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ADSORBING DANGER: CARBON MATERIAL COMBATTING ORGANOPHOSPHATE

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Abstract: *Organophosphates are a class of compounds known for their use as chemical warfare agents. These agents have been utilized in military contexts due to their ability to act as nerve agents, disrupting the nervous system's function. However, beyond their military application, organophosphates pose significant risks to human health and the environment. Exposure to these compounds can lead to severe neurological effects and even death in high concentrations. Moreover, organophosphates can persist in the environment, contaminating soil, water, and air, posing long-term risks to ecosystems and public health. Therefore, developing effective strategies for removing organophosphates is crucial. This study investigates the efficacy of carbon material in removing organophosphate malathion from aqueous systems. Carbon material was characterized using SEM and EDX. Experimental results were analyzed using four nonlinear isotherm models: Freundlich, Langmuir, Temkin, and Dubinin-Raduskevic model. The study revealed that 1 g of the examined material could adsorb 18.92 mg of malathion at 25°C. Furthermore, neurotoxicity was accessed, and it was found that treatment with the adsorbent led to a reduction in toxicity. The findings underscore the promising role of carbon material as an effective adsorbent for removing malathion.*

Keywords: *malathion, adsorption, neurotoxcity.*

1. INTRODUCTION

Organophosphate compounds, such as malathion (**Figure 1**), are used as chemical warfare agents because they disrupt the nervous system by inhibiting acetylcholinesterase (AChE), an essential enzyme for nerve function [1]. This inhibition leads to the accumulation of acetylcholine, causing continuous nerve signal transmission, resulting in muscle spasms, respiratory failure, and potentially death [2].

Malathion is an organophosphate insecticide commonly used to control insects in agricultural and residential areas [3]. Though malathion has relatively low toxicity to humans and mammals, it can transform into a more toxic compound, malaoxon, through oxidation by environmental factors such as air and sunlight or through metabolic processes in organisms [4]. This transformation involves replacing malathion's sulfur atom with an oxygen atom, significantly increasing its potency as an acetylcholinesterase inhibitor and, thereby, its toxicity [5]. Environmental conditions, like high temperatures and certain microbes, can accelerate this conversion, raising concerns about potential health risks. Therefore, while malathion is generally safe when used correctly, the possibility of malaoxon formation necessitates careful monitoring and management to prevent harmful effects on humans and non-target organisms [6].

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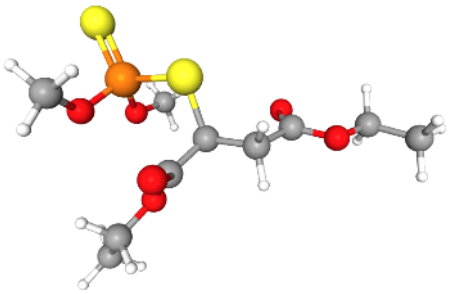

Figure 1. Structure of malathion

Removing these compounds from the environment is crucial because their high toxicity poses severe risks to human health and ecological systems. Persistent soil, water, and air contamination can lead to long-term exposure, affecting populations and wildlife and disrupting ecosystems. Therefore, effective removal strategies are essential to mitigate these hazards and ensure public and environmental safety [7, 8].

Various methods have been investigated for eliminating organophosphates, including biodegradation, photocatalysis, electrochemical treatment, membrane separation, and oxidation. Among these, adsorption has gained attention for its simplicity and cost-effectiveness [7].

Different types of materials can be used to remove organophosphate from the environment. Activated carbon, in particular, has proven highly effective due to its large specific surface area, porosity, thermal stability, and low reactivity with acids and bases. Carbon materials produced from agricultural, industrial, or biomass waste carbonization also present a sustainable and efficient option for organophosphate removal [9, 10].

The study aims to investigate the efficacy of carbon material in removing the organophosphate malathion from aqueous systems. This includes determining the carbon material's adsorption capacity for malathion and evaluating its potential for reducing toxicity.

2. MATERIALS AND METHODS

2.1. Material synthesis

Viscose fibers were used as the precursor. These fibers were thoroughly washed with distilled water before use. Post-washing, they were centrifuged using a spin dryer for 15 minutes and then dried at 90 °C for 24 hours in a drying cabinet.

The carbonization process involved loading 100 – 400 g of the precursor into a chamber furnace (HTK 8 W, Carbolite Gero GmbH, Germany). After evacuating the chamber, a nitrogen flow of 250 L h^{-1} was introduced. The sample was heated to 850 °C at a rate of 1.0 °C min^{-1} and held at that temperature for 30 minutes. Cooling to room temperature was conducted under a nitrogen atmosphere.

Following carbonization, the activation process occurred in a rotary kiln (RSR-B 120/500/11, Nabertherm GmbH, Lilienthal, Germany). For this, 10 g of the carbonized material was placed in the center of a quartz glass reactor. Initially, the setup was purged of air using N_2 at a flow rate of 100 L h^{-1}. The sample was then heated from room temperature to 770 °C under an N_2 flow rate of 50 L h^{-1} and maintained at this temperature for 30 minutes to ensure uniform heating throughout the reactor. Afterwards, the N_2 flow was stopped, and CO_2 was introduced at a flow rate of 45 L h^{-1} for 180 minutes. The activation process was completed by the termination of the CO_2 flow and restarting of the N_2 flow (50 L h^{-1}) until the kiln was cooled to room temperature.

