

Effect of Combining Bioremediation and Air Stripping on Soil Remediation System Using Synthetic Surfactants to Enhanced VOCs Desorption

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Abstract

The optimization of a MATLAB-based integrated model has been carried out. In this, a surfactant-enhanced hybrid bioremediation-air stripping system employed in the efficient removal of benzene, toluene, ethylbenzene, and xylene (BTEX) from petroleum-contaminated soils was investigated and compared with standalone bioremediation, air stripping, and conventional integrated treatment systems. Conventional remediation methods for volatile organic compounds (VOCs) rely on physicochemical and biological processes that primarily transfer BTEX from the solid phase into the gaseous phase without incomplete degradation. In this study, soil samples were collected from four locations within the NNPC/PPMC Suleja Depot, Niger State, Nigeria, and identified as clay, loamy, sandy and coarse-grained soils. The removal efficiency of the air stripping processes (ASPs), the bioremediation, and the hybrid treatment system was evaluated under varying operational conditions. The hybrid treatment configuration consisted of ASPs coupled with a bioreactor unit to enhance BTEX removal efficiency. BTEX was selected as the model compound for assessing system performance under different temperatures and surfactant formulations, namely MNS-1, MSDS-2, and MMS-4. Maximum BTEX recoveries were achieved within 1.5 h for ASPs and 30 days for bioremediation under controlled experimental conditions. The overall BTEX removal efficiencies increased from 47.12% - 56.74% for bioremediation, 45.68% - 50.66% for ASPs, and 64.29% - 83.26% for the hybrid system. The MATLAB-optimized hybrid model achieved superior removal efficiencies ranging from 96.84% - 98.71% as air velocity increased from 0.1 to 4.0 cm·s⁻¹ and 95.24% - 98.18%

for MMS-4 surfactant concentration rises from 0.01 to 3.00 wt% when temperature increased from 20°C to 50°C. A mass transfer and diffusion model was developed using MATLAB response surface methodology. The diffusion coefficient increased from 1.84 to 3.19 m²·s⁻¹ with increasing air velocity and temperature, indicating enhanced BTEX transport and volatilization. The results revealed the synergistic interaction between air stripping and bioremediation that improved BTEX desorption, biodegradability, and overall degradation efficiency. This implies that BTEX removal was strongly influenced by temperature and significant surfactant concentration.

Keywords

Surfactant, BTEX, Remediation Techniques, Bioremediation, Air Stripping, Hybrid Treatment System

1. Introduction

A comparative evaluation of surfactant-enhanced remediation techniques enables the selection of the most reliable, efficient, and environmentally sustainable method for the removal of volatile organic compounds (VOCs) present in petroleum contaminated soils. VOCs are characterized by their high vapour pressure and low water solubility, which enable rapid volatilization into the atmosphere and migration through soil and groundwater systems [1]. Common VOCs such as benzene, toluene, ethylbenzene, xylene (BTEX), chlorinated hydrocarbons, and industrial solvents pose serious environmental and public health risks due to their toxicity, carcinogenicity, persistence, and contribution to atmospheric photochemical reactions [1] [2]. Their uncontrolled release has become a major global environmental concern because of their role in groundwater contamination, air pollution, ecosystem degradation, and adverse human health effects. VOCs contamination in petroleum contaminated soils and groundwater has intensified the need for soil treatment techniques capable of achieving these VOCs removal. In petroleum producing states, communities and industrialized zones, accidental oil spills, leakage from underground storage tanks, refinery discharges, turnaround maintenance and improper hazardous waste management practices have significantly contributed to the accumulation of VOCs in the soil environments [1] [3]. These VOCs exhibit strong behaviour between soil, water, and gaseous phases, thereby complicating remediation efforts and increasing the long-term effect due to environmental exposure. VOCs are organic chemicals characterized by high vapour pressure and significant volatility under ambient environmental conditions. These VOCs are the aromatic hydrocarbons collectively known as BTEX that generally possess relatively high Henry's constants, enhance their volatility and promote efficient removal through soil remediation processes. Thus, Henry's constant strongly determines desorption efficiency of soil remediation, performance, mass transfer rate and remediation strategy selection [2] [3]. Besides Henry's con-

stant, VOC removal is influenced by vapour pressure, solubility, Soil organic matter, molecular weight, biodegradability, soil moisture content, temperature, air-flow rate and surfactant concentration. VOCs and their removal based on Henry's constant are presented in **Table 1**.

Table 1. VOCs removal based on Henry's constant.

VOC contaminant	Henry's constant (atm·m ³ /mol)	Air stripping efficiency	Bioremediation efficiency	Treatment technique
Benzene	5.5×10^{-3}	Excellent	High	Air stripping + Bioremediation
Toluene	6.6×10^{-3}	Excellent	Very high	Integrated remediation
Ethylbenzene	7.9×10^{-3}	Excellent	Moderate high	Air stripping
Xylene	6.0×10^{-3}	Very good	Moderate	Bioremediation
Trichloroethylene	1.0×10^{-2}	Excellent	Moderate	Air stripping
Vinyl Chloride	2.7×10^{-2}	Outstanding	Low	Vapor extraction
Phenol	3.2×10^{-7}	Poor	Excellent	Bioremediation
Naphthalene	4.4×10^{-4}	Moderate	Moderate	Surfactant biodegradation
Chlorobenzene	3.4×10^{-3}	Very good	Moderate	Air stripping

Table 1 displayed VOCs removal efficiency that depends on Henry's constant and volatility, where highly VOCs favour air stripping, while low-volatility VOCs such as phenol require enhanced biological remediation techniques. Henry's constant significantly influences VOCs removal by controlling VOCs volatilization, phase transfer, and desorption efficiency, where higher Henry's constants enhance air stripping, bioremediation and integrated treatment systems during remediation processes [3]. Air stripping shows high removal efficiency for VOCs possessing high Henry's constants due to enhanced volatilization and mass transfer characteristics. Bioremediation offers moderate-to-high treatment efficiency through microbial degradation of biodegradable VOCs into harmless end products such as carbon dioxide and water [1]-[3]. The process supports environmentally sustainable remediation by minimizing secondary waste generation and promoting ecological enhancement. Surfactant-enhanced removal improves the extent of remediation for strongly adsorbed VOCs by increasing contaminant desorption and bioavailability. This technique enhances the effectiveness of integrated remediation systems, particularly in low-permeability soils where conventional methods may exhibit limited efficiency. The selection of the right treatment techniques is essential for maintaining environmental compliance, control regulations and meeting permissible discharge standards established by regulatory agencies for air, soil, and groundwater quality protection [4]. The regulatory bodies such federal ministry

of environment, national environmental standard and regulations enforcement agency (NESREA), National Oil Spill Detection and Response Agency (NOSDRA), Standards Organization of Nigeria (SON) and Petroleum Regulatory Commissions (NUPRC and NMDPRA) enforce National Environmental (Air Quality Control) Regulations, while global standards are guided by the world health organization (WHO), environmental protection agency (EPA) and European union (EU) directives have established stringent discharge limits and remediation standards focus at minimizing VOCs emission and protecting ecological and human health systems [2] [4].

VOCs and removal efficiency are directly related through the physicochemical and biological characteristics of the contaminants, which determine how effectively they can be transferred, degraded, extracted, or transformed during remediation and treatment processes. The conventional remediation techniques for petroleum contaminated soil include thermal desorption, adsorption, chemical oxidation, soil vapour extraction, air stripping, membrane separation, and biological treatment methods [5] [6]. Among these techniques, air stripping has gained considerable industrial acceptance due to its operational simplicity and effectiveness in transferring these VOCs from solid to gaseous phases through enhanced mass transfer mechanisms as shown in **Figure 1**.

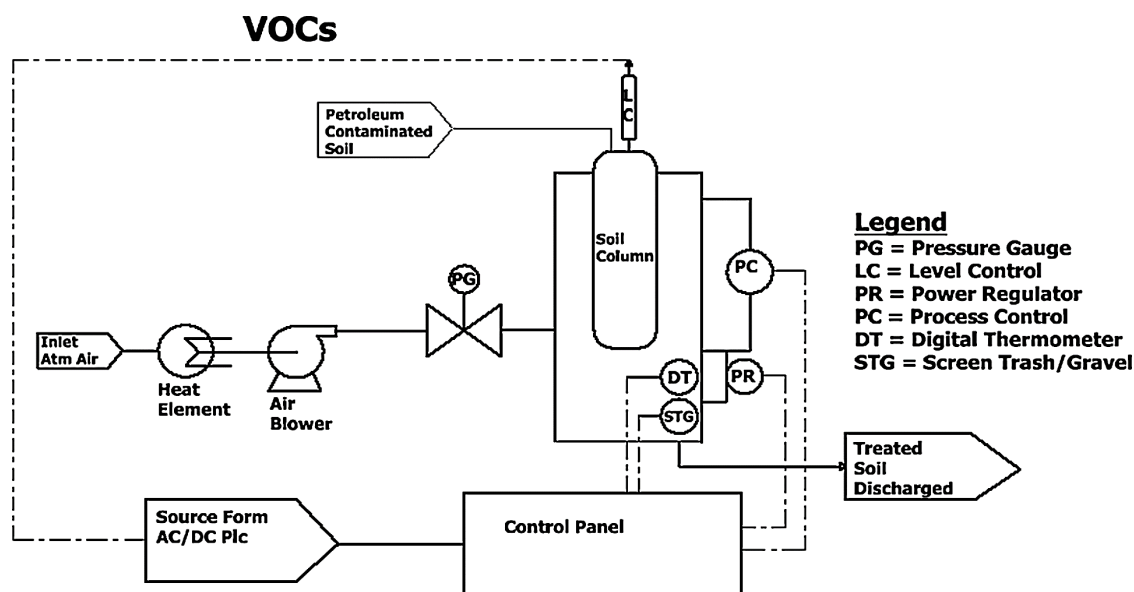


Figure 1. Schematic diagram of the soil column air stripping system.

Figure 1 presents an air stripping facility that facilitates VOCs desorption by increasing the interfacial contact between contaminated soil and air, thereby promoting volatilization of dissolved contaminants. However, conventional air stripping systems are often associated with several operational and environmental limitations, including incomplete contaminant removal, high energy demand, secondary air pollution generation, and reduced efficiency when treating strongly adsorbed VOCs [3] [5]. These VOCs transfer from solid to gaseous phases without

destruction but relocate these VOCs rather than achieving complete remediation.

Bioremediation techniques have emerged as environmentally sustainable options for VOCs treatment due to their ability to biologically degrade VOCs into less harmful end-products like carbon dioxide, water, and biomass [3] [6]. Biological remediation processes utilize naturally occurring microorganisms to metabolize contaminants under aerobic or anaerobic conditions. **Figure 2** shows a bioremediation process by facilitating biodegradation of petroleum contaminated soil under the influence of temperature, air aeration, moisture, and nutrient supply to enhance microbial activity [7]. This process is widely recognized for its ease operation, low environmental footprint, and applicability to diverse soil types but its efficiency as a standalone process is frequently constrained by the limited bio-availability of VOCs, slow microbial degradation, nutrient limitations, and inhibitory effects arising from high VOCs concentration. The mass transfer resistance between VOCs bound soil particles and microbial populations often restricts biodegradation efficiency in highly contaminated soils. Recently, there is a shift toward an integrated treatment system with surfactant solution in order to enhance the overall VOCs removal efficiency. Surfactant solution offers the potential for improving VOCs desorption, volatilization and biodegradation efficiency.

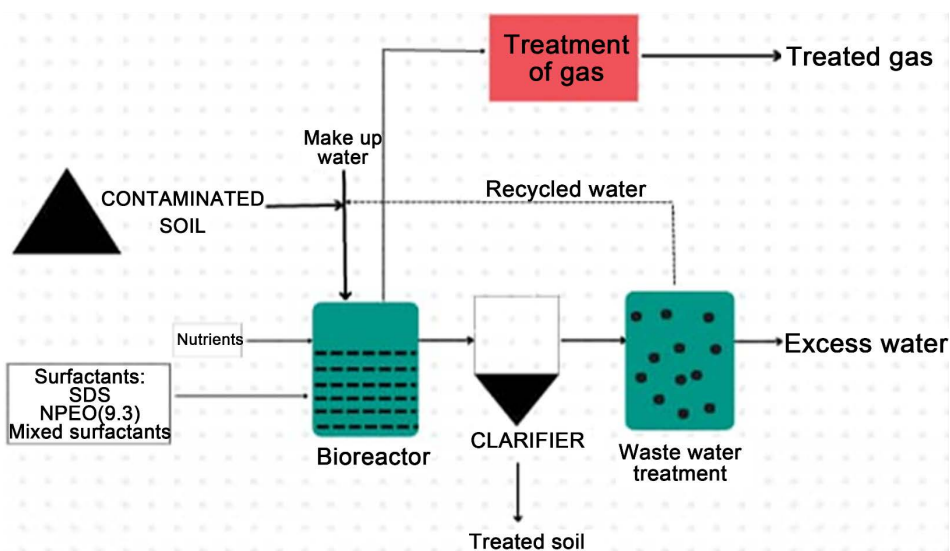


Figure 2. Schematic diagram of bioremediation process.

The effectiveness of integrated treatment systems largely depends on VOCs bioavailability, surfactant-assisted desorption behaviour, and the interaction between physicochemical operating parameters and microbial degradation processes [4] [7]. Synthetic surfactants have attracted considerable attention as remediation-enhancing agents due to their ability to reduce surface and interfacial tension, increase contaminant solubility and improve VOCs desorption from contaminated matrices [5] [8]. Nonionic surfactants such as Nonylphenyl Ethylate (NPEO_{9.3}) while anionic surfactants such as Sodium Dodecyl Sulfate (SDS) are widely investigated as shown in **Table 2** for environmental remediation applica-

tions because of their emulsification properties, micelle formation capability, and enhanced contaminant mobilization characteristics [6] [9]. The combined application of nonionic and anionic surfactants may further improve contaminant removal through synergistic interactions that enhance solubilization and mass transfer processes. Despite these advantages, uncertainties remain regarding the comparative performance of individual and mixed surfactant systems in integrated air stripping-bioremediation processes, particularly under varying operational conditions and contaminant concentrations as shown in **Table 2**.

Table 2. Surfactant performance relevant to BTEX removal efficiency.

