



WASTE-DERIVED CARBON MATERIAL FOR MALATHION ADSORPTION

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Abstract: Widespread use of toxic organophosphate malathion raises the need to develop efficient procedures for its elimination from the environment. The acute neurotoxicity of malathion is associated with irreversible inhibition of acetylcholinesterase, the enzyme involved in signal transduction in the nervous system. Its inhibition leads to different neurological disorders. Various methods have been applied for the removal of malathion from water, but one of the most promising is adsorption. We used waste-derived activated carbon material as an adsorbent for malathion. It was shown that 1 g of investigated material is capable of adsorbing 5.514 mg of malathion at 25°C. The toxicity of all samples was decreased after the treatment with the adsorbent. The kinetics of the batch adsorption removal of malathion from aqueous solutions was also investigated. Results showed that malathion adsorption onto activated carbon followed the pseudo-first-order kinetics model most appropriately under the given experimental conditions, with the constant rate value of 0.56248 mg g⁻¹ min⁻¹.

Keywords: malathion, activated carbon, kinetics, toxicity.

1. INTRODUCTION

Organophosphate pesticides (OPs) are phosphoric acid esters and are commonly used as insecticides to control pests. Unfortunately, OPs are highly toxic to humans and animals because they inhibit the enzyme acetylcholinesterase (AChE) [1].

Malathion is a broad-spectrum organophosphate insecticide for agricultural, industrial and domestic use. People could be exposed to malathion by inhalation, dermal contact, diet, and water. In addition, oxidative desulfurization in the liver converts malathion to malaaxon, further resulting in acetylcholinesterase inhibition in nervous tissue [2]. At the same time, malaaxon is considered 22 times more toxic than its thio-analog malathion during acute dietary exposure and 33 times more toxic by all routes of exposure in short- and medium-term exposure [3].

To reduce the impact of OP on health and the environment, there are various methods to eliminate them. These include biodegradation, photocatalysis, electrochemical treatment, membrane separation, oxidation, and adsorption. Among the mentioned methods, adsorption is especially attractive for research and application because it is simple and economically acceptable [4]. Various materials can be used to remove pesticides, such as mesoporous monetite, mineral surfaces, activated carbon and zeolites, carbon-based materials, graphene, and others [5]. However, activated carbon is the most commonly used adsorbent to remove OP compounds due to its large specific surface area, porosity, thermal stability, and low acid/base reactivity. To use different carbon materials for the adsorption of OP, special attention is paid to those obtained by the carbonization of waste materials from agriculture, industry or biomass [6].

This paper aims to examine the adsorption kinetics of malathion on porous waste-derived carbon material. Also, the toxicity of malathion solution after the treatment over time has been investigated. It is of interest to create useful solutions for its removal from water. In addition, AChE activity in malathion solution before and after adsorbent treatment was monitored.

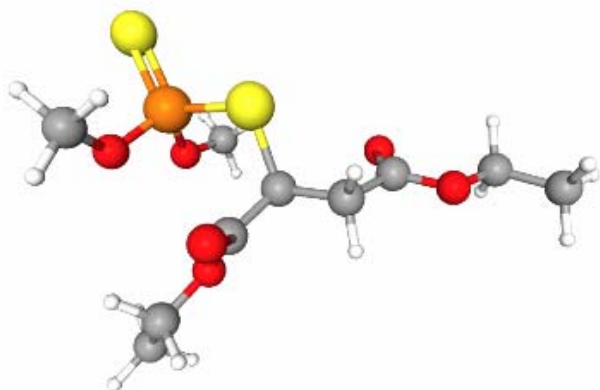


Figure 1. The structure of malathion.

