Original Article

Evaluating rhamnolipid-enhanced washing as a first step in remediation of drill cuttings and petroleum-contaminated soils

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HIGHLIGHTS

- Soil washing is an innovative approach to treatment of waste streams.
- Temperature has a significant effect on rhamnolipid enhanced soil washing.
- Drill cuttings and petroleum-impacted soil show similar optimum washing conditions.
- Maximum total petroleum hydrocarbon reduction in drill cuttings was 76.8%.
- Maximum total petroleum hydrocarbon reduction in soil was 58.5%.

GRAPHICAL ABSTRACT
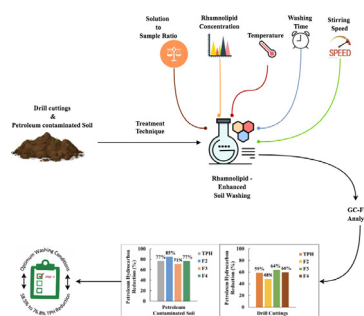
ABSTRACT

Environmental pollution by petroleum hydrocarbons (PHCs) is a severe and widespread problem impacting human health and the environment. To combat this issue, innovative and sustainable treatment methods are required. This research study investigated rhamnolipid-enhanced washing of drill cuttings and petroleum-contaminated soil obtained from northeastern British Columbia in Canada. The efficiency of PHC reduction was analysed and quantified via a Gas Chromatography equipped with a Flame Ionization Detector. Optimum washing conditions for both drill cuttings and petroleum-contaminated soil were temperature of ~23.5 °C (room temperature), rhamnolipid concentration of 500 mg/L, and a washing time of 30 min. The optimum stirring speed and solution-to-sample ratio for drill cuttings and petroleum-contaminated soil were 100 rpm; 1:1, and 200 rpm; 4:1 respectively. The maximum PHC reduction recorded for total petroleum hydrocarbon and PHC fractions – F2, F3 and F4 were 76.8%, 85.4%, 71.3% and 76.9% respectively for drill cuttings and 58.5%, 48.4%, 63.5% and 59.8% respectively for petroleum-contaminated soil. The results strongly suggest that soil washing is an effective step in the reduction of PHC and can be used as a first step in the treatment of drill cuttings and petroleum-contaminated soils.

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Introduction

Environmental pollution by petroleum hydrocarbons (PHCs) is a severe and widespread problem. Soil contamination by PHCs result in significant human health, plant life, animal and environmental defects with rising public concerns [1–4]. Furthermore, environ-

mental pollution is considered to be a major impediment to sustainable development and has become an increasingly important topic for decision makers in economical, industrial and political considerations [5,6].

Drill cuttings produced in the petroleum industry are a major waste management problem due to the types of contaminants and volumes generated. Drill cuttings are produced during petroleum exploration, extraction and production. The excavated materials when mixed with oil-based drilling fluids pose to be potentially long-term contaminants, particularly when they are not properly managed [7–10]. PHC contaminated soils accumulate in the environment due to leaks from storage tanks, aged pipelines and waste disposal sites [3,11] during the exploration, extraction, transportation, and storage of crude oil and its various derivatives. Environmental damage also arises due to the intentional discharge of oil and oily wastes into the environment [5]. With the modern economy's continued dependence on petroleum alongside increasing world demand for fuel, contamination from these sources pose to be a continuing environmental risk [12–14], also potentially leading to increased economic losses [5]. The widespread use of PHCs has invariably led them to be a persistent and long-standing source of soil pollution [15]. Therefore, soil contamination by PHCs is of increasing social, sanitary, environmental and economic concern [16].

Soil washing is a mechanical technique or physical process which removes contaminants from soils using liquids [5,17,18]. This technique is normally performed with water and may or may not involve the use of additives such as biosurfactants [1,19]. Soil washing utilizing biosurfactants is not characterized by the metabolic activities of biosurfactants or the effect of biosurfactants on the properties of the microbial cell-surface. Rather, it depends on the chemical-physical properties of the biosurfactants [20]. Soil washing techniques are site-specific as they depend on the soil characteristics (e.g. organic and inorganic material content and particle size distribution) [21], and the type of hydrocarbon contaminant(s) present. Due to this specificity, research is important to provide potentially useful universal guidelines in the selection of biosurfactants [22]. Soil washing is described by Urum et al. [13] as a potentially innovative remediation or treatment approach because its full-scale application in the treatment of crude oil contaminated soil is limited. It has the added advantage of being less time-consuming than other remediation techniques such as bioremediation and phytoremediation. The approach is also cost-effective [13]. The application of biosurfactants has also been reported to enhance contaminant flushing by reducing the hydrophobic hydrocarbon content in the contaminated soils [23]. Furthermore, soil washing also allows recovery of large volumes of contaminants [13].

Biosurfactant application in soil washing is investigated based on the identified advantages and physiochemical characteristics of biosurfactants which make them better matched to environmental applications [21]. When compared to synthetic (chemically synthesized) surfactants, biosurfactants display excellent surface activity, higher selectivity, higher biodegradability and less adverse environmental impact. The excellent surface activity makes biosurfactants excellent dispersing agents and emulsifiers [20,24–26]. In addition, they display high activity at extreme conditions of salinity, temperature, and pH. Biosurfactants are environmentally compatible, have lower toxicity and can be released into the environment without resulting in further damage from residues. Thus, removal of biosurfactants from effluents before disposal is not required. Furthermore, biosurfactants can be synthesized from renewable feedstocks such as industrial wastes and by-products [20,21,23,24]. The ability of biosurfactants to be produced from waste substrates also lowers the cost of production and reduces the polluting effects of biosurfactant production processes [2,20].

Major disadvantages of synthetic surfactants are their resistance to biodegradation and their toxicity [4]. The rhamnolipid biosurfactant selected for this work is one of the best-known and well-described glycolipid compounds. Glycolipids are the most-studied and best known microbial surfactants [24–28] and have attracted significant commercial interest [29]. Rhamnolipid has been commercialized by some companies such as Jeneil Biotech Inc., AGAE Technologies USA and Rhamnolipids Companies Inc. [29], thus making it a viable option with potential for being applied on an industrial scale.

Innovative remediation processes are a necessity, and the ultimate goal of a sustainable future is the ability to re-use treated waste streams [2]. The burden of disposal of drill cuttings and petroleum-contaminated soil is reduced when the waste streams are treated to levels that permit re-use [2,30]. The present work was aimed at investigating the effectiveness of soil washing utilizing rhamnolipid biosurfactants in the reduction of PHCs present in drill cuttings and petroleum-contaminated soils obtained from northeastern British Columbia (BC) in Canada. The residual concentrations were also compared to Canadian regulatory standards, to provide insight into acceptable disposal strategies and/or possibilities of re-use.

Material and methods

Property of contaminated samples

Drill cuttings

Drill cuttings (DC) were obtained from Tervita Silverberry Landfill, Fort St. John, BC. The initial total petroleum hydrocarbon (TPH) concentration of the sample was 5939 mg/kg. The concentrations of the petroleum hydrocarbon fractions – F2, F3 and F4 fractions were also analyzed. Initial concentrations of F2 fraction (representing C10–C16), F3 fraction (representing C16–C34) and F4 fraction (representing C34–C50) were 2334 mg/kg, 3350 mg/kg and 255 mg/kg respectively.

