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COMPARATIVE STUDY OF THERMALLY MODIFIED PEAT AND BARK-BASED SUBSTRATES FOR HEAVY METAL REMOVAL FROM WASTEWATER

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Wastewater generated from drilling fluid treatment, oil exploitation, and refinery processes is strongly contaminated with heavy metals, necessitating efficient remediation strategies. This study investigates the effectiveness of two thermally modified natural sorbents – potting soil (bark) and peat – for the removal of Cu, Cr, Cd, and Pb from industrial effluents. Both materials were thermally treated at 105 °C to achieve a stable hydrophobic state before testing their retention efficiency over a 24-hour period. Metal concentrations were determined using flame atomic absorption spectrometry (FAAS) for Cu(II) and graphite furnace atomic absorption spectrometry (GFAAS) for Cd, Pb, and Cr. Results indicated that the bark-based substrate achieved superior retention, particularly for Pb and Cr, reaching near-quantitative removal (>99%) within the first hour. In contrast, peat showed lower efficiency for Cd (15%) compared with the 97% achieved by the modified bark. A numerical model using fourth-order polynomial equations was developed to simulate adsorption kinetics, revealing that the superior performance of the bark-based material is linked to its higher hydrophobicity and favorable pH. This study demonstrates that modified natural sorbents offer a sustainable and cost-effective alternative to conventional chemical or thermal separation technologies.

Keywords: metals, natural sorbents, peat, bark, modelling, atomic absorption spectrometry

1. Introduction

Wastewater generated during the treatment of drilling fluids, oil extraction, and refinery distillation processes is characterized by complex contamination with heavy metal ions. The presence of copper (Cu), chromium (Cr), cadmium (Cd), and lead (Pb) results from crude oil migration within deposits and subsequent transport and processing phases. Efficient removal of these toxic elements is essential to facilitate the reuse of industrial water or to comply with natural discharge regulations [1].

Current separation technologies, such as thermal or chemical precipitation, are often cost-prohibitive, and the development of non-conventional, 100% natural, biodegradable sorbents has gained attraction as an economical and flexible alternative [2].

Among these, peat and bark-based materials are of particular interest because of their high organic matter content, which includes humic substances (complex molecules derived from decayed plant material) and non-humic substances such as carbohydrates (sugars) and amino acids (building blocks of proteins) [3].

The literature indicates that natural materials such as tree bark, chitosan, and peat can exhibit significant adsorption capacities, with values reported as high as 76 mg/g Cr (III) for peat and 1587 mg/g Pb for lignin. In many studies, the performance of these organic sorbents is highly sensitive to their degree of hydrophobicity and the accessibility of their binding sites. While peat is traditionally valued for carbon sequestration, its efficacy in adsorbing specific heavy metal ions from multicomponent industrial mixtures remains to be investigated [4].

A critical research gap exists in the systematic comparison of commercially available, thermally modified Romanian peat with bark-based substrates [5]. Specifically, there are limited data on how thermal treatment at 105 °C alters the kinetic performance and

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equilibrium stability of these readily accessible materials in a competitive, multi-metal environment [6].

The organic structures of peat and bark, which are rich in functional groups such as carboxyl and phenolic groups, allow the efficient adsorption of heavy metal ions. Processes such as ion exchange, pore diffusion, and chelation contribute to the mechanisms of metal retention in wastewater.

Some natural sorbents, such as pyrolusite and sawdust, have demonstrated high efficiencies in the removal of ions such as Pb(II), Cd(II), and Cu(II). Modified materials, including zeolites treated with metal particles or functionalized carbon nanotubes, show significantly improved adsorption capacities [7].

Recent studies show that factors such as pH, humidity, thermal treatments, and chemical modifications significantly influence adsorption efficiency. Overall, natural and modified sorbents represent efficient, economical, and versatile solutions for the treatment of water contaminated with heavy metals [8].

This study aims to systematically compare the adsorption kinetics and equilibrium stability of commercially available, thermally modified Romanian peat and bark-based substrates in multi-metal industrial wastewater. We hypothesize that thermal modification significantly enhances the hydrophobicity of bark-based substrates relative to standard peat, resulting in superior initial kinetics and overall removal efficiency for lead and chromium [9].

This investigation is of significant industrial importance because identifying an efficient, readily available natural sorbent can significantly reduce the operational costs of treating oil-industry effluents while ensuring compliance with stringent environmental safety standards.

2. Materials and methods

The simulated wastewater was prepared as a multi-metal mixture to accurately reflect industrial competition for active sites. Analytical-grade salts (>99% purity), including $CuCl_2$, $Cr(NO_3)_3$, $CdCl_2$, and $Pb(NO_3)_2$, were utilized to prepare the solutions.