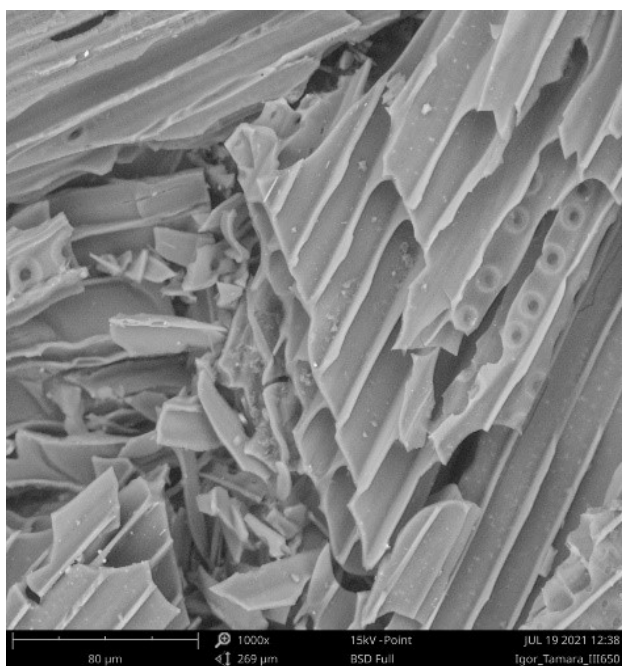


Figure 2. SEM micrography of investigated adsorbent.

2. EXPERIMENTAL

2.1. Chemicals

Acetylcholinesterase from electric eel, acetylthiocholine iodide (ASChI), and 5,5'-dithio-bis-(2-nitrobenzoic acid) (DTNB) were purchased from Sigma-Aldrich St. Louis, MO, USA. Potassium-hydrogen phosphate ($K_2HPO_4 \cdot 3H_2O$) and acetonitrile were purchased from Merck KgaA, Germany. Malathion (> 98% purity) was purchased from Pestinal®, Sigma-Aldrich, Denmark. The working pesticide solutions were prepared by diluting the

$1 \times 10^{-4} \text{ mol dm}^{-3}$ stock solutions in water. The pesticide stock solutions were held in the refrigerator until used. All chemicals were used without further purification. Deionized water was used throughout.

2.2. Material synthesis and adsorption experiments

Used rodent litter was dried for 24 h at 90 °C. Then, it was carbonized in a chamber furnace under a nitrogen atmosphere with a heating rate of 5.0 °C min⁻¹ and held isothermal for 60 min at 650 °C. The obtained carbon material was dispersed in double-distilled water (2 mg cm⁻³), and the desired amount of malathion stock solution was added to provide the targeted concentration of adsorbent and OP. Then, the vessel containing the adsorbent + malathion mixture was placed on a laboratory shaker and left for 1, 3, 5, 7, 10 min at 25 °C. After incubation, the mixture was centrifuged for 10 min at 14 500 rpm, and the supernatant was filtered through a nylon filter membrane.

2.3. UPLC analysis

For measuring the concentration of malathion, Waters ACQUITY Ultra Performance Liquid Chromatography (UPLC) system, coupled with a tunable UV photodiode array (PDA) detector controlled by the Empower software, was used. Chromatographic separations were run on an ACQUITY UPLC™ BEH C18 column with the dimensions 1.7 μm, 100 mm × 2.1 mm (Waters). Malathion solutions were analyzed under isocratic conditions with a mobile phase consisting of 60% acetonitrile and 40% water (v/v). The eluent flow rate was 0.20 cm³ min⁻¹, and the injection volume was 5 mm³. Optical detection for malathion was done at 200 nm. Under described conditions, the retention time of OP was (3.15±0.05) min. Malathion concentration in the analyzed samples was determined using the linear calibration curves constructed using standard pesticide solutions in a wide concentration range. The described method was previously optimized and cross-validated using the in-house developed protocols and, as such, used in this and our previous works on malathion determination.

2.4. SEM analysis

The waste-derived activated carbon material morphology was studied using a scanning electron microscope (SEM) JEOL JSM-5800 (JEOL, Ltd., Akishima, Tokyo, Japan). The sample is placed on carbon tape (which is adhesive on both sides - on one of the adhesive side of the tape with tweezers, powder of homogenized sample is applied). The other side of the adhesive tape is glued to the sample carrier, and then the sample carrier, together with the sample, is placed in the chamber SEM, and then the appropriate measurement is performed.

