD_5 ratio (>3) indicates complex organic matter in the PW, which is resistant to degradation. This poses challenges for PW treatment, often necessitating specific pre-treatment before biological methods can be applied (26,27). Oil in liquid effluents is present in four forms: free-floating (>150 μm), dispersed (50–100 μm), emulsified (<50 μm), and dissolved. Free-floating and dispersed oils can be removed by gravitational separation, whereas emulsified and dissolved oils require other methods (28). The sorption process involves mechanisms such as absorption, adsorption, and ion exchange. Absorption occurs when a substance is dissolved or trapped within sorbent material or through adsorption, whereas adsorption involves the accumulation of substances at the interface of two phases (29). Adsorption is a well-established technology offering high pollutant removal efficiency, operational flexibility, simple installation, and low maintenance requirements. Activated carbon is a widely used adsorbent for removing contaminants from wastewater, but it has limitations, such as high costs and the need for frequent regeneration when treating highly contaminated wastewater (30-32). The various adsorbents employed include bone char, clay, zeolites, carbon nanotubes, polymers, rubber materials, wool fibers, and straw (33,34). The drawbacks of these adsorbents include poor selectivity, as they adsorb both water and oil, and clogging and fouling caused by oil or grease, which significantly reduce their adsorption capabilities (35). Therefore, there is a need for an advanced sorbent that can selectively separate oil or water. Polymeric sorbents are gaining attention for the removal of emulsified oil from industrial wastewater. Experiments were conducted to evaluate the resin's capacity to adsorb emulsified oil from synthetic PW. The results show that polymeric beads exhibited a capacity of 301 ± 27 mg/g, suggesting their suitability for industrial wastewater treatment (36). Polyurethane (PU), a synthetic polymer, is known for its effective phase separation properties, making it relevant for oil-water separation applications. It exhibits excellent abrasion, tear, and flexural resistance and superior mechanical properties (37). Research indicates that TPU and PU-based sorbents are highly effective for hydrocarbon removal from water, demonstrating significant potential for produced water treatment. These sorbents exhibit superior sorption capacities (up to 55 g/g), reusability (up to 200 cycles), and cost-effectiveness compared to polypropylene and other polymer sorbents. In contrast, natural sorbents, while more biodegradable, have lower sorption capacities and reusability (38-40).

Bioregeneration of polymers after pollutant absorption enhances their applicability in environmental bioremediation. Studies demonstrate that solid polymer-based pollutant extraction, followed by bioregeneration and sorbent reuse, effectively treats crude oil-contaminated media (41).

Although polyurethane effectively absorbs hydrocarbons from contaminated water and supports bioremediation capability in two-phase bioreactors, its use as an adsorbent in a packed bed column remains unexplored. The lack of direct studies on TPU for produced water indicates a need for further research, yet current evidence supports PU sorbents as a viable option for oil and gas PW treatment. The objective of this research was to evaluate the effectiveness of thermoplastic polyurethane (Desmopan® 5377A) sorbent in removing HEM from synthetic PW, considering the effects of salt concentration, initial pH, and surfactant concentration.

Materials and Methods

Materials

This experimental study was conducted at a laboratory scale. Crude oil, sourced from the Idealo Crude Oil Transfer

Center in northwestern Iran, served as the hydrocarbon source. Poly oxyethylene sorbitan monooleate (Tween 80), a non-ionic surfactant, was added to disperse the oil into the aqueous phase. Tween 80, which is uncharged, facilitates solubilization, emulsification, and dispersion. Synthetic produced water (PW) was prepared using distilled water, crude oil, sodium chloride, and Tween 80 surfactant.

Thermoplastic polyurethane (Desmopan® 5377A, Leverkusen, Germany) was used as a polymeric sorbent. It is a hybrid ether/ester-based material that combines the advantages of ether- and ester-based polyurethanes. The mean size of beads ($n=10$) was $5.0\times4.4\times2.0$ mm ($W\times L\times H$). Additionally, sulfuric acid and sodium hydroxide were used to adjust the initial pH of PW. All other chemicals used in this research were supplied by Merck (Darmstadt, Germany) and Ameretat (Tehran, Iran).

