



Evaluation of polymeric adsorbents via fixed-bed columns for emulsified oil removal from industrial wastewater

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ABSTRACT

Polymeric adsorbents (PAs) have been gaining increased attention for application in industrial wastewater (WW) treatment. However, most studies on evaluating PAs specifically for emulsified oil removal are currently limited to performance screening through batch mode testing. Hence, this paper presents a thorough fixed-bed assessment of advanced PAs for the removal of emulsified oil from industrial WWs. A unique custom-built column setup was developed with a continuous test protocol that involves both adsorption and regeneration of media. A robust procedure was also established to automatically prepare a representative synthetic produced water (PW) containing the oil-water emulsions. Four cutting-edge PAs were evaluated, out of which two being tested for the first time targeting emulsified oil removal. Experimental tests were conducted to address resin capacity, regeneration efficiency, and performance reproducibility in repeat cycles. PA2 treated 168 ± 58 bed volumes (BVs) achieving the lowest capacity of 44 ± 14 mg/g. Higher comparable capacities were observed for PA1 and PA3 at ~100 mg/g, yet PA1 was found capable of treating 807 ± 3 BVs against 548 ± 115 BVs measured for PA3. PA4 treated 1219 ± 86 BVs with a capacity of 301 ± 27 mg/g which indicate its strong potential for industrial WW treatment application. This performance data can provide a reference for comparison when testing other novel resins for emulsified oil removal. Future studies will focus on testing PAs using real PW and evaluating their long-term performance via pilot testing.

1. Introduction

Significant volumes of industrial wastewater (WW) are produced within the oil and gas (O&G) industry. Produced water (PW) is considered one major byproduct stream that is generated during the O&G drilling operations at an average of 3–4 barrels per barrel of oil extracted [1–4]. Over the past years, conventional treatment technologies were applied on PW targeting the removal of suspended solids and free/dispersed forms of total oil and grease (TOG) [5]. Nevertheless, several recent drivers associated with environmental regulations restricting the PW injection volumes and the oil-in-water discharge limits have instigated the need for finding innovative solutions for beneficial reuse application. Emulsified oil is one complex form of oil in PW at which the oil molecules are strongly bonded to the water molecules in presence of a surface-active agent. Emulsified oils are not removed by conventional technologies and require applying advanced treatment. One of the best

available advanced technologies applied for water recycling purposes are membrane processes due to their compactness, high removal performances of organics, and their low consumption of energy. However, associated shortcomings include pretreatment requirements and membrane fouling which limit their lifespan [1,5–7]. Adsorption processes are also classified under advanced treatment and have been gaining increasing attention in fields of water treatment. Key advantages of adsorption processes include their simplicity, ease of operation, media selectivity, and resin recyclability [8,9].

There are various types of adsorptive media applied for oil-water separation. Activated carbon is a traditional adsorbent known for its ability to remove selective types of contaminants [10,11]. Still, the associated high production and regeneration costs of activated carbon are considered key disadvantages limiting its application. Therefore, in seek of more cost efficient alternatives, multiple studies focused on exploring the use of natural adsorbents such as zeolites [12–15] and

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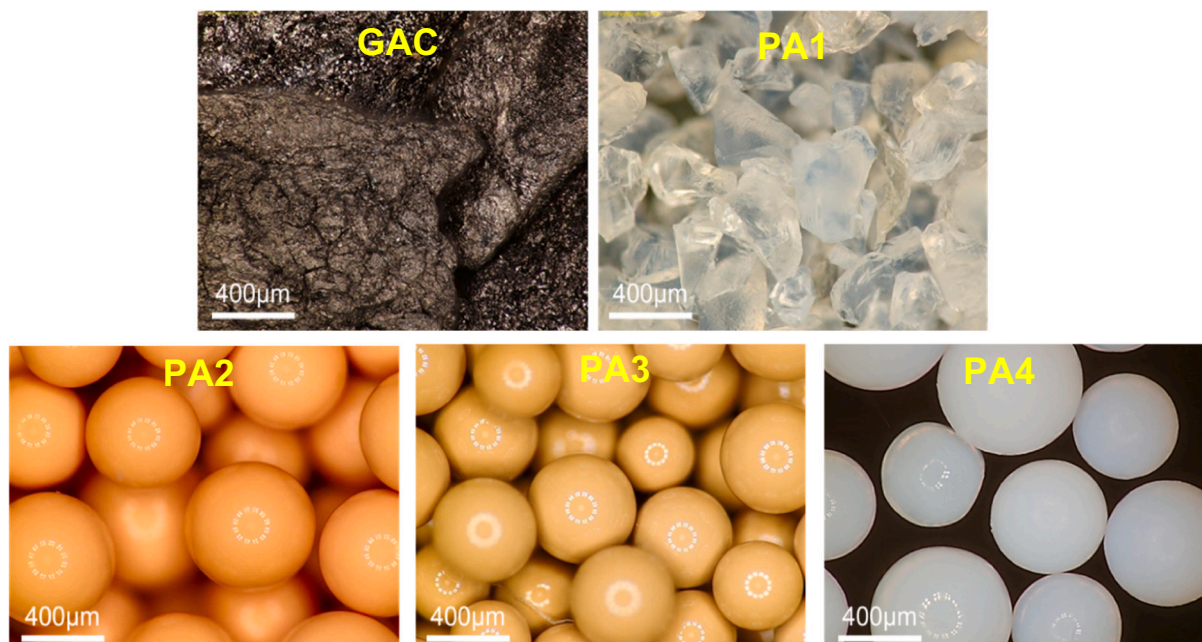


Fig. 1. Microscope analyses on tested media.

other industrial or agricultural waste materials [16–22]. Nevertheless, limitations on their local availability, selectivity, and recyclability restrict their application within the O&G industry. A more practical alternative is the use of advanced synthetic polymeric adsorbents (PAs) that are not tailored to strongly bind with the solute as activated carbon, which allows for applying simpler regeneration means such as solvent extraction [23,24].

Different parameters are considered when evaluating the performance of an adsorptive media at bench scale level. Adsorption processes are known to be affected by the change of several operating conditions mainly including contact time, feed concentration, dosage, pH, and salinity. As reported by many studies, batch mode testing is typically conducted to assess the effect of varying the aforementioned parameters on the resin performance [25–28]. It is also critical from an industrial perspective to assess the adsorbent retention capacity, cleanability, and replacement frequency. Fixed-bed column testing is required for such evaluation. The standard ASTM D6586–03(2021) method describes a rapid small-scale column test (RSSCT) for predicting the performance of granular activated carbon (GAC) at a scaled-down test version of either a pilot or a full scale adsorber. In this method, equations and results from batch testing are employed to calculate the RSSCT operating parameters while considering full-scale operating conditions. From the RSSCT, the breakthrough profile and the carbon usage rate can be estimated, yet the methodology does not assess the resin regeneration efficiency and performance reproducibility [29].

To the authors knowledge, available bench scale studies in the area of applying PAs for emulsified oil removal from PW have only involved partial assessment of the adsorbent performance via batch mode testing [18,19,30–34]. For example, Albatrni et al. evaluated the performance of various commercial resins targeting emulsified oil removal in batch tests without considering their regeneration efficiency [35]. Felipe Rocha et al. tested commercial cationic, anionic, and mixed polystyrene resins using synthetic vegetable oil in water emulsions at batch mode only [36]. Additionally, Abou Chacra et al. tested modified graphene magnetite for emulsified oil removal in both batch and column test modes using synthetic and real PWs, yet regeneration efficiency and performance reproducibility were not adequately addressed [27]. Another key component in evaluating the resin performance involves the use of a representative feed solution. Since access to actual

wastewater is limited due to availability and associated health and safety concerns, the use of synthetic wastewater has become more applicable for bench scale evaluations [25,34,36–41]. The use of a suitable oil source is also crucial. As confirmed by Dardor et al., synthetic PW recipes involving the use of vegetable or refined oils are not representative in mimicking the characteristics and behavior of actual PW [42]. Thus, crude oil from O&G operation was used in this study for preparing the oil-in-water emulsions in the synthetic PW targeting tertiary treatment application.

