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Synthesis and Application of a New Calix[4]arene Based Impregnated Resin for the Removal of Endosulfan from an Aqueous Environment

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ABSTRACT: The present work describes the synthesis of new 5,11,17,23-tetrakis[(propylthio)methyl]-25,26,27,28-tetrahydroxycalix-[4]arene (**3**) based impregnated resin, its characterization, and sorption behavior for the removal of endosulfan from water. The impregnated resin was characterized through various analytical techniques such as Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and gravimetric analysis. The sorption efficiency of resin was checked through batch as well as column experiments. Different parameters such as pH, contact time, sorbent dosage, and temperature for the sorption of endosulfan were optimized as 2, 60 min, 3 mg, and 293 K, respectively. Freundlich and Langmuir sorption isotherms were applied to the data to validate the sorption process. The Thomas model was used to calculate the kinetic coefficient (k_{TH}) and maximum sorption capacity (q_o) of the resin, which were (3.40 and 3.46) $mL \cdot mg^{-1} \cdot min^{-1}$ as well as (0.338 and 0.318) $mg \cdot g^{-1}$ for α- and β-endosulfan, respectively. Besides this, Lagergren and Morris–Weber equations for kinetic studies show that sorption follows the pseudofirst-order rate equation. The developed sorption method has been applied to polluted surface water samples with a percent removal of 99.5 ± 1 % for both endosulfan isomers.

INTRODUCTION

Persistent organic pollutants (POPs) are a set of toxic chemicals; most of them are pesticides that persist in the environment for a long period of time. They circulate globally via the atmosphere, oceans, and other pathways.[1] Although, the pesticides are a class of POPs that play a vital role in the crop production and protection, but the residues left in the food chain pose a lot of problems. Because, some polar pesticides have a good tendency to leach down and runoff with rainwater from soil and contaminate the groundwater as well as fresh waters, which affect the environment. Consequently, they have been linked to adverse effects on human health such as cancer, reproductive disorders, and damage to the nervous or immune systems.[1−3]

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide), a member of cyclodiene family of persistent organic pollutants, is a well-known pesticide. It is a mixture of two stereoisomers, α-endosulfan and β-endosulfan (Figure 1), in the range of (64 to 70) % and (29 to 32) %, respectively.[4] It is a neurotoxic and an endocrine disruptor being used in many countries to control insects such as the Colorado potato beetle, cabbageworm, pests on fruits, vegetables, and tea as well as on nonfood crops such as tobacco and cotton.[5] In addition to its agricultural use, it is applied as a wood preservative and for the control of home garden pests such as the tsetse fly.[6] It is sold under the trade names Thionex, Thiodan, Phaser, and Benzoepin. It is marketed by Bayer Crop Science, Makhteshim-Agan, and Drexel Company among others. Because of its high potential for bioaccumulation and toxic effects for humans and the environment, such as accumulation in fatty tissues, long-range transport, difficulty to degrade, long half-life of isomers, and its degradation products (greater than 2 months in water and greater than 6 months in soil), the United Nations Environmental Protection Agency (UNEPA) has classified endosulfan as a highly toxic chemical.[7,8] World Health Organization (WHO) drinking water quality standards permits a maximum 20 $\mu g \cdot L^{-1}$ for endosulfan,[9] whereas the limit of a single pesticide is 0.1 $\mu g \cdot L^{-1}$, while for the total amount of pesticides it is 0.5 $\mu g \cdot L^{-1}$.[10]

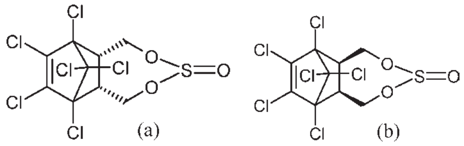

Figure 1. Molecular structures of (a) α-endosulfan and (b) β-endosulfan.

To lessen human risks and environmental pollution, regulations for drinking water are required. The wide range of organic pollutants in use makes research extremely difficult for producing a single method of removal for these pollutants that applies universally. Several methods for the removal of this toxic pollutant have been used to solve environmental problems, for example, combined ozone and UV irradiation,[11] biological degradation,[11] chemical oxidation with ozone,[12] and photodegradation.[13] However, sorption is found to be one of the best methods for the removal of organic pollutants.[14] Various natural as well as synthetic adsorbents have been used for the removal of endosulfan from water systems such as sal wood charcoal,[15] electrodialysis membranes,[16] carbon slurry,[17] wood charcoal,[18] wheat straw,[19] peach-nut shell,[20] natural organic substances,[21] mesoporous cyclodextrin-silica nanocomposite,[22] pore expanded mesoporous silica,[23] and chitosin-based molecularly imprinted polymers[24] and much more.[25−33] Some of these adsorbents are economically good. However, most of them are not regenerable and are prepared through tedious methods. They also pose an environmental threat because of their disposal in the atmosphere.

Polymeric adsorbents are highly porous in structure; their internal surfaces can adsorb and then desorb a wide variety of

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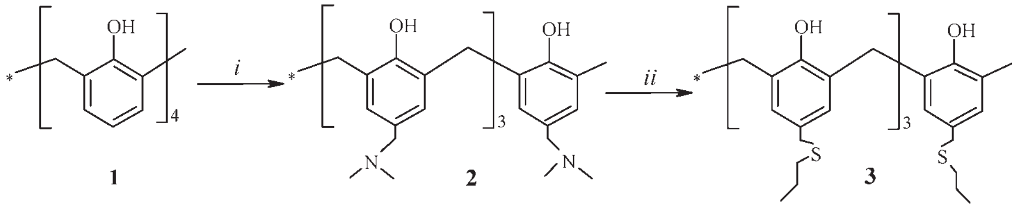


Figure 2. Synthetic scheme of calix[4]arene thioalkyl derivative (3).[41]

different species depending on the environment in which they are used. Amberlite XAD-4 is a cross-linked polymeric adsorbent, which has excellent sorption properties for neutral small molecules onto its macroreticular structure and higher surface area. These structures provide excellent chemical, physical, and thermal stability and selectivity. The modification with calixarenes enhances their sorption efficiency, which makes them the best choice for the removal of a variety of pollutants.[34,35] The calixarenes represent an important class of macrocyclic compounds due to their potential for forming host−guest complexes with cations and anions as well as neutral guest species.[36,37] The rigid three-dimensional macrocyclic structure of calix[4]arene is a versatile platform for designing a receptor that binds to a molecule via multiple interactions.[38,39] A variety of calixarene derivatives can be developed for the recognition of various toxic pollutants.[40,41] Thus, the present study describes a convenient method for the modification of Amberlite XAD-4 resin by the impregnation of calix[4]arene thioalkyl derivative (**3**) and investigation of its sorption efficiency through batch and column sorption methods to remove endosulfan from aqueous environment. This work presents the synthesis of a novel impregnated resin for the recovery of endosulfan from the environment.

