

Article

Mass-Balance Validation in Bench-Scale Gravimetric Sorption Testing: A Case Study on Zeolite and Clay for Used Motor Oil and Diesel Fuel

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Abstract

Gravimetric sorption testing is widely used to screen candidate sorbents for petroleum hydrocarbon remediation. Using a five-material Romanian sorbent screening as a case study, this study demonstrates why explicit mass-balance validation should be mandatory in such protocols. Natural zeolite, clay, peat, wood sawdust, and hops were tested against used motor oil and diesel fuel under a standardized protocol. A mass-balance check showed that results for peat, wood sawdust, and hops implied hydrocarbon uptakes exceeding the physically available mass; because the underlying raw records could not be located, these three datasets were excluded, illustrating the kind of error such validation is designed to catch. The validated result is a two-material comparison: for used motor oil and diesel fuel, respectively, clay and zeolite showed the higher sorption capacity (1.210 ± 0.016 g/g vs. 1.170 ± 0.010 g/g, Welch's *t*-test, $t(6.7) = -4.78$, $p = 0.0022$; and 1.444 ± 0.005 g/g vs. 1.352 ± 0.031 g/g, $t(4.2) = 6.51$, $p = 0.0023$), a reversal consistent with, but not confirmed by, a pore-size- and viscosity-selective sorption hypothesis. Both materials showed low inter-replicate variability ($CV < 2.3\%$), confirmed by Mann–Whitney U tests ($p = 0.0079$ for both hydrocarbons). Because measured capacities are three- to thirteen-fold higher than literature values for raw clinoptilolite and bentonite, these results are presented as protocol-specific bench-scale rankings rather than generalizable material properties. This study is offered as a worked example of validation-first data screening in gravimetric sorption testing; deeper characterization and re-measurement of the excluded materials are identified as next steps.

Keywords: petroleum hydrocarbon sorption; indigenous sorbents; zeolite; clay; oil spill remediation; gravimetric capacity; mass-balance validation; statistical analysis



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1. Introduction

Petroleum hydrocarbon contamination represents one of the most pervasive and persistent forms of environmental pollution worldwide. Accidental spills from road tankers, pipelines, ships, offshore platforms, and underground storage tanks discharge significant volumes of crude oil and refined products into terrestrial and aquatic ecosystems each year [1,2]. The consequences are severe: hydrocarbons suppress biodiversity, disrupt physical and biochemical soil processes, accumulate in food chains, and pose direct risks to human health through acute and chronic exposure pathways [3,4].

Rivers, lakes, and wetlands located near roads, refineries, and fuel depots are particularly vulnerable, as water movement accelerates the dispersion and penetration of pollutants into sediments and riparian soils [2]. In Romania, the Someș, Mureș, and Olt river basins—situated near major transport corridors and legacy industrial zones—are recognized as high-risk areas for accidental petroleum contamination, necessitating readily available, cost-effective, first-response sorbent materials.

Conventional remediation approaches—including soil vapor extraction [5,6], chemical oxidation [7,8], and soil washing [9]—are technically complex, energy-intensive, and economically prohibitive for small-scale emergency response. Growing scientific and practical interest has therefore emerged in low-cost, locally available sorbent materials capable of rapidly immobilizing spilled hydrocarbons at the point of release [1,10,11].

Indigenous natural materials—including lignocellulosic agricultural residues (straw, sawdust, hops), natural fibers (hemp, wool), and mineral sorbents (zeolites, clays, peat)—have demonstrated promising sorption performance due to their abundance, biodegradability, and intrinsic physicochemical affinity for organic compounds [1,10,11]. Romania possesses significant reserves of several such materials: clinoptilolite zeolite (Rupea, Brașov), bentonite (Orașu Nou, Satu Mare), kaolin clay (Șuncuius, Bihor), and large volumes of agricultural and timber processing residues available at negligible cost.

Despite the growing literature on natural sorbents, explicit mass-balance validation of gravimetric sorption results is not consistently reported or applied as a standard quality-control step, and rigorously controlled comparative studies with full statistical validation under standardized conditions remain limited for materials available in the Romanian regional context. The present study addresses both gaps by: (i) screening the gravimetric sorption performance of five indigenous Romanian sorbents for used motor oil and diesel fuel under a single standardized protocol; (ii) applying an explicit, pre-specified mass-balance validation check to the resulting dataset as a mandatory quality-control step, and restricting quantitative statistical analysis to the subset of materials whose results proved consistent with the physical mass balance—a step that, in this dataset, caught three material–hydrocarbon combinations whose reported values were not physically possible, illustrating the practical necessity of this check; (iii) statistically comparing the validated materials using both parametric (Welch’s *t*-test) and non-parametric (Mann–Whitney U) methods, appropriate for the resulting two-group comparison; and (iv) contextualizing the validated results within published literature ranges for natural sorbents, while explicitly flagging the resulting magnitude discrepancy as an open question requiring further verification rather than a confirmed finding. The primary contribution of this study is accordingly methodological—a worked demonstration of validation-first data screening in gravimetric sorption testing—illustrated through the zeolite–clay bench-scale result that survived this validation.