Based on the above, this study capitalizes on existing knowledge provided in literature and the authors' experience from the O&G industry and delivers a thorough fixed-bed performance assessment of various advanced PAs applied for the removal of emulsified oil from PW. A representative synthetic PW recipe was used in various media evaluations which addressed retention capacity, cleanability, and performance reproducibility in successive testing cycles. Cutting-edge PAs, some of which exclusively examined for this specific application, were evaluated at similar conditions and their performance was compared.

2. Materials and methods

2.1. Selection and characterization of adsorbents

2.1.1. Adsorbents

Several established and/or cutting-edge adsorbents were selected for evaluation including:

- **GAC:** 1240 W, coal-based, steam activated, Norit®. GAC is known as an established adsorbent applied for oil-water separation hence it was selected as a benchmark for performance comparison.
- **PA1:** is a PA structured with bonded benzene rings to a siloxane backbone. Several pilot and field trials have been conducted confirming the applicability of PA1 in removing different types of hydrocarbons from industrial waters [43]. Hence, PA1 was considered for evaluation.
- **PA2:** are red-brown polymeric solid beads. Various studies have evaluated PA2 in either batch or column modes for the removal of different types of contaminants [25,44–48]. PA2 was selected for

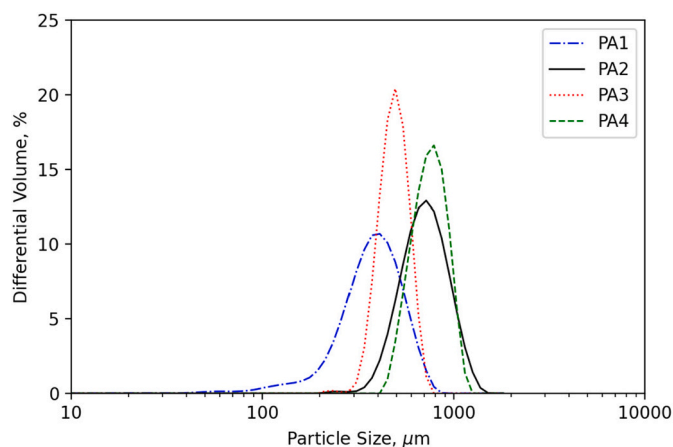


Fig. 2. Particle size distribution for the different resins evaluated.

evaluation to thoroughly assess its performance in removing emulsified oil under representative industrial conditions.

- **PA3:** brown/light brown polymeric solid beads. Similar to PA2, PA3 has been also tested for a variety of applications [23,49–51]. In terms of organics, studies so far were limited to the removal of naphthenic acids [25]. Therefore, this study will be the first to evaluate the performance of this polymeric resins targeting emulsified oil removal.
- **PA4:** white polymeric solid beads. PA4 applications were focused on food, textile, and pharmaceutical industries [52]. Thus, this study will also be the first to assess the performance of PA4 for the removal of emulsified oil.

2.1.2. Microscope imaging

Microscope analyses comparing the surface structure of the tested adsorbents were performed as shown in Fig. 1. PA2, PA3, and PA4 were all found to possess 3-D spherical shapes at different particle size distributions. PA1 particles were found to be more heterogeneous with a wider size distribution range. Prior to performance testing, GAC particles were sieved to a blend of 14/16 mesh sizes in order to remove fine particles and avoid pressure build within media bed. This size range agrees with the observed bigger particles for GAC when compared to the other adsorbents. In addition, the surface of GAC particles was confirmed to be porous as reported by other studies [53].

2.1.3. Particle size distribution

Particle size analysis was conducted to determine and compare the size distributions for PA1, PA2, PA3, and PA4. As seen in Fig. 2, overall, the particles range from 70 to 1100 μm . PA3 has the narrowest distribution (coefficient of variation (CV): 17.3 %) with an average particle size (mean) of 513 μm and standard deviation (SD) of 88 μm . PA4 also has a narrow distribution (CV: 27.1 %), but larger particles compared to PA3; the mean size for PA4 is 836 μm with a SD of 227 μm . PA2 (CV: 27.6 %) has a mean particle size of 759 μm and SD 209 μm ; having a close similarity to PA4. Lastly, PA1, which has the widest distribution (CV: 36 %) has a mean particle size of 405 μm with a SD of 144 μm . The evaluated resins had very uniform particle sizes, the majority above 100 μm which prevent excessive pressure drops within the resin bed. PA1's distribution included the smallest particles, but they were still large enough for column testing. Since all the resins have particle size within a close range, the void fraction in the columns is expected to be similar for all the resins.

2.2. Chemicals

In this study, deionized (DI) water was supplied by Milli-Q ultrapure water system (integral, 10, Merck- Millipore) at a resistivity of 18 $\text{M}\Omega$

Table 1

Analytical & advanced characterization methods.

Parameter	Instrument
Conductivity/pH	Orion 3 Star meter
Total organic & inorganic carbon, total nitrogen (TOC, IC, TN)	TOC analyzer (TOC-V, Shimadzu)
Total oil & grease (TOG)	TD560, Turner Designs
Particle size distribution	Beckman and Coulter Analyzer, Model LS13320
Microscope imaging	Olympus DSX1000

Table 2

Water quality of synthetic PW.

Parameter	Unit	Synthetic PW
pH	–	7.8
Conductivity	ms/cm	7.2
TOC	mg/L	125
O&G	mg/L	100
Cl^-	mg/L	2265
Na^+	mg/L	1000
SO_4^{2-}	mg/L	50
K^+	mg/L	50
Mg^{+2}	mg/L	62
Ca^{+2}	mg/L	300
NH_4^+	mg/L	10
HCO_3^-	mg/L	100

cm. Salts for preparing the brine solution were all obtained from Sigma Aldrich at 99 % purity including: sodium chloride, calcium chloride dihydrate, magnesium chloride hexahydrate, potassium chloride, sodium sulfate, ammonium chloride, and sodium bicarbonate. A medium grade – crude oil from O&G operation ($^\circ\text{API}$: 38.7 and density at 25 $^\circ\text{C}$: 0.825 g/mL) was used as the oil source in the synthetic PW. Emulsions were formed using a surfactant namely sodium dodecyl sulfate (SDS) acquired from Thermo Fischer Scientific. Several reagents were tested for media regeneration including Ethanol, toluene, methanol, acetone, and isopropyl alcohol (CHROMASOLV[®], for HPLC, $\geq 99.9\%$) which were all obtained from Thermo Fischer Scientific. Sodium hydroxide pellets – NaOH and hydrochloric acid 37 % were acquired from Sigma Aldrich and used for pH adjustment.

2.3. Analytical & advanced characterization methods

Table 1 lists the analytical methods used in this evaluation for performance tracking as well as for adsorbent media characterization.

2.4. Preparation of synthetic PW

A representative synthetic PW recipe that was developed in earlier studies [5,42] was used for the oil-water separation tests. The recipe includes three main components: a low saline matrix (i.e. brine at total dissolved solids (TDS): ~ 3800 mg/L) mimicking the salinity of a gas field PW [54], crude oil from O&G operation and a surfactant (SDS) used to disperse the crude oil into the saline aqueous phase in a ratio of 5:1 (oil to surfactant). Adsorption processes are classified under tertiary treatment with influent oil concentrations at ~ 30 mg/L. However, since this study targets conducting a comprehensive performance evaluation of the adsorbent, a recipe of higher oil content (~ 100 mg/L) was developed to enable saturating the media while using practical volumes of feedwater at bench level. To prepare the synthetic PW, 500 mL of brine mimicking the ionic compositions specified in Table 2 was prepared using DI water and salt concentrations calculated previously [5,42]. Then, ~ 17 mg of SDS and 0.1 mL of crude oil were added to the brine. The mixture was then magnetically stirred at 1000 rpm for 1 h and the final solution was stored in a glass bottle and used immediately in the oil-water separation tests. A summary of the analytical results for the

