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CARBON-BASED ADSORPTIVE MATERIALS FOR MITIGATION OF ORGANOPHOSPHATE CONTAMINANTS IN AQUATIC SYSTEMS

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Abstract: *Rapid industrialization and technological advancement have significantly increased the presence of hazardous chemicals in environmental matrices, posing risks not only to public health and ecosystems but also to environmental and water security. Among these contaminants, organophosphate compounds represent a critical class of toxic substances. While primarily used as agricultural pesticides, organophosphates share structural and toxicological features with certain nerve agents, making their environmental persistence and potential misuse a matter of concern within CBRN (Chemical, Biological, Radiological, and Nuclear) risk frameworks. Aquatic systems are particularly vulnerable, as wastewater discharges facilitate the transport of pesticides, synthetic dyes, and heavy metals into rivers, lakes, and groundwater reservoirs. The development of efficient, scalable, and low-cost remediation materials is therefore essential for both environmental protection and strategic water safety management. This study investigates the adsorption of chlorpyrifos onto bio-derived carbon materials synthesized via controlled carbonization of waste biomass. The objective was to assess their removal efficiency and evaluate their potential applicability in defensive water purification systems designed for contamination response and preventive risk mitigation. Material characterization was conducted using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) surface area analysis to determine morphology, surface chemistry, and porosity. Adsorption experiments were monitored by ultra-performance liquid chromatography (UPLC) at three operational temperatures (22 °C, 30 °C, and 35 °C). Adsorption efficiency and equilibrium time were determined to assess operational feasibility under variable environmental conditions. The results provide mechanistic insight into interactions between organophosphate compounds and carbon-based materials and support the development of bio-derived adsorbents as cost-effective components in resilient water treatment systems relevant to environmental security and CBRN preparedness.*

Keywords: *chlorpyrifos, nerve agents, bio-derived carbon materials, adsorption.*

1. INTRODUCTION

Surface water pollution is a growing environmental problem that significantly affects ecosystems, human health, and biodiversity. Organophosphate pesticides, which are primarily used in agriculture to control pests and increase yields, stand out among the many pollutants degrading water quality. They do not decompose spontaneously in nature, adversely affect aquatic ecosystems, and are highly toxic to living organisms [1]. They reach the waters through runoff from agricultural lands, where they can remain for a long time, and through interactions with other substances in the water, more toxic compounds can form. Exposure to organophosphate pesticides is associated with many health diseases, both in humans and animals [2].

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The aim of this work was to investigate the adsorption of chlorpyrifos (CHP) on carbon materials obtained from biowaste. The adsorption of these substances was investigated at different concentrations, three temperatures, and various contact times, with a constant amount of material. A carbon material derived from biowaste, obtained by carbonizing used rabbit litter, was used as an adsorbent. Morphological characterization of the material was performed using a scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Functional surface groups were identified using Fourier transform infrared spectroscopy (FTIR), and the material's specific surface area was also examined using BET (Brunauer-Emmett-Teller) analysis.

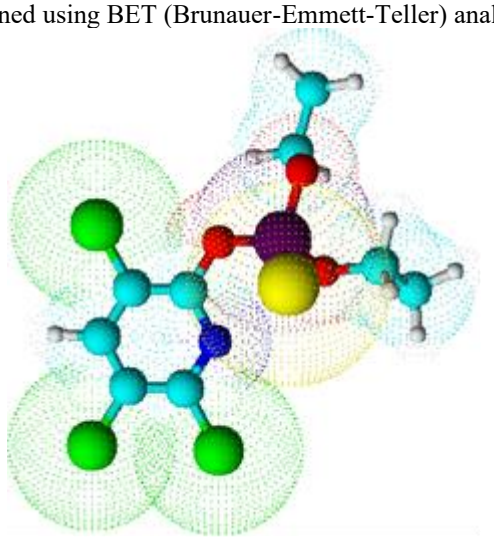


Figure 1. Chemical structure of CHP

CHP (Figure 2**)** adsorption on carbon materials was monitored experimentally using ultra-high-performance liquid chromatography (UPLC). Contaminant and carbon material suspensions were incubated for a specified period of time at three different temperatures, after which the time required for equilibrium to be established will be determined, after which no further CHP adsorption on the adsorbent will occur. Adsorption efficiency will be tested at a constant carbon material concentration.

