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Removal of malathion from aqueous solution using De-Acidite FF-IP resin and determination by UPLC–MS/MS: Equilibrium, kinetics and thermodynamics studies

Mu. Naushad *, Z.A. ALOthman, M.R. Khan *

Advanced Materials Research Chair, Department of Chemistry, College of Science, Bld #5, King Saud University, Riyadh, Kingdom of Saudi Arabia

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ABSTRACT

In the present study, De-Acidite FF-IP resin was used to remove a highly toxic and persistent organophosphorus pesticide (malathion) from the aqueous solution. Batch experiments were performed as a function of various experimental parameters such as effect of pH (2–10), contact time (10–120 min), resin dose (0.05–0.5 g), initial malathion concentration (0.5–2.5 μg mL^{-1}) and temperature (25–65 °C). The concentration of malathion was determined using a sensitive, selective and rapid ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) method. The uptake rate of malathion on De-Acidite FF-IP resin was rapid and equilibrium established within 40 min. Kinetics studies showed better applicability for pseudo-second-order model. The equilibrium data was fitted to Langmuir and Freundlich isotherm models and the isotherm constants were calculated for malathion. The values of thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) were computed from the Van't Hoff plot of ln K_C vs. $1/T$ which showed that the adsorption of malathion was feasible, endothermic and spontaneous. The regeneration studies were carried out which demonstrated a decrease in the recovery of malathion from 95% to 68% after five consecutive cycles. Breakthrough and exhaustive capacities of malathion were found to be 1.25 mg g^{-1} and 3.5 mg g^{-1}, respectively.

1. Introduction

Pesticides are worldwide used to adjust the growth of the plants, prevent agriculture from a variety of damage and increase the production of crops. In spite of their numerous merits, the increasing use of pesticides in agriculture and domestic activities for controlling pests is also polluting the environment day by day [1,2]. Pesticides are among the most dangerous environmental pollutants because of their stability, mobility, capable of bioaccumulation and long-term effects on living organisms. The pesticides contaminate water through agricultural, domestic and industrial activities. When these pesticides are introduced into the environment through spraying on crops, some part of these chemicals stays in the area where it is applied and transported to various environmental compartments [3]. They may reach streams or groundwater through spillage, leaching, aerial transport and adsorbed by plants and eatable vegetables which are the main sources of pesticides exposure in living organisms [4]. In water, these compounds can undergo transformations leading to the production of substances of even greater toxicity [5]. According to European Community Drinking Water Directive, the guideline for pesticides concentration in water for human consumption is 0.1 μg L^{-1} [6]. Organophosphorous pesticides are known to be highly toxic agricultural chemicals which are widely used in plants protection. Common organophosphorous pesticides are dimethoate, methylparathion, phosphamidon, fienitrothion, malathion, monocrotophos and phorate [7]. Among these pesticides, malathion is one of the most toxic and persistent organophosphorus pesticides which has caused serious environmental problems [8]. Individuals can also be exposed to malathion if they live near landfills where malathion has been dumped or near water containing malathion that washes off nearby land. Exposure to high amounts of malathion in the air, water and food may cause difficulty in breathing, vomiting, chest tightness, diarrhea, blurred vision, salivation, watery eyes, dizziness, sweating, headaches, loss of consciousness and even death. Therefore, it is highly important to reduce and eliminate these life threatening compounds from environment before they discharged and their levels in water must be monitored continuously, especially in sources of drinking water. The use of wide range of pesticides makes them enormously difficult to produce a single method for pesticide disposal that applies universally. So, several methods either independent or in conjunction have been used for the

* Corresponding authors. Tel.: +966 14674198.
E-mail addresses: shad81@rediffmail.com (Mu. Naushad), mrkhan078@gmail.com (M.R. Khan).

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removal of pesticides including chemical oxidation with ozone [9], biological degradation [10], Fenton degradation [11], coagulation [12], photo degradation [13], combined ozone and UV irradiation [14] and adsorption [15–17]. But, adsorption is considered to be relatively more effective to other traditional techniques due to low operating cost, reusability of the adsorbent, improved selectivity for specific adsorbates and ability to treat wastes in more concentrated form [15,16]. Several authors have been successfully studied a variety of cost-effective and locally available adsorbents for the removal of different types of pesticides [17–21]. Nevertheless, there are some disadvantages associated with these type of adsorbents viz. incompatible for column operation because of non-granulometric nature which results in chocking of industrial columns, adsorption of pesticides at low levels, high regeneration cost and the generation of carbon fines. In addition, other techniques like reverse osmosis, nanofiltration and advanced oxidation processes are vulnerable due to the formation of undesirable oxidation byproducts and membrane fouling [22]. Although, synthetic resins are comparatively expensive but can be designed to achieve higher degrees of selectivity and adsorption capacity for certain compounds than activated carbon. Anion exchange resins have shown strong potential for the removal of natural organic matter (NOM) and pesticides [23,24].

Nevertheless, several studies have been carried out on pesticide removal using ion-exchange resins, but the malathion removal using such resins is still limited. Inconsideration of the advantages associated with ion-exchange resins, the efforts have therefore been made in our laboratory for the removal of malathion from aqueous solutions using a strongly basic anion exchange resin (De-Acidite FF-IP). The effects of several operating parameters such as pH, contact time, resin dose, initial malathion concentration and temperature were investigated to reach at optimum conditions for the adsorption process. The malathion concentration was determined using a sensitive, precise and rapid method based on UPLC–MS/MS. The kinetics, isotherms and thermodynamics for the adsorption of malathion on De-Acidite FF-IP resin were also carried out to determine the mechanisms involved in the adsorption process.