■ EXPERIMENTAL METHODS

Reagents. All solvents/reagents used for the synthesis and preparations of solutions were of analytical grade, while ethanol and acetone were distilled. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system (Elga model classic UVF, UK). The Amberlite XAD-4 resin (styrene-divinylbenzene copolymer), surface area 725 $m^2 \cdot g^{-1}$, pore diameter 4 nm, and bead size ranging from 20 to 50 mesh was supplied by Fluka (Buchs, Switzerland). The resin obtained from the supplier contains organic and inorganic material. Therefore, before impregnation, the resin was precleaned with distilled acetone (3 times), then with distilled ethanol, finally dried at 313 K, and stored in a polyethylene container. For the pH (2 to 12) adjustment, NaOH and HCl (0.1 M) solutions were used. Standard endosulfan was purchased from Bayer Pesticides Company, Pakistan with 99 % (w/w) purity. The thioalkyl derivative of calix[4]arene (**3**) was synthesized according to a previously reported method (Figure 2).[42]

Instrumentation. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicollet AVATAR 5700 FT-IR spectrometer using KBr pellets [spectral range from (4000 to 400) cm^{-1}]. Melting points were determined on a Gallenkamp apparatus in a sealed capillary. Scanning electron microscopic (SEM) studies were performed using a JSM-6380 instrument. For pH measurements, an Inolab pH 720 (Germany) with a glass electrode and an internal reference electrode was used. A Gallenkamp mechanical shaker with a temperature controller was used for the batch sorption study. A glass column (16 cm × 6 mm) was used for column sorption study. The percentage of sorption was calculated from differences of detector response of GC μECD (Agilent 7890 A system, USA).

Impregnation of the Calix[4]arene Thioalkyl Derivative. A sample of 10 g of XAD-4 resin was taken in a 250 mL round-bottom flask. A sample of 50 mL of ethanol and 0.4 g ($5.1 \cdot 10^{-4}$ mol) of ligand **3** was added, and the mixture was continuously stirred for 120 h. After that, resin was filtered and washed with water to remove unimpregnated ligand. The ligand content was checked after solvent evaporation through gravimetric analysis. A maximum amount of ligand **3** impregnated onto dry resin was 0.35 g ($4.52 \cdot 10^{-4}$ mol), that is, $4.52 \cdot 10^{-5}$ $mol \cdot g^{-1}$.

Sample Preparation and Analysis. Stock solution of endosulfan was prepared according to the standard methods. Working samples were made by adding required stock solution to the predetermined quantity of distilled water. All experiments were performed with a stock solution of 1 $mg \cdot L^{-1}$, which was prepared as fresh after every 10 days.

The extraction of endosulfan was carried out by the liquid−liquid partition method, in which water samples were extracted with 10 mL of ethylacetate/*n*-hexane (1:1) in a 50 mL separating funnel. During extraction,the separating funnel was shacked for 5 min and allowed to settle for 5 min followed by the collection of upper organic layer in a 25 mL conical flask. The separated organic layer was treated with anhydrous sodium sulfate to absorb any trace of moisture present in the extracted sample. The sample was filtered through Whatman filter paper (0.45 μm). The extracted endosulfan samples were analyzed by GC-μECD. Instrumental conditions were as previously reported.[42]

Sorption Procedures. The uptake of endosulfan onto modified resin was characterized by the sorption efficiency of resin which was determined through static and dynamic sorption methods, as a function of the material present in the solution. The kinetics of sorption and factors that affect the sorption process were also studied.

Static Method. Sorption was determined by the batch method, which permits a convenient evaluation of parameters that influence the sorption process. The study was carried out for endosulfan isomers at room temperature, that is, 297 ± 1 K. The sample solution (10 mL) containing endosulfan isomers (0.3 $mg \cdot L^{-1}$) was taken in a 25 mL conical flask. The modified resin (3 mg) was added, and the mixture was equilibrated for a fixed period of time (60 min). The resin was filtered, and the sorbed endosulfan isomers were extracted with ethylacetate/*n*-hexane (1:1) followed by analysis through GC μECD. The sorption of endosulfan isomers was calculated as follows:

$$\%\text{sorption} = \frac{H_i - H_f}{H_i} \cdot 100 \tag{1}$$

where H_i and H_f are peak heights before and after the sorption, respectively. Likewise the percentage sorption of pure Amberlite XAD-4 was also calculated. The maximum batch sorption capacity

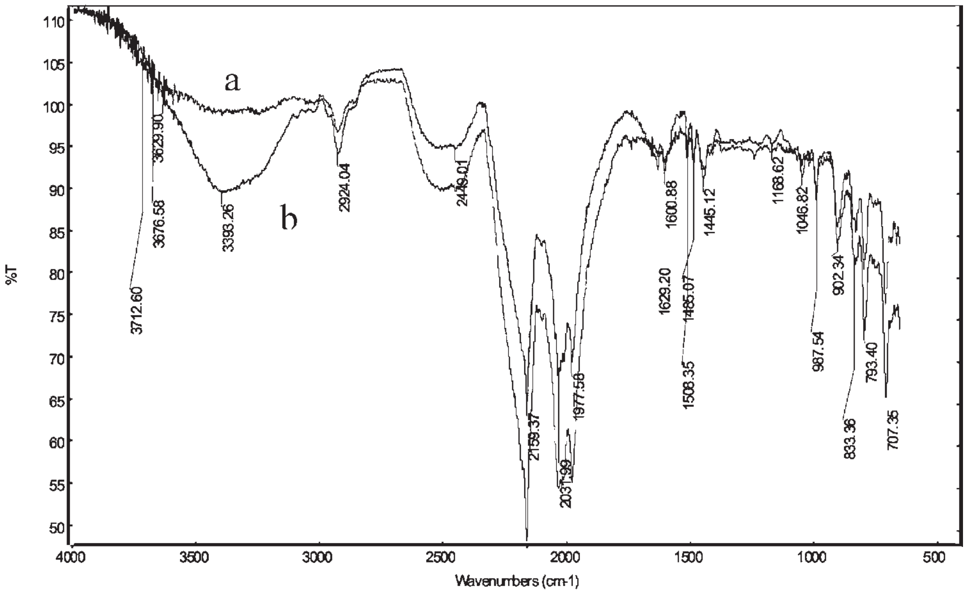


Figure 3. FT-IR spectra of (a) pure Amberlite XAD-4 and (b) impregnated resin.