2. Materials and Methods

2.1. Sorbent Materials and Hydrocarbons

Five indigenously available sorbent materials were selected: natural zeolite (clinoptilolite, commercially labeled Spectrum), local clay (bentonite), peat (commercially sourced), wood sawdust (mixed softwood from local timber processing), and dried hops (*Humulus lupulus*, agricultural residue). Zeolite and clay were used in their as-supplied granular form (approximately 3–4 mm particle size), rather than ground to a fine powder; this is a methodological detail relevant to the interpretation of the sorption-capacity magnitude discussed in Section 4.5, since most comparable literature studies used fine-powder forms. All materials were air-dried to constant mass prior to testing to eliminate humidity effects on initial weight measurements. Two petroleum hydrocarbons were used as contaminants:

(i) used motor oil (SAE 15W-40, density ≈ 0.88 g/mL, collected from a commercial automotive service workshop in Cluj-Napoca, Romania), selected for its high density and viscosity representative of heavy industrial contamination; and (ii) diesel fuel (EN 590 [12], density ≈ 0.84 g/mL), selected to simulate light hydrocarbon spill scenarios with higher dispersal capacity. All five materials were initially selected for experimental testing; as detailed in Section 2.3, gravimetric data for three of these materials did not pass mass-balance validation and were excluded from the analyses reported in Section 3. Throughout this manuscript, “indigenous” refers to the geological or agricultural origin of the raw material within Romania (e.g., domestically mined zeolite and clay deposits, locally generated agricultural residues), rather than to the absence of commercial processing or distribution; both zeolite and clay used here were obtained through commercial suppliers sourcing Romanian deposits, consistent with how such materials would realistically be procured for field deployment.

2.2. Standardized Gravimetric Protocol

Sorbent materials were completely air-dried and weighed to a standard dry mass of 30.00 ± 0.01 g per replicate using a calibrated precision balance (readability 0.01 g; Environmental Engineering laboratory, Technical University of Cluj-Napoca, Cluj-Napoca, Romania). Hydrocarbon was then dispensed into transparent plastic containers at a fixed volume of 50 mL per test using calibrated graduated glass syringes (same laboratory), and the pre-weighed sorbent was introduced into the container and left in static contact with the hydrocarbon for 15 min without forced agitation. The saturated sorbent was subsequently removed and drained for 5 min on fine-mesh filter paper to eliminate superficially accumulated hydrocarbon, and then reweighed; the mass difference (Δm) was recorded as the quantity of hydrocarbon absorbed. All tests were performed in five replicates ($n = 5$) per material–hydrocarbon combination, and arithmetic means and standard deviations were calculated for each material. This procedure was applied identically across all material–hydrocarbon combinations to ensure comparability of results.

All experiments were conducted at room temperature (20–25 °C). Sorption capacity (SC, g/g) was calculated as follows:

$$SC \text{ (g/g)} = (m_f - m_i) / m_i$$

where m_f is the final mass (g) after drainage, and m_i is the initial dry mass (g).

2.3. Data Validation and Exclusion Criteria

Prior to statistical analysis, all reported gravimetric results were checked against the physical mass balance imposed by the fixed hydrocarbon dose (50 mL) and hydrocarbon density (approx. 0.88 g/mL for used motor oil; approx. 0.84 g/mL for diesel fuel), which bounds the maximum physically possible sorption capacity at approximately 1.47 g/g for used motor oil and 1.40 g/g for diesel fuel, assuming complete uptake of the entire available hydrocarbon volume. Gravimetric results for peat, wood sawdust, and hops exceeded this physical upper bound for one or both hydrocarbons, indicating that these datasets could not be reconciled with the documented single-dose protocol. The magnitude of this exceedance is recalled by the authors as reaching approximately 1.8 g/g for at least one material–hydrocarbon combination; we state explicitly that this figure derives from the authors’ recollection rather than from a preserved calculation sheet or raw dataset, and is reported only as an approximate indication of scale, not as a documented value (Table S1, Section S1.4). The qualitative conclusion motivating exclusion—that the reported uptakes for these three materials were physically inconsistent with the single-dose protocol, regardless of the precise magnitude by which the bound was exceeded—does not depend

on this recalled figure and is the basis for the exclusion decision below. The full mass-balance calculation underlying the physical bound itself—the assumed hydrocarbon density range, the fixed dose volume and dry sorbent mass, and the resulting maximum physically possible uptake for each hydrocarbon—is given in Table S1 (Supplementary Materials) for transparency and independent verification by the reader. Before excluding these three datasets, we considered whether the excess uptake could instead be explained by container residue, incompletely drained free liquid retained at the container base, drainage-time variability between replicates, or a balance/tare error common to a batch of measurements. However, because the raw laboratory records for these three materials—individual replicate values, drainage times, and any contemporaneous notes—could not be located, none of these candidate explanations could be systematically evaluated or ruled out, and we could not distinguish a data-transcription or recording error from a genuine deviation from the documented protocol. This inability to audit the discarded values against a specific cause, rather than only against the physical mass-balance bound, is itself acknowledged as a data-quality limitation of the present study (Section 4.5). Given this, no principled basis existed for adjusting, correcting, or selectively retaining any subset of these results; any such adjustment would itself constitute an unverifiable, ad hoc modification of the reported data. We therefore consider full exclusion of these three material datasets to be the only methodologically defensible option, and have applied it accordingly, rather than adjusting or partially retaining them. Repeating the gravimetric measurements for these three materials under a documented, mass-balance-verified protocol—with drainage time, container tare, and replicate-level values all explicitly logged—is identified as a priority for future work (Section 4.5). The remaining two materials—zeolite and clay—yielded gravimetric results consistent with the physical mass balance for both hydrocarbons across all $n = 5$ replicates, with no statistical outliers detected (Grubbs test, $p > 0.05$), and were retained for the full analysis presented below.

