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COMPREHENSIVE ASSESSMENT OF THE EFFECTIVENESS OF REMEDIATION OF PETROLEUM-CONTAMINATED SOILS FOLLOWING AN ACCIDENTAL OIL SPILL

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This paper presents the results of a comprehensive assessment of the effectiveness of remediating soils contaminated with light petroleum products following the destruction of fuel storage tanks at an oil depot in the urban-type settlement of Borodianka, Kyiv Region, Ukraine, during military operations. The study employed an integrated methodology combining field hydrogeological investigations, mathematical modeling of contaminant migration within the vadose zone, laboratory analyses, and an experimental evaluation of an integrated remediation technology consisting of free-phase petroleum product recovery, decantation, and vacuum distillation. The remediation performance was quantitatively evaluated using a set of integrated indicators, including the contamination reduction coefficient, residual contamination coefficient, environmental hazard reduction coefficient, integrated potential migration hazard index, and the mass balance of recovered petroleum products. The proposed remediation technology reduced the average concentration of petroleum hydrocarbons in soil from 43,640 mg kg^{-1} to 2,180 mg kg^{-1}, corresponding to an overall remediation efficiency of 95%. The overall contamination reduction coefficient reached 20.0, whereas the decantation and vacuum distillation stage alone achieved a reduction coefficient of 8.61. The calculated environmental hazard reduction coefficient indicates a substantial decrease in the risk of secondary contamination of both soils and groundwater. These findings demonstrate the effectiveness of the integrated remediation approach for mitigating the environmental consequences of accidental petroleum spills and provide a scientific basis for the development of technological guidelines for the reclamation of petroleum-contaminated sites. *Key words:* petroleum products; soil contamination; accidental oil spill; free-phase recovery; decantation; vacuum distillation; soil remediation; environmental efficiency; mass balance.

Комплексна оцінка ефективності очищення забруднених нафтопродуктами ґрунтів після аварійного розливу. Соколов А.В.

Означені результати комплексної оцінки ефективності очищення ґрунтів, забруднених світлими нафтопродуктами внаслідок аварійного руйнування резервуарів на нафтобазі в смт Бородянка Київської області під час воєнних дій. Дослідження виконано на основі поєднання польових гідрогеологічних досліджень, математичного моделювання процесів міграції забруднювачів у зоні аерації, лабораторних випробувань та експериментальної оцінки ефективності комплексної технології очищення, що включає механічне вилучення вільної фази нафтопродуктів, декантацію та вакуумну дистиляцію. В дослідженнях виконано кількісну оцінку ефективності очищення із застосуванням системи інтегральних показників, що передбачають означення коефіцієнту зниження забруднення та залишкового забруднення, коефіцієнт екологічної небезпечності, інтегральний індекс потенційної міграційної небезпеки та масовий баланс вилучених нафтопродуктів. Під час виконання досліджень, відповідних регламентних робіт встановлено, що застосування комплексної технології забезпечило зниження середньої концентрації нафтопродуктів у ґрунті з 43640 до 2180 мг/кг, що відповідає загальній ефективності очищення 95%. При цьому, коефіцієнт зниження забруднення становив 20,0, а безпосередньо для стадії декантації та вакуумної дистиляції – 8,61. Розрахований коефіцієнт зниження екологічної небезпеки свідчить про істотне зменшення ризику вторинного забруднення ґрунтів і підземних вод. Отримані результати підтверджують доцільність застосування комплексного підходу до ліквідації наслідків аварійних розливів нафтопродуктів та можуть бути використані при розробленні технологічних регламентів рекультивації забруднених земель. *Ключові слова:* нафтопродукти, забруднення ґрунтів, аварійний розлив, механічне вилучення, декантація, вакуумна дистиляція, ремедіація, екологічна ефективність. масовий баланс.

Introduction. Accidental releases of petroleum products remain one of the most serious anthropogenic threats to the geological environment. Damage to storage tanks containing light petroleum products (LRPPs) results in the rapid infiltration of low-viscosity hydrocarbons through the vadose zone, followed by their accumulation as floating free-product lenses at the groundwater table. Such contamination sources are characterized by high mobility, long-term persistence, and the ability to generate extensive zones of secondary contamination affecting both soils and groundwater [1]. The remediation of petroleum-contaminated sites has become particularly important in Ukraine following the onset of the full-scale military invasion, during which numerous fuel storage and energy infrastructure facilities were damaged or destroyed [2]. The destruction of tank farms resulted in large-scale releases of gasoline and diesel fuel, causing extensive contamina-

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tion of soils, the vadose zone, and groundwater systems. Under these circumstances, conventional remediation techniques frequently prove inadequate because they fail to ensure the efficient removal of both free-phase and sorbed petroleum hydrocarbons. In addition, many existing technologies require costly equipment, involve substantial energy consumption, and often exhibit limited overall remediation efficiency [3].