Q of modified resin was calculated through following eq 2.[43]

$$Q = \frac{V(C_o - C_f)}{M} \qquad (2)$$

where V is volume of solution (L), C_o and C_f are the initial and equilibrium concentrations of endosulfan in water ($\text{mg}\cdot\text{L}^{-1}$), respectively, and M is the mass of sorbent (g).

Dynamic Method. A column study was carried out for determining the suitability of the adsorbent and the eluting solvent. A Pyrex glass column was packed with a small filter paper of column diameter at the bottom followed by a small amount of glass wool and 0.003 g of resin, and finally filter paper of same diameter was placed at the top to prevent any loss of the resin during the sample loading. A solution of appropriate concentration of endosulfan was passed through the column at optimized flow rate, that is, 1 $\text{mL}\cdot\text{min}^{-1}$. The concentration of endosulfan in the column effluents was determined by GC μECD.

The breakthrough curve (A) is used to obtain the area by integrating the plot of sorbed concentration C_s ($\text{mg}\cdot\text{L}^{-1}$) versus t (min) that can be used to find total sorbed endosulfan quantity q_{total} (mg) in the column for a given concentration and at given flow rate by using eq 3;

$$q_{\text{total}} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{\text{total}}} C_{\text{ads}}\,\mathrm{d}t \qquad (3)$$

whereas the total amount of endosulfan isomers sent to column m_{total} is calculated from eq 4;

$$m_{\text{total}} = \frac{C_o Q t_{\text{total}}}{1000} \qquad (4)$$

total percent removal of endosulfan from water through column (column performance) can be calculated from eq 5.[44]

$$\text{total removal }\% = \frac{q_{\text{total}}}{m_{\text{total}}} \qquad (5)$$

q_{total} is the total sorbed quantity of endosulfan, and m_{total} is the total amount of endosulfan sent to the column.

RESULTS AND DISCUSSION

Characterization of Impregnated Resin. The impregnated resin has been characterized by FT-IR and SEM.

FT-IR Analysis. The FT-IR spectra of the plain XAD-4 and impregnated resin are shown in Figure 3. The FTIR spectra before and after impregnation provided information regarding the surface groups that participated in the impregnation and also clearly indicated that sorption occurred on the surface of XAD-4. IR spectrum of impregnated resin (b) shows the peak at 3393 cm^{-1}, which correspond to the presence of the alcohol (O−H) functionality.

From this observation it can be concluded that **3** has been impregnated onto the surface of XAD-4 resin. The IR spectrum of pure resin (a) does not show any such peak.

SEM Analysis. In this work, SEM is used to study the morphological changes on the surface of adsorbent resin in its various forms (i.e., pure and impregnated), which are shown in Figure 4. The morphology of the impregnated resin shows some important observations. The coverage of the surface of the resin due to the impregnation of the calixarene molecules is evident from the formation of white layer(s) (cloud) of uniform thickness and coverage.

Sorption Studies. The two forms of endosulfan isomers are well-separated and quantified down to trace levels using the given set of GC conditions by μECD as a detector. This facilitate examining the sorption behavior of impregnated resin toward the two isomeric forms of endosulfan. Various parameters that may affect the removal of endosulfan from aqueous environment were studied.

Effect of pH. The influence of pH plays a key role in all chemical processes. In this study the sorption behavior of impregnated resin for the uptake of endosulfan isomers was determined in the pH ranging from 2 to 12, using the solution of constant concentration with shaking speed 125 rpm (Figure 5). The results shows that the percentage of sorption increases with decreasing pH and the maximum sorption occurs at pH 2, which is due to the fact that hydrogen ion concentration affect the surface properties of the sorbent. At very low pH values, the surface of the sorbent would be surrounded by the hydronium ions and sorbent surface becomes

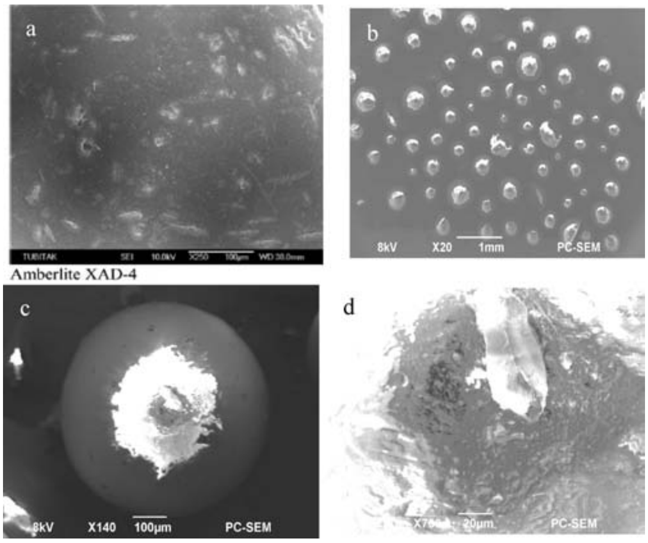


Figure 4. SEM micrographs of (a) pure resin (8 kV, 100 μm, 20×), (b) impregnated resin (8 kV, 100 μm, 20×), (c) single impregnated resin particle (8 kV, 100 μm, 140×), and (d) single impregnated resin particle (8 kV, 20 μm, 700×).