2.4. Statistical Analysis

Because the validated dataset comprises two sorbent materials (zeolite and clay), pairwise comparisons were performed using Welch's independent-samples t -test (which does not assume equal variances), applied separately to each hydrocarbon type, to test the null hypothesis that the two materials produce equal mean sorption capacity. Degrees of freedom were calculated using the Welch–Satterthwaite equation and are reported to one decimal place alongside each test statistic in Section 3. Effect sizes are reported as Cohen's d , calculated from the pooled standard deviation; given the small per-group sample size ($n = 5$), these estimates carry wide uncertainty and should be interpreted as indicative of a large, consistent separation between materials under this protocol rather than as precise population effect-size estimates. Given the small per-group sample size ($n = 5$), we treated the normality assumption underlying Welch's t -test with caution: Shapiro–Wilk tests were run on each of the four material–hydrocarbon groups as an exploratory check, while recognizing that such tests have very low statistical power at $n = 5$ and cannot definitively confirm normality. Three of the four groups showed no evidence against normality (zeolite/motor oil, $W = 0.821$, $p = 0.119$; clay/motor oil, $W = 0.987$, $p = 0.967$; clay/diesel, $W = 0.885$, $p = 0.332$); the zeolite/diesel group showed a significant deviation ($W = 0.684$, $p = 0.0065$), attributable to the limited measurement resolution of the underlying data (values reported to two decimal places, producing several tied replicate values, e.g., 1.44 recorded three times among five replicates) rather than necessarily reflecting a non-normal underlying process. Because this result raised a legitimate concern about the normality assumption for at least one comparison, we additionally performed the Mann–Whitney U test, a distribution-free rank-based test that does not assume normality, as a

robustness check for both hydrocarbon comparisons; results are reported alongside the Welch's *t*-test results in Section 3.3. Welch's test remains the primary reported comparison, consistent with our a priori analysis plan, because it is more appropriate for continuous gravimetric data and provides an effect-size estimate (Cohen's *d*); the Mann–Whitney result is reported as a confirmatory secondary check. Statistical significance was set at $\alpha = 0.05$.

2.5. Note on Sorption Kinetics

A preliminary kinetic analysis was attempted using mass measurements reconstructed at fixed time points (0, 3, 6, 9, 12, 15 min) rather than by continuous online monitoring. Because this approach does not constitute direct time-resolved experimental measurement, the resulting kinetic parameters are not reported as experimental evidence in this manuscript; see Section 4.5 for further discussion of this limitation and the requirements for a methodologically sound kinetic study.

3. Results

3.1. Sorption Capacity of Used Motor Oil

Table 1 presents the individual replicate values, means, and standard deviations for zeolite and clay tested with used motor oil. Both materials showed consistent inter-replicate performance, with coefficients of variation below 1.31%.

Table 1. Gravimetric sorption capacity of zeolite and clay for used motor oil under this specific protocol (coarse 3–4 mm granules, 5 min gravity drainage; g hydrocarbon/g dry sorbent; *n* = 5 replicates; values in the final column expressed as mean $\pm$ SD). See Section 4.5 for discussion of the magnitude of these values relative to the literature.

Material	Test 1 (g/g)	Test 2 (g/g)	Test 3 (g/g)	Test 4 (g/g)	Test 5 (g/g)	Mean $\pm$ SD (g/g)
Zeolite (clinoptilolite)	1.18	1.16	1.17	1.16	1.18	1.170 $\pm$ 0.010
Clay (bentonite)	1.20	1.19	1.21	1.22	1.23	1.210 $\pm$ 0.016

Clay exhibited a significantly higher mean sorption capacity than zeolite for used motor oil under this protocol (1.210 $\pm$ 0.016 g/g vs. 1.170 $\pm$ 0.010 g/g; Welch's *t*-test, $t(6.7) = -4.78$, $p = 0.0022$, Cohen's *d* = 3.02).

3.2. Sorption Capacity for Diesel Fuel

Table 2 presents the sorption capacities for diesel fuel of zeolite and clay.

Table 2. Gravimetric sorption capacity of zeolite and clay for diesel fuel under this specific protocol (coarse 3–4 mm granules, 5 min gravity drainage; g/g; *n* = 5 replicates). See Section 4.5 for discussion of the magnitude of these values relative to the literature.

Material	Test 1 (g/g)	Test 2 (g/g)	Test 3 (g/g)	Test 4 (g/g)	Test 5 (g/g)	Mean $\pm$ SD (g/g)
Zeolite (clinoptilolite)	1.45	1.44	1.44	1.45	1.44	1.444 $\pm$ 0.005
Clay (bentonite)	1.38	1.39	1.34	1.32	1.33	1.352 $\pm$ 0.031

For diesel fuel, zeolite ranked significantly higher than clay under this protocol (1.444 ± 0.005 g/g vs. 1.352 ± 0.031 g/g; Welch's t -test, $t(4.2) = 6.51$, $p = 0.0023$, Cohen's $d = -4.11$), reversing the ranking observed for motor oil. A possible mechanistic explanation for this inversion is discussed as a literature-informed hypothesis, not yet directly verified in these samples, in Section 4.1.

Figure 1 illustrates the gravimetric sorption capacities of zeolite and clay for both hydrocarbons, and Figure 2 presents the comparative sorption performance of the two materials across both petroleum hydrocarbons tested.