PHC sub-fractions are defined by the US Total Petroleum Hydrocarbons Criteria Working Group. There are four fractions defined in equivalent carbon (C) numbers. These are Fraction 1 (F1: C6–C10), Fraction 2 (F2: C10–C16), Fraction 3 (F3: C16–C34), and Fraction 4 (F4: C34–C50) [31].

Petroleum-contaminated soil

Petroleum-contaminated soils (PCS) were obtained from Back-to-Earth Remediation facility, located 42.5 km north of Prince George, BC. The soil was classified as exceeding the BC Contaminated Sites Regulation (CSR) Commercial and or Industrial land-use standards. The initial total petroleum hydrocarbon concentration was 3276 mg/kg. Initial concentrations of F2 fraction (C10–C16), F3 fraction (C16–C34) and F4 fraction (C34–C50) were 577 mg/kg, 2365 mg/kg and 334 mg/kg respectively.

Both samples were stored in a refrigerator at 4 °C to minimize degradation, reduce the abiotic loss of hydrocarbons, and maintain moisture [32,33]. Samples were oven-dried at 50 °C for 2–3 d and sieved using 850 μm # 20 ASTM E-11 specification sieve (Cole-Parmer Canada Company, Montreal, Quebec, Canada) to remove stones and coarse particles prior to hydrocarbon analysis and treatment.

Chemicals

All chemicals used were HPLC grade with a minimum of 97% purity.

Biosurfactant

Commercial rhamnolipid biosurfactant (R90–100, 90% purity)) produced by AGAE Technologies LLC (Corvallis, Oregon, USA) was purchased from Sigma-Aldrich Canada Co. (Oakville, Ontario, Canada). The critical micelle concentration (CMC) value for the rhamnolipid used was computed as 100 mg/L at 23 °C. The rhamnolipid decreased the surface tension of water to 30 mN/m.

Determination of critical micelle concentration

Serial dilutions of the rhamnolipid solutions were prepared in concentrations ranging from 10 mg/L to 800 mg/L. The upper limit was capped at 800 mg/L after constant surface tension values were observed [34]. Each test was conducted in quadruplicate, and the average calculated. The surface tension was measured using a Surface Tensiomat (model 21, Fisher Scientific, Ottawa, Ontario, Canada) at room temperature (approximately 23 °C). For accuracy, the values were measured in triplicate. Critical micelle concentration (CMC) of surfactants in aqueous solutions is dependent on temperature, water hardness and electrolyte [21]. The CMC of rhamnolipid was determined by plotting the graph of the surface tension versus the log of the rhamnolipid concentration [34,35]. The CMC was observed as the point beyond which further increase in biosurfactant concentration did not result in a decrease in the surface tension of water [34].

Biosurfactant enhanced soil washing

In the present study, the Taguchi experimental method was used for experimental design that allowed all five factors to be tested at various levels at the same time (Table 1). Each experimental level was carried out in triplicate. The biosurfactant concentrations tested were at and above the CMC of the rhamnolipid biosurfactant used. Five parameters that influence hydrocarbon removal with biosurfactants were investigated at five levels each. The parameters were: temperature, rhamnolipid concentration, washing time, stirring speed, and solution-to-sample ratio (S/S

ratio). S/S ratio represents the volume of the rhamnolipid solution to the mass of sample, reported as mL/g.

DC and PCS were dried at 50 °C for about 24 h and sieved with 20 μm ASTM E-11 specification sieve (Cole-Parmer Canada Company, Montreal, Quebec, Canada) to remove stones and coarse sand particles. Subsequently, 5 g of samples were weighed into 125 mL Erlenmeyer flasks and covered with aluminum thin foils. The samples in the Erlenmeyer flasks were placed in environmental growth chambers few hours before treatment to pre-condition the samples to the treatment temperature. The growth chambers had been pre-set to the appropriate temperature 48 h before the washing began.

The appropriate volume based on the test solution-to-sample ratio (1:1, 2:1, 3:1, 4:1 and 5:1) and concentration of biosurfactant solution (100, 200, 300, 400 and 500 mg/L) were added to the samples in the Erlenmeyer flasks. Equal-sized magnetic stirring bars (VWR International Co., Mississauga, Ontario, Canada) were placed in the flasks and experiments conducted at the temperature levels tested (10, 20, 30, 40 °C and room temperature). For samples washed at 30 °C and 40 °C, the flasks were placed on a hot plate magnetic stirrer (VWR International Co., Mississauga, Ontario, Canada). After washing the samples at the specified washing time (10, 30, 60, 180 and 360 min) and stirring speed (100, 150, 200, 250 and 300 rpm), the soil particles in the flasks were allowed to settle for 3 h after which the biosurfactant solution was pipetted off. Pipettes were used to transfer the supernatant rather than decanting to reduce the loss of samples. The samples were then rinsed using distilled water under the same treatment conditions used for the biosurfactant treatment with the exception of washing time. Rinsing was conducted for a duration of 10 min for all samples. Rinsing ensures oil is removed from the wall of the flasks, biosurfactant is removed from the samples, and emulsions are not formed in the process of extracting residual hydrocarbons from the samples using solvents [8,36]. After rinsing, the soil particles were allowed to settle for 3 h after which the rinse solution was pipetted off and the samples air-dried. Room temperature for the washing treatment averaged 23.5 °C. The washed samples were stored at 4 °C until hydrocarbon extraction.

Table 1
Taguchi experimental design for rhamnolipid washing of drill cuttings and petroleum-contaminated soil.

Experiment No.	Temperature (°C)	Rhamnolipid Concentration (mg/L)	Washing Time (min)	Stirring Speed (rpm)	Solution-to-Sample Ratio (mL/g)
L1	10	100	10	100	1:1
L2	10	200	30	150	2:1
L3	10	300	60	200	3:1
L4	10	400	180	250	4:1
L5	10	500	360	300	5:1
L6	20	100	30	200	4:1
L7	20	200	60	250	5:1
L8	20	300	180	300	1:1
L9	20	400	360	100	2:1
L10	20	500	10	150	3:1
L11	30	100	60	300	2:1
L12	30	200	180	100	3:1
L13	30	300	360	150	4:1
L14	30	400	10	200	5:1
L15	30	500	30	250	1:1
L16	40	100	180	150	5:1
L17	40	200	360	200	1:1
L18	40	300	10	250	2:1
L19	40	400	30	300	3:1
L20	40	500	60	100	4:1
L21	room	100	360	250	3:1
L22	room	200	10	300	4:1
L23	room	300	30	100	5:1
L24	room	400	60	150	1:1
L25	room	500	180	200	2:1

Petroleum hydrocarbon extraction and analysis

Samples were oven dried at 50 °C for 2–3 d and sieved using 850 μm # 20 ASTM E-11 specification sieve (Cole-Parmer Canada Company, Montreal, Quebec, Canada) prior to hydrocarbon analysis and treatment. Hydrocarbon was extracted using a mechanical extraction method. The method used was adapted from the Canadian Council of Ministers of Environment (CCME) reference method for the Canada-wide standard for PHCs in soil [37]. To extract hydrocarbon from the contaminated samples, 2 g of prepared samples were weighed into 20 mL clear glass vials (VWR International Co., Mississauga, Ontario, Canada) with 10 mL of 1:1 n-hexane/acetone added. The vials were arranged on a platform shaker (New Brunswick Scientific, Edison, New Jersey, USA) for mechanical extraction for 1 h at 250 rpm. The vials were allowed to settle for 90 min before transferring the supernatant into a 40 mL-vial using transfer pipettes. The extraction was repeated three more times, with the last cycle run for 140 min, to achieve a minimum solvent/dry soil ratio of 20:1 as specified by the method.

