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Removal of carbofuran and methylparathion from aqueous media through calix[4]arene-based impregnated resin

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ABSTRACT

The present study explores the synthesis of impregnated resin and its adsorption efficiency for the removal of carbofuran and methylparathion from aqueous media through static and dynamic adsorption methods. Different factors that affect the adsorption process were optimized as pH 5, adsorbent dosage 30 mg and agitation time 45 min for carbofuran and 60 min for methylparathion. The adsorption data were found to be best fitted with Freundlich isotherm and follow pseudo-second-order kinetic model. In addition to this, it was found from intraparticle diffusion model which explores that the adsorption of both pesticides may involve the film diffusion process as the rate limiting step. Thomas model rate constant (k_{TH}) was found to be 0.0015 $cm^3\,mg^{-1}\,min^{-1}$ for both pesticides, whereas maximum solid-phase concentration (q_0) was found to be 22.58 and 34.05 $mg\,g^{-1}$ for carbofuran and methylparathion, respectively, through dynamic adsorption study. The resin can be regenerated and reused effectively for real water samples.

Keywords: Calixarenes; Adsorption; Isotherms; Kinetics; Thermodynamics

1. Introduction

Contamination of surface and ground water by pesticides reduces its usefulness because many of these compounds are toxic to both humans and animals. Contamination is mainly due to increase in the use of pesticides for enhancing the agriculture yield of different crops. These pesticides and their degradation products get transported through air and water to various environmental compartments and bring dangerous environmental and health effects on humans and animals [1]. Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-N-methylcarbamate) and methylparathion (O,O-dimethyl-O-p-nitrophenyl phosphorothioate) are two well-known pesticides used (Fig. 1) worldwide to kill the insects in the crops and are often found in surface and ground water. Food and Agriculture Organization has banned the use of methylparathion because of high risk to workers. It is also called “cotton poison” used in cotton, vegetables, and soybean crops worldwide. According to Agency for Toxic Substances and Disease Registry, half-life of methylparathion is one month in natural water, which is enough to be toxic for many organisms living in water. Careless disposal of empty containers and washing of equipments contribute toward the contamination of ground water. It can also enter into body through eating food, drinking, and swimming in contaminated water. When it enters in body, liver can convert methylparathion into more hazardous

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compound called "methylparaoxon." Exposure to the very high level of such toxic pesticide for a short time may cause death, loss of consciousness, dizziness, confusion, headaches, difficult breathing, chest tightness, blurred vision, and sweating [2].

Carbofuran belongs to group of carbamate derivatives, widely used for controlling of soil dwelling, foliar-feeding insects, and rodents. It is known to be more persistent than other organophosphate insecticides. World Health Organization specified the standard limit of carbofuran as $3\,\mu g\,L^{-1}$. It is toxic, carcinogenic, and non-biodegradable; therefore, it is frequently detected in surface and ground water due to anthropogenic activities [3]. It is soluble in water and is highly mobile in soil, thereby having high potential for ground water contamination.

Various methods have been used to treat water contaminated with methylparathion and carbofuran. These treatment methods are bacterial degradation [4], nanofiltrationn and reverse osmosis membrane [5], photodegradation [6], nanomaterial [7], anaerobic-membrane bioreactor technology [8] precipitation, filtration, membrane process [9], electrochemical [10] etc. Each method has its own merits and demerits. Currently, adsorption methodology is found to be simple, cheap, and effective method for the removal of organic pollutants from aqueous system. Various adsorbents such as fertilizer and steel industry wastes [11], organobentonites [12], date seed activated carbon [13] chestnut shells [14], banana stalks activated carbon [15] and few synthetic adsorbents such as mesoporous cyclodextrin-silica nanocomposite [16], pore expanded mesoporous silica [17] and chitosan-based molecularly imprinted polymers [18] and modified silica [19] are reported in literature.

Calix[n]arene is a well-known class of cyclo-oligomeric compounds in the field of supramolecular chemistry that provides a three dimensional platform, which can be modified at upper or lower rim (phenolic groups) to synthesize different derivatives with specific shape and selectivity for guest molecules. However, due to multi-functionality, they are widely impregnated or immobilized on the solid polymeric supports for the removal of toxic heavy metals such as arsenic [20], Cr(IV) [21], and Pb(II) [22] and few organic molecules such as azodyes [23], aromatic amines [24], and hexachlorocyclohexane isomers [25] from aqueous media. The impregnation of calixarene moiety onto the polymeric support enhances the adsorption capacity of the resin [26]. Thus, the present study focuses on the preparation of calix[4]arene-based impregnated polymeric substrate and investigation of its adsorption performance towards the removal of carbofuran and methylparathion from aqueous media through batch and column methods.