Relevance of the Study. Recent studies indicate that the most promising approach to the remediation of petroleum-contaminated soils is the application of integrated remediation technologies that combine mechanical recovery of the mobile free-phase petroleum products, physicochemical treatment methods, and thermal processing. Such integrated technological solutions provide substantially higher remediation efficiency than individual treatment methods and significantly reduce the time required for the restoration of contaminated sites [4]. However, the majority of published studies have focused on individual remediation techniques, including mechanical recovery, soil washing, bioremediation, thermal desorption, and chemical oxidation [5, 6]. Considerably less attention has been devoted to the comprehensive quantitative assessment of the performance of multistage remediation technologies, particularly with respect to environmental hazard reduction, contaminant migration potential, petroleum hydrocarbon mass balance, and integrated indicators of environmental performance.

A particularly important unresolved issue is the quantitative evaluation of the contribution of individual technological stages to the overall remediation outcome. In current practice, the effectiveness of accidental petroleum spill remediation is generally assessed only by comparing the final petroleum hydrocarbon concentrations in the treated soil. In contrast, the individual efficiencies of mechanical recovery, decantation, and vacuum distillation are rarely quantified separately. Consequently, this approach provides limited opportunities for optimizing remediation process design and selecting the most effective treatment technologies for specific engineering-geological and hydrogeological conditions.

Relationship to Scientific and Practical Challenges. This study presents the results of comprehensive field and laboratory investigations conducted at an oil storage facility in the urban-type settlement of Borodianka, Kyiv Region, Ukraine, following the accidental destruction of storage tanks containing light petroleum products. Unlike most previous studies, the present research encompasses the entire remediation process, from delineating the contaminated area and mathematically modeling the migration of light non-aqueous phase liquids (LPP) [7, 8] to the quantitative evaluation of an integrated remediation technology using a system of comprehensive environmental performance indicators. The objective of this study is to comprehensively evaluate the effectiveness of remediating soils contaminated by accidental spills of light petroleum products through the combined application of free-phase petroleum product recovery, decantation, and vacuum distillation, using a system of integrated environmental indicators that characterize the degree of contaminant removal, reduction of environmental risk, and mitigation of the potential for contaminant migration.

Literature Review. A wide range of methodological approaches has been developed for evaluating the effectiveness of petroleum-contaminated soil remediation. The most commonly applied assessment criteria include reductions in total petroleum hydrocarbon (TPH) concentrations, biodegradation rates, residual toxicity, environmental risk, and changes in the physicochemical properties of soils following remediation. More recently, increasing attention has been given to integrated assessment frameworks that combine technological, environmental, and economic performance criteria to provide a more comprehensive evaluation of remediation effectiveness [9,10]. Despite these advances, existing studies primarily assess the final remediation outcome rather than the effectiveness of individual technological stages. Furthermore, relatively few investigations quantify reductions in environmental hazard and contaminant migration potential while simultaneously evaluating the mass balance of recovered petroleum products. This gap limits objective comparisons among remediation technologies and complicates the optimization of integrated remediation strategies.

Research Gap. A major unresolved issue is the development of a comprehensive methodological framework for quantitatively assessing the effectiveness of petroleum-contaminated soil remediation based on a system of integrated performance indicators. Such indicators should simultaneously characterize contaminant removal efficiency, residual anthropogenic impact, environmental risk, and the potential for secondary contaminant migration.

To address this challenge, the present study proposes a comprehensive system for evaluating the performance of an integrated remediation technology combining free-phase petroleum product recovery, decantation, and vacuum distillation. The proposed framework incorporates the following key indicators: contamination reduction coefficient; residual contamination coefficient; environmental hazard coefficient; environmental risk reduction coefficient; integrated potential migration index; and mass balance of recovered petroleum products. Together, these indicators provide a comprehensive quantitative assessment of remediation performance and environmental effectiveness.

