



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



Mohamed Abdelaty Habila^{a,*}, Zeid Abdullah ALOthman^a, Saad A. Al-Tamrah^a,
Ayman Abdel Ghafar^a, Mustafa Soylak^b

^a Advanced Materials Research Chair, Chemistry Department, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia

^b Erciyes University, Fen Fakultesi, Department of Chemistry, 38039 Kayseri, Turkey

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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.

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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

* Corresponding author. Tel.: +966 595184785.

E-mail address: mhabila@ksu.edu.sa (M.A. Habila).

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.

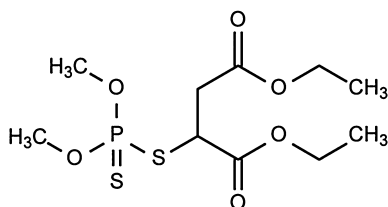
Experimental

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 \times 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



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

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 .

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

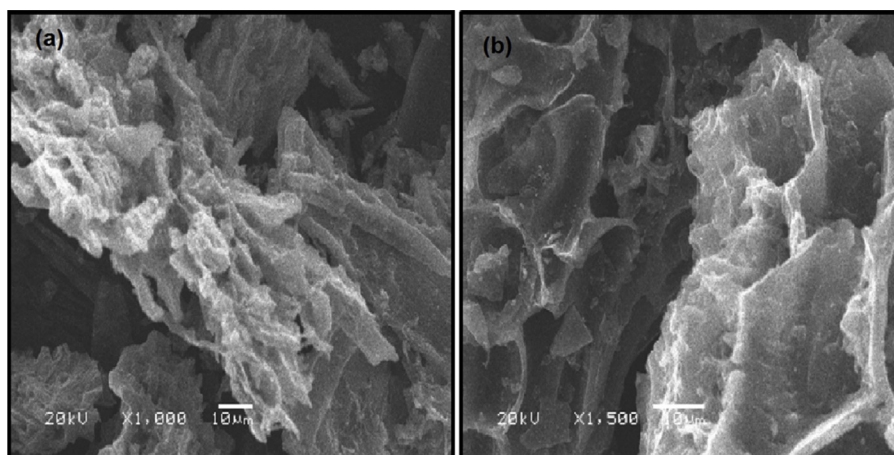


Fig. 1. Scanning electron microscope image of the prepared AC (a) at magnification of 1000 and (b) at magnification of 1500.

0.03 g of activated carbon and then equilibrated in a thermostat-shaking assembly (model MSW 275) at 30 °C and 200 rpm. After equilibrating, the concentration of remaining malathion in the solution was measured using HPLC–MS (Waters, Milford, MA, USA). The amount of malathion per unit weight of adsorbent, q_e (mg g^{-1}), was calculated using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of malathion in solution (mg L^{-1}), V is the solution volume (L), W is the weight of the adsorbent (g) and q_e is the adsorption capacity (mg g^{-1}).

The effect of shaking time on the adsorption of malathion was examined at four different initial concentrations (4, 8, 12 and 16 mg L^{-1}) of malathion at 25 °C, 0.03 g of adsorbent and the selected pH. At predetermined times; the solution of the specified flask was filtered using Whatman no. 42 filter paper and analyzed.

Results and discussion

Characterization of the prepared activated carbon

In the present work, Activated carbon was prepared by copyrolysis of agricultural and municipal solid wastes. Scanning electron microscope image is shown in Fig. 1a and b, which reveals

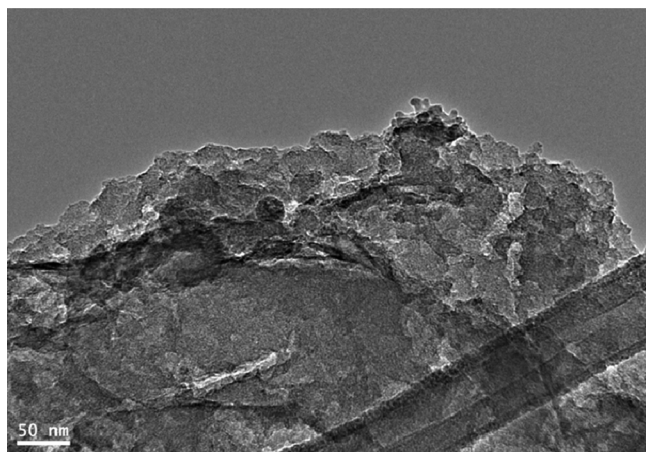


Fig. 2. Transmittance electron microscope image of the prepared AC.