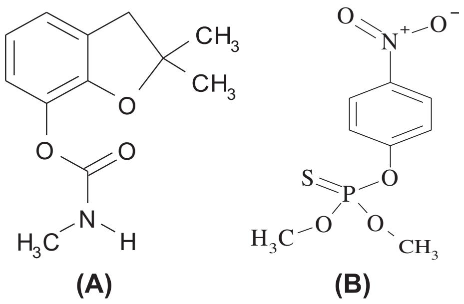

Fig. 1. Molecular structures of carbofuran (A) and methylparathion (B).

2. Material and methods

2.1. Reagents

Analytical thin layer chromatography was performed on precoated silica plates (SiO_2 and PF254). The pH (1–11) was adjusted through HCl/NaOH solution. Standard methylparathion (MP), carbofuran (CF), and Amberlite XAD-4 (surface area of $750\,m^2\,g^{-1}$, pore diameter 1–3 nm, and bead size 20–50 mesh) were purchased from Fluka (Germany), The surface area, pore diameter and mesh size were quoted by the supplier. The resin was washed with distilled water and ethanol before use. XAD-4 was modified and calix[4]arene was synthesized according to previously reported method [27,28]. All reagents/solvents used for the synthesis of calix[4]arene and calix[4]arene-based modified XAD-4 were of analytical grade. All solutions were prepared in double-distilled deionized water, which has been passed through Millipore Milli-Q Plus water purification system (Elga model classic UVF, UK).

2.2. Instrumentation

FT-IR spectra were recorded on a Thermo Nicolate 5700 FT-IR spectrometer as KBr pallets. Elemental analysis of impregnated resin was performed using Thermo Flashea CHNS analyzer. Melting point was determined through Gallenkamp melting point apparatus model MFB, 595, 010 M, England. The percent adsorption was calculated from differences of detector response of double-beam UV–visible spectrophotometer. The pH was measured with Inolab pH meter 720 (Germany) with glass electrode and internal reference electrode. A Gallenkamp thermostat automatic mechanical shaker model BKS 305-101, UK, was used for batch adsorption study. A glass column (10 cm × 6 mm) was used for column adsorption study.

2.3. Impregnation of calix[4]arene

A 5 g AmberliteXAD-4 was washed with distilled water and acetone; subsequently, it was nitrated using 10 mL concentrated HNO_3 and 25 mL concentrated H_2SO_4 for about 40 min in round-bottom flask just above room temperature. Nitrated XAD was then poured into ice cold water. It was filtered and washed until it become free from acid. Nitrated resin was reduced using $SnCl_2$:$2H_2O$ (15 g) and 15 mL HCl (conc) in 40 mL ethyl alcohol, the mixture that was refluxed for 10 h; subsequently, it was washed with double-distilled water followed by 2 M NaOH, so as to remove $(R–NH3)_2$ $SnCl_4$ from amino resin. For impregnating (physical attachment) of calixarenes, 5 g of modified XAD was taken in 250-mL round-bottom flask contains 0.5 g calix[4]arene in 100 mL ethanol. The mixture was continuously stirred for 130 h. After that, resin was washed with water and ethanol so as to remove free calixarene (Fig. 2). Physically attached calixarenes content were checked by weighting the resin before and after the impregnation reaction.

2.4. Characterizations

The impregnated resin was characterized by FT-IR, elemental and gravimetric analysis and also by static and dynamic adsorption methods.

2.4.1. Fourier transform infrared study

Fourier transform infrared spectroscopy is an efficient method to characterize the surface functionality of polymeric surfaces. Therefore, surface functionality of calix[4]arene impregnated Amberlite XAD-4 resin was characterized through this method. Fig. 3 shows the infrared spectra of pure XAD-4 (A) and impregnated resin (B). The prominent broad band at 3421.8 cm^{-1} represents the OH stretching of calix[4] arene, and the band at 1,383 cm^{-1} represents amino group of modified XAD-4. It has also been observed that slight displacement takes place in the band of an aromatic ring from 1,598 cm^{-1} in pure XAD to 1,611 cm^{-1} may be due the polarization in the electronic clouds of aromatic rings. These results confirm the attachment of calixarenes with modified XAD-4.

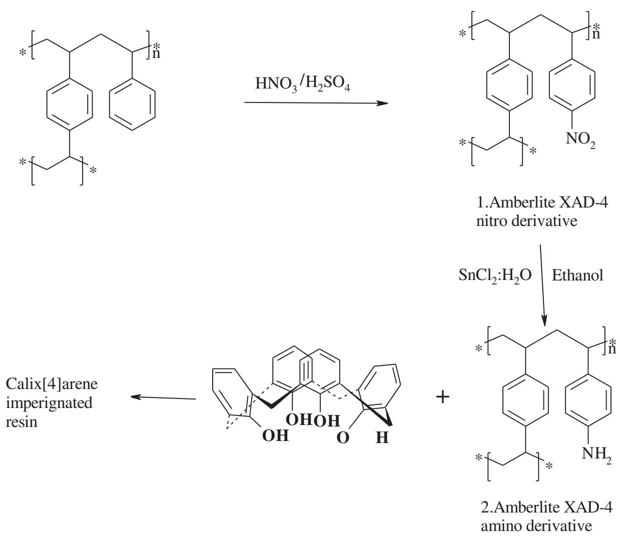

Fig. 2. Synthesis scheme of impregnated resin.

