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Effect of Petroleum Contamination on Soil Properties and the Removal Efficiency of Volatile Organic Compounds Using Air-Stripping System

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Abstract

A pilot-scale research study was investigated using soil column air stripping (SCAS) system to deal with petroleum contaminants with high concentration of volatile organic chemicals (VOCs) generated in the petroleum production and refining process, and the impacts of stripping temperature and gas-solid volume ratio on the maximum recovery of VOCs were investigated by a bench air stripping experiments, MATLAB programming and comparison with literature data'. This research compared air stripping results with theoretical models implemented in MATLAB, examining the interactive effects of air-to-soil ratio and temperature on the removal efficiency of VOCs through the use of a stripping facility called soil column air stripper. Various analyses were performed to assess how the air-to-soil ratio and temperature influence VOC removal efficiency. Increasing the air-to-soil ratio from 2.4 L/min to 12 L/min improved VOC recovery efficiency, rising from 30.46% to 47.10% after one hour of venting. The VOCs recovery efficiency was attained at 47.85% after approximately 1.5 hours at 12 L/min with unheated air. The use of unheated air at 24°C showed limited effectiveness in VOCs removal, with elimination rates significantly influenced by temperature; at 45°C, recovery efficiency increased from 33.82% to 66.03% after two hours of air stripping. The MATLAB experimental model indicated an increase in mass transfer coefficient from 0.170×10^{-5} *to* 0.198×10^{-5} s^{-1} *corresponding to temperature increasing from 24°C to 45°C respectively. The Henry's law constant increased from 238.59 to 893.36 atm with the same corresponding temperature rise. Over 99% of VOCs removal efficiencies were obtained for all combinations of temperature and air-to-soil ratio. The findings from air stripping approach showed stripping of VOCs from petroleum contaminated soil can be influence by temperature and air-to-soil ratio while MATLAB experimental model underscored air-to-soil ratio between 2.4 and 21.6 as the most efficient operating point at temperature 20* ^{O}C *to 50* ^{O}C*. This showed the effectiveness and accuracy of MATLAB programming over air stripping experiment with an advantage over the conventional method used in literature. The model demonstrated excellent fit and accuracy, evidenced by an* R^2 *of 0.98 and a root mean square error (RMSE) recorded 0.001. ANOVA variance results further validated the statistical significance of the model, with the predicted values all align closely with the experimental data. The results indicated that VOCs removal efficiency dependent on temperature with air-to-soil ratio but other soil factors may have a significant challenge in the practical application of preheated air.*

***Keywords**: Volatile organic chemicals; Soil column air stripper; Air stripping; Mass transfer.*

1.0 Introduction

Soil contamination from various volatile organic chemicals (VOCs) has become a serious environmental problem in Nigeria Today. These contaminants enter the soil through pipeline leaks, above and underground storage tanks spills and hazardous waste disposal [1]. The effective management of petroleum-contaminated soils is crucial, necessitating the development of assessment tests to gauge contamination levels and the use of treatment systems for the removal of VOCs. Common cleanup technologies for petroleum-contaminated soils include excavation, solvent extraction, reverse osmosis, and bioremediation, among others. Additionally, soil cleanup can be accomplished through air stripping techniques, utilizing both soil column air stripping (SCAS) and gas chromatography fitted with flame ionization detector (GC-FID) [1, 2]. The SCAS system is a distinctive remediation technique that reliance on air stripping operation to meet remediation goals. Air stripping is simple, easy to operate and effective in VOCs removal. These VOCs, which include aliphatic hydrocarbons (AHCs), polycyclic aromatic hydrocarbons (PAHs), and benzene, toluene, ethylbenzene, and xylenes (collectively known as BTEX) found in gasoline, as well as chlorinated hydrocarbons such as trichloroethylene and chloroform posse an environmental challenge [2, 3]. The behavior of these VOCs can be analyzed to predict their fate and transport in the environment, thereby influencing their removal rates during air stripping. Common types of air strippers include packed columns, tank aeration systems, spray fountains, sieve trays, and diffused aeration systems. The flow configuration during operation of soil column air stripper as concurrent, crosscurrent, or countercurrent is an important issue that require critical study, ensuring VOCs removal from soil by increasing the surface area of the contaminated soil that is exposed to air, which facilitates the transfer of VOCs from the solid phase to the gaseous phase.

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In a soil column, contaminated soil is distributed over the column from the conical hopper at the top of column while air is injected from below in counter-current mode operation using an air blower. The treated soil is collected from the bottom of the column while the VOCs rich air is released at the top to the surrounding through a level control for further treatment [3]. It is important to introduce soil column type of air stripper for VOCs removal from contaminated soil by increasing the surface area of the soil that is exposed to air. Subsequently compare the innovative SCAS and with MATLAB program to investigate the effects of operating variables such as temperature and gas-solid ratio on the removal efficiency of VOCs in a laboratory scale soil column air stripper [1, 3]. Air stripping schemes and the process variables can influence VOCs removal efficiency [3, 4]. Air stripping methods have demonstrated success with steam stripping and packed columns as well as using preheated air.

Applying this technique in remediating soil with different soil textures, can it be applicable or it will become a difficult task. In this approach, air is injected into the column, the soils will not allow the injected air to penetrate into the soil matrix very readily, leading to low removal efficiency. Because the traditional approaces of removing VOCs from the unsaturated zone do not work well in fine soils, alternative approaches must be taken. One of these approaches must be evaluated (using preheated air) and monitor the soil whether the contamination will not pose a risk to human health or the environment. SCAS system is a new remedial technology that is not known but it is very feasible for handling less volatile VOCs such as vinyl chloride, tetrachloroethylene, carbon tetrachloride, 1,1,1-dichloroethane, trichloroethylene (TCE), toluene, benzene, and chloroform, among others. The key variable in managing VOC-contaminated soil is Henry's law constant (H), along with the physicochemical properties of the VOCs. A list of VOCs and their air stripping potential based on K_H is provided in Table 1.

Table 1: List of selected VOCs, Henry's constant and their nature of volatilization

VOCs	**Formula**	**Mw (g/mol)**	**VP (Pa-m^3.mol^{-1})**	**Henry's constant**
Vinyl chloride	C_2H_3Cl	62.50	3.9 x 10^{O}	50
Aliphatic	C_6H_{12}	84.16	9.6 x 10^{-2}	1.25
Tetrachloroethylene	C_2Cl_4	165.83	7.7 x 10^{-2}	1
Toluene	$C_6H_5CH_3$	92.14	1.5 x 10^{-2}	0.2
Benzene	C_6H_6	78.11	4.1 x 10^{-4}	0.3
Ammonia	NH_3	17.031	6.2 x 10^{-4}	0.008
Polynuclear aromatic	Family	128 ≥300	5.6 x 10^{-5}	0.00073
Phenol	C_6H_5OH	94.11	3.8 x 10^{-7}	0.000005

Table 1 summarizes the VOCs and their relative ease of removal using soil column air stripping, the Henry law constant (H) will determine how appropriate air stripping can be as a remedial option. Process parameters such as temperature, air-to-soil ratio, loading rates, air stripper type, gas pressure drop and Henry's constant for VOCs was found to influence the VOCs removal efficiency. The countercurrent soil column air stripper

The countercurrent soil column air stripping provides a contact between the contaminated soil and the injected air in an assemble stripping device called SCAS system. In soil remediation, clean air is injected into the contaminated soil zone to volatilize and strip the VOCs, which are then removed by the carrier gas. The process has been found to be effective especially for treating the vadose zone of the soil contaminated with VOCs. Air stripping can be used for treatment of contaminated soil by petroleum or heavy metal [4].

