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Apple Waste Recovery to Remove Phthalate Residues from Water

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Abstract

Phthalates are recognized as emerging environmental contaminants and are classified as endocrine-disrupting chemicals, as they can induce various toxic effects in organisms and interfere with hormonal functions in biological systems, thereby posing significant health risks. In this study, contamination of environmental matrices with phthalate residues—including water, agricultural soils, and grapes—was investigated. In addition, the sorption behavior of dibutyl phthalate (DBP) and di-(2-ethylhexyl phthalate (DEHP) from aqueous solutions onto biochars derived from apple residues and functionalized with metal oxides (Fe_3O_4 and NiO), green-synthesized using plant extracts from *Urtica dioica* L. with the aim of their preliminary application in environmental remediation and the reduction of food-chain contamination risks. Several experimental series were conducted, including the determination of the sorption capacity of the biochars as a function of pH (3 - 9), characterization of adsorption isotherms at three temperatures (288 K, 298 K, and 308 K), and the thermodynamic parameters of adsorption. The experimental data were interpreted using the Langmuir and the Freundlich isotherm models. Furthermore, the thermodynamic parameters of the DBP sorption process onto the biochars, namely Gibbs free energy (ΔG_0), enthalpy (ΔH_0), and entropy (ΔS_0), were calculated.

Keywords

Apple Waste, Biochar, Metal Oxides, Water, Phthalates Decontamination

1. Introduction

Endocrine-disrupting chemicals (EDCs) are individual compounds or mixtures that can interfere with the normal functioning of hormones, leading to various diseases or even death. Estimates suggest that more than 24% of human diseases and disorders worldwide are attributable to environmental factors, which play a role in approximately 80% of the most fatal diseases, including cancer, cardiovascular diseases, and others. Environmental EDCs can contribute to hormonal imbalances that result in diabetes, neurological disorders, reproductive disorders, inflammation, and impaired immune function [1] [2]. Humans may be exposed to EDCs through a wide range of products and exposure pathways, including residues of plasticizers, pesticides, atmospheric pollutants, and industrial waste, among others [3]. Exposure to EDCs can be harmful at any age; however, it is particularly detrimental when it occurs during sensitive developmental periods, such as fetal development, childhood, adolescence, and pregnancy. Phthalates, recognized as ubiquitous EDCs, have been in use for more than 50 years, with an annual global production of approximately 6 million tonnes. They have numerous applications and are found in plastics, cosmetics, medical devices, and many other products. As a result, they are ubiquitous in everyday consumer goods, and their environmental impact is widely monitored [4]-[6]. Although these "emerging" contaminants are less persistent and less toxic than other priority substances (e.g., polychlorinated biphenyls, PCBs), their widespread presence across all environmental compartments underscores the need to reduce water and soil contamination in order to prevent the entry of these EDCs into the food chain [7].

The concept of the exposome encompasses the cumulative effects of environmental exposures on human health throughout the lifespan. Access to clean drinking water is considered a fundamental human right. Previous studies have identified more than 30 types of phthalates and their subtypes originating from various sources of contamination, including tap water, bottled water, water purification systems, and related sources [8]. As a vital component of daily intake, the abundance and diversity of phthalates in drinking water sources therefore raise concerns regarding the long-term safety of their consumption.

The World Health Organization (WHO) has established guideline values for acceptable levels of phthalates in drinking water; for example, limits of 1.3 and 3 μg/L have been set for di-(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP), respectively [9]. Studies conducted in various countries indicate that phthalate concentrations in raw water sources—and subsequently in tap water—range from 0.77 to 1438.20 μg/L [10], significantly exceeding the WHO-recommended limits. Such elevated concentrations may result in substantial lifetime exposure and accumulation of these compounds in the human body. In the face of severe water contamination, it is essential to develop effective remediation methods based on low-cost materials. Adsorption is a widely adopted technique for pollutant removal in wastewater treatment due to its relatively high efficiency, low cost, environmental friendliness, and operational simplicity [11]. The production of high-value materials such as biochar derived from agro-industrial waste represents a priority for maintaining ecological balance and is a key objective within the principles of the circular economy [12].

The properties of biochar are to some extent comparable to those of activated carbon, making it a reliable material for the removal of various impurities [13]. The selection of appropriate feedstocks and thermochemical conversion pathways is a decisive factor for achieving feasible biochar performance as an adsorbent [14]. Biochar is considered an efficient, environmentally friendly, and cost-effective material for the adsorption of typical pollutants from aqueous environments, including endocrine-disrupting chemicals [15].

The pollutant removal capacity of biochar can be further enhanced through activation or modification processes, as well as through novel combined treatment strategies aimed at effective pollution reduction [16]. The synthesis of biochar-based nanocomposites enables the combination of the advantages of biochar with those of nanomaterials. The resulting composites typically exhibit significant improvements in surface functional groups, pore structure, active surface sites, catalytic degradation capacity, and ease of separation [17].

