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Activated carbon from waste as an efficient adsorbent for malathion for detection and removal purposes

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ABSTRACT

The widespread use of pesticides leads to considerable attention for pesticide detection and removal. Therefore, in the first part of this work, a simple and facile solid phase extraction (SPE) procedure for separation of malathion from soil and water samples, has been established. Malathion was recovered at a pH of 2.0–3.0 with limit of detection (LOD) of 0.026 ng L^{-1}. While in the second part, the kinetics of the batch adsorption removal of malathion from aqueous solutions was investigated. Results showed that malathion adsorption onto activated carbon followed second order kinetics models most appropriately with adsorption capacity of 32.1 mg g^{-1}.

Introduction

Pesticides are harmful to human health due to their bad effects [1–3]. The Estimated Environmental Concentration (EEC) directive for the level of pesticides in water that is permissible for human consumption is 0.1 g L^{-1} [4]. Malathion (*O*,*O*-dimethyl thiophosphate of diethyl mercaptosuccinate) is one of the most important insecticides; it is often used in farms to kill mosquitoes and insects and in public health policy to control urban pests [5]. Malathion is the most widely used organophosphate insecticide in the USA, Saudi Arabia and Turkey [6–8]. Malathion is an organophosphorus compound that can cause childhood leukemia, anemia, and kidney failure as well as cholinesterase [9,10]. Baker et al. [11] reported that many malaria workers in Pakistan were affected by and suffered from exposure to isomalathion in 1976. Malathion is capable of inhibiting carboxyesterases in humans and animals. The insecticide enters the water system through human activities, such as agriculture and industry. Therefore, great attention is given by EPA and FDA to control the levels of malathion in the environment [12–14].

It is necessary to develop methods to monitor malathion in environmental samples that come into contact with humans and animals [15–17] as well as to seek effective removal techniques from wastewater [18–20]. To achieve accurate and sensitive determination of malathion, several pretreatment and sample preparation steps are required, because of the presence of interfering materials [21]. Therefore, a high-efficiency sample preparation and a low limit of detection are critical and must be respected when developing analytical methods [22,23]. The accuracy and reliability of the method are affected by the sample pretreatment procedure, including extraction and preconcentration [21]. The most commonly used sample pretreatment procedures are liquid–liquid extraction (LLE) [24], gel-permeation chromatography (GPC), and solid phase extraction (SPE) [25]. The LLE method consumes large amounts of solvents and its procedure take long time. On the other hand, SPE is simple, credible, and can achieve full extraction [26]. In addition, specific techniques are available to enable the optimization of the analytical conditions [26–32].

On the other hand, various adsorbents have been applied for removal of pollutants from wastewater [18–20,33–40]. All the materials studied have their own advantages and limitations and therefore, there is still a need for developing low cost adsorbents. The conversion of solid wastes such as biomass, waste cardboards, waste newspapers, plastics and industrial byproducts into

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activated carbon for wastewater treatment would improve the economic value by providing an alternative to costly activated carbon [41,42]. Most of published works based on activated carbon applications use one type of starting materials for preparing it [36–40], but for this work, activated carbon from mixed waste is applied. Herein, the purpose of this work is to maximize the environmental benefits by investigation of activated carbon prepared from different types of waste including palm, paper, and plastic wastes [43] as an efficient adsorbent for solid phase extraction (SPE) of malathion from environmental samples. In addition, to study the kinetics of the batch adsorption process for removal of malathion from wastewater. For extraction application, this work introduce the combination of the proposed SPE with ultra-pressure liquid chromatographic–mass spectrometric (UPLC–MS) to improve the method towards very low malathion residues in the environment. The influence of several important parameters, including the pH, eluent type, eluent volume, model solution flow rate, eluent flow rate, and sample volume, on the SPE method was investigated. For removal application, the kinetic of the batch adsorption process is evaluated using the pseudo first-order, pseudo second-order, and intraparticle diffusion models.

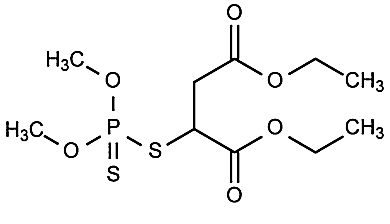
Experimental

Chemicals and reagent

HPLC-grade reagents and solvents were used in this work. The malathion standard (Scheme 1) (HPLC grade) and ACN were purchased from Sigma-Aldrich (St. Louis, MO, USA). Milli-Q water (Millipore, Bedford, USA) was used after filtration with 0.45 μm nylon filter paper. A stock solution of 10 mg L^{-1} of the malathion was prepared in a 1:2 (v/v) mixture of acetonitrile:water and stored at 4 °C [44]. The rest of the solutions were prepared by dilution of the stock solution. Activated carbon was prepared by co-pyrolysis of agricultural and municipal solid wastes as described in [43]. For scanning electron microscope (SEM) analysis, samples were mounted on an aluminum stub, coated with a thin layer of gold and then examined using Jeol (JSM-6380 LA) Japan. Transmission electron microscopy (TEM) images were obtained using a JEOL JSM-2100F electron microscope (Japan) operated at 200 kV. The surface area of the prepared AC sample was determined using N_2 sorption Quantachrome NOVA 4200 analyzer (USA). Fourier transformation infrared (FTIR) spectra of samples were recorded using a spectrophotometer (Thermo Scientific USA).