1.1 Soil Column Air Stripping

1.1.1 Description

Soil column air stripper is a cylindrical column device that is assemble for a specific application to treat the contaminated soil. Air enters at the bottom of the column, flows upward through the column at a very high efficiency. The contaminated soil is introduced at the top of the column (conical hopper) and flows downward by gravity. The air mixed with VOCs are discharged through the top while the treated soil is collected at the bottom through the sprue. The dimension of the column is 1.10 m height, 0.10 m diameter, the volume is 0.055 m^3 and the maximum capacity of feedstock per column is 2.5 kg.

1.1.2 Theory of operation

The soil column air stripper force air through contaminated soil and work best on VOCs that can easily evaporate. The contaminated soil is poured into the column and sprayed over the column by aid of the conical hopper. The soil poured down to the bottom of the column under gravity, a blower at the bottom blows air upwards at a countercurrent mode. The VOCs change from a solid to a gas phase (evaporate) as the air passes through the falling soil. The air carries the removed VOCs gases to the column outlet into the atmosphere and exit or treated. The clean soil is collected at the bottom of the column. A typical soil column air stripper is shown in Figure 1.0.

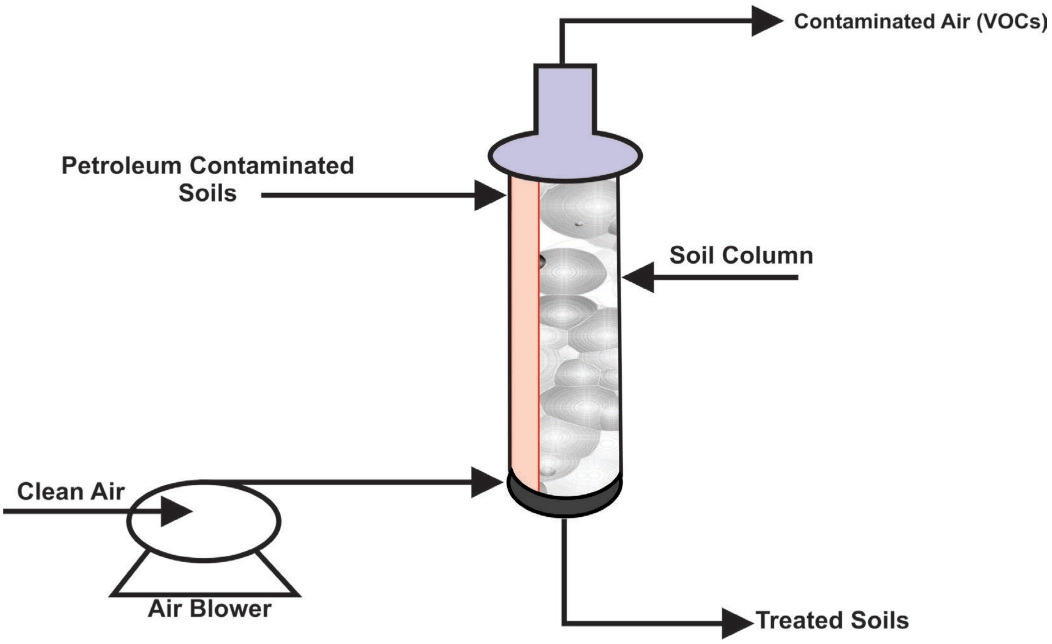

Figure 1: A schematic diagram of soil column air stripper [6]

The removal efficiency of VOCs in Figure 10 is highly dependent on temperature and we need to know the VOCs boiling temperature within the soil pore. For most VOCs, elevated air temperatures will improve the removal efficiency. If higher removal efficiency is required, the height of the column will be increased. The height affects the structural stability, so to maintain the same removal efficiency; the column height can be reduced by increasing the column diameter.

1.2 VOCs Removal Efficiency Analysis

Air stripping is a technique that uses an air stripper for VOCs removal from contaminated soil by increasing the surface area of the contaminated soil that is exposed to air, and it is widely used for the removal of VOCs from contaminated soil where petroleum activities and operation occurs [5]. The types of air stripper depend on the applicability of each technique that is based on its performance as reported in engineering literatures, information vendor and professional experience with the stripping facility [5, 6]. Treatment methods for VOCs recovery focus more on industrial contaminated soils and this require an innovative type of stripping facility to achieve the remedial objectives [6]. Air stripping technique still remains most useful where there is an economic interest in higher concentrations of valuable VOCs through recovery. A significant amount of VOCs recovery was recorded using air stripping as reported in the literature [7].

Recent investigations have explored different remediation strategies for petroleum-contaminated soils. For example, Oto-Obong *et al.* [8] conducted bench-scale laboratory experiments for determination of air stripping effectiveness for removal of VOCs from benzene-contaminated soils using air stripping technology was verified. Their findings demonstrated that operational parameters such as grain size, air-flow rate, and temperature significantly enhanced benzene recovery efficiency, increasing removal from 49% to 65%, and up to 70% with prolonged operational time. Similarly, Yakubu *et al.* [6] evaluated the interactive effect of temperature, surfactant addition, and grain size on the performance of a soil column air stripper for the removal of VOCs from petroleum-contaminated soils. The experimental results showed an increasing injected air temperature, combined with 0.1 wt% surfactant solution, showed an improved VOCs removal efficiency from 21.20 % to 37.29 % for AHCs and up to 81.45% for PAHs. More recently, Alexander *et al.* [4] investigated the bioremediation of engine oil and grease contaminated soils using compost manure, finely granulated corncob, and blended groundnut shell. Their study examined the mechanisms through which these organic amendments enhanced biodegradation in each treatment case.

Previous studies have examined the impact of operating parameters on removal performance using the stripping facility. Generally, VOCs removal efficiency is influenced by factors including temperature, air-to-soil ratio, solid loading rate, type of air stripper (size, depth, and diameter), pressure drop, and the contaminant's Henry's law constant [6, 7, 8]. Despite all the optimization efforts, conventional air stripping techniques often exhibit relatively low VOCs removal efficiencies in the remediation of contaminated source. Pilot-scale air stripping experiment is required to provide a practical performance of a counter-current soil column air stripper and its behavior during mass transfer. The mass transfer relationships and the effects on removal efficiencies can be increased by varying operating parameters. Several computer-based models are considered for further investigation and better understanding on the interactive effects of temperature and air-to-soil ratio on VOC

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removal efficiency using a MATLAB-based approach. Other investigations were performed using gas chromatography with flame ionization detector (GC-FID), and stripping facility to separate VOCs contaminant and to compare to MATLAB simulation.

The goal of this research study was to determine the VOCs removal efficiency from soil samples collected from petroleum disposal waste and to compare the performance of MATLAB simulation with a pilot-scale SCAS system. Firstly, to determine the hydrocarbons concentration in the contaminated soil. Next, to determine the performance of the soil column air stripper for the removal of the identified contaminants and next to determine the effects of operating variables on the removal efficiency of VOCs in a laboratory scale soil column air stripper and the application of MATLAB design model with the response surface plot to determine the interactive effect of these variables on the highest VOCs removal efficiency.

2.0 Henry's Law and the Mass-Transfer Coefficient

Countercurrent SCAS system is described by the term air stripping. The theoretical concept produces a condition in which a large surface area of the fine soil to be treated is exposed to air, which promotes transfer of the VOCs from the solid phase to the gaseous phase. This occurs because under normal conditions the concentration of the VOCs in ambient air is much lower than the concentration in contaminated soil [5, 8]. The removal process of VOCs from solid liquid proceeds through the following steps; transfer from the solid to the interface, transfer across the interface and transfer away from the interface into a new phase as follows:

2.1 Theoretical Investigation

The key process parameters required to find the VOCs removal efficiency include:

(a) Henry's constant

The Henry's law constant is an important parameter affecting the performance of SCAS system and contaminant diffusivity. This is defined as the ratio of the contaminant at equilibrium in the solid phase, Cs, to the contaminant in the gaseous phase, C_G, as shown in equation 1.

$$\mathrm{H} \rightleftharpoons \frac{C_G}{C_S} \tag{1}$$

where H - Henry's law constant. H define how appropriate air stripping can be as a remedial option as a function of temperature and follows Van't Hoff's relationship given in the integrated form [5, 8].

$$\mathrm{Log\ H} = \frac{\Delta H^o}{RT} + \mathrm{C} \tag{2}$$

where ΔH^o - enthalpy change resulting from the dissolution of VOCs in soil; R - the universal gas constant; T - the absolute temperature and C - a compound dependent constant.