2. Experimental

2.1. Chemicals and materials

Solvents and chemicals were of HPLC or analytical grade. Cross linked polystyrene based strongly basic anion exchange resin De-Acidite FF-IP (Cl^- form, SRA 65, 14–52 mesh size, 3%–5% cross-linking) was purchased from the Permutit company Ltd. (London, England). Malathion (diethyl 2-[(dimethoxyphosphorothioyl) sulfanyl] butanedioate) with molecular formula $C_{10}H_{19}O_6PS_2$ and formula weight of 330 g mol^{-1} was obtained from BDH chemicals Ltd. (Poole, England). Formic acid for mobile preparation was obtained from Panreac (Barcelona, Spain) and other chemicals used were of analytical reagent grade. Water was purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Glassware used were supplied by Schott (Duran, Germany), cleaned with distilled water followed by Milli-Q water and dried at 40 °C.

To remove the adhered impurities from the resin surface, it was washed with Milli-Q water for five times followed by drying at 40 °C for 10 h. The dried resin was stored in desiccator until used. Stock solution of malathion (100 μg mL^{-1}) was prepared in methanol and used for further dilutions. Standard solutions of malathion at different concentration levels (0.01–1 μg mL^{-1}) were prepared for calibration curves. Standards and samples were filtered through a 0.22 μm PVDF syringe filter (Membrane solutions, Texas, USA) before being injected into the UPLC–MS system.

2.2. Instrumentation and MS conditions for the analysis of malathion

Malathion separation was performed on a Waters ultra-performance liquid chromatography system (UPLC), equipped with a quaternary pump system (Milford, MA, USA), using an Acquity BEH C_{18} column (50 mm × 2.1 mm i.d., 1.7 μm particle size) (Waters, Milford, MA, USA). Optimum separation was achieved in isocratic mode with mobile phase consisting of acetonitrile 80% and water 19.99% with 0.1% of formic acid. The mobile phase flow rate was 400 μL min^{-1} and sample injection volume was 5 μL.

The UPLC system was coupled to a Quattro Premier triple quadrupole mass spectrometer (Micromass, Milford, MA, USA) consisting of electrospray ionization (ESI) source. The mass spectrometer (MS) instrument was operated in the positive mode and the data was acquired in multiple reaction monitoring (MRM) form using the protonated molecular ion of malathion as a precursor ion. Source working conditions were as follows: cone voltage, 22 V; capillary voltage, 3.0 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}. Nitrogen 99.99% purity, Peak Scientific, model NM30LA nitrogen generator (Inchinann, UK) and high purity argon (99.99%, Speciality Gas Centre, Jeddah, Saudi Arabia) were used as cone and collision gases, respectively. An Oerlikon rotary pump, model SOGEVAC SV40 BI (Paris, France) provided the primary vacuum to the mass spectrometer. The MRM transition as well as the collision energy voltage applied for the analysis is summarized in Table 1. Data acquisition was carried out using Waters MassLynx V4.1 software (Milford, MA, USA).

2.3. Quality assurance and quality control

To evaluate the performance of the UPLC–MS/MS method, quality parameters such as limit of detection (LOD) (signal-to-noise ratio, 3:1) and limit of quantification (LOQ) (signal-to-noise ratio, 10:1) linearity, intraday and interday precision were studied. The LOD and LOQ were obtained 0.02 ng mL^{-1} and 0.07 ng mL^{-1}, respectively. The obtained LOD and LOQ values were calculated by analyzing three replicates of a blank sample (Milli-Q water) spiked with malathion at low level (0.05 μg mL^{-1}). Calibration curves based on the peak area were constructed. They were linear across the level range studied (0.01–1 μg mL^{-1}) and the correlation coefficients (r^2) were >0.998 for the analyzed compound. The intraday (run-to-run precision) was estimated from five replicate injections of a standard (0.5 μg mL^{-1}), on the same day and interday (day-to-day precision) was determined by five replicate injections of the aforementioned standard along three consecutive days. These determinations were evaluated on the basis of the calculation of the relative standard deviation (RSD) of the peak area values. The RSD values obtained for intraday and interday were 1.63% and 2.13%, respectively. The obtained quality parameters values confirmed that the method was successful which was required for accurate malathion analysis.

2.4. Instrumental characterization

Scanning electron microscopy (SEM) analysis method was employed to observe the surface physical morphology of

Table 1
MRM parameters used with the triple quadrupole instrument*.

Analyte	Precursor ion $[M+H]^+$ m/z	Quantification Product ion (m/z)	Confirmation Product ion (m/z)	Collision energy voltage (V)
Malathion	330	127	99	22

* Dwell time was 0.025 ms.

De-Acidite FF-IP resin (before and after the adsorption of malathion) using a high-performance scanning electron microscope (JSM-6380 LA, Japan).

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique which utilizes X-rays that are emitted from the specimen when bombarded by the electron beam to identify the elemental analysis or chemical characterization of a sample. The EDS of De-Acidite FF-IP resin before and after the adsorption of malathion was recorded.

A Nicolet 6700 FTIR Thermo Scientific spectrometer was used to record the spectra of De-Acidite FF-IP resin before and after the adsorption of malathion. 10 mg (dry mass) of De-Acidite FF-IP resin was thoroughly mixed with 100 mg (dry mass) of KBr and ground to a fine powder. A transparent disc was made by applying a pressure of 80 psi in a moisture free atmosphere. The FTIR absorption spectra were recorded from 450 cm^{-1} to 4000 cm^{-1}.

2.5. Adsorption batch experiments

The adsorption of malathion on De-Acidite FF-IP resin was studied by batch experiments using Erlenmeyer flasks of 50 mL capacity covered with teflon sheets to prevent the introduction of any foreign particle contamination. The adsorption measurements were made in triplicate and average values were reported. The optimization for the adsorption of malathion was achieved by varying the parameters such as equilibration time, pH, initial malathion concentration, dose of resin and the working temperature. When the equilibrium was attained after each experiment, the samples were withdrawn from the shaker and 1 mL of malathion solution from each sample was filtered through a 0.22 μm PVDF filter and injected into UPLC–MS system to determine the concentration of malathion. The adsorption capacity of De-Acedite FF-IP resin for malathion was determined using the following equation [25].

