An efficient calix[4]arene based silica sorbent for the removal of endosulfan from water

Sibghatullah Memon [a,b], Najma Memon [b], Shahabuddin Memon [b,*], Yawar Latif [b]

[a] Dr. M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro 76080, Pakistan
[b] National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

ARTICLE INFO

ABSTRACT

The present work explores sorption behavior of calix[4]arene based silica resin to remove α and β endosulfan isomers from aqueous solution. The efficiency of resin was checked through both batch and column sorption methods. In both methods, the sorption parameters, i.e. pH, equilibrium time, shaking speed and sorbent dosage were optimized as 2, 60 min, 125 rpm and 50 mg, respectively. Freundlich and Langmuir sorption isotherm models were applied to validate the sorption process. The data obtained in both models reveal that the sorption is favorable. Column sorption data were analyzed through Thomas model to calculate kinetic coefficient k_{TH} and maximum sorption capacity q_o of the resin, which were found to be 6.18 and 5.83 cm^3 mg^{-1} min^{-1} as well as 1.11 and 1.08 mg g^{-1} for α and β endosulfan, respectively. Kinetics of sorption shows that it follows pseudo second order rate equation. The optimized method has also been applied to real water samples and the results show that calix[4]arene based silica resin is an effective sorbent to remove endosulfan from waste waters.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Persistent organic pollutants (POPs) are considered as substances which posses strong resistance to photolytic, chemical and biological degradation. They are semi-volatile, highly toxic, persistent and travel long distance through air and water. They have low solubility in water but high solubility in fats therefore; they can bio-accumulate in fatty tissues. Semi-volatility of these compounds enables them for long range transport in the atmosphere. This leads to contamination of water, soil and agriculture products [1].

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepine-3-oxide) is an organochlorine pesticide. It is used as an insecticide under different trade names like thiodan, thionex, endosan, endosulfan, etc. This pesticide is used for various crops in developing countries like Pakistan, India, Bangladesh, etc., in order to enhance agriculture production. Due to its dangerous effects for human and environment such as accumulation in fatty tissues, long range transport, difficult to degrade, long half life of isomers and its degradation products (greater then 2 months in water and greater then 6 months in soil) [2]. United Nations Environmental Protection Agency (UNEPA) classified endosulfan highly toxic [3] while WHO consider endosulfan as a moderately hazardous [4] pollu-

tant. According to Pesticide Action Network (PAN) International endosulfan fulfills the requirement of persistent organic pollutants (POPs). Therefore, it is proposed to be listed in Stockholm Convention [5]. Recently, it was observed that endosulfan isomers (Fig. 1) can cause endocrine disruption in both terrestrial and aquatic organisms. Excessive and improper applications can cause physical disorder, mental disturbance and death in farm workers, particularly in developing countries [6]. A global ban on the use and manufacturing of endosulfan is being considered through Stockholm Convention on persistent organic pollutants (POPs) [7]. WHO recommended limit of single pesticide is 0.1 μg dm^{-3}, while for total amount of pesticide it is 0.5 μg dm^{-3} [8].

Various methods have been utilized to remove endosulfan and related environmental pollutants from water such as biodegradation through Aspergillus sydoni [9], bionitrification and sand filter system [10], anaerobic-membrane bioreactor technology [11]. Removal of endosulfan from water using sorption methodology is current area of research due to its simplicity and effectiveness. Various sorbents such as Sal wood char coal [12], natural organic substances [13], wheat straw [14], peach-nut shells [15], and carbon slurry [16] are reported. However, very few synthetic sorbents are reported in the literature for the removal of pesticides from water such as mesoporous cyclodextrin-silica nanocomposite [17], pore expanded mesoporous silica [18] and chitosin based molecularly imprinted polymers [19].

Calixarenes are a class of synthetic cyclo-oligomers possessing cup like shape with defined upper and lower rim and central annu-

* Corresponding author. Tel.: +92 22 2772065; fax: +92 22 2771560.
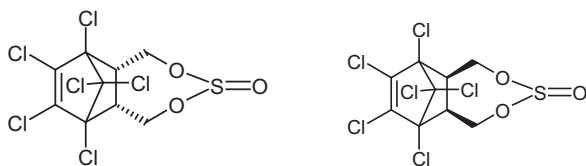*E-mail address:* shahabuddinmemon@yahoo.com (S. Memon).

Fig. 1. Molecular structure of α and β endosulfan.

lus. Its upper and lower rim can be functionally modified to form various derivatives to function as guests for various toxic metals or neutral molecules [20] such as Pb(II), chromium(VI), arsenic(V), carcinogenic aromatic amines, amino acid derivatives and azodyes from aqueous systems [21–23]. The immobilization of calixarene moiety onto the polymeric support enhances the sorption capacity of the resin [24–26]. Present work deals with the investigation of sorption efficiency of synthesized calix[4]arene based silica resin through batch and column sorption methods to remove endosulfan from aqueous system.

2. Materials and methods

2.1. Reagents

All reagents/solvents used for the synthesis and preparation of solutions were of analytical grade. Analytical thin layer chromatography (TLC) was performed on precoated silica plates (SiO$_2$, PF$_{254}$). The pH (2–12) was adjusted through 0.1 M HCl/NaOH solution using pH meter. Standard endosulfan was purchased from Bayer Pesticides Company, Pakistan with 99% purity. Silica (240–400 mesh) was obtained from Fluka Germany. p-tert-Butylcalix[4]arene was synthesized according to previously reported method [27,28]. All solutions were prepared in double distilled deionized (DDI) 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. Melting point was determined through Gallenkamp melting point apparatus model MFB, 595, 010M, England. The % sorption was calculated from differences of detector response of GC μECD (Agilent 7890 A system, USA). The pH was measured with Inolab pH 720 (Germany) with glass electrode and internal reference electrode. A Gallenkamp thermostat automatic mechanical shaker model BKS 305-101, UK was used for batch sorption study. A glass column (16 cm × 6 mm) was used for column sorption study.