Preparation of synthetic PW

To prepare the PW, a volume of 25 mL of crude oil was diluted to 1000 mL with distilled water, and the concentrations of salt and surfactant, as well as the pH, were adjusted based on the experimental design. The prepared solution was mixed for 2 hours using a magnetic stirrer and then allowed to stand for 8 hours to allow separation of excess oil from the water phase. Subsequently, using a peristaltic pump, the synthetic PW was withdrawn from beneath the crude oil layer for experimental use. To determine the initial HEM content in each run, 100 mL of the PW was extracted and quantified using EPA Method 1664B (42).

Setup of the sorption system

The sorption column was designed and implemented as shown in Figure 1.

The sorption capacity of the polymer beads for crude oil (0.16 g/g crude oil/polymer) was reported in a previous study (43). Desmopan® 5377A polymer beads (60 g) were poured into the 150 mL glass column. The inlet and outlet flow rates of the glass column were adjusted to ensure the column was filled with PW. The flow rate of PW delivered by the peristaltic pump was 31.8 mL/min. This was the maximum flow rate that allowed the packed bed to process produced water (PW) without overflow. The volume of the PW passed through the packed bed sorption column totaled 650 mL.

Analysis

HEM in PW comprises oil, grease, and other non-polar organic compounds that are extractable by *n*-hexane, as defined by U.S. Environmental Protection Agency (EPA) Method 1664. The liquid-liquid extraction method (EPA Method 1664B) was used to measure HEM, as described below. Briefly, the sample is treated with sulfuric acid to lower the pH to below 2. Then, the sample is extracted 3 times with n-hexane using a separatory funnel. The n-hexane is then removed by distillation, yielding HEM, which is dried and gravimetrically determined. EPA Method 1664B measures HEM in the range of 5–1000

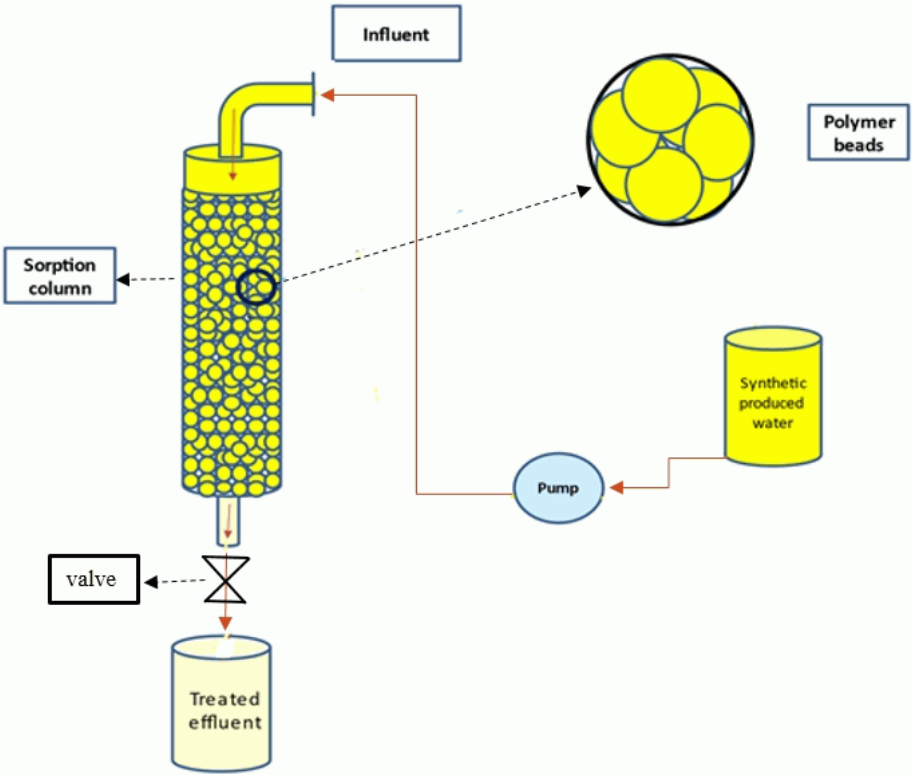

Figure 1. Diagram of sorption column setup

mg/L (42).