the porous structure and the roughness of the surface, some of them similar to cavities. Fig. 2 showed the transmittance electron microscope image which reveals the micro tubular porous structure of the prepared AC. The surface area of the prepared AC sample was determined using N_2 sorption and it was found to be $115.17 \text{ m}^2 \text{ g}^{-1}$. The prepared AC was examined to determine the surface functional groups on the surface by FTIR spectra. It showed bands at approximately 3600 cm^{-1} , which indicate the presence of the O–H group. Bands around 3400 cm^{-1} reveals the presence of N–H group. Bands around 2920 cm^{-1} are related to the CH stretch. Bands at 1700 cm^{-1} indicated the presence of C=O stretching. Bands at $1600, 1550 \text{ cm}^{-1}$ indicate the presence of aromatic ring in the carbon structure.

Optimization of the solid phase extraction conditions

Effect of pH

The most important parameter affecting SPE is the pH of the sample solution [47–50]. The effect of pH on the recovery of malathion from activated carbon columns was studied over a pH range of 2.0–10.0. The results are shown in Fig. 3. Malathion was quantitatively recovered over the pH range of 2.0–3.0. Therefore, all further experiments were performed at pH 2.5 using a phosphate buffer to adjust the pH of the solutions.

Effect of eluent type

The recovery percent for acetonitrile, ethanol, methanol, DMF and ethyl acetate (with a 3 mL eluent volume) were 49.5, 26.5, 68.8, 8.3 and 96.8%, respectively. Therefore, ethyl acetate was chosen for elution in further studies. These results are in

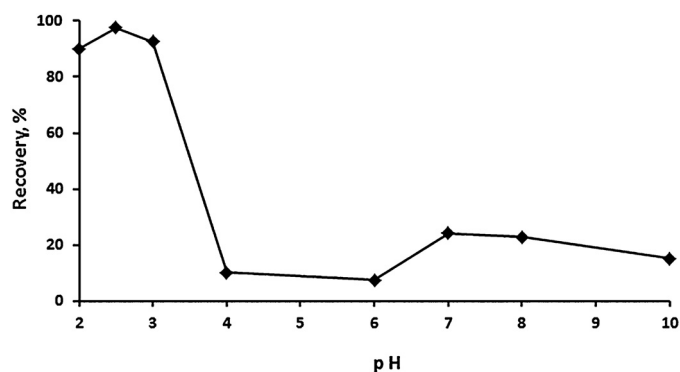
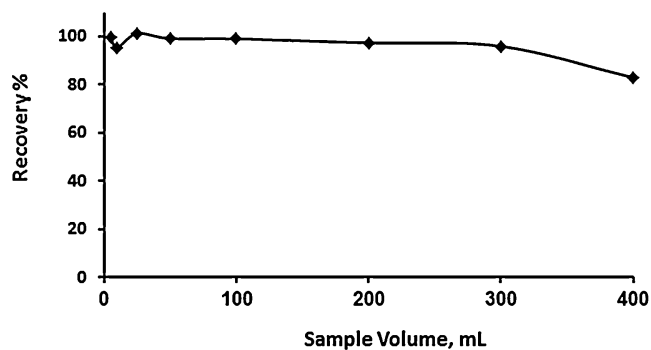


Fig. 3. The effect of pH on the recovery of malathion from activated carbon column.

Fig. 4. The effect of sample volume ($N = 3$).

agreement with that of Gándara, [26], who reported the elution of malathion with ethyl acetate. The influence of the volume of ethyl acetate as the eluent on the recovery of the adsorbed malathion from activated carbon was also examined over the volume range of 2–7 mL. Quantitative recovery values were obtained for ethyl acetate in the range of 3–7 mL, and 3 mL of ethyl acetate was selected as the eluent for all subsequent experiments.

Effect of flow rate of sample and eluent solutions

The flow rate of the model solution through the stationary phase column is an important parameter affecting the duration of the procedure and the contact time of the solution with the solid phase [51]. The flow rate also affects the rate of analyte adsorption onto the solid phase [12]. The model solutions (30 mL) were passed through the column with rates ranging from 3 to 12 mL min⁻¹. The % recovery was quantitative at 3 mL min⁻¹; this flow rate was selected for further experiments. The flow rate of the eluent solution was investigated in the same range. At volumes >3.0 mL min⁻¹, the % recovery of the analyte were not quantitative (67%). For all further experiments, 3 mL min⁻¹ was used as the eluent flow rate.