2.3. Immoblization of p-tert-butylcalix[4]arene on silica

The process of immobilization was carried through previously reported procedure [29] with slight modifications. Silica (10 g) was dried at 200 °C in vacuum oven at 30 Torr, and then 25 cm^3 of 1 M solution of silicon tetrachloride in dry dichloromethane was added. Reaction mixture was made alkaline (in order to deprotonate the OH groups) by adding 3 cm^3 of triethylamine (cloudy mixture was obtained) and mixture was kept at room temperature for 18 h. Solvent was removed through rotary evaporator to get white powder. A 3 g of p-tert-butylcalix[4]arene was dissolved in toluene (30 cm^3), white powder was added to it, and 10 cm^3 of triethylamine was added to this solution, and was refluxed for 50 h. The reaction was operated through IR.

2.4. Sorption procedure

2.4.1. Batch sorption study

Batch sorption study of endosulfan on calix[4]arene based silica resin was carried out at room temperature. A 10 cm^3 of 0.3 μg cm^{-3} endosulfan solution at pH 2 was taken in glass stoppered bottle. A 50 mg of resin was added to it and was shaked on the horizontal shaker for an equilibrium time (60 min) at 125 rpm. The solution was filtered through Whatmann filter paper (0.45 mm). The % sorption was calculated through following equation:

$$\%Sorption = \frac{H_i - H_f}{H_i} \times 100 \qquad (1)$$

H_i and H_f are peak heights before and after the sorption, respectively. Same equation was used to calculate % sorption of pure silica as well. Maximum batch sorption capacity Q of modified resin was calculated through following Eq. (2) [30]:

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

where C_o and C_f are the initial and equilibrium concentrations of endosulfan in water (mg dm^{-3}), V is volume of solution (dm^3), M is mass of sorbent (g).

2.4.2. Column sorption study

Glass column for dynamic sorption experiments was prepared as follows. Column diameter size filter paper was inserted at the bottom followed by glass wool, then 50 mg of resin was placed in the column, finally filter paper was placed on the top of resin so as to prevent any loss of resin. Sorption efficiency of resin was calculated by passing 0.3 mg dm^{-3} of endosulfan solution at pH 2 at flow rate of 1 cm^3 min^{-1}.

The area under the breakthrough curve (A) obtained by integrating the sorbed concentration C_s (mg dm^{-3}) versus t (min) plot can be used to find total sorbed endosulfan quantity q_{total} (mg) in the column for a given feed concentration and at given flow rate by using Eq. (3):

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

Total amount of endosulfan isomers sent to column m_{total} is calculated from Eq. (4):

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

Total percent removal of endosulfan from water through column (column performance) can be calculated from total sorbed quantity of endosulfan q_{total} to the total amount of endosulfan sent to column m_{total} Eq. (5) [31]:

$$Total\%removal = \frac{q_{total}}{m_{total}} \times 100 \qquad (5)$$

2.4.3. Extraction and analysis of endosulfan

The aqueous filtrate was extracted through liquid-liquid partition method using 1:1 mixture of ethyl acetate and n-hexane in 50 cm^3 separating funnel. During extraction, separating funnel was shaked for 5 min and placed for 5 min followed by the collection of upper organic layer in 25 cm^3 conical flask. Before injecting organic phase into GC, traces of water were removed through anhydrous sodium sulfate. Sample was filtered through Whatman filter paper (0.45 μm) followed by the injecting of sample (2 μL) in GC-μECD instrument. Instrumental conditions were set as; injector temperature 250 °C with split ratio of 50 capillary column HP-5 from Agilent with 0.25 mm diameter and 60 m length; temperature programming initial oven temperature 70 °C hold for 1 min, with run time 25 °C min^{-1} till 280 °C, while detector was set at 320 °C and nitrogen
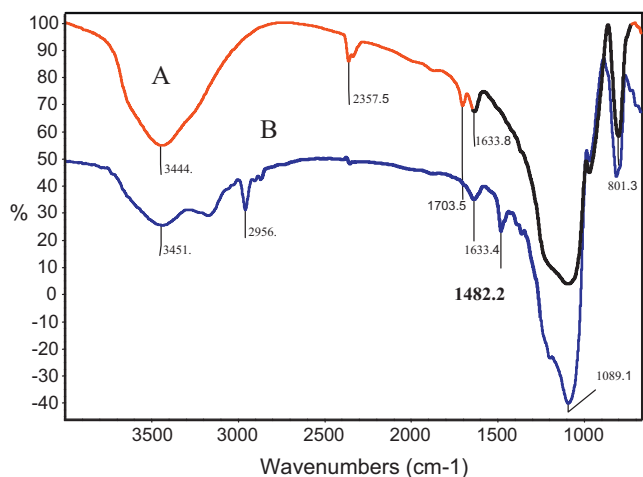
Fig. 2. FT-IR spectra: (A) pure silica and (B) silica immobilized with calix[4]arene.

was used as carrier gas at flow rate of 3 cm^3 min^{-1}. Under these conditions total run time was 14.4 min, while retention time of α and β endosulfan was found as 9.717 min and 10.203 min, respectively.