Scientific Novelty. This study presents, for the first time, a comprehensive methodological framework for evaluating the effectiveness of remediation of soils contaminated by accidental releases of light petroleum products. Unlike existing approaches, the proposed methodology is based on a system of integrated performance indicators that enables the simultaneous assessment of remediation efficiency, changes in environmen-

tal risk, residual anthropogenic impact, and the potential for contaminant migration. Furthermore, this study is the first to propose a unified set of interrelated quantitative indicators for evaluating an integrated remediation technology combining free-phase petroleum product recovery, decantation, and vacuum distillation. These indicators include the contamination reduction coefficient, residual contamination coefficient, environmental hazard coefficient, environmental risk reduction coefficient, integrated potential migration index, and the mass balance of recovered petroleum products. Collectively, they provide a scientifically robust and comprehensive framework for the quantitative evaluation of remediation performance and environmental effectiveness.

Materials and Methods. The experimental study was conducted at the territory of an oil storage facility located in the urban-type settlement of Borodianka, Kyiv Region, Ukraine, which was severely damaged during military operations in 2022. The destruction of the fuel storage tanks resulted in the accidental release of approximately 1,200 m^3 of light refined petroleum products (LRPPs), primarily gasoline and diesel fuel, leading to extensive contamination of the soil and the upper unconfined aquifer (Fig. 1).

The first stage of the investigation comprised an integrated program of field surveys, office-based analyses, and mechanical recovery of the mobile free-phase petroleum products. Field investigations included a reconnaissance survey of the contaminated site, geodetic positioning of observation points, drilling of nine exploratory boreholes (T1–T9), groundwater level measurements, field hydraulic tests using the bailer recovery method [8] (Fig. 2), and the collection of representative composite soil samples for laboratory analyses.

The office-based investigations involved a series of analytical calculations and numerical modeling procedures. In particular, the radius of LNAPL lens propagation was estimated using a simplified analytical multiphase flow model that accounted for both the spill volume and the average thickness of the free-product lens. Based on the calculated propagation radii, a spatial contamination model was developed to delineate the contaminated area, providing the basis for designing the mechanical recovery system for free-phase petroleum products (Fig. 3) [7].

Field investigations confirmed the formation of a localized petroleum contamination zone exceeding 4,000 m^2 in the central part of the oil storage facility. The spatial distribution of contaminants was primarily controlled by the soil grain-size composition, the characteristics of the artificially modified site topography, and the natural groundwater flow regime. Drilling of the obser-



Fig. 1. Fragments of the oil storage facility showing residual petroleum product contamination



Fig. 2. Observation boreholes containing free-phase petroleum products

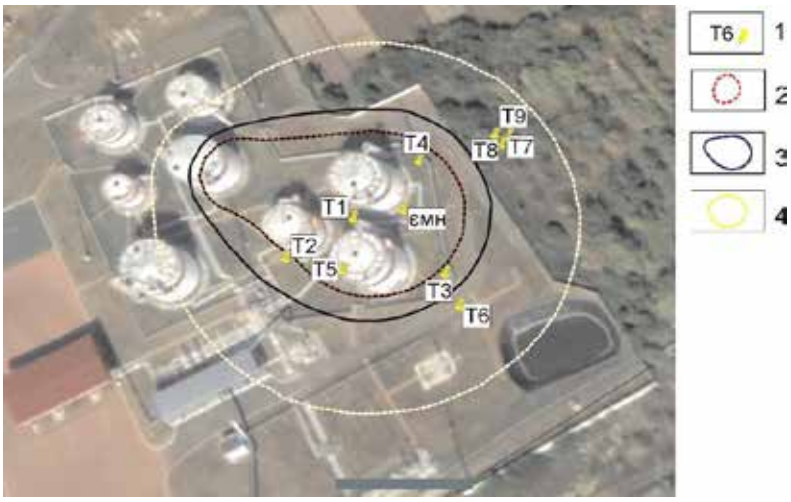


Fig. 3. Spatial approximation of the predicted distribution of petroleum products within the vadose zone, integrated with the coordinates of the observation boreholes and satellite imagery obtained from Google Earth

Legend: (1) field observation borehole; (2) contamination boundary corresponding to a free-product thickness of h_1 = 0.50 m; (3) contamination boundary corresponding to h_2 = 0.30 m; (4) contamination boundary corresponding to h_3 = 0.10 m.

vation boreholes confirmed the presence of a mobile light non-aqueous phase liquid (LNAPL) lens floating on the groundwater table. The thickness of the free-phase petroleum product varied from 0.10 to 0.50 m, depending on the distance from the damaged storage tanks. The maximum thicknesses were recorded within the central part of the spill area, in agreement with the results of the contaminant migration modeling.

