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Removal of Parathion from Aqueous Media Through *p-tert*-Butylcalix[4]arene Based Modified Silica

Sibghatullah Memon, Najma Memon and Shahabuddin Memon*

National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

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Abstract

This study explores, adsorption efficiency of *p-tert*-butylcalix[4]arene based modified silica to remove parathion from aqueous environment. The adsorption parameters, i.e. pH, concentration of pesticide solution, contact time and adsorbent dosage were optimized, as 10, 1 mg L^{-1}, 40 min and 0.04 g, respectively. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were used to evaluate the adsorption mechanism. Adsorption constants values of these models suggest that the adsorption of parathion is favorable and were found to be best fit with Freundlich isotherm. From the kinetic study it can be predicted that adsorption of parathion follows Ho and McKay model (pseudo-second order). Thermodynamic parameters, enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) have also been evaluated and were found as -132.25, 0.45, -4.14 $Jmol^{-1}$, respectively.

***Keywords*:** Calixarene; Parathion; Adsorption isotherms; Kinetics; Thermodynamics.

Introduction

Parathion (O,O-diethyl-O-(4-nitrophenyl) phosphorrothioate) is an organophosphorus pesticide It is used to remove pests in agriculture crops in Pakistan, due to its toxicity and risks of contact to birds and agricultural workers, and in reaction to the manufacturer's demand, Environmental Protection Agency (EPA) has declared the cancellation of all uses of parathion on agriculture crops, fruits and nuts [1]. Because of low vapor pressure and significant inhalation at ordinary temperature parathion get absorbed into the eyes, lungs and in blood streams through skin, which produces acute toxic effects [2]. The toxicity symptoms of parathion may develop seizures, skeletal-muscle paralysis, cardiac arrhythmias and respiratory failure, nausea, vomiting, abdominal cramps, diarrhea, and fecal incontinence**.** Due to increase in use of parathion and related pesticides in developing countries, like Pakistan, Bangladesh, India, etc., it further enhances serious human health and environmental problems, such as contamination of soil, surface and ground water. Therefore, it should be removed from aqueous environment.

Various techniques, such as, reverse osmosis [3], bioreactor technology [4], sand filter system [5] and gamma-irradiation [6] were used to remove pesticides from water. Currently, adsorption is being used as an important method to remove organic pollutants. In response to this different sorbents such as, fly ash [7], chestnut shells [8], watermelon peals [9], activated carbon [10], Dugesia dorotocephala [11], Fenton's reagent [12] and imprinted polymers [13] have been used effectively to remove pesticides from aqueous systems.

Consequently, due to the convenient one pot synthesis from cheap raw materials and regenerable nature of their impended resins; the calixarenes, a class of synthetic macrocyclic

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*Corresponding Author Email: shahabuddinmemon@yahoo.com

oligomers possessing cup like shape having defined upper and lower rims with central annulus have been widely used in adsorption processes. The upper and lower rim of calixarenes can be modified to synthesize different derivatives having varying cup-shaped cavities to function as guests for various toxic metals, neutral molecules and toxic anions [14]. Several studies have been reported to remove toxic species such as, recognition of chloride, bromide, iodide [15], fluoride [16], dichromate [17,18], methylene blue [19], Pb^{2+} [20], chromium(VI) [21], azodyes [23], a pesticide related 1-chloro-4-(trifluoromethyl)benzene [24] and neutral benzotrifluorides [25]. The present study reveals the determination of adsorption capacity, regeneration efficiency of calix[4]arene based modified silica for the removal of toxic pesticide (parathion) from aqueous environment.

Material and Methods

Reagents

Analytical thin layer chromatography (TLC) was performed on precoated silica plates (SiO2, PF254). The pH (2-12) was adjusted through HCl/NaOH solution using pH meter. Standard parathion and silica (240-400 mesh) were purchased from Fluka (Germany). *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[4]arene based modified silica was prepared according to previous method [26,27]. All reagents/solvents used were of analytical grade. Solutions were prepared in DDI (double distilled deionized) water, which was passed through Millipore Milli-Q Plus water purification system (Elga model classic UVF, UK).