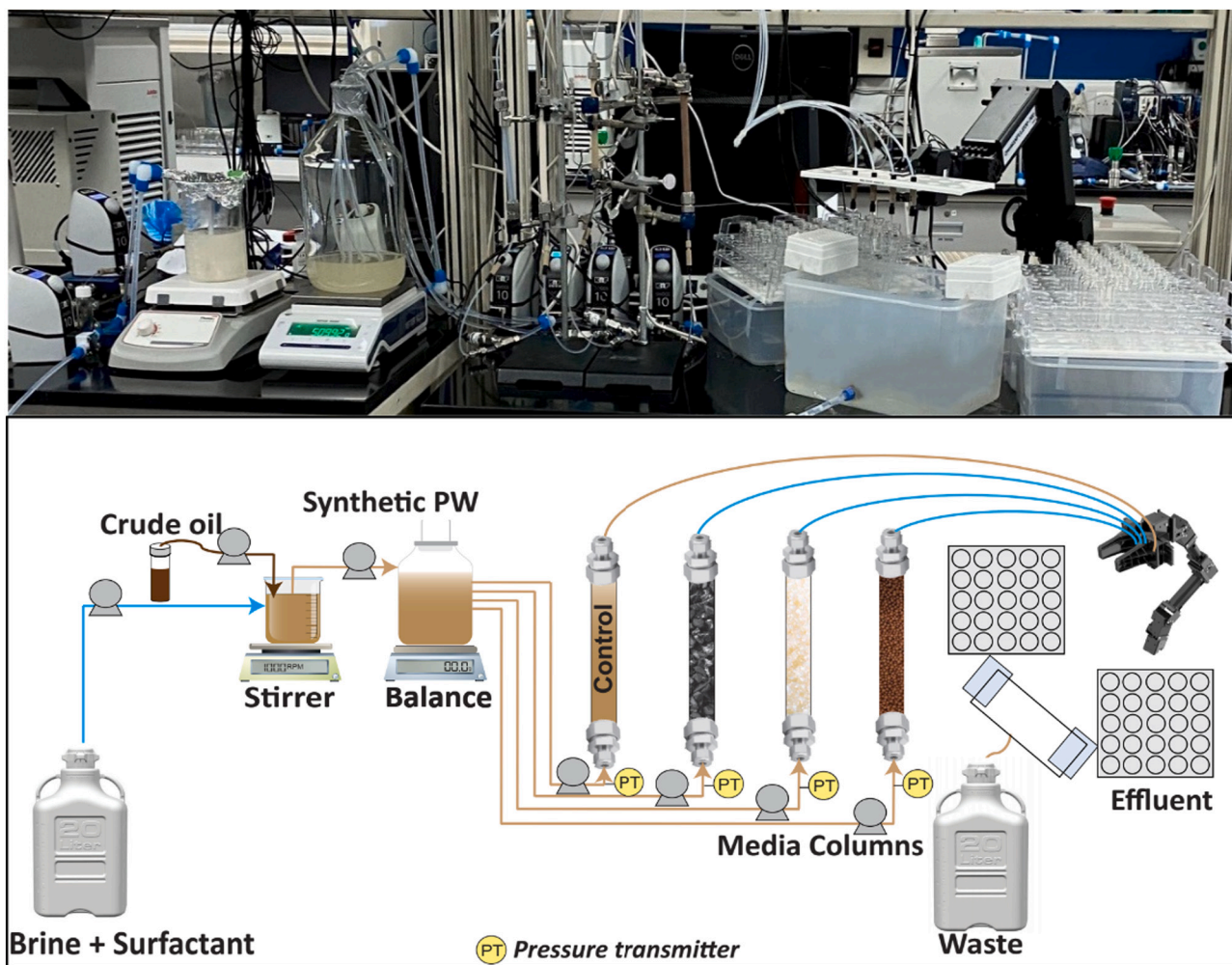


Fig. 3. Column test setup and diagram.

synthetic PW solution is shown in Table 2. Fig. S3 in the supporting information (SI) presents the particle size distribution for the PW. A mean droplet size of $2.72 \mu\text{m}$ was detected which is within the typical size range of oil-water emulsions of $<20 \mu\text{m}$ [42]. The impact of higher initial feed concentration was assessed in batch test mode at which a 30 mg/L TOC solution ($\sim 5 \text{ mg}$ of SDS and 0.03 mL of crude) was tested and compared to the 100 mg/L feed recipe.

2.5. Bench testing setup and protocol

2.5.1. Media preparation

Prior to testing, all adsorbents were cleaned to remove any organics or preservatives. For GAC, it was initially sonicated in DI water for 30 min (5–6 cycles for every 10 g media/250 mL DI water). GAC was then dried in the oven at $105 \text{ }^\circ\text{C}$ for 3 h. To avoid pressure build up in the column by fine particles, GAC was sieved (USA standard test sieve, Cole Parmer). A blend of 14 mesh (40 %) and 16 mesh (60 %) was used in testing. For PA1, PA2, PA3, and PA4, based on vendor recommendation, those resins were not expected to leach organics thus they were soaked in DI water for 24 h, rinsed with DI water before vacuum filtration through 0.45-micron filter and drying at $60 \text{ }^\circ\text{C}$ for 3 h. Other published studies have reported similar cleaning procedures [25].

2.5.2. Batch mode testing

Initially, batch tests were performed to assess the impact of changing operating conditions on the resin performance. Those conditions were also identified by other studies including contact time, initial feed

concentration, media dosage, and pH [35,55]. All batch tests were performed using 250-mL capped Erlenmeyer glass flasks and a shaker (VWR Scientific Advanced Orbital Shaker Model 3500) set at 200 rpm. Two “Control” samples were considered in testing. A feed control sample (i.e. feed PW with no resin) used in each test to track the change in feed concentration attributed to the testing method (e.g. shaking), and a resin control sample (resin with DI water) used to check the release of organics by the resin. TOC analyses were performed for measuring organic removals which were calculated considering both control samples. The range of conditions followed for every sub-batch test performed using 250 mL of feed volume includes:

- Contact time: 0–170 h
- Dosage: 100–5000 mg/L
- Feed TOC concentration: 30 and 100 mg/L
- pH: 4 (acidic), 7.8 (original PW), and 10 (basic). Adjusted using 0.1 M NaOH or 6 N HCl

2.5.3. Fixed-bed column testing

2.5.3.1. Setup. As shown in Fig. 3, different resins were evaluated using a custom-built unit consisting of 4 testing columns (PFA, Swagelok, diameter: 0.95 cm) each connected to a positive displacement pump (KNF, Switzerland). The setup was designed to operate using one control column (column without resin) and up to three resin columns tested simultaneously using a common feed solution. The control column was used to measure the change in feed TOC as it passes through the different

parts of the test setup (e.g. pumps, pipes, and glass wool). A pressure sensor (Omega Engineering, USA) was installed after each pump to record the operating pressure of each column. The outlet of every column was connected to an automatic sampling arm (Open Manipulator P, Robotics, South Korea) that collects samples at specific time intervals. The arm was programmed using the Robotic Operating System (ROS, Open-Source Robotics Foundation, USA) with a custom-made C++ code to specify the sampling location and timing. To avoid media floating, weighed amounts of glass wool (~45 mg) were added to the bottom and top of the column. The bed volume (BV) for all tested resins was set as ~10 mL (~14 cm as bed height). Masses of 6.8 g for GAC, 4.8 g for PA1, 3.0 for PA2, 3.6 for PA3, and 2.5 for PA4 were used.

2.5.3.2. Automated preparation of synthetic PW. The set-up incorporated an automated feed solution preparation system that prepared the synthetic PW solution based on the feed tank level. The feed tank was placed on an analytical balance (Mettler Toledo, USA) that was connected to a CompactRIO control system (cRIO 9068, NI, USA) programmed in LabVIEW (NI, USA). When the feed tank weight reaches a low set point, a positive displacement pump (KNF, Switzerland) transfers 500 mL of brine that already contains SDS to a mixing beaker placed on top of a stirred plate. Once the brine and SDS mixture has been transferred, another positive displacement pump (KNF, Switzerland) will turn on and transfer 100 μ L of oil to the beaker. The stirred plate is then automatically turned on by the control system and starts mixing the solution for 60 min at 1000 rpm. Once complete, the synthetic PW batch is transferred to the feed tank, located on top of a balance, increasing its weight above the set point.

2.5.3.3. Regeneration system. Solvent regeneration was performed using an Agilent High-performance liquid chromatography (HPLC) system (Agilent 1100, USA) that consists of a 4-channel gradient pump allowing inline mixing of up to 4 different solvents. Before the mixing point, the solvents flow through a degasser which removes any dissolved gases.