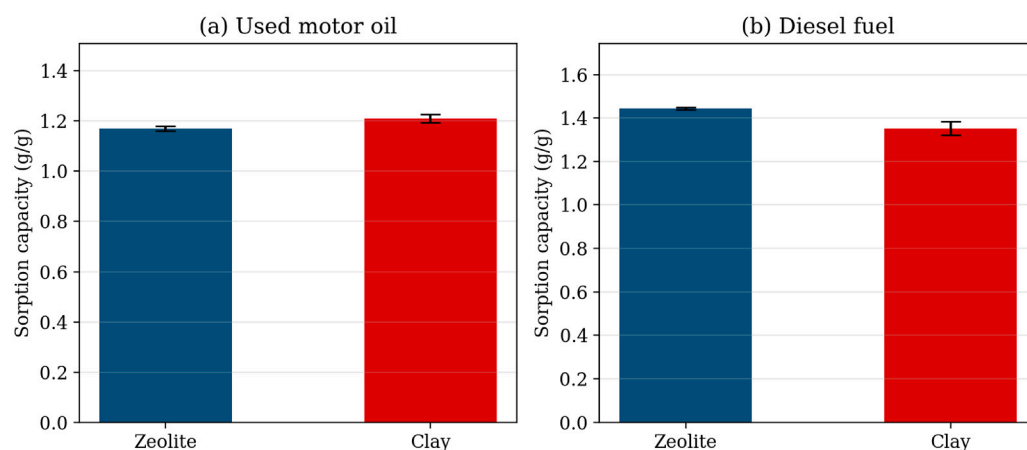


Figure 1. Gravimetric sorption capacity of zeolite and clay for (a) used motor oil and (b) diesel fuel (mean $\pm$ SD, $n = 5$ replicates; both inter-material differences significant, Welch's t -test $p < 0.01$).

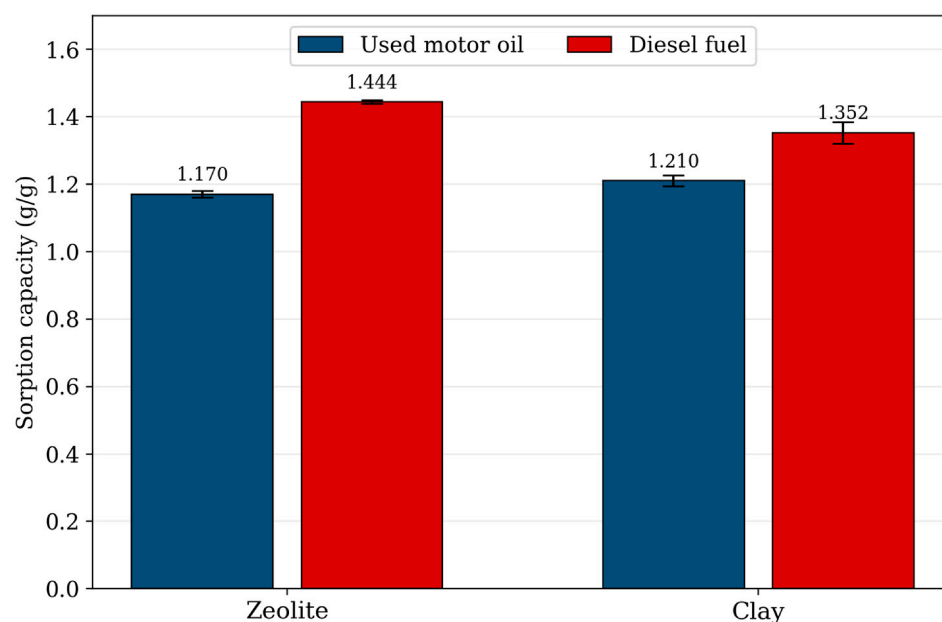


Figure 2. Comparative sorption performance of zeolite and clay for both petroleum hydrocarbons tested (mean $\pm$ SD; both pairwise differences $p < 0.01$).

3.3. Statistical Comparison of Results

Tables 3 and 4 present descriptive statistics and Welch's t -test results for zeolite and clay. Independent-samples t -tests revealed statistically significant differences between the two materials for both hydrocarbons tested.

Table 3. Descriptive statistics for used motor oil sorption capacity. Welch's *t*-test: $t(6.7) = -4.78$, $p = 0.0022$; Cohen's $d = 3.02$.

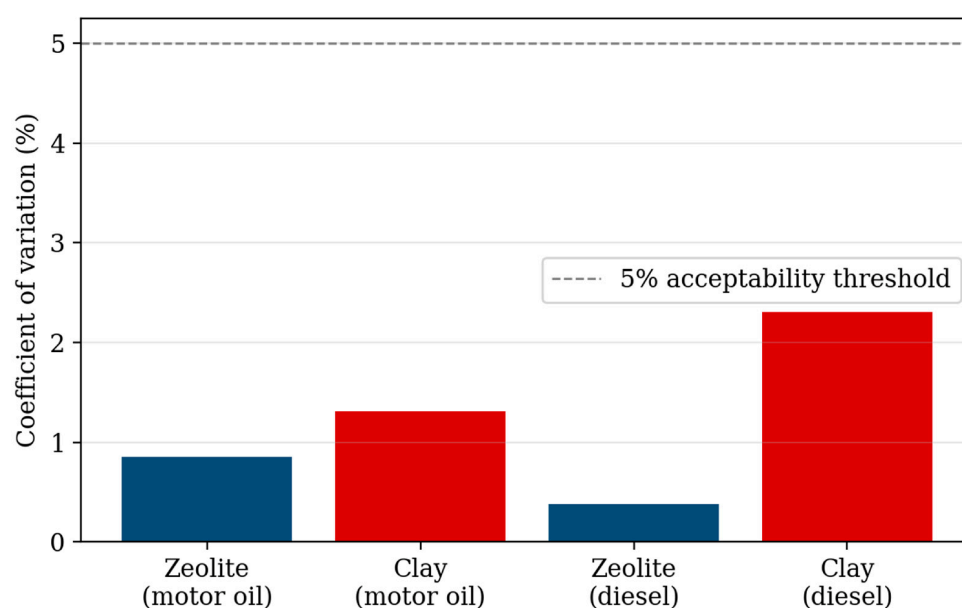
Material	n	Mean (g/g)	SD	CV (%)	95% CI
Zeolite	5	1.170	0.010	0.85	[1.161, 1.179]
Clay	5	1.210	0.016	1.31	[1.196, 1.224]

Table 4. Descriptive statistics for diesel fuel sorption capacity. Welch's *t*-test: $t(4.2) = 6.51$, $p = 0.0023$; Cohen's $d = -4.11$.