Instrumentation

Scanning Electron Microscopic (SEM) images were collected by using JSM-6490LV instrument. Thermo Nicolate 5700 FT-IR spectrometer was used to record FT-IR spectra as KBr pallets. Gallenkamp melting point apparatus model MFB, 595, 010 M, England was used to find melting point. GC µECD (Agilent 7890 A system, USA) was used for the calculation of percent adsorption from the difference of detector response. Inolab pH meter 720 (Germany) was used to check pH of solutions. A Gallenkamp thermostat automatic mechanical shaker model BKS 305-101, UK was used for adsorption study.

Batch adsorption procedure

A 10 mL of parathion solution (1.0 mg L^{-1}) having pH 10 was taken in conical flask, A 40 mg of *p-tert*-butylcalix[4]arene based modified silica was added in to it.. The flasks were agitated on the shaker to reach at the equilibrium point (40 min) at the speed of 125 rpm. The solution was filtered through Whatmann filter paper (0.45 mm). The filtrate was extracted as described in section 2.4. The percent adsorption was calculated through following equation;

$$\%Adsorption = \frac{Hi - Hf}{Hi} \times 100 \quad (1)$$

Here H_i and H_f is peak height before and after adsorption, respectively. Maximum batch adsorption capacity (A) of *p-tert*-butylcalix[4]arene based modified silica was find out by using through Eq. 2 [28].

$$A = \frac{V(C_o - C_e)}{M} \quad (2)$$

Where C_o and C_e is the initial and equilibrium concentration of target molecules in water (mg L^{-1}), V is volume of pesticide solution in (L), M is mass of modified silica (g).

Sample preparation and analysis of parathion

The sample was prepared by extracting parathion from aqueous filtrate through liquid-liquid extraction method. A mixture (1:1) of ethylacetate and n-hexane was placed in separating funnel containing 10 mL aqueous solution of parathion. In order to extract parathion separating funnel was occasionally shaken for 6 min. after few minutes upper organic layer was collected and dried using anhydrous sodium sulfate. Before injecting sample (2 µL) the dried sample was filtered through Whatman filter paper (0.45 µm) and injected in GC-µECD system. Instrumental conditions were set as; injector temperature 250 ^{o}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 ^{o}C hold for 1 min., with run time 25 ^{o}C min^{-1} till 280 ^{o}C, where it is hold for 5 min. While detector was set at 320 ^{o}C and nitrogen was used as carrier gas at flow rate of 3 mL min^{-1}. Under these conditions total run time was 14.4 min, while retention time of parathion is 9.67 min.

Results and Discussion

Surface study

In order to characterize adsorption of parathion on the surface of *p-tert*-butylcalix[4]arene based silica was analyzed through FT-IR and SEM study.