(b) Mass transfer rate

Mass transfer of VOCs across the gas-solid interface in an air stripper can occur through volatilization and induced by a mechanical surface aeration as described by equation (3):

$$\frac{dm}{dt} = -\ K_S.\mathrm{a}\,\frac{C - C_g}{H}\ \mathrm{A} \tag{3}$$

where $K_{s.a}$ is the overall mass transfer coefficient (s^{-1}), C is VOCs concentration (g/m^3), Cg is the gas phase VOCs concentration (g/m^3), H is Henry's constant (atm) and A is surface area (m^2). The rate constants for the local solid and gas phase transfers, k_S and k_G, respectively, are related to the overall transfer rate constant by

$$K_S.\mathrm{a} = \left(\frac{1}{K_S.\mathrm{a}} + \frac{1}{K_{Sa}\,H}\right)^{-1} \tag{4}$$

(c) Stripping factor

The stripping factor in mass transfer is a dimensionless parameter defined as the ratio of the solute's tendency to stay in the vapor phase to its tendency to stay in the solid phase (G/S) and its Henry's constant [4, 9]. This is used to evaluate stripping efficiency in an air stripper. The stripping factor (S) is defined by equation (5)

$$\mathrm{S} = \mathrm{H}\ [\mathrm{G}^{\circ}/\mathrm{S}^{\circ}] \tag{5}$$

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where: S - Air stripping factor (unitless) S^O - Soil flow rate (mol/s) G^O - Air flow rate (mol/s). The S is important in fining the ability of soil column to remove VOCs. Conditions that influence S include: For $S > 1$ (stripping), $S = 1$ (equilibrium) and $S < 1$ (absorption). For $S > 1$, signifies total removal of VOCs could be achieved when the column height is increased. Conversely, for $S < 1$, the SCAS system performance is limited by equilibrium and the rate fractional removal of VOCs.

(d) Concentration of effluent in soil

The concentration of the contaminant in the effluent soil (C_{out}) was determined using [9]

$$C_{out} = \frac{C_{in}\,(S-1)}{Exp\,\frac{NTU\,(S-1)}{S} - \frac{1}{S}} \qquad (6)$$

where: NTU: Number of Transfer Unit, S: stripping factor, C_{in}: influent concentration.

(e) Height of Transfer Unit

This measures the effectiveness of separation at a particular height which characterizes the efficiency of mass transfer from soil to air which as expressed by equation 7.

$$\text{HTU} = \frac{S_M}{K_{S,a}C_T} \qquad (7)$$

(f) Number of Transfer Unit

This is a performance equation required for achieving a desired separation. Where HTU - height of transfer unit (m), NTU – number of transfer unit introduced by Kavanaugh to characterize the difficulty of removing the VOCs contaminant from the solid phase [1, 8]. A single transfer unit gives the change of composition of the phases equal to the average driving force producing the change. It is expressed mathematically as:

$$\text{NTU} = \frac{z}{HTU} \qquad (8)$$

where column height Z (m) is calculated using equation 8.

2.2 Estimation of Operating Data

2.2.1 Mass transfer analysis

Mass transfer of VOCs occur through volatilization and it is induced by an air blower. The process of VOCs removal from solid to gas phase determine the effect of these process variables. The flow patter employ in this research work is counter-current mode. The mass balance analysis for a continuous stripping column is given by Figure 2.

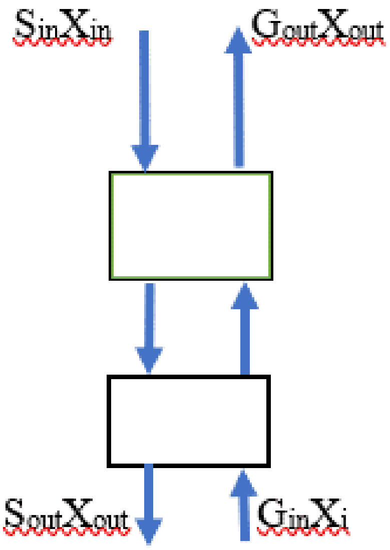

Figure 2: A countercurrent flow soil column air stripping

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Applying Henry's law, a mass balance of VOCs in and out of the soil column as shown in Figure 2:
Total moles in = Total moles out

$$S_iC_i + G_i\,y_i = S_oC_o + G_Oy_o \tag{9}$$

where G is the gas flux, S is the soil flow, C is the VOCs concentration in soil, and y is the VOCs concentration in air. Assuming an uncontaminated air supply,

y_i= 0, $C_i = C_o$ = C and $G_i = G_o$ = G

$$SC_o + Gy_o = SC_I + Gy_i \tag{10}$$

But for y_i= 0, this implies equation 11 becomes

$$Gy_o = SC_I - SC_o \tag{11}$$

$$\Rightarrow \frac{G}{S} = \frac{C_i - C_o}{y_o} = \frac{C_i - C_o}{C_o} \tag{12}$$

2.2.2 Air Stripper efficiency

The percentage removal of VOC is used to evaluate the efficiency of the air stripper. This was determined using (12) [6, 9]. Therefore, the percentage removal of the VOCs (η) is used to evaluate the efficiency of the air stripper and it is expressed as:

$$\eta = \frac{C_i - C_o}{C_i} \text{ x } 100\ (\%) \tag{13}$$

The percentage removal of the VOCs (η) is used to evaluate the efficiency of the soil column air stripper at a given column height necessary to achieve a treatment objective.

3.0 Material and Method

3.1 Pilot Scale Investigation

The pilot scale investigation was conducted using soil column air stripper system as shown in Figure 3. The soil column had an internal of 0.10 m diameter and 1.0 m column height, operating at a volumetric air-to-soil ratio of 2.4:1 and a Henry's law constant of 0.74. The initial influent VOCs concentration of 600 mg/kg was targeted for reduction to 5 mg/kg in the treated effluent soil. The mass-transfer coefficient is influenced by Henry's constant, air stripper configuration, operating temperature, and air-to-soil ratio. Equations (1–13) are proposed for optimizing the SCAS system based on mass-transfer relationships. Pilot-scale data are essential to obtain reliable parameters that govern VOCs removal efficiency under varying operational conditions. The effects of air-to-soil ratio and temperature on VOCs removal performance were systematically evaluated. An appropriate analytical program capable of identifying individual VOCs species and quantifying their concentrations in both influent and effluent soil samples were also employed. Table 2 and Figure 3 present the specifications of the soil column air stripper used to assess VOC removal for the research study.

Table 2: Air stripper specifications

S/N	Parameters	Unit of measurement	Values
1	Soil flow rate	l/min	2.4
2	Column volume	m^3	0.011
3	Stripping Area	m^2	0.01
4	Column Diameter	M	0.11
5	Column area	m^2	0.0095
6	Column height	M	1.1
7	Mass loading	Kg	2.5
8	Column material	Mm	Galvanized iron carbon

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Figure 3: Pilot scale soil column air stripping system

3.2 Experimental Procedure

The analytical methods employed in this research work is to determine VOCs concentration present in contaminated soil, this is to achieve high treatment efficiency using the stripping facility. The selected analytical program involves identifying and quantifying VOCs in the soil to be treated, the efficiency of the treatment process and the pilot scale stripping facility to determine the effects of varying the process parameters based on a reliable soil-quality.