2.2. Material characterization

The assessment of the structure and elemental composition of the samples was conducted using the PhenomProX Scanning Electron Microscope (SEM) from Thermo Fisher Scientific (Waltham, MA, USA), in combination with Energy Dispersive X-ray Analysis (EDX). Nicolet iS20 FT-IR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) was used for the FTIR spectra recording. The applied wavenumber range was from 4000 to 500 cm^{-1} with 64 scans and 4 cm^{-1} resolution.

2.3. Adsorption experiments

Adsorption experiments were conducted in stationary conditions, where adsorbent was initially dispersed in double-distilled water and then combined with organophosphate stock solution to achieve desired concentrations. The mixture underwent shaking and incubation at 25°C, followed by centrifugation and filtration of the supernatant through a nylon filter. Ultra-performance liquid chromatography (UPLC) was then used to analyze the malathion concentration post-adsorption. Uptake efficiency was calculated as follows:

$$\text{Uptake} = 100\% \times (C_0 - C_{eq})/C_0 \quad (1)$$

, where C_0 is the initial concentration of organophosphate, and C_{eq} is the concentration after adsorption. Control experiments were conducted without adsorbent. Malathion analysis utilized the Waters ACQUITY UPLC system with a photodiode array (PDA) detector, employing a mobile phase of 40% acetonitrile in water (v/v) and 60% pure acetonitrile.

2.4. Neurotoxicity of malathion

Measurements of AChE inhibition were conducted to monitor and quantify changes in the toxicity of malathion solutions pre- and post-adsorption. This assessment also aimed to explore any potential conversion of malathion into more toxic forms during hydrolysis, which could induce adverse effects even at concentrations below the detection threshold of UPLC. AChE activity was evaluated using a modified Ellman's procedure, wherein 1 U/mL AChE was exposed to malathion solutions before and after adsorption experiments at 37°C in 50 mmol

dm^{-3} PB pH 8.0 (final volume 0.650 cm^3). The enzymatic reaction was initiated by adding acetylcholine-iodide along with DTNB as a chromogenic reagent and allowed to proceed for 8 min before termination with 10% sodium dodecyl sulfate (SDS). Thiocholine, the enzymatic reaction product, reacted with DTNB, forming 5-thio-2-nitrobenzoate, the optical absorption of which was measured at 412 nm. Physiological effects were quantified through AChE inhibition, calculated as follows:

$$\text{AChE inhibition (\%)} = 100 \times (A_0\text{-}A)/A_0 \quad (2)$$

, where A_0 and A represent AChE activity in the absence of malathion and after exposure to malathion, respectively.

3. RESULTS AND DISCUSSION

3.1. Materials characterization

To investigate the morphology of the material, we used SEM. From **Figure 2**, it can be seen that the morphology of the sample is the same and reflects the morphology of precursor viscose fibers.

Figure 2. SEM micrograph of the carbon material

Also, the chemical composition of the material was investigated using EDX analysis. The material was found to have 91.83% carbon, 7.91% oxygen, 0.22% sodium and 0.05% sulfur.

From the FTIR spectra presented in **Figure 3**, it can be seen that two bands stand out. The first band at 1613 cm^{-1} represents the in-plane vibrations of sp^2 hybridized C=C bonds, while the second band at 1242 cm^{-1} is attributed to C–OH vibrations [11].

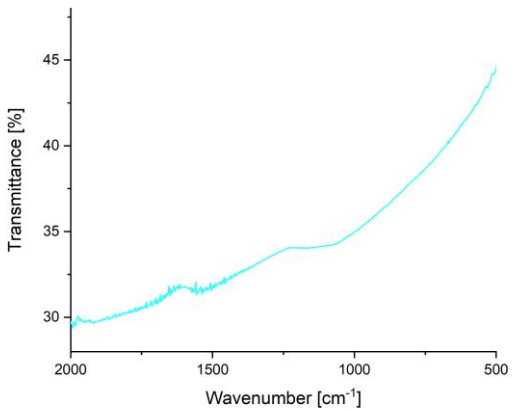

Figure 3. FTIR spectra of investigated carbon material

3.2. Adsorption isotherms

The thermodynamic aspects of the adsorption process for malathion were investigated by constructing adsorption isotherms and fitting experimental data to various adsorption isotherm models, each offering unique insights into the process. Freundlich (3), Langmuir (4), Temkin (5), and Dubinin-Radushkevich (6) models were employed for this analysis. **Figure 4** illustrates the experimental data points alongside the corresponding fits, while the fitted parameters are presented in **Table 1**.,

$$q_e = K_F C_e^{1/n} \quad (3)$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = \frac{RT}{b_T} \ln K_T C_e \quad (5)$$

$$q_e = q_{DR} e^{-K_{DR}\varepsilon^2} \quad (6)$$

where q_e (mg g^{-1}) represents equilibrium adsorption capacity, Ce (mg dm^{-3}) equilibrium adsorbate concentration, K_F (mg g^{-1} (mg $dm^{-3})^{1/n}$) and n Freundlich constants, K_L (dm^3 mg^{-1}) and q_{max} (mg g^{-1}) Langmuir constant and theoretical maximum adsorption capacity of the monolayer, b_T (J g mol^{-1} mg^{-1}) and K_T (dm^3 mg^{-1}) Temkin isotherm constant, q_{DR} maximum adsorption capacity, K_{DR} (mol^2 J^{-2}) constant associated with the mean free adsorption energy per mole of adsorbent, $\varepsilon = RT \times \ln(1 + 1/Ce)$.