Using the measured spill volume and the observed thickness of the free-product lens, the contaminated area was quantitatively estimated. The most probable extent of contamination was calculated to be 4,169 m², corresponding to an average LNAPL thickness of 0.30 m. The total volume of the mobile free-phase petroleum product was estimated at 1,250.7 m³, which closely matches the approximate spill volume determined during the engineering site assessment.

These findings provided the basis for designing the mechanical petroleum recovery system, determining the optimal number and spatial arrangement of recovery wells, and optimizing the subsequent remediation strategy.

The practical remediation of the contaminated site was implemented in two sequential stages. The first stage involved the mechanical recovery of the mobile free-phase petroleum products through the installation of 140 recovery wells with a total drilled length of 710 linear meters, followed by the extraction of the petroleum product–water mixture using the bailer recovery method. This initial mechanical recovery stage produced the most significant immediate environmental benefit. The average concentration of petroleum hydrocarbons in the soil decreased from 43,640 mg kg^{-1} to 18,760 mg kg^{-1}, corresponding to a reduction of approximately 57%.

Nevertheless, more than 42% of the initial contamination remained within the soil after mechanical recovery, indicating that this technique alone provides only limited remediation efficiency. These findings are consistent with previous international studies demonstrating that conventional mechanical recovery methods effectively remove only the mobile free-phase contaminants, whereas a substantial proportion of petroleum hydrocarbons remains adsorbed within the soil pore structure, requiring additional physicochemical treatment technologies for effective removal. This limitation provided the rationale for implementing a second remediation stage. The subsequent treatment involved a proprietary integrated remediation technology combining decantation and vacuum distillation. The primary objective of this stage was to remove the residual petroleum hydrocarbons adsorbed onto mineral soil particles that could not be extracted by mechanical recovery alone.

The treatment process consisted of several consecutive operations, including preliminary dispersion of the contaminated soil in an aqueous medium, intensive mixing of the resulting suspension, gravitational separation of the free petroleum phase by decantation, and the final removal of low-volatility hydrocarbon fractions by vacuum distillation under reduced pressure. Operating under vacuum significantly lowered the evaporation temperature of petroleum fractions, thereby reducing energy consumption while preventing thermal degradation of the mineral soil matrix.

To evaluate the performance of the proposed technology, five composite soil samples, each weighing 200 kg, were prepared to represent different contamination conditions across the study area. The total mass of the experimental material was 1,000 kg. Petroleum hydrocarbon concentrations were determined at three stages: prior to remediation, after mechanical recovery of the free-phase petroleum products, and following completion of the integrated remediation process.

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The average concentration of petroleum hydrocarbons in the contaminated soil immediately after the accidental spill was 43,640 mg kg^{-1}. Following mechanical recovery using the bailer method, the average concentration decreased to 18,760 mg kg^{-1}. Subsequent treatment by the combined decantation and vacuum distillation process further reduced the concentration to 2,180 mg kg^{-1} (Table 1).

The highest residual contamination was observed at sampling point T4, which corresponded to the highest initial petroleum hydrocarbon concentration and was most likely, associated with deeper contaminant penetration into the sandy soil matrix.

The results demonstrate that the second technological stage removed more than 88% of the residual petroleum hydrocarbons remaining after the initial mechanical recovery process. These findings confirm that mechanical recovery is effective primarily for the removal of the mobile free-phase petroleum products, whereas the combined physicochemical treatment efficiently removes capillary-bound and adsorbed hydrocarbons retained within the soil matrix. A summary of the experimental results is presented in Table 2.

As shown in Table 2, the final remediation performance was achieved primarily through the sequential application of the two technological stages. This treatment strategy is consistent with current international approaches to the remediation of LNAPL-contaminated sites, where maximum remediation efficiency is achieved only through the application of integrated treatment technologies rather than individual remediation methods [11].

To comprehensively evaluate the performance of the proposed remediation technology, a system of integrated performance indicators was developed. The assessment framework included the contamination reduction coefficient, overall remediation efficiency, efficiency of individual technological stages, residual contamination coefficient, integrated potential migration hazard index, and the mass balance of recovered petroleum hydrocarbons. The experimental data were processed using standard methods of mathematical statistics.