3.2.1 Soil characterization

The following properties of the soil samples were determined.

The selected soils were characterized using sieve analysis as described by ASTM D6913 standard size sieve. In this method, the soil samples were prepared and packed into the different size sieves as described by Abdullahi, 2015. The classification of soil particles ranging from 125mm down to 20μm was measured when the soil passes through sieves to capture the different size ranges. Subsequently other laboratory testing method were performed to access the level of permeability and infiltration rate.

3.2.2 Analysis of total volatile organic chemicals in soil by GC-FID

(a) Extraction process

The solid-liquid separation was done by shaker agitator machine while the total petroleum hydrocarbon quantifications (TPHs) were analyzed using GC–FID method. This method measures the aggregate concentration of extractable VOCs in solids based on boiling point ranges. This method is divided into two part, this include the extraction process and followed by GC-FID analysis [6, 8, 10].

(b) GC-FID analyses

The analytical method intended to assess the hydrocarbon concentration levels in soil samples by using a standards Varian model BV CP 3800 GC-FID equipped with a split/splitless injection port and Combi PAL auto sampler. The soil samples were taken into 2 mL chromatographic vial, injected and separated on a Varian Chrompack capillary column CP 5860 with 95% methyl and 5% phenyl-polysiloxane phase, (oven max tempt 350°C), WCOT fused silica, 30 m x 0.25 mm id and 0.25 μm film thickness with CP-Sil 8 CB low bleeds/MS coating. Carrier gas was helium 26 cm sec^{-1}. Temperature profile during the chromatographic analysis was recorded at 50°C for 3 minutes; 8°C/min to 320°C hold 15 minutes and detector at 320°C [6, 10]. The output signal was monitored on an installed computer connected to the GC-FID. The data was estimated by automated integration of the area under the resolved chromatographic profile [4, 10].

3.2.3 Research methodology

Figure 2 shows the stripping facility used for the air stripping experiments. The soil column air stripper is a cylindrical column mounted in the vertical position having dimension (100 cm height and 10cm diameter) which was packed uniformly with 2.50kg selected soil samples (gravel, sandy, loamy and clay) poured at top through a conical hopper position at angle 45$^{\mathrm{O}}$C which flow down (under gravity). A Multipoint thermocouple was placed at regular intervals along the suction line to watch over the thermocouple of the heat element and the temperature profile along the column height was measured by a digital thermometer while the pressure gradient across the soil column air stripper was quantified by pressure gauges placed at the end of the column. The device was operated using a batch mode where samples were intermittently fed from the top and filled to a level while the remaining space is to control high level of fluidization and off gas emission control. The outlet end of the column was fitted with a level control tube through which the off gas is channeled to power the reboiler. Steady air flow was provided to the soil column using an air blower. The air-flow rate was modulated by an adjusting valve on the blower. At the exit from the column, the vapours were passed through a level control unit before they were discharged, collected with the aid of an air bag and analyzed using GC/FID. The outlet end of the column was fitted with a fine wire mesh screens (50 μm diameter) to prevent soil from washed out. VOCs were selected as the contaminant and the air-flow rate was fixed for all experiments after 15 minutes of air stripping [6, 11]. The interactive effect of air injection temperature and air-to-soil ratio were studied to access VOCs removal efficiency from the stripping device. The schematic diagram describing all the step involves in this research methodology.

i. Determination of injected air temperature on VOCs removal efficiency

The effect of hot air on VOCs recovery was studied within a range of temperature (24–45^{O}C). The research procedure in section 3.2.3 was then repeated to determine the VOCs removal efficiency. Investigating the negative effect of spilled fuel on soils; it is important to reduce the soil concentration and alter the physicochemical properties of VOCs in soils.

ii. Determination of air-to-soil ratio on VOCs removal efficiency

The soil column air stripper presented in Figure 2 is equipped with an air blower, mass flow controller (rotameter), air heating element, and sampling ports for both soil and exhaust gas. The install heating system used to inject preheated air so as to maintain the column temperature. The procedure focuses on maximizing VOCs transport ($Ks.a$) by adjusting the gas pressure (via temperature) and the difference in concentration (via airflow). The select ranges for temperature, T_i = 20°C, while the air-to-soil ratio was at 2.4 L/min, this is to determine their interaction on VOCs removal efficiency. The air was injected at the lowest temperature and lowest air-to-soil ratio. The experiment was repeated for various combinations of temperature (T_1, T_2,…, T_n) and air-to-soil ratio of $(A/S)_1$, $(A/S)_2$,…,$(A/S)_n$ to determine the residual VOCs concentration.

iii. MATLAB programming model

A laboratory scale soil column air stripper used in this study is presented in Figure 2. The feedstock influent concentration of 620 mg/kg was fed into the column when the air-to-soil ratio range of 2.4 to 21.6 were considered to operate the stripping device at temperatures of 293K, 303K, 313K and 323K referred to as T_1, T_2, T_3 and T_4 respectively. The choice of temperature was based on VOCs boiling point temperature (BPT) the studies of Abdullahi *et al.* [10, 11] which reported that a convergence in the performance efficiencies occurs at temperature above 50^{0}C and high air-to-water ratios. The interactive effects of temperature and air-to-soil ratio on the removal efficiency were studied using advanced program simulation (MATLAB) from equations (2-13) with data obtained from literature [12]. The flowchart for simulation program logic flow is presented in Figure 4.

iv. Verification and validation

The verification and validation process for VOCs stripping of petroleum contaminated soils simulation followed a structured, iterative approach. The model's logic was verified using code reviews and visual animation audits. A step-forward feature and adjustable playback speeds allowed for precise tracking of entity sequences, while all code changes were documented for full traceability. The simulation was validated by comparing a simplified pilot model against experimental data. By validating a basic version before adding complex variables, the researcher ensured the model's core accuracy in simulating VOCs removal efficiency from petroleum-contaminated soils. These qualitative animations are shown in Figure 4 which is integrated with quantitative entity tracing for robust error detection. The model was benchmarked against experimental results to establish a reliable foundation, preventing compounding errors as the model's complexity increased for larger-scale petroleum-remediation scenarios.