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR

The immobilization of calixarene onto silica was confirmed through FT-IR spectroscopy. Fig. 2 shows that some additional bands appear in the spectra of pure silica, such as, stretching band at 2956 cm^{-1} indicate the presence of –CH$_3$ group while at 1633 cm^{-1} show the presence of substituted benzene and at 1482 cm^{-1} indicate the presence of substituted carbon. These peaks show that calix[4]arene get immobilized on the surface of silica.

3.1.2. SEM study

A morphological change on the surface of silica was observed through scanning electron microscope. Fig. 3(a) shows that the surface is smooth, while in Fig. 3(b) formation of some cracks and trough indicate that calix[4]arene immobilized to the silica surface. Fig. 3(c) shows that some wrinkles on the modified surface, which may be due to the sorption of endosulfan isomers.

3.2. Sorption studies

Endosulfan exists in two isomeric forms as α- and β-endosulfan. In given GC conditions, the two forms can be well separated and quantified down to trace levels by using μECD as detector. This facilitates to examine the sorption behavior of calix[4]arene based resin toward the two isomeric forms of endosulfan.
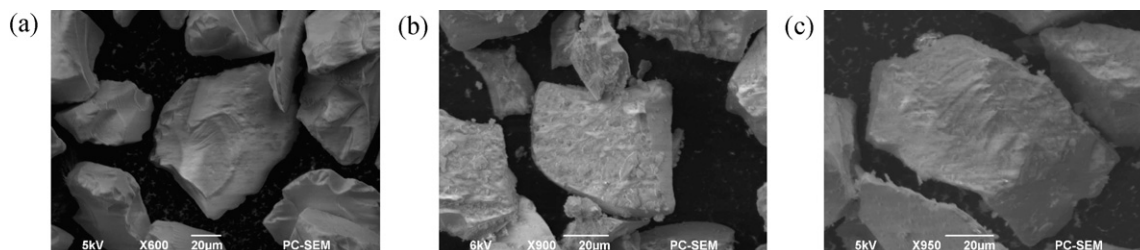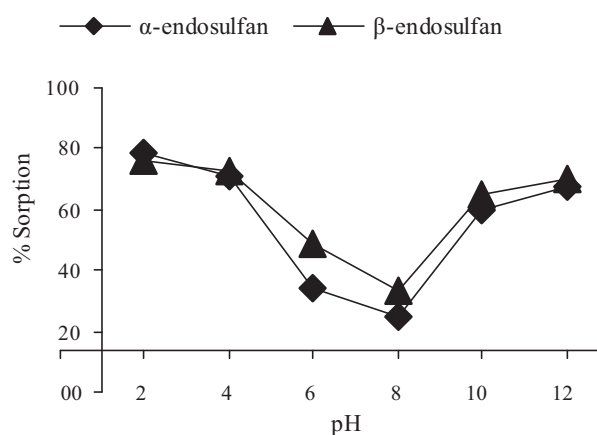

Fig. 4. Effect of pH on endosulfan uptake.

3.2.1. Effect of pH

The change in the pH of solution will change the properties of pesticide molecules as well as sorbent active sites [32]. The effect was observed from pH 2 to 12 using solution of constant concentration with shaking speed 125 rpm (Fig. 4). The plot shows that % sorption is higher at pH 2; it may be due to the calixarene molecule which attracts protonated endosulfan through cation-π interaction [33]. The sorption is lowest at 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 endosulfan molecule along with π-structure of calixarene moiety. The effect of pH on sorption of endosulfan on calixarene based silica resins seems to be a phenomenon governed by multitude of effects.

3.2.2. Effect of concentration of pesticides

Effect of concentration of endosulfan solution on % sorption was observed by diluting stock solution up to 0.05 mg dm^{-3} concentration at pH 2. Fig. 5 shows that with the decreasing concentration % sorption increases, which is due to the presence of fixed number of sorption sites for the host molecule.

3.2.3. Effect of contact time

Effect of contact time on the sorption of endosulfan was observed for an agitation time from 20 to 120 min. Equilibrium time was observed by shaking endosulfan solution at pH 2 in 50 cm^3 stoppered bottle using 20 mg of resin at the shaking speed of 125 rpm. Fig. 6 shows that % sorption increases with increasing contact time, and attains maximum value at 60 min; after that % sorption remain almost constant. Hence, further study was done at an optimized time of 60 min.

3.2.4. Effect of shaking speed

Sorption of α and β endosulfan was observed at pH 2 for an equilibrium time (60 min) at room temperature using 20 mg of resin

