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A highly efficient *p-tert*-butylcalix[8]arene-based modified silica for the removal of Hexachlorocyclohexane isomers from aqueous media

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ABSTRACT

Hexachlorocyclohexane (HCH) is an organochlorine insecticide that exists in various isomeric forms, where α-, β-, and γ-isomers are persistent and impart toxicity to water bodies. The current article explains about the removal of HCH using *p-tert*-butylcalix[8]arene-based modified silica. The modified silica is characterized through Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) and also by batch and column adsorption method for maximum removal efficiency. Variations in concentrations of HCH were monitored by GC-μECD. Various parameters that affect uptake like pH; agitation time, adsorbent dosage, and concentration of HCH were optimized as, pH 8, 60 min, 20 mg, and 1 mg L^{-1}, respectively. The adsorption data were found to be best fitted with Freundlich adsorption model and followed pseudo-second-order kinetic equation. From the Thomas model, kinetic coefficient (k_{TH} cm^3 mg^{-1} min^{-1}) values were found to be 0.054, 0.054, 0.049, 0.055 and maximum solid phase concentration (q_o mg g^{-1}) of hexachlorocyclohexane (HCH) isomers (α, β, γ, δ) on the modified silica which was calculated as 112.5, 110.8, 108.5, 114.2, respectively. The modified silica can be reused efficiently and under optimized conditions can effectively remove HCH isomers from real wastewater samples.

Keywords: Hexachlorocyclohexane (HCH); Isotherms; Kinetics; *p-tert*-butylcalix[8]arene

1. Introduction

Hexachlorocyclohexane (HCH) is an organochlorine synthetic chemical that exists in various isomeric forms (Fig. 1). The technical grade HCH is a mixture of five isomers that mainly contains α-HCH (53–70%), β-HCH (3–14%), γ-HCH (11–18%), δ-HCH (6–10%), and 0.5% other isomers. Its one isomer (γ-HCH) commonly called "lindane" has maximum insecticidal property which is used not only in the livestock, seed grains and wooden structures [1] but also as an insecticide for various vegetable crops, fruit, rodent control and for the treatment of mites and lice. The U.S. Food and Drug Administration have approved its use in three products for the treatment of scabies and lice (two shampoos and one lotion) [2]. Traces of HCH isomers (i.e. γ-HCH (Lindane), α-HCH and β-HCH) have persistence in environment, long range transport stability and bioaccumulation in fatty tissues, which causes adverse effects on human health. Therefore, these isomers are included in the annexes A, B, and C

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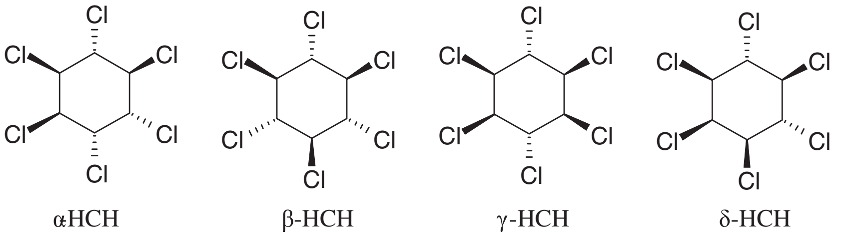

Fig. 1. Molecular structures of four HCH isomers.

in the Stockholm Convention on the persistent organic pollutants [1]. Exposure of HCH may cause various diseases in human and animals such as changes in the level of chromosomes, blood disorder, and liver/ kidney effects. The international agency for research on cancer (IARC) has considered that all isomers are possibly carcinogenic, while environmental protection agency (EPA) classified technical grade HCH as; γ-HCH/Lindane is carcinogenic, whereas α-HCH and β HCH are probable human carcinogen, which results in various diseases. EPA considers that drinking water should not contain HCH more than 0.02 μg L^{-1}. Occupational Safety and Health Administration (OSHA) regulates the level of γ-HCH at work place in eight hours daily work, not more the 0.5 mg L^{-1} [3].

Due to toxic effects of hexachlorocyclohexane (HCH) isomers on human and other animals various techniques, such as anaerobic degradation [4] biodegradation [5] reductive dechlorination using nanoparticles [6] and adsorption [7] are used to remove it from environment. Among these techniques, adsorption was found to be fast, simple, relatively low cost and an effective method for the removal of such persistent organic compounds from aqueous medium even at trace level. Consequently, some natural adsorbents such as biomimetic [8], activated carbon [9], wood charcoal [10], peach-nut shells [11] and few synthetic adsorbents such as triolein-embedded adsorbent [12], molecularly imprinted polymers [13], cyclodextrin polyurethane with carbon nanotubes [14] and mesoporous cyclodextrin-silica nanocomposites [15] etc, were used.

"Calix[n]arene" is a well-known class of cyclooligomeric 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 multifunctionality, they are widely impregnated or immobilized on the solid polymeric supports for the remediation of toxic heavy metals such as Pb(II), Cr(VI), As(V) [16–18] and organic pollutants such as azodyes, pesticide-related organic compounds as well as endosulfan isomers [19–21] from aqueous media. The immobilization of calixarene increases the adsorption capacity of modified silica. Thus, the present study focuses on the enhancement of adsorption capacity of solid polymeric support and exploration of its application for the removal of four isomers of technical grade HCH from aqueous media through batch and column methods.