The aim of the present study is to evaluate contamination of environmental matrices—namely water, agricultural soils, and grapes—with phthalate residues, as well as to analyze the sorption process of phthalate residues from aqueous solutions onto biochars derived from apple residues and functionalized with metal oxides (Fe_3O_4 and NiO) and plant extracts (ext). This work is intended to support the preliminary application of these materials in environmental remediation and to reduce the risks of food-chain contamination.

2. Materials and Analysis Methods

2.1. Materials Synthesis

The materials used for the removal of phthalates from wastewater—Biochar (A); Activated Biochar (A-ac); A-ac-Fe_3O_4; A-ac-NiO, A-ac-Fe_3O_4-NiO, RM1-HCl/Fe_3O_4 ext—were prepared according to the method of Bocşa, *et al.*, 2025 [18]. The biochar used was obtained from dried apple residues by calcination at 550˚C in an inert argon atmosphere, followed by chemical activation with 7.7 M NaOH solution and an additional calcination step at 700˚C. The activated material was subsequently treated with 0.1 M HCl in an ultrasonic bath and washed to neutral pH. The aqueous extract of Urtica dioica L. was obtained by infusion and characterized in terms of total polyphenol content and antioxidant capacity. The polyphenol content was 11.5 mg GAE/g dry plant, and the antioxidant activity was 5.524 mg TE/g dry plant. The extract was subsequently used for the functionalization of the proposed hybrid materials.

2.2. Detection and Quantification of Phthalates

2.2.1. Standards, Calibration Solutions and Sorption Conditions

For the analysis of environmental samples, calibration solutions were prepared using an equimolar mixture of the six studied phthalates ($\approx 5.0 \times 10^{-6}$ mol/dm^3), in accordance with ISO 8124-6, ensuring metrological traceability and comparability of results. In the sorption studies, solutions prepared from individual substances of high analytical purity were used, namely dibutyl phthalate (DBP, 99.8%), di(2-ethylhexyl) phthalate (DEHP, 99.7%), dimethyl phthalate (DMP, 99.6%), diethyl phthalate (DEP, 99.0%), dioctyl phthalate (DOP, 99.7%), benzyl butyl phthalate (BBP, 99.5%), Sigma-Aldrich (Germany) was used to prepare calibration and model solutions in order to evaluate the individual behavior of each phthalate.

The concentrations of DBP and DEHP solutions ranged from 0.24 to 0.57 mg/L, a range selected to reflect ecotoxicologically relevant levels and to highlight the efficiency of the sorbent. In each series of tests, the reduction of the contaminant concentration was compared with a control sample that was not exposed to the sorbent. The sorbent mass was varied between 2.23 and 6.83 mg to assess the influence of the sorbent-to-analyte ratio on adsorption capacity. Sorption experiments were conducted in sealed containers under constant stirring (250 rpm) for 20 min, a duration considered sufficient to reach adsorption equilibrium. The experiments were performed at 25˚C, 45˚C, and 65˚C to evaluate the influence of temperature on the adsorption mechanism and to distinguish between physical and chemical adsorption processes. After adsorption, the phthalates were extracted with chloroform, selected for its high solubility for hydrophobic compounds and compatibility with GC-MS analysis. The organic phase was separated and dried over anhydrous sodium sulfate to remove residual water, thereby ensuring the stability and accuracy of subsequent chromatographic determinations.

2.2.2. Chromatographic Conditions

Phthalate determination was carried out by gas chromatography coupled with mass spectrometry (GC-MS) using a Shimadzu GCMS-QP2010S system equipped with a COMBI PAL autosampler (CTC Analytics), ensuring high precision, reproducibility, and minimal injection variability. Chromatographic separation was achieved on a RESTEK Rtx-5MS fused-silica capillary column (30 m × 0.25 mm × 0.25 μm) with a nonpolar stationary phase (100% dimethylpolysiloxane), selected for its thermal stability, chemical inertness, and proven efficiency in separating low-polarity, semi-volatile phthalates. The oven temperature program was optimized to ensure complete analyte separation within a reasonable analysis time: an initial temperature of 150˚C (held for 1 min), followed by a ramp of 10˚C/min to 200˚C (held for 1 min), then a ramp of 20˚C/min to 280˚C, held for 10 min to elute higher-molecular-weight and high-boiling compounds. Helium (99.9990%) was used as the carrier gas at a constant flow rate of 1.0 mL/min. Samples were injected in split mode (ratio 5:1) to avoid column and detector overloading. Ionization was performed by electron impact (EI). The electron multiplier voltage was set to 130 V, and the injector, transfer line, and ion source temperatures were maintained at 260˚C, 280˚C, and 200˚C, respectively, to prevent analyte condensation and ensure stable ionization. Quantification was conducted in Selected Ion Monitoring (SIM) mode, chosen for its enhanced sensitivity and selectivity at low analyte concentrations. The analytical response was expressed as the ratio of the analyte peak area to that of the internal standard, thereby correcting for instrumental and injection variability and enabling robust calibration. The total GC-MS run time was approximately 25 min.