The extracted solution was cleaned up using a silica gel column to remove naturally occurring polar organics [37]. The tip of the glass column (30 cm length, 16 mm diameter) was plugged with glass wool (Sigma-Aldrich, Oakville, Ontario, Canada) and packed with activated silica gel (VWR International Co., Mississauga, Ontario, Canada) followed by anhydrous sodium sulfate (VWR International Co., Mississauga, Ontario, Canada) to a depth of 6.5 cm and 2.5 cm respectively. Silica gel was activated at 101 °C for 12 h and sodium sulfate dried at 400 °C for 4 h. Activated silica gel and dried sodium sulfate were placed in desiccators to cool before use. The packed column was pre-eluted with 20 mL of 1:1 dichloromethane/n-hexane (VWR International Co. BDH Chemicals, Mississauga, Ontario, Canada) to wet and condition the column, and the eluate discarded. The extracted solution was transferred into the column, followed by 20 mL of 1:1 dichloromethane/n-hexane to carry the sample through the column, with some of the solvent mixture used to rinse the vials into the column. The column was further flushed with 20 mL of 1:1 dichloromethane/n-hexane. The eluate was collected in 100 mL round bottom flasks.

Solvents were evaporated using a Heidolph Laborota 4000 rotary evaporator (Schwabach, Germany) at 35 °C and speed of 30 rpm and the extract transferred into 2 mL GC vials in dichloromethane for chromatographic analysis. The GC vials were clear vials (76-series, VWR International Co., Mississauga, Ontario, Canada) with caps (PTFE/Silicone/PTFE septa). This septum type was specifically used because it is resistant to dichloromethane and it minimizes volatilization losses.

GC-FID analysis

Total petroleum hydrocarbon (TPH) analysis was performed using an Agilent/HP 6890 Series Gas Chromatography (GC) equipped with a Flame Ionization Detector (FID) (Santa Clara, California, USA). The equipment was provided by Northern Analytical Laboratory Service (NALS), UNBC, Prince George, Canada. For the analysis of F2 and F3 fractions, a fused silica capillary column – Supelco 2-4080 SupelcoWax 10 capillary (Supelco Inc., Bellefonte, Pennsylvania, USA) with a length of 30 m, inside diameter of 0.32 mm and film thickness of 0.25 μm was used. The parameters used for analysis were; injection volume at 2.0 μL, injector temperature at 270 °C, detector temperature at 300 °C, split ratio at 10:1, helium gas used as carrier gas was maintained at 21.28 psi pressure and constant flow rate of 5.2 mL/min. Oven temperature started at 70 °C and was held for 2 min, ramped at 5 °C/min to

150 °C, and further increased at 10 °C/min to 270 °C and held for 25 min. Total run time for a sample analysis was 55 min.

For the F4 Fraction analysis, a Zebron ZB-1HT Inferno capillary column (Phenomenex Inc., Torrance, California, USA) with a length of 30 m, inside diameter of 0.32 mm and film thickness of 0.25 μm was used. The parameters used for analysis were injection volume at 1.0 μL, injector temperature at 320 °C, detector temperature at 300 °C, split ratio at 10:1, helium gas used as carrier gas was maintained at 9.52 psi pressure and constant flow rate of 1.4 mL/min. Oven temperature started at 130 °C and was held for 2 min, ramped at 30 °C/min to 270 °C, and further increased at 5 °C/min to 385 °C and held for 1 min. Total run time for a sample analysis was 30.67 min.

Decane (nC10), hexadecane (nC16), and tetratriacontane (nC34) (Sigma-Aldrich Canada Co., Oakville, Ontario, Canada) in dichloromethane at approximate concentrations of 20, 50, 100, 200 and 400 mg/L were used to run a 5-point calibration curve for retention time marking and for calculating average response factor. The concentration of each fraction for each sample extract was calculated by using the integration of all area counts within each fraction, the final volume of sample extract, dry weight of sample taken and the computed average response factor [37]. Pentacontane (nC50) (Sigma-Aldrich Canada Co. (Oakville, Ontario, Canada) was used for retention time marking for the F4 fraction analysis. Total petroleum hydrocarbon (nC10 to nC50) for this work is calculated as the sum of F2, F3 and F4 fractions.

The percentage of hydrocarbon removal was calculated using Eq. (1.1).

Petroleum Hydrocarbon Reduction (%)

$$= \frac{P.Hi - P.Hr}{P.Hi} \times 100 \qquad (1.1)$$

where

P.Hi = The initial concentration of petroleum hydrocarbon in the samples
P.Hr = The residual concentration of petroleum hydrocarbon in the samples
after treatment

Taguchi experimental method

The Taguchi method is applied in the design stage of experiments and processes, and in the analysis of process parameters. It allows combination of multiple factors at multiple levels. The Taguchi method uses orthogonal arrays to study entire processes with minimal number of experiments [38]. The Taguchi method was used in designing the experimental plan as it saves time and reduces the number of experiments and experimentation cost [39,40]. The signal-to-noise ratios and analysis of variance were used to investigate the effect of the washing parameters on petroleum hydrocarbon reduction (PHC).

Statistics

All triplicates of each experimental level were analyzed for residual PHC concentrations. The mean values and standard deviation were calculated for all experiment levels. Data were analyzed using the Minitab 17 software. The Error bars (when shown) represents standard deviation.

The optimal washing parameters and the optimal parameter combinations were obtained by analysis of the signal-to-noise (S/N) ratio. By using the S/N ratio, Taguchi experimental design identifies noises (i.e., outside influences) that affects the

experimental design [39]. The desired level of signal is compared to the background noise; the higher the S/N, the less prominent the noise is [40]. The "larger the better" situation is applied as the quality characteristic in the analysis of S/N ratio in this study because the larger the PHC reduction, the better the result. The highest S/N ratio gives the optimal level of the parameter tested [38,39].

The main effect plot is a plot or graphical representation that identifies the optimal level of each parameter based on the S/N ratio [39].

Analysis of variance (ANOVA) was used to determine the statistical significance and the level of importance of the parameters on PHC reduction. ANOVA was tested for $P < 0.05$ for significance.

Results and discussions

Drill cuttings

Total petroleum hydrocarbon (TPH) and hydrocarbon fractions reduction in drill cuttings

The highest reduction for TPH, F2 and F3 fractions was recorded at experiment L22. The highest reduction for F4 fraction was recorded at experiment L24 (Fig. 1).