The first performance criterion was the contamination reduction coefficient, which provides a quantitative measure of remediation efficiency and is defined as:

$$Kcr = \frac{C0}{C} \quad (1)$$

where: Kcr – is the contamination reduction coefficient; C0 – is the initial contaminant concentration; C – is the contaminant concentration after remediation.

Higher values of Kcr indicate greater environmental effectiveness of the remediation technology. Based on the experimental data,

$$Kcr = \frac{43640}{2180} \approx 20{,}02.$$

This result indicates that the petroleum hydrocarbon concentration in the soil decreased by more than twenty-fold following remediation.

The overall remediation efficiency was calculated using the conventional relationship:

$$\eta = \frac{C0 - C}{C0} 100\% \quad (2)$$

where: C0 – is the initial petroleum hydrocarbon concentration (mg kg^{-1}); C – is the concentration after remediation (mg kg^{-1}); η – (\eta) is the remediation efficiency (%).

Substituting the experimental values yields:

Table 1

Petroleum hydrocarbon concentrations in soil at different stages of the remediation process

Sampling point	After the spill, mg kg^{-1}	After mechanical recovery, mg kg^{-1}	After integrated remediation, mg kg^{-1}
T1	42000	18000	2100
T2	38500	16200	1850
T3	46700	20100	2300
T4	51200	22500	2700
T5	39800	17000	1950
Середнє значення	43640	18760	2180

Table 2

Changes in the average petroleum hydrocarbon concentration during the remediation process

Remediation stage	Concentration, mg kg^{-1}	Reduction relative to the initial concentration, %
Before remediation	43 640	-
After mechanical recovery	18 760	57,0
After decantation and vacuum distillation	2 180	95,0

$$\eta =. \frac{43640 - 2180}{43640} \times 100\% = 95{,}0\%.$$

Thus, the integrated remediation technology removed nearly the entire mass of light refined petroleum products from the contaminated soil. The achieved remediation efficiency exceeds that reported for most conventional remediation technologies, which typically range between 70% and 90%.

To assess the degree of residual contamination, the residual contamination coefficient was calculated using the following equation:

$$Kr = \frac{C}{C0} \quad (3)$$

where: Kr – is the residual contamination coefficient; C – is the petroleum

hydrocarbon concentration after remediation (mg kg^{-1}); C0 – is the initial petroleum hydrocarbon concentration before remediation (mg kg^{-1}).

Lower values of Kr indicate higher remediation efficiency. Based on the experimental data,

$$Kr = \frac{2180}{43640}\ 0{,}05.$$

This result indicates that only approximately 5% of the initial petroleum hydrocarbon content remained in the soil following completion of the remediation process.

To evaluate the environmental hazard associated with soil contamination, the environmental hazard coefficient (environmental risk coefficient) was calculated as:

$$R = \frac{C}{Cs} \quad (4)$$

where: R – is the environmental hazard coefficient; C is the measured contaminant concentration in the investigated medium; Cs - is the regulatory permissible concentration of the contaminant.

Using a regulatory threshold concentration of 1,000 mg kg^{-1}, the environmental hazard coefficient was R=43.64 before remediation and 2.18 after remediation. Thus, the potential environmental hazard of the contaminated site was reduced by more than twenty-fold following implementation of the integrated remediation technology.

Based on the calculated values of the environmental hazard coefficient, the contamination levels were classified according to the categories presented in Table 3.

Table 3

Environmental hazard classification based on the environmental hazard coefficient

Environmental hazard coefficient (R)	Hazard level
$R \leq 1$	Acceptable
$1 < R \leq 10$	Moderate
$10 < R \leq 100$	High
$R > 100$	Extremely high

To characterize the migration potential of petroleum contaminants, the migration hazard index was calculated as:

$$I_м = \frac{Cw}{Cs} \quad (5)$$

where: IM – is the migration hazard index; Cw – is the petroleum hydrocarbon

concentration in the aqueous extract; Cs – is the petroleum hydrocarbon concentration in the soil.