Material	n	Mean (g/g)	SD	CV (%)	95% CI
Zeolite	5	1.444	0.005	0.38	[1.439, 1.449]
Clay	5	1.352	0.031	2.30	[1.325, 1.379]

For used motor oil, clay showed significantly higher sorption capacity than zeolite ($t(6.7) = -4.78$, $p = 0.0022$), with a large estimated effect size (Cohen's $d = 3.02$). For diesel fuel, the ranking reversed, with zeolite significantly outperforming clay ($t(4.2) = 6.51$, $p = 0.0023$, $d = -4.11$). Given the modest sample size ($n = 5$ per group), these Cohen's d values should be read as indicating a large, consistent separation between materials under this specific protocol rather than as precise population estimates; both comparisons nonetheless remained significant at the pre-specified $\alpha = 0.05$ threshold. As a distribution-free robustness check, motivated by the Shapiro–Wilk result for the zeolite/diesel group (Section 2.4), the Mann–Whitney U test was additionally applied to both hydrocarbon comparisons. This confirmed the Welch's *t*-test conclusion in both cases: for used motor oil, $U = 25.0$, exact $p = 0.0079$; for diesel fuel, $U = 25.0$, exact $p = 0.0079$ (both material groups were fully separated in rank, i.e., every clay replicate exceeded every zeolite replicate for motor oil, and the reverse for diesel). The agreement between the parametric (Welch's *t*-test) and non-parametric (Mann–Whitney U) results indicates that the observed material ranking does not depend on the normality assumption of the primary test.

Figure 3 summarizes the experimental reproducibility of the gravimetric measurements, expressed as the coefficient of variation for zeolite and clay across both hydrocarbon types.

**Figure 3.** Experimental reproducibility: coefficient of variation (CV%) for zeolite and clay across both hydrocarbon types. All CV values remain below 2.3%, well within the 5% acceptability threshold.

Consistent with the methodological note in Section 2.5, no kinetic-parameter table is reported here: the underlying time-resolved data were reconstructed from fixed-interval mass measurements rather than continuously monitored online, and therefore do not meet the standard required for experimental kinetic evidence. A properly instrumented, continuously monitored kinetic study is identified as a priority for future work (Section 4.5).

3.4. Comparison with Published Literature Values

To provide external literature context for the validated zeolite and clay results, Table 5 and Figure 4 compare our experimental sorption capacities with values reported for raw, unmodified clinoptilolite and bentonite tested against petroleum hydrocarbons in independent studies. As discussed in detail in Section 4.5, our values are 3–13 times higher than these literature values; we present this comparison transparently, including the discrepancy, rather than omit it, and direct the reader to Section 4.5 for a full discussion of possible explanations and the verification we recommend before the absolute magnitude of our results is relied on.

Table 5. Comparison of experimental sorption capacities with independent literature values.

Material	This Study (g/g)	Literature (g/g)	Hydrocarbon Tested (Literature)	Source
Zeolite (clinoptilolite)	1.170 (motor oil)/1.444 (diesel)	0.36	Used engine oil	Bandura et al. [13]
Clay (bentonite)	1.210 (motor oil)/1.352 (diesel)	0.090–0.125	Petroleum contaminants	Lepesbayeva et al. [14]

Source: own data compared with independent literature values from [13] and [14]. Note the substantial magnitude discrepancy discussed in Section 4.5.

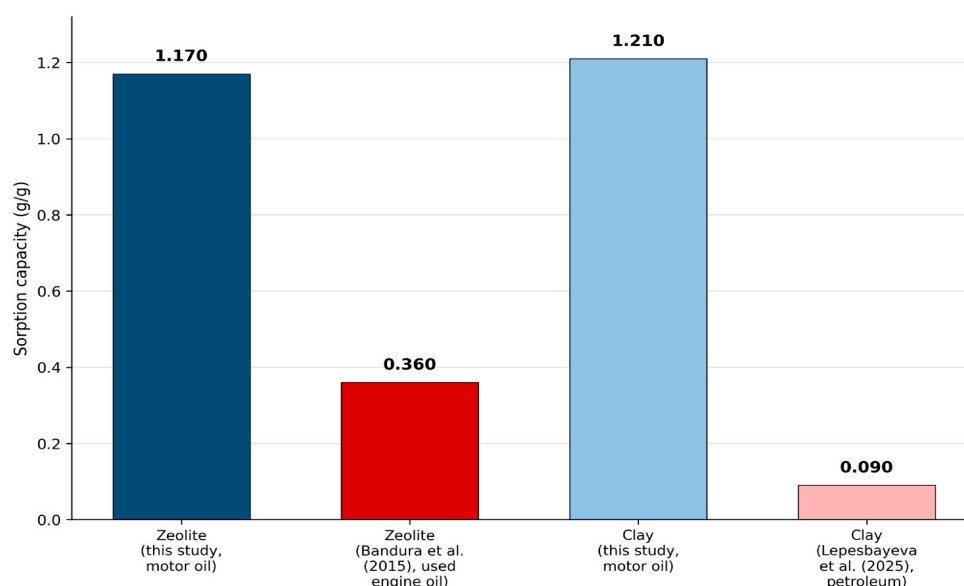


Figure 4. Visual comparison of experimental sorption capacities (this study) with independent literature values [13,14] for raw zeolite and clay. The gap between bars illustrates the magnitude discrepancy discussed in detail in Section 4.5.