Fig. 3. (a) SEM micrograph pure silica; (b) SEM micrograph of immobilized silica resin; (c) SEM micrograph of immobilized silica after sorption.
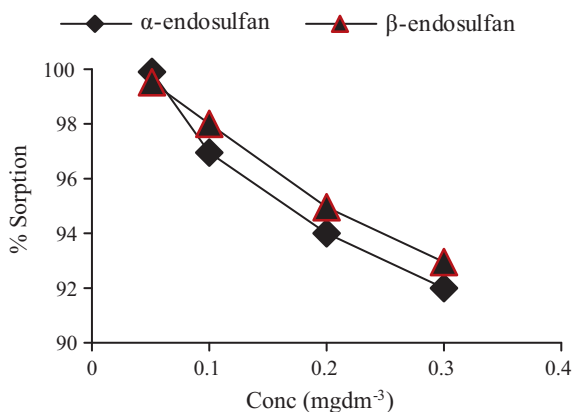
Fig. 5. Effect of concentration on endosulfan uptake (experimental conditions: sorbent dosage 0.02 g/10 cm³ at pH 2, contact time 100 min with shaking speed 125 rpm).
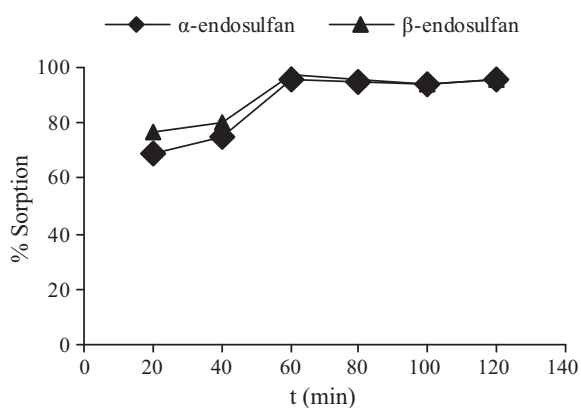

Fig. 6. Effect of contact time on endosulfan uptake (experimental conditions: sorbent dosage 0.02 g/10 cm³ at pH 2 with shaking speed 125 rpm using 0.3 mg dm⁻³ pesticides concentration).

from 25 to 150 rpm (Fig. 7). Results show that % sorption increases with rise in shaking speed and attains maximum value at 125 rpm, therefore, further studies were done at an optimized shaking speed.

3.2.5. Effect of sorbent dosage

Amount of sorbent dosage required for the maximum sorption of α and β endosulfan was studied at room temperature under opti-
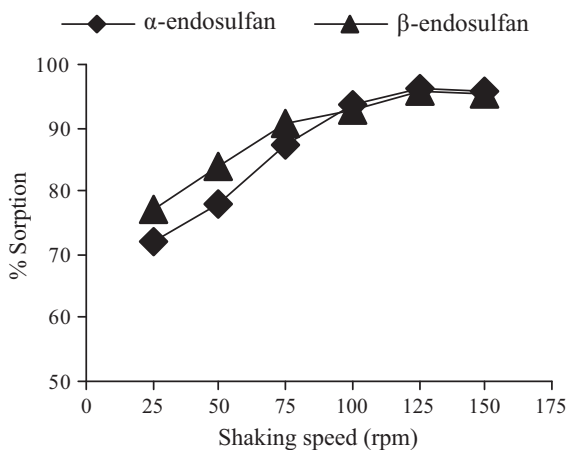

Fig. 7. Effect of shacking speed on endosulfan uptake (experiment conditions: sorbent dosage 0.02 g/10 cm³ at pH 2 using 0.3 mg dm⁻³ pesticides concentration for 60 min contact time).
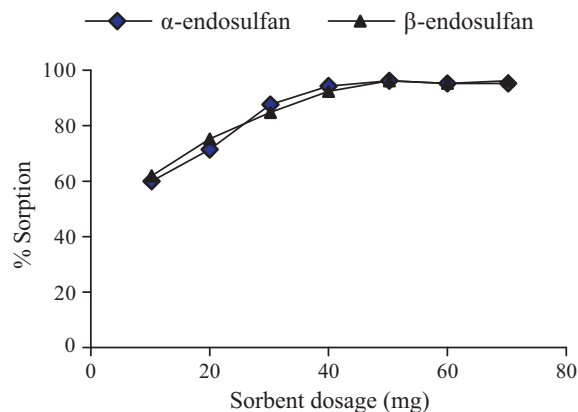

Fig. 8. Effect of sorbent dosage on endosulfan uptake (experimental conditions: 0.3 mg dm⁻³ pesticides concentration at pH 2 for 60 min using 125 rpm shaking speed).

mized conditions as shown above and at constant concentration of 0.3 mg dm⁻³. It was observed that with increase of sorbent dosage sorption was increased due to more active surface area to adsorb external particles and attains maximum value at 50 mg of resin (Fig. 8). Results show that 50 mg are sufficient to uptake maximum amount (98–99%) of α and β endosulfan from aqueous system.

Using these optimized conditions sorption efficiency of pure silica was checked. Results show that pure silica sorbs (40–45%) of α and β endosulfan from water. Therefore, it may be assumed that further sorption of endosulfan is due to the presence of calixarene cavity on the surface of silica.

3.3. Sorption isotherms

Various isotherms are used to determine the relationship between amount of substance adsorbed as a function of concentration in bulk solution at given temperature and under equilibrium conditions. From these isotherms Freundlich and Langmuir are very prominent to explain the nature of sorption [34]. The sorption data have been subjected to Freundlich and Langmuir isotherms to investigate nature of sorption of endosulfan on calixarene based resin.

3.3.1. Freundlich model

A multilayer sorption can be explained through this model, this involves the distribution of active sites that is the characteristic of heterogeneous surfaces. Eq. (6) is a linear form of this isotherm:

$$\log C_{ads} = C_m + \frac{1}{n}\log C_e \tag{6}$$

$1/n$ is sorption intensity, C_{ads} is an adsorbed concentration (mol g⁻¹), C_e is an equilibrium concentration (mol dm⁻³) and C_m is multilayer sorption capacity.