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where, C_o and C_e are the initial and equilibrium concentrations of malathion in solution (mg L^{-1}), respectively, V is the volume of solution (L) and m is the amount of adsorbent used (g).

2.6. Breakthrough capacity

0.2 g of De-Acidite FF-IP resin was taken in a glass column (0.6 cm internal diameter) with glass wool support. Malathion solution (1000 mL) of 1 μg mL^{-1} initial concentration (C_o) was passed through the column with a flow rate of 1 mL min^{-1}. The effluent was collected in 50 mL fractions and the amount of malathion (C) was determined in each fraction by UPLC–MS/MS. The breakthrough curve was obtained by plotting C/C_o vs. volume of the effluent.

2.7. Desorption and regeneration studies

Desorption studies were carried out by both the batch and column process. In the batch process, 50 mL of 1 μg L^{-1} malathion solution was treated with 0.5 g of De-Acidite FF-IP resin in Erlenmeyer flask using temperature controlled shaker incubator at 120 rpm for 1 h. After 1 h, De-Acidite FF-IP resin was washed several times with Milli-Q water to remove the excess of malathion. Then, De-Acidite FF-IP resin was treated with 50 mL of 0.01 M NaOH solution in another flask. The flask was again shaken in temperature controlled shaker incubator at 120 rpm (to desorb malathion) for 1 h. The solution was then filtered and injected into UPLC–MS system to determine the amount of malathion. In column process, 0.5 g of adsorbent was taken in glass column (0.6 cm internal diameter) with glass wool support. 50 mL of 1 μg L^{-1} malathion solution was passed through the column at flow rate of 1 mL min^{-1}. The resin in the column was washed several times by Milli-Q water in order to remove traces of malathion remained unadsorbed. 50 mL of 0.01 M NaOH solution was then passed through the column as an eluent. The effluent was collected in 10 mL fractions with a flow rate of 1 mL min^{-1} and the malathion desorbed were determined in each fraction.

The regeneration of any ion-exchange resin or adsorbent is directly related to the application potential of adsorption technology. For this study, 50 mL of 1 μg L^{-1} malathion solution was passed through the column containing 0.5 g of De-Acidite FF-IP resin on glass wool support at 1 mL min^{-1} flow rate. The column was washed several times with Milli-Q water to remove unadsorbed traces of malathion. To regenerate the column, 50 mL of 0.01 M NaOH solution was passed through the column as an eluent at 1 mL min^{-1} flow rate. The effluent was collected and desorbed malathion concentration was determined. The same procedure was repeated for five times.

3. Results and discussion

3.1. Characterization

SEM examination of De-Acidite FF-IP resin before and after adsorption of malathion was undertaken (Fig. 1) and it was found that the surface of De-Acidite FF-IP resin was clean and spherical shaped before adsorption. However, after adsorption of malathion, the surface became rough and malathion was adhered on the surface due to which the morphology has been changed. It was demonstrated from EDS study (Table 2) that Cl element was disappeared and some new element (S and P) were introduced after the adsorption of malathion which also confirmed the adsorption of malathion onto De-Acidite FF-IP resin.

The FTIR spectra of De-Acidite FF-IP resin before and after malathion adsorption are presented in Fig. 2. It was concluded from the Fig. 2 that the broad peak around 3400 cm^{-1} corresponded to the presence of interstitial water and hydroxyl groups [26]. A sharp peak at around 1400 cm^{-1} was due to the stretching vibration of C–N [27]. A weak peak at 2970 cm^{-1} was aroused owing to $–CH_2$ asymmetric stretching vibration. After adsorption of malathion, the peak at 1400 cm^{-1} (representative of the C–N group) was disappeared while the two new peaks at 1548 and 1600 were produced which may be due to P═S and C═O groups of malathion. It was also observed from our EDS results that S and P elements were introduced after the adsorption of malathion (Table 2).

3.2. Batch operations for the removal of malathion

3.2.1. Effect of contact time

The time dependent adsorption behavior was measured by performing a series of adsorption experiments at different contact times (10–120 min). It was observed that instant adsorption of malathion (76%) was achieved within 10 min and equilibrium was established after 40 min where the adsorption reached upto 91% (Fig. S1). It was noted that the adsorption increased rapidly in the initial stages and then became slow at later stages till the equilibrium was attained. This difference in the rate of adsorption may be due to the fact that initially all adsorbent sites were vacant so the adsorption was high. Later, due to the decrease in the number of adsorption sites on the resin as well as malathion concentration, the adsorption of malathion became slow. Fig. 3a and b shows the UPLC–MS/MS chromatograms of malathion standard solution (1 μg mL^{-1}) before and after adsorption (40 min), respectively. From these figures, it is