2.3. Thermodynamic Calculations

The sorption processes were described using two theoretical models: the Langmuir and the Freundlich models. The generalized form of the Langmuir isotherm is as follows:

$$A_e = \frac{A_0 k_l}{1+k_{l\,C_e}} C_e, \tag{1}$$

where A_e represents the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (μmol/g); C_e is the equilibrium concentration of the adsorbate in solution (μmol/L); k_l denotes the Langmuir equilibrium constant of sorption (L/μmol); A_0 is the monolayer adsorption capacity (μmol/g).

The linear form of the Langmuir isotherm is as follows:

$$\frac{C_e}{A_e} = \frac{1}{k_l A_0} + \frac{C_e}{A_0} \tag{2}$$

This allows the determination of A_0 and k_l values from the plot of $C_e/A_e = f(C_e)$.

The Freundlich isotherm describes non-ideal and reversible adsorption that is not limited by the formation of a monolayer of reactive molecules on the adsorbent surface [19]. This model applies to adsorption on heterogeneous surfaces with interactions between adsorbed molecules. It assumes that sites with higher affinity are occupied first. The Freundlich isotherm is expressed as follows:

$$A = K_F C_e^{\frac{1}{n}}, \tag{3}$$

where K_F is the Freundlich equilibrium constant, and the empirical parameter $1/n$ ranges between 0 and 1. The values of $1/n$ and $\ln K_F$ were determined from the graphical form of the Freundlich adsorption isotherm:

$$\ln A_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

The thermodynamic process of DBP sorption was described using classical equations:

$$\Delta G_0 = -RT \ln K, \tag{5}$$

$$\Delta G_0 = \Delta H_0 - T\Delta S_0, \tag{6}$$

where K is the thermodynamic equilibrium constant of the sorption process (dimensionless); ΔG_0 is the Gibbs free energy change of DBP sorption; ΔH_0 is the enthalpy change of the reaction; ΔS_0 is the entropy change associated with DBP sorption onto the biochar.

2.4. Statistical Analyses

All experiments were conducted in triplicate, and the mean and standard deviation were calculated. The results were considered statistically significant if $p <$

0.05, using Statgraphics software, Centurion XVI 16.1.17 (Statgraphics Technologies, Inc., The Plains, VA, USA).

3. Results and Discussions

An assessment of phthalate levels in environmental samples was conducted based on studies of natural water sources used for industrial water supply, as well as water subjected to various treatment stages at industrial facilities, such as softening. The levels of phthalate contamination in spring and lake waters within the Chișinău municipality, Republic of Moldova, are summarized for the water bodies listed in Table 1.

Table 1. Coordinates of sampling points and content of phthalates in water sources.

No.	Water source	Geographic coordinates		DBP, mg/dm^3	DEHP, mg/dm^3
		N/S	E/W		
1.	Spring “Tamara”	47˚0'49.68"	28˚48'45.61"	<0.005	<0.007
2.	Spring “St. Helena”	47˚2'37.49"	28˚47'30.17"	<0.005	0.008
3.	Spring Balkan highway	47˚3'8.73"	28˚46'20.61"	<0.005	<0.007
4.	Spring Dimo St.	47˚2'53.31"	28˚52'14.89"	<0.005	<0.007
5.	Spring “Chemertan”	47˚2'35.87"	28˚52'11.10"	<0.005	<0.007
6.	Spring Florilor St.	47˚3'14.29"	28˚51'13.63"	<0.005	0.011
7.	Durlesti stream	47˚1'3.55"	28˚49'10.79"	<0.005	<0.007
8.	Lake “Valea Morilor”	47˚1'16.79"	28˚48'52.19"	<0.005	<0.007
9.	Lake “La Izvor”	47˚2'46.03"	28˚47'24.20"	<0.005	<0.007
10.	Lake Arboretum	47˚2'0.54"	28˚48'48.64"	<0.005	<0.007
11.	Lake “Valley of Roses”	47˚0'5.66"	28˚51'16.84"	<0.005	<0.007
12.	Lake “Victoria”	46˚56'29.80"	28˚56'23.86"	<0.005	<0.007
13.	Lake Botanical Garden	46˚58'39.90"	28˚53'19.45"	<0.005	<0.007
14.	Byk River (Ghidighić St.)	47˚3'7.96"	28˚47'2.08"	0.027	0.033
15.	Byk River (Muncesti St.)	46˚56'33.10"	28˚56'56.80"	0.022	0.057

N—north; S—south; E—east; W—west; DBP—dibutyl phthalate; DEHP—di-(2-ethylhexyl) phthalate.