Design of experiments

Experiments were designed using the D-optimal method within the framework of response surface methodology (RSM). The concentrations of surfactant (Tween 80) and salinity (NaCl) were treated as continuous independent variables, while pH was designated as a discrete independent variable (factor). The range of independent variables was selected based on the average chemical composition of PW. The pH range of produced water depends on factors including chemical composition, dissolved gases (e.g., CO_2 or H_2S), organic matter, and reservoir conditions. The pH of produced water typically ranges from 4.5 to 8.5 (44,45). The salinity of produced water (PW) exhibits significant variation due to differences in reservoir geology, oil type, extraction methods, and reservoir location. It ranges from 10,000 to 350,000 ppm, with an average of 45,000 ppm (46,47). A study of gas-condensate oil-water emulsions evaluated three non-ionic surfactants. The optimal concentration, approximately 1000 mg/L, maximized oil recovery (48). The removal efficiency of HEM in a sorption column served as the dependent variable (response). The range of independent variables is shown in Table 1. By default, high levels of the independent variable were coded as +1, and low levels were coded as −1.

Thirty-six experiments (runs) were designed. In each experiment, samples were collected before and after to measure the HEM removal efficiency as the response variable. In this study, Design Expert 11 (Stat-Ease Inc., Minneapolis, USA) was used for the design of experiments, model development, evaluation of variable effects, and optimization of independent variables to achieve maximum HEM removal efficiency. To validate the reliability of the fitted model, confirmation experiments were conducted to compare predicted optimal values with experimental results.

The sequential backward elimination method was used to remove non-significant variables. The statistical properties of the model were evaluated using a normal probability plot, which displays the residuals (the differences between the predicted and observed values of the dependent variable for each run). This plot indicates whether the residuals follow a normal distribution. Deviations from this line, such as an S-shaped pattern, suggest that transforming the dependent variable's values may improve the model's fit.

Results

Experimental design and HEM removal efficiency using a polymeric sorbent column

Table 2 represents the designed experiments with variable levels (salinity, surfactant, and initial pH), and the corresponding HEM removal efficiency. The average concentration of HEM in PW prior to passing through the sorption column was 437 mg/L.

According to Table 2, the minimum and maximum HEM removal efficiency were 13.66 % (Run 12) and 75.07 % (Run 20), respectively. The highest removal efficiency was observed in the absence of salinity. Removing contaminants from PW is challenging, particularly because it typically contains varying levels of salinity. Achieving complete removal efficiency is not feasible in practice, underscoring the importance of optimizing the treatment conditions while accounting for salinity.

Statistical evaluation of polymer sorption experimental results

The value of the coefficient of determination (R^2) indicates the proportion of variance in the dependent variable that the independent variables can explain. Values of R^2 and adjusted R^2 are shown in Table 3. In this statistical analysis, the cubic model has the highest R^2 (0.9422) and adjusted R^2 (0.7469) compared to other models.

An ANOVA was conducted using the cubic model and its components (Table 4) to examine the relationships between the factors and dependent variables.

The *F*-value of 5.55 indicates that the model is statistically significant with only a 0.02% chance that an *F*-value this large could occur due to noise. In this case, C, AB, A^2, B^2, and B^2C are significant model terms. The model in Equation (1) effectively determines factor significance through coefficient comparison and provides a final model in terms of coded factors for predicting HEM removal efficiency.

$$\text{HEM removal efficiency (\%)} = 46.70 - 0.0808\,A - 2.55\,B + 0.1607\,C\,[1] + 13.96\,C\,[2] + 3.37\,C\,[3] - 6.18\,AB - 1.13\,BC\,[1] + 1.19\,BC\,[2] + 1.03\,BC\,[3] + 10.17\,A^2 - 16.21\,B^2 + 0.8892\,B^2C\,[1] - 16.19\,B^2C\,[2] - 2.92\,B^2C\,[3] \quad (1)$$

A: salinity, B: surfactant, and C: pH

The coded equation is useful for identifying the relative

Table 1. The details of the selected continuous and discrete independent variables