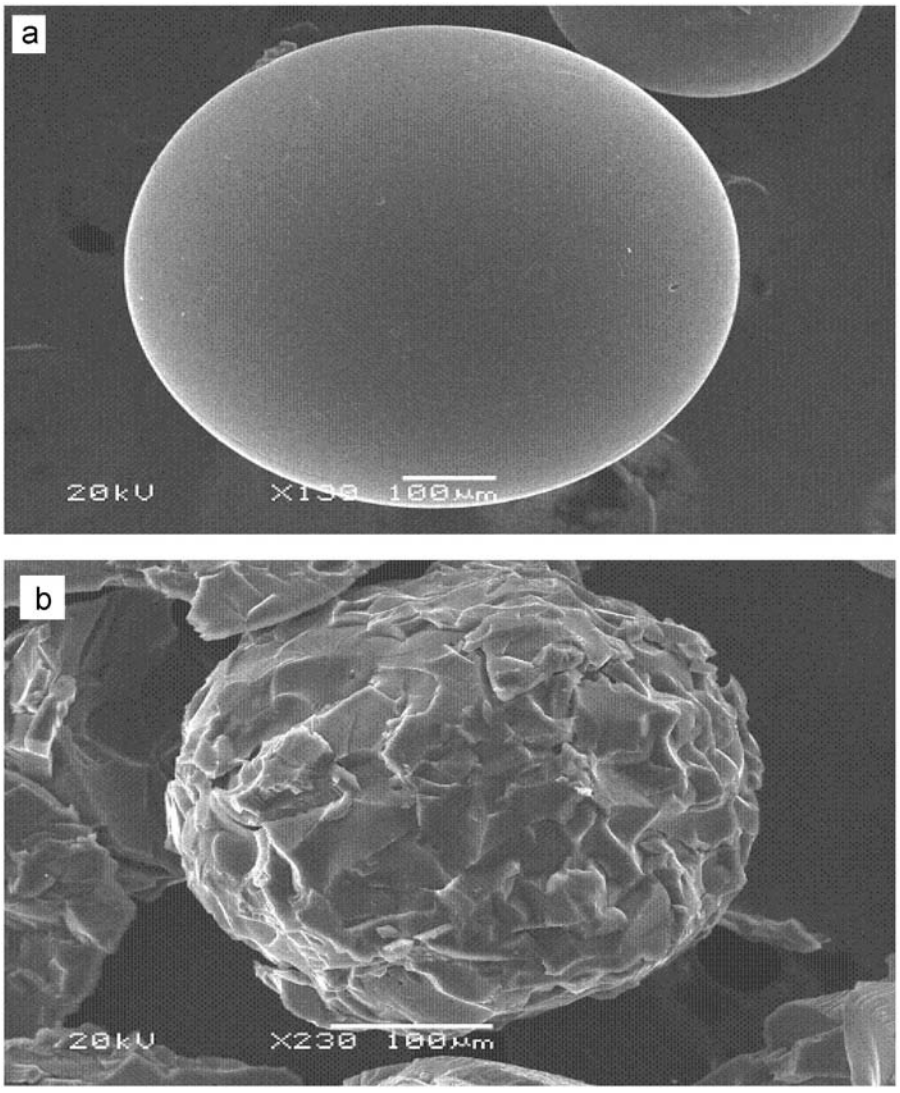

Fig. 1. Scanning electron micrographs of De-Acidite FF-IP resin (a) and malathion adsorbed De-Acidite FF-IP resin (b).

Table 2
EDS data of De-Acidite FF-IP resin before and after malathion adsorption.

Element	Mass %	
	Before adsorption	After adsorption
C	89.25	88.12
O	0.64	2.23
Al	0.61	0.58
Cl	9.09	–
N	0.41	0.22
S	–	5.72
P	–	3.13

apparent that the UPLC–MS/MS malathion chromatogram relative intensity decreased upto 91% after 40 min (Fig. 3b).

3.2.2. Effect of pH

For the adsorption process, the pH of the aqueous solution is one of the main variable parameters. The pH may affect the ionization degree of the sorbate and the surface property of the sorbent [28]. The influence of pH in the range of 2–10 was studied for 40 min. The pH of the solution was adjusted using $NaOH/HNO_3$ solutions. It is evident from Fig. S1, that percentage removal of malathion was increased from 91% to 96% with the increase in pH from 2 to 6. Beyond pH 6, the adsorption became constant. So, further studies were carried out at pH 6 (optimum pH). From the Fig. 3a and c, it is clear that the UPLC–MS/MS malathion chromatogram relative intensity decreased upto 96% at pH 6 (Fig. 3c).

3.2.3. Effect of resin dose

The effect of adsorbent dose on the removal of malathion was studied at different doses (0.05–0.5 g) by keeping the shaking time 40 min, pH 6 and initial malathion concentration 1 $\mu g\,mL^{-1}$. It is apparent from Fig. S1 that the removal of malathion increased from 90% to 96% when the De-Acidite FF-IP resin dose was increased from 0.05 g/20 mL to 0.2 g/20 mL. After dosage of 0.2 g/20 mL, there was no significant change in percentage removal of malathion. It may be due to the overlapping of active sites at higher dosage. So, 0.2 g/20 mL was considered as optimum dose and was used for further studies.

3.2.4. Adsorption kinetics

Adsorption kinetics describes the solute uptake rate at the solid–solution interface and evidently provides valuable information about the reaction pathways and mechanism of the reactions. The kinetics of malathion adsorption on De-Acidite FF-IP resin were analyzed using pseudo-first-order and pseudo-second-order models. The conformity between experimental data and the model