2.1. Samples

In this work, two natural sorbents were tested for the decontamination of water contaminated with heavy metals: high-quality peat enriched with a nutrient substrate (referred to as peat) and peat mixed with pine bark and natural animal manure (referred to as potting soil (bark)).

2.2. Adsorbent preparation

Two commercially available natural organic materials were sourced from Romania for evaluation: high-quality peat enriched with a nutrient substrate (peat) and a bark-based mixture containing pine bark and natural fertilizers (potting soil (bark)) (*Figures 1–4*).



Figure 1: Peat mixed with pine bark and natural fertilizers

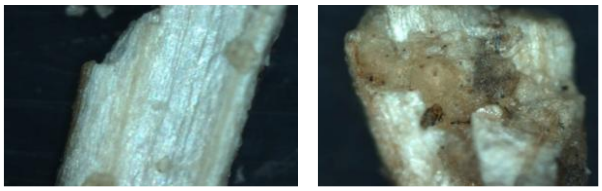


Figure 2: Microscopic image 10 x magnification of peat mixed with pine bark and natural fertilizers (flower soil)



Figure 3: Peat

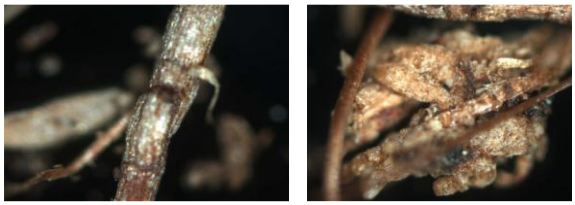


Figure 4: Microscopic image 10 x magnification of peat

2.3. Material characterization

The characteristics of the sorbents are presented in *Table 1*. To modify these materials from their native hydrophilic state to a hydrophobic form, both sorbents underwent thermal drying treatment at 105 °C in a laboratory oven until a stable moisture content was achieved. The main characteristics of the thermally

Table 1: Properties of potting soil (bark) and peat used in the experiment (data on the product label)

Property	Potting soil (bark)	Peat
Moisture %	12	11
pH (aqueous filtrate)	7.14	6.23
Conductivity mS/cm	1.291	0.82

Table 2: Characteristics of thermally modified peat

Property	Potting soil (bark)	Peat
Composition	Peat mixed with pine bark and natural fertilizers (flower soil)	High-quality peat enriched with nutrient substrate (peat)
Electrical conductivity (mS/cm)	0.02	max. 0.5
pH (aqueous filtrate)	5.5-6.5	5-6.5
Water holding (retention) capacity	75%	max. 65%
Nitrogen total (%)	0.8%	max. 1.4%

Table 3: Operating conditions for atomic absorption

Metals	λ (nm)	Detection limit (mg/L)	Limit of quantification (mg/L)
Cu	324	0.2011	0.7692
Cd	228	0.1000	0.8000
Pb	283	0.5558	2.0140
Cr	357	0.6155	2.332

modified peat are presented in *Table 2*. The final moisture content was recorded at 11% for peat and 12% for potting soil (bark) [5].

The properties of the thermally modified sorbents were analyzed to establish baseline characteristics of the aqueous filtrate, and pH was determined using a pH/Cond 340i glass electrode.

Conductivity was measured using a Consort C3030 multi-parameter analyzer. The post-treatment pH was 6.23 for peat and 7.14 for potting soil (bark), and the conductivity values were 0.82 mS/cm for peat and 1.291 mS/cm for potting soil (bark).

2.4. Reagents and materials

The initial concentration (C_0) of each heavy metal ion (Cu^{2+}, Cr^{3+}, Cd^{2+}, and Pb^{2+}) was fixed at 0.1 g/L (100 mg/L) within the same 2 L volume.

Adsorption tests were conducted at a constant room temperature (≈ 25 °C) to simulate standard industrial operating conditions. The mass-to-volume ratio was 200 g of the selected thermally modified sorbent added to 2 L of the multi-metal solution.

The chosen sorbent was added to 2 L of the multi-metal solution to establish a 1:10 solid-to-liquid ratio. The mixture was subjected to continuous mechanical stirring to ensure uniform exposure of the adsorbent surface to the metal ions. Aliquots of the solution were collected at five distinct time intervals (1, 2, 5, 8, and 24 hours). Immediately following sampling, the aqueous phase was separated from the adsorbent by filtration to halt further reactivity.