2.5. Neurotoxicity of malathion solutions

AChE inhibition measurements were performed to follow and quantify changes in the toxicity of malathion solutions before and after the adsorption. Also, this allows

us to investigate if there are any transformations of malathion into more toxic forms upon hydrolysis. These transformation products could exert harmful effects at concentrations below the detection limits of UPLC. AChE activity was assayed according to modified Ellman's procedure. The *in vitro* experiments were performed by exposing 1 U cm^{-3} AChE to malathion solutions before and after the adsorption experiments at $37 \text{ }^\circ\text{C}$ in 50 mmol dm^{-3} PB pH 8.0 (final volume 0.650 cm^3). The enzymatic reaction was started by adding acetylcholine-iodide in combination with DTNB as a chromogenic reagent and allowed to proceed for 8 min until stopped by 10% sodium dodecyl sulfate (SDS). The enzymatic reaction product, thiocholine, reacts with DTNB and forms 5-thio-2-nitrobenzoate, whose optical adsorption was measured at 412 nm. Physiological effects were quantified as AChE inhibition given as:

$$\text{inhibition}_{\text{AChE}} = 100 \times \frac{A_0 - A}{A_0} \quad (1)$$

where A_0 and A stand for the AChE activity in the absence of malathion and the one measured after the exposure to malathion, respectively.

3. RESULTS AND DISCUSSION

3.1. SEM analysis

To examine the three-dimensional structure of the selected adsorbent, SEM micrography was taken and shown in Figure 2. From Figure 2, it can be seen that despite carbonization, the investigated material retained its primary structure. The roughness of the material can also be seen in the picture.

3.2. Kinetics of adsorption removal of malathion from aqueous solutions

To determine the kinetic parameters of malathion adsorption on investigated carbon material, the tested adsorbent at a concentration of 1 mg cm^{-3} was incubated with malathion at a concentration of $5 \times 10^{-5} \text{ mol dm}^{-3}$ at $25 \text{ }^\circ\text{C}$ for 1, 3, 5, 7 and 10 min. The concentration of adsorbed malathion was calculated as the difference between its initial concentration (C_0) and the equilibrium concentration (C_e) of malathion measured by UPLC after removing the adsorbent. The obtained data were used to assess the kinetic parameters by the three kinetic models: pseudo-first-order model, pseudo-second-order model and interparticle diffusion model. The results are shown in Figure 3 and Table 1.

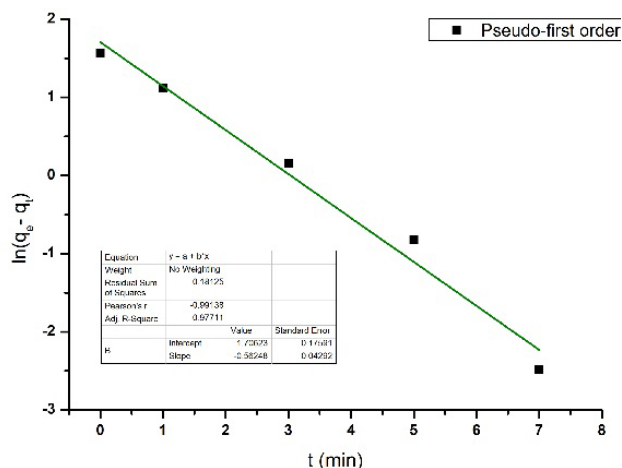


Figure 3a. The plot of pseudo-first-order for $5 \times 10^{-5} \text{ mol dm}^{-3}$ malathion and 1 mg cm^{-3} of adsorbent.

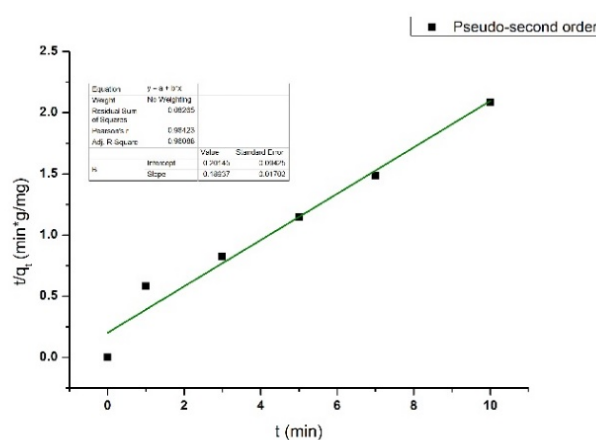


Figure 3b. The plot of pseudo-second-order model for $5 \times 10^{-5} \text{ mol dm}^{-3}$ malathion and 1 mg cm^{-3} adsorbent.