A plot of $\log C_{ads}$ versus C_e exhibit straight line, with slope $1/n$ and intercept C_m (Fig. 9)

3.3.2. Langmuir isotherm

This model is first quantitative theory of sorption involve the sorption takes place on the fixed number of sorption sites confined to mono molecular layer with no transfer of sorbate on the plane of surface. Data of sorption of endosulfan on calixarene based silica resin were fitted in the Langmuir isotherm linear form of Langmuir model used for analysis of sorption data:

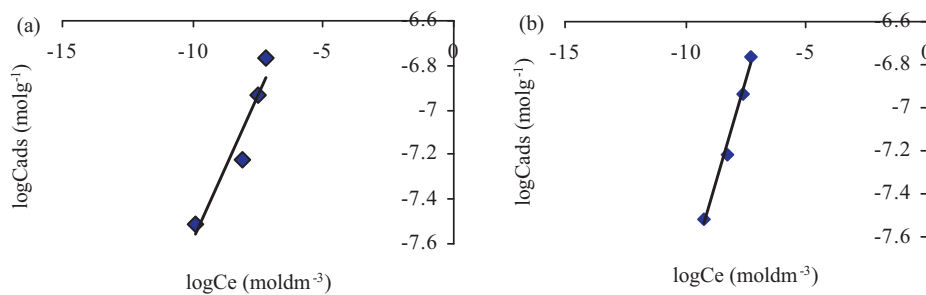$$\frac{C_e}{C_{ads}} = \frac{1}{Q_b} + \frac{C_e}{Q} \tag{7}$$

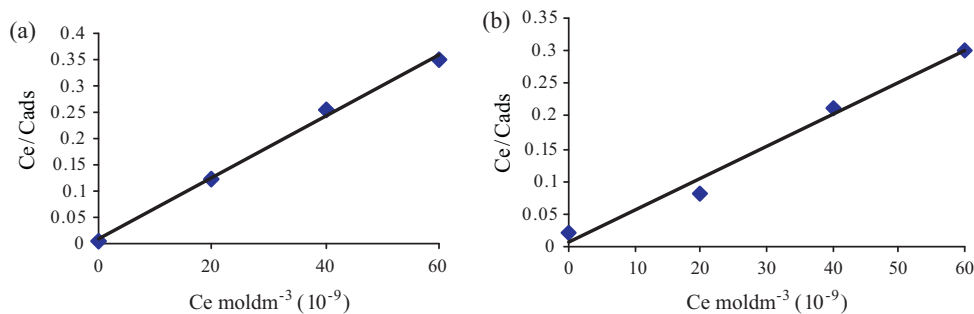**Fig. 9.** Freundlich sorption isotherm plot for (a) and (b) endosulfan on calixarene based silica resin.

Fig. 10. Langmuir isotherms of (a) and (b) endosulfan.

Q is monolayer sorption capacity (mol g^{-1}), b is an enthalpy of sorption (mol dm^{-3}), C_{ads} is sorbed concentration (mol g^{-1}), and C_e equilibrium concentration (mol dm^{-3}).

A plot of C_e/C_{ads} versus C_e exhibit straight line with slope $1/Q$ and intercept $1/Q_b$ (Fig. 10).

From the value of Langmuir constant b, a dimensionless parameter, called separation factor R_L was calculated through following equation:

$$R_L = \frac{1}{1 + bCi} \tag{8}$$

b is a Langmuir constant (dm^3 mol^{-1}).

The magnitude of sorption isotherm constants, gives an indication of favorability and unavoidability of sorption process. The values of constants obtained from both the sorption models are given in Table 1. The value of sorption intensity ($1 < n < 10$) indicates that sorption is favorable [35]. The corresponding value of n or the sorption of endosulfan isomers on calixarene based resin is 3.83 and 2.59, respectively, which show that the sorption is favorable. Moreover, calculated value of R_L is <1, which also indicates favorable sorption of endosulfan. In addition, Table 1 shows that the value of C_m is higher then Q, which indicate that sorption of endosulfan favors the Freundlich isotherm, along with this, the value of R^2 is higher in Freundlich then in Langmuir model.

Table 1
Isotherm constants and values of R^2 for isomers of endosulfan on calixarene based silica resin.

Isotherm	Isotherm parameter	α-Endosulfan	β-Endosulfan
Freundlich	Cm (mmol g^{-1})	0.0107	0.103
	$\frac{1}{n}$	0.261	0.3851
	R^2	0.916	0.992
Langmuir	Q (nmol g^{-1})	200	200
	b (mol dm^{-3})	9.6×10^7	1.11×10^7
	R^2	0.91	0.94

3.4. Column sorption

The efficiency of column is described through the concept of breakthrough curve. The position of curve depends upon solution concentration and flow rate. The breakthrough curves show the loading behavior of endosulfan to be removed from aqueous solution in a fixed bed and is usually expressed in terms of sorbed endosulfan concentration (C_s), inlet endosulfan concentration (C_i) and outlet endosulfan concentration (C_t) or normalized concentration defined as the ratio of effluent endosulfan concentration to inlet endosulfan concentration (C_t/C_o) as a function of time or volume of effluent.

The optimized conditions set for the batch sorption study were also used in column at flow rate of 1 cm^3 min^{-1} to remove endosulfan (0.3 mg dm^{-3}) from water through calixarene based silica resin (50 mg). Break through volume was calculated from plot of C_t/C_i versus V (cm^3). Fig. 11 shows that column achieved breakthrough at C_t/C_i = 0.21 and 0.22 for α and β endosulfan, respectively, with bed volume of 5 cm^3 and took approximately 25 cm^3 to exhaust.