Parameters	Nonyl phenol ethoxylate	Sodium dodecyl sulfate	Mixed surfactant
Surfactant type	Nonionic	Anionic	Nonionic-anionic
Symbol	NPEO _{9,3}	SDS	NA
Formula	C ₉ H ₁₉ C ₆ H ₄ (OCH ₂ CH ₂) _n OH	CH ₃ (CH ₂) ₁₀ -CH ₂ O-SO ₃ -Na	NA
Molecular weight	616 g/mol	288.38 g/mol	NA
CMC@25°C	0.059 mM	0.0082. Mm	0.05 - 1.0 mM
Purity	>99%	≥97% to ≥ 99%	>99%
Ph	5.0 - 7.0	7.0 - 9.0	7.0 - 7.5
Interfacial tension (mN/m)	3.24	2.74	3.51
CMC (g·L ⁻¹)	0.15	0.25	0.12
Performance	Excellent desorption	Excellent desorption	Synergistic effect

Table 2 provides a comparative evaluation of synthetic surfactants and their interfacial properties which can be applied for selecting the right surfactants that enhance treatment techniques targeting BTEX-contaminated systems. The important parameters are surface tension, interfacial tension, and critical micelle concentration (CMC) which play a fundamental role in governing volatilization efficiency, contaminant desorption from soil matrices, oxygen transfer rates, and microbial accessibility. The properties nonionic, anionic and mixed surfactants directly determine how effectively BTEX compounds are transferred from the solid phase into the gas phase and subsequently biodegraded. The selected surfactants have the tendency to improve BTEX removal efficiency during bioremediation, air stripping and integrated treatment systems.

Henry's constant strongly governs BTEX volatilization, air stripping efficiency, and VOCs transfer from aqueous and solid phases [7] [10]. Higher Henry's constant enhances vapor-phase partitioning and VOCs removal. Surfactant characteristics and interfacial properties presented in **Table 2** influence the selection of surfactant whether nonionic, anionic or mixed surfactants, improve VOCs solubilization, interfacial mass transfer, and desorption, thereby increasing BTEX mo-

bility, bioavailability, and overall remediation efficiency. It is interesting to know that soil remediation system can be influenced by surfactant behaviour and Henry's constant, both of which govern VOCs desorption, volatilization and biodegradation processes. Individual surfactants or mixed enhanced BTEX mobilization through reduction of surface tension and improved contaminant solubility within the soil matrix. Surfactants such as NPEO_{9,3} exhibited strong desorption capability due to their nonionic structure, while SDS promoted better microbial compatibility because of its biodegradable anionic nature. However, the mixed surfactant system showed superior performance as a result of synergistic interactions between the nonionic and anionic components, leading to enhanced micelle formation, improved contaminant transfer, and increased BTEX availability for treatment [8] [11]. Henry's law strongly affects BTEX volatilization during air stripping. BTEX compounds with higher Henry's constants showed greater transfer from the aqueous phase to the gaseous phase, resulting in rapid removal under increased airflow and temperature conditions. Air stripping efficiently removed volatile fractions, residual contaminants that remained within soil pores, limiting complete remediation [11]. Bioremediation complemented this process by degrading residual VOCs through microbial activity. Interestingly, the hybrid treatment system combining air stripping and bioremediation process to achieve the highest overall VOCs removal efficiency due to simultaneous enhancement of volatilization, BTEX removal and biological degradation mechanisms.

VOCs have been reported as major contaminants of soil environments, which is due to their toxicity and adverse ecological impacts [12] [13]. To reduce dependence on conventional fossil fuels and mitigate environmental contamination, hydrocarbon fuels have increasingly been blended with bio-based additives and biofuels [13] [14]. Various techniques have been employed for the removal of VOCs contaminants from contaminated soil media. One technique employed for the selective removal of contaminants is air stripping. Air stripping is one of the most effective and widely applied methods because of its simplicity, cost-effectiveness and high VOCs removal efficiency [14]. Other remediation techniques include bioremediation, surfactant enhanced treatment and other thermal desorption methods. The selection of a suitable treatment method depends on the physicochemical properties of the VOCs, site conditions, treatment objectives, and economic considerations. Among the notable recent contributions, Liu *et al.* [15] conducted an experimental assessment of surfactants on the remediation of petroleum contaminated soil and surface hydrophobicity of petroleum hydrocarbon degrading flora for removing VOCs; this provides a valuable insight into VOCs volatilization and transport behaviour under simulated subsurface conditions. Yakubu *et al.* [16] performed an experiment on the effect of temperature, surfactant and particle size distribution on the performance of a soil column air stripper for the removal of VOCs from petroleum polluted soils using process variables to improve VOC removal efficiency. The highest VOCs removal efficiencies recorded 67.29% for clay, 55.24% for loamy, 54.56% for sandy and 51.85% for coarse soil

when 0.1 wt% SDS surfactant and air temperature was elevated to 45°C while the combine effect surfactant, temperature and particle size which recorded approximate value of 70% - 80% VOCs removal efficiency. San-Valero *et al.* [17] investigated the performance of bioactive coating packed-bed bioreactors for the treatment of indoor VOCs such as n-hexane, toluene, and α -pinene. The study focused on improving biologically active coatings to enhance VOCs biodegradation and mass transfer in packed-bed systems. The experimental results recorded 50% for n-hexane, 80% removal for toluene while 70% removal was obtained for α -pinene. The empty bed residence times (EBRTs) values between 56 and 112 seconds and the inlet VOCs concentration was 9 - 15 mg·m⁻³. However, when the EBRT was reduced to 28 seconds, removal efficiencies suddenly declined due to reduced gas-liquid mass transfer and lower pollutant bioavailability. The One-dimensional wet scrubbing-catalytic ozonation process was conducted by Zhang *et al.* [18]. There were limitations in catalyst deactivation, ozone consumption, and reduced efficiency under fluctuating VOCs loading conditions. Although other research studies have independently examined air stripping, bioremediation, and surfactant-enhanced remediation techniques, limited research has comprehensively evaluated the comparative performance of standalone bioremediation, air stripping devices, and integrated air stripping-bioremediation systems using different classes of synthetic surfactants for VOCs desorption [19]. The existing treatment methods suffer from insufficient removal efficiency, operational instability, and increased treatment limitations. The recent research has shifted toward surfactant-enhanced remediation systems, where surfactants improve VOCs solubility, desorption, and mass transfer from soil matrices into mobile phases. Despite these advances, there exists a knowledge gap in combined interactions between surfactant chemistry, VOCs desorption mechanisms, and integrated remediation performance. The investigation showed that VOCs removal efficiencies exceeding 80% - 90% under optimized airflow and temperature conditions, yet these models largely neglect BTEX due to their low Henry's law constants and limited volatility. The optimization studies using response surface methodology (RSM) and computational tools have improved stripping efficiency but remain restricted to single-phase VOCs system without surfactant application. Surfactant-enhanced soil remediation (SESR) has shown significant improvements in BTEX desorption from 60% - 80% for BTEX when surfactant concentrations exceed the CMC, but quantitative modeling of surfactant-enhanced air stripping systems remains largely unexplored, particularly in the VOCs removal with gas-phase mass transfer. The research remains fragmented with most studies focusing independently air stripping, bioremediation, surfactant-enhanced desorption and oxidation processes [15] [20]. Interestingly, most studies rely on laboratory-scale experiments without predictive modeling capable of optimizing. The mixed surfactant systems under dynamic air stripping conditions remain insufficiently modeled, this is due to a lack of integrated computational analysis that couples with thermodynamics, and biodegradation processes into a unified predictive model. No existing study has

fully implemented MATLAB-based modeling to optimize surfactant-enhanced desorption [21], air stripping efficiency, and bioremediation performance for BTEX removal efficiency. Therefore, the novelty of this study lies in the development of an integrated surfactant-enhanced hybrid treatment system supported by a MATLAB design programming. This analysis evaluates BTEX desorption under varying surfactant types, concentrations relative to CMC, temperature conditions, and air-flow rates. Unlike previous empirical methods that integrate mass transfer theory, thermodynamic partitioning, and microbial degradation to optimize remediation performance.

The aim of this study is to develop and optimize a MATLAB-based integrated model for surfactant-enhanced hybrid treatment system for efficient BTEX removal from petroleum contaminated soils. The specific objectives are to evaluate the desorption performance of nonionic, anionic and mixed surfactant systems under varying operational conditions including surfactant concentration, temperature, and airflow; to develop a predictive MATLAB model incorporating mass transfer, thermodynamic parameters, and Henry's law behavior for BTEX desorption estimation and to investigate and optimize the hybrid bioremediation-air stripping system by quantifying synergistic effects between surfactant-enhanced desorption and microbial degradation.

2. Material and Methods

2.1. Description of Study Area

The study site is located at Suleja depot (09.2678°N, 007.1555°E) in Niger State, North Central, Nigeria and the coordinates of the sampling points (Table 3) with an average elevation of approximately 490 m above sea level. The site has been identified as requiring remediation due to significant contamination arising from petroleum-related activities (Figure 3). The main sources of contamination include petroleum distillates such as gasoline, diesel, and used oils, as well as wastewater

Table 3. Handheld GPS for identified locations, coordinates and its identified VOCs.

Sn	Sampling locations	GPS coordinates	Elevation (m)	Monitoring source	VOCs contaminant
1	Products pipeline entry point	09.25539N, 007.17071E	482	Assessment of pipeline leakage impact	BTEX, TPH, VOCs
2	Tank offloading manifold	09.25364N, 007.17118E	477	Evaluation of spill contamination	BTEX, diesel hydrocarbons
3	Lubricant yard	09.25455N, 007.17931E	490	Investigation of lubricant-related pollution	PAHs, lubricating oil residues
4	Oil-Water separation area	09.25473N, 007.17006E	483	Monitoring of wastewater contamination	BTEX, oily sludge, VOCs

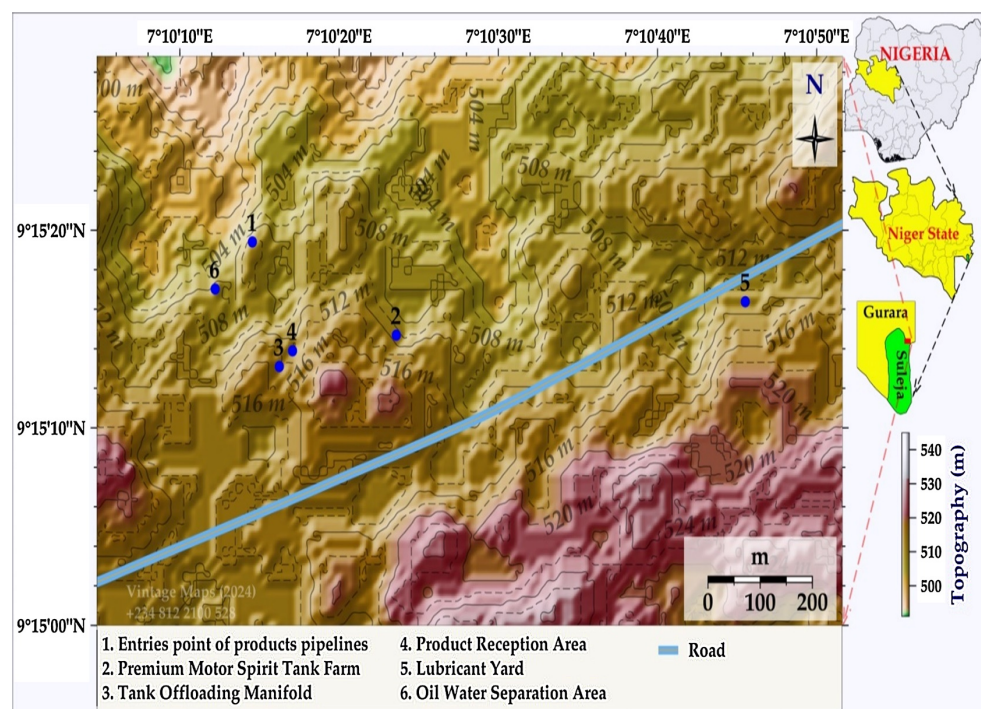


Figure 3. Map of the study area showing spatial distribution of contamination across sampling locations.

discharges. Field observations revealed visible signs of contamination, with soil exhibiting grey to black discoloration in several locations, indicating zones of high hydrocarbon saturation [16] [22]. The spatial distribution of contaminants, particularly VOCs, was found to be heterogeneous, varying with depth, subsurface geological characteristics, and the nature and volume of hydrocarbon releases. This identified sampling locations and their corresponding coordinates were determined using a handheld global positioning system (GPS) device to ensure accurate spatial referencing of all contaminated sites within the study area.

Soil samples were collected from different contaminated locations using a random sampling technique in order to obtain representative samples of the affected environment. At each sampling point, soil samples were obtained within a defined surface coverage area of approximately 4 cm × 5 cm. Sampling was conducted at two different depth intervals, namely 0 - 15 cm (topsoil layer) and 15 - 30 cm (subsurface layer), to evaluate the vertical distribution and migration characteristics of VOCs within the soil profile. The integration of sampling locations with site function and contamination sources provides the information used in identifying the remediation approach, the type of contamination, its distribution, and environmental conditions, thereby improving remediation efficiency and sustainability [22].

Table 3 presents the geographic clustering of the sampling locations, bearing, elevations and the contamination footprint. There was a slight variation in elevation (477 - 490 m) and this may influence hydrocarbons migration; horizontally and downslope movement toward lower areas like tank offloading manifold [19]

[22]. Each location represents a distinct contamination pathway requiring targeted remediation strategies. The product pipeline entry point and tank offloading manifold are prone to fresh hydrocarbon inputs from leaks and spills; these areas are suitable for rapid-response techniques such as air stripping and surfactant-enhanced air stripping to remove the VOCs. The lubricant yard, characterized by heavier oil fractions and persistent residues, may require bioremediation methods due to the lower volatility and higher adsorption of VOCs to soil organic matter (SOM). Meanwhile, the oil-water separation area is likely impacted by aged hydrocarbons and sludge, making it a candidate for an integrated treatment system to address BTEX and other VOCs found within the contaminated site.

2.1.1. Soil Sample Collection and Analysis

Random sampling technique was used to collect soil samples in each location (**Table 3**). Four composite auger samples were collected at two depths (0 - 15 and 15 - 30) cm, and a total of sixteen (16) samples were taken in the locations. The four (4) samples weighing 1 kg each, were collected from different depths. The sampling locations and coordinates were identified by GPS. The soil samples were collected from the experimental sites identified as representative soil fractions (**Figure 3**). The controlled soil samples were collected from Forestry area 100m away from the polluted site at the same depths and labeled E1, E2, E3, and E4. The soil samples were stored in plastic buckets and homogenized in a mixer and they were air-dried for 3 days before being selected for further analysis. The soil samples were obtained from the selected four locations named 1, 2, 3 and 4 as identified in **Figure 3**. The soil samples were stored in airtight polyethylene containers to prevent volatilization losses and transported to the laboratory for analysis. The selected soil samples were air-dried at ambient temperature; crushed gently to remove lumps and then carried out soil classifications (grain-size distribution) were carried out by sieving analysis that employed ASTM D6913/D6913M to obtain clay, loamy, sandy and coarse-gravel soils which represent sample A, B, C and D respectively. The representative soil samples were homogenized prior to laboratory analysis.