The calculated migration hazard index decreased from I_M = 436.4 before remediation to 21.8 after remediation. This substantial reduction indicates a marked decrease in the risk of groundwater contamination and the lateral migration of petroleum hydrocarbons beyond the boundaries of the accidental spill area. Consequently, the migration potential of the LNAPL within the vadose zone was reduced by nearly twenty-fold. Of particular significance is that this pronounced reduction was achieved primarily through the removal of adsorbed hydrocarbons, which constitute the greatest long-term threat to groundwater quality due to their persistence within the soil matrix. To further verify the technological performance of the proposed remediation process, a mass balance analysis was performed [12]. For the experimental soil batch with a total mass of 1,000 kg, the initial mass of petroleum hydrocarbons was 43.64 kg. Following completion of the remediation process, the residual hydrocarbon mass was reduced to 2.18 kg, indicating that 41.46 kg of petroleum hydrocarbons had been removed overall. Of this amount, approximately 24.9 kg was recovered during the mechanical extraction stage, whereas an additional 16.6 kg was removed during the combined decantation and vacuum distillation process. Consequently, the second technological stage accounted for nearly 40% of the total petroleum hydrocarbon removal (Table 4), despite treating only the residual, strongly adsorbed fraction of the contaminant.

These results demonstrate the high effectiveness of vacuum distillation as the final stage of the integrated remediation process.

Conclusions. An integrated framework for evaluating the effectiveness of remediation of petroleum-contaminated soils following accidental spills is proposed for the first time. The methodology is based on the combined application of a system of interrelated performance indicators, including the contamination reduction coefficient, residual contamination coefficient, environmental hazard coefficient, environmental hazard reduction factor, integrated migration hazard index, and petroleum hydrocarbon mass balance. Unlike existing assessment approaches, the proposed framework provides a comprehensive quantitative evaluation of both the technological and environmental performance of remediation and enables objective comparison of different remediation technologies using a unified set of evaluation criteria. The obtained results demonstrate that the effectiveness of petroleum-contaminated soil remediation depends

Table 4

Comprehensive evaluation of the integrated remediation technology

Indicator	Value
Initial petroleum hydrocarbon concentration	43 640 mg kg^{-1}
Residual petroleum hydrocarbon concentration	2 180 mg kg^{-1}
Overall remediation efficiency	95,0 %
Contamination reduction coefficient	20,02
Residual contamination coefficient	0,05
Environmental hazard reduction factor	20,02 fold
Total mass of recovered petroleum hydrocarbons	41,46 kg t^{-1} of soil
Mass removed by decantation and vacuum distillation	16,58 kg t^{-1} of soil

not only on the recovery of the free-phase light refined petroleum products (LRPPs), but also on the capability of the remediation technology to remove adsorbed and capillary-bound hydrocarbons, which represent the primary long-term source of secondary contamination of soils and groundwater. The field and laboratory investigations showed that mechanical recovery alone reduced the average petroleum hydrocarbon concentration only to 18,760 mg kg^{-1}, indicating that nearly 43% of the initial contaminant mass remained in the soil after completion of the first remediation stage.

The proposed integrated remediation technology reduced the average petroleum hydrocarbon concentration to 2,180 mg kg^{-1}, corresponding to an overall remediation efficiency of 95%. Unlike most previously published studies, the present work not only quantified the degree of contaminant removal but also performed a comprehensive assessment of environmental remediation performance using an integrated system of evaluation indicators. The contamination reduction coefficient reached 20.02, the residual contamination coefficient was 0.05, and the environmental hazard reduction factor also reached 20.02. The application of this integrated assessment framework makes it possible to evaluate remediation performance not only in terms of residual contaminant concentrations but also with respect to the potential for contaminant migration and its associated environmental impacts.

The petroleum hydrocarbon mass balance demonstrated that, of the initial 43.64 kg of petroleum hydrocarbons contained in one metric tonne of contaminated soil, only 2.18 kg remained after completion of all remediation stages. The total amount of petroleum hydrocarbons removed was 41.46 kg, of which 16.58 kg was recovered during the decantation and vacuum distillation stage. Consequently, the second technological stage contributed approximately 40% of the overall remediation efficiency, despite targeting only the residual, strongly sorbed fraction of petroleum hydrocarbons. This finding highlights the critical role of physicochemical treatment in achieving high remediation efficiency and minimizing the long-term environmental risks associated with residual petroleum contamination.

Practical Implications. The proposed methodology and the obtained results can be applied in the design and implementation of remediation projects addressing accidental petroleum spills at fuel and energy infrastructure facilities, transportation hubs, oil storage terminals, filling stations, fuel storage depots, and other potentially hazardous industrial sites. Furthermore, the proposed integrated assessment framework may serve as a scientific basis for the development of sector-specific technical guidelines, regulatory documents governing the evaluation of petroleum-contaminated soil remediation, and environmental audit procedures for sites affected by accidental petroleum spills.

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