The maximum PHC reduction rate for TPH, F2, F3 and F4 fractions was 76.8%, 85.4%, 71.3% and 76.9% respectively. Overall, the highest PHC reduction was observed in the F4 fraction, as reduction rates for all experiments were above 62%. Average reduction rate across all experimental levels for F4 fraction was 68.3%. Lowest PHC reduction rate for TPH, F2, F3 and F4 fractions was 27.8%, 50.3%, 6.9% and 61.9% respectively. For TPH, F3 and F4, the lowest reduction was recorded at L18 while L19 resulted in the lowest reduction of F2.

Residual PHC concentrations in drill cuttings

The highest residual TPH concentration in DC was 4348 mg/kg after rhamnolipid washing, largely due to the F3 fraction which was found to have the highest residual concentration at 3120 mg/kg. A common trend noticeable in the experiments conducted at room temperature were the high PHC reduction rates. Average reduction rates at room temperature for TPH, F2, F3 and F4 fractions were 76.0%, 84.7%, 70.2% and 73.6% respectively in drill cuttings. This trend was verified by ANOVA. Temperature was indicated as having a significant effect on rhamnolipid washing at a α-level (i.e., significance level) of 0.05 for TPH, F2 and F3 fraction. The P-values for temperature for TPH, F2 and F3 fraction were less than 0.05. While the P-value for effect of temperature in F4 fraction reduction was

higher than 0.05, the P-value for this factor was lower than all other four factors. For TPH reduction, the degree of significance of the factors in decreasing order, based on P-values were temperature, solution-to-sample ratio, washing time, stirring speed, and rhamnolipid concentration.

Yan et al. [8] observed an 85.2% reduction of TPH in drill cuttings from 85,000 mg/kg to 12,600 mg/kg. Rhamnolipid soil washing of drill cuttings in the present study yielded a maximum TPH removal of 76.8%. The results are comparable because according to Iturbe et al. [41], the rate of removal of PHC in soils is affected by the initial TPH concentration. The higher the initial TPH, the higher the removal rates and the removal efficiency of surfactants. Results reported by Lai et al. [4] for severely contaminated samples also showed higher removal efficiency than slightly contaminated soils despite the fact that similar treatment conditions were used. Thus, biosurfactant-enhanced washing has a high potential as an environmentally friendly option of removing bulk contaminants from soils [42].

Comparison of residual PHC concentrations with Canada-wide standards

The residual PHC concentrations were compared to the CCME 2008 Canada-Wide Standards (CWS) for PHCs in soils (PHC CWS) [43] presented in Table 2. The figures presented are at the Tier 1 generic numerical level, which are remedial standards for both surface and subsoils which occur in four different categories of land-use as at 2017. In the present study, the most stringent standards for F2, F3, and F4 fractions that consider protection of potable groundwater were adopted for comparison.

As shown by these results, this experiment indicates that rhamnolipid washing is an effective and time-efficient process for reducing the PHC content of drill cuttings. The ranges of residual concentrations in the samples were F2 = 342–1159 mg/kg, F3 = 960–3120 mg/kg and F4 = 59–97 mg/kg. The CGS standards were used for comparison since over 71% of the drill cuttings in this study had grain sizes greater than 250 μm. Canada-wide standards for petroleum hydrocarbons (PHC CWS) follows the American Society for Testing and Materials (ASTM) soil classification which classifies soil with a median grain size of >75 μm as coarse-grained soil [43].

When compared to standards in Table 2, residual concentrations for F2 and F3 fractions exceeded the standards for all four land-use categories, while F4 fractions were below the regulatory standards for all land-use categories. This again indicates the need for further remediation methods to reduce the PHC of F2 and F3 fractions to levels below the CWS when CCME standards are applied.
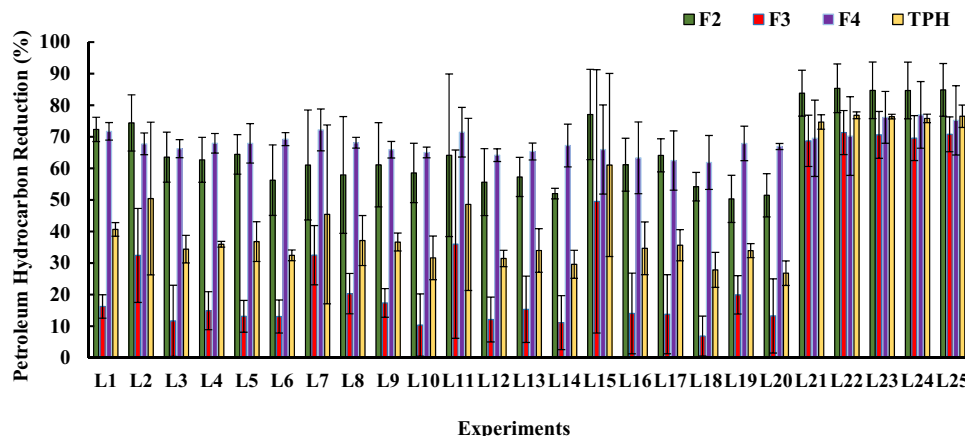

Fig. 1. Total petroleum hydrocarbon (TPH) and hydrocarbon fractions reduction of drill cuttings through rhamnolipid washing experiments.

Table 2

Canada-wide standards of petroleum hydrocarbon (in mg/kg) for surface soils.

Fraction	Soil texture	Land-use			
		Agricultural	Residential/ Parkland	Commercial	Industrial
F2	CGS	150	150	260	260
	FGS	150	150	230	230
F3	CGS	300	300	1700	1700
	FGS	1300	1300	2500	2500
F4	CGS	2800	2800	3300	3300
	FGS	5600	5600	6600	6600

CGS = Coarse grained soil.
FGS = Fine grained soil.

Optimal rhamnolipid washing conditions in drill cuttings

The optimal rhamnolipid washing conditions for TPH reduction were: temperature of 23.5 °C (room temperature), rhamnolipid concentration of 500 mg/L, washing time of 30 min, stirring speed of 100 rpm and S/S ratio of 1:1 (Fig. 2).

Using S/N ratios in TPH reduction, the factors are ranked from 1 (highest) to 5 (lowest) as temperature, washing time, S/S ratio, rhamnolipid concentration, and stirring speed. Based on ANOVA results, temperature showed a significant effect on rhamnolipid washing. Using the P-values, the degree of significance of all factors on TPH reduction in decreasing order were temperature, S/S ratio, washing time, stirring speed and rhamnolipid concentration. Optimal washing conditions for F2, F3 and F4 fractions are presented in Figs. 3–5.

Yan et al. [8] conducted rhamnolipid biosurfactant washing of drill cuttings. The authors found the optimal washing conditions to be a temperature of 60 °C, rhamnolipid concentration of 360 mg/L, washing time of 20 min, stirring speed of 200 rpm and liquid/solid ratio of 3:1. Optimal results from the present study are comparable and show a good fit to applications as lower stirring speed and S/S ratio will ultimately reduce application costs. Although the optimal rhamnolipid concentration in the present study was 500 mg/L, the highest TPH reduction was recorded at a concentration of 200 mg/L.

The hydrocarbon fractions, F2, F3 and F4 recorded different extents of removal. Even though the experimental conditions that resulted in the maximum reduction for TPH, F2 and F3 fractions were similar in each sample type, the optimal conditions based on the main effect plot varied. This observation is important because the regulatory standards used as the comparison in the present study (i.e., PHC CWS) expressed regulatory standards of hydrocarbon levels as F2, F3 and F4 fractions, not as TPH.