2.5. Adsorption studies

The remaining metal concentration in each filtrate sample was quantified via atomic absorption spectrometry (AAS). The Cu(II) concentration was determined using flame atomic absorption spectrometry (FAAS) with a ZEEnit 700P instrument, whereas Cd, Pb, and Cr were analyzed using graphite furnace atomic absorption spectrometry (GFAAS).

As shown in *Table 3*, specific wavelengths were used for the detection of Cu, Cd, Pb, and Cr, with the following calibration-curve equations: $y = 0.00527 + 0.0855x$ and $R^2 = 0.9982$ for Cu; $y = 0.00271 + 0.0461x$ and $R^2 = 0.9986$ for Cd; $y = 0.00166 + 0.0039x$ and $R^2 = 0.9960$ for Pb; and $y = 0.00389 + 0.0117x$ and $R^2 = 0.9957$ for Cr.

All experiments were performed in triplicate to ensure statistical reliability.

3. Results

The main objective of the study was to test the retention capacity of selected metals on the natural sorbents evaluated. *Figures 5–8*, illustrating metal retention on potting soil (bark) and peat, present data collected at room temperature.

Following the analyses, potting soil (bark) showed a cadmium retention capacity of 72% after the first hour and 97% after 24 hours, whereas peat showed progressively lower retention, starting at 3% in the first hour and reaching approximately 15% after 24 hours (*Figure 5*).

In the second experiment, the lead retention capacity of peat was 68% in the first hour and 83% after 24 hours. In contrast, potting soil (bark) showed a retention capacity of over 99% Pb in the first hour, and this value remained constant throughout the 24-hour period (*Figure 6*).

The third experiment analyzed copper retention (*Figure 7*), showing that the percentage retained by

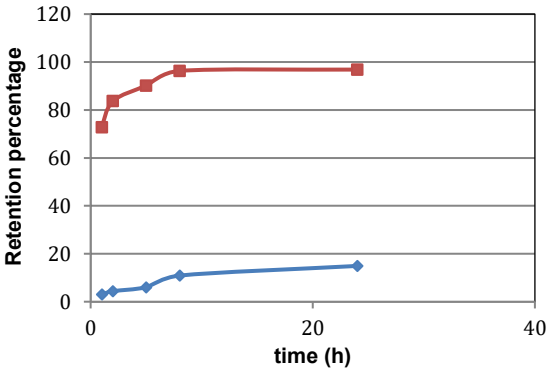


Figure 5: Cd retentions percentage (%) (■ bark, ◆ peat)

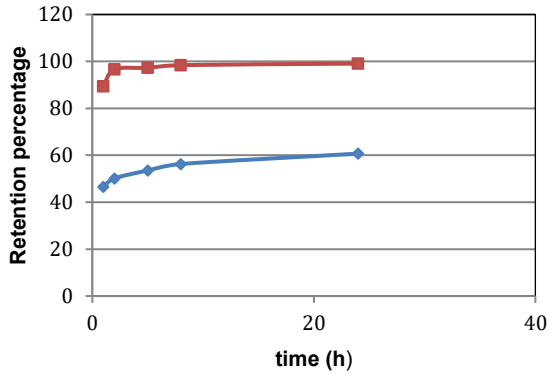


Figure 7: Cu retentions percentage (%) (■ bark, ◆ peat)

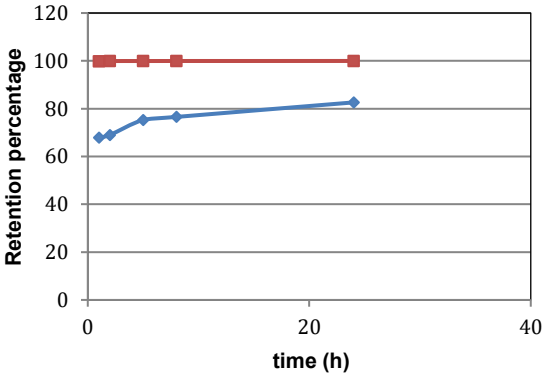


Figure 6: Pb retentions percentage (%) (■ bark, ◆ peat)

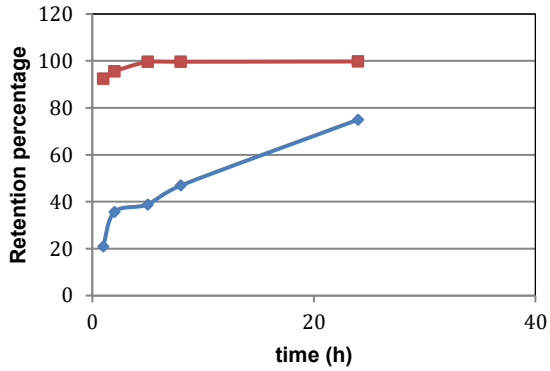


Figure 8: Cr retentions percentage (%) (■ bark, ◆ peat)

potting soil (bark) was higher than that obtained with peat. After the first hour, peat retained 47% Cu and reached 61% after 24 hours. Potting soil (bark) showed 90% retention in the first hour and then remained constant from the second hour, with 98–99% retention.