The results will be processed using the Dubinin-Radushkevich and Dubinin-Astakhov isotherm models to determine characteristic adsorption parameters and describe the adsorbent surfaces.

2. EXPERIMENTAL

2.1. Chemicals

Daily prepared working solutions of CHP in ethanol were used in the work, at concentrations ranging from 5×10^{-4} to 5×10^{-6} mol dm^{-3}, obtained by diluting the 1×10^{-1} mol dm^{-3} solution. Ethanol (C_2H_5OH) and acetonitrile (CH_3CN), HPLC grade, were obtained from J.T.Baker.

2.2. Methods

UPLC – Chromatographic analyses were performed on an ultra-high-performance liquid chromatography Waters ACQUITY system with a binary pump (Binary Solvent Manager), an automatic sampler (Sample Manager), and a detector (Photo Diode Array - PDA) in the wavelength range from 190 to 500 nm. Analyses were performed at a constant eluent composition (isocratic conditions). An ACQUITY UPLC TM BEH C18 chromatographic column was used as the stationary phase, and the mobile phase was 20% water, 80% acetonitrile.

Other laboratory equipment **–** included a Sartorius 2632 analytical balance and a Mettler technical balance. Eppendorf Research automatic pipettes were used to measure liquid samples. Samples were mixed on a Vortex V1 plus BOECO mixer and an Orbital shaker-Incubator Grant-bio ES-20 mixer at a constant, set temperature. Separation of the solid and liquid phases was performed using a Mini Spin PLUS centrifuge (Eppendorf) at 14,500 rpm. The samples were filtered using a KX Syringe Filter with a 13 mm diameter and a 0.22 µm pore size.

3. RESULTS AND DISCUSSION

3.1. Synthesis of carbon materials derived from biowaste

The carbon materials (CM) used as adsorbents were obtained from biowaste, by carbonizing the used rabbit litter. The first adsorbent includes all components of the spent litter (CM I), while the second contains unused sawdust (CM II). The first step in the synthesis process is to dry the biowaste in an oven at 90 °C for 24 h, after which they were carbonized in a furnace atmosphere at 650 °C for 1 h. At the end, carbon material suspensions were prepared in ethanol at a concentration of 2 mg cm^{-3} (suspension stock).

3.2. Characterization of carbon materials

SEM and EDX spectroscopy – The morphology of the carbon materials was analyzed using a SEM (JEOL, Ltd., Akishima, Tokyo, Japan). The homogenized sample powder was placed on a carbon support strip using tweezers, then introduced into the SEM chamber. The chemical composition of the investigated carbon materials was determined using EDX.

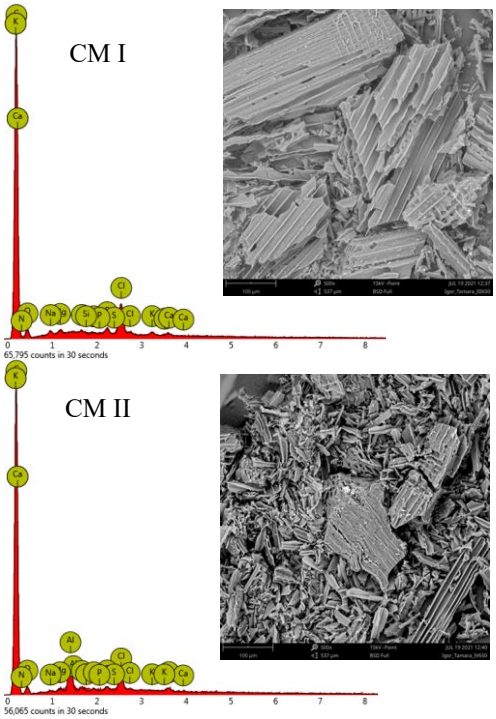


Figure 3. SEM micrograph and EDX spectrum of CM

From the micrographs shown in Figure 2, it can be seen that the primary structure of both materials is retained, and that they are rough and porous. Based on the spectra, the most abundant element is carbon, at 92.94% in CM I and 93.02% in CM II. In addition, the composition of CM I includes 5.26% oxygen and 1% chlorine. CM II also consists of oxygen with 4.59% and aluminum with 1.16%. Other elements, such as calcium, magnesium, silicon, and others, are present in trace amounts, that is, at levels below 1%.