2. Materials and methods

2.1. Reagents

Analytical thin layer chromatography (TLC) was performed on precoated silica plates (SiO_2, PF_{254}). The pH (2–10) was adjusted through 0.1 M HCl/NaOH solution. Standard parathion and silica (240–400 mesh size) were purchased from Fluka (Germany). *p-tert*-butylcalix[8]arene was synthesized according to previously reported method [22]. All reagents/solvents used for the synthesis of *p-tert*-butylcalix[8]arene and *p-tert*-butylcalix[8]arene-based modified silica were of analytical grade. 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 5,700 FT-IR spectrometer as KBr pallets. Scanning electron microscopic (SEM) studies were performed using JSM-6490LV instrument. Melting point was determined through Gallenkamp melting point apparatus model MFB, 595,010 M, England. The % adsorption was calculated from differences of detector response of GC μECD (Agilent 7890 System, USA). 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 sorption study. A glass column (16 cm × 6 mm) was used for column adsorption study.

2.3. Modification of silica with p-tert-butylcalix[8]arene

The process was carried out according to previously reported procedure [23] with slight improvement. A 5 g of silica (250–400 mesh size) was dried in vaccum followed by adding 1 M solution of $SiCl_4$ in dry CH_2Cl_2. A 1.5 cm^3 of triethylamine was added in reaction mixture in order to make it alkaline for deprotonation of OH group on silica surface. A cloudy mixture was obtained. This was placed at room temperature for 12 h followed by the removal of solvent through rotary evaporator. To this resulted white powder, 1.5 g of *p-tert*-butylcalix[8]arene dissolved in 50 cm^3 $CHCl_3$ was added followed by the addition of 5 cm^3 of triethylamine. The reaction mixture was refluxed for 60 h, and the reaction was periodically monitored by FT-IR. After modification, the silica was filtered and subsequently washed with 150 cm^3 hot $CHCl_3$, 100 cm^3 methanol and 100 cm^3 water in order to remove unreacted calixarene and other impurities.

2.4. Adsorption procedure

2.4.1. Static adsorption

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

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

H_i and H_f are peak height before and after adsorption, respectively. Maximum static adsorption capacity (q_{ad}) of *p-tert*-butylcalix[8]arene-based modified silica was calculated using Eq. (2)

$$q_{ad} = \frac{V(C_i - C_f)}{M} \qquad (2)$$

where C_i and C_f are the initial and equilibrium concentration of HCH isomers (mg L^{-1}), V is volume of solution in (L), M is mass of sorbent (g).

2.4.2. Dynamic adsorption

Dynamic adsorption study was carried out using (10 mm × 25 cm) size glass column containing 20 mg of adsorbent. Dynamic adsorption capacity of modified silica was calculated by passing 1 mgL^{-1} HCH standard solution at pH 8 and the flow rate 2 mL min^{-1}. The total adsorbed quantity of HCH isomers (mg) on the modified silica at a given concentration was calculated through Eq. (3)

$$q_{total} = \frac{QA}{1,000} = \frac{Q}{1,000} \int_{t=0}^{t=total} C_{ads} dt \qquad (3)$$

Here, Q is a flow rate, A is the breakthrough area (cross-sectional area of the bed, cm^2) is used to calculate the total adsorbed quantity (q_{total} in mg) of HCH isomers in column by intergrading the adsorbed concentration C_{ads} vs. time t.

2.5. Extraction of HCH isomers

For analysis through GC-μECD system, each sample of solution was extracted in mixture (3:2) of n-hexane and ethyl acetate. For this each, 10 mL sample solution was shaked with 6 mL mixture for 5 min and was placed vertically for 10 min in separating funnel so as to attain the equilibrium. After that upper organic layer was collected and traces of water was removed by using anhydrous sodium sulfate.

2.6. Analysis of HCH isomers

Each extracted sample was analyzed through GC-μECD system. The temperature programming was set as; initial oven temperature was 150°C held for 1 min, then temperature was increased at 15°C min^{-1} till 280°C, where it was hold for 1 min. The detector temperature was set as 320°C and N_2 was used as carrier gas at the flow rate of 3 mL min^{-1}. Under these conditions, 2 μLs of sample was injected in HP-5 capillary column at the split ratio of 50. Through this method, four isomers of HCH can be well separated and quantified. The retention times of four isomers were found to be 5.64, 5.96, 6.06, and 6.34 min for α, β, γ and δ isomer, respectively.