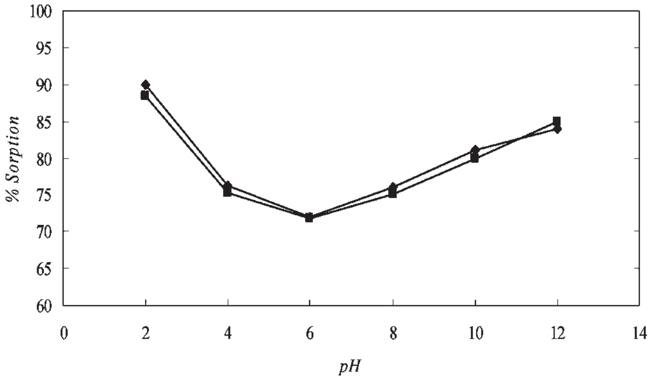


Figure 5. Effect of pH on sorption of ♦, α-endosulfan; ■, β-endosulfan isomers.

positively charged, and thus S and O bearing sites of endosulfan are electrostatically attracted toward the surface[45] due to a lone pair of electrons. Consequently, it is due to the calixarene molecule which may attracts protonated endosulfan through cation−π interaction[46] at low pH. The sorption is lowest at the near neutral pH region; this may be due to just intermolecular interaction between resin and endosulfan, while at more basic pH free phenolic groups are deprotonated, which may have some interaction with a endosulfan molecule along with the π-structure of calixarene moiety. Thus, the effect of pH on the sorption of endosulfan by calixarene-based resins seems to be a phenomenon governed by a multitude of effects.[41]

Effect of Concentration of Pesticides. The concentration study was carried out by diluting the stock solution in the range of (0.05 to 0.7) mg·L^{-1} at pH 2. Figure 6 shows that with increasing concentration the percentage of sorption decreases, which reveals that an increase in initial concentration decreases the percentage binding. These observations can be explained by the fact that, at very low concentrations of pesticide, the ratio of sorptive surface area to the total endosulfan molecules available is high, and thus, there is a greater chance for pesticide removal, while the case is reverse at higher concentrations. Thus, at low initial pesticide concentrations, the removal capacity is higher.

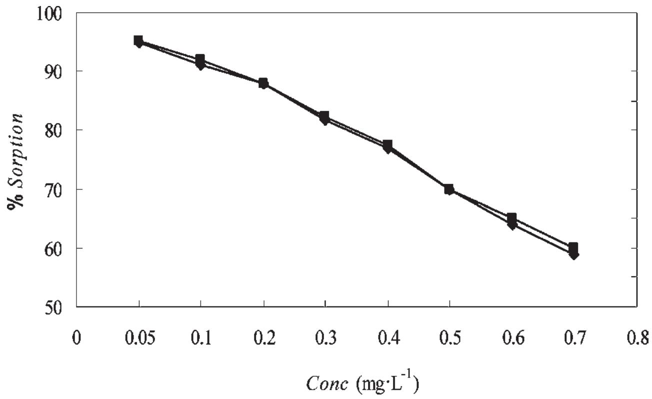


Figure 6. Effect of concentration on sorption of ♦, α-endosulfan; ■, β-endosulfan isomers.

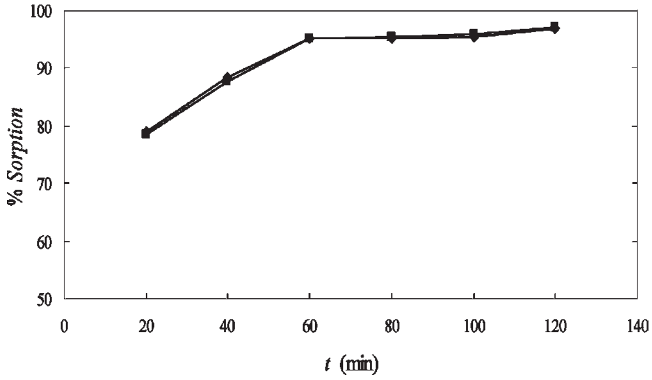


Figure 7. Effect of contact time on the sorption of ♦, α-endosulfan; ■, β-endosulfan isomers.

Effect of Contact Time. The equilibrium time was observed by agitating the solution from (20 to 120) min at pH 2 using 1 mg of resin at the shaking speed of 125 rpm. The Figure 7 reveals that the percentage of sorption increases with increasing contact time and attains maximum value at 60 min; after that the percentage of sorption remains almost constant. Hence, a further study was done at an optimized time of 60 min.

Effect of Sorbent Dosage. Sorbent dosage is an important parameter because this determines the capacity of a sorbent for a given initial concentration of sorbate. The study was carried out at pH 2 using resin [(0.5 to 20) mg] at the shaking speed of 125 rpm. Figure 8 reveals that the percent sorption increased very rapidly when the amount of the sorbent was increased from (0.5 to 0.3) mg, after that the percent sorption stayed almost constant up to 20 mg of sorbent dosage.

The sorption efficiency of pure Amberlite XAD-4 was also checked by using the above-mentioned optimized parameters, and it was observed that the percentage sorption with pure Amberlite XAD-4 was (50 to 55) % of α- and β-endosulfan from water, respectively; therefore it can be assumed that additional sorption was due to the impregnated thioalkyl derivative of calix[4]arene (3).

Effect of Temperature. To explain the thermodynamic behavior of sorption, the experiments were conducted at 293 K with intervals of 20 K at optimum conditions. Figure 9 shows that with increasing temperature the percentage of sorption decreases, which confirms the exothermic nature of the reaction.

Comparative Study. The maximum sorption capacity of impregnated resin has also been compared (Table 1) with other sorbents reported in literature.[14,16,19,41] It can be observed from the data that the sorption capacity of impregnated Amberlite-XAD-4 is much better than the previously reported studies. The superiority of the impregnated resin over other sorbents could be explained on the basis of economical viewpoint, the regeneration, and reusability of the resin, which in turn helps to avoid the environmental pollution with the advantage to recycle the sorbate material. Most of the sorbent materials used are not reused and create the disposal problems. It may also be demonstrated on the basis of the amount of sorbent dosage that the impregnated resin is more effective as compared with other sorbents, that is, only 3 mg of the resin is sufficient to sorb 99 % of endosulfan from 0.3 mg·L^{-1} sample solution. The present strategy has also been proven better than the previous one performed by our group.[41]

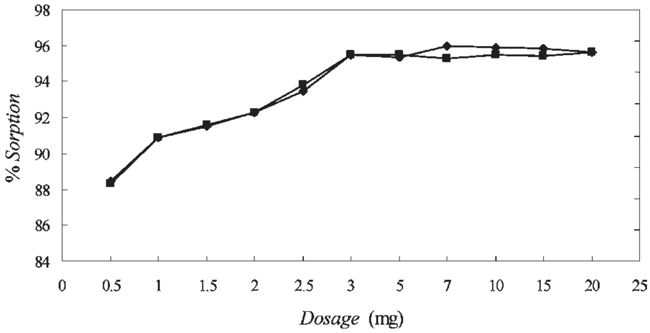


Figure 8. Effect of adsorbent dosage on the sorption of ◆, α-endosulfan; ■, β-endosulfan isomers.