Low concentrations of DEHP and DBP were detected in most water samples. With the exception of water from the Byc River, no elevated levels of phthalate residues were observed. Other phthalates were not detected, even in trace amounts. These results suggest that the absence of significant phthalate contamination in the water sources and lakes of Chișinău can likely be attributed to the region’s low industrial development and limited agricultural activity. Soil represents one of the primary environments for phthalate accumulation. The migration, transformation, and retention of these compounds are influenced by multiple factors, including soil properties, the composition and abundance of microorganisms, and the organic matter content. To identify potential sources of phthalate contamination in grapes, samples were collected from vineyards in the Ialoveni district and the Chişinău municipality (**Table 2**).

Table 2. Coordinates of sampling points and content of phthalates in soil samples.

No.	Sampling location	Geographic coordinates		Phthalate concentrations, mg/kg soil					
		N/S	E/W	DMP	DEP	DBP	BBP	DEHP	DnOP
1.	Young vineyard (Ialoveni district) municipality)	46˚58'02.8"	28˚47'15.8"	<0.01	<0.01	0.115	<0.01	<0.01	<0.01
2.	Fruiting vineyard (Ialoveni district)	46˚58'41.1"	28˚46'26.9"	<0.01	<0.01	0.080	<0.01	<0.01	<0.01
3.	Milestii Mici Plantation (1)	46˚55'23.6"	28˚48'49.7"	<0.01	<0.01	0.236	<0.01	0.925	<0.01
4.	Milestii Mici Plantation (2)	46˚59'29.82"	28˚47'26.08"	<0.01	<0.01	0.279	<0.01	0.279	<0.01
5.	Codru village (Chisinau municipality)	46˚59'01.3"	28˚46'41.8"	<0.01	<0.01	0.247	<0.01	<0.01	<0.01

N—north; S—south; E—east; W—west; DMP—dimethyl phthalate; DEP—diethyl phthalate; DBP—dibutyl phthalate; BBP—benzyl butyl phthalate; DEHP—di-(2-ethylhexyl) phthalate; DnOP—di-n-octylphthalate.

The results of phthalate analysis in soil revealed the presence of two compounds from this group: DBP and DEHP. DBP was detected in all soil samples, with concentrations ranging from 0.080 to 0.279 mg/kg. DEHP was detected only in samples collected from the Mileştii Mici vineyards, where its concentration substantially exceeded that of DBP. The highest total phthalate content was found in the soil from the Mileştii Mici vineyard, amounting to 0.925 mg/kg. These findings are consistent with international data [20] and confirm the presence of phthalate pollution associated with intensive agricultural activity. Previous studies [21] reported that the main phthalic acid contaminants detected in soil were DBP, DEHP, and DMP, accounting for 49.2%, 27.0%, and 12.4% of the total phthalate content, respectively. To evaluate phthalate contamination in plant material, grape samples were analyzed at harvest. The sampling locations and the DBP and DEHP content in destemmed grapes are presented in **Table 3**.

The experiment demonstrated that the majority of phthalate contamination in fruit occurs on the surface of the berries rather than within the bulk tissue. Ethanol rinsing (~96.4% *v/v*) of the fruit surface enabled the extraction of 89% - 100% of phthalates, compared with extraction from a homogenized mixture of crushed berries. These findings suggest that phthalate contamination of fruit—and consequently of the resulting must—arises not from migration through the plant's vascular system from the soil, but rather from vineyard practices such as spraying, irrigation with wastewater, application of contaminated soil, and other anthropogenic processes. DEHP was identified as the predominant contaminant among the o-phthalate esters, while other phthalate homologues were undetectable, even in trace amounts. The results of this study confirm that contamination of plant-derived food products with phthalate esters persists and should be considered in food safety assessments, consistent with the findings of numerous previous studies [22]-[25].

Table 3. The degree of contamination of grape fruits at the harvest period.

No.	Sampling location, vineyard	Geographic coordinates		DBP, mg/kg	DEHP, mg/kg
		N/S	E/W		
1.	Siret (Straseni district)	47˚07'23.27"	28˚43'58.98"	0.010	0.045
2.	Romanesti (Straseni district)	47˚14'4.16"	28˚43'7.26"	0.011	0.010
3.	Yavgur (Chimislia district)	46˚32'53.57"	28˚37'11.13"	<0.007	0.023
4.	Frumoasa (Calarasi region)	47˚19'34.72"	28˚23'58.72"	0.008	0.025
5.	Cahul district	45˚55'14.98"	28˚13'22.73"	<0.007	0.015

N—north; S—south; E—east; W—west; DBP—dibutyl phthalate; BBP—benzyl butyl phthalate; DEHP—di-(2-ethylhexyl) phthalate.