The fourth experiment assessed chromium retention on the materials (*Figure 8*). After the first hour, the porous structure of potting soil (bark) retained 92% Cr, and after five hours, it was possible to retain over 99% Cr. Peat substrate initially retained 21% Cr and reached 75% after 24 hours.

In *Table 4*, we proposed equations to determine the percentage of removal at any time between 1 and 24 hours for metals in wastewater using the two sorbents.

In our proposed model, y represents the percentage of metal removal, and x denotes the contact time in hours (valid for the interval $1 < x < 24$).

Table 4: Equation for determining the percentage of removal at any time (peat and bark)

Metals	Equation	Total metal removal percentage, %
	Peat	
Cu	$y = -0.0111x^4 + 0.4318x^3 - 4.684x^2 + 18.436x + 75.197$	96.5
Cd	$y = -0.0136x^4 + 0.5252x^3 - 5.7426x^2 + 24.635x + 53.396$	97.4
Pb	$y = -0.0003x^4 + 0.0103x^3 - 0.1113x^2 + 0.4361x + 99.405$	99.4
Cr	$y = -0.0009x^4 + 0.0442x^3 - 0.7452x^2 + 5.019x + 88.143$	98.7
	Bark	
Cu	$y = -0.0036x^4 + 0.1423x^3 - 1.5867x^2 + 7.419x + 40.589$	94.6
Cd	$y = -0.0028x^4 + 0.0968x^3 - 0.8331x^2 + 3.1735x + 63.56$	95.8
Pb	$y = 0.0037x^4 - 0.1322x^3 + 1.1141x^2 - 1.3025x + 68.157$	91.5
Cr	$y = -0.0237x^4 + 0.9084x^3 - 9.5818x^2 + 37.482x - 7.7947$	97.5

For most scenarios, the adsorption rate at 24 hours becomes negligible (approximately 0.01%/h), supporting the assumption that 24 hours is a sufficient contact time to achieve equilibrium. We calculated the equilibrium adsorption rate (Ve) for all eight scenarios at a contact time of x = 24 hours.

Lead adsorption on peat mathematically reached equilibrium, exhibiting a negligible rate of 0.001%/h. In contrast, lead adsorption on potting soil (bark) continued to show the highest positive rate at 24 hours (0.18%/h); this suggests that, although an efficiency of 91.53% was achieved, true equilibrium may require a longer contact time (e.g., 48 hours).

Regarding initial kinetics, chromium on potting soil (bark) maintained the highest rate at 18.77%/h, indicating very fast external mass transfer and rapid initial adsorption.

Conversely, the fastest kinetics on the peat substrate were observed for cadmium (14.88%/h), indicating a rapidly accessible surface area, whereas lead on peat exhibited the slowest overall initial kinetics at just 0.24%/h.

The equilibrium adsorption rate should be close to zero, indicating that equilibrium has been reached (*Table 5*) [8]-[9].

We used the following equation:

$$V_e = \frac{dy}{dx} = 4ax^3 + 3bx^2 + 2cx + d \qquad (1).$$

We also calculated the initial adsorption rate (V_{init}), which is given by the derivative of the polynomial function [10],[11]:

$$V_{init} = 4a + 3b + 2c + d \qquad (2).$$

This value indicates how quickly the metal removal process started in the first hour (%/h) (*Table 5*).

As previously established, although slow, this scenario achieves 99.74% removal in the first hour (an almost instantaneous process), making the instantaneous rate at x = 1 practically insignificant (*Table 5*).

The percentage of removal at 1 hour (y_1) is calculated by substituting x = 1 into the original polynomial equation [12]:

$$y = ax^4 + bx^3 + cx^2 + dx^1 + f = \\ = a + b + c + d + f \qquad (3).$$

Using the next equation, we calculated the adsorption capacity at equilibrium (*Table 6*):

$$q_e = \frac{C_0 y_e}{100\frac{m}{V}} \qquad (4).$$

We constructed the Langmuir isotherms based on the relationships shown in *Table 6* [13]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (5),$$

$$C_e = C_0 - q_e \frac{m}{V} = 100 - q_e \qquad (6).$$

Table 5: Calculated rate at x=24 h (*Equation 1*), initial absorption rate (V_{init}), and percentage of removal after 1 hour (y_1)