2.5.3.4. Experimental protocol. Performance assessments were conducted addressing the resin saturation, cleanability, and performance repeatability. The test protocol includes the following steps:

- Conditioning

As recommended by their vendor, PA1, PA3, PA2, and PA4 were all rinsed with ethanol using the HPLC system at flowrate of 1 mL/min. The alcohol conditioning step has been also utilized to dissolve the air trapped within the beads allowing the resin to settle before operation. The resin bed was then rinsed with DI water for 24 h. TOC analysis was performed on the effluent to ensure that ethanol was flushed out completely (i.e. TOC < 1 mg/L).

- Treatment

The resin was then tested using the synthetic PW while operating up to saturation to obtain the full resin breakthrough curve. Tests were performed using flowrate of 1 mL/min in a bottom to top flow direction. Effluent samples were collected by the arm every 2, 4, 6, or 8 h to be analyzed for both TOC and TOG. Such broad methodology of performance tracking resulted in generating enough data that better described the performance of the adsorbent. Since SDS prohibits biological activity [56], bacteriostatic preservatives were not added to the feed.

- Regeneration

Various studies have reported the use of solvents for adsorbent regeneration [25,27]. In this study, two factors were considered before selecting a suitable regenerant: the solubility of the crude oil used to

Table 3
Adsorption isotherm models.

Model	Expression	Linearized form	Plot
Kinetics			
PFO	$\frac{dq}{dt} = k_1(q_e - q)$	$\ln(q_e - q) = \ln(q_e) - k_1t$	$\ln(q_e - q)$ vs t
PSO	$\frac{dq}{dt} = k_2(q_e - q)^2$	$\frac{t}{q} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e}$	$\frac{t}{q}$ vs t
Isotherms			
Langmuir	$q_e = \frac{q_m b_0 C_e}{1 + b_0 C_e}$	$\frac{C_e}{q_e} = \frac{1}{b_0 q_m} + \frac{1}{q_m} C_e$	$\frac{C_e}{q_e}$ vs C_e
Freundlich	$q_e = K_f C_e^{1/n}$	$\ln(q_e) = \ln(K_f) + \frac{1}{n} \ln(C_e)$	$\ln(q_e)$ vs $\ln(C_e)$

prepare the feed PW in the solvent and the resin compatibility with that solvent. Approximately 0.5 mL of crude oil was mixed with various solvents namely methanol, acetone, ethanol, isopropyl alcohol, and toluene. The solubility of oil in the different solvents was compared and the one found suitable was selected to develop the complete regeneration procedure. Regeneration using the selected regenerant was performed using the HPLC system to utilize the gradient mixing of different solvents. Operation was carried out in reverse flow direction (i.e., top to bottom) at flow of 1 mL/min.

As a more representative approach for evaluating the performance of adsorptive media under industrial testing conditions, repeat test cycles (3 \times) of treatment followed by regeneration were conducted on each of the tested resins. A single test cycle was performed on GAC since it requires regeneration by thermal means (e.g. steam).

3. Theory and modeling

The influence of selected operating parameters like contact time, initial feed concentration, media dosage, and pH on the resin performance was studied in batch testing mode. In order to understand the impact of those parameters on the adsorption process and illustrate the resin adsorption mechanism, different predictive models were applied to forecast adsorption behaviors and describe generated equilibrium curves.

3.1. Adsorption kinetics

Batch tests studying the adsorption kinetics via varying the contact time between the solute and the adsorbent were performed for estimating the time required for the adsorption process to reach equilibrium. The equilibrium state can be defined as the condition where no further adsorption takes place at which the rate of solute adsorption from the solution to the adsorbent surface equals the rate of solute desorption from the surface of the adsorbent to the solution. Adsorption kinetic models are usually applied for predicting the adsorption equilibrium time and estimating the rate of the process [57]. Two commonly used kinetic models describing the process rate were employed for modeling experimentally obtained data including the pseudo first order (PFO) model proposed by Lagergren [58] and the pseudo second order (PSO) model [26]. Table 3 summarizes the expressions used for both kinetic models along with their linearized form.

3.2. Adsorption isotherms

Adsorption isotherms are typically applied for describing and understanding the adsorption process equilibrium and the relation between the amount of solute adsorbed per mass of adsorbent (q) and the residual solute concentration at equilibrium (C_e). In this study, two commonly applied isotherm models referred to as Langmuir and Freundlich were employed for data modeling. While Langmuir assumes the adsorption on homogeneous surfaces and provides prediction for monolayer adsorption mechanism, Freundlich is concerned with

heterogeneous surfaces and multilayer adsorption mechanism [16,31]. Table 3 lists expressions for both isotherm models along with their linearized form.

Where, q is the adsorption capacity in mg/g, k_1 is the PFO rate constant in h^{-1} , k_2 is the PSO rate constant in g/mg.hr, q_e is the adsorption capacity at equilibrium in mg/g, t is time in hr, q_m is the maximum adsorption capacity in mg/g, C_e is the effluent concentration at equilibrium in mg/L, b_0 is a Langmuir constant describing the net enthalpy of adsorption, K_f is a Freundlich equilibrium constant describing the adsorptive capacity, and n is a Freundlich constant indicating the affinity of adsorbate to the adsorbent surface. Typically, Freundlich constant n can be used to describe the adsorption process as unfavorable if $0 < n < 1$, favorable if $n > 1$, irreversible if $n = 0$, and linear if $n = 1$ [55].

3.3. Breakthrough curves: Thomas model

After batch mode testing, the performance of each adsorbent was evaluated in column test mode. Breakthrough curves describing the resin performance in terms of effluent concentration profile are generated and one of the most applied mathematical models known as Thomas model was used for performance prediction [59,60]. Thomas equation is described in Eq. (1):

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{th}q_m M}{Q} - k_{th}C_0 t\right)} \quad (1)$$

where k_{th} is a constant in L/mg.min, q is the maximum adsorption capacity in mg/g, C_0 and C are the feed and effluent concentrations in mg/L, M is the mass of sorbent in g, Q is the flowrate in mL/min, and t is time in min. The linearized form of Thomas model is expressed as Eq. (2):

$$\ln\left(\frac{C}{C_0} - 1\right) = \frac{k_{th}q_m M}{Q} - k_{th}C_0 t \quad (2)$$

By plotting $\ln\left(\frac{C}{C_0} - 1\right)$ vs t , Thomas parameters can be obtained from the resulted linear correlation using the slope (i.e. $k_{th}C_0$) and y-intercept (i.e. $\frac{k_{th}q_m M}{Q}$).

As a more representative parameter for industrial application, the breakthrough curves were presented in terms of the effluent to feed ratio (C/C_0) against the number of treated BVs.

3.4. Mass transfer zone (MTZ)

The MTZ is part of the breakthrough curve obtained from column testing. It develops across the axial direction of the bed and both the shape and the length of it are closely related to the performance of the adsorbent. MTZ is typically defined as the moving area across the resin bed where the adsorbate concentration varies between 5 % (breakthrough point) and 95 % (saturation point) of the feed concentration (C/C_0) [61]. In ideal scenarios, the mass transfer faces no resistance (i.e. instantaneous) signifying that the whole resin bed is being utilized efficiently during the treatment process. However, real case scenarios would involve several factors influencing the mass transfer within the bed including the adsorbent properties, the column depth, the adsorbate pH and concentration, and flowrate [62]. A slower mass transfer rate implies the formation of a wide MTZ within the bed requiring more BVs for media saturation. The wider the MTZ the bigger the fraction of unused resin bed upon reaching the breakpoint. The length of MTZ was calculated for each test cycle in order to understand the variation in the shape of the resulted breakthrough curves. First, BVs required for the C/C_0 ratio to reach 5 %, 95 %, and 100 % were identified from the breakthrough curve. After that Eq. (3) was applied to calculate the length of the MTZ as a % of the total bed length.

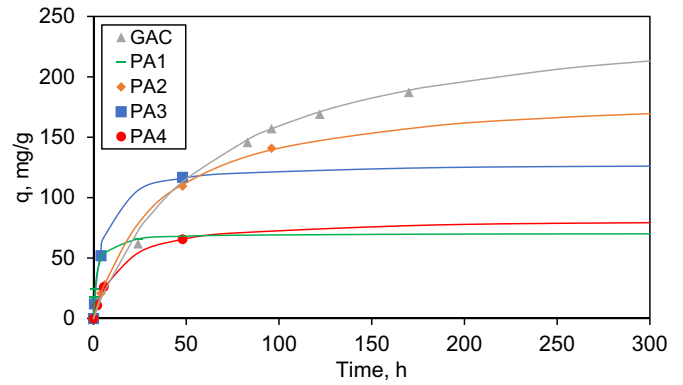


Fig. 4. PSO kinetics prediction and comparison with experimental data.