Independent variables	Unit	Actual values (coded value)					
Sodium chloride salinity	mg/l	0 (−1.00)	25000 (−0.50)	50000 (0.00)		75000 (0.50)	100000 (1.00)
Surfactant Tween 80	mg/l	0 (1.00)	300 (−0.50)	400 (−0.33)	600 (0.00)	800 (0.33)	1200 (1.00)
pH	-	4 (−5 1 −1)		6 (−1 −1 5)	7 (1 −1 −5)		9 (5 1 1)

Table 2. The designed experiments and results of the HEM removal efficiency using the sorption column

Run	Factor 1	Factor 2	Factor 3	Response
	A: Salinity mg/L	B: Surfactant mg/L	C: initial pH	HEM removal efficiency %
1	0	0	7	33.52
2	100000	800	4	66.29
3	100000	0	4	29.41
4	100000	0	4	34.38
5	100000	600	4	66.41
6	50000	1200	7	33.33
7	100000	0	9	51.67
8	50000	0	9	39.39
9	50000	0	7	45.83
10	0	1200	7	28.89
11	25000	600	7	27.98
12	25000	600	7	13.66
13	100000	1200	6	52.86
14	50000	0	6	40.52
15	0	1200	4	37.69
16	0	0	4	31.74
17	50000	300	4	28.57
18	100000	1200	7	22.60
19	100000	0	7	65.71
20	0	600	9	75.07
21	0	0	4	27.06
22	0	1200	6	50.91
23	50000	1200	9	33.71
24	100000	1200	4	32.92
25	50000	1200	6	24.43
26	0	0	6	20.80
27	0	1200	9	52.04
28	50000	1200	4	25.18
29	100000	0	6	54.55
30	100000	1200	9	18.42
31	0	800	6	65.38
32	0	400	4	70.55
33	75000	600	7	16.33
34	0	0	9	49.12
35	100000	400	6	54.44
36	75000	600	7	16.50

impact of factors by comparing their coefficients and predicting the response for specified factor levels. As shown in Equation (1), the interaction between surfactant concentration and pH (B^2C), with a coefficient of −16.19, has the largest negative impact on HEM removal efficiency. Conversely, salinity (A^2), with a coefficient of + 17.1, has the greatest positive impact on enhancing HEM removal efficiency.

Table 3. Model fit summary statistics

Source	Std. Dev.	R^2	Adjusted R^2	
Linear	17.12	0.1489	0.0070	
2FI	16.71	0.3778	0.0532	
Quadratic	14.58	0.5674	0.2791	
Cubic	8.64	0.9422	0.7469	Suggested
Quartic	5.61	0.9878	0.8934	Aliased

Interaction effect of salinity and surfactant (AB)

Figure 2 demonstrates that the efficiency of HEM removal is influenced by the interaction between salinity and surfactant concentration (AB). High surfactant concentrations reduce the effectiveness of salt in the salting-out process. In the absence of surfactants, increasing salinity does not significantly enhance hydrocarbon removal efficiency. However, increasing surfactant concentration beyond the optimum level decreases removal efficiency, particularly at high salinity.

Befkadu et al (49) report that the efficiency of hydrocarbon (HEM) removal in surfactant-enhanced soil washing depends on salinity and surfactant concentration. Their review indicates that salinity influences surfactant properties, such as micelle formation and adsorption, which interact with surfactant concentration to affect HEM removal efficiency, consistent with the findings of this study.

Interaction effect of surfactant and pH (B^2C)

Figure 3 illustrates the interaction effect of surfactant concentration and pH on removal efficiency, with the highest and lowest efficiencies observed at pH 9 and 7, respectively. Removal efficiency at pH 4, 6, and 9 increased with increasing surfactant concentration but decreased at concentrations above 600 mg/L. Other studies confirm that pH and non-ionic surfactant concentration interact to influence hydrocarbon removal, with an optimal surfactant concentration beyond which performance plateaus or declines (50).

Optimum condition and verification

The desirability function was used to optimize the independent variables and maximize HEM removal efficiency in synthetic PW using a polymeric sorbent. Table 5 presents the optimal variable values and the predicted maximum removal efficiency, corresponding to a desirability of 0.723.