2.4.2. Elemental and gravimetric analysis

The CHNS results show elemental percentage of impregnated resin, which was found 82.46% of carbon, 5.79% of hydrogen, and 3.46% of nitrogen while remaining 8.29% is expected to be oxygen present in the adsorbent. The gravimetric analysis was observed by considering the difference in the weight of adsorbent before and after the impregnation. It was estimated from the difference that more the 0.4 g of calixarenes get attached to the 5 g of modified XAD-4. In addition to these results, the adsorbent was also characterized through static and dynamic adsorption methods.

2.4.3. Static adsorption

The process of static adsorption of carbofuran and methylparathion was carried out at room temperature, using 10 mL of 10 mg L^{-1} standard stock solution of both pesticides to optimize pH, contact time, adsorbent dosage, and temperature. For each experiment, percent adsorption was calculated through Eq. (1).

$$\%\ \text{Adsorption} = \frac{A_i - A_f}{A_i} \times 100 \tag{1}$$

Here, A_i and A_f are the absorption maximum before and after adsorption, respectively. Maximum static adsorption capacity (q_a) of adsorbent was calculated using Eq. (2).

$$q_a = \frac{V(C_i - C_f)}{M} \tag{2}$$

where C_i and C_f are the initial and equilibrium concentration of both pesticides (mg L^{-1}), V is volume of solution in (dm^3), and M is mass of adsorbent (g).

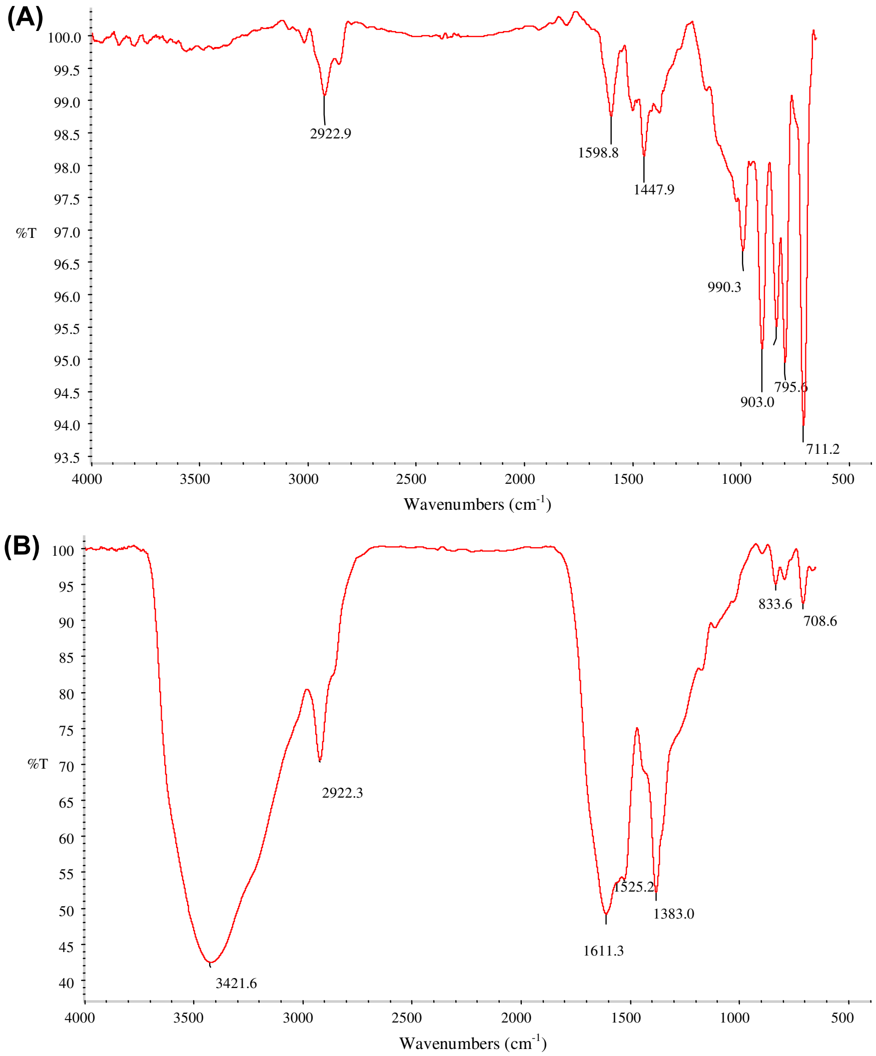

Fig. 3. Fourier transform infrared spectra (FT-IR) spectra. Pure XAD-4 (A) XAD-4 impregnated with calix[4]arene. (B).