Metals/ sorbents	Coefficients (a, b, c, d, f)	V_e (%/hours)	Stability	V_{init} (%/hours)	Stability	y_1 (%)
Cu/ peat	a=-0.0111, b=0.4318, c=-4.684, d=18.436, f=75.197	0.02	very stable	10.57	very stable	89.37
Cd/ peat	a=-0.0136, b=0.5252, c=-5.7436, d=24.635, f=53.396	0.01	very stable	14.48	very stable	72.79
Pb/ peat	a=-0.0003, b=0.5252, c=-5.7426, d=24.636, f=99.405	0.00	equilibrium	0.24	equilibrium	99.74
Cr/peat	a=-0.0009, b=0.0442, c=-0.7452, d=5.019, f=88.143	0.01	very stable	3.67	very stable	92.46
Cu/ bark	a=-0.0036, b=0.1423, c=-1.5867, d=7.419, f=40.589	0.01	very stable	4.71	very stable	46.56
Cd/ bark	a=-0.0028, b=0.0968, c=-0.8331, d=3.1735, f=63.56	0.01	very stable	1.45	very stable	65.99
Pb/ bark	a=-0.0037, b=-0.1322, c=1.1141, d=-1.3025, f=68.157	0.01	slightly increasing	0.86	slightly increasing	67.84
Cr/ bark	a=-0.0237, b=0.9084, c=-9.5818, d=37.482, f=-7.7947	0.01	very stable	18.57	very stable	20.99

Table 6: Equations for determining adsorption capacity at equilibrium (Langmuir, Freundlich, and Temkin isotherms)

Metals/ sorbents	y_e (%)	C_e (mg/L)	b (L/mg)	Langmuir isotherm equation	K_f	Freundlich isotherm equation	A_T	Temkin isotherm equation
Cu/ peat	96.53	3.47	0.29	$q_e = \frac{29 \cdot C_e}{1 + 0.29 \cdot C_e}$	51.81	$q_e = 51.81 \cdot C_e^{0.5}$	13.56	$q_e = 26.07 + 10 \cdot \ln C_e)$
Cd/ peat	97.41	2.59	0.40	$q_e = \frac{40 \cdot C_e}{1 + 0.40 \cdot C_e}$	60.55	$q_e = 60.55 \cdot C_e^{0.5}$	10.13	$q_e = 23.15 + 10 \cdot \ln C_e)$
Pb/ peat	99.40	0.60	16.57	$q_e = \frac{1657 \cdot C_e}{1 + 16{,}57 \cdot C_e}$	128.32	$q_e = 128.32 \cdot C_e^{0.5}$	22.21	$q_e = 30.91 + 10 \cdot \ln C_e)$
Cr/peat	98.67	1.33	7.42	$q_e = \frac{742 \cdot C_e}{1 + 7{,}42 \cdot C_e}$	85.67	$q_e = 85.67 \cdot C_e^{0.5}$	10.08	$q_e = 23.10 + 10 \cdot \ln C_e)$
Cu/ bark	94.61	5.39	0.18	$q_e = \frac{18 \cdot C_e}{1 + 0.18 \cdot C_e}$	40.75	$q_e = 40.75 \cdot C_e^{0.5}$	8.59	$q_e = 22.51 + 10 \cdot \ln C_e)$
Cd/ bark	69.87	30.13	0.03	$q_e = \frac{2 \cdot C_e}{1 + 0.03 \cdot C_e}$	12.72	$q_e = 12.72 \cdot C_e^{0.5}$	0.51	$q_e = -6.71 + 10 \cdot \ln C_e)$
Pb/ bark	91.53	8.47	0.11	$q_e = \frac{11 \cdot C_e}{1 + 0.11 \cdot C_e}$	31.47	$q_e = 31.47 \cdot C_e^{0.5}$	4.29	$q_e = 14.56 + 10 \cdot \ln C_e)$
Cr/ bark	97.49	2.51	0.40	$q_e = \frac{40 \cdot C_e}{1 + 0.40 \cdot C_e}$	61.57	$q_e = 61.57 \cdot C_e^{0.5}$	10.02	$q_e = 23.04 + 10 \cdot \ln C_e)$

We constructed the Freundlich isotherms based on the relationship shown in *Table 6* [14],[15]:

$$q_e = K_f C_e^{1/n} \quad (7).$$

We calculated the constant K_f based on the q_e and C_e values above, using a standard exponent of $1/n = 0.5$ (typical for adsorption on heterogeneous surfaces).