To verify the model's accuracy in predicting the highest removal efficiency, three additional experiments were conducted under optimal conditions. The average HEM concentrations entering and leaving the packed sorption column were 542 mg/L and 162 mg/L, respectively. The HEM removal efficiency was 68.9%, 71.6% and 69.3% in the three experiments, respectively. The average HEM removal efficiency across these experiments was 70.0%, closely aligning with the predicted removal efficiency

Table 4. Analysis of variance (ANOVA) for the prediction model of HEM removal efficiency using a sorption column

Source	Sum of squares	*df*	Mean square	*F* value	*P* value	Consideration
Model	8129.95	14	580.71	5.55	0.0002	*P* value≤0.05
A-salinity	9.21	1	9.21	0.0881	0.7695	*P* value≥0.05
B-surfactant	100.36	1	100.36	0.9600	0.3383	*P* value≥0.05
C-initial pH	1125.20	3	375.07	3.59	0.0309	*P* value≤0.05
AB	684.42	1	684.42	6.55	0.0183	*P* value≤0.05
BC	883.27	3	294.42	2.82	0.0640	*P* value≥0.05
A^2	573.04	1	573.04	5.48	0.0292	*P* value≤0.05
B^2	935.96	1	935.96	8.95	0.0069	*P* value≤0.05
B^2C	2926.37	3	975.46	9.33	0.0004	*P* value≤0.05
Residual	2195.44	21	104.54			
Lack of fit	2069.60	17	121.74	3.87	0.0995	*P* value≥0.05

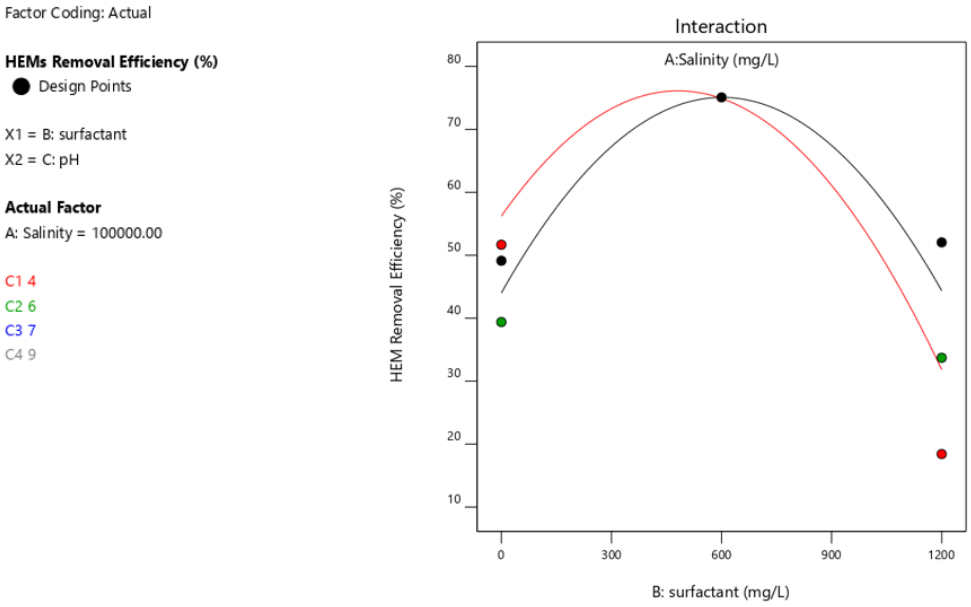

Figure 2. The interaction effect of salinity and surfactant (AB) on HEM removal efficiency

(76.1%) based on optimal model parameters. The percent error between the experimental mean HEM removal efficiency and the predicted value was less than 7.7%. Table 5. Optimized values of independent variables to maximize sorption of HEM from PW by using a polymer sorbent

Activated carbon is highly effective for removing HEM from oil and gas PW, with removal efficiencies typically ranging from 70% to 98% in various studies, and 85–95% in column adsorption systems. Combining sorbents, such as wool fibers and synthetic polymers, or integrating sorption with methods like coagulation or membrane filtration can enhance HEM removal efficiency (44).