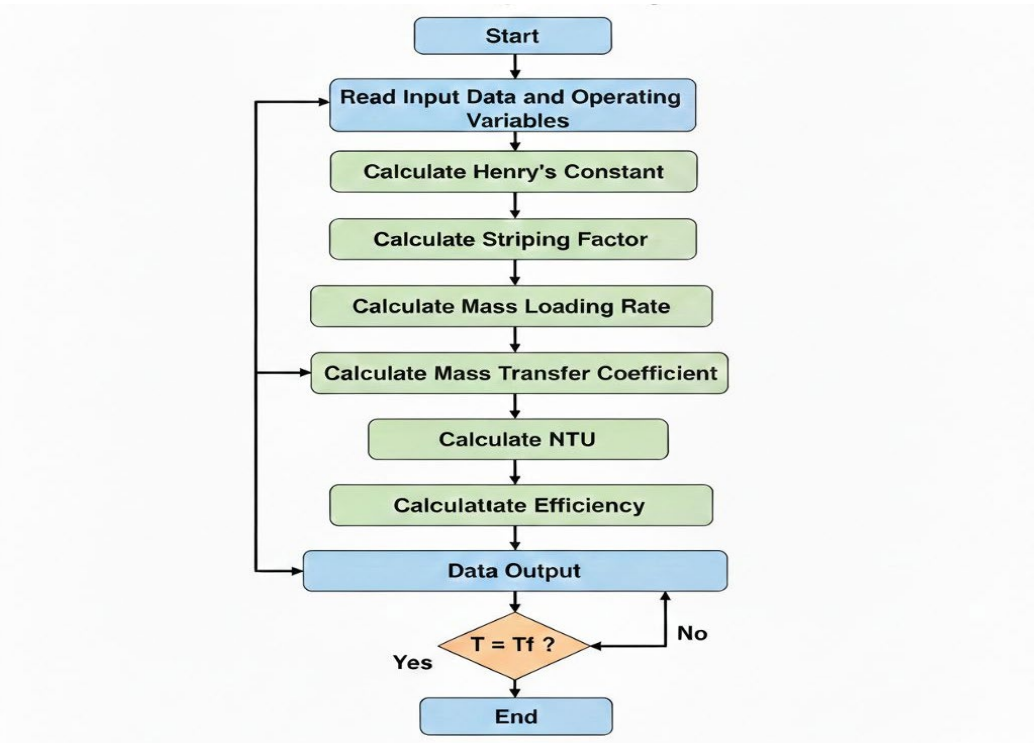

Figure 4: MATLAB simulation logic flow diagram

4.0 Results and Discussion

4.1 Physicochemical Properties of Soil Samples

The experiments were performed to correlate the influence of soil grain size distribution on air injection flow rate and VOC recovery efficiency. In all the experiments, VOCs was selected as the pollutants. The air-flow rate was constant for all experiments studied. The experiments were investigated by injecting air at the ambient temperature of 24°C. The characterization of the selected soils is presented in Table 3. While the concentrations of VOCs recovery from soil column air stripper are shown in Table 4.

Table 3: Physical properties of soil samples

Soil sample	Mean Grain Size (mm)	Permeability (mm^2)	Infiltration Rate (mm/hr)	Porosity (%)	Hydraulic Conductivity (m/s)	Transport Efficiency Index
Clay	1.1×10^{-2}	1.2×10^{-1}	3.056×10^{-6}	45.60	1.1×10^{-9}	0.11
Loamy	2.6×10^{-2}	6.8×10^{-10}	5.556×10^{-6}	37.50	1.3×10^{-6}	0.29
Sand	0.65	5.6×10^{-9}	8.333×10^{-5}	29.46	1.2×10^{-4}	0.75
Coarse	1.45	3.2×10^{-10}	3.083×10^{-1}	19.35	1.5×10^{-3}	0.94

Table 4: Concentration of VOCs recovery in location 1 using soil column air stripper

Soil samples	VOCs Conc. in soil sample prior to air stripping (mg/kg)	Residual VOCs in soil sample after air stripping (mg/kg)	Amount recovered in air (mg/kg)
Clay	114.87	60.21	54.66
Loamy	86.57	55.29	31.28
Sand	26.42	23.10	03.10
Coarse	21.79	13.21	08.58

Tables 3 and 4 results were considered to determine the influence of grain size distribution on flow characteristics during operation for the four selected soil samples. Coarse and sandy soils exhibit higher infiltration rates, facilitating rapid transportation of VOCs contaminant into the soils while clay exhibit very low infiltration and this limit VOCs volatilization. This implies, soil permeability and grain size strongly influence VOCs removal efficiency during volatilization. The fate and transport of VOCs from the immiscible and soil phases to the air phase used in this experiment as:

(a) Effect of soil grain size distribution

The experiments were conducted with four types of soil samples having a uniform grain size and contaminated with VOCs. The contaminated soil sample includes clay soils, loamy soils, sandy soils and coarse-grain soils.

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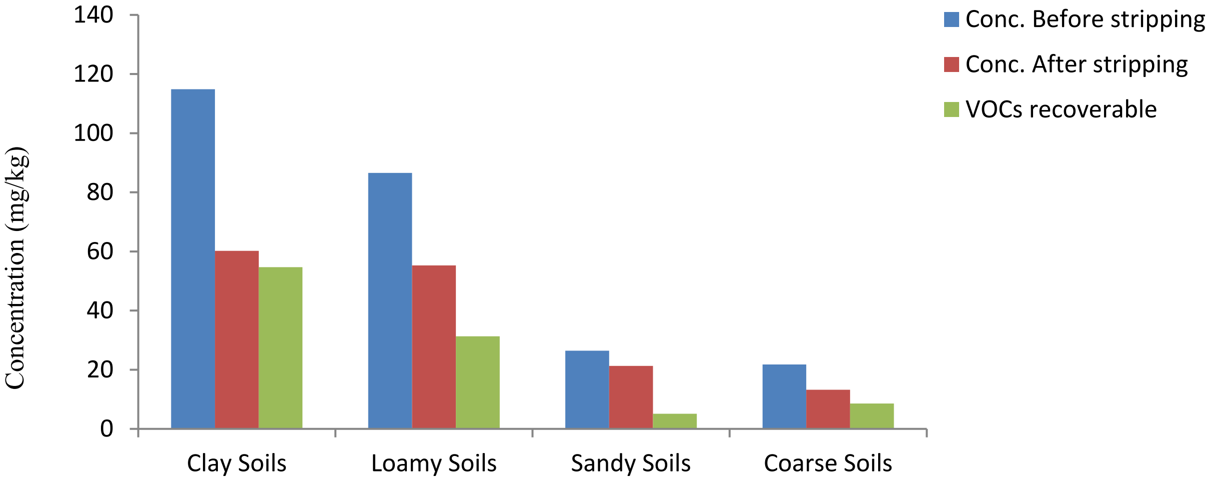

Figure 5: Effect of concentration on VOCs removal

Table 3 depicts variation as the particle size distribution increases from coarse to clay soils. The clay soils recorded the highest with 2.0 x 10^1 mm/g indicates the highest recording the highest VOCs holding capacity and conducting ability compared to other soil samples. The coarse soils have least holding capacity because of large surface area and large soil-permeability which was affected by the amount of clay present in soil samples [6, 9]. In all the selected soil samples, the contaminants distribution on the surface was observed to be inconsistent. This implies, different particle sizes with different level of infiltration rates (Table 4). Infiltration over a specific surface area causes a widespread contamination of soils and by VOCs such as petroleum and it products, this poses serious environmental and health hazards [6, 10]. The infiltration characteristics of gasoline and diesel fuels into undisturbed location are crucial in mitigating or remediating soil pollution. Furthermore, infiltration rate for fuel distillates decreased exponentially from 3.083 x 10^{-1} in coarse-grain to clay 3.056 x 10^{-6} mm/hr as wetting depth increased with time. Soil core size and bulk density both had significant effects on VOCs infiltration through the undisturbed soil cores; a smaller core size or a greater bulk density could reduce oil penetration to depth. It can be observed from Figure 5, there were system decreasing variation from 114.87 mg/kg clay, 86.57 mg/kg loamy, 26.42 mg/kg sandy and 21.79 mg/kg coarse-grain soils corresponding to the residual concentration of 60.21 mg/kg clay, 55.29 loamy, 23.10 mg/kg sandy and 13.21 mg/kg coarse-grain soils respectively and the VOCs recovery rates were inconsistent with sudden decrease. The variation of VOCs concentration with time of treatment showed trends similar to concentration after stripping. During air injection, clean air replaced polluted air within the column and the VOCs in the pores volatilized into the clean air, seeking to establish equilibrium [9, 10]. After the beginning of air injection, the VOCs concentration decreased rapidly with increasing time of treatment (evaporation phase) and approached a very low asymptotic value during the final stage of air injection (diffusion phase). During the beginning of air injection, the VOCs removal rate was higher in the coarser soil, as explained earlier. Beyond the initial stages of air injection, the VOCs removal rate was higher in finer soils because the grain surface area is relatively higher in finer soil [10].

(b) Effect of air stripping on VOCs removal efficiency

The efficiency of a soil column air stripper vapor depends on the properties of the soil, VOCs contaminant and on the process conditions for heated and unheated air, The VOCs properties affect the distribution from the immiscible phases to the air phase, Experiments were conducted with temperature of (24 – 45) ^{O}C while air-flow rates were kept constant (Tables 5 and 6).