Instrumentation and MS conditions

The chromatographic separation of the standard and sample solutions was carried out on a Waters ACQUITY ultra-performance liquid chromatographic (UPLC) system using a quaternary pump system using an ACQUITY BEH C_{18} column (100 mm × 2.1 mm i.d., 1.7 μm particle size) (Waters, Milford, MA, USA). Clear separation of all analytes was achieved by using a mobile phase consisting of a mixture of acetonitrile and water with 0.1% formic acid. A linear gradient of 40 to 50% acetonitrile (v/v) from 0 to 8 min was used at a flow rate of 0.45 mL min^{-1} and an injected sample volume of 1 μL.



Scheme 1. The chemical structure of malathion, mwt 330.36.

The UPLC system was coupled to a Quattro Premier triple quadrupole mass spectrometer (Micromass, Milford, MA, USA) using an electrospray ionization (ESI) source Z-spray. The MS instrument was operated in the positive mode, and the data were obtained in single-reaction monitoring (SIR) mode using the protonated molecular ion of each compound as the precursor ion. The working conditions of the source were as follows: cone voltage, 20 V; capillary voltage, 3 kV; source temperature, 120 °C; desolvation temperature, 300 °C; cone gas flow rate, 60 L h^{-1}; desolvation gas flow rate, 600 L h^{-1}; Collision Cell Entrance potential (CEP), 1 V; Collision energy (CE), 20; collision cell exit potential (CXP), 0.5 V; ionspray voltage (IS), 3000 V; curtain gas, nitrogen; temperature, 120 °C; ion source gas, Nitrogen; CAD gas, Argon; Quantifier of malathion, $330 > 127$; Qualifier of malathion, $330 > 99$. Nitrogen (99.99% purity, Peak Scientific, model NM30L LA nitrogen generator, Inchinann, UK) and high-purity argon (99.99%, Specialty Gas Centre, Jeddah, Saudi Arabia) were used as the cone and collision gases, respectively. An Oerlikon rotary pump, model SOGEVAC SV40 BI (France), provided the primary vacuum to the mass spectrometer. The data acquisition and processing were carried out by MassLynx V4.1 software.

SPE procedure

A Visiprep TM-DL SPE vacuum instrument from Supelco (Bellefonte, PA, USA) was used for the SPE procedure. The columns were filled with 200 mg of activated carbon using PTFE frits and were pretreated with 10 mL ACN and 20 mL of Milli-Q water. To preconcentrate the malathion solutions, it were passed through the column. The retained malathion was then eluted with three ml of ethyl acetate, filtered through PTFE filters (0.45 μm), and analyzed by UPLC/MS. Usually, the recovery of the analyte depends significantly on the type (polarity) of solvent used for elution [45]. Therefore, the influence of various eluents, including acetonitrile, ethanol, methanol, dimethyl formamide and ethyl acetate, on the quantitative desorption of malathion from the activated carbon column was investigated. The effect of sample volume on the recovery of malathion from the activated carbon column was investigated for the range of 5–400 mL using optimized conditions.

Sampling and extraction of the soil and wastewater samples

For sampling and extraction of the soil and wastewater samples, the procedures described in [46] were used with some modifications. Soil and wastewater samples were collected from farms near Riyadh city. Soil samples were taken in a jar and sealed with aluminum foil-lined lids, wastewater samples were taken in glass bottles covered with aluminum foil, the sample volume was approximately 1 L, then the samples were stored in dry ice until extraction procedure. For extraction of soil samples, 10 g was taken in a screw cap glass jar, then 200 mL mixture of acetone:hexane (1:4, v/v) was added and the jar was covered with aluminium foil, shaken for 1 h, the solution was filtered with glass fiber filter paper. The glass jar and the filter paper were washed with 50 mL acetonitrile. The 250 mL extracted solution was introduced to SPE procedure. For wastewater samples, 100 mL acetonitrile was added to 200 mL wastewater sample, and then the solution was introduced directly to SPE procedure.

Batch adsorption process for malathion removal

The batch adsorption experiments were performed in 250 mL conical flasks by mixing 80 mL of the malathion solution with