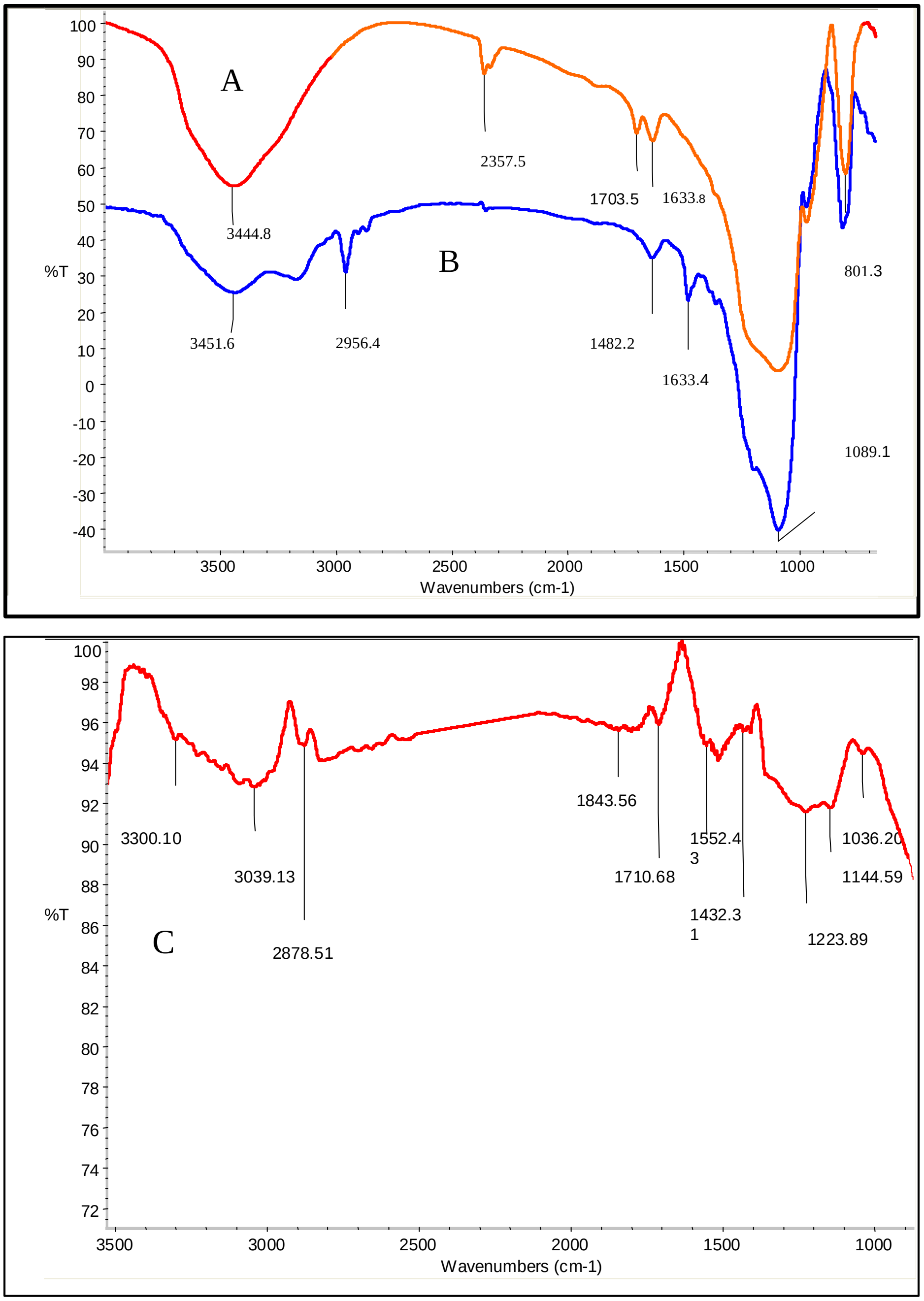


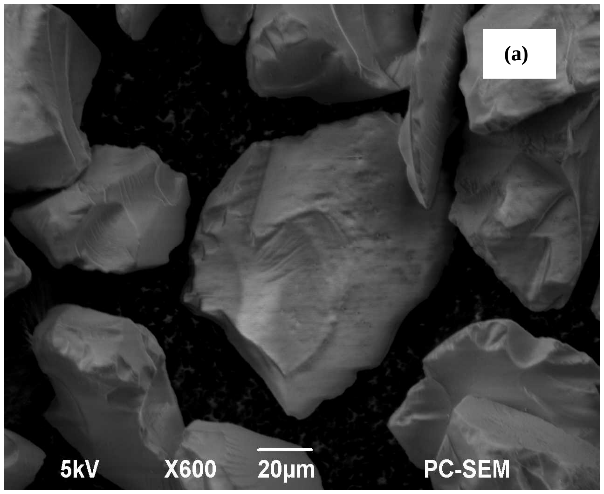
Figure 1. **FT-IR spectrum (A) pure silica, (B) *p-tert*-butylcalix[4]arene based modified silica (C) Modified silica after adsorption of parathion**