To mitigate environmental contamination, which inevitably contributes to contamination of the food chain, sustainable and cost-effective sorbents were developed based on biochar derived from apple residues and functionalized with metal oxides (Fe_3O_4 and NiO), green-synthesized using plant extracts from *Urtica dioica* L. Apple waste is considered biowaste and contributes to environmental pollution, as it is generated in substantial quantities during apple processing. Previous studies have demonstrated high adsorption efficiencies for paracetamol (57.54%), tartrazine (37.48%), and dibutyl phthalate (74.98%) [26].

The sorption performance of 6 experimental sorbent samples was evaluated for two phthalates, namely DBP and DEHP, since low concentrations of DEHP (0.007 - 0.057 mg/dm^3) and DBP (0.005 - 0.027 mg/dm^3) were detected in most of the tested water samples. The results of the analysis of phthalate residues in soil also revealed the presence of these compounds. DBP was detected in all soil samples, with concentrations ranging from 0.080 to 0.279 mg/kg. DEHP was identified as the predominant contaminant of fruits among o-phthalate esters (0.010 - 0.045 mg/kg), while other phthalate homologues were undetectable, even in trace amounts. According to the experimental results, as well as previous studies [20] [21], the main contaminants of the environmental objects were DBP and DEHP.

Figure 1 illustrates examples of the reduction in DBP mass spectral signal intensity in processed water samples compared with the control. For clarity, overlapping peaks have been separated along the time axis. Each DBP and DEHP peak in the chromatogram represents the combined signal of the analyte and its deuterated internal standard. **Figure 2** illustrates examples of the reduction in DEHP mass spectral signal intensity in treated water samples relative to the control. For clarity, overlapping peaks have been separated along the time axis.

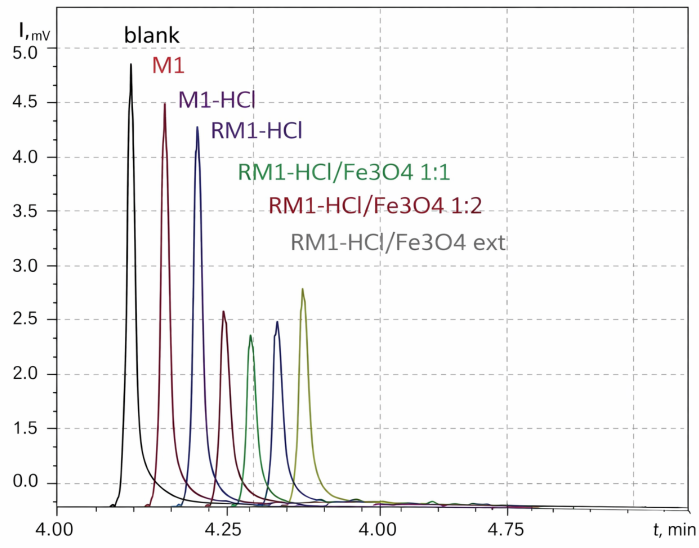


Figure 1. Visualization of the relative decrease in DBP mass spectrum signals following exposure to the indicated adsorbents: blank, M1, M1-HCl, RM1-HCl, RM1-HCl/Fe_3O_4 (1:1), RM1-HCl/Fe_3O_4 (1:2), RM1-HCl/Fe_3O_4 ext.