3. Results and discussion

3.1. Characterization

3.1.1. Fourier transforms infrared (FTIR) study

Fourier transform infrared spectroscopy is an efficient method to characterize the surface functionality of polymeric surfaces; therefore, modification of *p-tert*-butylcalix[8]arene on the surface of silica was confirmed through this method. Fig. 2 shows that some extra bands appears in the spectra of modified silica, such as the band at the 2959.9 cm^{-1} confirms the

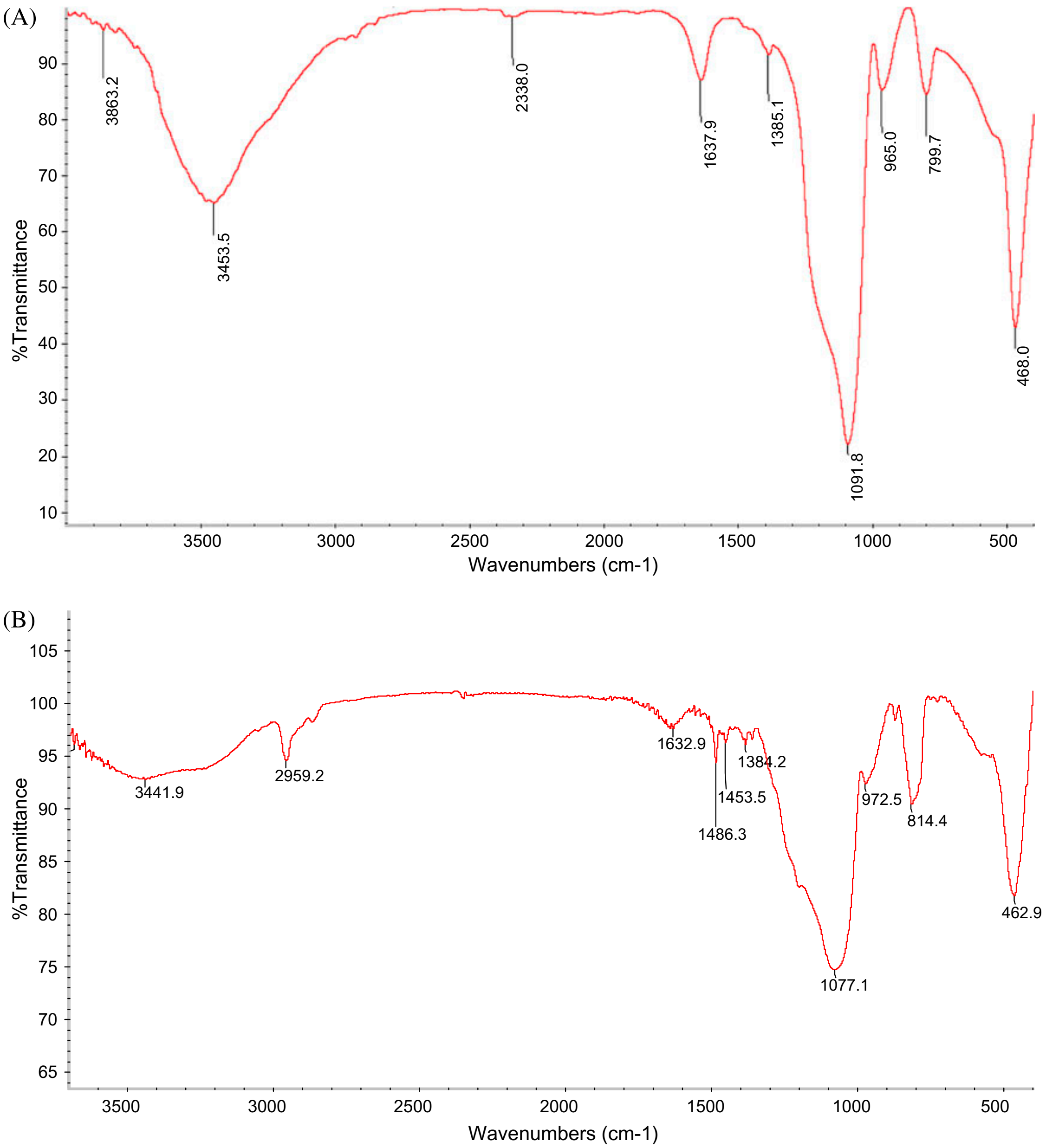

Fig. 2. FT-IR spectrum (A) Pure silica and (B) *p-tertbutyl*calix[8]arene based silica resin.

presence of –CH_3 group, whereas the band at 1651.9 and at 1486.6 cm^{-1} indicate the presence of substituted benzene ring and the substituted carbon, respectively. These results confirms that the *p-tert*-butylcalix[8]arene was successfully immobilized on the surface of silica.

3.1.2. Scanning electron microscopic (SEM) study

SEM is an advanced surface characterization tool for polymeric surfaces. In the present study, surface of silica was observed before and after immobilization of calixarene through this technique. Fig. 3 shows that some white spots are produced on the surface of silica due to calixarene moiety which enormously increases the surface active sites for the guest molecules.