Fourier transforms infrared (FTIR) study

Fourier transform infrared spectroscopy is an efficient method to analyze the surface functionality of polymeric surfaces. Therefore, modification of silica was operated through this method. (Fig. 1) is the FTIR spectrum of pure silica, modified silica and after adsorption of parathion. Results of Fig 1C shows that the band at 2878 cm^{-1} belongs to C-H stretching of *tert*-butyl group and the bands at 1552 cm^{-1} and 1432 cm^{-1} indicate the presence of NO_2 groups, while the band at 1036cm^{-1} is of the C-O stretching in the parathion molecule. From these results, it is confirmed that molecules of parathion have been adsorbed on the surface of modified silica.

Scanning Electron microscopy (SEM)

The adsorption is a surface phenomenon, the speed and extent of adsorption is specific to some molecules is influenced by surface area, pore size and surface functional groups. Adsorption of parathion on *p*-*tert*-butylcalix[4]arene based modified silica was also confirmed through SEM images. (Fig. 2) is the SEM micrograph of pure silica, modified silica and after adsorption of parathion. It can be seen from the images of modified silica that surface is rough and having large number of active sites, whereas the surface become smooth and posses some wrinkles after adsorption which is due to the some external material, i.e. parathion.



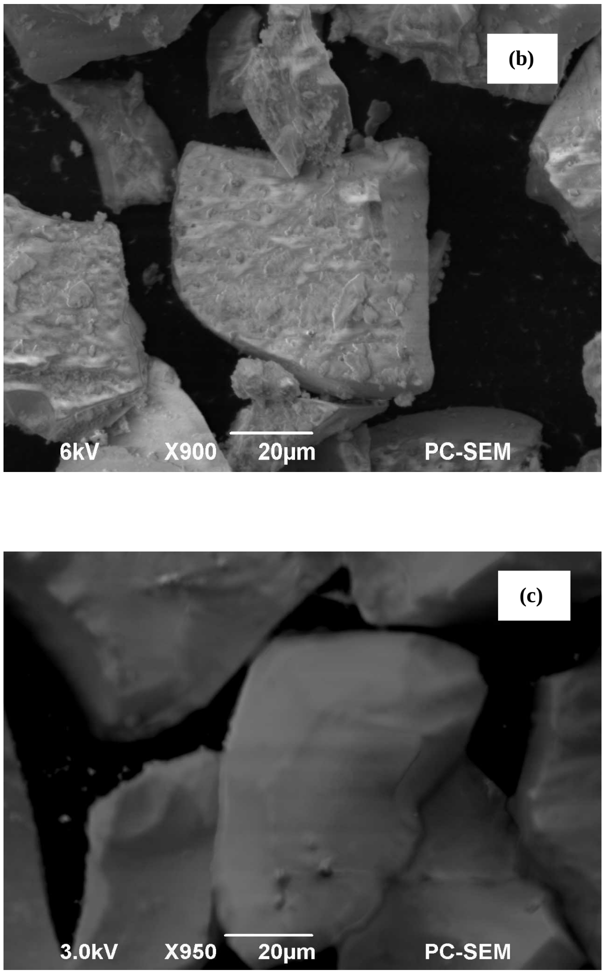


Figure 2. **Scanning electron microscopic (SEM) micrographs (a) pure silica (b) *p-tert*-butylcalix[4]arene based modified silica (c) modified silica after adsorption of parathion**

pH study of adsorption of parathion

Effect of pH on percent adsorption of parathion using modified silica was observed from pH 2-12. (Fig. 3) shows that percent adsorption is low in acidic region which may be due to weak lipophilic interaction of parathion with neutral calixarene cavity. The adsorption is found to be maximum at pH 10 which may be due to the deprotonation of OH free group of calixarene. This creates the dipole, therefore, considerable association is developed through dipole-dipole interaction between the parathion and calixarenes cavity immobilized on the surface of silica. In addition to this, lipophilic (alkyl group) of parathion may interacts with the lipophilic cavity of calixarene molecule at this pH [30].