We also constructed the Temkin isotherms based on the relationship shown in *Table 6* [13]:

$$q_e = B\ ln(A_T) + B\ ln(C_e) \quad (8).$$

We used a standard constant of $B = 10$ (related to the heat of adsorption) and calculated the binding constant A_T for each scenario using q_e and C_e [16].

$$A_T = e^{(\frac{q_e}{B} - \ln(C_e))} \quad (9).$$

In *Table 6*, the b value represents the affinity or binding energy between the metal and the sorbent.

A high b value (e.g., Pb on peat, $b = 16.57$) indicates a very strong affinity, explaining why lead removal was virtually instantaneous and reached 99.74% in one hour.

A low b value (e.g., Cd on bark, $b = 0.03$) indicates a weaker affinity, correlating with the lower initial retention performance of cadmium compared with other metals.

The mechanism of adsorption involves a combination of ion exchange and surface complexation with the organic matter (humic acids and peptides) present in the sorbents.

The thermal treatment at 105 °C specifically modifies the hydrophobicity of the materials, which was found to be much higher in potting soil (bark) than in peat, significantly influencing metal ion retention.

An analysis of the kinetic data reveals:

1. Almost instantaneous adsorption (Large discrepancy)

Lead on peat, with a discrepancy of 99.50%, represents the extreme case.

The affinity of peat for lead is so high that most of the available lead ions were adsorbed within the first few minutes.

The adsorption rate decreased drastically after $x = 0$, reaching 99.74% at $x = 1$ hour.

This is typical of controlled rapid ion exchange processes on surface sites.

2. Consistent adsorption (Small discrepancy)

Chromium on potting soil (bark), with a discrepancy of 2.22%, shows the best fit.

The initial rate (18.77%/hour) is very close to the actual percentage achieved (20.99%).

This suggests that the removal rate remained relatively constant (or changed slowly) during the first hour.

The process could be limited by rapid external diffusion followed by slow chemisorption or pore diffusion.

3. General case (Peat vs. soil)

Most of the peat scenarios have very large discrepancies. This indicates that peat has an abundance of readily accessible sites and that the polynomial model does not

adequately capture the rapid saturation kinetics in the first quarter of an hour.

The performance of the modified potting soil (bark) in this study shows significant improvements over several alternative low-cost sorbents reported in the literature.

Lead (Pb) retention on the bark-based substrate achieved near-quantitative removal (>99%) within the first hour. This surpasses the efficiency of pyrolusite, which also reaches 100% but often requires strictly controlled neutral pH conditions, and dried cabbage leaves, which reached 95.67% efficacy only after 120 minutes.

While some alternative sorbents remove up to 72.35% of Cd(II) at pH = 6, the modified bark in this study achieved 97% removal after 24 hours.

Chromium retention reached over 99% after five hours, which is higher than the 76 mg/g capacity typically reported for standard peat under isolated conditions.

A critical observation in this study is the substantial difference in performance between the two sorbents regarding cadmium: peat performed poorly (3–15%), whereas potting soil (bark) achieved near-quantitative removal for Pb and Cr.

The superior performance of the bark-based substrate is fundamentally linked to its higher degree of hydrophobicity following thermal treatment.

Furthermore, the bark substrate maintained a higher filtrate pH (7.14) than peat (6.23). Higher pH levels generally reduce the solubility of metal ions and decrease competition with protons (H^+) for active binding sites. In the multi-metal mixture used (0.1 g/L of each salt), the poor retention of Cd on peat suggests a low affinity in the presence of competing ions. The Pb and Cr ions exhibit higher binding energies for the carboxyl and phenolic functional groups present in the organic matrix, effectively displacing Cd through a competitive ion-exchange mechanism. A special analysis is dedicated to structural encapsulation because the bark material's complex organic composition likely provides more heterogeneous and stable binding sites for Pb and Cr, allowing for the observed 'instantaneous' adsorption that characterized these specific interactions.

This surpasses the efficiency of pyrolusite, which also reaches 100% but often requires strictly controlled neutral pH conditions, and dried cabbage leaves, which reached 95.67% efficacy only after 120 minutes. While some alternative sorbents remove up to 72.35% of Cd(II) at pH = 6, the modified bark in this study achieved 97% removal after 24 hours.

4. Discussion

The comparative analysis highlights a stark contrast between the two sorbents, driven primarily by their degree of hydrophobicity and functional group accessibility.

The most significant performance gap was observed for cadmium; the bark substrate achieved 97% removal after 24 hours, whereas peat reached only 15%.

This low efficiency for cadmium on peat (3–15%) suggests intense competition for active sites in a multi-metal mixture.