Under optimum conditions, column performance of sorbent was calculated using Eq. (5) and found to be 87% and 88% for α and β endosulfan, respectively.

3.5. Thomas model

Successful design of column requires the knowledge of concentration time profile or breakthrough curve for effluent and maximum sorption capacity. 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 that the rate deriving force obeys second order reversible reaction kinetics [36]. 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 following linear form:

$$\ln \left(\frac{C_0}{C} - 1 \right) = \frac{k_{TH} q_0 A}{Q} - \frac{k_{TH} C_0}{Q} V_{eff} \tag{9}$$
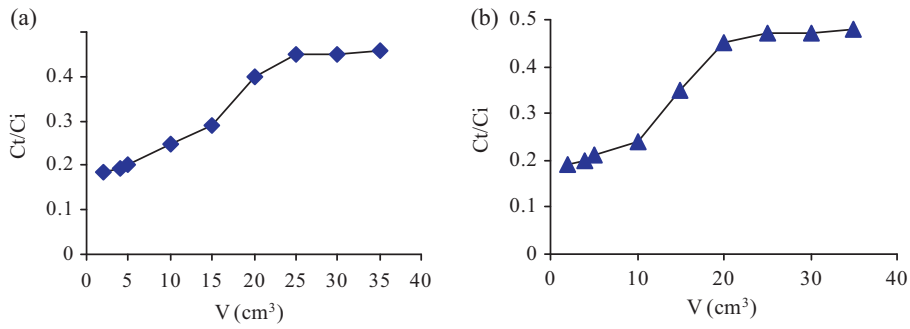
Fig. 11. Break through curve of (a) and (b) endosulfan.

C_0 is initial concentration of endosulfan (mg dm^{-3}), C is the effluent concentration (mg dm^{-3}), k_{TH} is Thomas model rate constant (cm^3 mg^{-1} min^{-1}), q_o maximum solid phase concentration of solute (mg g^{-1}), A is the amount of material sorbed (mg), Q is flow rate (cm^3 min^{-1}), and V_{eff} is effluent volume (cm^3). V_{eff} can be calculated from following equation:

$$V_{eff} = Q t_{total}$$

Q is flow rate (cm^3 min^{-1}) and t_{total} stands for maximum flow time (min).

Thomas model rate constant k_{TH} (6.18, 5.83) and q_o (maximum solid phase concentration) of solute (1.11, 1.08) with coefficient of determination R^2 (0.905, 0.979) 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 (Fig. 12).

Thomas model suggests that a column can uptake 1.11 and 1.08 mg g^{-1} of α and β endosulfan if operated at 6.18 and 5.83 cm^{-3} min^{-1}.

3.6. Kinetics of sorption

Efficiency of sorption process can be evaluated through the kinetics study of process. Lagergreen [37] and Ho [38] kinetic equations were used to examine the experimental data which considered that sorption is either pseudo first order or pseudo second order reaction, respectively.

Pseudo first order rate constant was determined through following equation:

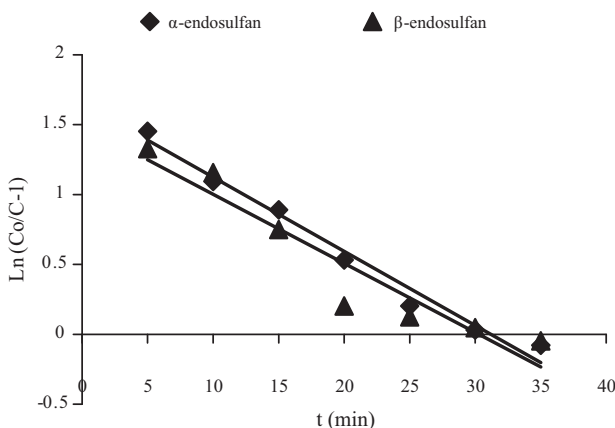$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{10}$$

q_e and q_t are the amount of endosulfan sorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the first order rate constant.

Fig. 13 shows the kinetic study of α and β endosulfan on the resin, under optimized conditions, while evaluating the effect of agitation time on % sorption. Langergreen plot of $\log(q_e - q_t)$ versus agitation time t (min) exhibit straight line with co-efficient of determination (R^2) values 0.511 and 0. 477, for α and β endosulfan, respectively.

Data was investigated through pseudo second rate mode given by Ho and McKay.

Pseudo second order rate equation:

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

Fig. 14 shows plot of t/q_t versus t exhibit straight line with (R^2) value for α endosulfan is 0.991 and for β is 0.994, from which it
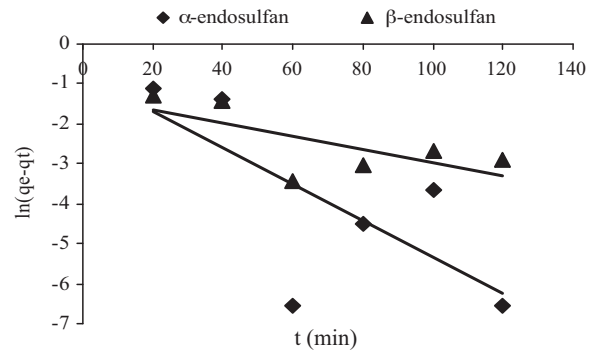

Fig. 13. Langergreen plot for alpha and beta endosulfan.