Table 5: Overall VOCs removal efficiency with unheated air at 24 ^{o}C using air stripping

Soil Samples	Conc. in Soil Before Air Stripping (mg/kg)	Residual VOCs After Air Stripping (mg/kg)	Conc. of VOCs Remaining in Air	Amount Recovered (%)
Clay	211.95	105.53	101.42	47.85
Loamy	204.84	108.37	96.47	47.1
Sandy	105.38	65.5	39.88	37.84
Coarse	91	62.53	28.47	30.46

Table 6: Overall VOCs removal efficiency with heated air at 45 ^oC using air stripping

Soil samples	Conc. in soil before stripping (mg/kg)	Residual VOCs after stripping (mg/kg)	Conc. of VOCs in remaining in air	Amount recovered (%)
Clay	211.95	72.03	139.92	66.03
Loamy	204.84	69.91	134.93	65.87
Sandy	105.38	50.52	54.86	52.06
Coarse	91.00	60.22	30.78	33.82

Tables 5 and 6 present a clear linear relationship of VOCs removal efficiencies among soil samples for unheated and heated air during air stripping. The preheated air flow created by the air stripping enhances the percentage of VOCs removals of 66.03%, 65.87%, 52.06% and 33.82% corresponding to clay, loamy, sandy and coarse-grain soils respectively. The lowest percentage of VOCs removals recorded were 47.85%, 47.10%, 37.84% and 30.46% respectively for an unheated air. This means that the efficiency of VOCs removed efficiencies were influenced by temperature, subsequently the mean particle size increases from clay to coarse soils so the VOCs removal efficiencies decrease geometrically even without temperature increase [10, 11]. It can be observed from Tables 5 and 6, the VOCs concentration in the effluent air maintained a significantly higher value in the case with preheated air. The VOCs removal rate with preheated air was higher than with unheated air (Figure 6). After an hour of air stripping, it was found that approximately 66.03% and 65.87% of VOCs for clay and loamy soils were removed with the preheated air, while only 47.85% and 47.10% of the VOCs were stripped from clay and loamy soils with unheated air. The remediation time was substantially reduced when the air was preheated.

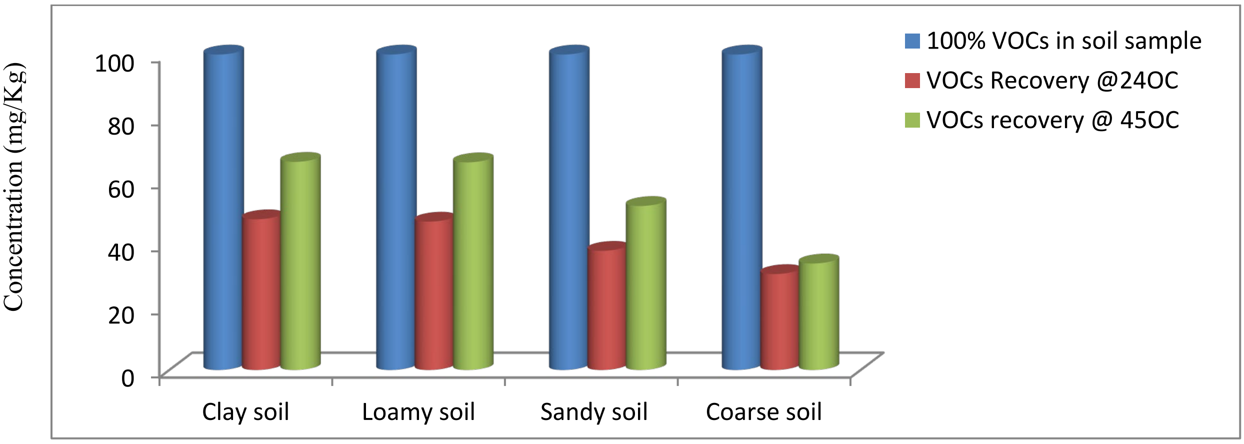

Figure 6: Effect of temperature on VOCs concentration in the effluent air

Figure 6 provides the VOCs removal efficiencies results for heated and unheated air. The results are selected and compared with MATLAB programming that allows the user to input the air stripping process parameters. The advance programming software displays the effectiveness and the result align closely with the experimental data on the removal efficiencies of VOCs at different temperatures and air-to-soil ratios.

4.2 MATLAB Simulation in Air Stripping Application

The performance and accuracy of a model depends on how close the results are to the laboratory practical results. The simulation results on VOCs removal efficiency need to be verified for temperature, air-to-soil ratio and combinations of temperature and air-to-soil ratio as presented in Tables 7 and 8.

Table 7: VOCs removal efficiencies for combination of temperatures and air-to-soil flow rates

Temperature/Air-to-soil ratio	Q = 323 K	Q = 373 K	Q = 423 K	Q = 473 K
2.4	99.0963	99.7345	99.8938	99.8984
4.8	99.2600	99.8493	99.8945	99.8985
7.2	99.4207	99.8599	99.8951	99.8995
9.6	99.5242	99.8653	99.8954	99.8995
12.0	99.5942	99.8694	99.8957	99.8996
14.4	99.6435	99.8731	99.8960	99.8996
16.8	99.6797	99.8755	99.8962	99.8997
19.2	99.7066	99.8775	99.8963	99.8997

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Temperature/Air-to-soil ratio	Q = 323 K	Q = 373 K	Q = 423 K	Q = 473 K
21.6	99.7275	99.8792	99.8965	99.8997

Table 8: Influence of temperature (T) and air-soil ratios (G/S) on absorption factor (R) of VOCs

Temperature/Air-to-soil ratio	Q =294 K	Q =305 K	Q =314 K	Q =325 K
2.4	1.41	2.47	4.04	6.32
4.8	1.58	2.75	4.38	6.98
7.2	1.76	3.02	4.91	7.65
9.6	1.93	3.30	5.35	8.31
12	2.10	3.86	5.78	5.97
14.4	2.27	3.86	6.22	9.63
16.8	2.44	4.13	6.65	10.30
19.2	2.61	4.31	7.08	10.96
21.6	2.78	4.69	7.52	11.62

Increasing the temperature on VOCs removal efficiency were identified to be more significant at temperatures between 40 and 45°C than at 50°C while air-to-soil ratios is at 2.4 – 21.6. Table 7 showed VOCs removal efficiencies increase non-linearly with process parameters. Tables 7 and 8 presents the simulation data for MATLAB simulation and the variables that influence the performance of SCAS system. The variables include temperature, air-to-soil ratio, Henry's constant, and the mass transfer coefficient. The result predicts the effectiveness of SCAS system by identifying the optimum operating conditions at difference temperatures and air-to-soil ratios.

Air-to-soil ratio influence

Figure 7 shows the trend of removal efficiencies of VOCs at different air-to-soil ratios and temperatures. At any given temperature, increase in air-to-soil ratio results in higher VOCs removal efficiency. This is because, increased air flow rate increases the interfacial area, decreases gases phase resistance and hence increase the mass transfer efficiency. Previous research studies considered show similar result [10, 12]. Another effect of increased air-to-soil ratio is that, it causes a decrease in partial pressure of the solute in the gas phase, decreases its solubility and improves its removal efficiency. More also, the capacity for transfer of VOCs relative to equilibrium condition in an air stripper is known as H which increases with temperature and air-to-soil ratio as shown in Table 8. The result also shows that the trend becomes less significant at high temperatures (20 - 50) ^{O}C where the difference in percentage removal under different air-to-soil ratio becomes smaller [6, 11, 12]. At these conditions, the maximum removal efficiency is reached because the combined effect of high temperature and high air-to-soil ratio accelerate mass transfer of VOCs between the solid and the gas phase. This phenomenon shows a similar result obtained by Yakubu *et al.,* [6] in the air stripping of VOCs in a pilot scale soil column air stripper. However, the air-to-soil must be chosen to maximize transfer while keeping pressure gradients under normal levels. Excessively high air-to-soil ratio will result in flooding while reducing the column diameter is to avoid flooding [12].