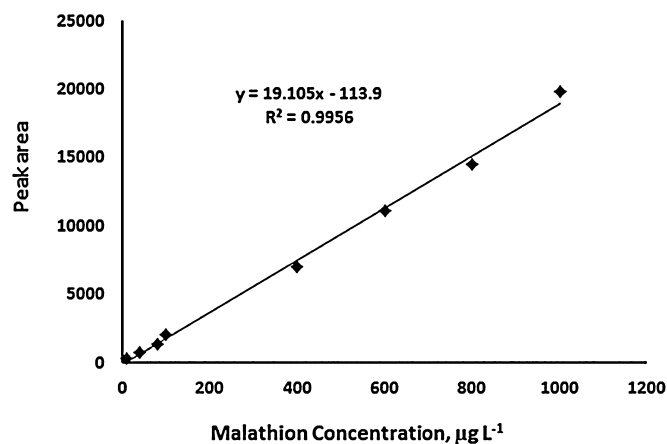


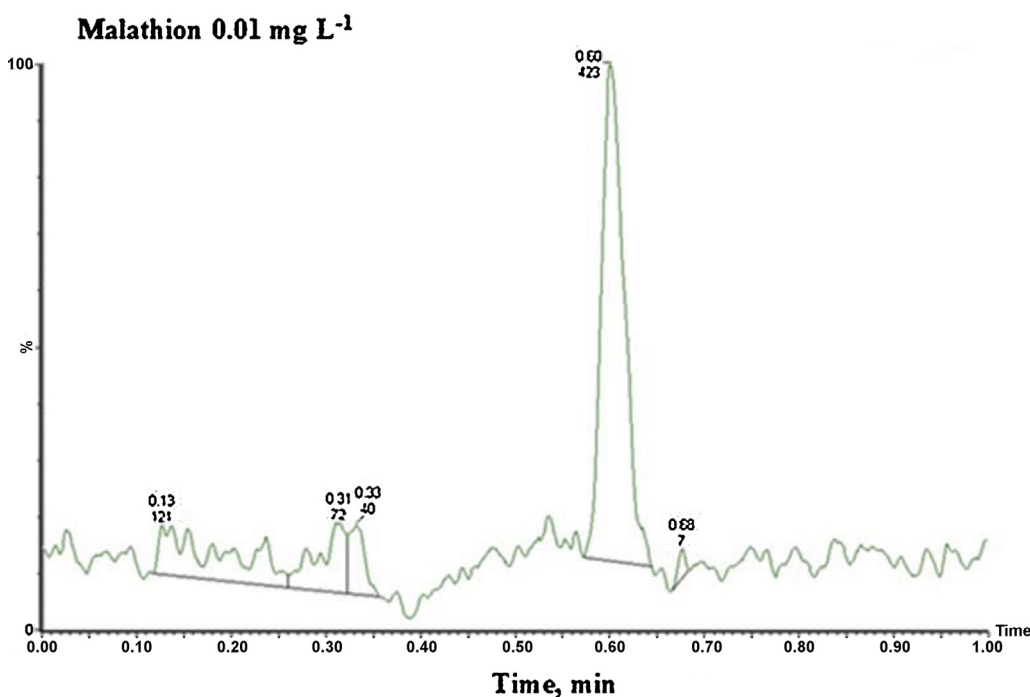
Fig. 5. Calibration curve for malathion.

Influence of sample volume

Quantitative recoveries were obtained for malathion over a sample volume range of 5–300 mL, as shown in Fig. 4. The concentration of malathion solution used for this test is 2 µg L⁻¹, this means the cartridge (0.5 g activated carbon) adsorbed 20 µg of malathion.

Analytical features

The adsorption capacity (loading capacity) of the prepared activated carbon was studied using a batch procedure and found to be 32 µg g⁻¹. The reproducibility of the proposed SPE procedure was investigated by a standard solution containing 1 µg L⁻¹ of malathion ($n = 5$). The relative standard deviation (RSD%) was found to be lower than 4.9%. The calibration curve is shown in Fig. 5. Linearity in the malathion solution was maintained in the range from 10 to 1500 µg L⁻¹. Precision studies were done at 1 µg L⁻¹ level of malathion by performing five replicates. The chromatograms of a malathion standard solution (0.01 mg L⁻¹) is shown in Fig. 6 which reveal the sensitivity of the instrument to

Fig. 6. Chromatogram of a malathion standard (0.01 µg L⁻¹).