BET analysis – In order to determine the specific surface area of the carbon material, an automatic volumetric sorption analyzer (Sorptomatic 1990 Finnigan) was used. The analysis was performed using isothermal adsorption of nitrogen at 77.13 K. Before adsorption, the samples were degassed in a vacuum for 4 h at 90 °C and 16 h at 200 °C.

The value of the specific surface for CM I is S_{BET} = 10 m^2g^{-1} while for CM II, S_{BET} = 487 m^2g^{-1}. It is observed that the second material has almost 50 times greater specific surface area compared to the first.

FTIR – In order to determine the characteristic functional groups present in the adsorbents, a Nicolet iS20 FT-IR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) was used. The wavelength range was from 4000 to 500 cm^{-1}, with 64 scan/a every 4 cm^{-1}.

The band assignments were made in accordance with the literature [3].

Each functional group has a characteristic position on the FTIR spectrum (Table 1). Each band present corresponds to a specific vibration of the particular chemical bond of the given material.

Table 2. Characteristic functional groups of CM I and CM II

Band position (cm^{-1})	Functional group	Type of vibration
617	O-H free	deformation
655	-COOH	deformation
702	-COOH	deformation
863	C-H aromatic out-of-plane	bending
887	C-H aromatic out-of-plane	bending
1033	C-H aromatic compounds	deformation
1110	C-O	deformation
1380	C-N	stretching
1458	C-H skeletal vibration aromatic ring	deformation
1589	C=C skeletal vibration of aromatic ring	stretching

CM I and CM II have common peaks originating from the C-H bending vibration, the -COOH deformation vibration and the O-H free, deformation vibration. However, in the FTIR spectrum of CM II, a bathochromic shift of the C-H and -COOH bands can be observed. The cause of this phenomenon may lie in the different chemical compositions of these two materials. Despite the shift of the two mentioned characteristic bands, the O-H vibration occurs in both materials at the same position. In addition, CM I contains a band characteristic of the C=C stretching vibration, which is not present in the spectrum of CM II. CM II is also characterized by various deformation vibrations, including C-H and C-O, and by one C-N stretching vibration.

3.3. Adsorption of pesticides on carbon materials at different temperatures

The adsorption of CHP was investigated at 22 °C, 30 °C, and 35 °C, with a constant amount of adsorbents, over a pesticide concentration range of 5×10^{-4} to 1×10^{-6} mol dm^{-3}. The experimental data were fitted using the nonlinear forms of the Dubinin-Radushkevich and Dubinin-Astakhov isotherm models, as shown in Figure 4. The corresponding adsorption parameters, which provide insight into the surface characteristics and adsorption behavior of the adsorbents, are summarized in Table 3.

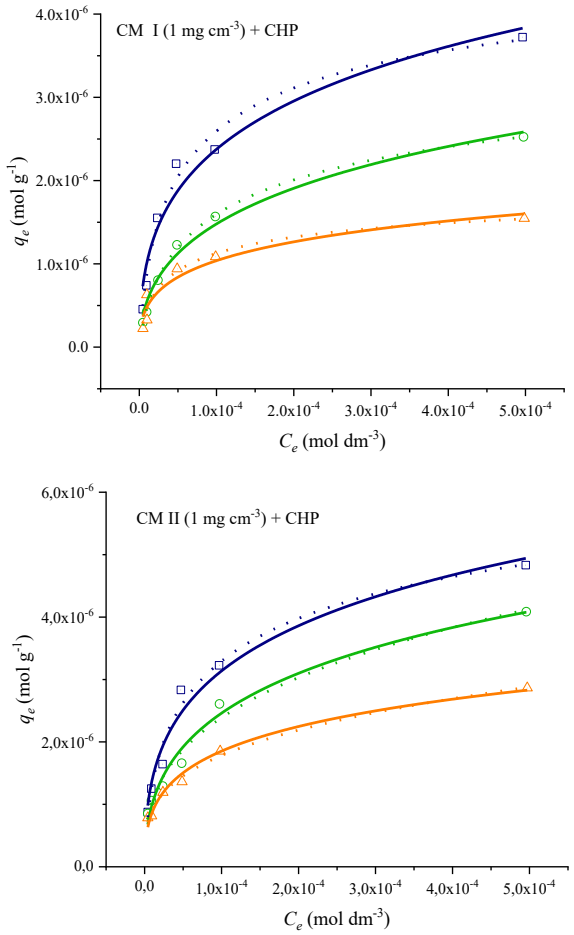


Figure 5. Nonlinear forms of isotherms applied to the adsorption process of CHP on CM:

The obtained results for the adsorption of CHP on both carbon materials indicate that the process can be well described by the Dubinin-Radushkevich and Dubinin-Astakhov isotherm models at all temperatures (Figure 6). It can be observed that CM II exhibits a higher adsorption capacity for CHP compared to CM I.

Table 4. Parameters of adsorption isotherm models for adsorption, obtained by fitting experimental data

***T*/°C**	***22***	***30***	***35***
Dubinin – Radushkevich *CM I*			
q_{DR}/mol g^{-1} ×10^6	11 ± 2	8,5 ± 0,9	4,0 ± 0,8
K_{DR}/mol^2 kJ^{-2}	260 ± 30	300 ± 20	230 ± 40
E_a/J mol^{-1}	44 ± 3	41 ± 2	46 ± 4
χ^2×10^{14}	7,23928	1,21053	2,10462
R^2	0,95958	0,98599	0,9324
Dubinin – Radushkevich *CM II*			
q_{DR}/mol g^{-1} ×10^6	13 ± 2	12 ± 2	7,0 ± 0,6
K_{DR}/mol^2 kJ^{-2}	240 ± 20	270 ± 20	230 ± 10
E_a/J mol^{-1}	45 ± 2	43 ± 2	46 ± 2
χ^2×10^{14}	6,55679	3,69693	1,05219
R^2	0,97612	0,98031	0,98633
Dubinin – Astakhov *CM I*			
q_{DA}/mol g^{-1} ×10^6	4,6 ± 0,7	3,8 ± 0,3	1,9 ± 0,6
n	5 ± 2	4 ± 0,4	5 ± 2
E_a/J mol^{-1}	26 ± 1	23,8 ± 0,6	26 ± 2
χ^2×10^{14}	3,27003	16,6068	1,87611
R^2	0,98631	0,99856	0,9548
Dubinin – Astakhov *CM II*			
q_{DA}/mol g^{-1} ×10^6	7 ± 2	32 ± 9	40 ± 10
n	3 ± 1	1 ± 1	0,9 ± 0,8
E_a/J mol^{-1}	24 ± 2	10 ± 2	6 ± 5
χ^2×10^{14}	5,68135	4,29678	8,0718
R^2	0,98448	0,98283	0,99213

Based on the q_{max} values derived from the isotherm parameters, the maximum amount of adsorbed CHP decreases with increasing temperature (Table 5). The Dubinin-Radushkevich model indicates that the adsorption is predominantly physical (E < 8 kJ mol^{-1}), while the Dubinin-Astakhov model provides a better fit to the experimental data, likely due to surface heterogeneity of the adsorbents (n ≠ 2) [4].

4. CONCLUSION

In this study, the adsorption of CHP onto carbon materials derived from biowaste was investigated at 22 °C, 30 °C, and 35 °C. SEM analysis confirmed a rough, porous morphology for both materials, while BET results showed a considerably higher specific surface area for CM II than for CM I. Accordingly, CM II generally exhibited better adsorption performance.

The Dubinin-Radushkevich and Dubinin-Astakhov isotherm models successfully described the adsorption process. The calculated adsorption energies indicate that CHP adsorption is predominantly physical, while the applicability of the Dubinin-Astakhov model suggests the importance of surface heterogeneity.

The adsorption capacity decreased with increasing temperature, indicating that CHP adsorption was more favorable at 22 °C. Although the obtained adsorption capacities were moderate, the results show that low-cost carbon materials derived from biowaste have potential for mitigating organophosphate contaminants in aquatic systems. Further optimization of precursor selection, carbonization conditions, porosity, and surface chemistry is needed to improve their adsorption efficiency and

practical applicability.

Acknowledgment

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