2.1.2. List of Reagents, Materials and Equipment

Chemicals and reagents are essential materials used in environmental and laboratory analyses to facilitate sample preparation, extraction, treatment, and analytical determination of contaminants. In studies involving petroleum-contaminated soils, nonionic surfactant, anionic surfactant, mixed surfactant formulation, de-ionized water (distil water) and solvents for extraction, soil auger, hand spade, disposable gloves, sample plastic containers, polythene bags, refrigerator, compost manure, finely granulated corn cob, groundnut shell powder (blended), distilled water, soil samples, microbial consortia (native or augmented bacteria), nutrients (nitrogen and phosphorus sources) and others.

GPS Navigator (surveying the topography of the soil), Gas Chromatography—Flame Ionization Detector (GC-FID), Soil Column Air Stripper (SCAS) system,

bioreactor, mechanical aeration, moisture control units, pH meter, pressure gauge, digital thermometer, shaker agitator sand sieves.

2.2. Laboratory Analysis

The samples were collected into polythene bags, sealed stored in the laboratory fridge at 4°C which is used for further analysis. The laboratory analysis includes preparation of surfactant solutions, investigation of the physicochemical properties, bioremediation process (bioreactor), air stripping process, soil samples extraction and subsequently followed by Varian 3700 GC/FID method.

2.2.1. Preparation of Surfactants by Gravimetric and Dilution Process

The preparation of surfactants by gravimetric (weighing) and dilution is a standard procedure in the laboratory for formulating solutions, testing, and measurements by mass to determine concentration. Two surfactants (NPEO_{9,3} and SDS) were considered individually and mixed to enhance the removal efficiency of VOCs during soil remediation experiment and their effects were evaluated on VOCs residual after remediation. The preparation process for a mixed surfactant requires exact gravimetric measurements followed by dilution with solvents.

1) Standard surfactant solution

The preparation of anionic and nonionic surfactants include analytical solid grade surfactant samples, distilled water, a beaker, a stirring rod and others. In order to prepare a standard surfactant solution for the experimental runs, the concentrations of the surfactant stock solutions used in this experiment were 0.01, 0.1, 1.0, 1.1, 1.2 and all 1.2 wt % respectively. In order to increase the experimental samples, control samples were taken to the laboratory prior to the experimental work. The analytical grade solid surfactant weighed 1 g, 5 g, 10 g and 100 g were dissolved individually in a 100 ml water, to get a modified surfactant solution with the final concentration by volume of 1%, 5%, 10% and 100% (w/v) respectively. The calculation for standard surfactant solutions at different concentrations for the soil remediation experiment is based on 1000 g of solution. The surfactant concentration is calculated using (1)

$$\text{wt\%} = \frac{\text{Mass of Surfactant}}{\text{Total Mass of Solution}} \times 100 \quad (1)$$

The mixture was stirred vigorously until an analytical crystal solid surfactant completely dissolved then followed by filtration to form a solution. The surfactant sample was specifically added to a beaker containing the appropriate volume of deionized water under a prescribed condition for NPEO_{9,3} modified as MNS-1, SDS formed MSDS-2 while Zwitterionic modified to form MZN-3 surfactants. The standard surfactant samples of MNS-1, MSDS-2 and MZN-3 were obtained with a desired working concentration.

2) Synthetic mixed surfactant solution

The preparation of two analytical grade surfactants was achieved by measuring an equal amount of solid grade surfactant (at ratio 1:1) by taking into considera-

tion the reaction parameters (temperature, time and concentration). The analytical grade solid surfactants accurately weighed 1 g, 5 g, 10 g and 100 g of an equal amount of NPEO_{9,3} and SDS then dissolved in 100 ml of distilled water and adjusted the final volume by mixing to get a clear solution with desire concentration known as MMS-4. The mixed surfactant solution was kept in a room under a controlled condition, to ensure that the reaction is completed. This procedure was repeated to achieve the optimum conditions for wider application.

2.2.2. Physicochemical Characterization of Contaminated Soil Samples

Prior to the application of bioremediation and air stripping treatments, the contaminated soil samples were systematically characterized to establish baseline physicochemical conditions and assess their suitability for integrated remediation processes. This characterization provides essential input parameters for evaluating contaminant mobility, microbial activity, and mass transfer behaviour within the soil matrix. All analyses were conducted in accordance with relevant ASTM standard methods to ensure accuracy, reproducibility, and comparability with established environmental engineering practices (Table 4).

Table 4. Soil physicochemical methods and its ASTM standards.

Parameters	Test methods	Principle	Equipment	References
Soil pH	ASTM D4972	Ion exchange	pH meter	[19] [23]
Bulk Density	ASTM D7263	Density	Oven-dried core	[24] [25]
Electrical conductivity	ASTM D1125 ASTM D4646	Electrolysis	Conductivity meter	[24] [25]
Total Porosity	Derived from ASTM D425	Density	Calculated using bulk and particle density	[24] [25]
Permeability	ASTM D5084	Darcy's law	falling permeability tests	[24] [25]
Total Nitrogen	ASTM D5373 ASTM D5291	Titration	Combustion-based analytical methods	[24] [25]
Phosphorus Content	ASTM D5198 ASTM D6919	Solubility	Chemical extraction by spectrophotometric	[24] [25]
Microbial Population	ASTM D5465	Oxidation	Serial dilution and plate count techniques	[24] [25]
Water Holding Capacity	ASTM D7367	Capillary Action	Ability to retain moisture against gravity.	[24] [25]

Table 4 presents the physicochemical and biological parameters that are used to evaluate the properties of the soil sample and its influence on contaminant transport and behaviour, nutrient status, and microbial viability. These properties govern the effectiveness of hybrid bioremediation-air stripping systems by controlling volatilization efficiency, microbial degradation rates, and mass transfer dynamics. Establishing these baseline conditions ensures that remediation design, modeling, and performance assessment are grounded in reliable and reproducible

environmental data.

2.2.3. Determination of BTEX Concentration in Soil Samples

1) Extraction process

This method employed ASTM D4547 and operates on the principle that organic contaminants exhibit higher solubility in selected organic solvents to enhance analyte recovery from soil matrices. Solvent extraction removes BTEX, total petroleum hydrocarbons (TPHs) from contaminated soil matrices [26]. A 220 g of soil sample was weighed accurately and poured into an extraction flask containing the soil sample. A mixture of organic solvents was then added to the soil sample, which includes n-hexane, methanol, dichloromethane, acetone and pentane. The flask was tightly sealed during agitation to prevent solvent leakage and volatilization losses. The solvent penetrates the pores and interstitial spaces of the contaminated soil, dissolving adsorbed petroleum hydrocarbons attached to soil particles. The soil-solvent mixture in the extraction flask was subjected to mechanical agitation using a shaker mechanical stirrer for a period of 30 minutes. The mixture is allowed to settle, to separate the solid soil particles from the liquid solvent extract. The supernatant containing dissolved petroleum hydrocarbons is carefully decanted or filtered through filter paper or membrane filters to remove suspended solids. The solvent extraction is employed to isolate BTEX from soil, followed by gas chromatography-flame ionization detection (GC-FID).

2) Gas chromatography-flame ionization detection analysis

The purified extract obtained after solvent extraction and cleanup is transferred into amber glass vials for instrumental determination using GC-FID. The GC-FID is a reliable analytical technique for the separation, identification, and quantification of VOCs, particularly BTEX constituents, due to its high sensitivity, precision, and selectivity for hydrocarbon compounds [25] [26]. Analytical performance parameters include detection limits, recovery efficiency and precision; this is evaluated in accordance with EPA Method 8021B for BTEX analysis. During analysis, approximately 1 - 2 μ L of the purified extract is injected into the gas chromatograph through split or splitless injection mode. The injector temperature is maintained between 200°C - 250°C to ensure rapid vaporization of analytes. An inert carrier gas, commonly helium or nitrogen, transports the vaporized compounds through a capillary column where separation occurs according to differences in boiling point, volatility, and interaction with the stationary phase. Benzene elutes first, followed by toluene, ethylbenzene, and xylene isomers. The separated compounds are detected in the FID system through combustion in a hydrogen-air flame, generating ion currents proportional to hydrocarbon concentration. Quantification was achieved using a certified BTEX standard and the final concentrations are reported in mg/kg dry soil.

2.3. Methodology

2.3.1. System Operation and Conditions

Consider a case to strip out BTEX using bioreactor, SCAS and hybrid bioreactor-

SCAS system. The feed rate is 1000 kg/s. Top product VOCs removal between 99 to 99.99% and less than 1% VOCs in the bottom product. A bioreactor operates under a controlled biological, chemical, and physical conditions to enhance the remediation of petroleum-contaminated soil. The process involves loading contaminated soil into the reactor, followed by the addition of water, nutrients, microorganisms, and surfactants to improve contaminant desorption and biodegradation. Continuous aeration supplies the oxygen required for aerobic microbial activity, while agitation ensures uniform mixing and mass transfer. Temperature and pH are carefully regulated to optimize microbial growth and VOCs removal efficiency. Typical operating temperatures range from 20°C - 50°C, with pH maintained between 6.5 and 8.0. Regular monitoring of BTEX concentration and process parameters ensures effective system performance (**Table 5**). In air stripping, the injected air temperature falls between 20°C - 50°C, the blower discharge at a pressure that is less than 1 atm while the heater outlet temperature was 44°C. These conditions affect the operation of the soil column air stripper as shown in **Table 5**.

Table 5. Bioreactor components, dimensions and their units.

Component	Unit	Dimension
Reactor vessel volume	L	2 - 10
Reactor height	cm	25 - 50
Internal diameter	cm	10 - 20
Working liquid volume	%	60% - 80% of total reactor volume
Soil loading capacity	kg	0.5 - 3
Air diffuser diameter	cm	2 - 5
Sampling port diameter	cm	0.5 - 1.0
Mixing shaft length	cm	15 - 30
Impeller diameter	cm	4 - 8
Air tubing diameter	cm	0.5 - 1.0

The surfactant enhanced techniques were operated using a batch mode where the soil samples were intermittently fed from the top and filled to a certain height while the remaining space was left empty for oxidation and fluidization control. At the exit point, the vapours were discharged or collected for further analysis by GC-FID.

2.3.2. Procedure

1) Bioremediation process

For the bioremediation process, a laboratory-scale bioreactor was charged with contaminated soil and amended with nutrient supplements to stimulate indigenous hydrocarbon-degrading microorganisms. Synthetic surfactants comprising nonionic, anionic, and mixed surfactant systems were introduced at predetermined concentrations to enhance hydrocarbon solubilization and bioavailability.

Table 6. Soil column air stripper, dimensions and their units.

Sn	Components	Units	Dimensions
1	Air stripper type		Soil column
2	Film thickness	mm	12
3	Column height	mm	1000
4	Column diameter	mm	100
Operating parameters			
5	i. Pressure drops	N/m ²	12.03
	ii. Henry's constant	-	0.73
	iii. Stripping factor	-	1.41
	iv. Influent concentration	mg/kg	270.3
	v. Air-to-soil ratio	-	2.4

Moisture content, pH, aeration, and temperature were maintained within controlled conditions between 20 °C and 50 °C throughout the treatment period. Periodic mixing was carried out to ensure uniform microbial activity as shown in **Figure 2**. The pH was maintained near neutral conditions (pH 6.5 - 7.5) to support microbial growth. Moisture content was controlled to maintain sufficient microbial activity and oxygen diffusion. The nutrition ratio of 100% Carbon: 10% Nitrogen: 1% Phosphorus was added to maintain microbial metabolism and cellular synthesis. Sufficient oxygen was supplied into the reactor for aerobic bioremediation and hydrocarbon oxidation. Oxygen and water were the key factors that improve the growth of microbes and increase moisture content of the contaminated soil during bioremediation, the number of replicate (n) for this process was four (4) for all soil samples. Finally, the effect of contaminant concentration, soil permeability, retention time, microbial population density, and surfactant concentrations was verified to significantly affect degradation performance. Continuous monitoring of these parameters ensures stable operating conditions, enhanced hydrocarbon removal, and improved remediation efficiency.

2) Air stripping process

The soil column air stripper is a cylindrical column mounted in the vertical position having dimensions (1100 cm height and 10 cm diameter) which was packed uniformly with 1 kg selected soil samples (gravel, sandy, loamy and clay) poured at the top through a conical hopper positioned at an angle 45 °C which flows down (under gravity). A Multipoint thermocouple was placed at regular intervals along the suction line to monitor the temperature of the heat element and a digital thermometer was inserted into the column to monitor the temperature profile along the column height while the pressure gradient across the soil column was measured using pressure gauges placed at one end of the column. The soil column was operated using a batch mode where the soil samples were intermittently fed from the top and filled to a certain height while the remaining space was left empty for

VOCs 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 (**Figure 1**). The soil column air stripper dimensions and operating conditions are tabulated in **Table 6**. 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 for further analyses. The outlet end of the column was fitted with a fine wire mesh screens (50 μm diameter) to prevent soil from washed out. BTEX were selected as the contaminant and the air-flow rate was fixed for all experiments after 1 hour of air stripping. The effect of air injection temperature and surfactant concentrations was studied to determine the performance of the soil column air stripper through BTEX removal efficiency. The schematic diagram describing all the step involves in this research methodology is shown in **Figure 1** and **Figure 2**. To determine the BTEX concentration in the soil, the soils were analyzed using gas chromatograph fitted with a flame ionization detector (Varian 3700 GC/FID).

3) Integrated bioremediation-air stripping system

The integrated treatment method consisted of two steps remediation of BTEX contaminated soil employing air stripping to remove BTEX contaminants using an air blower. Each experimental run contained 1 kg of homogenized soil sample. A standard surfactant sample of MNS-1, MSDS-2 and MMS-4 were obtained with a desired working concentration to accelerate the transfer of BTEX from the soil phase to gaseous phase. The soil-surfactant mixture was maintained for duration of 1 hour prior to air stripping. After 1.3 hours of air stripping stage, the residual contaminated soil was further treated through a bioreactor using bioremediation process for 28 days. All treatment stages were optimized a temperature between 20°C - 50°C using homogenized contaminated soil. The initial BTEX concentrations before treatment was determine using GC-FID method. The process condition is presented in **Table 7**.