Conversely, lead and chromium achieved near-quantitative removal on the bark, likely due to a higher affinity for the carboxylic and phenolic groups abundant in its lignin-rich matrix. Lead adsorption on the bark substrate was virtually instantaneous, maintaining over 99% retention from the first hour.

This strong interaction is reflected in the high Langmuir affinity constant (b = 16.57 L/mg for lead on peat), indicating a significantly higher binding energy compared with other divalent cations.

The fourth-order polynomial model accurately captured the system's non-linear kinetics. Chromium on bark exhibited the fastest initial kinetics (18.57%/h), indicating high surface availability and rapid external mass transfer.

Most scenarios reached a stable equilibrium within 24 hours (V_e = 0.01%/h), confirming that this duration is sufficient for industrial applications. Furthermore, the bark-based scenarios for copper, cadmium, and lead demonstrated maximum Langmuir adsorption capacities exceeding 106 mg/L, suggesting that they can handle higher pollutant loads than peat, which was capped at approximately 100 mg/L.

The bark's superior performance is fundamentally linked to its enhanced hydrophobicity from thermal modification and its higher initial filtrate pH of 7.14, compared with peat's pH of 6.23.

This higher pH likely facilitated the retention of metals such as chromium and lead by promoting surface complexation or localized hydrolysis.

To fully validate these mechanisms, future studies should utilize Fourier-transform infrared spectroscopy (FTIR) to identify the specific carboxyl and phenolic groups responsible for metal binding.

Additionally, Brunauer–Emmett–Teller (BET) surface area analysis could provide a physical basis for the bark's superior retention capacity.

Finally, investigating these sorbents under dynamic flow conditions in fixed-bed columns will be essential for simulating industrial wastewater treatment plants.

5. Conclusions

This study evaluated the retention capacity of heavy metals from simulated oil-industry wastewater using two thermally modified natural sorbents.

The following conclusions are derived directly from the experimental results and numerical modeling:

Sorbent performance and efficiency: potting soil (bark) demonstrated superior overall performance compared with peat, achieving near-quantitative removal (>99%) for Pb and Cr within 5 hours.

Kinetic modeling: The application of a fourth-order polynomial model effectively simulated the non-linear adsorption process.

Lead on peat reached an equilibrium of 99.74% removal almost instantaneously (within 1 hour), while

chromium on bark exhibited the highest initial mass transfer rate of 18.5% within 1 hour.

Adsorption capacity and affinity: calculation of the maximum Langmuir adsorption capacity q_m and the affinity constant b confirmed high site selectivity, particularly for Pb on peat (b = 16.57 L/mg). The bark-based substrate showed higher theoretical removal thresholds (>106 mg/L) for several metals.

Economic viability (low-cost treatment): The use of commercially available natural materials, modified through simple low-temperature thermal drying (105 °C), confirms this technique as a low-cost alternative to expensive industrial chemical precipitation or thermal separation technologies.

Performance disparity: The significant gap in Cd retention – where peat achieved only 15% compared with 97% for bark – is attributed to the superior hydrophobicity and favorable pH (7.14) of the modified bark matrix, which reduces proton competition and enhances metal sequestration in multi-metal environments.

Scope of findings: While the sorbents showed high removal capacity, this study focused strictly on adsorption kinetics and equilibrium. Dedicated investigations into sorbent regeneration, reusability, and dynamic flow conditions remain subjects for future research to further optimize the industrial lifecycle of these materials.

FTIR and functional groups: We acknowledged that Fourier-transform infrared spectroscopy (FTIR) analysis would help identify the active functional groups. Peat and bark contain complex organic structures such as humic acids, carbohydrates, and peptides. The retention of metals occurs through chemical bonds formed with this organic fraction.

Surface area and microscopy: While not provided in the initial draft, the 'superior retention capacity' of the bark-based substrate is likely linked to its porosity and specific surface area. Thermal treatment at 105 °C was used to modify these characteristics and obtain a hydrophobic material.

REFERENCES

[1] Ciufu, A.-G., Chis, T.-V., & Dobre, T. (2015). Adsorption of crude oil using biosorbents in accidental oil spills. *Bulletin of Romanian Chemical Engineering Society*, *2*(2), 46–51.

[2] Popiţa, G., Varga, I., Modoi, C., Haţegan, R., & Popovici, A. (2011). Heavy metal contamination assessment and its environmental impact in the area of rural waste disposals in Cluj county, Romania. *Hungarian Journal of Industry and Chemistry, 39*(2), 271–278. https://doi.org/10.1515/423.