Table 4

Media ranking based on PSO kinetics (from fastest to slowest).

Rank	Media	PSO adsorption rate, K_2 (g/mg-h)
1	PA1	8.51E-03
2	PA3	1.56E-03
3	PA4	9.63E-04
4	PA2	1.57E-04
5	GAC	6.41E-05

$$\%MTZ = \frac{BV_{95\%} - BV_{5\%}}{BV_{100\%}} \times 100\% \quad (3)$$

4. Results and discussion

4.1. Batch test results

Prior to column test evaluations, initial performance screening tests were conducted in batch mode which involved assessing the effect of varying contact time, initial feed concentration, media dosage, and pH on the adsorbent performance.

4.1.1. Effect of contact time

It is important to measure the time required by each resin to reach its equilibrium adsorption capacity. In this test, the contact time for the five tested adsorbents (GAC, PA1, PA2, PA3, and PA4) was varied between 0 and 170 h while fixing other operating conditions (i.e. feed TOC of ~100 mg/L, pH at 7.8 and dosage of 1000 mg/L). Experimental data were modeled using the adsorption kinetic models namely PFO and PSO. In agreement with several adsorption studies [63], the PSO was found to better predict experimental results for all tested adsorbents. Fig. 4 compares the PSO kinetic predictions which were used to estimate the most suitable contact time for reaching adsorption equilibrium. PA1, PA3, and PA4, were found to reach equilibrium faster than GAC and PA2. For those three adsorbents, 48 h was measured as the optimum contact time. Although longer test durations were required for GAC and PA2 to reach equilibrium, similar contact time (48 h) was employed for the subsequent assessments for the purpose of maintaining comparable testing conditions. As per the kinetic rate ranking in Table 4 comparing the PSO rate constant (k_2) from fastest to slowest. GAC and PA2 came last in the rank as both adsorbents required more time before reaching equilibrium. PA1 was found to have the fastest rate followed by PA3, and PA4.

4.1.2. Effect of media dosage

The effect of varying the resin dosage on the adsorption capacity was also evaluated. Multiple dosages were tested for each resin while fixing initial feed TOC (100 mg/L), pH (7.8), and contact time

Table 5
Langmuir and Freundlich R² comparison.

Media	GAC	PA1	PA2	PA3	PA4
R ²					
Langmuir	0.9887	0.5925	0.9435	0.2062	0.8024
Freundlich	0.8236	0.9743	0.6692	0.9084	0.8338

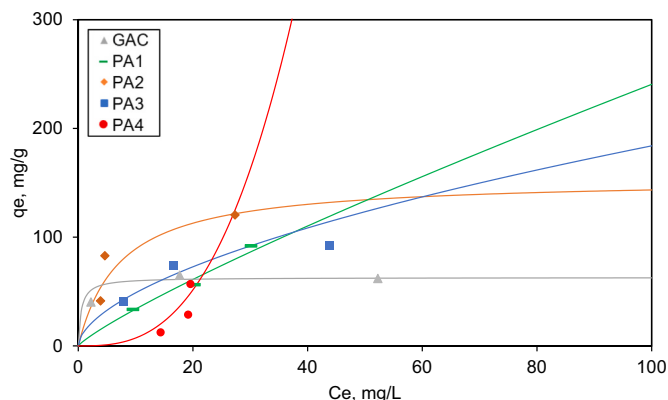


Fig. 5. Adsorption isotherm predictions for GAC, PA1, PA3, PA4, and PA2 against experimental data.

(determined in Section 4.1.1 as 48 h). Both Langmuir and Freundlich adsorption isotherms were used to fit obtained experimental data in which the R² for each model was compared as shown in Table 5. Freundlich isotherm was found to better correlate with experimental data obtained for PA1, PA3 and PA4. GAC and PA2 on the other hand were both better represented by Langmuir isotherm. Based on that, the relation between the equilibrium adsorption capacity and effluent concentration (Ce) was predicted and compared for all tested resins as shown in Fig. 5. Based on Freundlich constant n describing the

favorability of solute adsorption on the resin, all tested resins were representing favorable behavior (i.e. n > 1) to varying extents except for PA4.

Results for the evaluation of impact of feed TOC concentration and pH can be found in the SI. Increased removal performances were attained at lower initial feed concentration. This is attributed to the fact that the resin becomes saturated at higher feed concentrations, thus smaller number of adsorption sites for the remaining oil to be adsorbed are available. Such performance has been verified by other studies evaluating this parameter on different resins [20]. As for pH, results were found to agree with other studies verifying the improved adsorption performances at lower pH values [64].

4.2. Fixed-bed column test results

4.2.1. Selection of regeneration solvent

To select a suitable regenerant, the solubility of crude oil used in this study was tested in different solvents as shown in Fig. 6 A. The crude oil was found soluble only in toluene. Selected resins were all confirmed to be compatible with toluene thus it was selected as the main regenerant. Since the resin beds are initially running on DI water, and to be able to displace toluene attached to the resin, ethanol that is miscible with both water and toluene was used to displace toluene and then DI water was used to displace ethanol. Using the HPLC system, regeneration was carried out using the sequence of solvent blends (as present flow) and timings shown in Fig. 6 B. Each full regeneration cycle takes ~380 min (~6.3 h). The switch between solvents (ethanol and toluene) was done gradually within a period of 1 h. For example, 60 min (from 70 min to 130) were used for the gradual switch from ethanol to toluene before subjecting the bed to pure toluene for another 60 min. Such procedure was developed based on trial and error which was found to be the most efficient in cleaning the tested resins. Each resin bed was further rinsed for at least 24 h using DI water before starting the next cycle. TOC analysis was conducted on the column effluent to ensure that no residual organics are being released by the resin (i.e. TOC is <1 mg/