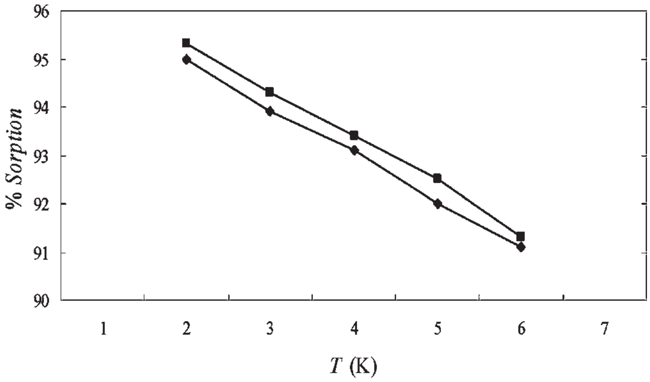


Figure 9. Effect of temperature on the sorption of ◆, α-endosulfan; ■, β-endosulfan isomers.

Characterization of Resin through Sorption Isotherms. Sorption isotherms are often used as empirical models to describe the equilibrium of the sorption of a material on surface.[47] They are obtained from measured data by means of regression analysis and show the relationship between amounts of material sorbed as a function of concentration in the solution. The most frequently used isotherms are Freundlich and Langmuir isotherm.

Freundlich Sorption Model. This model is used to describe the sorption process on heterogeneous and microporous adsorbent surfaces and assumes that various types of active sites adsorb/interact simultaneously. Equation 6 is a linear form of this isotherm;

$$\log C_{\mathrm{ads}} = C_{\mathrm{m}} + \frac{1}{n}\log C_{\mathrm{e}} \tag{6}$$

where C_{ads} is the adsorbed concentration (mol·g^{-1}), C_{m} is the multilayer sorption capacity, $(1/n)$ is sorption intensity, and C_{e} is an equilibrium concentration (mol·L^{-1}). A plot of log C_{ads} versus C_{e} exhibits a straight line with the slope $(1/n)$ and intercept C_{m} as shown in Figure 10.

Langmuir Sorption Isotherm. Langmuir theory relates to an ideal case, when the sorption process occurs on an energetically homogeneous surface, without mutual interactions between molecules of the sorbate.[48,49] The model was fitted for the sorption of endosulfan isomers on impregnated resin; eq 7 is the linear form of the Langmuir sorption isotherm.

$$\frac{C_{\mathrm{e}}}{C_{\mathrm{ads}}} = \frac{1}{Qb} + \frac{C_{\mathrm{e}}}{Q} \tag{7}$$

where C_{e} is the equilibrium concentration (mol·L^{-1}), C_{ads} is the adsorbed concentration (mol·g^{-1}), Q is the monolayer sorption capacity (mol·g^{-1}), and b is an enthalpy of sorption (mol·L^{-1}). A plot of $(C_{\mathrm{e}}/C_{\mathrm{ads}})$ versus C_{e} exhibits a straight line with slope $(1/Q)$ and intercept $(1/Qb)$ (Figure 11).

The separation factor, R_{L}, can be calculated from the value of Langmuir constant b, through eq 8.

$$R_{\mathrm{L}} = \frac{1}{1 + bCi} \tag{8}$$

Favorability and unavoidability of sorption process can be calculated from the sorption isotherm constants. The value of sorption intensity $(1 < n < 10)$ indicates that sorption is favorable. The corresponding value of n or the sorption of endosulfan isomers on impregnated resin is 2.17 and 2.59, respectively, which show that the sorption is favorable. Moreover, the favorable sorption of endosulfan isomers is also indicated from the calculated value of R_{L}, that is, < 1. In addition, the value of R^2 is higher in Langmuir then in the Freundlich model, which indicate that the sorption of endosulfan favors the

Table 1. Comparative Sorption Capacity Study of Calix[4]arene Based Impregnated Resin

	dosage of sorbent		temperature	Q_{m}	
name of sorbent	g	pH	K	mmol·g^{-1}	ref
sal wood charcoal	20	6.6−5.4	303	$4.3\cdot10^{-8}$	14
carbon slurry	0.025	6.5	298	$9.0\cdot10^{-6}$	16
peach-nut shells	0.1	6	303	0.27 ± 0.029	19
calix[4]arene based silica	0.05	2		$200\cdot10^{-6}$	41
new calix[4]arene-based impregnated resin	0.003	2	293	$111\cdot10^{-6}$	this work

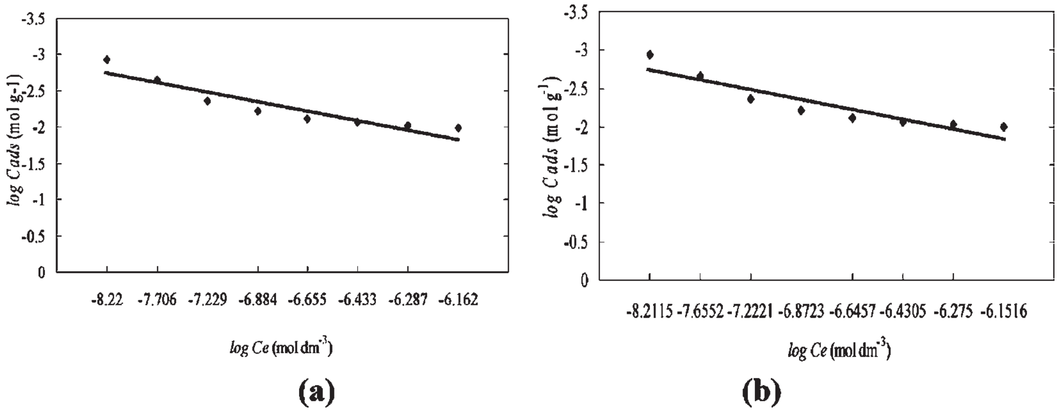


Figure 10. Freundlich sorption isotherms of (a) α-endosulfan and (b) β-endosulfan on impregnated resin.

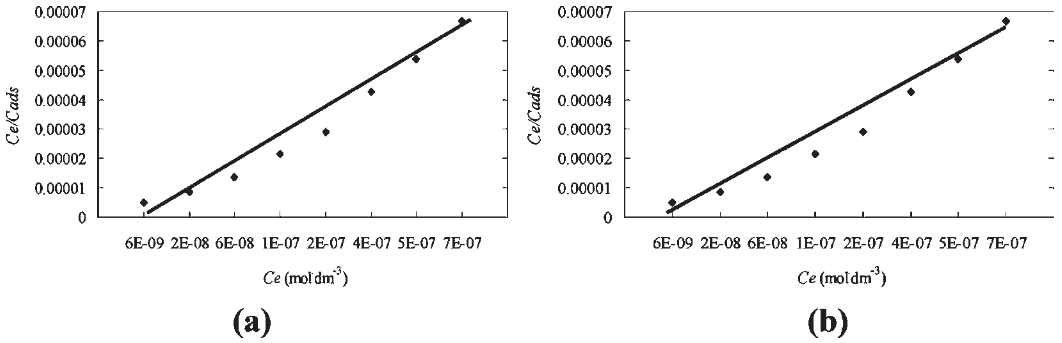


Figure 11. Langmuir sorption isotherms of (a) α-endosulfan and (b) β-endosulfan on impregnated resin.