3.2. Adsorption parameters

3.2.1. Effect of pH

In this study, pH of solution was varied from 2–10 for all the isomers. Each sample was shacked for one hour containing 20 mg of adsorbent. Fig. 4 shows that pH 8 is an optimum value for removal of all considered isomers. The pH has noticeable effect on the

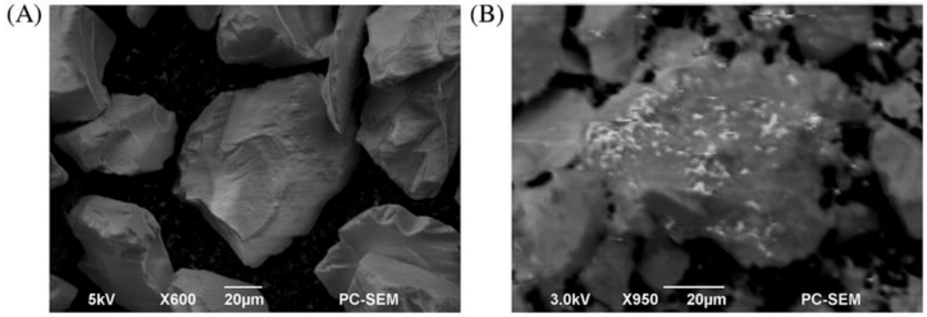

Fig. 3. Scanning electron microscopic images of (A) pure Silica and (B) *p-tert-butyl*calix[8]arene immobilized silica resin.

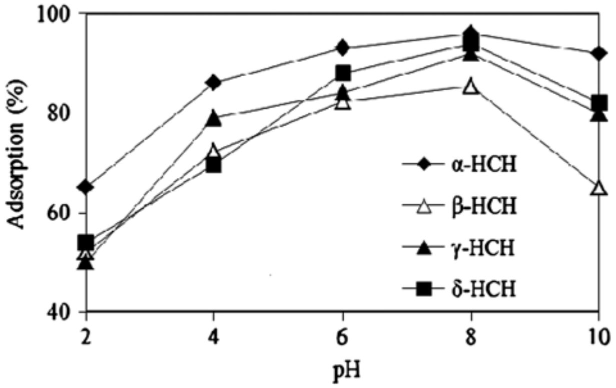

Fig. 4. Effect of pH on the adsorption of HCH isomers.

adsorption sites of sorbent as well as on the structure of adsorbate molecules (change in pH affect induced dipole of adsorbate molecule). Therefore, adsorption capacity of modified silica greatly changes with the change in pH of the solution. This behavior may be because of maximum lipophilic interaction of calixarene cavity with lipophilic chlorinated guest molecules [24]. At slight basic pH, the hydroxide ions repels highly electronegative chlorine atoms hence produce an induced dipole, which may be responsible for the adsorption of HCH molecules Under optimized conditions, the adsorption efficiency of pure silica was found significantly lower (less than 40% for all isomers) as compared to modified silica.

3.2.2. *Effect of adsorbent dosage*

Amount of adsorbent has considerable effect on % adsorption for finding maximum adsorption capacity under optimized conditions. This effect was observed by using 5–35 mg L^{-1} of modified silica at pH 8 and using 10 mL of 1 mg L^{-1} of each HCH isomer. Fig. 5 shows that 20 mg of modified silica is an efficient to remove more than 85% of all considered isomers from 1 mg L^{-1} aqueous solution.

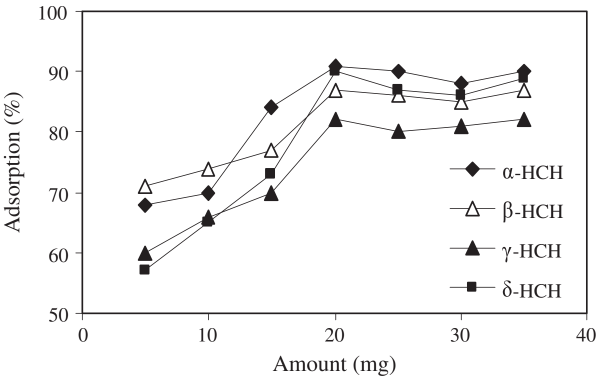

Fig. 5. Effect of adsorbent dosage on the adsorption of HCH isomers.

3.2.4. *Effect of HCH concentration*

Effect of concentration of HCH isomers on % adsorption was observed from 0.5–2 mg L^{-1} solution at pH 8 using 5 mg of modified silica. Fig. 6 illustrates that as the concentration of solution increases the % adsorption of target molecules decreases. This indicates that there are of solution increases the % adsorption of target molecules decreases. This

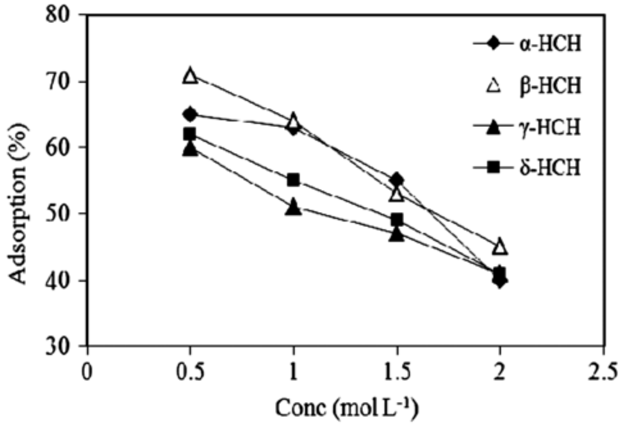

Fig. 6. Effect of concentration on adsorption of HCH isomers.

indicates that there are fixed number of adsorptive sites available on the modified silica, which can effectively remove four isomers of HCH from aqueous solution at low concentration.