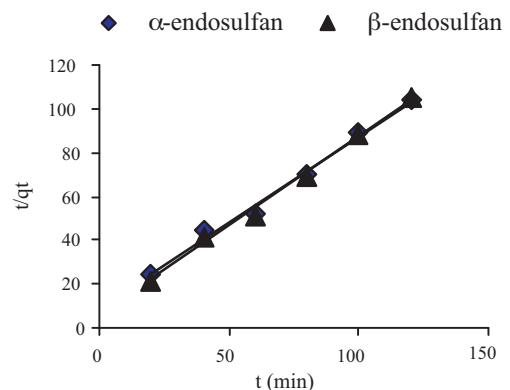**Fig. 12.** Plot of $\ln((C_0/C)-1)$ vs. t.

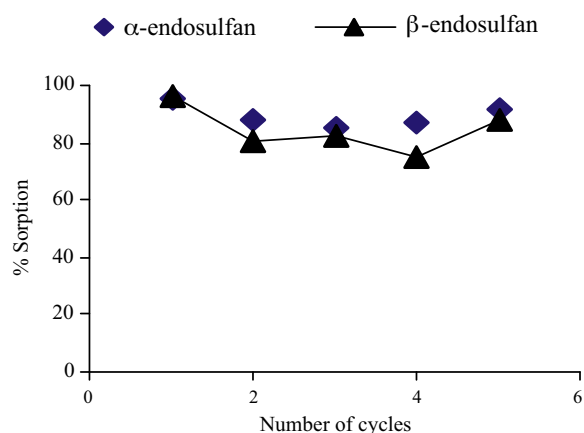**Fig. 14.** Ho and McKay plot for alpha and beta endosulphan.

Fig. 15. Effect of number of cycles on endosulfan uptake.

Table 2
Amount found and percent removal of α and β endosulfan from real water samples with calix[4]arene based silica resin.

Sample	Amount found		% Removal	
	α endosulfan (mg dm^{-3})	β endosulfan (mg dm^{-3})	α endosulfan	β endosulfan
A	2.67	2.52	89.6	92.2
B	5.08	4.93	91.9	94.1

was concluded that sorption of endosulfan follows pseudo second order kinetics.

3.7. Sorbent regeneration

For regeneration studies, 10 cm^3 of 0.3 mg dm^{-3} of α- and β-endosulfan was sorbed on 0.05 g of resin. Sorbent was regenerated by shaking with 5 cm^3 of 1:1 mixture of n-hexane and ethyl acetate for 10 min. Sorbent efficiency of resin for % recovery was checked for 5 cycles. Percent recovery of resin was found 89.68 ± 4.03% and 84.38 ± 7.9 for α and β-endosulfan, respectively (Fig. 15).

3.8. Application of proposed method

The proposed method was applied to agriculture run-off water samples. Water samples were collected from two different areas of district Matiari, Sindh, Pakistan. Sorption of α and β endosulfan was checked under optimized conditions. The % sorption was calculated from difference in peak height of detector response. Sorbed endosulfan was recovered by shaking sorbent for 10 min in 1:1 mixture of n-hexane and ethyl acetate. The results of % sorption and % recovery are shown in Table 2. Table shows that calix[4]arene based silica resin can effectively remove endosulfan from water.

4. Conclusion

Sorption efficiency of immobilized calix[4]arene based silica resin was investigated to remove endosulfan isomers from aqueous solution. Results of sorption experiment shows that calix[4]arene based silica resin is more efficient then pure silica. The sorption process was found to be pH dependent, while cation–π interactions play an important role for removal of endosulfan isomers from aqueous solution. Other factors, like, contact time and shaking speed also affect sorption efficiency of synthesized resin. Sorption results show that Freunlich sorption isotherm was found to be best fitted to sorption data following pseudo second order rate

equation. On the other hand Thomas model suggests that column sorption is more efficient then batch method. An excellent regeneration for at least five times with slight up-down in sorption capacity indicates that calix[4]arene based resin is highly applicable for the removal of endosulfan from agriculture/industrial waste water.