Table 2. Isotherm Constants and Values of Regression Coefficient (R^2) for Isomers of Endosulfan

		C_m		
isotherms	isomers of endosulfan	$\text{mmol}\cdot\text{g}^{-1}$	$1/n$	R^2
Freundlich	α-isomer	0.908	0.4608	0.9823
	β-isomer	0.909	0.4624	0.9805
		Q	B	
		$\text{mmol}\cdot\text{g}^{-1}$	$\text{mol}\cdot\text{L}^{-1}$	R^2
Langmuir	α-isomer	$112\cdot10^{-6}$	$8.9\cdot10^{-4}$	0.9918
	β-isomer	$111\cdot10^{-6}$	$8.8\cdot10^{-4}$	0.9932

Langmuir isotherm. The values of constants obtained from both of the sorption models are given in Table 2.

Column Sorption. The column study was carried out to remove the endosulfan isomers, which shows that the impregnated resin is homogeneous in nature. By using the conditions optimized through batch experiments at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ (0.3 $\text{mg}\cdot\text{L}^{-1}$) from water through impregnated resin (3 mg). The breakthrough capacity, exhaustion capacity, and degree of column utilization have been evaluated from breakthrough curves, as shown in Figure 12.

A relatively high sorption capacity then batch capacity has been observed, which is generally attributed to relatively more time interaction between the adsorbent and the sorbate surface with column. The total percent removal of endosulfan isomers through column was found to be 96.3 % and 95.6 % for α- and β-endosulfan isomers, respectively.

Thomas Model. The successful design of a column requires the knowledge of the concentration time profile or breakthrough curve for effluent and maximum sorption capacity. The Thomas model is one of the most commonly used methods to describe the column sorption data. This model assumes Langmuir kinetics of sorption—desorption, and no axial dispersion is derived with sorption so the rate-deriving force obeys second-order reversible reaction kinetics. Column sorption data were fitted to Thomas model to determine the Thomas rate constant (k_{TH}) and maximum solid-phase concentration (q_o). The model has the following linear form:

$$\ln\left(\frac{C_o}{C} - 1\right) = \frac{k_{\text{TH}} q_o A}{Q} - \frac{k_{\text{TH}} C_o}{Q} V_{\text{eff}} \tag{9}$$

C_0 is the initial concentration of endosulfan ($\text{mg}\cdot\text{L}^{-1}$), C the effluent concentration ($\text{mg}\cdot\text{L}^{-1}$), k_{TH} is the Thomas model rate constant ($\text{mL}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$), q_o the maximum solid phase concentration of solute ($\text{mg}\cdot\text{g}^{-1}$), A the amount of material sorbed (mg), Q the flow rate ($\text{mL}\cdot\text{min}^{-1}$), and V_{eff} the effluent volume (mL). V_{eff} can be calculated from the following equation,

$$V_{\text{eff}} = Qt_{\text{total}} \tag{10}$$

Q is the flow rate ($\text{mL}\cdot\text{min}^{-1}$), and t_{total} stands for the maximum flow time (min).

The Thomas model rate constant k_{TH} (3.40, 3.46) and q_o (maximum solid phase concentration) of solute come out to be 0.338 and 0.318 $\text{mg}\cdot\text{g}^{-1}$ with a coefficient of determination R^2 (0.9586, 0.9439) for α- and β-endosulfan, respectively. These constants were calculated from the plot of $\ln((C_0/C) - 1)$ against t (min) at constant flow rate (Figure 13).

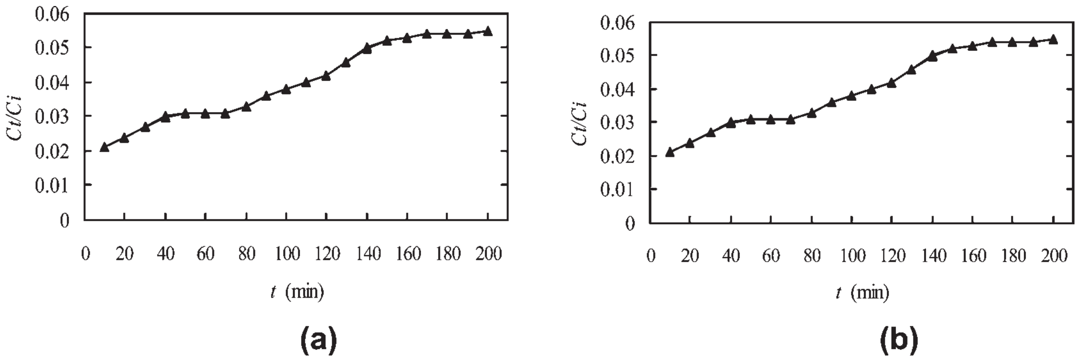


Figure 12. Breakthrough curves of (a) α-endosulfan and (b) β-endosulfan.

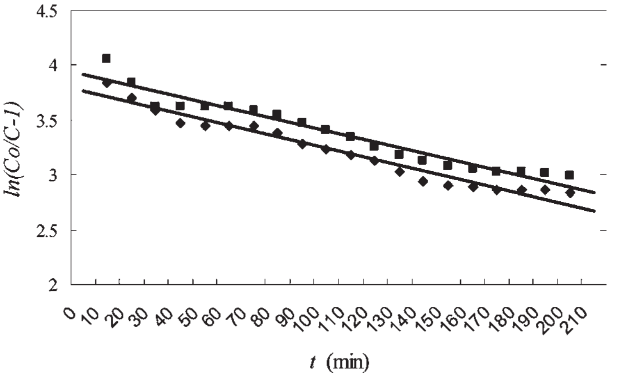


Figure 13. Plot of $\ln((C_o/C) - 1)$ vs t.