Based on ANOVA results at a significance level of 0.05, only temperature showed a significant effect on rhamnolipid washing for the reduction of TPH, F2 and F3 fractions; no individual factor showed a significant effect on rhamnolipid washing for the F4 fraction. Temperature, however, had the lowest P-value for the F4 fraction.

Interactions between test parameters

Interaction plots were used to investigate the interaction between temperature and the other four washing parameters-rhamnolipid concentration, washing time, stirring speed and S/S ratio on TPH reduction during rhamnolipid washing of drill cuttings. The interaction plots were similar, with all parameters responding distinctly to the room temperature. At room temperature, all the test parameters at all levels display high S/N ratio. At all parameter levels, the lines showed a distinct pattern which indicates that response of the parameters changes as temperature changes. This is an indication that the factors interact.

Petroleum-contaminated soil

Total petroleum hydrocarbon (TPH) and hydrocarbon fractions reduction in PCS

The highest reduction for TPH, F2 and F3 fractions in petroleum-contaminated soil was recorded at experiment L2. The highest reduction for F4 fraction was recorded at experiment L25. The
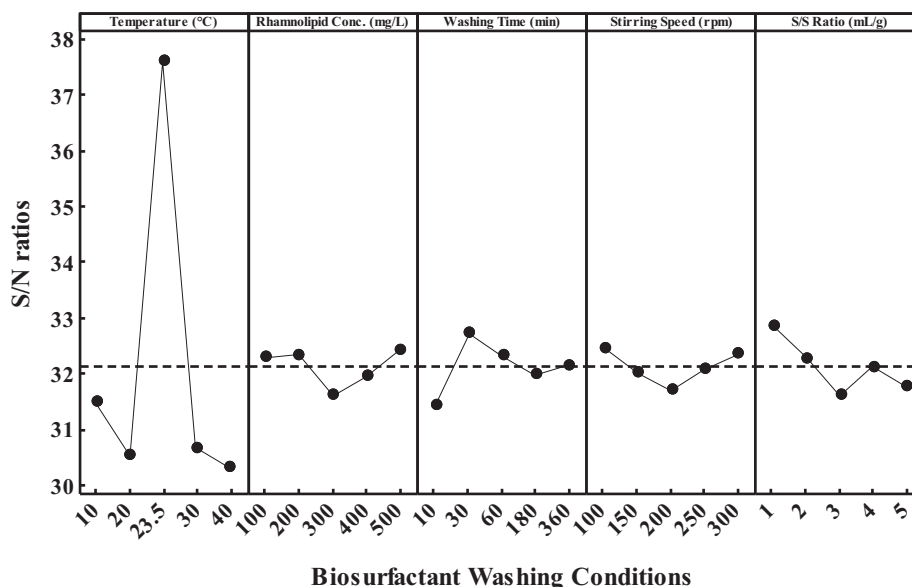
Fig. 2. Main effects of test parameters on total petroleum hydrocarbon reduction in drill cuttings through rhamnolipid washing treatment.
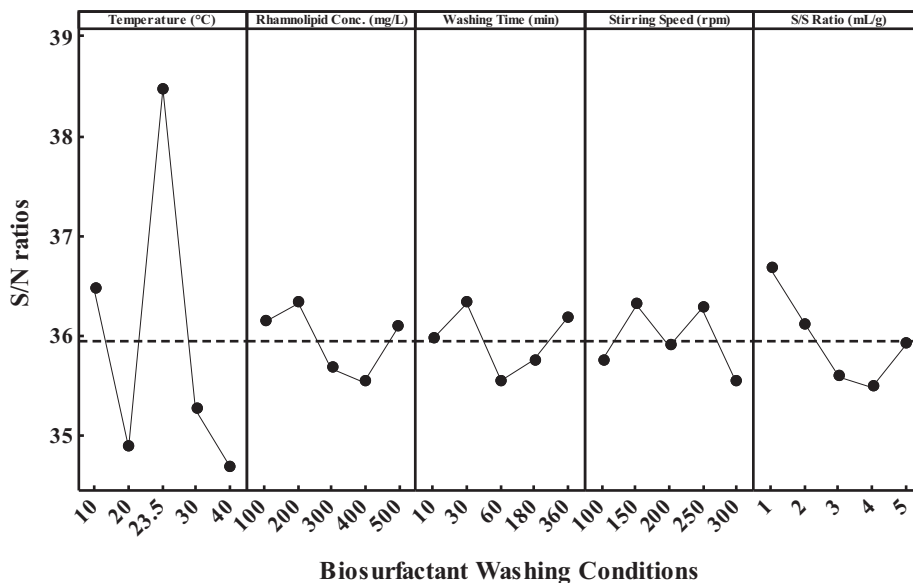
Fig. 3. Main effects of test parameters on F2 fraction reduction in drill cuttings through rhamnolipid washing treatment.
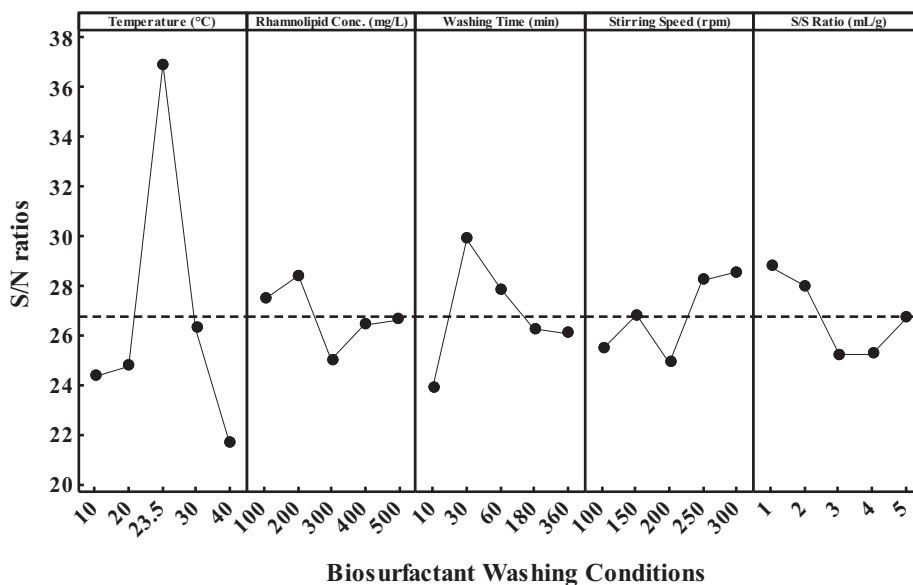

Fig. 4. Main effects of test parameters on F3 fraction reduction in drill cuttings through rhamnolipid washing treatment.

maximum PHC reduction rate for TPH, F2, F3 and F4 fractions was 58.5%, 48.4%, 63.5% and 59.8% respectively. Overall, the highest PHC reduction was observed in the F3 fraction, as reduction rates for all experiments were above 49%, and average reduction rate across all experimental levels was 56.4% (Fig. 6). Lowest PHC reduction rate for TPH, F2, F3 and F4 fractions was 41.4%, 15.3%, 49.2% and 26.8% respectively. For TPH, F2 and F3 the lowest reduction was recorded at L7, while L17 resulted in the lowest reduction of F4.