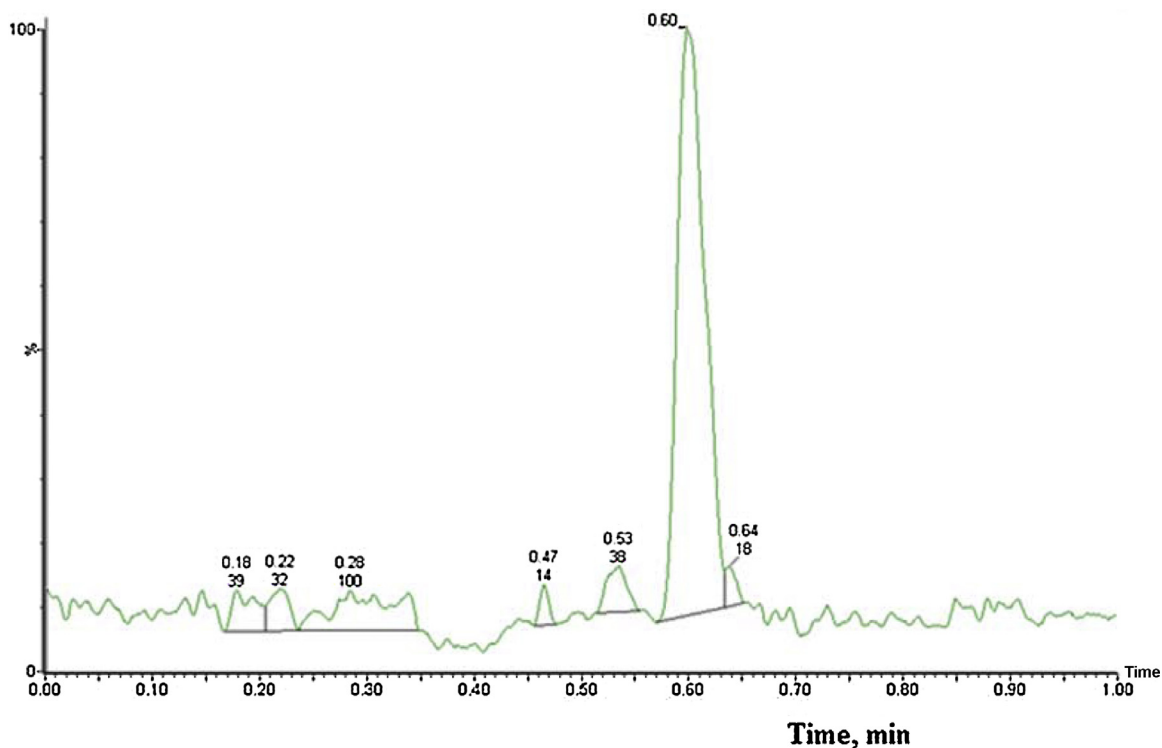


Fig. 7. Chromatogram of soil samples.

detect malathion with clear peak at this concentration. In addition, the chromatogram confirms the need to preconcentration steps to enable the determination of malathion at very trace levels (below 0.01 mg L^{-1}) in some environmental samples. In order to ensure the applicability of the method for detection of malathion in samples with different matrix, the chromatogram of soil and water samples after extraction is shown in Figs. 7 and 8, respectively. The

clear peak for soil and water samples at the same retention time of the standard malathion solutions is obtained which reveal the successful of extraction method. This analytical method was validated by evaluating the preconcentration factor, the limit of detection (LOD) and the limit of quantification (LOQ) [50]. The preconcentration factor is calculated as the ratio between initial sample volume (300 mL) and last extracted solution volume