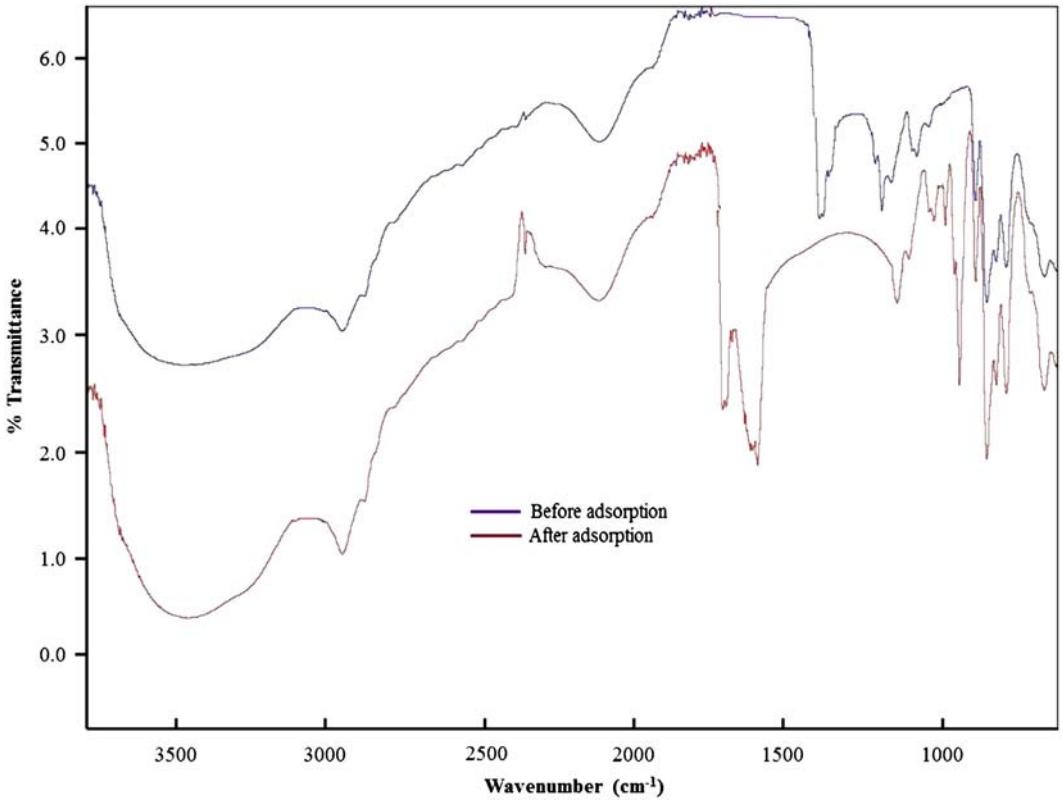

Fig. 2. FTIR spectra of De-Acidite FF-IP resin before and after malathion adsorption.

predicted values was expressed by the correlation coefficients. A relatively high r^2 value indicated that the model successfully described the kinetics of malathion adsorption.

3.2.4.1. The pseudo-first-order equation. The rate constant K_1 for the adsorption of malathion at different concentrations (1, 2 and 3 μg mL^{-1}) was studied by Lagergren rate equation [29].

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (2)$$

where, q_t and q_e are the amounts of malathion adsorbed at time t, and at equilibrium, respectively. The values of rate constant K_1 were determined from the slope of the plot log $(q_e - q_t)$ vs. t.

3.2.4.2. The pseudo-second-order equation. The pseudo-second-order kinetic rate equation was given by Ho and Mckay [30]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where, K_2 is the pseudo-second-order rate constant. The values of K_2 for all studied concentrations were determined from the intercepts of the plot t/q_t vs. t. Fig. 4a and b show the plots for Lagergren-first-order and pseudo-second-order kinetic models, respectively. The parameters obtained for two models are presented in Table 2. It is apparent from Table 3 that the values of r^2 of pseudo-first-order model were slightly lower than the pseudo-second-order model which indicated that pseudo-second-order model was better obeyed than pseudo-first-order model.

3.2.5. Effect of initial concentration and adsorption isotherms

The effect of initial malathion concentration on the percentage adsorption of malathion onto De-Acidite FF-IP resin was performed by the batch method and the result is presented in Fig. S2. It is evident from Fig. S2 that the percentage removal of malathion decreased from 98% to 80% as the concentration of malathion increased from 0.5 μg mL^{-1} to 2.5 μg mL^{-1}. The higher uptake of malathion at lower concentration may be attributed to the availability of more active sites on the surface of the De-Acidite FF-IP resin for lesser number of adsorbate (malathion) species.

Adsorption isotherm studies are imperious to describe the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. In this study, two adsorption isotherm models (Langmuir and Freundlich) were used for the adsorption of malathion onto De-Acidite FF-IP resin.

The Langmuir model assumes that the uptake of adsorbate molecules occurs on a homogenous surface with a finite number of adsorption sites by monolayer adsorption without any interaction between adsorbed molecules [31]. Once a site is occupied by adsorbate molecules, no further adsorption can occur at that site. The surface will reach the saturation point and the maximum adsorption of the surface will be achieved. To ensure equilibrium conditions, the linear form of the Langmuir isotherm model was applied to the experimental data as

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (4)$$

where, q_e is the amount of malathion adsorbed (mg g^{-1}), C_e is the equilibrium concentration of malathion (mg L^{-1}), Q_0 and b are the Langmuir constants related to maximum monolayer adsorption capacity and energy of adsorption, respectively.

The values of Q_0 and b have been evaluated from the intercept and slope of linear plots of $1/q_e$ vs. $1/C_e$, respectively (Table 4). It is clear from Table 4 that b values were higher at higher temperatures which showed endothermic nature of malathion adsorption.

The adsorption capacity of De-Acidite FF-IP resin for the removal of malathion was compared with those of other