[3] Deng, S., Zhang, X., Zhu, Y., & Zhuo, R. (2024). Recent advances in phyto-combined remediation of heavy metal pollution in soil. *Biotechnology Advances, 72*, Article 108337. https://doi.org/10.1016/j.biotechadv.2024.108337

[4] Li, C., Sanchez, G. M., Wu, Z., Cheng, J., Zhang, S., Wang, Q., Li, F., Sun, G., & Meentemeyer, R. K. (2020). Spatiotemporal patterns and drivers of soil contamination with heavy metals during an intensive urbanization period (1989–2018) in southern China. *Environmental Pollution*, *260*, Article 114075. https://doi.org/10.1016/j.envpol.2020.114075

[5] Ciufu, A.-G., & Chis, T.-V. (2014). Application of natural sorbents in oil spill cleanup. *Bulletin of Romanian Chemical Engineering Society*, *1*(2), 15–28.

[6] Yadava, K. P., Tyagi, B. S., & Singh, V. N. (1991). Effect of temperature on the removal of lead(II) by adsorption on China clay and wollastonite. *Journal of Chemical Technology and Biotechnology*, *51*(1), 47–60. https://doi.org/10.1002/jctb.280510105

[7] Abdul Raheem, N., Selvaraj, G.-K., Karuppanan, K., Ganesan, G., Soorangkattan, S., Subramanian, B., Ramamurthy Baluraj, S., Rajaiah, D. K., & Hasan, I. (2025). Bioremediation of heavy metals by an unexplored bacterium *Pseudoxanthomonas Mexican* strain GTZY isolated from aerobic-biofilm wastewater system. *Environmental Science and Pollution Research, 32*(37), 22036–22050. https://doi.org/10.1007/s11356-024-34602-1

[8] Aljohani, M. S., Alnoman, R. B., Alharbi, H. Y., Al-Anazia, M., & Monier, M. (2024). Designing of a cellulose-based ion-imprinted biosorbent for selective removal of lead (II) from aqueous solutions. *International Journal of Biological Macromolecules*, *259*(2), Article 129145. https://doi.org/10.1016/j.ijbiomac.2023.129145

[9] Abu-Shahba, M. S., Mansour, M. M., Mohamed, H. I., & Sofy, M. R. (2022). Effect of biosorptive removal of cadmium ions from hydroponic solution containing indigenous garlic peel and mercerized garlic peel on lettuce productivity. *Scientia Horticulturae*, 293, Article 110727. https://doi.org/10.1016/j.scienta.2021.110727

[10] Mohamed, H. I., Ullah, I., Toor, M. D., Tanveer, N. A., Ud Din, M. M., Basit, A., Sultan, Y., Muhammad, M., & Rehman, M. U. (2025). Heavy metals toxicity in plants: understanding mechanisms and developing coping strategies for remediation: a review. *Bioresources and Bioprocessing*, *12*(1), Article 95. https://doi.org/10.1186/s40643-025-00930-4

[11] Chatterjee, S., Mukherjee, A., & Ranganathan, S. (2023). Metal-microbe interactions and their implications in bioremediation. *Frontiers in Cellular and Infection Microbiology*, *13*, Article 1121230. https://10.3389/fmicb.2023.1121230

[12] Chernyshova, I., Slabov, V., & Kota, H. R. (2023). Emerging application of biosurfactants in metal extraction. *Current Opinion in Colloid & Interface Science*, *68*, Article 101763. https://doi.org/10.1016/j.cocis.2023.101763

[13] Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, *156*(1), 2–10. https://doi.org/10.1016/j.cej.2009.09.013

[14] Pradas, E. G., Sánchez, M. V., Cruz, F. C., Viciana, M. S., & Pérez, M. F. (1994) Adsorption of cadmium and zinc from aqueous solution on natural and activated bentonite. *Journal of Chemical Technology and Biotechnology*, *59*(3), 289–295. https://doi.org/10.1002/jctb.280590312

[15] Pan, F., Meng, Q., Luo, S., Shen, J., Chen, B., Khan, K. Y., Japenga, J., Ma, X., Yang, X., Feng, Y. (2017) Enhanced Cd extraction of oilseed rape (*Brassica napus*) by plant growth-promoting bacteria isolated from Cd hyperaccumulator *Sedum alfredii* Hance. *International Journal of Phytoremediation*, *19*(3), 281–289. https://doi.org/10.1080/15226514.2016.1225280

[16] Perveen, S., Parveen, A., Hussain, I., Rasheed, R., Mahmood, S., Ashraf, M. A., & Hassan, A. (2024) Nanotechnological approaches for restoring metalloid contaminated soil. In V. D. Rajput, A. Kumari, & T. M.. Minkina (Eds.), *Nano-bioremediation for water and soil treatment: An eco-friendly approach* (1st edition). Apple Academic Press.