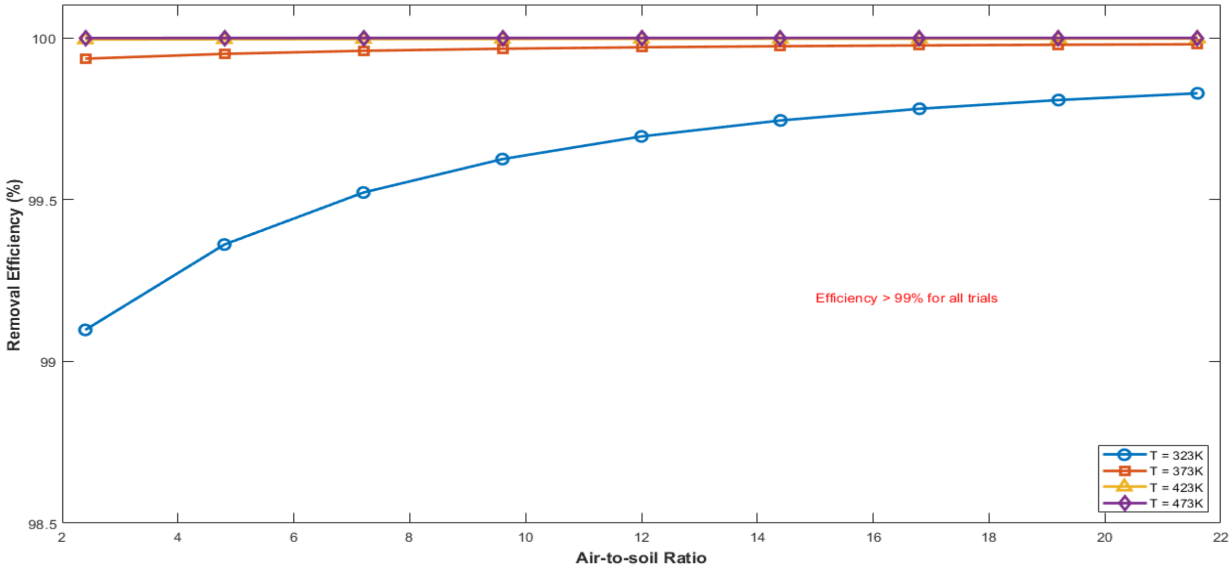

Figure 7: Influence of air-to-soil ratio on VOCs removal efficiency

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4.2.1 Temperature influence

The influence of temperature on the removal efficiency was considered within a temperature range of 293-323K and at different air-to-soil ratios as shown in Figure 6. The results also showed variation in temperature within 293 to 323K and for all air-to-soil ratios, an equilibrium removal efficiency of over 99 % is reached and further increase in temperature gives no significant change in removal efficiency. Figure 8 depicts the VOCs removal efficiency increases with increase in temperature at all air-to-soil flow rates. This is because an increase in temperature causes a decrease in the solubility of VOCs in soil pores and increases Henry's coefficient as shown in Table 9 and hence improves removal efficiency [1, 12].

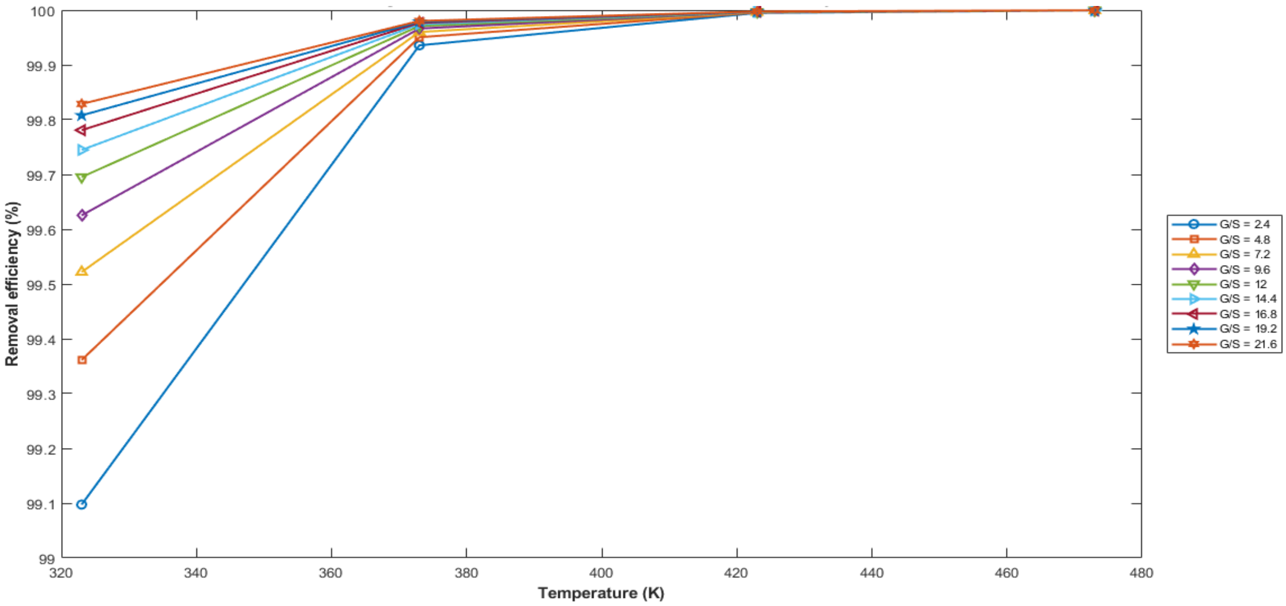

Figure 8: Influence of temperature on VOCs removal efficiency

Table 9: Change in mass transfer coefficient and Henry's constant with temperature

S/N	Parametric Properties	First Values	Second Values	Third Values	Fourth Values
1	Thermometer readings (K)	294	305	314	325
2	Coefficient of mass transfer (1/s) x10^{-5}	0.170	0.150	0.174	0.198
3	Henry's law constant (atm)	238.59	379.54	589.36	893.36

The parametric properties and the corresponding values on Henry's law constant and temperature will affect the desired VOCs removal efficiency as shown in Figure 9.0

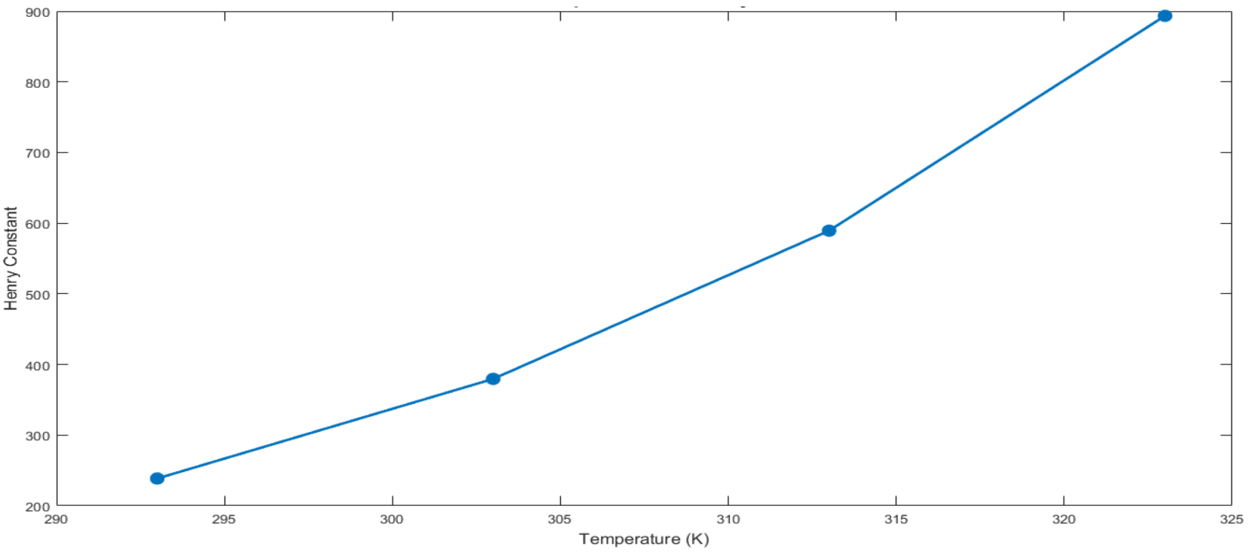

Figure 9: Influence of temperature on Henry's constant for VOCs

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4.2.2 Surface response analysis on the influence of temperature and air-to-soil ratio

The optimal parameters for independent and dependent variable were evaluated using response surface plot shown on Figure 10. The VOCs removal efficiency is considered as a function of dependent while the independent variables are the operating variables (temperature and air-to-soil ratio) use to achieve the high yield during air stripping process. The surface response plot defines the mass transfer of VOCs by volatilization processes and this is induced by mechanical aeration.