Research on aliphatic polyurethane foams, such as Desmopan, indicates that sorbent modification can enhance oil adsorption capacity. For instance, a laboratory study on polyurethane foam composites reported a maximum adsorption capacity of 29.5 g/g for diesel (a proxy for heavy end mixture components) when modified with activated carbon. Unmodified polyurethane exhibited a lower capacity (20–25 g/g), yet still surpassed many conventional sorbents, such as cotton or polypropylene (51).

Produced water often contains a mixture of organic and inorganic materials, and its properties depend significantly on the geological location and formation of the field, the lifetime of its reservoirs, the type of hydrocarbon produced, and the chemicals used in oil and gas fields (44).

Consequently, results from studies using real versus synthetic PW may vary. Table 6 presents examples of natural, modified natural, and synthetic adsorbents used for PW treatment, showing their efficiency in removing petroleum hydrocarbons. Some studies report general

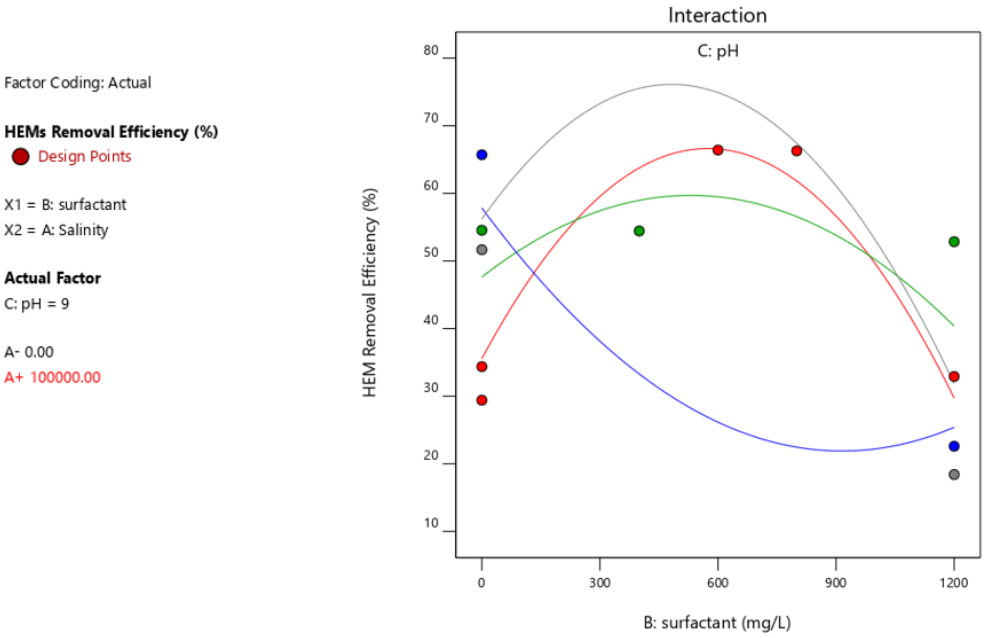

Figure 3. The interaction effect of surfactant and pH (B^2C) on HEM removal efficiency

Table 5. Optimized values of independent variables to maximize sorption of HEM from PW by using a polymer

Number	Salinity mg/L	Surfactant mg/L	pH	HEM removal efficiency (%)	Desirability
1	100000	482	9	76.1	0.723

oil removal rather than HEM specifically, although HEM is a subset of oil and grease, rendering these results applicable to HEM removal. Variations in initial HEM concentration, water types (e.g., brackish versus produced water), and test duration complicate direct comparisons.

The highest removal efficiencies (>99%) were observed with exfoliated graphite, likely owing to its optimized surface properties and hydrophobicity. Commercial sorbents, such as powdered activated carbon and zeolite, are widely used but less effective, with removal efficiencies of 58–73% for oil contaminants. Natural sorbents, such as straw, show promise, particularly for crude oil, but straw modified with methoxytrimethylsilane does not consistently improve performance.