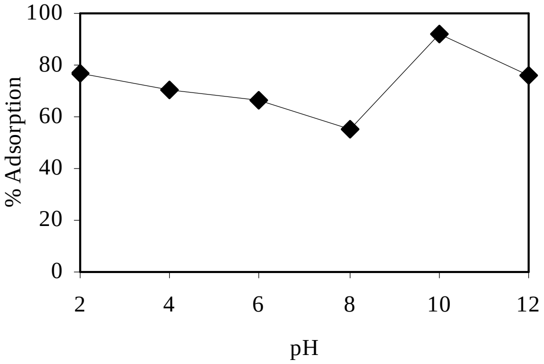


Figure 3. **Effect of pH on adsorption of parathion**

Adsorbent dosage study

Adsorption was significantly affected by the quantity of adsorbent. Effect of amount of adsorbent on percent adsorption of parathion using the *p-tert*-butylcalix[4]arene based modified silica is shown in (Fig. 4). Graph shows that percent adsorption increases with increase of adsorbent dosage and attains maximum value at 40 mg. This may be due to increase in adsorbent active sites on surface.

Under optimized conditions maximum batch adsorption capacity was found to be 0.025 mol g^{-1} calculated by using equation 2.

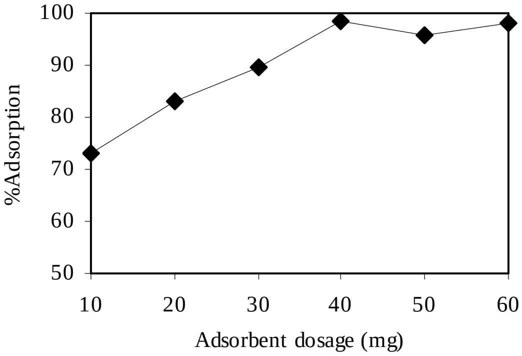


Figure 4. **Effect of adsorbent dosage on parathion adsorption**

Adsorption isotherms

Concentration effect on adsorption of parathion using *p-tert*-butylcalix[4]arene based modified silica resin was observed using optimized conditions at room temperature. The grapgh was plotted between percent adsorption and initial concentration of parathion (Fig. 5). Results show that modified silica was found to be an efficient up to 1.0 mg L^{-1}. After that percent adsorption decreases as the concentration increases, which shows that modified silica has some specific sites that become saturated up to 1.0 mgL^{-1} while using optimized conditions.

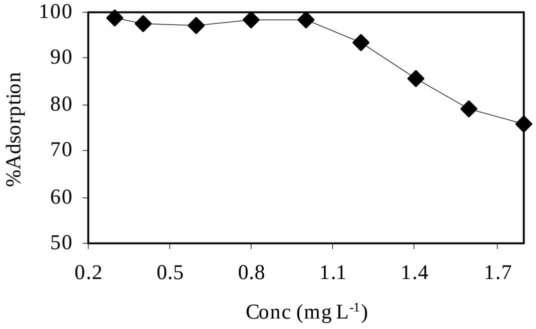


Figure 5. **Effect of initial concentration on parathion adsorption**

Adsorption isotherm is a critical way to evaluate the adsorption capacity as well as adsorbate- adsorbent interaction [31]. Various adsorption isotherms were used to determine the relationship between the adsorbent dosage and percent adsorption as a function of concentration under optimized conditions. Adsorption data was analyzed through Freundlich; Langmuir and Dubinin–Radushkevich D-R isotherm models to examine the nature of adsorption of parathion on the *p-tert*-butylcalix[4]arene based modified silica.