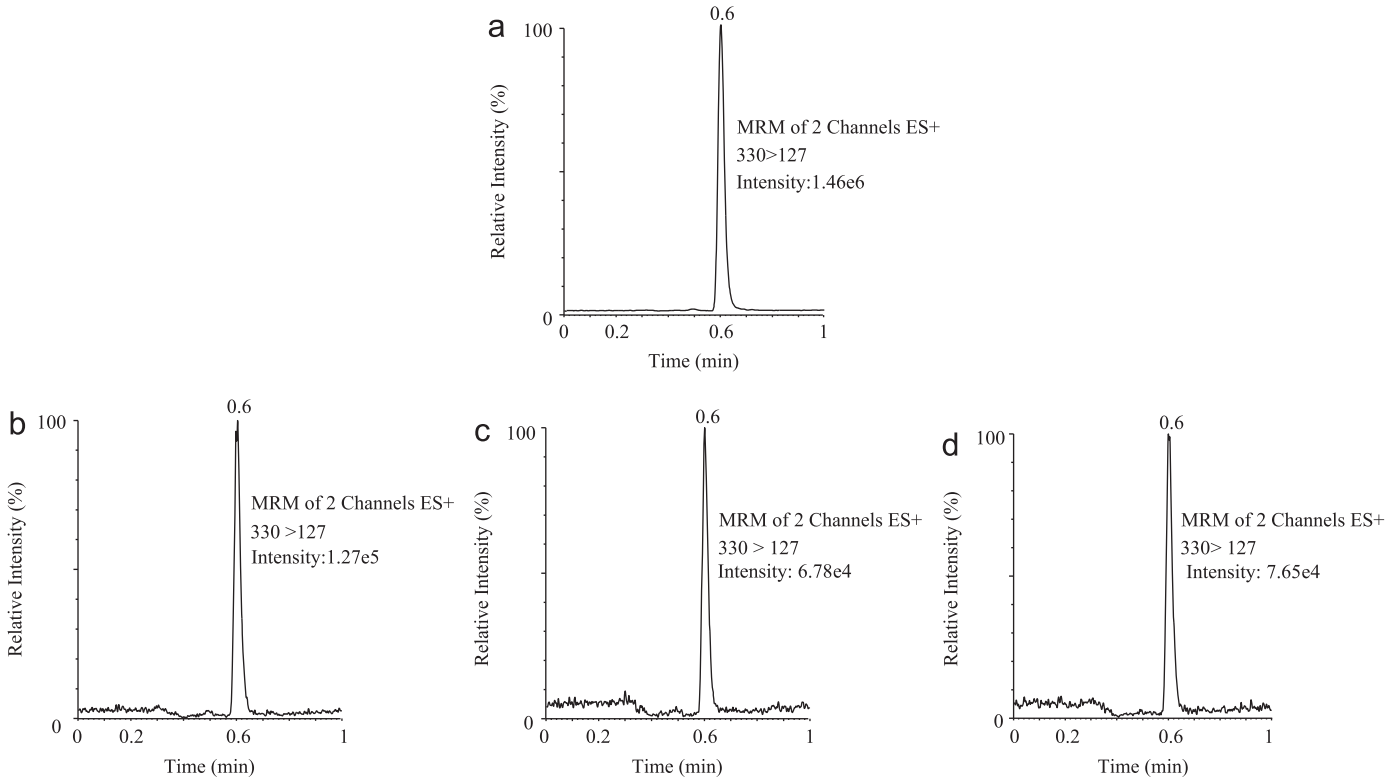

Fig. 3. UPLC–MS/MS chromatograms of malathion standard 1 μg mL^{-1} (a), time 40 min (b), pH 6 (c) and temperature 55 °C (d).

adsorbents reported in the literature [32] and the values are shown in Table 5. It is clear from Table 5 that the adsorption capacity of De-Acidite FF-IP resin was higher than the reported values which suggested that De-Acidite FF-IP resin was a promising material for the removal of malathion from aqueous solutions.

In order to predict the adsorption efficiency of the adsorption process, the dimension less equilibrium parameter was determined by using the following equation [33]:

$$R_L = \frac{1}{1 + bC_o} \tag{5}$$

where, C_o (mg L^{-1}) is the lowest initial malathion concentration and b is Langmuir constant (L mg^{-1}). The value of $R_L < 1$ represents favorable adsorption, $R_L > 1$, unfavorable adsorption and $R_L = 1$, linear isotherm. The value of R_L in the present study was also less than one which indicated a favorable adsorption.

The Freundlich isotherm is an empirical equation and based on the assumption that the adsorbate molecules adsorbs onto the heterogeneous surface of an adsorbent. The adsorption data of malathion was also analyzed by the Freundlich model. The logarithmic form of the Freundlich model is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n}\ln C_e \tag{6}$$

where, q_e is the amount of malathion adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the malathion (mg L^{-1}), K_f and n are the Freundlich adsorption constants which indicate the adsorption capacity and measure of the deviation from linearity, respectively. The Freundlich isotherm constants (K_f and n) were determined from the intercept and slope of the linear plots of log q_e vs. log C_e, respectively. The value of K_f was increased with the increase in temperature which also demonstrated the endothermic nature of the adsorption process. The value of n is not only a measure of the deviation from linearity, nonetheless inform about the heterogeneity degree of the sorption sites. As n approaches zero, the surface site heterogeneity increase. In this study, $n > 1$ suggested the favorable adsorption of malathion [34] on De-Acidite FF-IP resin (Table 4). Figs. S3(a) and S3(b) present the plots for Langmuir and Freundlich adsorption isotherm models, respectively. The parameters obtained for two models are presented in Table 4. The higher values of r^2 in the case of Freundlich model indicated the better applicability of this model.

3.2.6. Thermodynamic studies

The temperature influences the adsorption equilibrium and its variations produce a displacement from or toward the phase the solubility of the molecules (if in liquid phase) and their diffusion within the pores of the adsorbent materials [35]. The effect of varying temperature on the adsorption of malathion was studied using optimum dose of De-Acidite FF-IP resin. The results are represented as percentage removal of malathion vs. temperature (Fig. S4). The percentage removal of malathion increased from 93% to 96% with increase in the temperature from 25 °C to 65 °C. The continuous increase in the percentage removal of malathion indicated that the adsorption process was endothermic and chemical in nature. It is apparent from Fig. 3a and d that UPLC–MS/MS malathion chromatogram relative intensity after adsorption at 55 °C (Fig. 3d) decreased upto 96%.