The adsorption efficiency of pure silica was also checked under optimized conditions and was compared with modified silica, the results shows that pure silica can only remove less the 40% of all HCH isomers.

3.3. Adsorption equilibrium study

Study of adsorption equilibriums is used to evaluate the interaction between adsorbent and adsorbate molecules and adsorption capacity of silica surface [25]. Most well-known adsorption isotherms, that is, Freundlich and Langmuir is used to find adsorption pattern of four HCH isomers on *p-tert*-butylcalix[8] arene-based modified silica.

Freundlich adsorption isotherm expresses the formation of multimolecular layer on the heterogeneous surface this was tested through the following linear form of Eq. (4);

$$\ln C_{\mathrm{ad}} = \ln C + \frac{1}{n}\ln C_{\mathrm{e}} \tag{4}$$

C_{ad} is adsorbed concentration in molg^{-1}, C is multimolecular adsorption capacity, $\frac{1}{n}$ is adsorption intensity, and C_{e} is an equilibrium concentration. The graph was plotted between lnC_{ad} versus C_{e} which gives straight line (Fig. 7(A)).

The adsorption pattern of HCH isomers were also checked 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 this model is Eq. (5)

$$\frac{C_{\mathrm{e}}}{C_{\mathrm{ad}}} = \frac{1}{Qb} + \frac{C_{\mathrm{e}}}{Q} \tag{5}$$

Here, Q is monolayer adsorption capacity (molg^{-1}), b is adsorption enthalpy (molL^{-1}), where as C_{e} and C_{ad} is equilibrium and adsorbed concentration, respectively. A plot of $\frac{C_{\mathrm{e}}}{C_{\mathrm{ad}}}$ versus C_{e} gives straight line with slope $\frac{1}{Q}$ and interceptt $\frac{1}{Qb}$ (Fig. 7(B)).

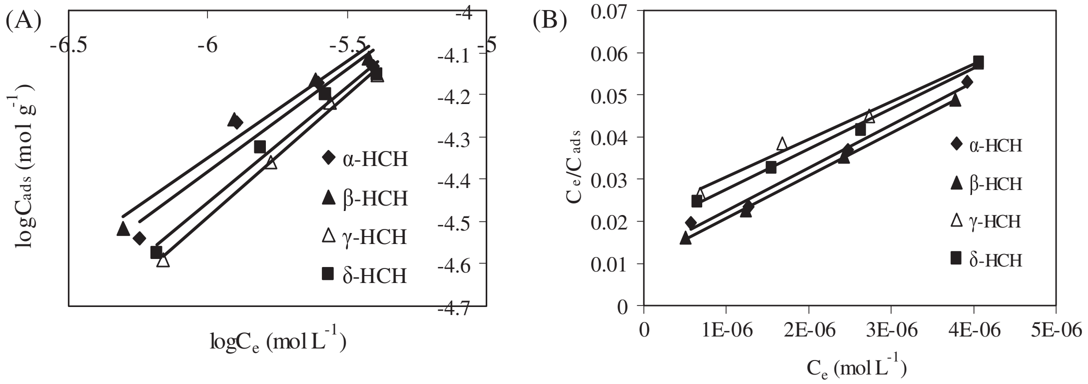

Fig. 7. (A) Freundlich isotherms of HCH isomers and (B) Langmuir isotherms of HCH isomers.

Table 1
Isotherm constants and values of regression co-efficient (R^2) for adsorption of HCH isomers

Isotherm	Isotherm parameter	α-HCH	β-HCH	γ-HCH	δ-HCH
Langmuir	Q_{m} (mmolg^{-1})	0.0097	0.0099	0.103	0.102
	b	8.34×10^5	9.31×10^5	5.40×10^5	4.12×10^5
	R^2	0.99	0.99	0.98	0.99
Freundlich	C (mmolg^{-1})	0.339	0.041	0.157	0.108
	$1/n$	0.48	0.45	0.58	0.54
	R^2	0.92	0.96	0.99	0.97

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

$$R_{\mathrm{L}} = \frac{1}{1 + bG_{\mathrm{i}}} \tag{6}$$

Here, C_i is initial concentration of solution.

The values of adsorption constants of both the models are given in Table 1. The magnitude of these values gives an idea about the favorability and unfavorability of adsorption process [26]. The calculated values of adsorption intensity $(\frac{1}{n})$ is (> 0 and < 1) which shows that adsorption is favorable. Moreover, the calculated values of R_L is < 1. These values also indicate that that adsorption is favorable. In addition to this, the values of multilayer adsorption capacity (C) is higher then monolayer adsorption capacity (Q_m), these values supports that adsorption of four isomers of HCH isomers on *p-tert*-butylcalix[8]arene follows multilayer adsorption path way, i.e. Freundlich adsorption model.