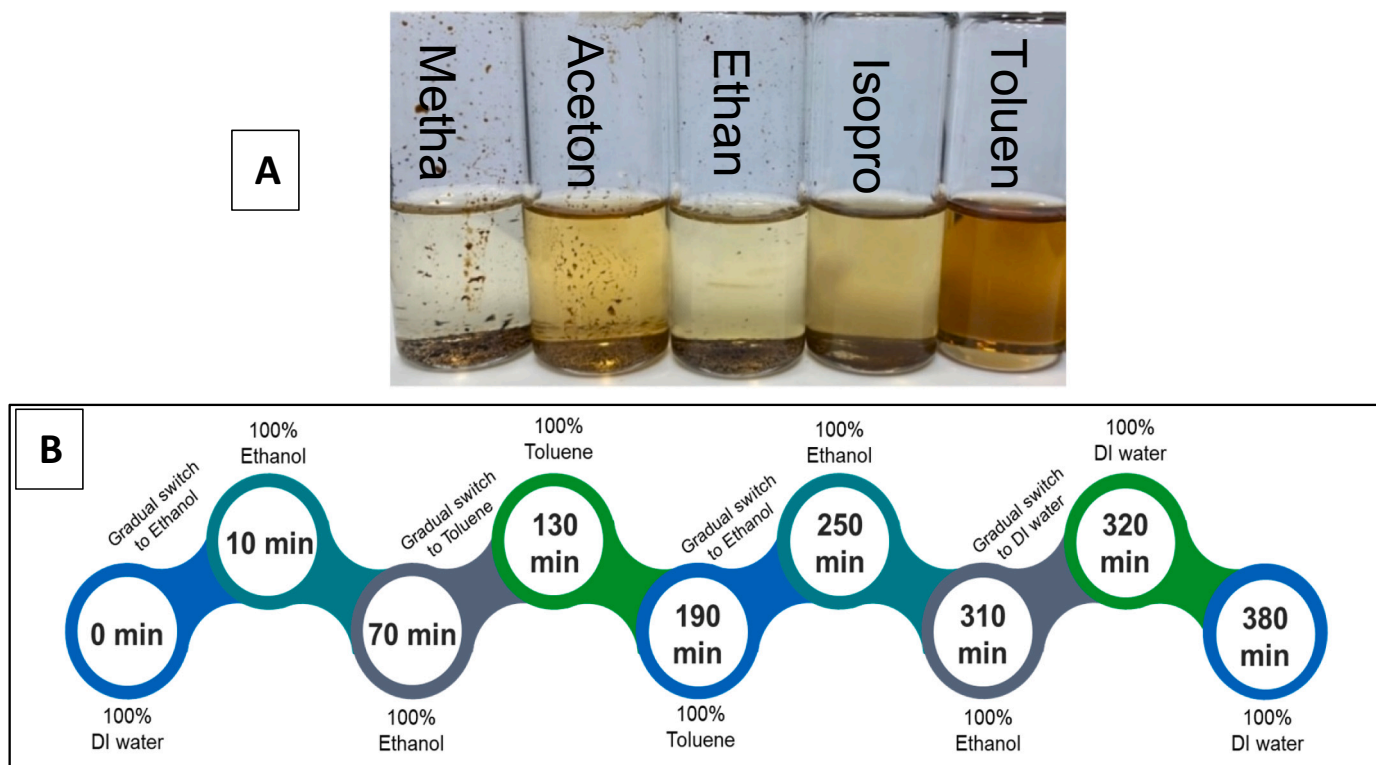


Fig. 6. A: Crude oil solubility in various solvents and B: Solvent regeneration protocol using HPLC.

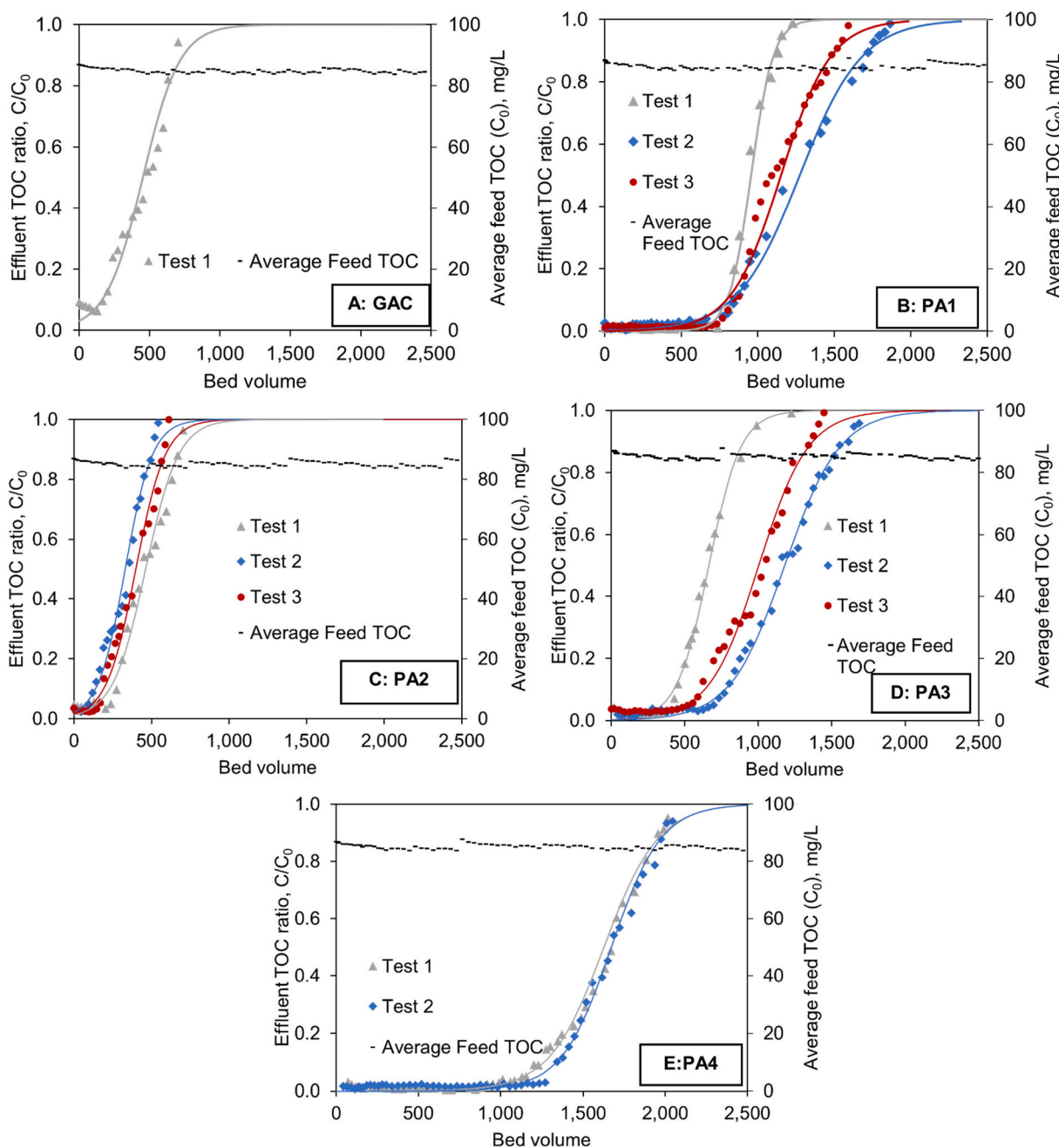


Fig. 7. Breakthrough profiles for tested adsorbents.

Table 6

Thomas model prediction for maximum capacity compared to experimental data.

Media	Max. adsorption capacity	Test 1	Test 2	Test 3
		mg/g		
GAC	Thomas model	52	–	–
	Experimental	55	–	–
PA1	Thomas model	125	151	165
	Experimental	124	163	179
PA2	Thomas model	119	97	109
	Experimental	115	95	103
PA3	Thomas model	134	221	209
	Experimental	136	219	210
PA4	Thomas model	380	429	–
	Experimental	381	427	–

L).

4.2.2. Performance evaluation

Performance evaluation tests were initially performed on GAC, being the standard adsorbent, and then on multiple commercial polymeric adsorbents including resins which were exclusively tested for emulsified oil removal application in this study.

4.2.2.1. GAC. Fig. 7 A presents the breakthrough profile for GAC. Feed samples from the control column were analyzed for TOC and around ~30 % drop was detected. Based on that, reported C/C₀ ratios for all tested media were corrected for the control's TOC. As compared in Table 6, Thomas model predictions for the maximum adsorption capacity was found comparable (i.e. <10 % deviation) to experimental results for the single test cycle performed on GAC. Adsorption treatment in industrial applications is typically carried out up to the start of the

Table 7
MTZ comparison.

Test	Media	MTZ, cm	MTZ, %
1	PA1	3.8	27 %
2		7.5	53 %
3		7.0	49 %
1	PA2	8.9	63 %
2		10.6	75 %
3		9.1	64 %
1	PA3	6.2	44 %
2		8.0	57 %
3		8.8	62 %
1	PA4	6.0	43 %
2		5.0	36 %

Table 8
Performance summary up to breakpoint.

Media	BVs treated	Adsorption capacity		Average permeate	
	#	mg/g	mg/cm ³	TOC (mg/L)	TOG (mg/L)
GAC	95	13	8.9	6.6	5.1
PA1	807 ± 3	111 ± 15	53 ± 7	1.1 ± 0.1	0.23 ± 0.03
PA2	168 ± 58	44 ± 14	13 ± 4	4.5 ± 1.3	4.0 ± 1.3
PA3	548 ± 115	100 ± 12	36 ± 4	2.1 ± 0.6	1.5 ± 0.3
PA4	1219 ± 86	301 ± 27	75 ± 7	0.98 ± 0.07	0.49 ± 0.14

breakpoint - 5 % of feed concentration- for purposes related to maintaining effluent quality. Thus, the resin treatable bed volumes, the adsorption capacity, and the permeate quality (TOC and TOG) were all compared based on data obtained up to the breakpoint. Table 8 compares the experimental adsorption capacities normalized per mass and bed volume for GAC up to the breakpoint. GAC's capacity was measured at 13 mg/g (8.9 mg/cm³). Permeate from the GAC column had TOC of 6.6 mg/L and TOG of 5.1 mg/L confirming the passage of oil to the effluent.