Dubinin-Radushkevich (D-R) isotherm

This isotherm model is used to differentiate physical and chemical adsorption phenomenon by estimating the porosity and energy of adsorption, it is differ from Langmuir isotherm that it is used to characterize whole surface but not the homogenous which involve the same binding sites throughout the surface. The linear form of this model is Eq. 3.

$$\ln C_{ad} = \ln X_m - \beta\varepsilon^2 \qquad (3)$$

Here X_m stand for maximum adsorption capacity of adsorbent (mol g^{-1}), C_{ad} is the quantity of parathion adsorbed on the modified silica (mol g^{-1}). β is a constant calculated from the slope of $\ln C_{ad}$ against ε^2 and is used to find out the adsorption energy. ε Polanyi adsorption potential which can be evaluated by using Eq 4,

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{4}$$

Here T is temperature in Kelvin, C_e is an equilibrium concentration of parathion solution (mol L^{-1}), R is a gas constant (kJ mol^{-1} K^{-1}). Polanyi theory assumes the layer by layer attachment target molecules to the pores of adsorbent leads to form condensed adsorption films on the microporous adsorbent.

The plot of $\ln C_{ad}$ versus ε^2 is a straight line with a slope β and intercept X_m (Fig. 6(a)). The adsorption energy for the transfer of one mole of parathion from infinity to the surface of the modified silica can be obtained by using Eq. 5;

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

Freundlich model

This model assumes the formation of multi molecular layer through the distribution of active sites that is the characteristic of heterogeneous surfaces. The linear form of this model can be represented through Eq. 6.

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

Here C_{ad} is a adsorbed concentration (mol g^{-1}), $\frac{1}{n}$ is adsorption intensity, C_e stands for equilibrium concentration (mol L^{-1}), while C_m represents a multilayer adsorption capacity.

The plot of $\log C_{ad}$ versus $\log C_e$ reveal straight line, with slope $\frac{1}{n}$ and intercept C_m (Fig 6(b)).

Langmuir isotherm

This model is first quantitative theory of adsorption involve the adsorption takes place on fixed number of adsorption sites confined to mono molecular layer with no transfer of adsorbate on the plane of surface. Data of adsorption of parathion on *p-tert*-butylcalix[4]arene based modified silica were fitted in the Langmuir isotherm model. The linear form of this adsorption isotherm is shown in Eq 7.

$$\frac{C_e}{C_{ad}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{7}$$

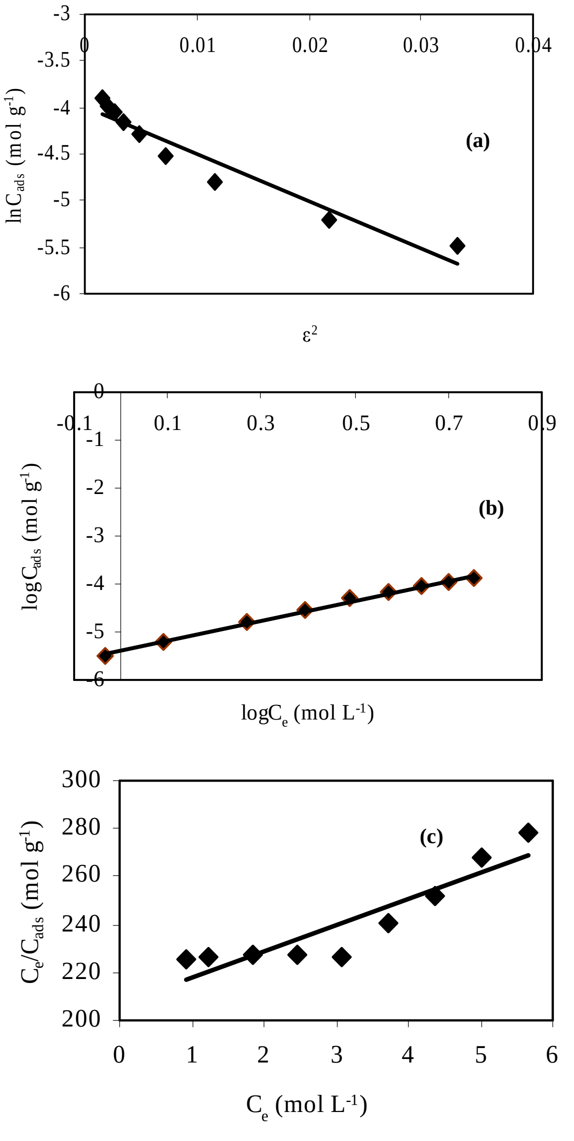


***Figure 6.* (a) D-R Adsorption isotherm of parathion, (b) Freundlich adsorption isotherm of parathion (c) Langmuir adsorption isotherms of parathion**