Synthetic sorbents maintain efficiency over multiple cycles through squeezing, distillation, or bioregeneration, unlike some natural sorbents that degrade (38). A key advantage of polyurethane, such as FlexFoam200, is its reusability for up to 200 cycles, enhancing cost-effectiveness. Although activated carbon retains 95% of its capacity after 40 cycles, it does not match polyurethane's longevity. In real-world conditions, such as seawater, activated carbon's capacity drops significantly (from 72 g/g to 16.23 g/g), whereas polyurethane exhibits superior performance (55).

Discussion

Based on the findings of this study, under optimized conditions, a maximum HEM removal efficiency of 70.25% was achieved at a salt concentration of 100 g/L, a surfactant concentration of 482 mg/L, and an initial pH of 9.

From a scalability perspective, polyurethane fixed bed columns provide a promising, cost-effective, and sustainable solution for hydrocarbon removal and produced water treatment, with high adsorption capacity, antibacterial properties, and recyclability (39,56,57). Polyurethane absorbs hydrocarbons by allowing them to diffuse into its porous network. This process is often explained by the Fickian diffusion model, in which hydrocarbons diffuse into the polymer matrix over time (58). The primary driving force for sorption in polyurethane is van der Waals forces between hydrocarbons and the polymer chains. Variations in polyurethane composition modestly influence sorption capacity, indicating that physical forces predominate over chemical bonding (59,60).

Salting-out primarily increased HEM removal efficiency. HEM removal efficiency was lowest at pH 7. The interaction between surfactant concentration and pH indicates that increasing the Tween 80 concentration enhances HEM removal efficiency at pH 4, 6, and 9 up to an optimal concentration, beyond which the efficiency decreases. As shown in Figure 2, the interaction between salinity and surfactants enhances oil droplet stability, reduces oil-water interfacial tension, and alters the zeta potential of oil droplet surfaces, primarily due to surfactants (2). The emulsions' composition varied by oil type, oil quantity, and surfactants (61). The emulsifying

Table 6. Comparisons of adsorbents in terms of efficiency of removing hydrocarbons from produced water

Sorbent	Oil removal efficiency	Conditions	Source
Exfoliated graphite (EG)	>99% (from 278 mg/L to 1.2 mg/L)	Sorption column of EG Actual produced water	(52)
Powdered activated Carbon (AC)	72.98%	Synthetic produced water Initial oil concentration 40 ppm, 0.5 g sorbent dose, flow rate 1.25 mL/min. Fixed-bed-column	(53)
Granular activated Carbon (AC)	64.87%	Synthetic produced water Initial oil concentration 40 ppm, 0.5 g sorbent dose, flow rate 1.25 mL/min. Fixed-bed-column	(53)
Zeolite	58.58%	Synthetic produced water Initial oil concentration 40 ppm, 0.5 g sorbent dose, flow rate 1.25 mL/min. Fixed-bed-column	(53)
Straw	57.0% (34.9 to 15.0 mg/L over 14 days)	Synthetic produced water Crude oil in brackish water	(54)
Wood Shavings modified with methoxytrimethylsilanes	42.0% (40.6 to 23.6 mg/L over 14 days)	Synthetic produced water Crude oil in brackish water	(54)
Straw modified with methoxytrimethylsilanes	9.0% (15.5 to 14.1 mg/L over 14 days)	Synthetic produced water Crude oil in brackish water	(54)

properties of Tween 80 depend on factors such as pH and ionic strength. In solid lipid nanoparticle solutions, aqueous stability and dispersibility increase with pH and decrease with electrolyte concentration (62).

Previous studies demonstrated that Tween 80-stabilized emulsions remain stable across a pH range of 2–9, with no observed changes in microstructure. Increasing NaCl concentration from 0 to 100 mM in Tween 80-stabilized oil-in-water emulsions slightly increases average particle size, with no additional increase at higher salt concentrations. This effect results from the dehydration of the hydrophilic polyoxyethylene head groups of the non-ionic surfactant due to salt addition (63).