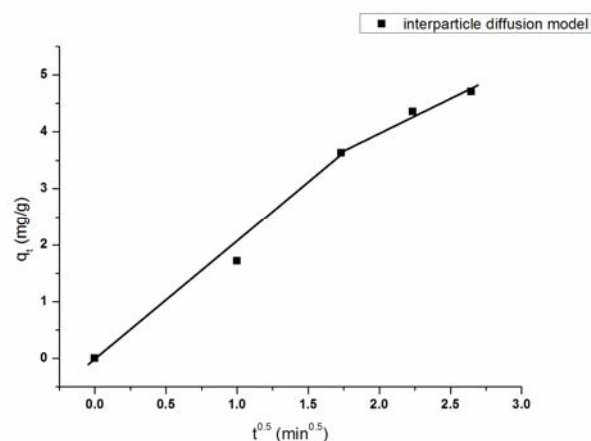


Figure 3c. The plot of the interparticle diffusion model for $5 \times 10^{-5} \text{ mol dm}^{-3}$ malathion and 1 mg cm^{-3} adsorbent.

Table 1. Kinetic parameters of the pseudo-first-order, pseudo-second-order and interparticle diffusion models for 5×10^{-5} mol dm⁻³ malathion and 1 mg cm⁻³ of investigated adsorbent

Parameters	Pseudo-first order	Pseudo-second order	Interparticle diffusion model
k^*	0.56248	0.17801	1.87393
R^2	0.97711	0.96088	0.97829

* (min^{-1}) for pseudo-first order, ($\text{mg g}^{-1} \text{min}^{-1}$) for pseudo-second order and ($\text{mg g}^{-1} \text{min}^{-1/2}$) for interparticle diffusion model

Based on the presented results, it was found that 1 g of test material is capable of adsorbing 5,514 mg of malathion. Besides, the obtained results showed that the adsorption of malathion on the selected adsorbent follows the pseudo-first-order kinetic model under the given experimental conditions with a rate constant of 0.56248 min^{-1} . Also, the interparticle diffusion kinetics model was applied to elucidate the diffusion mechanism. The two divided linear plots suggest the diffusion process occurs via two steps. The first segment of the plot denotes boundary layer diffusion, in contrast to the second segment representing interparticle diffusion of malathion throughout the open cavities of the adsorbent. The value for constant was $1,874 \text{ mg g}^{-1} \text{min}^{-1/2}$ at 25°C .

3.3. Neurotoxicity of malathion solutions

The toxicity of the malathion solution was assessed by the AChE inhibition assay as described in section 2.5. The results are given in Figure 4. Toxicity measurement data showed that under the given experimental conditions, in all cases, there is a decrease in the toxicity of the malathion solutions after the adsorption treatment. This process does not fabricate more toxic products that would more strongly inhibit AChE.

5. CONCLUSION

Activated carbon obtained from waste was used to remove malathion from the water. Based on the presented results, it was found that 1 g of test material is capable of adsorbing 5,514 mg of malathion. Also, the results showed that the adsorption of malathion on the corresponding adsorbent follows the pseudo-first-order kinetic model under given conditions, with a rate constant of 0.56248 min^{-1} . Furthermore, toxicological analysis of aqueous malathion solutions after the treatment with adsorbent showed descending trend, which means no more toxic products are formed during this process. Therefore, the removal of malathion using the tested adsorbent was successful.

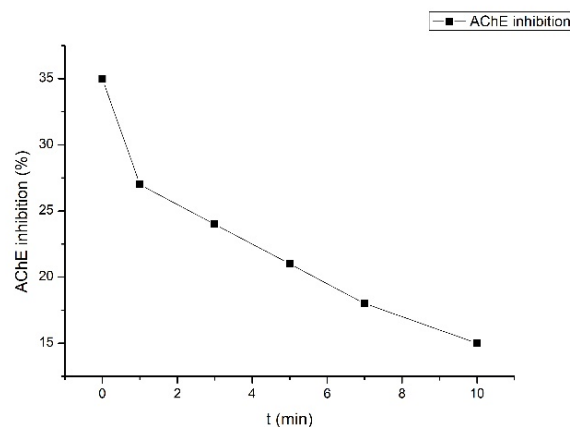


Figure 4. Toxicity of malathion solution after 0, 1, 3, 5, 7 and 10 min of contact with adsorbent. The initial malathion concentration was 5×10^{-5} mol dm⁻³.

Acknowledgments

This work was partially supported by the Ministry for Science of the Republic of Serbia (Grant no. 451-03-9/2022-14/200017).

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