Kinetics of Sorption Study. The kinetics of sorption is an important parameter used for modeling the efficiency of process. A simple kinetic analysis of the sorption is evaluated by employing the kinetic data to different equations, namely, Morris–Weber, Lagergren (pseudofirst-order equation), and Ho and McKay (pseudosecond-order equation).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{Lagergren model} \tag{11}$$

$$q_t = R_d\sqrt{t} \quad \text{Morris–Weber model} \tag{12}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad \text{Ho and McKay model} \tag{13}$$

The Lagergren model was tested by plotting $\log(q_e - q_t)$ versus time, where q_e is the amount of endosulfan sorbed ($mg \cdot g^{-1}$) at equilibrium and q_t at time t (min), and k (min^{-1}) is the first-order rate constant.

q_t is the sorbed concentration in $mol \cdot g^{-1}$ at time t, which was plotted against $(t)^{1/2}$ to test the Morris–Weber equation.

Figure 14 shows the kinetic study of α and β endosulfan on the resin under optimized conditions, while evaluating the effect of agitation time on percent sorption. Plot of $\log(q_e - q_t)$ versus agitation time t (min) exhibit straight line with the coefficient of determination (R^2) having values 0.945 and 0.914, for α- and β-endosulfan, respectively.

Meanwhile, the same data were evaluated through the Morris–Weber model where q_t was plotted against $(t)^{1/2}$ that exhibits a straight line with the coefficient of determination (R^2) having values of 0.8485 and 0.8343, for α- and β-endosulfan, respectively, as shown in Figure 15.

Data were also investigated through pseudosecond-order rate model given by Ho and McKay. Figure 16 shows a plot of (t/q_t) versus t, which exhibits a straight line with (R^2) 0.9996 and 0.9995 values for α- and β-endosulfan, respectively.

From these kinetic model observations, it can be concluded that the kinetics follows the Ho and McKay model that elucidates the pseudosecond-order kinetics of the sorption of endosulfan isomers on impregnated resin.

Thermodynamics of Sorption Study. Thermodynamics is the science of energy conversion involving heat and other forms of energy. To study the thermodynamics of sorption of endosulfan on impregnated resin, three basic parameters, free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated. The values of these parameters are compiled in Table 3.

The effect of temperature on the sorption of endosulfan isomers was studied in the range of (293 to 333) K at optimum conditions. The plot of $\ln K_c$ versus $1/T$ gives a straight line with a coefficient of determination (R^2), 0.9919 and 0.9951 for α- and β-isomers, respectively, as shown in Figure 17. The values of ΔH and ΔS could be evaluated from the values of slope and intercept by using the following eq 14.[45]

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{14}$$

where K_c is the equilibrium constant, which is related to the van't Hoff equation.[47]

K_c is calculated from the values of sorption at different temperatures by the formula;

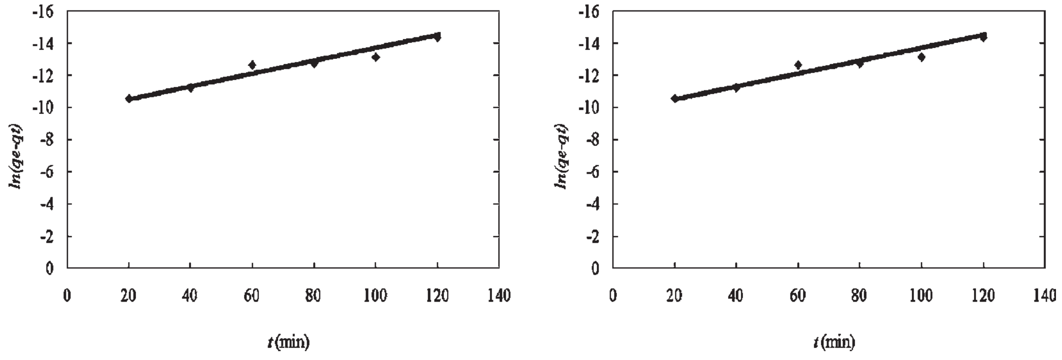
$$K_c = \frac{F_e}{1 - F_e}$$

where F_e is the fraction sorbed at equilibrium.

The change in free energy (ΔG) could be calculated by using the following eq 15;

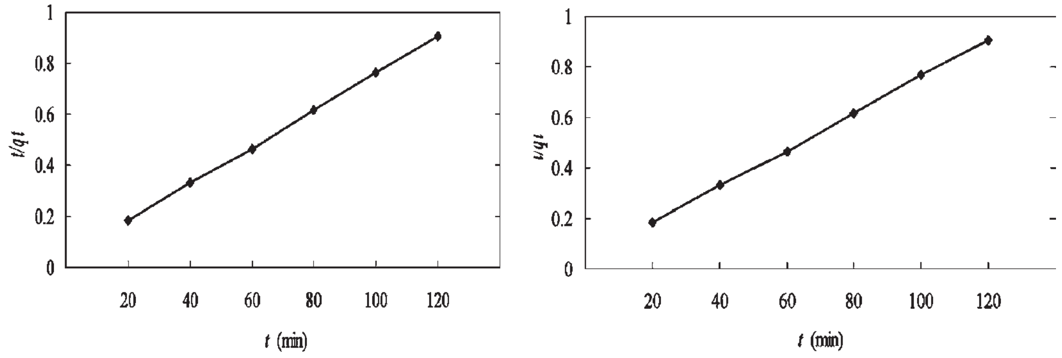
$$\Delta G = -RT \ln K_c \tag{15}$$

The negative value of free energy (Table 3) of endosulfan relates to the feasibility of sorption on impregnated resin, and a little decrease in the values of ΔG was observed with the increase in temperature, which reveals less sorption of endosulfan isomers at higher temperatures and shows that the reaction is less spontaneous at higher temperatures. Consequently, the negative value of ΔH shows that the reaction is exothermic in nature. Meanwhile, during the sorption process, molecules of endosulfan get attached through coordination with the binding sites of sorbent surface which results in the loss of degree of freedom,



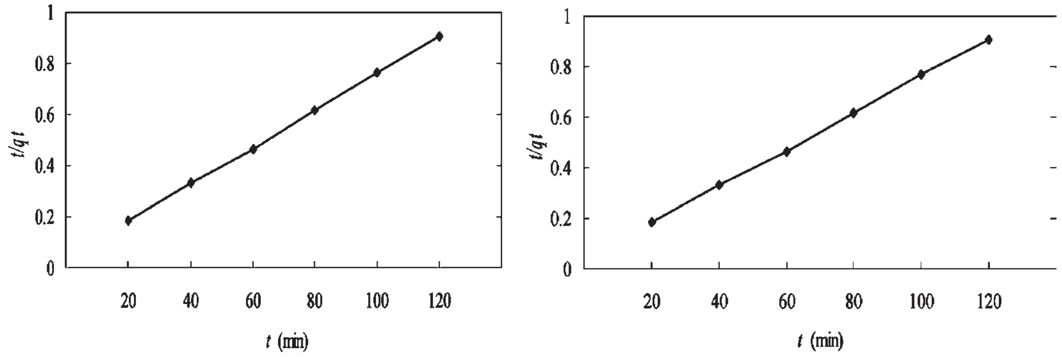
(a) **(b)**

Figure 14. Lagergren model of (a) α-endosulfan and (b) *β*-endosulfan.