3.4. Kinetics of adsorption study

This is an important parameter for evaluating adsorption mechanism followed by adsorbate molecules to attach on the surface of adsorbent. The effect of agitation time was observed from 15–120 min using 20 mg of modified silica to evaluate the kinetics of adsorption. Fig. 8 is the time profile for the removal of HCH isomers on to modified silica. The figure shows that % adsorption increases with rise in agitation time and gradually reached at equilibrium after 60 min for all HCH isomers. There after % adsorption will almost remain constant. Hence, 60 min was considered as optimum time for further examination.

Kinetic study for the adsorption of HCH isomers on modified silica was checked through the various kinetic models namely the Langergren (pseudo-first order kinetic) [27], Ho and McKay model (pseudo-second-order kinetic) [28] and Morris Weber (intraparticle diffusion model) [29,30].

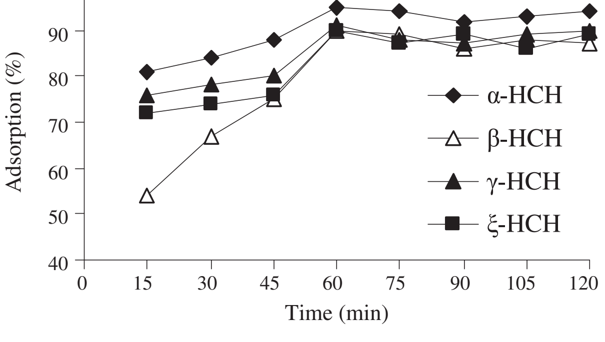

Fig. 8. Effect of agitation time on the adsorption of HCH isomers.

The linear form of these models is shown in Eqs. (7)–(9), respectively

$$\log(q_{\mathrm{e}} - q_t) = \log q_{\mathrm{e}} - \frac{k_1 t}{2.303} \quad \text{(Langergren model)} \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{t}{q_{\mathrm{e}}} \quad \text{(Ho and McKay)} \tag{8}$$

$$q_t = R_{\mathrm{d}} t^{0.5} \quad \text{(Morris Weber)} \tag{9}$$

In all these models, q_e and q_t are the quantity of HCH isomers adsorbed at equilibrium and at time t, respectively. While k_1, $k_{2,}$ and R_d are the rate constants for Langergren Ho and McKay and Morris Weber kinetic models, respectively.

Pseudo-first-order kinetic equation was observed by plotting $\log(q_e - q_t)$ versus t. Pseudo-second-order kinetic model was checked from the graph between $\frac{t}{q_t}$ versus t. Finally, Morris Weber was observed by plotting graph between q_t versus $t^{0.5}$.

The best fit model for detecting the mechanism of adsorption of HCH isomers on modified silica was decided from their regression coefficient values (R^2) calculated from corresponding plot of Fig. 9.

Table 2 shows that the regression coefficient (R^2) values for the Ho and McKay model is higher than for the Langergren model. From this, it can be predicted that the adsorption of HCH isomers follows pseudo-second-order kinetic. The Morris Weber plot represents multilinearity relation. Fig. 10 (C) shows that three steps are involved in the adsorption processes. The first step is the transport of HCH molecules to the surface of adsorbent. Second step is the diffusion of HCH molecules from the outer surface to the active sites of adsorbent. Final step is an equilibrium stage where the HCH molecules get adsorbed on the active sites of adsorbent. Due to decreasing of solute concentration, the intraparticle diffusion rate get slower at the third step.

3.5. Thermodynamics of adsorption

The temperature has considerable effect on the adsorption of guest molecules. This effect on the adsorption of HCH isomers was investigated in the temperature range 283–293 K under optimized conditions (Fig. 10).