4. Discussion

4.1. Mechanistic Interpretation of Sorption Performance

The directly measured findings of this study are the gravimetric sorption-capacity values (Sections 3.1 and 3.2) and the statistical comparisons between materials (Section 3.3);

these are reported without qualification. The explanations offered below for why these differences occur are, by contrast, literature-informed interpretations rather than findings demonstrated in this study, and are flagged as such throughout this section.

A possible explanation for the higher motor oil sorption capacity of clay relative to zeolite is the layered, high-surface-area structure generally reported for bentonite (montmorillonite), whose interlamellar spacing and edge sites are known from the literature to accommodate viscous, high-molecular-weight hydrocarbon fractions such as those present in used motor oil. We emphasize that this interpretation is offered as a plausible hypothesis consistent with the gravimetric ranking observed, and not as a mechanism directly demonstrated in this study: no BET surface area, FTIR, or SEM measurements were performed on the specific material batches used here (Section 4.5), and the generic pore/surface parameters cited below are drawn from the literature on clinoptilolite and bentonite in general rather than from characterization of our own samples. Directly relevant in this regard, Lepesbayeva et al. [14] applied FTIR, SEM, XRD, and ζ -potential analysis to bentonite and a bentonite-vermiculite composite specifically for petroleum sorption from water, confirming that adsorption is governed by the physicochemical characteristics of the clay surface layers; this is the closest direct precedent in the literature for the clay-based mechanism we propose, though it was not performed on our own material batch.

Similarly, zeolite's viscosity-selective behavior—ranking below clay for motor oil but above clay for diesel—would be consistent with a pore-size-selectivity mechanism: the rigid micropore channels typically reported for clinoptilolite (aperture on the order of ~ 4 Å in the literature) would be expected to restrict penetration of the larger, more viscous molecular fractions typical of used motor oil, while accommodating smaller diesel molecules more readily. As with the clay interpretation above, this remains a literature-informed hypothesis rather than a confirmed mechanism for the present samples, since no direct pore-structure or surface characterization was performed on our own batch. The closest direct precedent in the literature is Favvas et al. [15], who performed a complete physicochemical characterization of raw clinoptilolite (EDXRF, FTIR, XRD, SEM, and N₂ adsorption) in direct contact with diesel and other hydrocarbon-based fuels, confirming the mesoporous, low-specific-surface-area structure of natural clinoptilolite that underlies the pore-size-selectivity hypothesis proposed here; this study, however, addressed fuel dehydration rather than hydrocarbon sorption capacity and was not performed on our own material batch. Confirming our specific hypothesis would still require BET, FTIR, and/or SEM analysis of the zeolite and clay batches used in this study, which we identify as a priority for follow-up work (Section 4.5).

The use of zeolite and clay as petroleum sorbents is well-documented in the broader mineral-sorbent literature: natural clinoptilolite has been reported to sorb used engine oil and diesel through a predominantly physical, mesopore-controlled mechanism [13], and has been shown to retain reusable sorption performance over repeated sorption–thermal regeneration cycles [16]. Bandura et al. [17] reviewed a broader set of natural and synthetic mineral sorbents, including both zeolites and clays, for petroleum-substance removal, providing additional literature context for the mineral-sorption mechanisms proposed above. We note that absolute sorption-capacity values reported in this literature for raw, unmodified clinoptilolite and bentonite are generally lower than those obtained in the present study; this discrepancy is discussed as an open question in Section 4.5 and should be taken into account when comparing the present dataset with the wider literature.

A preliminary kinetic assessment was attempted but could not be reported as experimental evidence, because the underlying time-resolved data were reconstructed rather than directly measured (Section 2.5); the rate-limiting mechanism for both materials, therefore, remains to be established through a properly instrumented kinetic study (Section 4.5).

4.2. Statistical Rigor and Reproducibility

The large effect sizes observed (Cohen's $d = 3.02$ for motor oil; $d = -4.11$ for diesel) and low coefficients of variation ($CV < 2.3\%$ for both materials and hydrocarbons) indicate that the zeolite–clay ranking differences are unlikely to be attributable to measurement noise alone, despite the modest sample size ($n = 5$ per group) that remained after data validation. We note that statistical significance establishes the reliability of the observed difference in gravimetric performance and does not, by itself, establish or confirm the underlying physicochemical mechanism, which remains at the hypothesis level, as discussed in Section 4.1.

4.3. Romanian Resource Context and Circular Economy

Romania has domestic reserves of both mineral materials evaluated in this study: natural zeolite (clinoptilolite) and clay (bentonite) are both mined domestically at low cost and require only basic processing (drying, sizing). The complementary hydrocarbon selectivity of the two materials identified in this bench-scale screening (clay for motor oil; zeolite for diesel) is a promising finding for potential future integration into spill-response inventories; however, consistent with the bench-scale scope of the present study (Section 4.5), we do not consider the current dataset sufficient to recommend specific logistics or deployment planning, and testing under realistic environmental matrices would be a necessary precondition for any such recommendation.