Here b is a constant related to binding energy of parathion (mol L^{-1}), C_e equilibrium concentration (mol L^{-1}), Q is monolayer adsorption capacity (molg^{-1}), C_{ad} is adsorbed concentration (molg^{-1}).

The plot of $\frac{C_e}{C_{ad}}$ versus C_e show straight line with slope $\frac{1}{Q}$ and intercept $\frac{1}{Qb}$, (Fig 6(c)).

From the value of Langmuir constant *"b"*, a dimensionless parameter called separation factor R_L can be calculated through Eq.8.

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

Table 1 show the isotherm constants values.

***Table 1*. Isotherm constants and values of R^2 for parathion on *p-tert*-butylcalix[4]arene based modified silica.**

Isotherm	parameter	parathion
Freundlich	Cm (µmolg^{-1})	4.17
	$\frac{1}{n}$	0.48
	R^2	0.9927
Langmuir	Q (µmolg^{-1})	0.09
	b (dm^3 mol^{-1})	0.053
	R^2	0.832
Dubinin-Radushkevich (D-R)	X_m (µmol g^{-1})	101.3
	E (J mol^{-1})	10.2
	R^2	0.9289

The constant terms of D-R, Langmuir and Freundlich isotherm were evaluated from their respective slopes and intercepts. The calculated values of dimensionless parameter, i.e. separation factor R_L were found to be lies in the range of 0.94-0.74 at the concentration range from 0.3 mgdm^{-3} to 1.8 mgdm^{-3}. (The favorable range is $0 < R_L < 1$) from this it can be predicted that adsorption is favorable at all the concentrations. Whereas the calculated value of frendlich constant "*n*" is found to be 2.06 (The favorable range $1< n < 10$) from this it can be predicted that adsorption of parathion on the surface of modified silica is favorable. The smaller value of "n" indicates the smaller changes in the adsorbent efficiency over different equilibrium concentration. The saturation limit, X_m, represent total specific microscopic volume of the adsorbent, where as, constant β shows adsorption energy for the transfer of one mole of solute from infinity to the surface of adsorbent. Of all the isotherms, from the higher value of C_m and R^2 for the Freundlich isotherm it can be predicted that adsorption of parathion is best fitted to this model. Along with this it can also be evaluated that the surface of adsorbent is heterogeneous. Therefore parathion adsorbs *via* multilayer adsorption process. Moreover, according to A. U. Itodo and H. U, Itodo values of free energy for the physiosorption lie in the region of 1-20kJmol^{-1}[32]. Therefore the calculated value also supooting the physiosorption.

Kinetic study of adsorption

The effect of contact time on percent adsorption of parathion was observed at pH 10 from 10 to 120 min using 1.0 mgL^{-1} solution of parathion. (Fig. 7) shows that percent adsorption increases with the rise in agitation time and attains maximum value at 40 min. after that percent adsorption becomes constant.

In order to look at the mechanism adsorption Lagergren model (pseudo first order) [33] and Ho and McKay model (pseudo second order) [34] kinetic models were used. The linear form of pseudo first order kinetic model is Eq. 9.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

Here k_1 (min^{-1}) is the pseudo first order rate constant, q_e is the quantity of parathion adsorbed (mg g^{-1}) at equilibrium and q_t is the quantity of parathion adsorbed at time t (min).