The TPH removal rates recorded in the present work is comparable to results presented by Lai et al. [4]. Maximum TPH removal with rhamnolipid washing for TPH contaminated soil with an initial concentration of 3000 mg/kg was given as 23.4% at a concentration of 0.2 mass%. Iturbe et al. [41] reported comparable results with on-site soil washing of PHC contaminated soil with initial average TPH of 9172 mg/kg. About 83% TPH removal was observed with soil washing. Biosurfactant soil washing in the research was carried out in multiple steps until the final TPH

concentration required was achieved. Whereas, the rhamnolipid soil washing process used in the present study was conducted only once and it gave reduction values as high as 58.5% for PCS.

Residual PHC concentrations in petroleum-contaminated soil

It was observed that after rhamnolipid washing, residual TPH concentration in the sample was below 1920 mg/kg, largely due to F3 fraction, as the highest residual concentration for this fraction was recorded as 1203 mg/kg (L7). Based on the results, this experiment indicates that rhamnolipid washing is an effective and time-efficient procedure for reducing the PHC content of petroleum-contaminated media.

Comparison of residual PHC concentrations with Canada-wide standards

The ranges of residual concentrations in the PCS were found to be: F2 = 298–486 mg/kg, F3 = 864–1203 mg/kg and F4 = 134–244 mg/kg. When compared to Table 2, residual concentrations
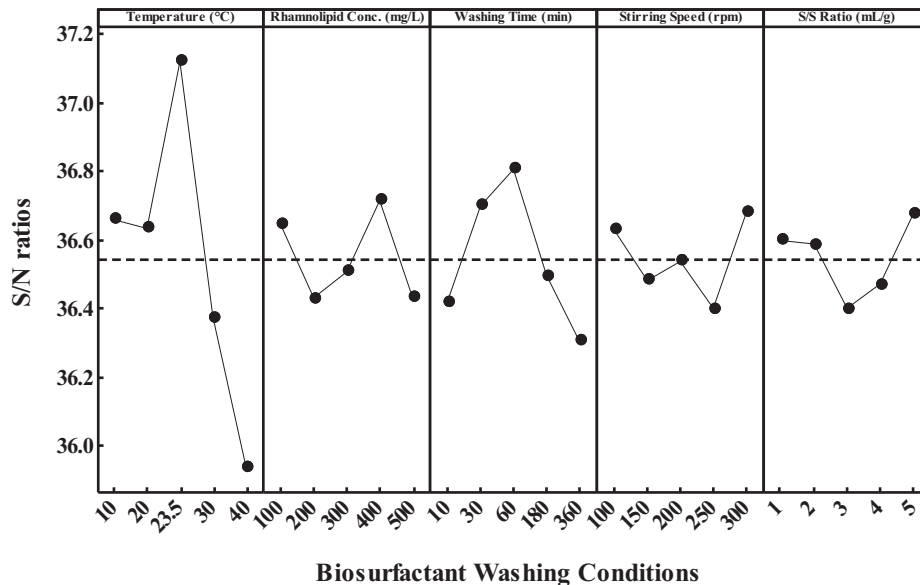
Fig. 5. Main effects of test parameters on F4 fraction reduction in drill cuttings through rhamnolipid washing treatment.
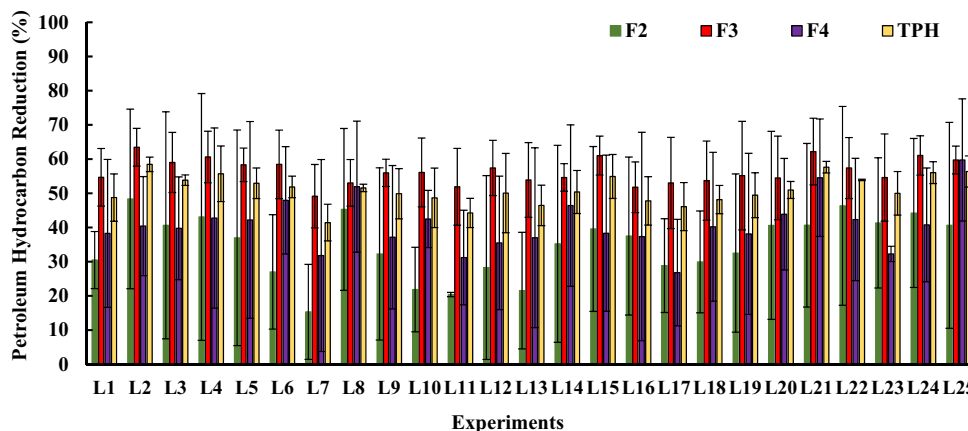

Fig. 6. Total petroleum hydrocarbon (TPH) and hydrocarbon fractions reduction in petroleum-contaminated soil through rhamnolipid washing experiments.

for F2 fractions exceeded the standards for all four land-use categories, while F3 fractions exceeded the standards for agricultural and residential/parkland land-use but were below the standards for commercial and industrial land-use. F4 fractions, on the other hand, were all below the regulatory standards. These residual concentrations indicate the need for further remediation methods to reduce the PHC of F2 and F3 fractions to levels below the CWS.

Optimal rhamnolipid washing conditions in petroleum contaminated soil

Using S/N ratios in TPH reduction, the parameters are ranked from 1 (highest) to 5 (lowest) as temperature, S/S ratio, washing time, rhamnolipid concentration, and stirring speed. The optimal rhamnolipid washing conditions for TPH reduction in PCS as shown in Fig. 7 were: temperature of 23.5 °C (room temperature), rhamnolipid concentration of 500 mg/L, washing time of 30 min, stirring speed of 200 rpm and S/S ratio of 4:1.

Based on ANOVA results, at a significance level of 0.05, no individual factor showed a significant effect on rhamnolipid washing. Temperature, however, had the lowest P-value for TPH, F2 and F3. For F4 fraction, rhamnolipid concentration had the lowest P-value.

For overall TPH reduction, the degree of significance, based on P-values in decreasing order, were temperature, washing time, solution-to-sample ratio, rhamnolipid concentration and stirring speed. Optimal washing conditions for F2, F3 and F4 fractions are presented in Figs. 8–10.

The pattern of change of S/N ratio for F2 reduction was similar to TPH for parameters- temperature, rhamnolipid concentration and washing time, with some minor differences. The pattern of change of S/N ratio for F3 reduction was similar to TPH for all parameters with some minor differences, despite the difference in the optimum conditions that gave the best reduction in TPH and F3 fraction.

Variability among the replicates as depicted by the error bars in Figs. 1 and 6 for both drill cuttings and petroleum contaminated soil was high. The experimental variability could have been due to changes in the laboratory conditions during biosurfactant washing or sampling variability.