References

[1] http://www.who.int/ipcs/assessment/en/pcs_95_39_2004_05_13.pdf.
[2] http://www.ipen.org/ipenweb/documents/poprc/documents/endosulfan/pop/screening/criteria.
[3] U.S. EPA, Re registration Eligibility Decision for Endosulfan, 2002, 738-R-02 013.
[4] http://www.wpro.who.int/NR/rdonlyres/A68749B9-8F06-4361-BCDC-E74FAAF12912/0/Endosulfan_HSG1_1998.pdf.
[5] http://www.panna.org/documents/endosulfanProposalStockholm.pdf.
[6] U.S. Department of health and human services, Toxicological profile for endosulfan, 2000.
[7] http://www.ejfoundation.org/pdf/end_of_the_road.pdf.
[8] http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/index.html.
[9] S. Goswami, K. Vig, D.K. Singh, Biodegradation of α and β endosulfan by Aspergillus sydoni, Chemosphere 75 (2009) 883–888.
[10] S. Aslan, Combined removal of pesticides and nitrates in drinking waters using biodenitrification and sand filter system, Process. Biochem. 40 (2005) 417–424.
[11] X. Yiping, Z. Yiqi, W. Donghong, C.L. Junxin, W. Zijian, Occurrence and removal of organic micropollutants in the treatment of landfill leachate by combined anaerobic-membrane bioreactor technology, J. Environ. Sci. 20 (2008) 1281–1287.
[12] P.C. Mishra, R.K. Patel, Removal of endosulfan by sal wood charcoal, J. Hazard. Mater. 152 (2008) 730–736.
[13] H.E. Bakouri, J. Morillo, J. Usero, A. Ouassini, Potential use of organic waste substances as an ecological technique to reduce pesticide ground water contamination, J. Hydrol. 353 (2008) 335–342.
[14] S. Aslan, A. Turkman, Simultaneous biological removal of endosulfan (α+β) and nitrates from drinking waters using wheat straw as substrate, Environ. Int. 30 (2004) 449–455.
[15] G.Z. Memon, M.I. Bhanger, M. Akhtar, Peach-nut shells—an effective and low cost adsorbent for the removal of endosulfan from aqueous solutions, Pak. J. Anal. Environ. Chem. 10 (2009) 14–18.
[16] V. Gupta, I. Ali, Removal of endosulfan and methoxychlor from water on carbon slurry, Environ. Sci. Technol. 42 (2008) 766–770.
[17] R. Sawicki, L. Mercier, Evaluation of mesoporous cyclodextrin-silica nanocomposites for the removal of pesticides from aqueous media, Environ. Sci. Technol. 40 (2006) 1978–1983.
[18] A. Sayari, S. Hamoudi, Y. Yang, Applications of pore expanded mesoporouus silica. Removal of heavy metal cations and organic pollutants from wastewater, Chem. Mater. 17 (2005) 212–216.
[19] Q. Yu, S. Deng, G. Yu, Selective removal of perfluorooctane sulfonate from aqueous solution using chitosan-based molecularly imprinted polymer adsorbents, J. Water Res. 42 (2008) 3089–3097.
[20] L.J. Bauer, C.D. Gutsche, The formation of complexes of calixarenes with neutral organic molecules in solution, J. Am. Chem. Soc. 107 (1985) 6063–6069.
[21] I.B. Solangi, S. Memon, M.I. Bhanger, Synthesis and application of a highly efficient tetraester calix[4]arene based resin for the removal of Pb2+ from aqueous environment, Anal. Chim. Acta 638 (2009) 146–153.
[22] I. Qureshi, S. Memon, M. Yilmaz, Estimation of chromium(VI) sorption efficiency of novel regenerable *p-tert* butylcalix[8]arene octamide impregnated Amberlite resin, J. Hazard. Mater. 164 (2009) 675–682.
[23] S. Erdemir, M. Bahadir, M. Yilmaz, Extraction of carcinogenic aromatic amines from aqueous solution using calix[*n*]arene derivatives as carrier, J. Hazard. Mater. 168 (2009) 1170–1176.
[24] I. Qureshi, S. Memon, M. Yilmaz, An excellent arsenic(V) sorption behavior of *p-tert*-butylcalix[8]areneoctamide impregnated resin, C. R. Chimie (2010), doi:10.1016/j.crci.2010.02.007.
[25] T. Oshima, R. Saisho, K. Ohe, Y. Baba, K. Ohto, Sorption of amino acid derivatives on calixarene carboxylic acid impregnated resins, React. Funct. Polym. 69 (2009) 105–110.
[26] M.A. Kamboh, I.B. Solangi, S.T.H. Sherazi, S. Memon, Synthesis and application of calix[4]arene based resin for the removal of azo dyes, J. Hazard. Mater. 172 (2009) 234–239.
[27] C.D. Gutsche, B. Dhawan, K.H. No, R. Muthukrishnan, The synthesis, characterization, and properties of the calixarenes from p-tert-butylphenol, J. Am. Chem. Soc. 103 (1981) 3782–3792.
[28] C.D. Gutsche, L.G. Len, The synthesis of functionalized calixarenes, Tetrahedron 42 (1986) 1633–1640.

[29] A. Katz, P.D. Costa, A.C.P. Lam, J.M. Notestein, The first single-step immobilization of a calix-[4]-arene onto the surface of silica, Chem. Mater. 14 (2002) 3364–3368.
[30] K. Vijayaraghavan, D. Prabu, Potential of *Sargassum wightii* biomass for copper(II) removal from aqueous solutions, J. Hazard. Mater. B137 (2006) 558–564.
[31] N. Ozturk, D. Kavak, Sorption of boron from aqueous solutions: batch and column studies using fly ash, J. Hazard. Mater. B127 (2005) 81–88.
[32] G.Z. Memon, M.I. Bhanger, M. Akhtar, The removal efficiency of chestnut shells for selected pesticides from aqueous solutions, J. Colloid Interf. Sci. 315 (2007) 33–40.
[33] B.S. Creaven, D.F. Donlon, J. McGinley, Coordination chemistry of calix[4]arene derivatives with lower rim functionalisation and their applications, Coord. Chem. Rev. 253 (2009) 893–962.
[34] G.Z. Memon, M.I. Bhanger, J.R. Memon, M. Akhtar, Sorption of methyl parathion from aqueous solutions using mango kernels: equilibrium, kinetic and thermodynamic studies, J. Bioremediation 13 (2009) 102–106.
[35] M.S. Bilgili, Adsorption of 4-chlorophenol from aqueous solutions by xad-4 resin: isotherm, kinetic, and thermodynamic analysis, J. Hazard. Mater. B137 (2006) 157–164.
[36] H.C Thomas, Heterogeneous ion exchange in a flowing system, Am. Chem. Soc. 66 (1944) 1466–1664.
[37] Lagergreen, About the theory of so called sorption of soluble substances, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.
[38] Y.S. Ho, Citation review of Lagergreen kinetic rate equation on sorption reaction, Scientometrics 59 (2004) 171–177.