This was further supported by calculating thermodynamic parameters. The change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) for adsorption were calculated using the following equations [36–39]:

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{7}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

where, ΔH^0 and ΔS^0 are the changes in entropy and enthalpy of adsorption, respectively, T is temperature (K) and R is the gas

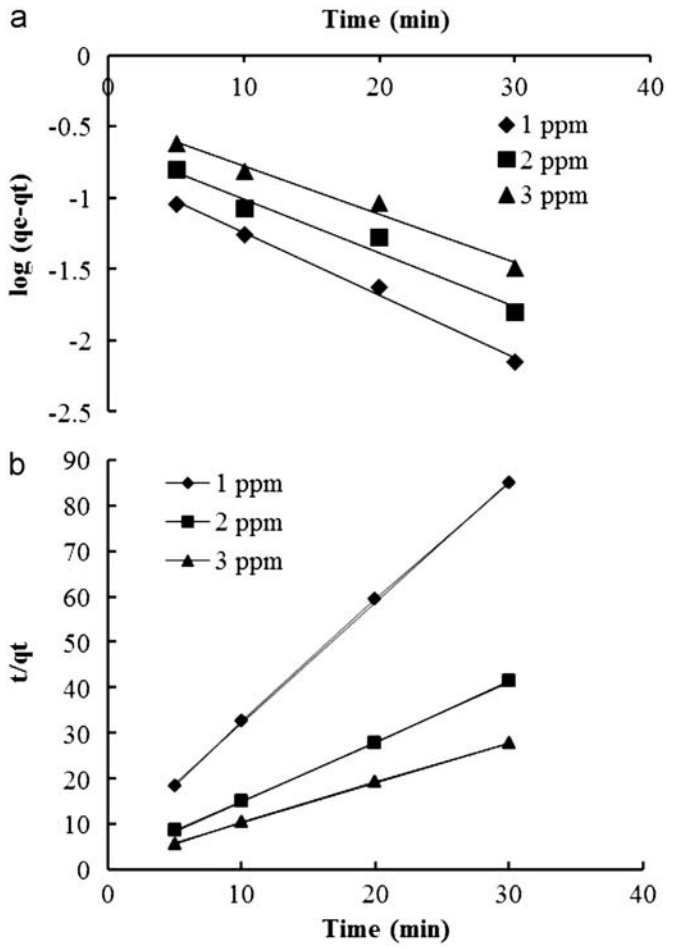

Fig. 4. Plots of kinetic models, pseudo-first-order (a) and pseudo-second-order (b) for the adsorption of malathion onto De-Acidite FF-IP resin.

Table 3
Rate constants for pseudo-first-order and pseudo-second-order equations obtained from the graph for different initial concentrations.

Order of reaction	Initial concentration ($\mu g\ mL^{-1}$)	Slope	Intercept	Rate constant	Correlation coefficient (r^2)
Pseudo-first-order	1	−0.043	−0.812	0.099	0.994
	2	−0.037	−0.632	0.085	0.968
	3	−0.033	−0.447	0.075	0.977
Pseudo-second-order	1	2.65	5.82	1.21	0.999
	2	1.31	1.81	0.95	0.999
	3	0.88	1.49	0.52	0.999

constant (8.314 J mol^{-1} K^{-1}). A plot of ln K_c vs. $1/T$ for malathion was linear and represented graphically in Fig. 5. The K_c value was calculated using the following equation [36,37]:

$$K_c = \frac{C_e}{C_o} \tag{9}$$

where, C_e and C_o are the amount of malathion adsorbed per unit mass of resin and in aqueous phase, respectively. The values of ΔH^0 and ΔS^0 were evaluated from the slope and intercept of a linear Van't Hoff plot which are given in Table 4. It is clear from Table 4 that the values of ΔH^0 is positive (27.89 KJ mol^{-1}) which also indicated the endothermic process of adsorption and the value of ΔS^0 was positive which illustrated that malathion adsorption caused disorderness in the system. The value of ΔG^0 indicated the degree of spontaneity of the adsorption process and a more negative value showed an adsorption process which was favorable energetically. The increase in ΔG^0 with increasing temperature showed that the adsorption was more favorable at high temperature.

3.2.7. Breakthrough capacity

The amount of De-Acidite FF-IP resin required for complete removal of malathion was found by determining the breakthrough capacity. Breakthrough curve of malathion (Fig. 6) indicated that 250 mL of 1 $\mu g\ L^{-1}$ malathion solution could be passed through the column without detecting malathion in the effluent. The breakthrough capacity of malathion was found 1.25 mg g^{-1} which was higher than the adsorption capacity (0.96 mg g^{-1}) obtained by batch study. The column was completely exhausted after passing 700 mL of 1 $\mu g\ L^{-1}$ malathion solution (exhaustive capacity 3.5 mg g^{-1}).

3.2.8. Desorption and regeneration studies

To keep the processing cost down it is very important to carry out the desorption and regeneration studies. Desorption study of malathion was carried out by the batch and column processes using 0.01 M NaOH solution as an eluent. It was found that the adsorption of malathion by the batch and column processes was 96% and 99%, respectively which was not too different. However, the recovery of malathion was poor by batch process (63%) as compared to column process (95%).

The regeneration studies were also carried out using 0.01 M NaOH solution. It is apparent from Fig. 7 that the recovery of malathion decreased from 95% to 68% after five successive cycles. These results demonstrated promising regeneration potential of the De-Acidite FF-IP resin which showed that this resin could be used again and again without any appreciable lose in the percent adsorption of malathion.