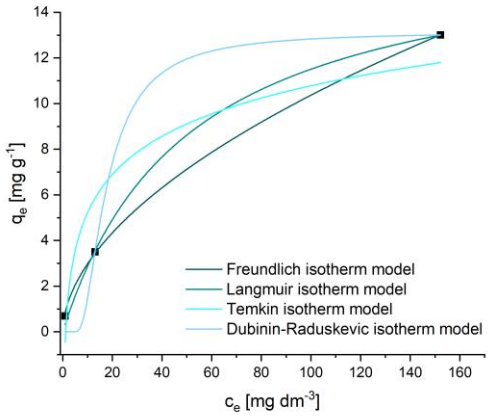

Figure 4. Adsorption isotherms for malathion removal at 25°C

Table 1. Parameters for the adsorption of malathion onto carbon material using Freundlich, Langmuir, Temkin, and Dubinin-Radushkevic isotherm at 25°C

Parameters	
Freundlich isotherm	
n	1.81
K_F ((dm^3 mg^{-1})$^{1/n}$)	0.81
χ^2	0.026
R^2	0.999
Langmuir isotherm	
K_L (dm^3 mg^{-1})	0.01
q_{max} (mg g^{-1})	18.92
χ^2	0.334
R^2	0.988
Temkin isotherm	
K_T (dm^3 mg^{-1})	0.74
b_T (J g mol^{-1} mg^{-1})	1082.67
χ^2	6.825
R^2	0.755
Dubinin-Raduskevic isotherm	
q_{DR} (mg g^{-1})	13.02
K_{DR} (mol^2 J^{-2})	1.05×10^{-4}
E (J mol^{-1})	69.13
χ^2	5.602
R^2	0.799

From the parameters presented in **Table 1**, it can be concluded that the Freundlich isotherm model best fits the experimental data, indicating predominantly physisorption on the heterogeneous surface of carbon material. The n value in the Freundlich isotherm model is 1.81, indicating the adsorption process's favorable nature. Additionally, analysis based on the Dubinin-Radushkevich model, specifically the calculated adsorption free energy per mole of adsorbent (E < 8 kJ mol^{-1}), verifies that the adsorption process of malathion is predominantly physisorption, indicating the absence of chemical bond formation between malathion and the investigated activated carbon material.

3.3. Neurotoxicity of malathion solutions

The toxicity of the malathion solution was evaluated using the AChE inhibition assay described in Section 2.4., with results presented in **Figure 5** and **Table 2**. Data from toxicity assessments indicated a consistent reduction in the toxicity of malathion solutions following adsorption treatment under the specified experimental conditions. Importantly, this process did not generate more toxic byproducts that would lead to stronger inhibition of AChE.

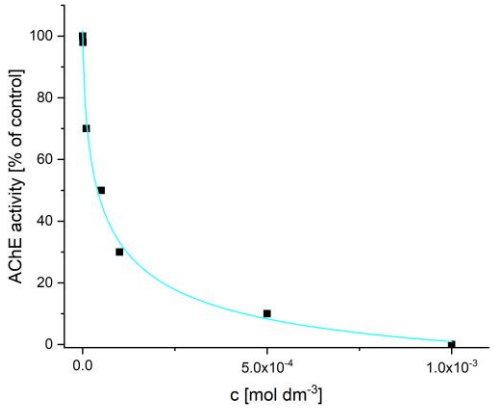

Figure 5. The dependence of AChE activity inhibition from malathion concentration

Table 2. AChE inhibition of malathion solution

C (mol dm^{-3})	AChE inhibition (% of control)
2.5×10^{-6}	5,00
2.5×10^{-5}	22,39
5×10^{-5}	26.64
1.25×10^{-4}	47.63
2.5×10^{-4}	63.41

4. CONCLUSION

Activated carbon material derived from viscose fibers was employed to remove malathion from water, demonstrating promising results. Specifically, 1 gram of the investigated material exhibited the capability to adsorb 18.92 mg of malathion. Moreover, the adsorption process followed the Freundlich isotherm model under the given conditions, indicating that the adsorption process is most likely physisorption onto the heterogenous surface of carbon material. Additionally, toxicological analysis of aqueous malathion solutions post-treatment with the adsorbent revealed a declining trend in toxicity, indicating the absence of more toxic byproducts formed during the process. Thus, the removal of malathion utilizing the tested adsorbent proved to be successful.

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