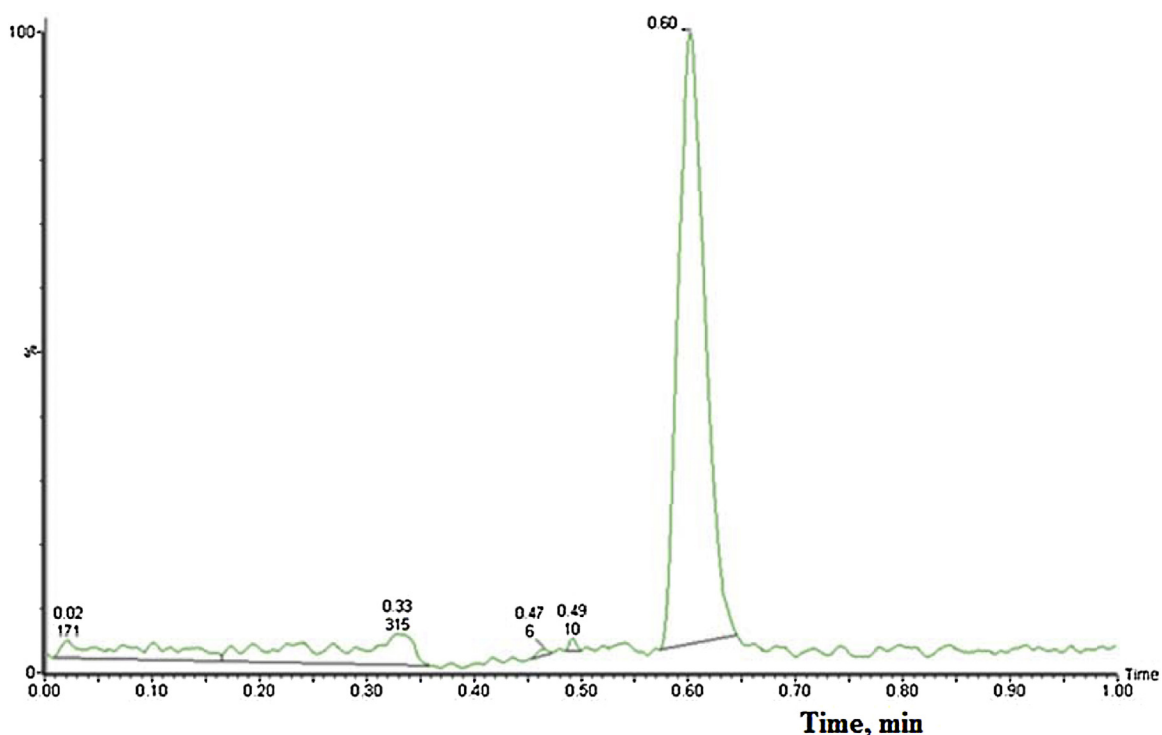


Fig. 8. Chromatogram of waste water samples.

(3 mL), so it was calculated here as 100. The LOD was evaluated here as the ratio of three times the standard deviation of ten blank readings with respect to the pre-concentration factor. It values of was found to be 0.026 ng L^{-1} . This low LOD is due to combination of SPE with high preconcentration factor and the advanced instrument such as UPLC–MS. The limit of quantification (LOQ) was evaluated here as the three times the LOD. It values of was found to be 0.078 ng L^{-1} .

Application to real samples

The SPE procedure was applied to the determination of malathion in environmental samples (soil and agricultural wastewater). The reliability of the proposed method was determined by spiking known concentrations of malathion into the real samples. The results of this experiment are shown in Table 1. The % recovery was calculated based on the standard malathion solution equal to the spiked one. Results indicate the high efficiency of SPE procedure for malathion analysis. Analysis was performed with three replicates to ensure the precision (repeatability) of the method. Good agreement was found between the amounts of malathion that were added and measured; the percent recovery was $>95.7\%$. These results reveal the accuracy of the SPE procedure and also indicate that the method is matrix-independent.

Comparison of malathion recovery with other extraction methods from the literature

As shown in Table 2, the proposed SPE in this work showed high efficiency, low detection limit and acceptable recovery percent compared to other preconcentration method from the literature.

Application for malathion removal from aqueous solutions

The effect of contact time

The amount of malathion adsorbed onto activated carbon was studied as a function of shaking time at different initial

Table 1
Malathion recovery from spiked soil and agricultural wastewater samples.

	Concentration spiked ^a	Concentration found ^a	Recovery %
Soil samples (n=3)	0	0	
	1.63	1.61 ± 0.5	98.8
	1.50	14.8 ± 6	98.7
	58.2	58.2 ± 11	100
	151.1	150.9 ± 39	99.9
Agricultural wastewater samples (n=3)	0	0	
	16.3	16 ± 1	98.2
	145	145 ± 3	100
	582	557 ± 52	95.7
	1511	1498 ± 128	99.1

^a Concentrations are expressed as $\mu\text{g kg}^{-1}$ for soil sample (ng L^{-1}), for water sample.

Table 2
Comparison of malathion recovery with other extraction methods from the literature.