2.4.4. Dynamic adsorption

Dynamic adsorption study was carried out using (6 mm × 10 cm) size column containing 30 mg of adsorbent. Dynamic adsorption capacity of adsorbent was calculated by passing standard solution at pH 5 and the flow rate 2 mL min^{-1}. The total adsorbed quantity (mg) of carbofuran and methylparathion on calix[4] arene impregnated resin at a given concentration was calculated through Eq. (3).

$$q_{\text{total}} = \frac{QA}{1,000} = \frac{Q}{1,000}\int_{t=0}^{t=\text{total}} C_a \mathrm{d}t \tag{3}$$

Here, Q is a flow rate, A is the breakthrough area, used to calculate the total adsorbed quantity (q_{total} in mg) of carbofuran and methylparathion in column by intergrading the adsorbed concentration C_a vs. time t.

3. Results and discussion

3.1. Adsorption parameters

3.1.1. Effect of pH

Change of pH has noticeable effect on the adsorption sites of resin as well as it alter the properties of pesticide molecules, as a result, adsorption capacity greatly changes with the change in pH of the solution. Adsorption may also become more complicated due to the surface functional group of adsorbent. In this study, effect of pH on the adsorption of carbofuran and methylparathion was observed by varying solution pH from 1–11 using 10 mL aqueous solution of both pesticides at room temperature. Each sample was agitated for one hour containing 20 mg of adsorbent.

Fig. 4 shows that adsorption behavior of carbofuran and methylparathion. It was found to be highest in the acidic medium; this may be due to the protonation of easily available oxygen atoms in the carbofuran and methylparathion. Protonation increases the polarity of molecule, which results in increasing intermolecular association between adsorbent and adsorbate. At high pH hydroxyl group may become deprotonated which may results the creation of repulsive forces between the negatively charged calixarenes and negatively charged target molecules. Therefore, adsorption become poor as pH increases from acidic to basic media. This suggests that in acidic conditions surface of impregnated resin become protonated, which make strong association with pesticides molecules and at higher pH anionic surface has week interaction with target molecules [29].

3.1.2. Effect of initial concentration

In order to determine the effect of initial concentration of pesticides, solutions of different concentration were treated with resin till equilibrium time. Fig. 5 is graphical representation of concentration effect. It shows that as the concentration of pesticides increases percent adsorption decreases. This fact reveals that there is limited number of active sites available for the guest molecules on the surface of adsorbent. It may also be predicted that intermolecular association among adsorbate molecules increased due to increased concentration of adsorbate and also as a result of limited cavity size of calix[4]arene may have caused resistance to adsorption. In addition to this, it can be observed that at low concentration adsorption takes place at higher energy sites while at high concentration, it is takes place at low energy sites available, resulting in a decrease in percent adsorption of target molecules.

3.1.3. Effect of adsorbent dosage

The quantity of adsorbent is an important to determine the efficiency of adsorbent for the maximum removal of target molecules at a given initial concentration. In the present study, the adsorbent dosage was optimized at an optimized pH using 10 mL of stock solution of each pesticide at room temperature.

Fig. 6 shows that percent adsorption of carbofuran and methylparathion increases more than 90% by the increasing of adsorbent dosage from 5 to 30 mg and stays almost constant up to 50 mg. These results show that that there is a specific ratio between adsorbent dose and adsorbate concentration for the maximum removal of target molecules. In addition to this, it can be observed from the figure that continuous rise of percent adsorption takes place until it reached to the optimum point. This may happen due the continuous rise of adsorption sites and surface area with the increasing of dosage.

3.2. Adsorption isotherms

Study of adsorption equilibriums is a critical way to evaluate the interaction between adsorbent and adsorbate molecules and to determine adsorption capacity of resin. Most well-known adsorption isotherms, i.e. Freundlich, Langmuir, and Dubinin–Radushkevich (D–R), were used to find adsorption pattern of both pesticides on the resin.

Freundlich adsorption isotherm assumes the formation of multi molecular layer on the heterogeneous surface. This model was tested through the linear form of Eq. (4):

$$\ln C_a = \ln C + \frac{1}{n} \ln C_e \tag{4}$$

where C_a is adsorbed concentration in mol g^{-1}, C is multi layer adsorption capacity, $\frac{1}{n}$ is adsorption intensity, and C_e is an equilibrium concentration. The values of adsorption isotherm constants were evaluated from the graph obtained by plotting between ln C_a and ln C_e (Table 1).