4.2.2.2. PA1. Breakthrough profiles from three repeat test cycles for PA1 are presented in Fig. 7 B. As shown in Table 6, a notable increase in PA1 maximum capacity in cycles 2 and 3 was obtained which is attributed to the change in MTZ. Table 7 compares the MTZ length for PA1 in each test cycle. The MTZ length was only at 27 % of the total bed length in cycle 1 and increased to ~50 % in cycles 2 and 3 justifying the resulted increase in resin capacity. Focusing on the resin performance up to the breakpoint - 5 % of feed concentration, PA1 showed average capacity of 111 ± 15 mg/g (53 ± 7 mg/cm³). Table 8 compares the number of treatable bed volumes by PA1 measured at 807 ± 3. A standard deviation (SD) of 3 bed volumes for PA1 indicates the effectiveness of the applied regeneration in maintaining the resin performance for repeat test cycles. As predicted by the Freundlich isotherm, PA1 possesses a higher equilibrium retention capacity when compared to GAC. Both oil and surfactant were removed from the feed by PA1 at average permeate TOC of 1.1 mg/L and TOG of 0.23 mg/L. Images of PA1 bed during testing are shown in Fig. 8 A. In addition, microscope photos of exhausted and regenerated PA1 are shown in Fig. 8 B.

4.2.2.3. PA2. Resulted breakthrough curves for PA2 are shown in Fig. 7 C. Table 6 compares the estimated maximum adsorption capacity using Thomas model with experimental data. Both were found comparable and showed decreased capacities for cycle 2. This is mainly attributed to the number of treatable BVs before the breakpoint. From Fig. 7 C, only 95 BVs were treated by PA2 in cycle 2 against 238 and 170 BVs for cycles 1 and 3 respectively. As shown in Table 8. Average capacity of 44 ± 14 mg/g (13 ± 4 mg/cm³) was obtained. The higher SD for PA2 confirms the deviation in performance between the test cycles specifically in cycle 2. As expected, the virgin resin in the first test cycle showed the best performance whereas a better performance

representation is obtained upon conducting multiple test cycles. PA2 treatable BVs were estimated as 168 ± 58 BVs. In agreement with the batch results assessing the impact of contact time which indicated that PA2 showed similar kinetics to GAC, column performances for both resins showed comparable number of treatable BVs (considering PA2 SD). PA2 was also found to have higher retention capacity compared to GAC which is in alignment with model predictions from the dosage test (Fig. 5). Average permeate TOC was measured at 4.5 ± 1.3 and TOG at 4.0 ± 1.3.

4.2.2.4. PA3. Fig. 7 D compares the breakthrough curves obtained upon testing PA3 resin. It was noticed that both the breakpoint and the MTZ shape changed between cycles 1, 2, & 3. Thomas-estimated capacities are compared with experimental data in Table 6. The increase in measured capacities for cycles 2 and 3 are attributed to the increased number of treatable BVs before the breakpoint as well as to the increase in the length of MTZ (44 % to 62 %) as shown in Table 7. Focusing on the performance up to the breakpoint (Table 8), average capacity of 100 ± 12 mg/g (36 ± 4 mg/cm³) was obtained upon treating 548 ± 115 BVs. The obtained capacity is comparable to PA1 yet with less operable BVs and higher performance variability (i.e. SD). Average permeate TOC and TOG concentrations were higher than PA1 at 2.1 ± 0.6 and 1.5 ± 0.3 mg/L, respectively. Those initial tests results reflect the applicability of PA3 in removing emulsified oil under industrial conditions, which to the authors knowledge this is the first time this resin has been evaluated for this application. It was also found regenerable allowing it to be operated for multiple testing cycles. Images of PA3 bed throughout testing are shown in Fig. 9.

4.2.2.5. PA4. Fig. 7 E presents the resulted breakthrough curves for PA4 comparing cycles 1 and 2. Data from cycle 3 were non-representative due to increased column pressure drop- attributed to the glass wool-. Experimental maximum capacities were found equivalent to Thomas model prediction as shown in Table 6. Capacities of around 381 and 427 mg/g were measured for cycles 1 and 2 respectively. PA4 showed comparable performances in both cycles in terms of MTZ length and breakpoint confirming the effectiveness of applied regeneration method and the reproducibility of resin performance. PA4's average capacity up to breakpoint (Table 8) was estimated at 301 ± 27 mg/g (75 ± 7) with 1219 ± 86 treatable BVs. The resin produced excellent quality permeate at TOC and TOG of 0.98 ± 0.07 and 0.49 ± 0.14 mg/L respectively. As compared to PA1 and PA3, PA4 showed the highest retention capacity -consistent with Freundlich isotherm in Fig. 5- and the highest number of treatable BVs. Results from this evaluation signifies the promising potential of PA4 to be applied for the treatment of industrial oily wastewaters targeting emulsified oil removal application. Images of PA4 bed throughout testing are shown in Fig. 9.

Table 9 compares the performance of tested cutting-edge PAs in this study to other relevant products reported in literature. Since the current study has exclusively evaluated the performance of PAs targeting emulsified oil removal, the given comparison, listing adsorbents tested for other applications, is only intended to provide a relative performance range to be used for validating obtained results. The comparison confirms that the acquired performance data in this study specifically in terms of adsorption capacity were within reported ranges. This validates the applicability of the tested PAs in removing emulsified oil for industrial application.

It should be also emphasized that the performance evaluation data of various PAs for emulsified oil removal are presented as a target reference for the various global research teams who are currently developing innovative/novel media that are promising step change in performance for oil-water separation applications. The novel adsorption products, which may be enhanced with nanomaterials, should be compared to available products in terms of adsorption capacity, regeneration efficiency, performance reproducibility, resin stability, and perhaps other

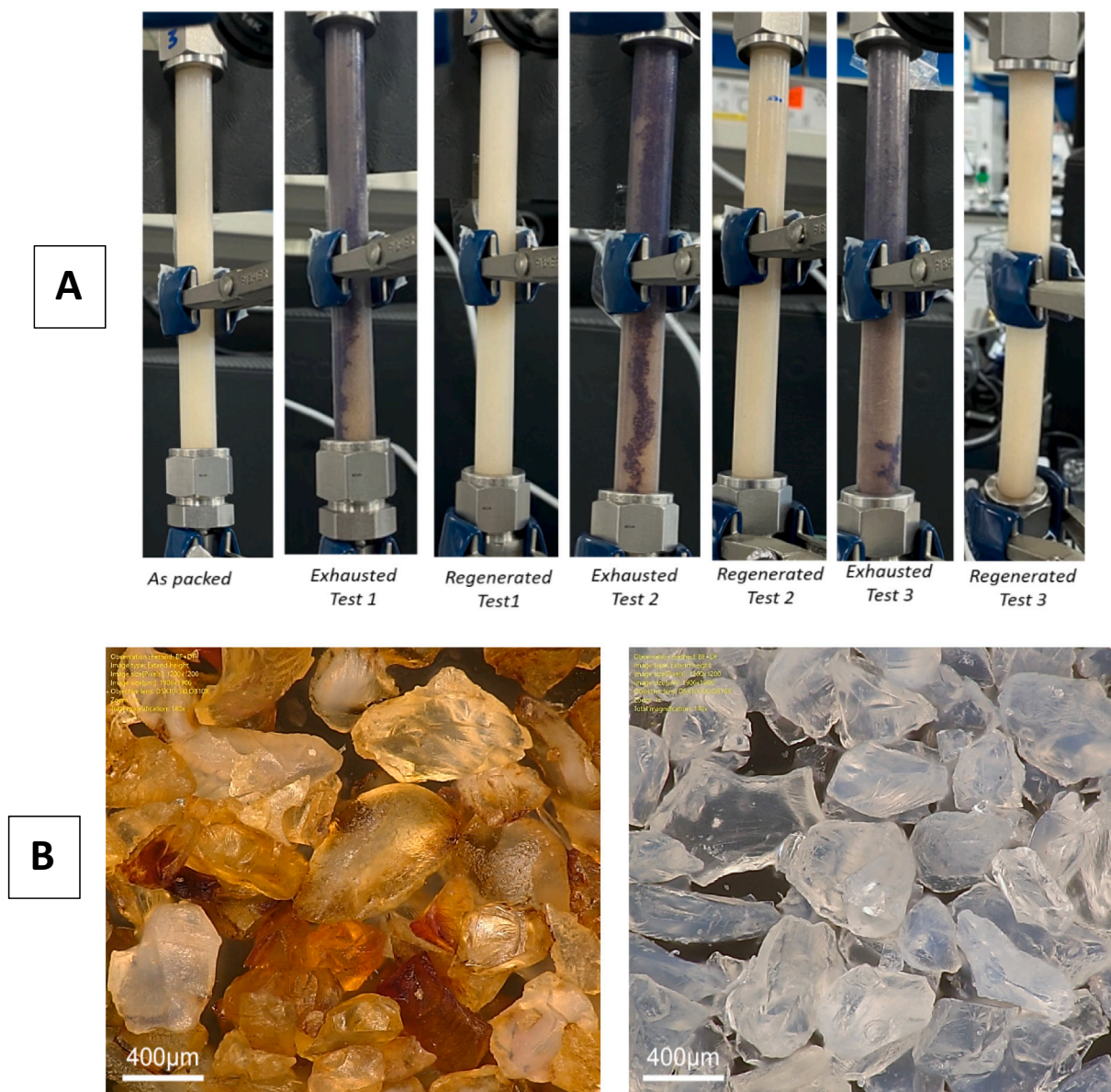


Fig. 8. A: images of PA1 throughout column testing and B: Microscope images of PA1, left exhausted and right after regeneration.