4.4. Operational and Logistical Considerations

Beyond gravimetric performance, practical deployment of zeolite and clay as spill-response sorbents depends on operational factors not captured by sorption capacity alone. Zeolite has been reported to retain comparable sorption performance over multiple sorption–combustion–regeneration cycles [16], suggesting a potential reusability advantage; whether clay (bentonite) tolerates similar thermal regeneration without structural degradation of its layered montmorillonite framework has, to our knowledge, not been systematically established and would need to be verified before regeneration is assumed for this material.

Both materials are handled and applied as fine mineral powders, which raises a common occupational consideration: prolonged inhalation of respirable crystalline silica, a documented carcinogen with binding occupational exposure limits in the European Union, is a recognized hazard associated with handling of silicate mineral powders in general. Field application of zeolite or clay sorbents should accordingly include standard dust-control measures (e.g., respiratory protection, minimizing aerosolization during application) consistent with existing occupational exposure regulations for mineral dusts, independent of which of the two materials is selected [18].

From a site-selection perspective, the hydrocarbon-dependent performance reversal identified in this study (Sections 3.1 and 3.2) offers a practical, low-cost decision rule: clay would be the preferred choice at sites dominated by heavier, more viscous contamination (e.g., used motor oil, industrial lubricants), while zeolite would be preferred where lighter fuels, such as diesel, predominate. Both materials are mined domestically in Romania (Section 4.3), so cost and availability are unlikely to be limiting factors relative to this performance-based selection criterion.

4.5. Limitations and Future Work

This study has several limitations that should be considered when interpreting the results. First, gravimetric data originally collected for peat, wood sawdust, and hops could not be reconciled with the mass balance imposed by the documented experimental protocol

(Section 2.3) and were excluded from analysis; the present study is therefore limited to zeolite and clay, and no conclusions can be drawn regarding the other three materials until their sorption capacities are re-measured under a fully documented, mass-balance-verified protocol. Second, the protocol employed a simplified gravimetric approach without advanced physicochemical characterization (BET surface area, FTIR, SEM), so the mechanistic interpretations offered in Section 4.1 remain inferential rather than experimentally demonstrated. Third, a preliminary sorption-kinetics analysis was attempted but is not reported quantitatively in this manuscript (Section 2.5): the underlying data were reconstructed from mass measurements at fixed time points rather than continuously monitored online, which does not meet the standard required for experimental kinetic evidence. A properly instrumented kinetic study, with continuous online monitoring of mass or concentration, is required before rate constants or reaction order can be reported for these materials. Fourth, all tests were performed on neat hydrocarbon in laboratory containers, without a soil, sediment, or water matrix, and without testing of reusability, secondary leaching, or saturated-sorbent disposal; the present results should accordingly be regarded as bench-scale sorption screening rather than direct evidence of field deployment performance. Future work should prioritize: (i) repeating the gravimetric measurements for peat, wood sawdust, and hops with a fully documented protocol and verified mass balance; (ii) direct BET/FTIR/SEM characterization of zeolite and clay; (iii) continuous, time-resolved kinetic monitoring; and (iv) testing under realistic environmental matrices.

A further limitation, identified during preparation of this study, concerns the absolute magnitude of the reported sorption capacities. Comparable literature studies on raw, unmodified clinoptilolite and bentonite report substantially lower sorption capacities for petroleum hydrocarbons (on the order of 0.3–0.9 g/g for zeolite [13,15] and 0.09–0.125 g/g for unmodified bentonite [14]) than the values obtained here (1.17–1.44 g/g for zeolite; 1.21–1.35 g/g for clay), a discrepancy also presented directly in Table 5 and Figure 4. While the values reported in this study satisfy the mass-balance check described in Section 2.3, mass-balance consistency confirms only physical possibility and does not, by itself, establish agreement with typical literature magnitudes. One plausible, mechanistically coherent explanation, consistent with the materials actually used in this study, is particle size: the zeolite and clay were tested as coarse granules (approximately 3–4 mm), rather than the fine powders typically used in the cited literature studies. Coarse granular beds have substantially larger interparticle void space than fine powders, in which liquid can be retained by capillary bridging and surface tension between grains rather than true absorption into the material; under the 5 min drainage time used in this protocol (Section 2.2), such interparticle liquid may not fully drain, inflating the apparent sorption capacity relative to studies using fine powders with more complete drainage. We present this as a plausible hypothesis consistent with the known particle size of our materials, not as a confirmed explanation: it has not been directly tested here, and would require a dedicated experiment (e.g., comparing drainage times, or comparing granular versus powdered forms of the same material batch) to verify. We recommend this as a specific, testable priority for follow-up work, alongside independent replication of the zeolite and clay measurements and direct BET surface area characterization of the specific batches used.

4.6. On the Scope and Contributions of This Study

The reduction in this study, over the course of revision, from an original five-material screening to a validated two-material comparison, together with the removal of the unsupported kinetic-parameter table (Sections 2.5 and 3) and the explicit labeling of the pore-size/viscosity mechanism as a literature-informed hypothesis rather than a demonstrated finding (Section 4.1), reflects a deliberate editorial choice made during revision,