According to this model, if value of adsorption capacity $1/n$ is >0 and <1, then the adsorption is favorable. The calculated value (shown in Table 2) of

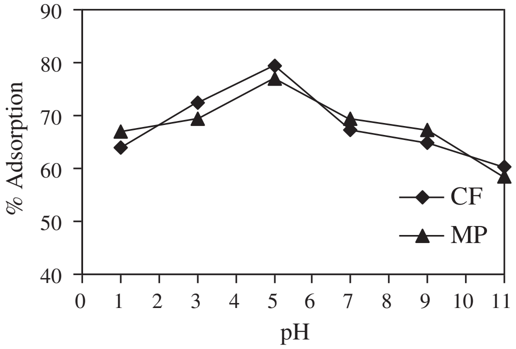

Fig. 4. Effect of pH on the Adsorption of carbofuran and methylparathion (conditions: initial concentration 10 mg L^{-1}, adsorbent dosage 30 mg).

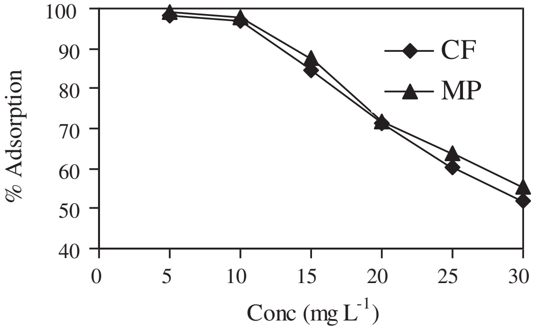

Fig. 5. Effect of initial concentration for the removal of carbofuran and methylparathion (consitions: pH 5, adsorbent dosage 30 mg).

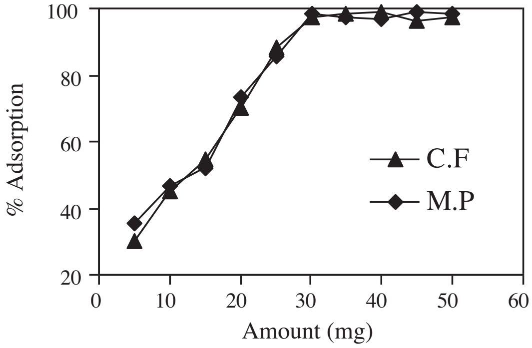

Fig. 6. Effect of adsorbent dosage for the removal of carbofuran and methylparathion (conditions: pH 5, initial concentration 10 mg L^{-1}).

adsorption capacity for both pesticides lies in range of favorable adsorption.

The adsorption pattern of carbofuran and methylparathion was also investigated through Langmuir model. This isotherm assumes the formation of monomolecular layer on the homogenous surface, which does not involve interaction among adsorbate molecules. Linear form of Langmuir model is Eq. (5).

$$\frac{C_e}{C_a} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{5}$$

Here, Q is monolayer adsorption capacity (mol g^{-1}), b is adsorption enthalpy (mol L^{-1}), whereas C_e and C_a is equilibrium and adsorbed concentration, respectively. A plot of C_e/C_a vs. C_e gives straight line with the slope $1/Q$ and intercept $1/Qb$.

The dimensionless parameter called separation factor (R_L) can be evaluated from the Langmuir constant b using Eq. (6):

$$R_L = \frac{1}{1 + bC_i} \tag{6}$$

Here, b is the Langmuir constant and C_i is initial concentration of solution.
If,

(1) $R_L > 1$ then isotherm is unfavorable.
(2) $R_L = 1$ then isotherm is linear.
(3) $0 < R_L < 1$ then isotherm is favorable.
(4) $R_L = 0$ then isotherm is irreversible.

The calculated value of R_L for carbofuran and methylparathion follows third condition i.e. $0 < R_L < 1$ which indicate that adsorption is favorable.

D–R is more general to differentiate the physical/chemical adsorption phenomenon, as it does not assume homogenous surface. This isotherm is used to evaluate the porosity of adsorbent and apparent energy required to migrate adsorbate molecules to the surface of adsorbent. The linear form of this model is Eq. (7).

$$\ln C_a = \ln X_m - \beta\varepsilon^2 \tag{7}$$

Here, C_a is the total amount of carbofuran and methylparathion adsorbed on the adsorbent surface (mol g^{-1}), X_m represent theoretical maximum adsorption capacity of adsorbent (mol g^{-1}). β is D-R isotherm constant. ε Polanyi adsorption potential which can be calculated through Eq. (8),