Method	LOD	% Recovery	Refs.
Cleanert-PEP	4 ng L^{-1}	59.5–94.6	Ma et al. [52]
SPE			
SPE-GC/MS	0.03	97.8	Lambropoulou, Sakellariades and Albanis [53]
SPE	–	80–100	Beyers and Carlson [54]
SPME	5 ng L^{-1}	71–114	Used et al. [55]
SDE	5 ng L^{-1}	91–104	Ahmadi et al. [56]
SPE	0.026 ng L^{-1}	95.7	This study

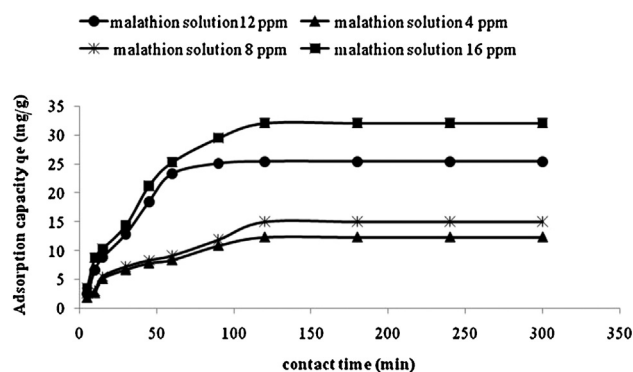


Fig. 9. Effect of contact time on malathion adsorption onto activated carbon prepared from mixed wastes.

concentrations at 30°C , and desired pH (2.5). The effect of contact time for four different concentrations (4, 8, 12 and 16 ppm) of malathion adsorption by activated carbon is given in Fig. 9. It is evident from the figure that the amount of malathion adsorbed increases with increasing contact time. Further, the adsorption was rapid in the early stages and then gradually decreased to become constant after the equilibrium point. The saturation point is almost reached at 120 min. At this point, the amount of malathion desorbing from the activated carbon is in a state of dynamic equilibrium with the amount of the malathion being adsorbed on the activated carbon. The amount of malathion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent. The removal of malathion was found to be dependent upon the initial concentration. The amount of malathion adsorbed, q_e (mg g^{-1}), increased with an increase in the initial concentration. In this study, the amount malathion adsorbed at equilibrium increased from 12.3 to 32.1 mg g^{-1} with the increase in the initial malathion concentration from 4 to 16 ppm. The mass transfer driving force becomes larger when the initial concentration increased and hence resulting in higher adsorption of malathion. However, the removal of malathion becomes independent on the initial concentration, in case of very low values of the initial concentration due to the large ratio of available activated carbon surface to initial malathion concentration.

Batch kinetic studies

Adsorption kinetics provides valuable information about the reaction pathways and mechanism of the reactions. In order to examine the controlling mechanism of the adsorption process, the pseudo first-order, pseudo second-order, and intraparticle diffusion models [57–59] were applied to analysis the experimental data of malathion adsorption on the prepared activated carbon. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

The pseudo-first order kinetic model. The linearized-integral form of the pseudo first-order model [57], is generally expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where q_e and q_t are the amounts of malathion adsorbed (mg g^{-1}) at equilibrium and at time t , respectively, and k_1 is the rate constant of first order adsorption (min^{-1}). Straight lines were obtained by plotting $\log(q_e - q_t)$ against t , as shown in Fig. 10. The values of the rate constant k_1 and q_e at four different initial concentrations were obtained from the slopes and intercepts of the plots, respectively, and presented in

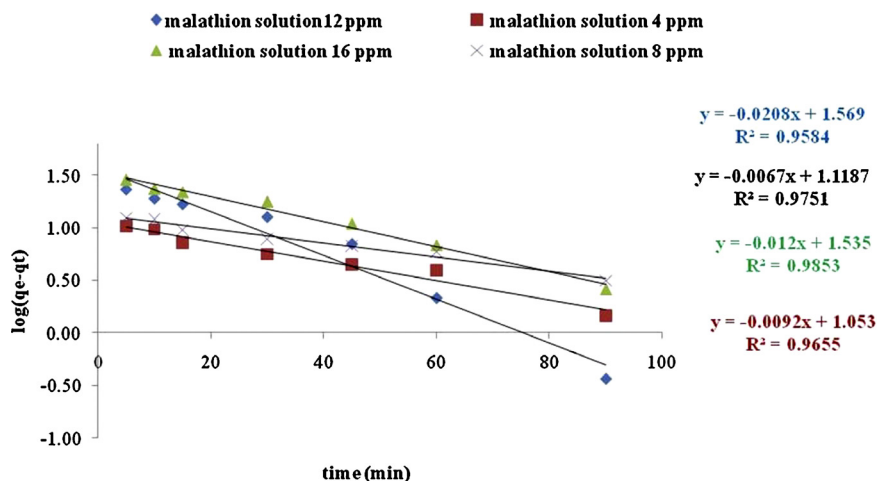


Fig. 10. Lagergren first order plot for malathion adsorption onto activated carbon prepared from mixed wastes.