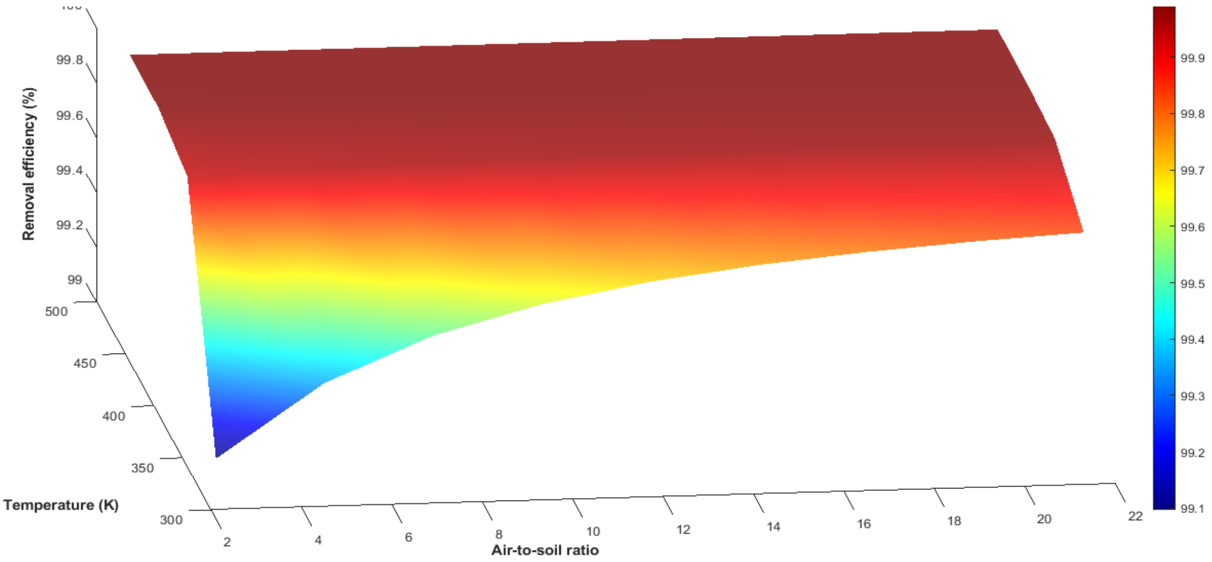

Figure 10: Surface plot removal efficiencies at different temperatures and air-to-soil flow rates

The simulating VOCs recovery using air stripping technique with soil samples contaminated with VOCs is broken down by physicochemical processes with an R^2 value of 0.98 and a root mean square error (RMSE) of 0.001, the model account for 98% of the variability in the experiment data with negligible error. These metrics, supported by a significant p-value (<0.05), suggest that the model effectively captures the experimental trends despite inherent measurement limitations. Figure 10 showed the interactive effect of operating variables on the removal efficiency. The result revealed about 99.8% VOCs removal efficiency was achieve by increasing the temperature and we need to know the hydrocarbon composition and their TBP. For most VOCs, elevating the injected air temperatures will improve the removal efficiency [11]. This implies that air stripping of VOCs from petroleum contaminated soil is most dependent on temperature and moderately other factors like column height, grain size and air-to-soil ratio. The 3D surface plot depicts the relationship between the operational parameters and VOCs removal efficiency.

In summary, the stripping device operates at a very high removal efficiency (> 99%), MATLAB program achieved higher level of VOCs of removal efficiency than experiment approach. The reason for this would not be far from the fact that the MATLAB program is similar to the experimental approach because these results absolutely agrees with the experiment approach which has a very high level of accuracy of almost 98%. The Air-to-soil ratio is identified between 2.4 to 21.6 as the critical driver for performance improvement, showing a logarithmic growth pattern where initial increases yield significant gains before reaching a point of diminishing returns. The simulation result on the varying effect of H on removal efficiency, influent/effluent concentrations profiles along the column height, this predict a better performance on mass transfer coefficients compared to traditional correlations [12].

5.0 Conclusion

The effect of Henry's constant, stripping factor, temperature and air-to-soil volume ratio on VOCs removal rate was investigated by using air stripping method to treat high concentration VOCs contaminated soil produced in petroleum and refining processes. The countercurrent SCAS system and MATLAB simulation programming was used to verify VOCs removal efficiency. This study led to the following conclusions:

The soil characterization showed that VOCs were present with a very high concentrations of 211.954 mg/kg clay, 198.805 mg/kg loamy, 178.196 mg/kg sandy and 136.775 mg/kg coarse-grain soils respectively (in all contaminated locations). For location 1 having dominance (114.87 mg/kg of clay, 86.57 mg/kg loamy, 26.42 mg/kg and 21.79 mg/kg coarse-grain soil) over other locations due to high activity and operations.

The VOCs removal efficiencies at 47.85%, 47.10%, 37.84% and 30.46% recorded a corresponding residual VOCs after air stripping of 105.53 mg/kg clay, 108.37 mg/kg loamy, 65.50 mg/kg sandy and 62.53 mg/kg coarse-

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gravel soils were attained after 1 hour of air stripping with unheated air while with preheated air, it showed decrease in residual VOCs within the soil pores with rise in average recovery efficiency of 66.03%, 65.87%, 52.06% and 33.82% while rising the treatment temperature from 24 ^{O}C to 45^{O}C after 1 hour. The VOCs recovery with preheated air was observed to increase with time as the soil grain size decreases. The results presented so far shows the variation of recovery efficiency with time of treatment for the four selected soil samples.

The VOCs recovery efficiency is impacted by air-to-soil flow rate as presented in Table 6. At lower ratios, the efficiency curve rises steeply from 2.4 to 7.2 while increasing the ratio from 7.2 to 21.6 showed a sharp jump from 99.4% to 99.8997%. The VOCs removal efficiency increases rapidly as temperature rises for injected air into the soil column air stripper. Higher temperatures correlate with higher removal efficiency, particularly visible at the peak of the graph (dark red zone) shown in Figure 8 and less time was required to reach maximum recovery efficiency than with unheated air.

The integration of MATLAB simulation programming with response surface methodology demonstrated a significant enhancement in VOC removal efficiency, achieving values exceeding 99%. This performance was higher than the experimental results obtained for under unheated (47.89%) and heated (66.03%) air conditions, confirming the superior predictive capability and optimization strength of the model. The combined interaction of temperature and air-to-soil flow rate, as illustrated through response surface analysis, highlights optimal operating conditions that consistently the yield removal efficiencies above 99%. In addition, the MATLAB-based simulation and optimization approach provides a robust, efficient, and reliable tool for enhancing VOCs removal efficiency for soil remediation, offering significant improvements over conventional approach and the response surface plot showed the interactive effect of these factors.

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