Table 1
Isotherm constants values of carbofuran and methylparathion

Isotherm with parameters	Carbofuran (CF)	Methylparathion (MP)
Langmuir isotherm		
Q_m (m mol g^{-1})	0.725	0.0057
b	6.5×10^5	7.1×10^5
R^2	0.99	0.99
Freundlich isotherm		
C (m mol g^{-1})	0.609	0.0441
$1/n$	0.2055	0.1954
R^2	0.95	0.96
Dubinin–Radushevish (D–R)		
X_m (mg g^{-1})	4.96×10^{-7}	5.44×10^{-8}
E (kJ mol^{-1})	18.9	19.6
R^2	0.92	0.94

Table 2
Constants and regression coefficient (R^2) values of Lagergren, Ho and McKay and Morris-Weber models for adsorption of carbofuran and methylparathion

Kinetic model and parameters	Carbofuran (CF)	Methylparathion (MP)
Pseudo first-order		
k_1 min^{-1}	0.0396	0.052
q_e (mg g^{-1})	3.5×10^{-10}	1.05×10^{-9}
R^2	.0.702	0.867
Pseudo second-order		
k_2 (g mg^{-1} min^{-1})	1312.33	403.22
q_e (mg g^{-1})	0.0001788	0.0001906
R^2	0.998	0.991
Morris–Weber model		
R_d	8.79	13.61
C	94.11	43.31
R^2	0.965	0.943

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

Here, R is a general gas constant (kJ mol^{-1} k^{-1}), T is temperature in Kelvin, and C_e is an equilibrium concentration of adsorbate in solution (mol L^{-1}). The plot of ln C_a versus ε^2 is a straight line with a slope β and intercept X_m (Fig. 7(c)). The mean free energy of adsorption required for the transfer of one mole of solute from infinity to the surface of the adsorbent; it can be calculated through Eq. (9),

$$E = \frac{1}{\sqrt{-2\beta}} \tag{9}$$

The nature of adsorption can be estimated from the value of apparent free energy of adsorption. According to A.U. Itodo and H.U. Itodo, the typical values of free energy for the physio-sorption lie in the region of 1–20 kJmol^{-1}. [30] The calculated value of energy (Table 2) lies in the range of physio-sorption. Therefore, it can be predicted that the adsorption of carbofuran and methylparathion involves the weak intermolecular forces (dipole–dipole interaction).

3.3. Kinetics of adsorption study

This is an important parameter for evaluating adsorption mechanism followed by target molecules to attach on the surface of adsorbent. The effect of agitation time was examined from 15–120 min using 30 mg of impregnated resin in order to evaluate the kinetic models. Fig. 7 is the time profile for the removal of carbofuran and methylparathion on impregnated resin. It can be observed that the percent adsorption increases with rise in agitation time and gradually reached at equilibrium point. After 45 and 60 min, no further adsorption takes place for carbofuran and methylparathion, respectively. Further study was done under optimized conditions.

Kinetic study for the adsorption of target molecules on the impregnated resin was analyzed through the various kinetic models namely the Lagergren's (pseudo-first-order kinetic) [31], Ho and McKay (pseudo-second-order kinetic) [32], and Morris Weber (intraparticle diffusion model) [33].

The linear form of these models is shown in Eqs. (10)–(12), respectively.

Lagergren's model:

$$\log\,(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{10}$$

Ho and McKay:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

Morris Weber:

$$q_t = R_d t^{0.5} \tag{12}$$

In all these linear equations, q_e and q_t are the amount of carbofuran and methylparathion adsorbed at equilibrium and at time t, respectively. While k_1, k_2, and R_d are the rate constants for Lagergren's, Ho and McKay and Morris Weber kinetic models, respectively.

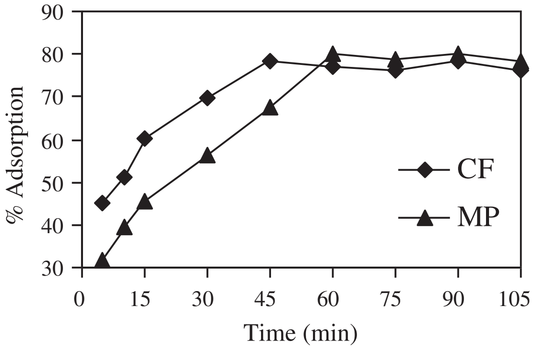

Fig. 7. Effect of agitation time for the removal of carbofuran and methylparathion (conditions: pH 5, initial concentration 10 mg L^{-1}).

Pseudo-first-order kinetic equation was observed by plotting log ($q_e - q_t$) vs. t Fig. 8(a), and the graph of pseudo-second-order kinetic model was plotted between t/q_t vs. t Fig. 8(b); finally, Morris Weber was observed by plotting graph between q_t vs. $t^{0.5}$ Fig. 8(c).