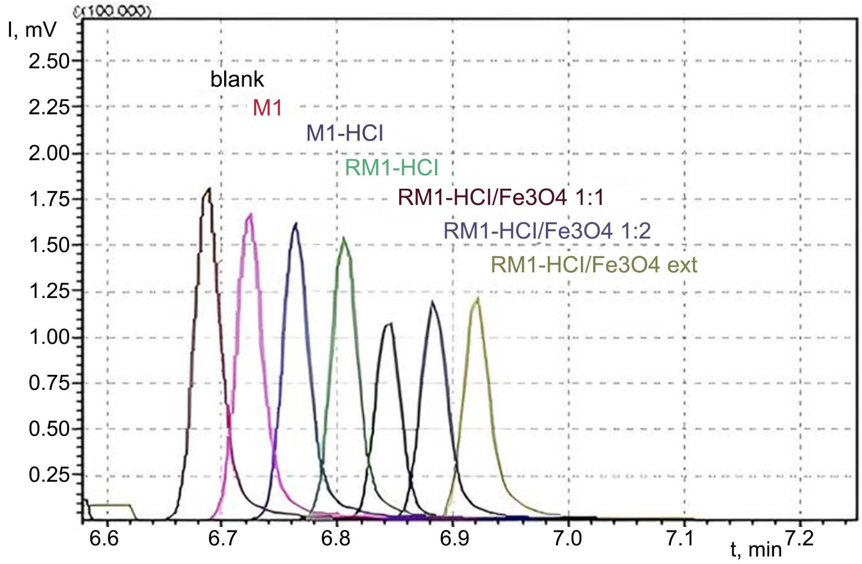


Figure 2. Visualization of the relative decrease in DEHP mass spectral signals following exposure to the specified adsorbents: blank, M1, M1-HCl, RM1-HCl, RM1-HCl/Fe_3O_4 (1:1), RM1-HCl/Fe_3O_4 (1:2), RM1-HCl/Fe_3O_4 ext.

The difference in phthalate concentrations between the treated samples and the control was used to calculate the mass of phthalate adsorbed per corresponding mass of sorbent for each measurement. Table 4 shows the relationship between the average sorption capacities of the tested adsorbents for DBP and DEHP.

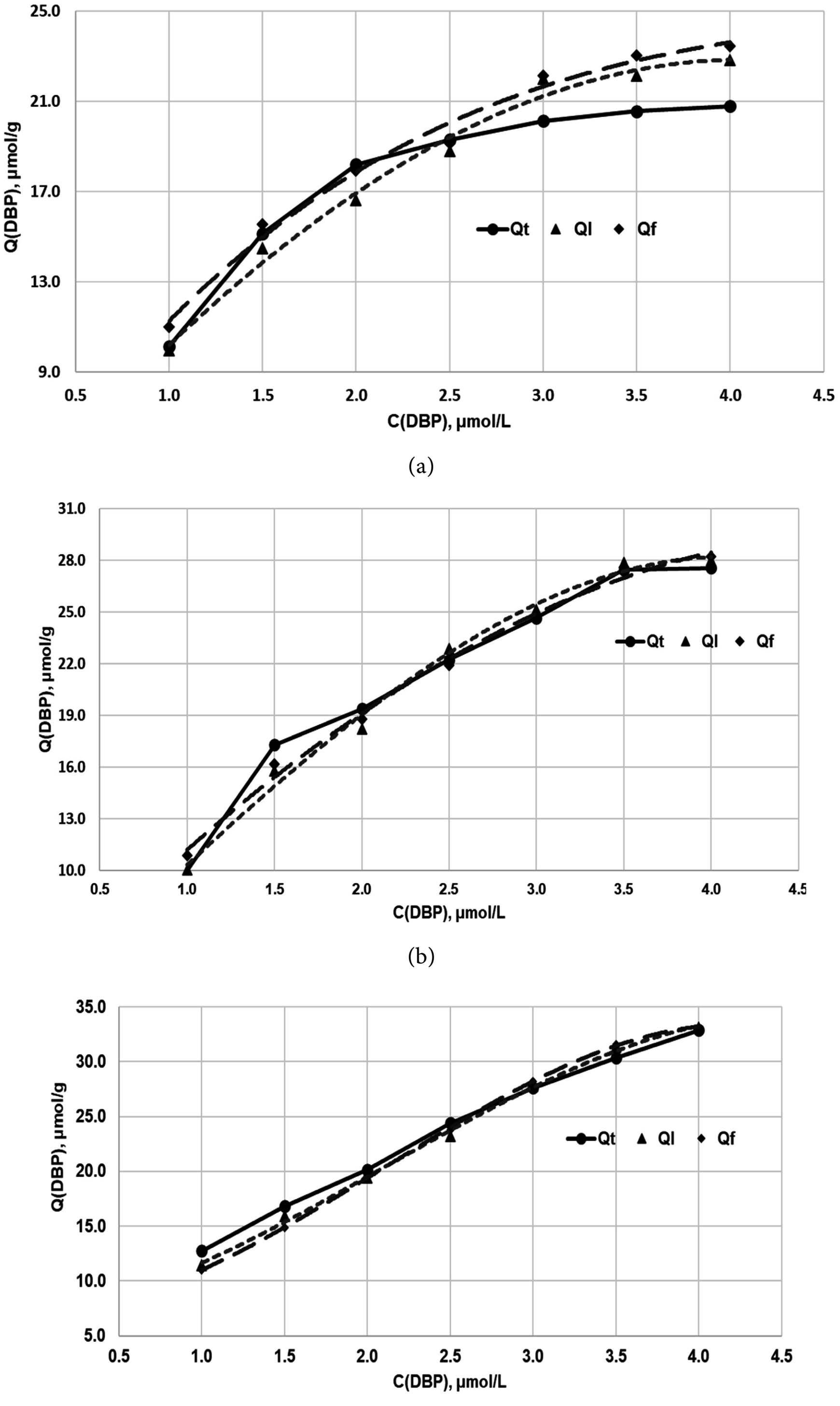
Table 4. Average sorption capacities of the tested adsorbents.