Table 7. Hybrid treatment operating condition sequence.

Sn	Process parameters	Values	S.I unit
1	Sequence	Air stripping - bioremediation	-
1	Soil mass per run	1.0	Kg
2	Initial BTEX concentration	70.18, 93.29, 49.30 and 57.53	mg/kg
3	Temperatyure	20, 30, 40 and 50	°C
4	Surfactant type	MMS-4	-
5	Surfactant dose	0.01 - 1.5	wt%
6	Contact time before stripping	1.0	Hour
7	Air stripping duration	1.30	Hours
8	Bioremediation duration	28	Days
9	Number of replicates	$n = 4$ for each soil sample	-

The sequential treatment improves hydrocarbon bioavailability and microbial degradation efficiency. The synergy between both processes accelerates contaminant removal, reduces treatment time, and enhances remediation performance. The hybrid treatment system offers a sustainable, efficient, and cost-effective approach for restoring petroleum-contaminated soils. Air stripping reduces volatile hydrocarbon concentration, while bioremediation degraded residual contaminants, resulting in improved overall remediation efficiency and accelerated treatment performance. The removal efficiencies (η) of the treatment system were calculated using Equation (1)

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (2)$$

The above procedure was repeated for identified soil samples from locations.

1000 cm³ of 0.1 wt% of MNS-1, MSDS-2 and MMS-4 surfactant solutions were added individually to the treatment techniques and allowed to drain until equilibrium was reached. It was then saturated with water and was allowed to drain under gravity. The procedure was then repeated to determine the BTEX removal. The effect of temperature on VOCs removal efficiency was studied at a temperature range of 20°C - 50°C. The procedure was then repeated in order to reduce its concentration and alter the chemical composition of the BTEX in soils so as to enhance volatilization efficiency and mobility.

4) MATLAB Design simulation and optimization for BTEX removal

i. Design model

The MATLAB design model is developed to simulate, optimize, and predict the removal efficiency of BTEX compounds under varying surfactant types and temperature conditions within a hybrid bioremediation-air stripping system. The model combines experimental data, statistical analysis, kinetic modelling, and response surface optimization. The design analysis focuses on reducing interfacial tension and contaminant viscosity while increasing solubility, thereby accelerating BTEX desorption during soil remediation process. The pilot-scale experiments integrating bioremediation and air stripping processes, as presented in figure 2 and figure 3, were used to validate the model. The system was assumed to operate at an influent concentration of 114.87 mg/kg of VOCs, combined with varying surfactant concentrations of 0.01, 0.1, 1.0, and 1.1 wt%, corresponding to temperatures of 20°C, 30°C, 40°C and 50°C, denoted as Q1, Q2, Q3, and Q4, respectively. The selection of temperature conditions was based on [27], which reported convergence in performance efficiency at temperatures above 50°C, even at relatively low surfactant concentrations during VOCs air stripping.

ii. Data collection

Data collection for this study is conducted through controlled laboratory experiments aimed at assessing the effects of synthetic surfactants and temperature on BTEX removal efficiency in an integrated bioremediation-air stripping system. Petroleum-contaminated soil samples are collected from selected polluted locations and prepared under standard laboratory procedures. The samples are air-

dried at ambient conditions, homogenized, and sieved in accordance with ASTM standard methods to eliminate coarse particles, stones, and debris before treatment and analysis [26] [27]. Subsequently, the processed soil samples are separated into experimental batches and introduced into laboratory-scale reactors or treatment columns. Different surfactant systems, including nonionic, anionic, and mixed surfactants, are applied under varying temperature conditions ranging from 20°C to 50°C. Operational parameters and BTEX concentrations are monitored systematically throughout the remediation process for performance evaluation and data analysis. The prepared soil samples are divided into experimental batches and transferred into laboratory-scale hybrid bioremediation-air stripping columns. The synthetic surfactants are applied independently to the contaminated soil systems, namely nonionic surfactants, anionic surfactants, and mixed surfactants. The surfactants are introduced at predetermined concentrations above their critical micelle concentration (CMC) to enhance BTEX desorption, solubilization, and microbial accessibility. The remediation experiments are conducted at controlled temperatures of 20°C, 30°C, 40°C and 50°C respectively. The BTEX removal efficiency is calculated as:

$$\text{Removal Efficiency} = \frac{C_i - C_f}{C_i} \times 100\% \quad (3)$$

where C_i = Initial BTEX concentration and C_f = Final BTEX concentration.

iii. Programming development

The experimental data obtained from laboratory analysis are imported into MATLAB using matrix and table functions. Each variable is assigned as an independent or dependent parameter. The independent variables are temperature (10°C - 50°C), surfactant type, surfactant concentration, airflow rate and retention time and the dependent variable is BTEX removal efficiency (%). The data are organized into MATLAB arrays and processed using scripts and Simulink models. The hybrid treatment combines:

$$\text{Overall BTEX Removal} = \text{Air stripping contribution} + \text{Biodegradation contribution} + \text{Synergistic enhancement} \quad (4)$$

The predictive model should estimate BTEX desorption rate, volatilization efficiency, microbial degradation rate, overall removal efficiency and synergistic factor.

- Model equations

Mass transfer model

BTEX desorption during air stripping is governed by the mass transfer coefficient in Equation (4):

$$\frac{dC}{dt} = -K_{sa} (C - C^*) \quad (5)$$

where C = BTEX concentration in liquid/soil phase, C^* = equilibrium concentration and K_{sa} = volumetric mass transfer coefficient. The mass transfer coefficient depends on air velocity:

$$K_{sa} = \alpha V^\beta \quad (6)$$

where V = air velocity (cm/s) and α, β = empirical constants. Increasing air velocity from 0.1 - 4.0 cm/s increased removal efficiency toward 99.9995%, confirming enhanced interfacial mass transfer.

Henry's law desorption model

BTEX volatilization follows Henry's law:

$$C_g = HC_s \quad (7)$$

where C_g = gas phase concentration, C_s = aqueous phase concentration and H = Henry's constant.

Temperature dependence:

$$H_T = H_{298} e^{-\Delta H_R \left(\frac{1}{T} - \frac{1}{298} \right)} \quad (8)$$

As temperature increases BTEX vapor pressure increases, Henry's constant increase and volatilization improves. This explains the higher efficiencies observed from 293 K to 323 K.

Surfactant-enhanced desorption model

Surfactants improve micellar solubilization, BTEX desorption and bioavailability. The enhancement factor can be modeled as:

$$E_s = 1 + K_s S \quad (9)$$

where E_s = surfactant enhancement factor, K_s = surfactant constant and S = surfactant concentration (wt%). Increasing MMS-4 surfactant concentration from 0.01 - 1.1 wt% significantly improved removal efficiency. Near-complete BTEX removal (>99.999%) was observed at higher temperatures and surfactant loadings. This confirms that surfactants enhanced BTEX desorption kinetics and increased contaminant accessibility.

Biodegradation kinetics

The biodegradation process is represented using first-order kinetic equations:

$$C_t = C_0 e^{-kt} \quad (10)$$

where C_t = BTEX concentration at time t , C_0 = Initial concentration, k = Biodegradation rate constant and t = Time.

Temperature Dependency Model

The effect of temperature on biodegradation and volatilization is simulated using Arrhenius equations:

$$k = A e^{-\frac{E_a}{RT}} \quad (11)$$

where A = Frequency factor, E_a = Activation energy and R = Gas constant and T = Absolute temperature. This model predicts the increase in BTEX volatilization and microbial activity as temperature increases.

Hybrid synergy model

The synergistic effects between air stripping, surfactant desorption and microbial degradation can be quantified using equation

$$SF = RHRA + RB \quad (12)$$

where SF = synergy factor, RH = hybrid removal efficiency, RA = air stripping efficiency and RB = biodegradation efficiency. The interpretation for $SF > 1 \rightarrow$ synergistic interaction, $SF = 1 \rightarrow$ additive behaviour and $SF < 1 \rightarrow$ antagonistic behaviour.

MATLAB optimization maximizes SF to limit temperature, airflow constraints, surfactant dosage and oxygen availability.

Response surface methodology (RSM)

MATLAB Response Surface Methodology tools are used to evaluate the interactive effects of surfactants and temperature on BTEX removal efficiency. A quadratic polynomial model is developed:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \quad (13)$$

where Y = BTEX removal efficiency, X_1 = Temperature, X_2 = Surfactant concentration/type and β = Regression coefficients. The model identifies individual effects of variables, interaction between temperature and surfactants and optimum operating conditions. The interaction between mixed surfactants and temperature is particularly significant due to its influence on micelle formation and solubilization capacity. At temperatures above the CMC threshold, increased thermal energy enhances surfactant mobility and reduces solution viscosity, thereby promoting the formation of mixed micelles with improved stability and solubilization efficiency. Nonionic surfactants contribute to reduced toxicity and improved compatibility with microbial systems, while anionic surfactants enhance electrostatic interactions and desorption strength. Simulation models capture these synergistic interactions, revealing optimal temperature and surfactant combinations that maximize BTEX removal efficiency.

3. Results and Discussion

3.1. Physicochemical Characteristic of Surfactant Solutions

Physical and chemical characteristics of these three surfactants; MNS-1, MSDS-2 and MMS-4 were extensively investigated and verified according to the American Standard of Testing and Measurement (ASTM) [27] [28]. The resulting surface tension, CMC values and pH values vary depending on the specific surfactant type and mixed formulations. Note that the mass of water = total mass of solution – mass of surfactant. The result of optimum conditions as well as yield and micro-analysis of prepared surfactants are presented in **Table 8**.

Table 8 presents MNS-1, MSDS-2, MZN-3 and MMS-4 surfactants obtained through dilution with deionized water under a controlled condition to reach the target volume concentration at 25°C - 30°C. The advantage of MMS-4 over MZN-3 is the formation of a good yield characterized by lower CMC at 25°C compared to MNS-1 and MSD-2. The performance of MNS-1 and MSD-2 compared to other types of surfactants has been recorded in the literature when use in the remediation of petroleum contaminated soils [28]. The MMS-4 characteristics, properties

and concentration showed a better performance and high remediation efficiency compared to other types of surfactants. Some advantages and disadvantages of MMS-4 surfactants were evaluated. This implies that MMS-4 can be effectively utilized for the treatment of VOCs in petroleum contaminated soil.

Table 8. Synthetic surfactant formulations and their performance.

Surfactant type	Mass of surfactant (g)	Mass of water (g)	Surfactant conc. (wt%)	Surface tension, (mN/m)	CMC @ 24°C (g/L ⁻¹)	pH value
MNS-1	1.00	999.00	0.1	35	0.15	7.20
MSDS-2	15.00	985.00	1.5	33	0.25	7.30
MZN-3	8.00	992.00	0.8	30	0.31	7.35
MMS-4	1.00	999.00	0.1	17	0.10	7.40

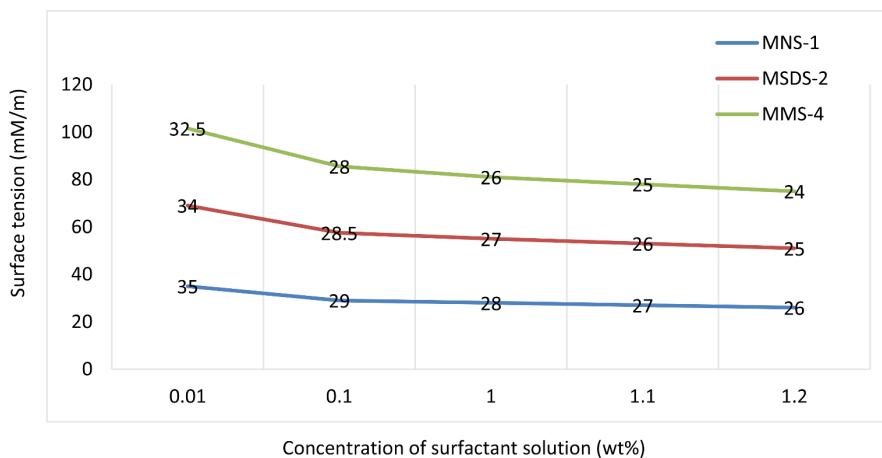


Figure 4. Graph of surface tension against surfactant concentration.

It can be seen from **Figure 4** that at a concentration of 0.1%, MNS-1 reduced the surface tension of water to 28 mN/m while MSDS-2 reduced the surface tension of water to 28.5 mN/m. Interestingly, 0.1% MMS-4 achieved a reduction of 29 mN/m, showing higher removal efficiency than other types of surfactants. The mixed surfactants (MMS-4) with molar concentrations of 0.01, 0.05, 0.08 and 0.1wt% showed a gradual reduction in surface tension from 35 to 29 mN/m, showing higher VOCs efficiency for various soil remediation applications. It can be observed from the graph as surfactant concentration increases, surface tension decreases until the CMC is reached, after which it remains relatively constant between 29 and 34 mN/m depending on the type of surfactant. Temperature on the other hand generally lowers the surface tension further. This suggests that the MSS-4 can perform effectively for the desorption of VOCs in soil samples than other synthetic surfactants [28]. The MMS-4 has a better property among other surfactant solutions to remove toxic VOCs in soil. The result revealed that MMS-4 will operate beyond MNS-1, MSDS-2, MZN-3 and subsequently improve the treatment efficiency of these toxic BTEX in soils.

3.2. Physicochemical Behaviour of Petroleum-Derived Contaminants in Soil Matrix

3.2.1. Preliminary Analysis on Soil Samples

Preliminary information regarding the extent of hydrocarbon pollution and establishes the contamination profile used for evaluating remediation efficiency during subsequent treatment processes. The simultaneous occurrence of BTEX indicates the presence of mixed petroleum hydrocarbon contamination commonly associated with hydrocarbon handling activities. Because BTEX compounds are highly volatile and toxic and their presence represents a significant environmental and public health concern. The selected physicochemical properties of the soil samples are presented in **Table 9**.

Table 9. Selected physicochemical properties of soil samples.