(a) **(b)**

Figure 15. Morris–Weber model of (a) α-endosulfan and (b) *β*-endosulfan.



(a) **(b)**

Figure 16. Ho and McKay model of (a) α-endosulfan and (b) *β*-endosulfan.

and thus the decrease in the value of ΔS could be elucidated, which in turn becomes temperature-independent because after sorption there will be no effect of temperature on ΔS. Since the sorption of endosulfan is exothermic in nature at all temperatures through coordination onto the surface of the resin, therefore, it could be apparently understood that the change in enthalpy (ΔH) is also temperature-independent.

Sorbent Regeneration. The regeneration study of α- and *β*-endosulfan isomers was carried out by sorption of 10 mL of 0.3 $\text{mg} \cdot \text{L}^{-1}$ on 3 mg of impregnated resin. The sorbent was regenerated by shaking with 5 mL of mixture of *n*-hexane and ethyl acetate (1:1) for 10 min. The sorbent efficiency of resin for percent recovery was checked for five cycles. The percent recovery of resin was found to be 92.5 ± 2.03 % and 92.6 ± 7.9 % for α-endosulfan and *β*-endosulfan, respectively (Figure 18).

Application to Real Water Samples. To study the application of the impregnated resin, the samples of agricultural soil

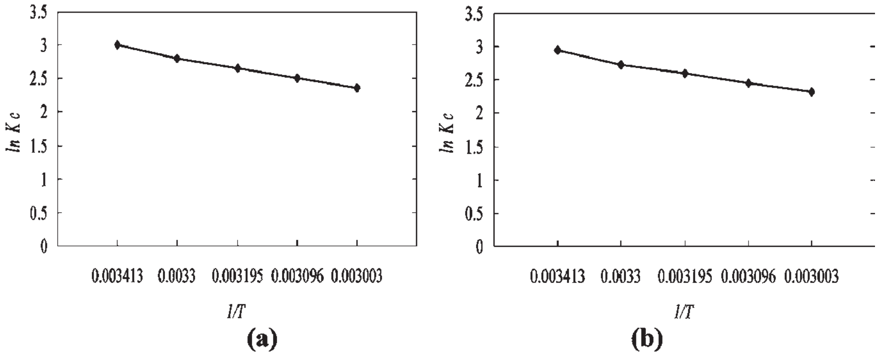


Figure 17. Thermodynamics of (a) α-endosulfan and (b) β-endosulfan.

Table 3. Thermodynamic Parameters for the Sorption of Endosulfan on Calix[4]arene-Based Impregnated Resin

	temp	ΔG^o	ΔH^o	ΔS^o
endosulfan	K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
α-isomer	293	−7.32754		
	303	−6.83217	−3833.78	−13.06
	313	−6.45187		
	323	−6.11704		
	333	−5.72387		
β-isomer	293	−7.16921		
	303	−6.65668	−3642.554	−12.409
	313	−6.3358		
	323	−5.9467		
	333	−5.66319		

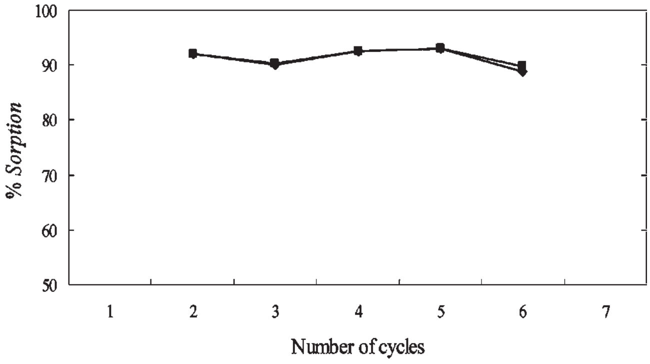


Figure 18. Effect of the number of cycles on the uptake of ♦, α-endosulfan; ■, β-endosulfan isomers.

sprayed with endosulfan were collected from the vicinity of Jamshoro, Pakistan. The soil was washed with water and was filtered to remove any particulate. The water filtered from soil was finally extracted with ethylacetate/*n*-hexane (1:1) followed by GC analysis to check amount of endosulfan in it. The sorption of α- and β-endosulfan was carried out under optimized conditions (Table 4).

CONCLUSION

The present study demonstrates that newly synthesized calix[4]-arene thioalkyl derivative-based Amberlite XAD-4 resin is more efficient for the removal of endosulfan isomers from an aqueous environment than the reported materials. Various parameters like shaking time, dosage of sorbent, and concentration of sorbate were optimized and it has been observed that the sorption is favorable at various pH particularly at pH 2. The sorption data were evaluated by Freundlich and Langmuir isotherm models. The value of $1/n$ from the Freundlich sorption isotherm proposes that the sorption capacity of impregnated resin is better for lower concentration solutions, whereas the R_L values from the Langmuir sorption isotherm depict the favorability of sorption process, and this model was also found to be best fitted with sorption data. The kinetic results suggest the pseudosecond-order nature of the sorption process, while the thermodynamic parameters, that is, ΔH, ΔS, and ΔG determined for endosulfan, indicate the exothermic and spontaneous nature of sorption. The study may be helpful to design large scale plants for the application of impregnated resin that can effectively be regenerated and reused to remove endosulfan isomers from agriculture/industrial wastewaters.

Table 4. Amount Found and Percent Removal of α- and β-Endosulfan from Real Water Samples with Calix[4]arene-Based Impregnated Resin

	amount found		removal (%)	
samples	α-endosulfan ($mg \cdot L^{-1}$)	β-endosulfan ($mg \cdot L^{-1}$)	α-endosulfan	β-endosulfan
A	0.995	1.101	99.5	98.5
B	0.115	0.202	98.9	98.5

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