factors such as durability, costs, etc. It is important that the comparison of various adsorptive media for oil-water separation is based on the use of a representative synthetic produced water mimicking industrial conditions, which is a key feature of this study.

5. Conclusions

This study presented a broad performance evaluation of several cutting-edge PAs applied for the removal of emulsified oil targeting industrial application. Batch mode and fixed-bed column tests were conducted in this study for thorough media evaluation given that other studies were limited to partial performance screening via batch testing only. Evaluation was carried out using a fully automated custom-built column setup, a representative synthetic PW solution, and a testing procedure that involves both adsorption and regeneration of media. Four adsorbents were assessed; two of which being tested for the first time for such application. Experiments addressed resin capacity, regeneration efficiency, and performance repeatability in repeat cycles. Key findings include:

- 1- Batch tests investigating the impact of contact time revealed that PA1 showed the fastest kinetics followed by PA3, PA4 and then PA2. GAC was proven to be the slowest.
- 2- Batch tests examining the impact of media dosage showed Freundlich isotherm better represented the adsorption behavior of PA1, PA3, and PA4 whereas Langmuir was found to better predict the behavior of PA2 and GAC.
- 3- Batch tests assessing the impact of feed concentration and pH were found to agree with other studies in obtaining improved performances at lower feed concentrations and pH.
- 4- Fixed-bed column testing of GAC resulted in capacity of ~ 13 mg/g upon treating 95 BVs. Comparably, 168 ± 58 BVs were treated by PA2 but at improved capacity of ~ 44 mg/g.
- 5- Fixed-bed column testing of PA1 and PA3 yielded comparable capacities at ~ 100 mg/g yet both differed in performance repeatability and their treatable BVs. 807 ± 3 BVs vs. $\sim 548 \pm 115$.
- 6- Fixed-bed column testing of PA3 and PA4 revealed promising results for industrial application with PA4 showing capacity at ~ 301 mg/g via operating 1219 ± 86 BVs.

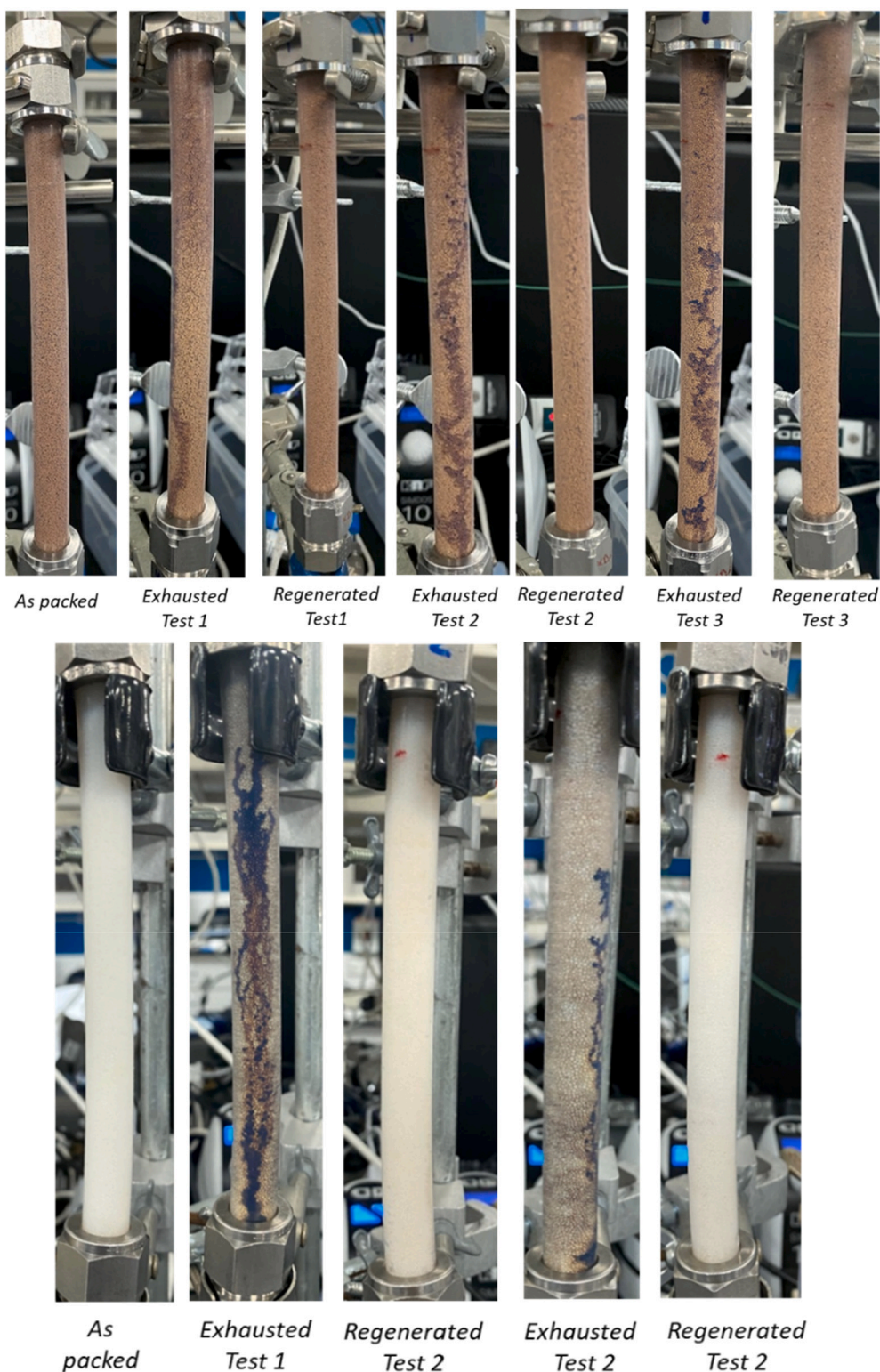


Fig. 9. Images of PA3 (top) and PA4 (bottom) throughout column testing.

- 7- PA1 and PA4 were both able to remove the oil emulsions at TOG <1 mg/L. Effluents at TOG >1 were detected for GAC, PA2, and PA3.
- 8- Solvent regeneration using toluene and ethanol was proven effective in restoring the performance of all tested PAs.

adsorption resins for emulsified oil removal using representative synthetic PW solution. Future studies will focus on evaluating the performance of PAs using real PW from O&G operation. Pilot testing would also be required in the next stage to evaluate operating costs including media, durability, and replacement projections.

It is proposed that the performance evaluation data presented in this study be used as a reference for comparison upon assessing other novel

Table 9
Performance comparison of PAs.

Study	Adsorbent	Contaminant	Regeneration	Capacity, mg/g
This study	PA1	Emulsified oil	Toluene & ethanol	111 ± 15
	PA2			44 ± 14
	PA3			100 ± 12
	PA4			301 ± 27
[43]	ProSep Osorb	Dispersed/ Dissolved oil	Steam & natural gas	300
[25]	Optipore L493	Naphthenic acid	Methanol & caustic	57
[25]	Macronet 202	Naphthenic acid	Methanol & caustic	120
[65]	Purosorb PAD428	Polyphenols	Water & ethanol	48

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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