not an unaddressed deficiency. We state directly what this study is and is not. It is not a materials-characterization study: it does not report BET surface area, FTIR, SEM, or XRD data on the specific zeolite and clay batches used, and the mechanistic interpretation offered in Section 4.1 is explicitly flagged throughout as inferential. It is not a kinetics study: no rate constants or reaction orders are reported as experimental findings, because the underlying time-resolved measurements do not meet that standard (Section 2.5). What this study does report, and validate to a level we believe is defensible, is narrower and more specific: (i) a documented case in which a mass-balance check applied to real gravimetric data caught three material–hydrocarbon datasets that were physically inconsistent with the stated protocol and could not otherwise have been distinguished from valid results by inspection alone; (ii) a fully auditable account of what could and could not be verified about the resulting data-quality gap (Table S1), rather than a silent correction or an unqualified exclusion; and (iii) a statistically robust, mass-balance-consistent bench-scale ranking of two domestically available materials against two hydrocarbons, confirmed by both parametric (Welch’s *t*-test) and non-parametric (Mann–Whitney U) tests, with the interpretive limits of that ranking stated explicitly rather than implied to be more general than the evidence supports (Section 4.5). We recognize that this is a narrower contribution than the mechanistic, multi-material characterization study the manuscript originally set out to be. We consider it nonetheless a genuine and useful contribution in its own right: mass-balance validation is a low-cost, broadly applicable quality-control step that is not universally applied in the gravimetric sorption literature, and a worked example—including the process of catching, documenting, and transparently reporting a real data-quality failure, rather than only its theoretical description—has practical value for other researchers designing or auditing similar bench-scale protocols, independently of whether the underlying sorption mechanism is further characterized in future work.

5. Conclusions

This study set out to screen five indigenously available Romanian sorbent materials for petroleum hydrocarbon remediation under a standardized gravimetric protocol, and, in the course of doing so, to demonstrate the practical necessity of explicit mass-balance validation as a quality-control step for gravimetric sorption data. During data validation, gravimetric results for three materials (peat, wood sawdust, hops) were found to imply hydrocarbon uptakes exceeding the maximum physically available in the test system and were excluded from analysis (Section 2.3)—a worked example of the kind of error that such validation is designed to catch. The validated finding of this study is accordingly a two-material comparison, based on zeolite and clay, summarized below; the results should be read as a protocol-specific bench-scale ranking rather than as verified, generalizable material properties (Section 4.5), and the study’s primary contribution is methodological rather than material-characterization in scope (Section 4.6).

1. Clay (bentonite) achieved significantly higher sorption capacity than zeolite for used motor oil under this protocol (1.210 ± 0.016 g/g vs. 1.170 ± 0.010 g/g; Welch’s *t*-test, $t(6.7) = -4.78$, $p = 0.0022$, Cohen’s *d* = 3.02).
2. Zeolite (clinoptilolite) achieved significantly higher sorption capacity than clay for diesel fuel under this protocol (1.444 ± 0.005 g/g vs. 1.352 ± 0.031 g/g; Welch’s *t*-test, $t(4.2) = 6.51$, $p = 0.0023$, Cohen’s *d* = -4.11), reversing the ranking observed for motor oil. This reversal is consistent with a pore-size- and viscosity-selective sorption hypothesis, which remains a literature-informed interpretation rather than a mechanism directly verified by surface or pore characterization of the present samples (Section 4.1).

3. Both materials showed low inter-replicate variability, with all coefficients of variation below 2.3%, which is within commonly accepted reliability thresholds for gravimetric sorption testing.
4. Welch's independent-samples *t*-test indicated that both inter-material differences are statistically significant ($p < 0.01$) with very large effect sizes, suggesting that the observed ranking differences are unlikely to be attributable to measurement noise alone; the underlying physicochemical mechanism remains a literature-informed hypothesis rather than a directly confirmed explanation (Section 4.1).
5. A preliminary kinetic assessment was attempted but is not reported as quantitative evidence in this study because the underlying data were reconstructed rather than continuously measured; establishing the sorption rate law for zeolite and clay under properly instrumented, time-resolved conditions is identified as a priority for future work (Section 4.5).
6. The exclusion of three of the five originally tested materials underscores the importance of explicit mass-balance validation in gravimetric sorption studies; this study makes both the validated dataset and the rationale for exclusion transparent, and identifies the re-measurement of peat, wood sawdust, and hops under a mass-balance-verified protocol as a priority for future work.
7. Both zeolite and clay are abundantly available in Romania and require minimal processing. Their complementary hydrocarbon selectivity (clay for motor oil, zeolite for diesel) is a promising bench-scale finding that warrants testing under realistic environmental matrices (soil, sediment, or water surface conditions; Section 4.5) before any recommendation regarding field deployment in spill-response scenarios.

These results provide a mass-balance-validated, protocol-specific bench-scale ranking of zeolite and clay as candidate sorbents for used motor oil and diesel fuel, and, more broadly, a worked demonstration of why explicit mass-balance validation is a necessary quality-control step in gravimetric sorption testing (Section 4.6). Because the absolute capacities measured are substantially higher than comparable literature values for raw clinoptilolite and bentonite (Section 4.5), direct verification of the reported magnitudes—for example, longer drainage times, granular-versus-powder comparisons, and empty-container controls—is identified as a prerequisite before these values are used for material ranking beyond this exact protocol. Testing under realistic environmental matrices, extending the validated dataset to the remaining candidate materials under a corrected and fully documented protocol, and direct physicochemical characterization are identified as further immediate next steps before this line of research can support field-deployment recommendations.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/app16167865/s1>, Data S1: Raw gravimetric replicate values (validated dataset: zeolite and clay); Table S1: Mass-balance calculation underlying the exclusion of peat, wood sawdust, and hops (Section 2.3), including the assumed hydrocarbon density range, the fixed dose volume and dry sorbent mass, the resulting maximum physically possible uptake for each hydrocarbon, and an explicit statement of which candidate causes of the excess apparent uptake (container residue, retained free liquid, drainage-time variability, balance/tare error) could and could not be evaluated, given the available laboratory records.

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