Properties	Clay soil	Loamy soil	Sandy soil	Gravel soil
pH Level	4.80	5.01	5.06	5.24
Bulk Density (g/cm ³)	1.67	1.38	1.25	1.00
Electrical Conductivity (μS/cm)	145	121	101	89
Total Organic Carbon (%)	3.65	3.27	1.94	0.60
Total Porosity (%)	45	25	21	18
Permeability (m ²)	2.6×10^{-11}	5.6×10^{-9}	4.2×10^{-8}	8.1×10^{-7}
Moisture Content (%)	32.5	24.8	15.6	8.4
Nitrogen Content (%)	0.28	0.22	0.14	0.05
Phosphorus Content (mg/kg)	18.6	14.2	9.5	4.1
Microbial Population (CFU/g $\times 10^5$)	8.4	6.9	4.8	2.1
Water Holding Capacity (%)	58	42	28	12

The physical parameters presented in **Table 9** provide strong evidence suggesting the presence of BTEX contamination within the investigated soil samples. The observed pH values ranging from 5.2 - 6.8 indicate slightly acidic conditions commonly associated with petroleum hydrocarbon degradation and the formation of organic acids during microbial oxidation processes [27] [28]. Moisture content values between 18% - 35% further suggest hydrocarbon influence, as petroleum-coated soil particles tend to alter pore structure and increase water retention capacity. Electrical conductivity values of approximately 120 - 450 μS/cm indicate elevated ionic concentrations resulting from hydrocarbon-related chemical interactions within the soil matrix. The bulk density values ranging from 1.45 - 1.78 g/cm³ and porosity values between 30% - 42% display structural modification of the soil due to hydrocarbon adsorption and pore blockage [28]. Reduced porosity may limit oxygen diffusion and negatively affect soil aeration, which is characteristic of petroleum-contaminated soils. Organic carbon content values of 3.5% - 8.9% also strongly support hydrocarbon accumulation because BTEX compounds

and other petroleum fractions contribute to total organic carbon levels. Furthermore, the dark coloration, oily texture, and strong petroleum odor observed in the samples provide visible and sensory indications of hydrocarbon contamination that strongly suggest the presence of BTEX and other related petroleum hydrocarbons in the contaminated soils. These findings justify that further chemical characterization is required using analytical techniques such as GC-FID to accurately quantify BTEX concentrations and assess the severity of contamination prior to remediation.

3.2.2. GC-FID Analysis for Concentration Profile and Distributions of Hydrocarbons

The GC-FID results presented in **Tables 10-14** clearly indicate significant contamination of the soil samples by both PAHs and BTEX, with concentrations beyond the maximum limit. These values are environmental concerns, particularly when compared to typical regulatory thresholds, which often recommend much lower permissible limits for aromatic compounds in agricultural or residential soils.

1) Concentration profile and distributions of PAHs in soil samples

The GC-FID results in **Table 10** showed a significant contamination of soil samples by PAHs, with total concentrations ranging from 15.28 to 26.90 mg/kg, exceeding typical regulatory limits for soils. The distribution of light PAHs (2 - 4 ring compounds) shows concentrations of 25.18 mg/kg (clay), 24.43 mg/kg (loamy), 19.18 mg/kg (sandy), and 14.53 mg/kg (coarse-grained soils). These compounds are associated with petrogenic contamination and are characterized by high mobility, bioavailability, and toxicity [28]. Higher concentrations in clay and loamy soils are attributed to greater organic matter content and surface area,

Table 10. GC-FID quantification of light PAHs (mg/kg) in untreated soil samples.

Hydrocarbons	Clay	Loamy	Sandy	Coarse-grain
Naphthalene	2.17	0.72	1.05	1.37
Acenaphthylene	2.77	0.49	0.32	0.25
Fluorene	2.21	0.95	0.40	0.02
Phenanthrene	1.86	0.70	0.36	0.40
Anthracene	5.60	7.54	3.60	5.79
Fluoranthene	6.81	9.14	7.60	5.14
Pyrene	2.31	2.62	2.32	2.05
Benzo[c]phenanthrene	0.80	0.71	0.20	0.81
Benz(a)Anthracene	0.12	0.07	0.05	0.01
ChryseneBenzo[k]fluoranthene	1.51	1.45	1.46	1.44
Benzo[b+j]fluoranthene	0.00	0.00	0.00	0.00
Σ 2 - 4 PAHs rings	25.18	24.43	19.18	14.53

enhancing adsorption, while sandy soils exhibit lower concentrations due to reduced adsorption capacity and higher permeability, promoting leaching [28] [29]. The dominant compounds include fluoranthene (5.14 - 9.14 mg/kg), anthracene (3.70 - 7.54 mg/kg), and pyrene (2.05 - 2.62 mg/kg), indicating toxic and persistent contamination with potential ecological and human health impacts. The low levels of benz(a)anthracene and benzo[c]phenanthrene suggest the presence of more complex aromatic structures at reduced concentrations [28] [30].

Table 11. GC-FID quantification of heavy PAHs (mg/kg) in untreated soil samples.

Hydrocarbons	Clay	Loamy	Sandy	Coarse-grain
3-Methylcholanthrene	0.00	0.00	0.00	0.00
Indeno[1,2,3-cd]pyrene	0.00	0.00	0.00	0.00
Dibenzo[a,h]Anthracene	0.14	0.36	0.63	0.42
Benzo[ghi]perylene	0.00	0.00	0.00	0.00
Dibenzo[a,h]pyrene	0.00	0.00	0.01	0.00
Dibenzo[a,i]pyreneDibenzo[a,i]pyrene	0.15	0.13	0.13	0.17
Dibenzo[a,l]pyrene	0.00	0.00	0.00	0.00
Benzo[e]pyrene	0.13	0.13	0.11	0.16
Benzo[a]pyrene	0.01	0.00	0.00	0.00
Σ 5 - 6 PAHs rings	1.72	0.62	0.88	0.75

Table 11 presents heavy PAHs (5 - 6 ring compounds) with concentrations of 1.72 mg/kg (clay), 0.62 mg/kg (loamy), 0.88 mg/kg (sandy), and 0.75 mg/kg (coarse-grained soils), giving a total of 3.97 mg/kg (Σ 5 - 6 PAHs). Although lower than light PAHs, these compounds are highly toxic, persistent, and carcinogenic. Their environmental significance lies in their resistance to biodegradation, tendency to accumulate in soils and sediments, and long-term persistence [30]. The dominant heavy PAHs include dibenzo[a,h]anthracene with 0.36 - 1.44 mg/kg, dibenzo[a,i]pyrene with 0.13 - 0.17 mg/kg, and benzo[e]pyrene recorded 0.11 - 0.16 mg/kg and trace amount of benzo[a]pyrene. The absence of some compounds suggests low occurrence, degradation and limited formation pathways.

The distribution of PAHs in soil samples, serves as a strong litmus indicator of hydrocarbon contamination and the possible coexistence of BTEX. The elevated contamination levels reflect the level of fuel distillates infiltration into the soil matrix [29] [30]. Such contamination adversely alters soil physicochemical properties, reduces microbial activity, and diminishes soil fertility. In addition, prolonged exposure to PAHs and BTEX compounds poses severe human health challenges such as respiratory complications, liver or kidney damage and cancer. This implies an urgent need for effective soil remediation and environmental monitoring strategies is required to prevent further degradation and protect human life [30] [31].

2) Concentration profile and distributions of BTEX in soil samples

The evaluation of BTEX distributions in petroleum-contaminated soils reveals that these compounds are highly volatile and mobile, often creating significant contamination in soil and groundwater. The findings indicate that BTEX concentrations frequently exceed environmental standards, with spatial distribution strongly influenced by soil type, depth, and the source of contamination groundwater.

Table 12. GC-FID quantification of heavy BTEX (mg/kg) in untreated soil samples.

Hydrocarbons	Clay	Loamy	Sandy	Coarse-grain
Benzene	56.14	57.87	49.30	57.53
Toluene	0.00	8.37	0.00	0.00
Chlorobenzene	0.00	6.58	0.00	0.00
Ethybenzene	0.00	6.26	0.00	0.00
m+y Xylene	6.90	7.01	0.00	0.00
O-Xylene	5.83	5.84	0.00	0.00
1,3-Dichlorobenzene	0.00	0.00	0.00	0.00
1,4-Dichlorobenzene	1.32	1.35	0.00	0.00
1,2-dichlorobenzene	0.10	0.00	0.00	0.00
Σ BTEX (mg/kg)	70.18	93.29	49.30	57.53

Table 12 presents the GC-FID quantification of BTEX compounds in untreated soil samples with varying soil textures. Loamy soil recorded the highest total BTEX concentration (93.29 mg/kg), indicating greater hydrocarbon retention due to its balanced pore structure and organic matter content. Sandy soil showed the lowest contamination level (49.30 mg/kg), likely due to higher permeability and lower adsorption capacity. Benzene was the dominant contaminant across all soil types, while toluene, chlorobenzene, ethylbenzene, and xylenes were mainly detected in loamy soil. The total concentration of BTEX was observed to be 270.30 mg/kg (**Table 12**). They are toxic, capable of contaminating groundwater, causing respiratory, neurological, and reproductive health disorders [31]. Therefore, effective soil remediation is essential, with bioremediation and integrated treatment system is considered as sustainable alternative.

3.3. Performance of Soil Remediation Techniques for BTEX Removal Efficiency

The reduction of BTEX concentrations in petroleum-contaminated soils is essential due to their toxic and hazardous nature discussed in this session. In this session, bioremediation, air stripping and hybrid bioremediation-air stripping techniques were employed to evaluate their effectiveness in BTEX removal efficiency from soil samples. Data obtained from the different treatment technique were an-

alyzed and the interpretation of results throughout the remediation process.

3.3.1. Impact of Surfactants and Temperature Conditions on Bioremediation System

Surfactants and temperature are operational factors that influence the removal efficiency of BTEX during bioremediation processes. Surfactants enhance the solubility and mobility of VOCs, thereby improving their availability for microbial degradation and volatilization while temperature significantly affects remediation performance by influencing microbial activity, mass transfer rate and volatilization. The residual BTEX concentrations were obtained when MNS-1, MSDS-2 and MMS-4 solutions were used across all soil samples at control conditions as shown in **Table 13** and **Table 14**.

Table 13. Overall BTEX removal in soil samples using bioremediation under unheated air conditions with 0.1wt% synthetic surfactants.

Soil sample/ Influent Conc. in mg/kg	Nigeria EPA for BTEX residual in soil (mg/kg) [25]	Residual BTEX with MNS-1 (mg/kg)	Residual BTEX with MSDS-2 (mg/kg)	Residual BTEX with MMS-4 (mg/kg)
Clay (70.18)	0.10	53.59	56.60	52.20
Loamy (93.29)	0.05	67.25	70.05	60.10
Sand (49.30)	0.01	40.40	42.36	35.53
Coarse (57.53)	0.005	33.42	35.28	29.38

Table 14. Overall BTEX removal in soil samples using bioremediation under heated air conditions with 0.1wt% synthetic surfactants.

Soil sample	Nigeria EPA for BTEX residual level in soil (mg/kg)	Residual BTEX with MNS-1 (mg/kg)	Residual BTEX with MSDS-2 (mg/kg)	Residual BTEX with MMS-4 (mg/kg)
Clay	0.10	46.15	51.75	40.13
Loamy	0.05	60.57	65.37	52.51
Sand	0.01	34.79	39.53	30.52
Coarse-grain	0.005	29.42	33.50	24.31

Table 13 and **Table 14** present the comparative residual concentrations of BTEX in different soil types after treatment under unheated and heated air conditions using three remediation systems: MNS-1, MSDS-2, and MMS-4. The results indicate that soil texture, treatment configuration, and operating temperature significantly influenced the remediation performance. Under unheated air conditions, the residual BTEX concentrations remained substantially higher than the EGASPIN/EPA permissible residual limits for all soil samples. It can be observed that loamy soil exhibited the highest residual BTEX concentrations, with values of 67.25 mg/kg, 70.05 mg/kg, and 60.10 mg/kg for MNS-1, MSDS-2, and MMS-4 respectively. This behavior may be attributed to the moderate porosity and higher organic matter

retention characteristics of loamy soils and low temperature, which enhance adsorption and reduce volatilization and biodegradation rates of BTEX compounds [30] [31]. In contrast, coarse-grain soils showed the lowest residual concentrations, ranging from 24.31 - 33.50 mg/kg, due to their higher permeability, larger pore spaces, and improved oxygen transfer that enhanced contaminant removal. Among the remediation systems, MMS-4 consistently produced the lowest residual BTEX concentrations across all soil types, indicating superior remediation efficiency [31]. For example, in sandy soil, MMS-4 reduced BTEX concentration to 30.52 mg/kg compared to 34.79 mg/kg and 39.53 mg/kg obtained with MNS-1 and MSDS-2 respectively. The improved performance of MMS-4 suggests that the surfactant composition and mass transfer characteristics enhanced BTEX desorption and volatilization from contaminated soil matrices.

Table 13 showed a noticeable reduction in residual BTEX concentration with heated air for all soil samples. The residual concentration in clay soil using MMS-4 decreased from 52.20 mg/kg under unheated conditions to 40.12 mg/kg under heated conditions, representing a substantial improvement in remediation performance. Similar trends were observed for loamy, sandy, and coarse-grain soils. This is because coarse and sandy soils possess higher air permeability and lower adsorption capacities, allowing greater contaminant mobilization and stripping efficiency [31] [32]. This implies that clay soils retained higher residual concentrations due to low permeability, smaller pore spaces, and stronger adsorption onto clay mineral surfaces. The results revealed a significant reduction in BTEX concentrations after treatment above Nigerian EGASPIN/EPA permissible limits [32]. BTEX removal was enhanced but complete remediation was not achieved within the experimental conditions. This implies, additional treatment approaches may be required to attain regulatory compliance.