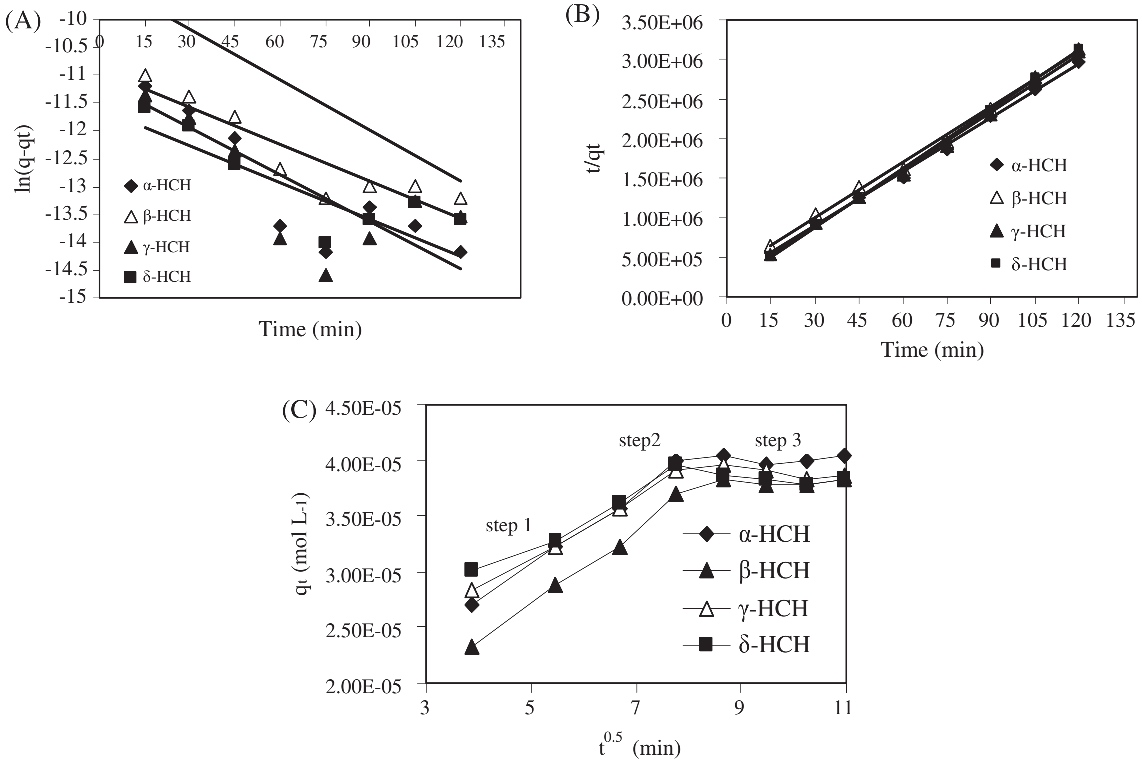

Fig. 9. Kinetic plots: (A) Langergren model, (B) Ho and Mckay model, (C) Morris Webber model.

Table 2
Regression co-efficient values for kinetic models

	R^2			
	α-HCH	β-HCH	γ-HCH	δ-HCH
Langergren	0.410	0.656	0.544	0.548
Ho and McKay	0.998	0.993	0.998	0.996
Morris weber	0.981	0.982	0.983	0.981

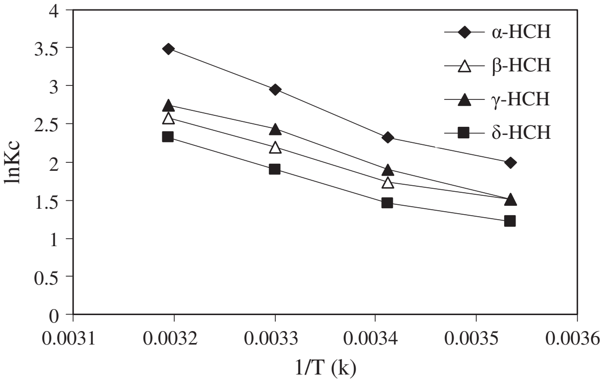

Fig. 10. Effect of temperature on the adsorption of four HCH isomers.

The thermodynamic parameters ΔH, ΔS, and ΔG can be calculated from the Eqs. (10) and (11), respectively.

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

$$\Delta G = -RT \ln K_c \tag{11}$$

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.

The ΔH values show that the adsorption of HCH isomers is endothermic in nature. This fact illustrates that the adsorption takes place through the diffusion process as the temperature increased the rate of mass transfer increases toward the modified silica and hence adsorption increased with the rise in temperature. On the other hand, the values of entropy change (ΔS) show that the rise in randomness at the interface of adsorbent. Both the negative value of ΔG and positive value of ΔS confirm that the adsorption of HCH isomers on modified silica is spontaneous process.

Table 3
Values of thermodynamic terms (ΔG, ΔH, ΔS) for HCH isomers

HCH	Temp (K)	ΔG (J mol^{-1})	ΔH (J mol^{-1})	ΔS (J mol^{-1})
α	283	−4.69	37.29	146.6
	293	−5.64		
	303	−7.42		
	313	−9.05		
β	283	−3.57	26.95	107.3
	293	−4.23		
	303	−5.54		
	313	−6.73		
γ	283	−3.57	31.32	123.1
	293	−4.63		
	303	−6.15		
	313	−7.16		
δ	283	−2.85	27.64	107.2
	293	−3.53		
	303	−4.79		
	313	−6.03		

3.6. Dynamic adsorption study

The optimized conditions of batch adsorption were used to evaluate the efficiency of modified silica 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. 11 shows the breakthrough curve of four HCH isomers. This can be expressed as a ratio of normalized concentration (C_t/C_i) as a function of time or effluent volume. Breakthrough curve of HCH isomers shows that the loaded column gets saturated after passing 130 cm^3 of 1 μgcm^{-3} HCH solution in 65 min.