Effect of individual test parameters on PCS
Effect of temperature. The optimal temperature condition for TPH, F2 and F4 fraction removal in PCS was room temperature (approximately 23.5 °C) and 10 °C for F3 fraction. The signal-to-noise (S/N)
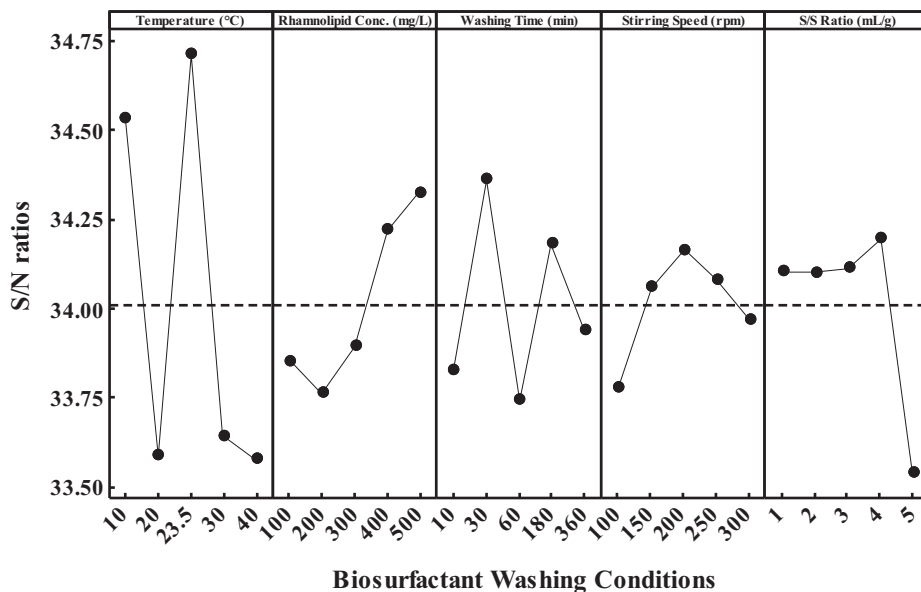
Fig. 7. Main effects of test parameters on total petroleum hydrocarbon reduction in petroleum-contaminated soil through rhamnolipid washing treatment.
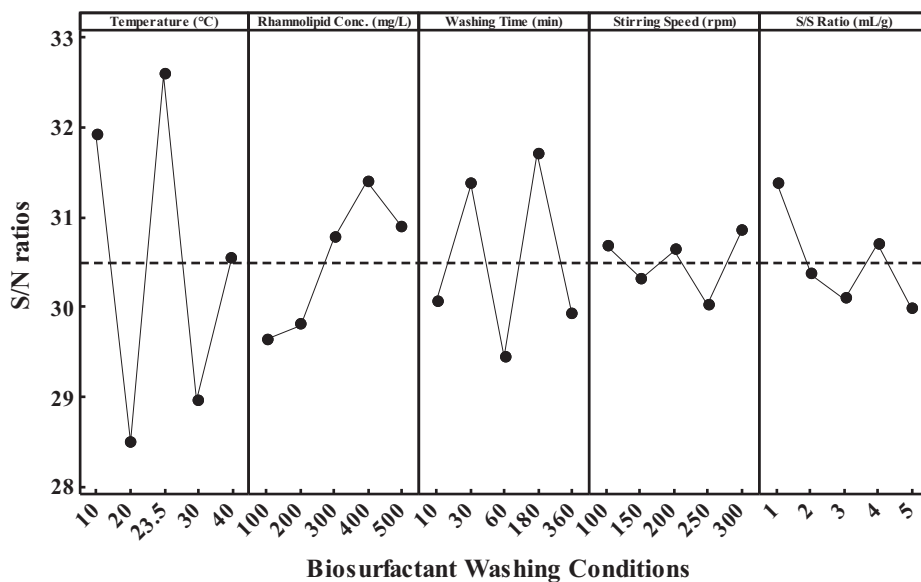

Fig. 8. Main effects of test parameters on F2 fraction reduction in petroleum-contaminated soil through rhamnolipid washing treatment.

ratios for 10 °C and room temperature in F3 fraction reduction were observed to be close: 35.32 and 35.18 respectively. It was observed that increase in temperature from 10 °C to 20 °C led to a decrease in TPH, F2, F3, F4 fractions. Further increase in temperature to room temperature showed an evident increase in hydrocarbon reduction. For TPH, F2 and F3 fractions, a further increase in temperature from room temperature to 40 °C decreased the rate of hydrocarbon reduction. For F2 fraction, on the other hand, increase from room temperature to 30 °C reduced the PHC reduction rate while a subsequent increase in temperature to 40 °C led to increased hydrocarbon removal. Temperature is an important factor because the process of desorption and dissolution which affects PHC removal are dependent on temperature [8].

According to Paria [15], in the presence of surfactants, solubilization of organic compounds is significantly affected by temperature. The author further states that for non-ionic and ionic surfactants, the degree of solubilization increases with tempera-

ture up to an optimum temperature where maximum solubilization is observed. However, the hydrophilic chain length affects the optimum temperature. The results observed from the present study reflect different optimum temperatures depending on the hydrocarbon fraction.

Effect of rhamnolipid concentration. Optimal rhamnolipid concentration for PHC reduction of TPH, F3 and F4 fractions was 500 mg/L, and 400 mg/L for F2 fraction. Similarly, the observed removal rate showed a different trend with F2 fraction than with TPH, F3 and F4 fractions. With F2 fraction, increase in rhamnolipid concentration from 100 mg/L to 400 mg/L increased the removal of hydrocarbon, further increase to 500 mg/L resulted in a decrease in hydrocarbon reduction. TPH, F3 and F4 fraction all responded identically to increase in rhamnolipid concentration. The rate of hydrocarbon reduction reduced initially with an increase in rhamnolipid concentration to a point. After that point, further increase of rham-
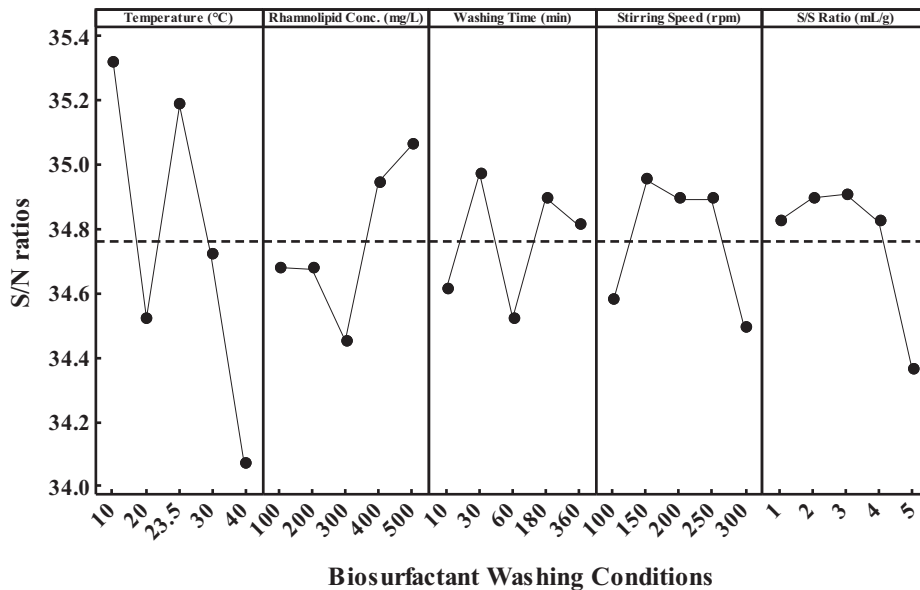
Fig. 9. Main effects of test parameters on F3 fraction reduction in petroleum-contaminated soil through rhamnolipid washing treatment.
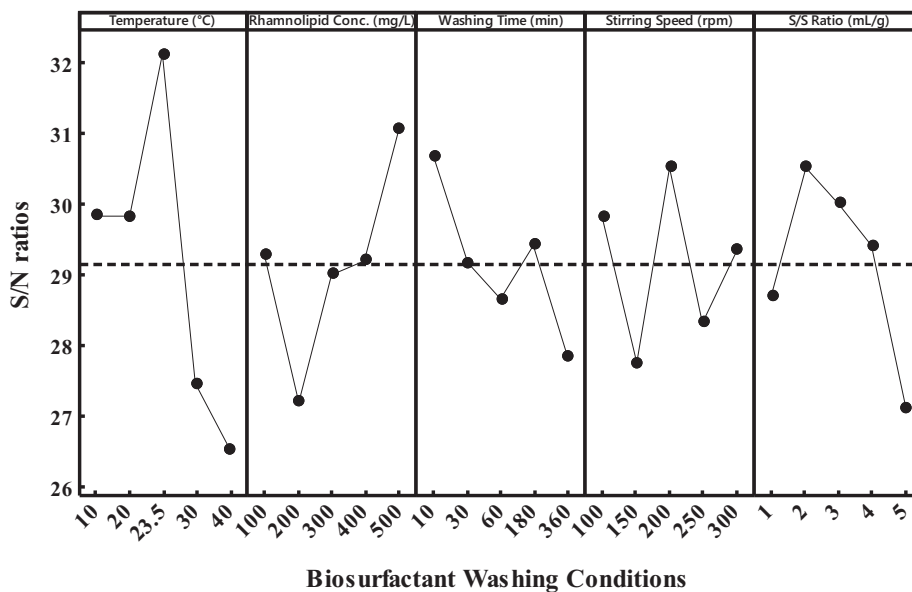