Figure 5 depicts the comparative distribution of residual BTEX concentrations relative to the EPA control values for different soil samples subjected to bioremediation under preheated air conditions. The result compares the remediation efficiencies of MNS-1, MSDS-2, and MMS-4 treatment systems across soil samples with EPA control values within 99.85% - 99.99%, for a strict regulatory requirement for BTEX remediation in contaminated soils, suggesting a complete compliance with EPA standards under an experimental condition. Among the remediation techniques, MSDS-2 consistently produced the lowest residual BTEX percentages across most soil types, particularly in clay soils (26.26%) and sandy soils (31.29%). This indicates that the MSDS-2 treatment configuration enhanced BTEX degradation and the removal efficiency is effectively than other systems under preheated air conditions. MMS-4 exhibited the highest residual BTEX percentages in all soil categories, with values reaching 56.74% in coarse-grain soils and 52.14% in sandy soils while clay and loamy soils recorded 47.12% and 50.17% respectively. This suggests that MMS-4 surfactant contributed to BTEX reduction and its removal efficiency recorded the highest under temperature conditions [32]. The addition of compost manure, finely granulated corn cob, and blended

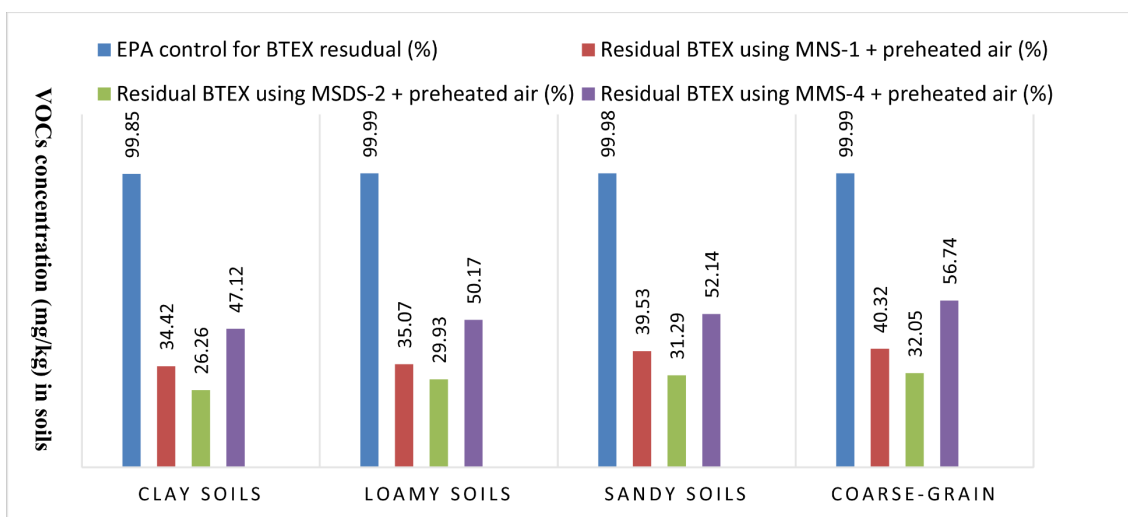


Figure 5. BTEX removal efficiencies for bioremediation with heated air across soil samples.

groundnut shell enhanced microbial growth and activity, improved soil aeration and porosity, increased hydrocarbon bioavailability, accelerate TPH degradation and reduce remediation time. Researcher is recommending the use of air stripping techniques as an alternative technique to bioremediation since BTEX possess high vapor pressures and low boiling points; this can be effectively remove BTEX.

3.3.2. Impact of Surfactants and Temperature Conditions on Air Stripping System

The combined effect of temperature and surfactant concentrations on the BTEX removal rate were studied for both heated and unheated air at a temperature of 20°C - 50°C, this parameter was considered as measure to test the air stripping experiments. The variation of BTEX concentration and removal efficiency with time of treatment showed a similar trend as presented in **Table 15** and **Table 16**.

Table 15 and **Table 16** present the residual BTEX concentrations in petroleum-contaminated soil samples treated by air stripping under unheated and heated air conditions in the presence of 0.1 wt% synthetic surfactants. The results generally indicate that air stripping achieved only moderate removal of BTEX compounds

Table 15. Overall BTEX removal in soil samples using air stripping under unheated air conditions with 0.1wt% synthetic surfactants.

Soil sample/ Influent Conc. in mg/kg	Nigeria EPA for BTEX residual level in soil (mg/kg)	Residual BTEX with MNS-1 (mg/kg)	Residual BTEX with MSDS-2 (mg/kg)	Residual BTEX with MMS-4 (mg/kg)
Clay (70.18)	0.10	48.57	51.01	46.19
Loamy (93.29)	0.05	61.55	69.69	61.12
Sand (49.30)	0.01	47.80	45.26	40.52
Coarse (57.53)	0.005	41.52	43.87	36.35

Table 16. Overall BTEX removal in soil samples using air stripping under heated air conditions with 0.1wt% synthetic surfactants.

Soil sample	Nigeria EPA for BTEX residual level in soil (mg/kg)	Residual BTEX with MNS-1 (mg/kg)	Residual BTEX with MSDS-2 (mg/kg)	Residual BTEX with MMS-4 (mg/kg)
Clay	0.10	46.35	47.45	35.11
Loamy	0.05	59.55	61.36	49.44
Sand	0.01	33.76	36.53	30.53
Coarse-grain	0.005	28.42	30.52	24.30

when compared with the results in **Table 15** and **Table 16** for bioremediation system. The reductions in BTEX concentrations were observed across all soil samples, the BTEX residual concentrations values remained significantly higher than the Nigeria EPA permissible residual limits, demonstrating the limited efficiency of air stripping as a standalone remediation technique [31] [33].

For an unheated air conditions in **Table 14**, the residual BTEX concentrations ranged from 36.35 - 69.69 mg/kg across the different soils and surfactants. The highest residual concentration was observed in loamy soil treated with MSDS-2 (69.69 mg/kg), while the lowest was recorded in coarse-grain soil treated with MMS-4 (36.35 mg/kg). The poor performance in clay and loamy soils can be attributed to their smaller pore spaces, higher organic matter content, and stronger adsorption capacity, which restrict the volatilization and migration of BTEX compounds during air stripping. Coarse-grain and sandy soils exhibited comparatively lower residual concentrations because their larger pore structures and higher permeability enhanced contaminant desorption and volatilization. For heated air conditions in **Table 15**, BTEX removal improved slightly in all soil samples. The residual concentrations decreased to 24.30 - 61.36 mg/kg, indicating that elevated temperature enhanced contaminant volatilization and mass transfer [31] [33]. The improvement was particularly noticeable in sandy and coarse-grain soils, where MMS-4 reduced BTEX residual concentrations to 30.53 mg/kg and 24.30 mg/kg, respectively. Heating likely increased the vapour pressure and diffusion rate of volatile hydrocarbons, thereby improving stripping efficiency. Despite improvement in BTEX removal efficiencies for air stripping with preheated air, the results still remained substantial compare to bioremediation system across all soil samples. This observation provides strong evidence that air stripping alone is insufficient for complete remediation of petroleum contaminated soils and this necessitate the application of an integrated treatment system.

Figure 6 presents the comparative distribution of residual BTEX concentrations after treatment by air stripping under both unheated and heated air conditions in the presence of synthetic surfactants. The results clearly shows that air stripping contributed to a reduction in BTEX concentration level across all soil samples and the residual BTEX concentration of 35.11 mg/kg clay, 49/44 mg/kg loamy, 30.53 mg/kg sandy and 24.30 mg/kg coarse-grain soils remained higher than

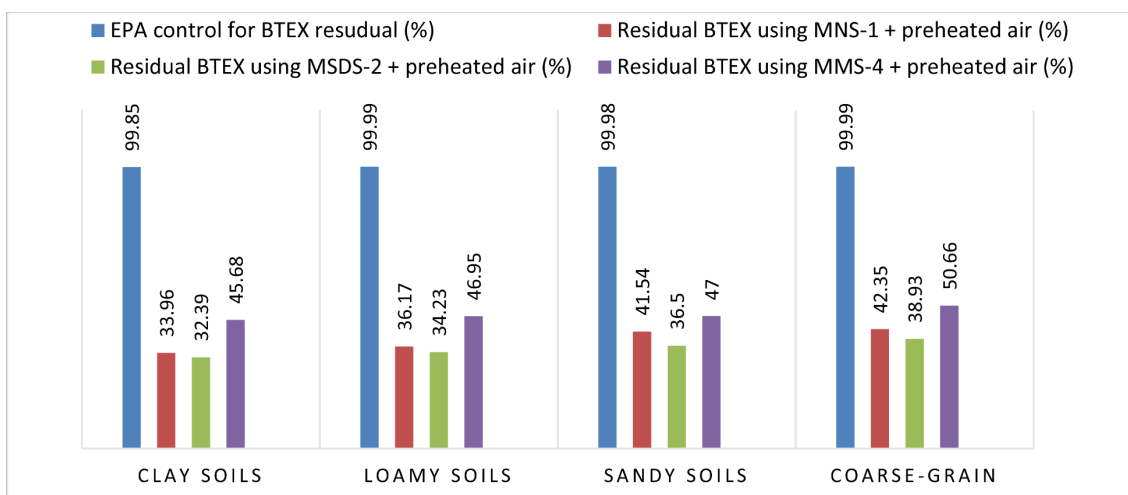


Figure 6. BTEX removal efficiencies for air stripping with heated air across soil samples.

Nigeria EPA permissible limits which represent 45.68% clay, 46.95% loamy, 47.00% sandy and 50.66% coarse-grain soils when MMS-4 was used. These results are higher than when MNS-1 and MSDS-2 were used. This indicates that injecting preheated air into air stripper performed better than unheated air stripping in all soil samples. This improvement was attributed due to an increase in temperature, which enhanced volatilization, vapor pressure, and mass transfer of BTEX from the solid phase into the gaseous phase [31] [33]. Sandy and coarse-grain soils were observed to have lower residual BTEX concentration values; this may be due to their higher porosity, permeability, and lower adsorption characteristics while clay and loamy soils retained higher BTEX concentrations (fine soil particles and higher organic matter contents), thereby restricting BTEX desorption and volatilization during the stripping process. This limitation explains why air stripping alone could not achieve acceptable cleanup levels. The results therefore suggest a synergistic integration of bioremediation and air stripping option that could provide superior remediation performance for treatment exercise [33]. The combined treatment exercise would enhance overall remediation efficiency, shorten treatment duration, and improve compliance with Nigerian environmental regulatory standards.

3.3.3. Impact of Preheated Air with Various Surfactants Condition on Integrated Treatment System

The combined effect of temperature and surfactant concentrations on BTEX removal rate were studied at the temperature of 20°C to 50°C, these parameters were considered as measure to test the enhanced hybrid remediation experiments. The BTEX removal efficiency in soil samples using MNS-1, MSDS-2 and MMS-4 solutions with preheated air was investigated. The properties of the selected soil samples and their corresponding removal efficiencies are presented in **Table 17** and **Table 18**.

Table 17 and **Table 18** present the comparative residual BTEX concentration

Table 17. Overall BTEX removal in soil samples using integrated treatment system under unheated air conditions with 0.1wt% synthetic surfactants.

Soil sample/ influent conc. in mg/kg	Nigeria EPA for BTEX residual level in soil (mg/kg)	Residual BTEX with MNS-1 (mg/kg)	Residual BTEX with MSDS-2 (mg/kg)	Residual BTEX with MMS-4 (mg/kg)
Clay (70.18)	0.10	40.50	43.95	35.14
Loamy (93.29)	0.05	53.48	60.64	52.05
Sand (49.30)	0.01	39.73	38.21	31.47
Coarse (57.53)	0.005	33.45	36.81	31.30

Table 18. Overall BTEX removal in soil samples using integrated treatment system under heated air conditions with 0.1wt% synthetic surfactants.

Soil sample	Nigeria EPA for BTEX residual level in soil (mg/kg)	Residual BTEX with MNS-1 (mg/kg)	Residual BTEX with MSDS-2 (mg/kg)	Residual BTEX with MMS-4 (mg/kg)
Clay	0.10	38.29	41.38	25.06
Loamy	0.05	51.49	55.29	30.38
Sand	0.01	25.70	30.47	15.48
Coarse-grain	0.005	20.36	24.44	08.25

in contaminated soils treated with preheated air under three treatment conditions. The results clearly demonstrate that soil texture, thermal conditions, and treatment configuration significantly influence the efficiency of BTEX removal. In all the soil samples, the residual BTEX concentrations after treatment remained lower than the EPA control values, confirming the effectiveness of the remediation systems. However, substantial variations were observed on the four soil samples and treatment approaches compare to the predictive control values. The result revealed a major limitation on the conventional experimental approach to dynamically regulate treatment parameters such as airflow rate, heating temperature, surfactant dosage, oxygen transfer, and treatment duration in real time. Variations in these operational conditions may have contributed to fluctuations in residual BTEX concentrations observed among the soil samples. It can be observed that sandy and coarse-grain soils exhibited higher residual BTEX concentrations, especially under MMS-4 treatment conditions where values increased to 73.09% and 83.26%, respectively. The higher residual levels in coarse-grain soils may be attributed to rapid air passage and insufficient BTEX contact time during treatment [33]. Sandy soils also tend to promote faster volatilization but may reduce the interaction between BTEX, microorganisms and surfactants, thereby limiting overall degradation efficiency. These findings indicate that soil permeability and pore structure strongly influence treatment performance under preheated air conditions.

Figure 7 further confirms the effectiveness of the integrated remediation approach through the significant reduction in BTEX residual concentration values and the corresponding increase in BTEX removal efficiencies across the investigated soil samples. The EPA control values remained nearly constant between 99.85% and 99.99%, indicating extremely high contamination levels before treatment, whereas the integrated treatment systems produced substantial decreases in residual BTEX concentrations. The lowest residual BTEX concentrations were recorded under the combined application of MSDS-2 synthetic surfactant and preheated air, with clay soil showing a residual concentration of 41.04% and loamy soil recording 40.73%. These reduced concentration values correspond to significantly higher BTEX removal efficiencies compared with the untreated control and individual remediation techniques. The advantage of MNS-1 and MSDS-2 achieved average BTEX removal efficiencies of 51.07% and 44.81% under hybrid treatment system while MMS-4 reached up to 72.02%. Lower efficiencies were observed with standalone using MMS-4 with approximately 52% bioremediation and 47% for air stripping system under preheated conditions. This presents a clear performance gap in favour of the integrated system. The integration of air stripping and bioremediation, when enhanced with MMS-4 surfactant, provides a highly effective remediation strategy for petroleum-contaminated soils. The improved performance is linked to increase mass transfer, reduced interfacial resistance, and enhanced degradation of low molecular weight hydrocarbons [33] [34]. Integrated organic amendments to the hybrid system provide synergistic effects that improve the VOCs removal efficiency compared with unheated air condition. The results suggest that an optimal performance can be achieved through optimization process with the aid of a design models and a surface response plot, with precise process variables such as surfactant concentration, temperature, and airflow to interact. Such optimization not only maximizes remediation efficiency but also ensures environmental safety and ensured a reliability of the hybrid mixed-surfactant system.