The salting-out effect can explain the improved hydrocarbon removal efficiency with increasing salinity. Salting-out extraction is a technique that separates molecules based on their solubility in a solvent. This method involves adding a high concentration of salt to a solution to induce phase separation by disrupting the homogeneous mixture (64). While the salting-out effect drives hydrocarbons toward the polymer-water interface, the surfactant partially counteracts this effect by enhancing solubilization. This occurs because the surfactant lowers surface tension and facilitates hydrocarbon solubilization (65). Interactions between surfactant and salt concentrations have been observed by other researchers. It was reported that high surfactant concentrations led to more efficient removal of dye molecules (methyl orange) due to increased reverse micelle formation. When 3% $CaCl_2$ was used instead of 1%, dye removal efficiency increased with higher surfactant concentrations. This was because the salting-out effect reduced the critical micelle concentration (CMC) of the surfactant (66).

The interaction between pH and surfactant, as shown in Figure 3, can be attributed to the micelle effect. The micelle effect is a phenomenon in which surfactant molecules cluster around hydrophobic compounds, such as total petroleum hydrocarbons (TPHs), enhancing their solubility in water. The efficiency of TPH removal by micelles is influenced by the concentration of surfactants used. Surfactant molecules can exist as monomers, micelles, hemimicelles, or admicelles, depending on their concentration. Higher surfactant concentrations enhance interactions between Tween 80 and water at a specific temperature (67). The concentration at which micelles begin to form is known as the CMC. The CMC of Tween 80 in pure water is approximately 13.0 mg/L (68). The CMC of surfactants varies with pH, as they possess both hydrophilic and hydrophobic characteristics. Solution pH can affect the ionization of the surfactant's hydrophilic groups, altering the molecule's overall charge. This change in charge can affect the ability of surfactant molecules to form micelles, ultimately altering the CMC of surfactants (69).

Tween 80's emulsifying properties are influenced by pH (70). A study examined the effect of pH on the stability of an emulsion formed by Tween 80 and gas condensate. At 25 °C, the emulsion was more stable at pH 7 than at higher pH levels (e.g., pH 8–10) and exhibited greater stability at lower pH levels (e.g., pH 4–6) (71).

Previous experimental research has shown that the adsorption of a non-ionic surfactant, Triton X-100, can block a substantial proportion of micropores (<2 nm) and mesopores (2–50 nm) in activated carbons. Specifically, 80%–90% of micropores and 20%–60% of mesopores were blocked, an effect attributed to the larger size of the surfactant molecules or their aggregates relative to the pore dimensions (72). Therefore, the reduced removal efficiency at high surfactant concentrations may result from surfactant-oil aggregates blocking polymer pores. Furthermore, polymeric absorbents can serve as a pre-treatment option to reduce hydrocarbon levels in PW, offering a viable solution for treating complex contaminated wastewater.

This research is limited by its focus on synthetically produced water, which may not fully represent the complexity of real-world produced water compositions. Additionally, the maximum HEM removal efficiency indicates incomplete pollutant removal, suggesting limitations in the sorbent's capacity or the method's applicability for comprehensive treatment. Ongoing research into modified polyurethanes and optimized system designs, validated through pilot-scale trials, is essential for overcoming these challenges and enabling widespread adoption of sustainable produced water treatment practices.

Conclusion

This study demonstrates that the quantity of surfactant significantly affects the removal of n-hexane extractable material (HEM) from synthetic produced water (PW) using a polymeric sorbent (Desmopan® 5377A). Increasing the concentration of Tween 80 enhances HEM sorption up to an optimal level (482 mg/L), beyond which sorption efficiency declines. The emulsifying properties of Tween 80 are influenced by the pH of the PW, necessitating careful selection of the pH range to optimize sorption performance. Surfactant concentration critically impacts HEM removal efficiency: insufficient concentrations fail to form micelles, leading to incomplete removal, while excessive concentrations form micelles that hinder efficiency. Additionally, in the absence of surfactants, increasing salinity does not significantly enhance hydrocarbon removal efficiency. Research should aim to scale up the sorption process for industrial use, including analyses of surfactant costs, pH control, and sorbent regeneration, with pilot studies assessing integration into current produced water treatment systems.

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Authors's contributions

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Competing interests

The authors declare that they have no competing interests.

Ethical issues

The ethics committee has ethically approved this project with the registration code IR.ZUMS.REC.1397.298.

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