Table 3

Kinetic constant parameters obtained for malathion adsorption on activated carbon prepared from mixed wastes.

C_i (ppm)	Pseudo-first order				Pseudo-second order			Intraparticle diffusion model		
	$q_{e,exp}$ (mg g ⁻¹)	k_1 (10 ⁻³) (min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_2 (10 ⁻⁴) (g (mg min) ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_{id} (mg (g min) ⁻¹)	C (mg g ⁻¹)	R^2
4	12.32	0.021	11.29	0.95	13.9	2.2×10^{-3}	0.99	1.16	-0.24	0.97
8	15.03	0.015	13.14	0.97	17.45	1.4×10^{-3}	0.98	1.35	-0.57	0.97
12	25.4	0.047	37.06	0.95	28.9	1.14×10^{-3}	0.98	2.8	-2.03	0.95
16	32.11	0.027	34.2	0.98	37.03	7.7×10^{-4}	0.99	3.34	-2.62	0.98

Table 3. Results showed that there are differences between the experimental q_e (12.32, 15.03, 25.4 and 32.11 mg g⁻¹) and the calculated q_e (11.29, 13.14, 37.06 and 34.2 mg g⁻¹) in case of initial malathion concentration of 4, 8, 12 and 16 ppm, respectively.

The pseudo second-order kinetic model. The parameters of pseudo second-order adsorption kinetic rate equation is expressed [58] as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

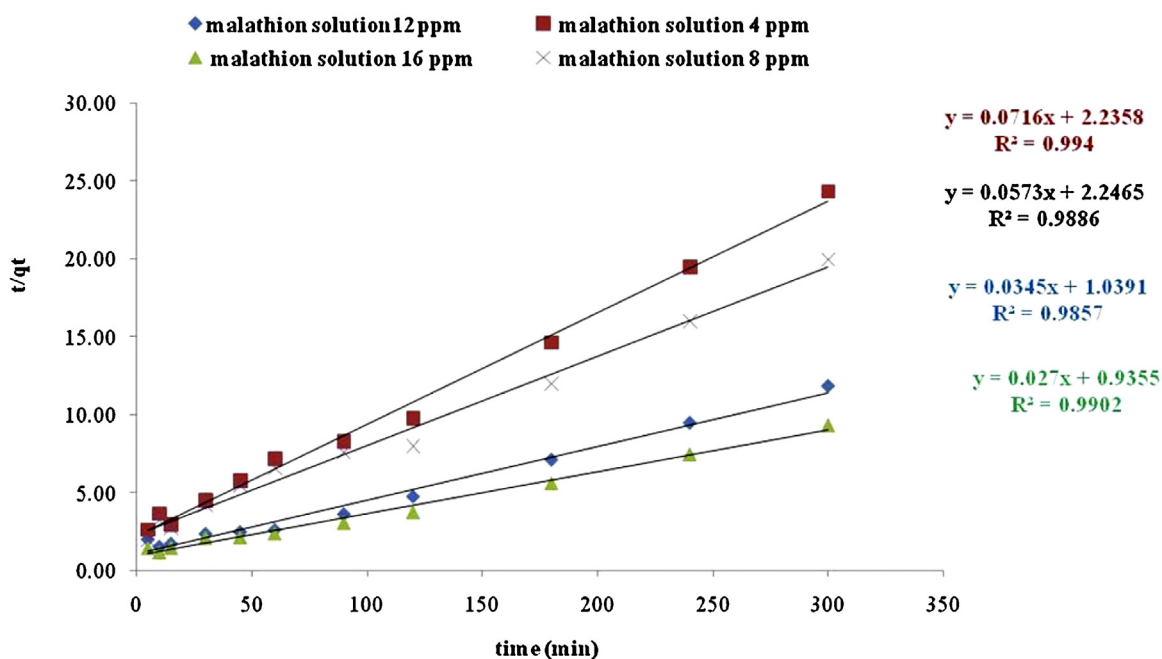


Fig. 11. Pseudo-second order plot for malathion adsorption onto activated carbon prepared from mixed wastes.