3.6.1. Thomas model

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 rate constant (k_{TH} cm^3 mg^{-1} min^{-1}) and maximum solid phase concentration (q_o, mg g^{-1}). The linear form of this model is shown in Eq. (12);

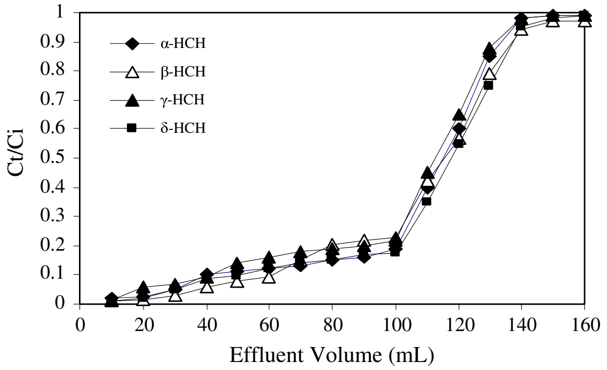

Fig. 11. Breakthrough curves of HCH isomers.

$$\left(\ln\frac{C_i}{C_e} - 1\right) = \frac{k_{TH} q_o A}{Q} - \frac{K_{TH} C_i}{Q} V_{eff} \tag{12}$$

Here, C_i and C_e are the initial and effluent concentration (mg L^{-1}), respectively. A is the quantity of material adsorbed, Q is flow rate (cm^3 min^{-1}), and V_{eff} is the effluent volume, which can be calculated from the Eq. (13);

$$V_{eff} = Qt_{total} \tag{13}$$

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

Values of Thomas rate constant (k_{TH}) and maximum solid phase concentration (q_o), is shown in Table 4. These values are calculated from the plot of ($\ln\frac{C_o}{C} - 1$) versus V_{eff}.

3.7. Comparative study

Adsorption capacity of calix[8]arene-based modified silica is compared with those of other adsorbents reported in the literature, that is, bagasse fly ash [31], clinoptilolite [32] and powdered activated carbon (PAC) [33]. Results show that the adsorption capacity of synthesized material is much better than of other adsorbents (Table 5). Superiority of modified silica can be observed from the amount of adsorbent. Few grams of modified silica can remove four isomers of HCH from aqueous solution.

3.8. Regeneration of modified silica

The adsorbent were efficiently regenerated in the 1:1 mixture of ethylacetate and n-hexane by shaking it

Table 4
Thomas model constants

HCH	k_{TH} (cm^3 mg^{-1}min^{-1})	q_o (mg g^{-1})	R^2
α	0.052	112.5	0.94
β	0.052	110.8	0.94
γ	0.049	108.5	0.92
δ	0.055	114.2	0.93

Table 5
Comparative study of *p-tertbutyl*calix[8]arene based modified silica for removal of lindane

Adsorbent	Dosage ($g\,L^{-1}$)	Removal (%)	Temperature (K)	Q_m ($mg\,g^{-1}$)	Reference
Bagasse	5	95	298	0.251	[31]
Clinoptilolite	10	65	298	0.244	[32]
PAC	2.5	99	298	255	[33]
Modified Silica	2	99	298	103	Current study

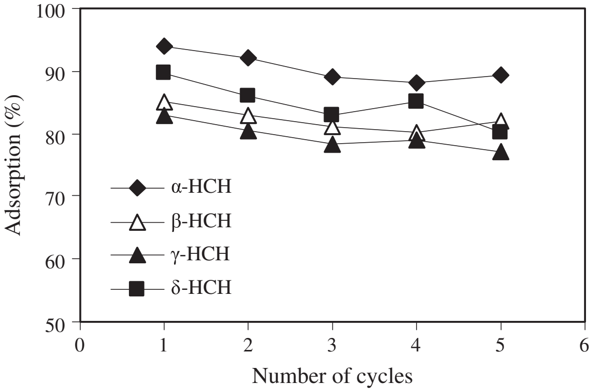

Fig. 12. Effect of number of cycles on HCH uptake.

for just 10 min. The efficiency of regenerated adsorbent was observed for 5 cycles. The average% recovery of modified silica was found to be 90.46 ± 2.47, 82.26 ± 1.84, 79.6 ± 2.27, 84.74 ± 3.46 for α, β, γ, and δ HCH, respectively (Fig. 12).

3.9. Application to spiked agriculture run-off samples

To find the environmental application of three samples of agriculture, run-off water was collected from Sindh University Jamshoro and filtered. The water samples were spiked with the 5 $\mu g cm^{-3}$ HCH standard stock solution. The batch adsorption process was repeated for three samples under optimized conditions to find the removal efficiency of modified silica. The results of % removal of four isomers are shown in Table 6.

Table 6
% Removal of HCH isomers from spiked real water samples

Sample	HCH	% Removal
	α	79.2
A	β	83.2
	γ	78.7
	δ	81.5
	α	80.3
B	β	84.6
	γ	79.5
	δ	83.2
	α	80.4
C	β	85.6
	γ	86.1
	δ	82.9

4. Conclusion

It may be concluded that *p-tert*-butylcalix[8]arene based modified silica is an efficient sorbent for the removal of HCH isomers from aqueous systems. The results of adsorption parameters show that it is best fitted to Freundluich isotherm and follows pseudo second order kinetics involving intraparticle diffusion mechanism. Thomas model reveals that column packing is much more effective to remove isomers then the batch method. Under optimized condition, it is conveniently applicable to real environmental samples and can be reused effectively.

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