4. Conclusion

From the obtained results, it can be concluded that De-Acidite FF-IP resin was an excellent material for the removal of malathion from the aqueous solution which adsorbed malathion upto 96% within 40 min. The concentrations of malathion before and after the adsorption processes were determined using a sensitive, selective and rapid UPLC–MS/MS. The kinetics data were best fitted in pseudo-second-order rate equation as evident from the values of r^2. The adsorption isotherm studies showed that Freundlich model was better fitted. The negative values of ΔG^0 suggested that the adsorption was spontaneous in nature. The positive value of ΔH^0 and ΔS^0 indicated that the endothermic adsorption process and malathion adsorption caused the randomness in the system. The adsorbed malathion was recovered using 0.01 M NaOH solution and the regenerated De-Acidite FF-IP resin was effectively used upto five consecutive cycles with the loss of only 4% in the percent adsorption of malathion. Breakthrough and exhaustive capacities of malathion were found 1.25 mg g^{-1} and 3.5 mg g^{-1}, respectively. In view of all these outcomes, it can be concluded that De-Acidite FF-IP resin was very worthwhile and reproducible for the removal of malathion from aqueous solution.

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Table 4
Adsorption isotherm constants and thermodynamic parameters for malathion adsorption on De-Acidite FF-IP resin.

Temperature (°C)	Langmuir constants			Freundlich constants				Thermodynamic parameters			
	Q_o (mg g^{-1})	b (L mg^{-1})	r^2	$1/n$	n	K_f	r^2	K_c	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
25	16.39	0.077	0.989	0.95	1.05	1.14	0.999	1.12	−0.15	27.89	0.094
35	9.43	0.17	0.994	0.89	1.12	1.25	0.998	1.42	−1.095		
45	1.32	2.85	0.996	0.74	1.35	1.41	0.998	2.27	−2.04		
55	0.99	6.67	0.982	0.67	1.49	1.57	0.996	3.00	−2.98		

Table 5
Comparison of adsorption capacity for the removal of malathion using different adsorbents.

Adsorbents*	% Removal	Adsorption capacity (mg g^{-1})	References
Bentonite	31.50	5.75	[32]
Kaolin	15.34	2.80	[32]
Montmorillonite	42.28	7.95	[32]
DTA–M	57.33	10.50	[32]
TTA–K	32.50	5.85	[32]
TTA–M	67.00	12.60	[32]
CP–M	77.80	14.20	[32]
De-Acidite FF-IP resin	93.00	16.39	Present study

* DTA—dodecyltrimethylammonium; TTA—tetradecyltrimethyl ammonium; CP—cetylpyridinium; M—montmorillonite and K—Kaolin.

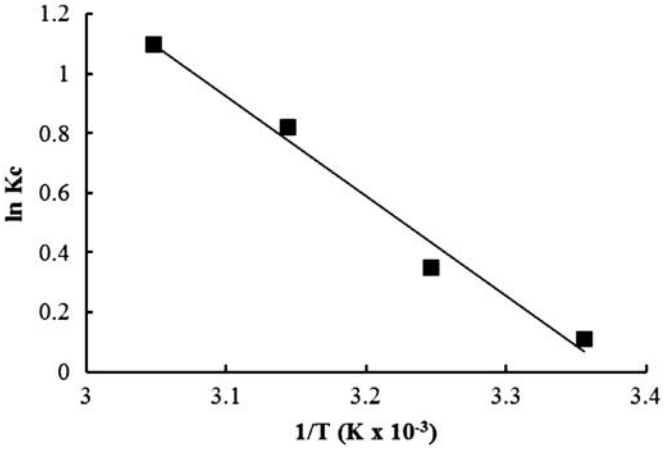

Fig. 5. Van't Hoff plot ln K_c vs. $1/T$ ($K \times 10^{-3}$) for the adsorption of malathion onto De-Acidite FF-IP resin.

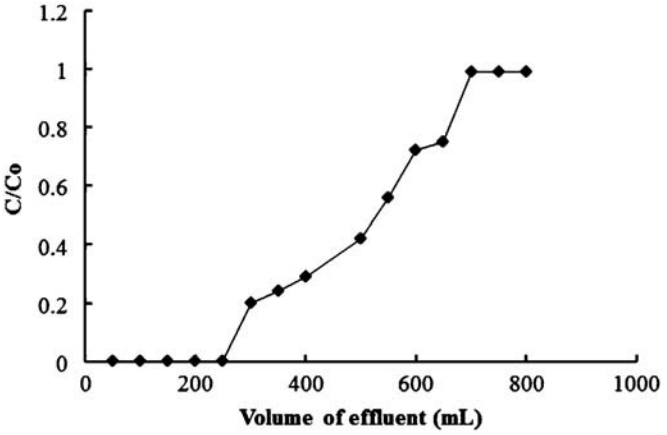

Fig. 6. Breakthrough capacity curve for the adsorption of malathion onto De-Acidite FF-IP resin.

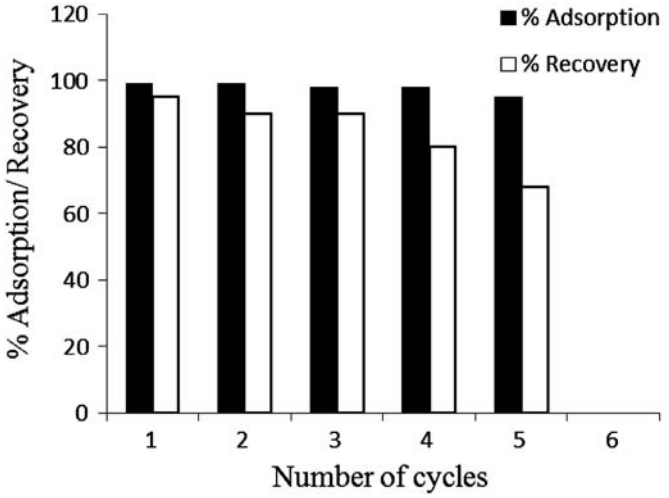

Fig. 7. Column studies to regenerate the De-Acidite FF-IP resin using 0.01 M NaOH as an eluent.

Appendix A. Supporting information

Supplementary information associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.04.015.

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