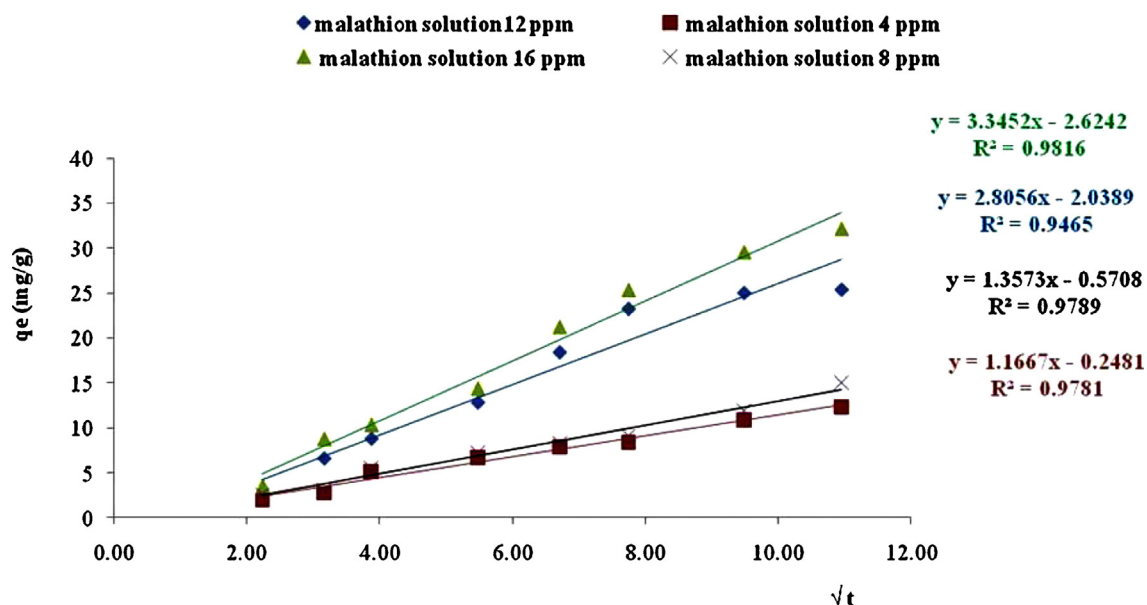


Fig. 12. Intraparticle diffusion model plot for malathion adsorption onto activated carbon prepared from mixed wastes.

The plots of t/q_t versus t , gave linear plots Fig. 11. The values of q_e and k_2 were determined from the slopes and intercepts of the plots, respectively, and are listed in Table 3. The experimental q_e (12.32, 15.03, 25.4 and 32.11 mg g^{-1}) are nearer to the calculated q_e (13.9, 17.45, 28.9 and 37.03 mg g^{-1}) in case of initial malathion concentration of 4, 8, 12 and 16 ppm, respectively.

The intraparticle diffusion model. The intraparticle diffusion model was tested to identify the diffusion mechanism [59], is expressed as in the following equation:

$$qt = k_{id}t^{1/2} + C \quad (4)$$

where k_{id} is the intraparticle diffusion rate constant ($\text{mg g min}^{1/2}$), C is the intercept (mg g^{-1}).

The plot of q_t versus $t^{1/2}$ gave straight line and the values of k_{id} were calculated from the slopes of the plots. Values of C gave an idea about the thickness of boundary layer, i.e., the larger the intercept, greater the contribution of the surface sorption in the rate controlling step. The data for malathion adsorption onto activated carbons applied to intraparticle diffusion model is shown in Fig. 12, and the results are given in Table 3.

It is clear from Table 3 that among these three models, pseudo-second order kinetic equations had high R^2 values and also the experimental q_e is in accordance with calculated q_e . For pseudo-first order kinetic model the experimental q_e are not in good agreement with calculated q_e . In the view of these results, it can be said that the pseudo second order kinetic model provided a good correlation for the description of the mechanism of sorption of malathion in contrast to the other models.

Conclusions

In this work, environmental benefits have been valorized by applying activated carbon from wastes sources as low cost starting materials for various environmental applications. Sensitive detection of malathion is achieved by combination of SPE with UPLC–MS. This combination offered many advantages for the monitoring as well as research studies of malathion; the proposed method provide fast determination, simple procedure, inexpensive packaging material and low detection limits. The SPE method was

successfully applied to the extraction of malathion from agricultural wastewater and soil samples. The optimized condition for maximum recovery was at sample pH of 2.5 and a sample volume of 300 mL, with elution by 3 mL of ethyl acetate. In addition, the activated carbon from waste showed high efficiency in removal of malathion from aqueous solutions. By optimizing the adsorption process, results showed that maximum adsorption capacity was 32.1 mg g^{-1} . The kinetics of malathion adsorption followed pseudo-second order rate expressions.

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