Sample	Average sorption capacities, μmol/g	
	DBP	DEHP
M1	1.61 ± 0.02^{a}	0.10 ± 0.01^{a}
M1-HCl	3.90 ± 0.05^{b}	0.54 ± 0.01^{b}
RM1-HCl	14.41 ± 0.12^{d}	1.00 ± 0.01^{c}
RM1-HCl/Fe_3O_4 1:1	16.54 ± 0.09^{f}	2.62 ± 0.0^{e}
RM1-HCl/ Fe_3O_4 1:2	15.86 ± 0.21^{e}	2.53 ± 0.02^{e}
RM1-HCl/ Fe_3O_4 ext	13.42 ± 0.16^{c}	2.40 ± 0.01^{d}

Values represent means of three replicated trials, ±standard deviation. Different letters ($^{a-f}$) designate statistically different results ($p < 0.05$).

The adsorption mechanism can be either physical or chemical, primarily depending on the aromatic or specific functional groups and the polarity of both the biochar and the organic pollutants. Biochar is known to strongly influence the adsorption of organic contaminants. In physical adsorption, the process is determined by intermolecular attractions and electrostatic forces between the biochar and the pollutants, whereas chemical adsorption relies on specific chemical interactions, such as π-π interactions, hydrogen bonding, and coordination bonds [16]. The sorption phenomena can be further classified according to the following mechanisms [26]: 1) hydrogen bonding, 2) electrostatic interactions, 3) hydrophobic interactions, and 4) non-covalent electron donor-acceptor π interactions. The observed differences in the adsorption behavior of DBP and DEHP are likely attributable to their distinct hydrophobicities, molecular masses, and three-dimensional structures.

Nanometal oxides exhibit high surface energy and a large specific surface area; however, their fine-grained nature often leads to aggregation and passivation. Nanometal oxide-biochar composites combine the distinct advantages of biochar and nanometal oxides, demonstrating considerable potential as adsorbents [26]. All tested sorbents displayed a narrow pore size distribution, with the primary pore size around 4 nm, attributed to the carbon component of the composites. In samples containing Fe_3O_4, a multimodal pore size distribution was observed, with larger pores ranging from 5.8 to 8 nm, likely corresponding to the Fe_3O_4 phase. In contrast, for A-ac-NiO, only 4 nm pores were detected, associated with the carbon matrix, indicating that NiO did not form large grains or a porous structure [18]. Sorption isotherms describe the relationship between the amount of adsorbed substance and its concentration in the equilibrium solution, providing insight into the interactions between the adsorbate and adsorbent (Figure 3).



(a)

(b)

(c)

Figure 3. Sorption isotherms on biochar samples: (a) A-ac; (b) A-ac-Fe_3O_4 (1:1); (c) A-ac-Fe_3O_4 (1:2). Experimental conditions: T = 298 K, pH = 6.2.

Two theoretical models are commonly used to describe sorption processes: Langmuir and Freundlich. The Langmuir model assumes that adsorption reaches a maximum corresponding to a saturated monolayer of molecules on the adsorbent surface, and is frequently applied to phthalate sorption [19] [27]. This model further assumes a fixed number of adsorption sites, reversible adsorption, no interaction between adsorbed molecules, and cessation of adsorption once saturation is achieved.

The shape of sorption isotherms provides a first experimental indication of the nature of a specific adsorption phenomenon. According to the classification of isotherms into four main types—L, S, H, and C [28]—the DBP isotherms exhibited an L-shaped curve. This L-shape indicates minimal competition between the solvent and adsorbate for adsorption sites, with the longitudinal axes of adsorbed molecules lying parallel to the adsorbent surface. Experimental data were best described by the Langmuir adsorption model for biochar samples (1 - 3). The monolayer saturation capacity ranged from 35 to 56 μmol/g, and the experimentally obtained adsorption values closely matched the theoretical Langmuir predictions. Adsorption was further supported by the Freundlich model, with empirical 1/n values between 0.52 and 0.68.

For biochar samples 3 - 5, adsorption increased with temperature (**Table 5**), indicating the endothermic nature of the process. In contrast, samples 1 - 2 exhibited a maximum adsorption at 45˚C (318 K).

Table 5. Experimental DBP adsorption values at different temperatures (pH = 6.2).

No.	Biochar	DBP adsorption, μmol/g		
		25˚C (298 K)	45˚C (318 K)	65˚C (338 K)
1	A-ac	20.732	32.683	17.509
2	A-ac-Fe_3O_4-1:1	27.913	32.568	16.066
3	A-ac-Fe_3O_4-1:2	34.127	33.840	34.323
4	A-ac-Fe_3O_4-ext-1:1	22.481	34.087	35.145
5	A-ac-Fe_3O_4-ext-1:2	10.997	20.654	31.607

DBP—dibutyl phthalate.