Fig. 10. Main effects of test parameters on F4 fraction reduction in petroleum-contaminated soil through rhamnolipid washing treatment.

nolipid concentration resulted in increased PHC removal. This is similar to results obtained by Chaprão et al. [44] and Lai et al. [4]. The authors observed that with an increase in rhamnolipid concentration, the solubility of crude oil increased. The efficiency of removal of PHC from soils and the concentration of rhamnolipid were observed to be positively correlated.

The effect of biosurfactant concentration is important because biosurfactant acts differently relative to their concentration. Some biosurfactants are more effective at concentrations below the CMC while some are more effective at concentrations above the CMC. While removal efficiency of rhamnolipids and surfactin were shown by Lai et al. [4] to increase with increase in concentrations above the CMC, at concentrations above CMC, lecithin and tannin could not increase crude oil solubilization [44]. CMC is the biosurfactant concentration at which micelles start to form solubilization [44]. The concentrations of rhamnolipid used for this experiment

were at and above the CMC value. The overall results are similar to what is reported in literature, rhamnolipid was more effective at concentrations above CMC.

Effect of washing time. Optimal rhamnolipid washing time for reduction of TPH, F2, F3 and F4 fraction were 30 min, 180 min, 30 min and 10 min respectively. Washing time for TPH and F3 fraction were the same, an observation that aligns with F3 fraction having the highest impact on TPH reduction. Washing time is an important test parameter as sufficient treatment time is required for effective removal of PHCs [44]. Chaprão et al. [44] tested contact times of 5, 10, 20 and 1440 min. In general, increase from 5 to 1440 min resulted in a decrease in oil removal performance through biosurfactant washing. This is similar to results presented in this study. The overall trend showed a reduced PHC reduction rate at higher treatment times. 5 – 10 min under agitation was

considered sufficient for PHC reduction by Chaprão et al. [44]. The authors infer an interaction between agitation/stirring speed and contact time. P-values (probability values) for washing time and stirring speed presented by ANOVA results were not close. However, an interaction plot of washing time and stirring speed showed non-parallel lines which reflected a level of interaction between the factors. Lai et al. [4] also found that PHC removal efficiency did not vary sufficiently with changes in treatment time from 1 d to 7 d. Rather, similar removal efficiency was recorded for both 1 d and 7 d, and in some cases, a decrease in TPH removal was reported at 7 d. It can be inferred from the results that rhamnolipid washing is time efficient; a factor that contributes positively in the potentials of combining this technique with other time-consuming remediation methods.

Effect of stirring speed. Optimal stirring speed for removal of TPH, F2, F3 and F4 fraction were 200, 300, 150 and 200 rpm respectively. The highest stirring speed is recorded for F2 fraction. A review of the S/N ratios, however, shows that S/N ratios for 100, 200 and 300 rpm are quite close. These were 30.68, 30.63 and 30.85, which indicates that increasing stirring speed from 100 to 300 does not effectively contribute to an increase in F2 fraction reduction. The results indicate that lower values of stirring speed tested (levels 1–3) are sufficient for PHC reduction. Lai et al. [4] reported shaking speed of 100 and 200 rpm as increasing the TPH removal efficiency in the washing experiment conducted. At 0 and 5 rpm shaking speed, TPH removal efficacy recorded by the authors was about 5%. Lai et al. [4] noted the need for caution when testing the effect of agitation. Although the authors tested for shaking speed (while this experiment tested stirring speed), it was advised that the level of agitation applied should not be too high. This is to ensure that the level of agitation employed is just enough to ensure efficient contact between PHC and the biosurfactants. Vigorous agitation, on the other hand, could result in PHC removal mainly due to mechanical detachment. Thus, overstating the removal efficiency of the biosurfactants added. Chaprão et al. [44] tested four biosurfactant types and recorded varying results on the effect of agitation on PHC removal during biosurfactant washing. Only three of the four biosurfactants tested showed better removal rates with agitation. Results from the authors indicate that effect of agitation depends on the type of soil, the type of surfactant and the concentration of the biosurfactant.

Effect of solution-to-sample ratio. TPH, F2, F3 and F4 fractions all showed different optimal conditions for S/S ratio. The optimal conditions were 4:1, 1:1, 3:1, 2:1 for TPH, F2, F3, and F4 fractions respectively. Yan et al. [8] and Urum et al. [36] reported a ratio of 3:1 as the optimal value for S/S ratio. According to Yan et al. [8], a ratio of 3:1 is an acceptable value when considering the economic and operational aspects of biosurfactant washing.

Conclusions

In this study, rhamnolipid-enhanced soil washing of two different soil types was evaluated. Taguchi experimental design was employed to study the effect of temperature, rhamnolipid concentration, washing time, stirring speed and solution-to-sample ratio as potentially vital parameters for rhamnolipid-enhanced soil washing.

Washing of drill cuttings and petroleum-contaminated soil has been demonstrated as an effective treatment method to reduce PHC concentrations in petroleum-contaminated soils and drill cuttings. A potential benefit of soil washing is reduced process time; however, the need for additional treatment processes is recognized to ensure that the residual levels of contaminants in impacted media can be reduced to levels within provincial and/or federal regulatory standards. This makes biosurfactant washing an efficient first step that can be applied singly to reduce PHC concentrations in contaminated soil/media; or in addition to a time-consuming secondary remedial process such as biodegradation.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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