The best fit model for detecting the mechanism of adsorption of carbofuran and methylparathion on modified XAD-4 was determined from their regression coefficient values (R^2) calculated from corresponding plot of Fig. 8 (Table 2). The calculated values of these models show that the adsorption of carbofuran and methylparathion follows pseudo-second-order kinetic model, whereas Fig. 8(c) shows that the adsorption takes place in three steps. The first step is the faster which involves the transfer of target molecules to the surface of adsorbent through film diffusion process. The second step is slower than first step, in which the diffusion of target molecules takes place in to the pores of adsorbent. The last step is slowest among three steps. Therefore, it is considered as the equilibrium stage where with the lapse of time no adsorption takes place. Further, it can be predicted from the figure that the linear portion of the graph was not passed through the origin which represents that pore diffusion is not the limiting step but the film diffusion may be the rate limiting step which means adsorption takes place on the surface calix[4]arene appended resin rather than inside pores.

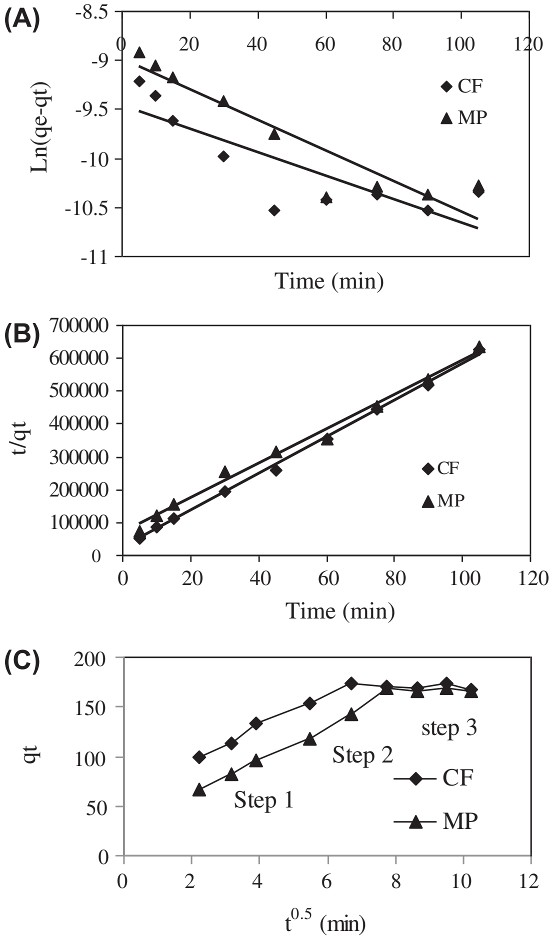

Fig. 8. Kinetic models for carbofuran and methylparathion (A) Langergren model; (B) Ho and McKay model; (C) Morris Weber model.

3.4. Thermodynamics of adsorption

The temperature has considerable effect on the adsorption of target molecules to the surface of adsorbent. It was investigated in the temperature range 283–293 k under optimized conditions for both pesticides (Fig. 9).

The thermodynamic parameters ΔH, ΔS, and ΔG can be calculated from the Eqs. (13) and (14), respectively.

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{13}$$

$$\Delta G = -RT \ln K_c \tag{14}$$

Here, K_c is equilibrium constant, where as ΔH, ΔS, and ΔG is the change in enthalpy, entropy, and free energy, respectively. R is the gas constant and T is the temperature, at which adsorption takes place. The values of thermodynamic parameters are shown in Table 3.

Thermodynamic parameters are used to evaluate the nature of adsorption. The value of enthalpy change (ΔH) reveals that the adsorption of carbofuran and methylparathion is an exothermic process due to the formation weak association forces between the adsorbate molecules and adsorbent active sites. On the other hand, the negative values of change in the free energy (ΔG) show that the adsorption of carbofuran and methylparathion is a spontaneous process.

3.5. Dynamic adsorption study

The optimized conditions of batch adsorption were used to evaluate the efficiency of impregnated resin in the column. This can be determined from the knowledge of break through curve, which determines the exhaustion capacity and the degree of column saturation Fig. 10 is break through curve of carbofuran and methylparathion. This can be expressed as a ratio of normalized concentration (C_t/C_i) as a function of time or effluent volume. Break through curve of carbofuran

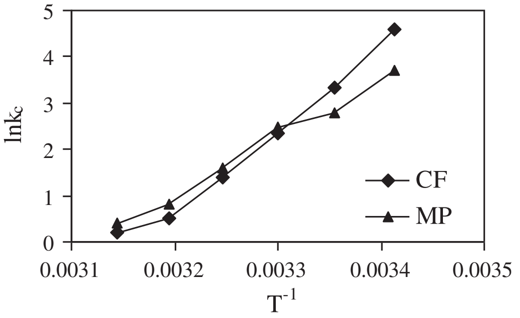

Fig. 9. Effect of temperature for the removal of carbofuran and methylparathion (conditions: pH 5, initial concentration 10 mg L^{-1}, adsorbent dosage 30 mg).

and methyparathion shows that the loaded column gets saturated after passing 120 mL of 10 mg L^{-1} solution of both pesticides in 60 min.