The thermodynamic parameters of DBP sorption on biochars—Gibbs free energy (ΔG_0), enthalpy (ΔH_0), and entropy (ΔS_0)—were subsequently calculated. For all samples and at the three analyzed temperatures, the ΔG_0 values were negative, indicating that the DBP sorption process on biochars is spontaneous (**Table 6**).

The differences in Gibbs free energy values indicate that samples 2 - 3 exhibit a higher affinity of biochar for DBP. The ΔG_0 values show little variation with increasing temperature, consistent with previous reports [29]. The negative enthalpy (ΔH_0) confirms that DBP sorption on biochars is exothermic. Sorption processes are accompanied by changes in the entropy of the system, determined by the reorganization of sorbate molecules at the sorbent-fluid phase interface. In most cases, sorption involves the transition of molecules from a more disordered to a more ordered state on the sorbent surface, which leads to a decrease in entropy ($\Delta S < 0$), associated with the limitation of molecular degrees of freedom [30]. Such behavior is typical for activated carbon, in part because water molecules are released by molecular exchange between DBP molecules and functional groups on the carbon surface. Analysis of the entropy change, correlated with enthalpy and Gibbs free energy, provides essential information on the spontaneity of the process and the nature of the interactions involved.

Table 6. Thermodynamic parameters (ΔG_0, ΔH_0, ΔS_0) for DBP sorption on biochars.

No.	Biochar	T, K	ΔG_0, kJ/mol	ΔH_0, kJ/mol	ΔS_0, J/(mol·K)
1	A-ac	298	−5.803	−51.19	−191.25
		318	−9.917		
		338	−6.092		
2	A-ac-Fe_3O_4-1:1	298	−20.682	− 24.72	−111.3
		318	−18.456		
		338	−12.897		
3	A-ac-Fe_3O_4-1:2	298	−28.373	−27.64	−90.3
		318	−26.567		
		338	−28.886		
4	A-ac-Fe_3O_4-ext-1:1	298	−12.564	−95.38	−98.4
		318	−10.596		
		338	−9.385		
5	A-ac-Fe_3O_4-ext-1:2	298	−11.851	−16.95	−17.11
		318	−13.562		
		338	−11.968		

For enthalpy-driven adsorption ($\Delta H_0 < 0$, $\Delta S_0 < 0$), the sign of ΔG_0 can change during the adsorption process. Previous studies have shown that at high or near-saturation loadings, the enthalpy of adsorption decreases [31]. As adsorption approaches saturation, few new adsorption sites are occupied, resulting in a small change in entropy (ΔS_0); consequently, the term $-T\Delta S_0$ is not expected to vary significantly or strongly influence ΔG_0. Under these conditions, $\Delta G_0 = \Delta H_0 - T\Delta S_0$ may become positive due to the decrease in ΔH_0. Nevertheless, the negative enthalpy continues to favor adsorption of molecules.

4. Conclusions

Studies have shown that DBP and DEHP are the most frequently detected phthalate residues in environmental samples from the Republic of Moldova. Although water from Chisinau city sources generally does not raise concern—with the exception of the Byc River—significant phthalate concentrations have been detected in some vineyard soils, attributed to agricultural practices and treatments.

Analysis of grapes from various plantations during the harvest period confirmed the presence of these residues. To prevent contamination of the food chain, it is essential to develop efficient sorbents capable of reducing the cumulative effects of exposure to environmental residues on human health. Access to clean drinking water is a fundamental human right, and biochar derived from apple waste and activated with nanooxides represents a promising approach in this context.

The adsorption behavior of DBP and DEHP on the developed biochar differs considerably due to the specific molecular properties of each compound: aqueous solubility (11.2 mg/L for DBP and 0.003 mg/L for DEHP), molecular dimensions (length/width: 1.265/1.229 nm for DBP and 1.388/1.032 nm for DEHP), and octanol-water partition coefficient (4.61 for DBP and 7.5 for DEHP). Previous studies reported stronger adsorption of DEHP, attributed to its higher hydrophobicity and lower solubility in water. Similarly, DEHP was adsorbed more effectively than DBP on magnetic and non-magnetic chitosan/PVA hydrogels, with adsorption governed by hydrogen bonding, complexation, and hydrophobic interactions. In contrast, for the apple biochar examined in this study, DBP was predominantly adsorbed, likely due to steric factors and the compact structure of the DBP molecule. This observation is consistent with the L-shaped adsorption isotherms, which indicate that the molecules are arranged parallel to the biochar surface.

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Conflicts of Interest

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

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