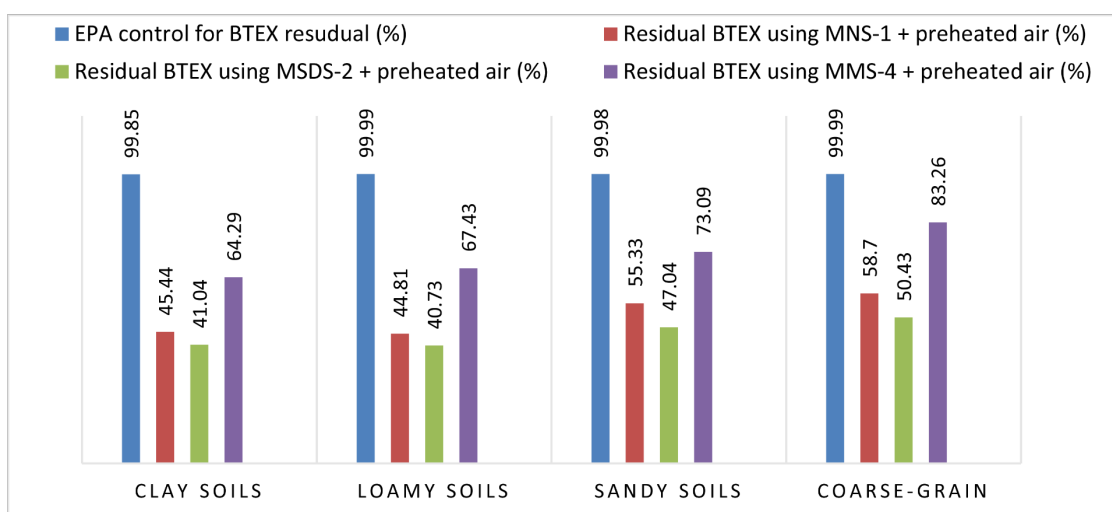


Figure 7. BTEX removal efficiencies for integrated treatment system with heated air.

3.4. MATLAB-Based Design Optimization for Hybrid Treatment System

3.4.1. Removal Efficiency

BTEX removal Efficiency of the model depends on how close the predicted values are to the practical results. The simulation data in **Table 18** and **Table 19** showed a good prediction of BTEX removal. **Table 19** and **Table 20** showed that over 98% BTEX removal efficiencies were obtained for all the combinations of air flow velocity and temperature. **Figure 8** present studies on hybrid treatment system for BTEX at low air velocity (0.1 - 4.0) were verified to determine the effect of temperature on injected air. The result shows that a removal efficiency of 72.51% and 98.71% were obtained for air velocities of 0.1 to 4.0 cm/s at 20°C to 50°C respectively. More also, very high BTEX removal efficiencies (over 98%) were achieved using MMS-4 and hybrid treatment system as shown in **Table 19**.

The process variables have a direct impact on BTEX volatilization rate and desorption efficiency during hybrid treatment process. The response surface plot

Table 19. Simulated BTEX volatilization rate (%) under different temperature and air velocity.

Air velocity (cm/s)	283 K	293 K	303 K	313 K	323 K
0.1	72.51	81.63	89.44	93.61	96.84
0.5	74.26	83.27	90.85	94.57	97.12
1.0	76.44	84.95	91.72	95.18	97.46
1.5	77.83	85.92	92.34	95.73	97.71
2.0	79.16	86.84	92.88	96.15	97.95
2.5	80.25	87.56	93.36	96.44	98.16
3.0	81.11	88.21	93.84	96.73	98.37
3.5	81.86	88.75	94.16	96.98	98.54
4.0	82.44	89.26	94.53	97.22	98.71

Table 20. Simulated BTEX desorption efficiency (%) influenced by 0.1 wt% MMS-4 surfactant.

MMS-4 SC (wt%)	293 K	303 K	313 K	323 K
0.01	71.52	83.27	91.63	95.24
0.05	73.84	84.65	92.54	95.82
0.10	75.92	85.76	93.16	96.37
0.50	77.41	86.63	93.74	96.81
1.00	78.86	87.34	94.16	97.12
1.50	79.95	88.05	94.61	97.43
2.00	80.76	88.62	94.96	97.71
2.50	81.42	89.04	95.22	97.95
3.00	81.95	89.46	95.54	98.16

in **Figure 8** revealed an increasing temperature and airflow enhanced BTEX volatilization due to improved mass transfer and increased contaminant vapor pressure. Higher temperatures reduced soil contaminant interactions and accelerated diffusion of volatile BTEX from the soil matrix into the gaseous phase, thereby increasing air stripping efficiency. This implies that increase in airflow promoted contaminant transport and minimized vapor accumulation around soil particles.

Figure 9 depicts MMS-4 concentration and contact time exhibited strong

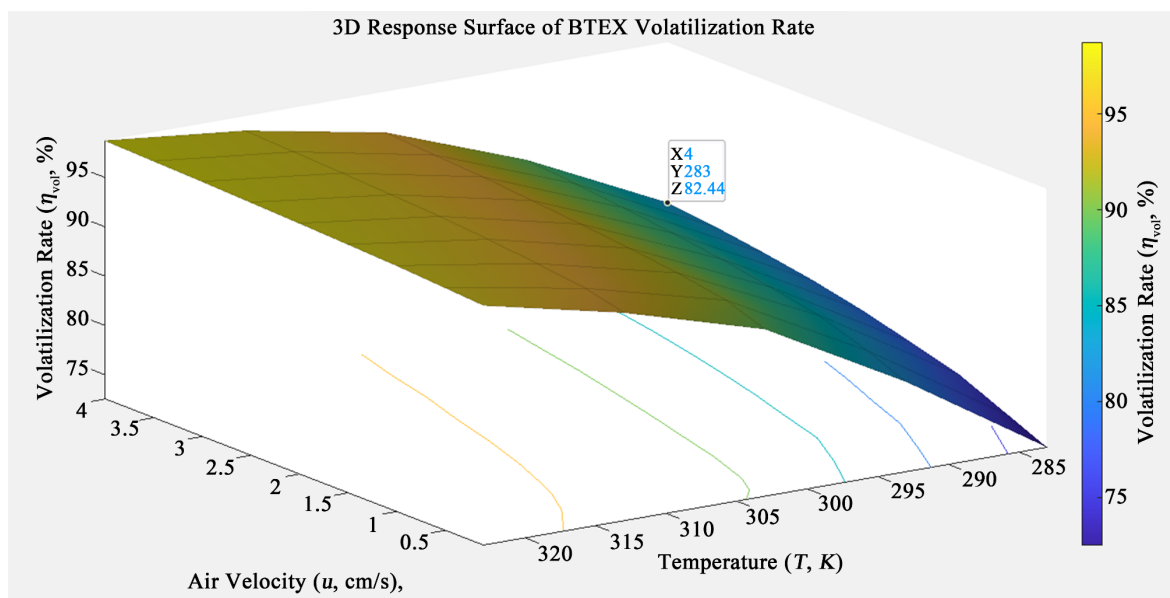


Figure 8. 3D response surface of BTEX volatilization rate.

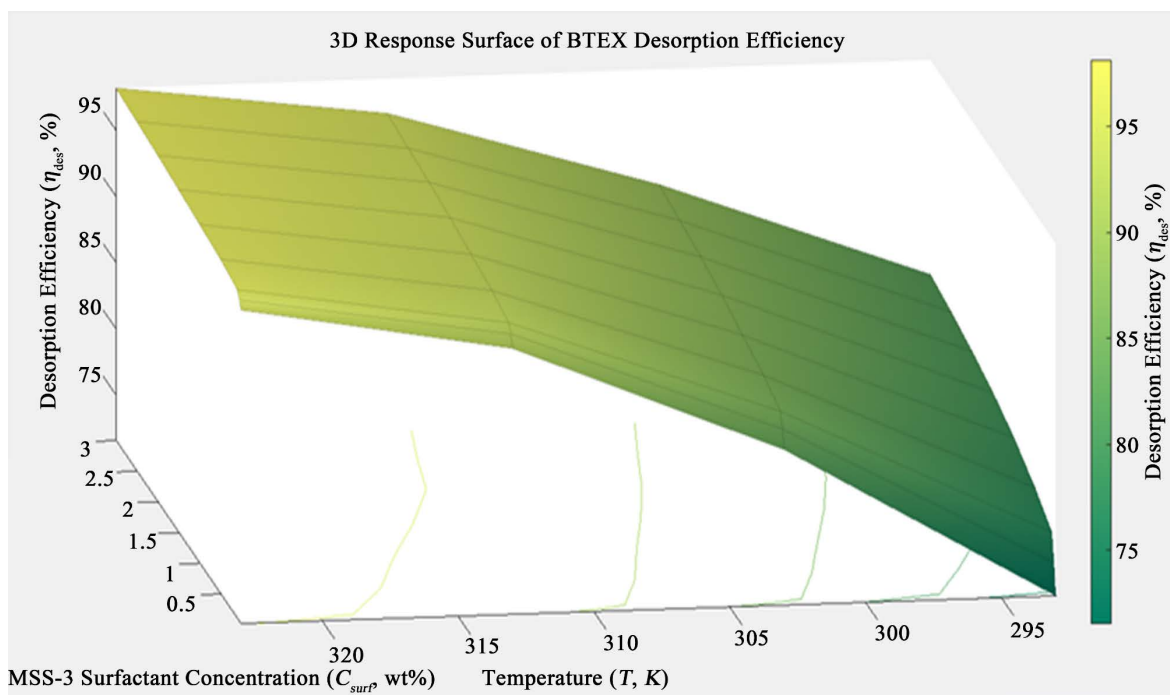


Figure 9. 3D response surface of BTEX desorption efficiency.

positive effects on BTEX removal. Increasing MMS-4 dosage above the CMC enhanced solubilization and mobilization of BTEX compounds from soil pores. The MMS-4 showed superior performance due to synergistic interactions between nonionic and anionic surfactants, resulting in improved micelle formation and interfacial activity [34]. The curved response surfaces further indicated significant interaction effects among the variables, confirming that optimum remediation performance depends on the combined influence of temperature, air velocity, surfactant concentration and treatment duration.

3.4.2. Effect of Air Velocity

BTEX removal efficiency at different air velocities corresponding with their temperatures is presented in **Table 21**. At any given temperature, increase in air velocity results in higher BTEX removal efficiency. The result on enhanced hybrid treatment optimization for BTEX desorption at low air velocities (0.1 - 4.0) cm/s between 283K to 323K and the mass transfer coefficient per unit time was verified suggesting BTEX desorption rate was influenced by temperature and air velocity.

Table 21. Simulated mass transfer coefficient as a function of temperature and air velocity.

Air velocity (cm/s)	283 K	293 K	303 K	313 K	323 K
0.1	0.118	0.164	0.213	0.248	0.286
0.5	0.126	0.176	0.228	0.266	0.304
1.0	0.139	0.189	0.244	0.281	0.321
1.5	0.151	0.201	0.257	0.295	0.335
2.0	0.164	0.214	0.271	0.308	0.348
2.5	0.175	0.226	0.284	0.321	0.361
3.0	0.186	0.238	0.297	0.334	0.373
3.5	0.197	0.249	0.309	0.346	0.385
4.0	0.208	0.261	0.322	0.359	0.398

The simulation effect of temperature and air velocity on the treatment of soil samples showed a progressive increase in the mass transfer coefficient indicating enhanced contaminant transport from the soil matrix into the gaseous phase. **Table 21** presents the lowest operating condition of 283 K and 0.1 cm/s, the mass transfer coefficient was 0.118, whereas the highest value of 0.398 was obtained at 323 K corresponding to 4.0 cm/s. This substantial increase confirms the strong dependence of volatilization and interfacial transport processes on thermal and hydrodynamic conditions.

Figure 10 presents the nonlinear interaction between temperature and air velocity through the 3D surface plot. The steep gradient observed at higher operating conditions that indicates strong interaction effects and confirms continuous increases in temperature and air velocity that produce greater enhancement in mass transfer performance than individual parameter variation alone [33] [34].

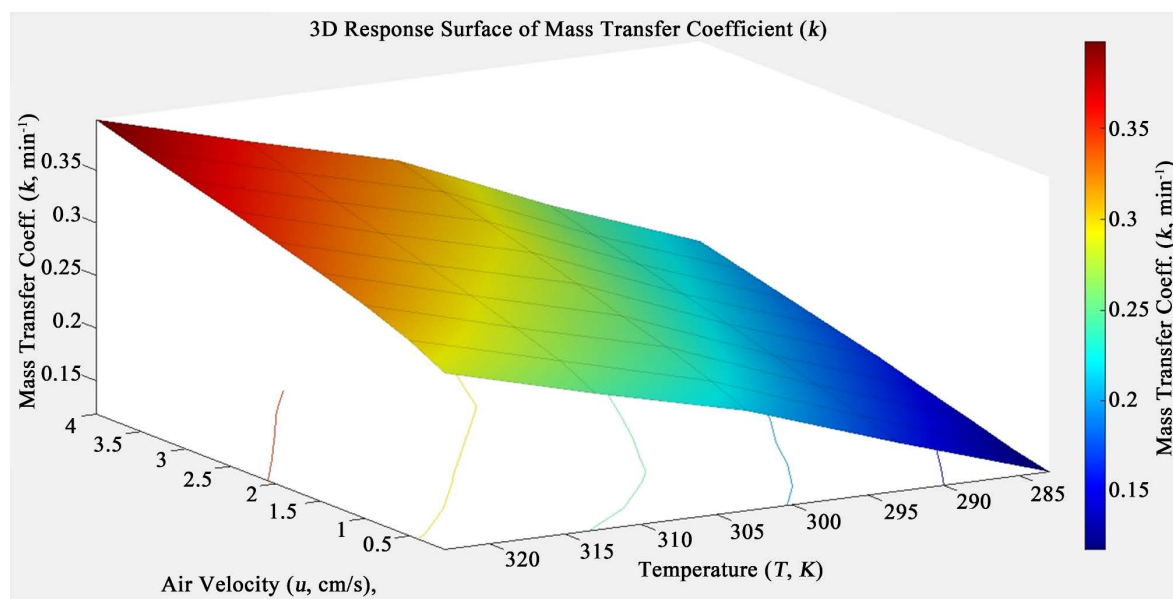


Figure 10. 3D response surface of mass transfer coefficient.

The response surface also suggests the existence of optimal operational regions for maximizing BTEX removal efficiency while minimizing transport limitations. These trends support the effectiveness of integrating preheated air and air velocity optimization in hybrid treatment systems. Higher mass transfer coefficients directly correspond to improved BTEX volatilization and removal efficiency, which are critical for air stripping and hybrid treatment application. The result also shows that the trend becomes less significant at high temperatures (283 K - 323 K) where the difference in BTEX removal under different air velocity becomes smaller. At these conditions, the maximum removal efficiency is reached because the combined effect of high temperature and high air velocity accelerate mass transfer of BTEX between the solid and the gas phase. The air velocity must be chosen to maximize transfer while keeping pressure gradients under normal levels. Excessively high air velocity will result in flooding [34].