3.5.1. Thomas model

In order to determine the maximum adsorption capacity of column, it requires the knowledge of concentration time profile or breakthrough curve. This model assumes no axial transfer of adsorbed molecules on the surface, and the adsorption rate follows the second order reversible reaction kinetics. The adsorption data of column were subjected to be analyzed through this model to determine the Thomas model rate constant (k_{TH} cm^3 mg^{-1} min^{-1}) and maximum solid-phase concentration (q_0 mg g^{-1}). The linear form of this model is shown in Eq. (15):

$$\left(\ln\frac{C_\mathrm{i}}{C_\mathrm{e}}-1\right)=\frac{k_{\mathrm{TH}}q_0A}{Q}-\frac{K_{\mathrm{TH}}C_\mathrm{i}}{Q}V_{\mathrm{eff}} \tag{15}$$

Here, C_i and C_e is the initial and effluent concentration (mg L^{-1}), respectively. A is the quantity of material adsorbed, Q is flow rate (mL min^{-1}), and V_{eff} is the effluent volume, which can be calculated from the Eq. (16):

$$V_{\mathrm{eff}}=Qt_{\mathrm{total}} \tag{16}$$

where Q is flow rate and t_{total} is stands for maximum flow time.

Table 3
Thermodynamic constant terms for the adsorption of carbofuran and methylparathion

Thermodynamic parameter	Carbofuran (CF)	Methylparathion (MP)
ΔG (Jmol^{-1})	−5.12	−4.92
ΔH (kJmol^{-1})	−1.37	−1.01
ΔS (Jmol^{-1})	−4.33	−3.14

Values of Thomas model rate constant and maximum solid-phase concentration were calculated from the plot of $\left(\ln\frac{C_0}{C}-1\right)$ vs. V_{eff}. From this, Thomas model rate constant (k_{TH}) was found to be 0.0015 cm^3 mg^{-1} min^{-1} for both pesticides, whereas maximum solid-phase concentration (q_0) was found to be 22.58 and 34.05 mg g^{-1} for carbofuran and methylparathion, respectively.

3.6. Regeneration of resin

The impregnated resin was regenerated in environmental grade ethylacetate having 99.5% purity for recycling of same adsorbent in order explores its reloading efficiency. It can be evident from Fig. 11 that the resin can be reloaded for about three cycles. After that, the adsorption capacity of resin decreased.

3.7. Application to agriculture real water samples

In order to discover environmental applications of synthesized resin, three real water samples were collected from sprayed lawn area of Sindh University, Jamshoro. Each sample was filtered and spiked with 10 mg L^{-1} of standard solution of carbofuran and methylparathion. The batch adsorption procedure was repeated for all samples under optimized conditions. Percent removal of both pesticides from the three samples was found to be more than 82%. These values indicate that the resin is an efficient to remove majority of carbofuran and methylparathion from real water samples.

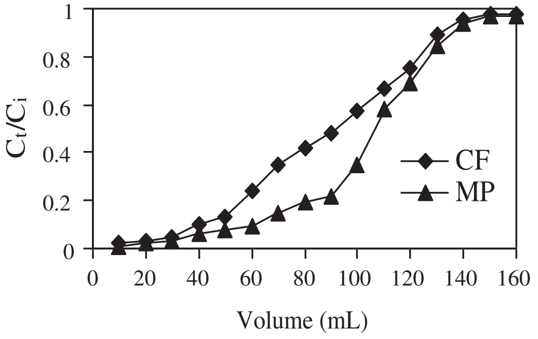

Fig. 10. Breakthrough curve for the removal of carbofuran and methylparathion from aqueous media.

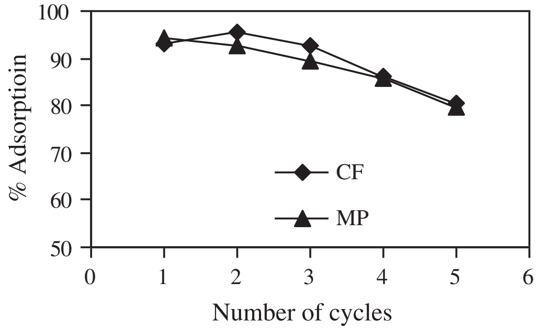

Fig. 11. Effect of number of cycles for the removal of methylparathion and carbofuran.

4. Conclusion

It can be summarized from the results that carbofuran and methylparathion can be effectively removed from aqueous environment using synthesized impregnated resin through batch and column adsorption methods. The adsorption process found to be multilayer and multistep following pseudo-second-order kinetic model and may involve film diffusion process as the rate limiting step. The synthesized material found to be reusable and can be applied for real water samples using optimized conditions.

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