3.4.3. Effect of Temperature

The effect of temperature on BTEX removal efficiency was considered within a temperature range of 283 K - 323 K and at different air velocity as shown in **Table 22**. The response surface also suggests a mass transfer performance in hybrid treatment system compared to individual parameter variation alone (**Figure 11**).

A graphical representation of the effect of temperature on diffusion coefficient for BTEX removal efficiency under the operating conditions is shown in **Figure 11**.

Figure 11 showed linear progressive plots between temperature and BTEX diffusion coefficient, with the coefficient increasing from approximately 1.84 to $3.19 \times 10^{-10} \text{ m}^2/\text{s}$ as temperature increased from 283 K to 323 K. The high correlation coefficient ($R^2 = 0.9967$) confirms that increasing temperature significantly enhances molecular diffusion and BTEX mobility within the soil matrix [35].

Table 22. Simulated BTEX diffusion coefficient under different temperature conditions.

Temperature (K)	Diffusion coefficient (m ² /s)
283	1.84
293	2.11
303	2.46
313	2.81
323	3.19

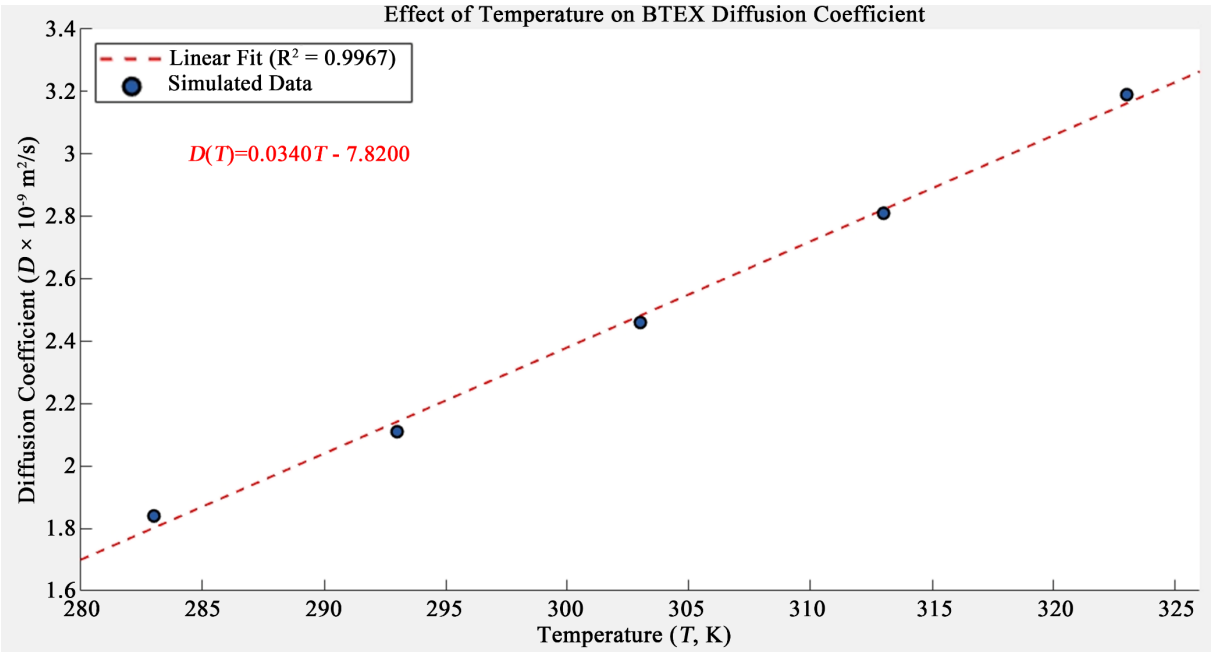


Figure 11. Effect of temperature on diffusion coefficient for BTEX.

Higher temperatures increase the average kinetic energy of the BTEX molecules, thereby increasing diffusion rates and reducing resistance to BTEX movement through soil pores. The increase from 1.84 cm²/s at 283 K to 2.46 cm²/s at 303 K implies a moderate enhancement in volatilization and BTEX transport, while further increases to 2.81 cm²/s and 3.19 m²/s at higher temperature between 313 K and 323 K, this confirmed accelerated diffusion behavior. Another effect of increased temperature is that, it causes an increase its solubility and improves its removal efficiency. More also, the capacity for transfer of BTEX relative to equilibrium condition in hybrid treatment system is the stripping factor (s) which increases with temperature and air velocity and subsequently reduce the concentration level BTEX presence in soil matrix [35].

3.4.4. Residual BTEX Concentration

Residual BTEX concentration decreased with increasing temperature and air velocity due to enhanced diffusion, volatilization, and mass transfer processes. Higher thermal and airflow conditions improved BTEX removal efficiency by ac-

celerating BTEX transport from solid phase to the gaseous phase using hybrid treatment system as shown in **Table 23**.

Table 23. Simulated residual BTEX concentration (mg/kg) after integrated treatment.

Temperature + Air velocity	Residual BTEX Concentration (mg/kg)
283 K + 0.1 cm/s	4.52
293 K + 1.0 cm/s	2.84
303 K + 2.0 cm/s	1.37
313 K + 3.0 cm/s	0.62
323 K + 4.0 cm/s	0.18

Interestingly, increased temperature and air velocity are expected to significantly reduce residual BTEX concentration through improved volatilization and BTEX removal efficiency. **Figure 12** also showed that at high temperature (283 to 323 K) and for all air velocity resulted in an equilibrium reduction of BTEX concentration from 4.25 mg/kg at 283k and 0.1cm/s to 0.18 mg/kg at 323k and 4.0 cm/s which recorded an overall removal efficiencies 98.16% when air velocity was constant and 98.71% when air velocity was at 4.0cm/s. But over 4.0cm/s gives no significant change in removal efficiency. The removal efficiency increases with increase in temperature and 0.1 wt% MMS-4 dosage for all experimental conditions [34] [35]. This is because an increase in temperature and air velocity causes a decrease in the solubility of BTEX compounds and increases air velocity and hence reduces BTEX concentration level in soil matrix (improves removal efficiency).

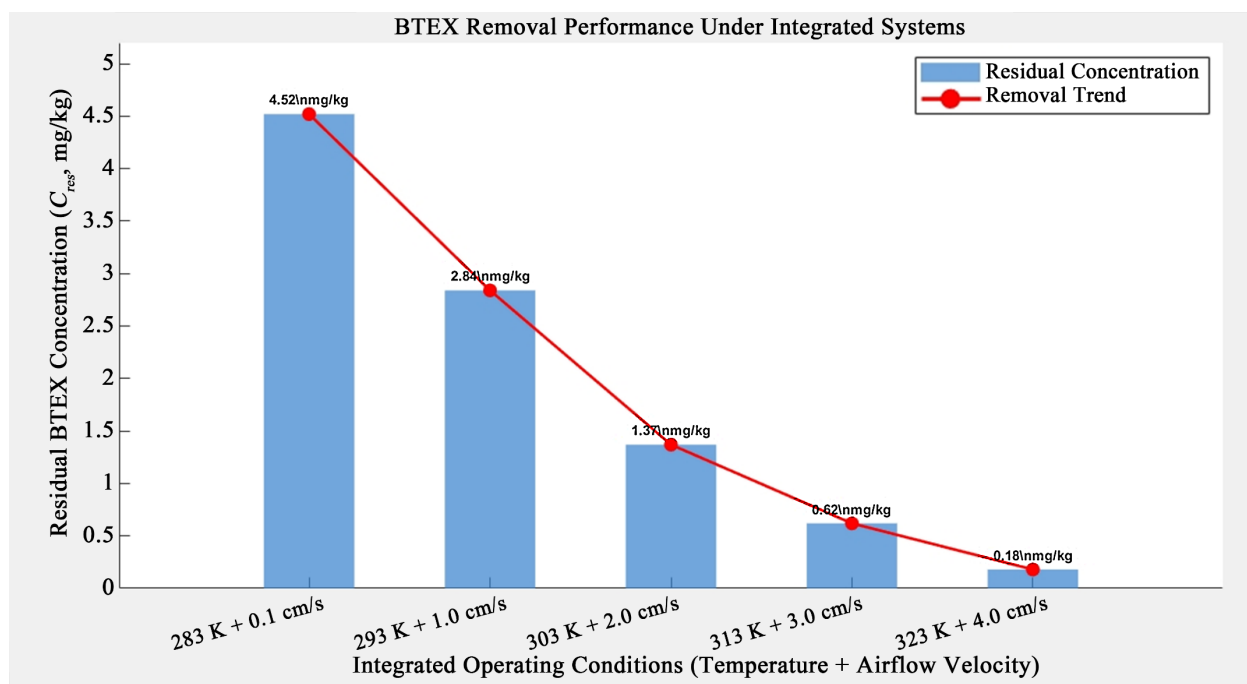


Figure 12. BTEX removal performance under hybrid treatment system.

3.5. Model Validation for Simulation Results

Hybrid air stripping and bioremediation system is essential for process optimization, scale-up, and performance evaluation that showed that hybrid system performs better than the standalone methods with an error metric such as R^2 , RMSE (percent deviation) and BTEX removal efficiency.

Table 24. Comparison between experimental and-Matlab predicted BTEX removal efficiency.

Treatment techniques	Experimental removal efficiency (%)	Matlab predicted removal efficiency (%)	Percentage deviation (%)	R^2	RMSE
Air stripping	47.00 ± 3.66	50.66	4.12	0.945	2.87
Bioremediation	52.14 ± 4.60	56.74	2.82	0.957	2.34
Hybrid system	73.09 ± 10.17	83.26	4.06	0.972	1.6
Matlab + optimized Hybrid system	73.09 ± 10.17*	98.16 - 98.71	18.01 - 18.55	0.997	0.74

R^2 : Coefficient of determination and RMSE: Root Mean Square Error.

Table 24 provides the basic for evaluating the experimental results obtained on air stripping, bioremediation, and the hybrid treatment achieved BTEX removal efficiencies ranging from 45.68% to 83.26%. MATLAB simulations predicted higher BTEX removal efficiencies from 98.16% to 98.71% under optimized operating conditions. The high coefficient of determination at $R^2 > 0.99$ and low RMSE values indicates strong agreement between the model and experimental observations. The apparent increase in BTEX removal efficiency does not represent direct experimental performance but rather the theoretical optimum predicted by the model after simultaneous optimization of process variables such as air flow rate, contact time, surfactant dosage, and microbial activity (**Table 7**). The MATLAB results interpret the maximum achievable performance within the model constraints rather than experimental validated results.

Despite the promising results obtained from the hybrid treatment system, several limitations were observed. First, the experiments were conducted under controlled pilot scale conditions, which do not replicate the environmental factors encountered in the field applications, such as fluctuating temperature, moisture content, and natural airflow patterns. Secondly, the contaminated soil used in this study was relatively homogeneous compared to field soils, which often exhibit significant spatial variability in texture, organic matter content, permeability, and contaminant distribution. Such heterogeneity can influence contaminant transport and BTEX removal efficiency. The surfactant enhanced BTEX desorption, residual surfactant persistence in the soil may affect long-term soil quality, microbial activity, or contaminant mobility if not adequately removed. Furthermore, the optimized model was developed and validated using pilot scale generated data and

some specific operating conditions. The direct transfer of the model to field-scale soil remediation may be challenged by soil heterogeneity, hydrogeological conditions, contaminant aging, operational costs, and technique limitations. Therefore, pilot-scale and field-scale investigations are recommended to verify the applicability, robustness, and scalability of the proposed hybrid treatment system under real environmental conditions.

In summary, the experimental effect of MMS-4 and temperature on soil remediation techniques employed recorded overall BTEX removal efficiencies of (47.12% - 56.74%) for bioremediation system, (45.68% - 50.66%) for air stripping system and (64.29% - 83.26%) for hybrid treatment system compared to (96.84% - 98.71%) for Matlab design + hybrid treatment system when air velocity varied from 0.1 - 4.0 cm/s at the interval of 10°C - 50°C. The results showed that over 95% BTEX removal efficiencies were obtained for all the combinations of Matlab design and hybrid treatment system under the influence of air temperature and surfactant concentration. This is an indication of the effectiveness and reliability of the process compared to results obtained from the literature. This implies that temperature effect is more dominant than the effect of surfactant dose on the removal of BTEX for either standalone air stripping or bioremediation systems.

4. Conclusions

MATLAB hybrid treatment system was developed and evaluated using a combination of air stripping and bioremediation techniques under the influence of surfactant solutions and temperature for the treatment of BTEX presence in petroleum contaminated soils. The application of surfactant solution at a prescribed process condition has improved microbial metabolism which increased the treatment efficiency of toxic BTEX. The integration of air stripping and bioremediation techniques greatly improved the removal efficiency of BTEX when compared to air stripping and bioremediation techniques for heated and unheated air under natural environmental conditions.

The analyses of soil samples using GC-FID showed that BTEX concentrations in the entire representative soil samples corresponding to 70.18 mg/kg clay, 93.29 mg/kg loamy, 49.30 mg/kg sandy and 57.53 mg/kg, mg/kg coarse-grain soils respectively. MMS-4 showed a high superiority over MNS-1 and MSDS-2 for surfactant enhanced bioremediation and air stripping systems. The experimental effect of MMS-4 and temperature on soil remediation techniques employed recorded overall BTEX removal efficiencies of (47.12% - 56.74%) for bioremediation system, (45.68% - 50.66%) for air stripping system and (64.29% - 83.26%) for hybrid treatment system compared to (96.84% - 98.71%) for Matlab modeling design + hybrid treatment system when air velocity varied from 0.1 - 4.0 cm/s and temperature rises between 10°C - 50°C. The results revealed the accuracy and effectiveness of MATLAB + hybrid treatment system compared to air stripping, bioremediation and hybrid treatment techniques. MATLAB + hybrid treatment system is considered a good remedial option when the temperature rises from 10°C to

50°C. The application of MNS-1, MSDS-2 and MMS-4 surfactants increases the BTEX removal efficiency in soil samples but MMS-4 showed superiority over MNS-1 and MSDS-2 in all soil samples. The treatment performance of bioremediation, air stripping, hybrid system and hybrid + Matlab relies on temperature, air flow rate and surfactant concentration. Optimizing these factors in each case will lead to higher treatment efficiency without causing negative effects on the environment.

Author Contributions

Stephen YAKUBU contributions include conceptualization, methodology, investigation, experimental design, data collection, data analysis, and original manuscript preparation. Adeola Grace OLUGBENGA: Experimental validation, manuscript review and editing. Yetunde Mariyam ALADEITAN.: Supervision and critical review of the manuscript while Abdullahi ZAKARI; Supervision and editing of manuscript.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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