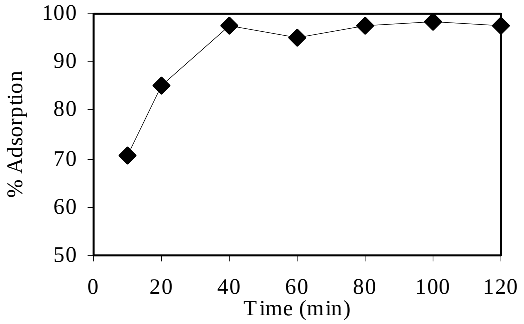


***Figure 7.* Effect of contact time on parathion adsorption**

Fig. 8. A is the Plot of $\log(q_e - q_t)$ versus contact time t (min) show straight line with co-efficient of determination (R^2) 0.5981 for the adsorption of parathion on the modified silica.

Kinetic data was also examined through Ho and Mc Kay model (pseudo second order). The linear form of this model can be represented through Eq. 10.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

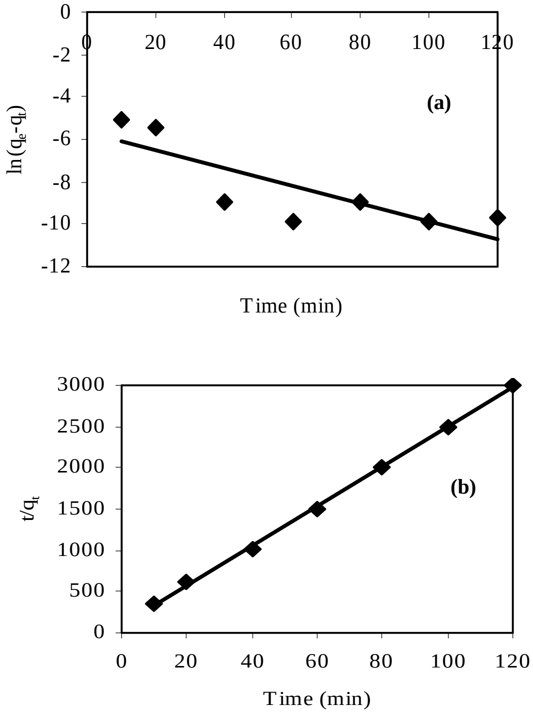


***Figure 8.* (a) Langergren kinetic model, (b) Ho and Mc-Kay kinetic model**

Fig 8. B shows plot of $\frac{t}{q_t}$ versus t exhibit straight line with value R^2 0.9987 for the adsorption of parathion.

The values of R^2 for Lagergren (pseudo first order) and Ho and McKay (pseudo second order) kinetic models are 0.5981 and 0.9987, respectively. From these values it can be predicted that adsorption of on the modified silica parathion follows pseudo second order kinetic equation. Moreover, the values of kinetic constants (K_1 and K_2) for Lagergren and Ho and McKay models were found to be 0.096 and 22.72 respectively. High value of Ho and McKay model supports that parathion follows pseudo second order kinetic equation.

Thermodynamics of adsorption

Temperature has appreciable effect on the adsorption process. Temperature effect on the adsorption of parathion was analyzed at 293, 303, 313, 323, 333 K, under optimized conditions using Eq. 11.

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (11)$$

$$\Delta G = -RT \ln K_c \qquad (12)$$

Thermodynamic parameters such as ΔH, ΔS, ΔG and T are enthalpy, entropy, Gibbs free energy and temperature, respectively. Whereas, K_c can be calculated by using equation 13,

$$K_c = P_e / 1 - P_e \qquad (13)$$

Here P_e is fraction of parathion adsorbed at equilibrium. Values of thermodynamic constants ΔH (-132.2 $Jmol^{-1}$) and ΔS (0.45 $Jmol^{-1}$) were calculated from the slope and intercept of (Fig. 9) respectively. These values indicate that the adsorption of parathion is an exothermic process. Eq. 12 is used to calculate the value of Gibbs free energy (ΔG), which is evaluated as, – (3.14, 4.41, 5.82, 8.11, 11.19 kJ mol^{-1}). The negative value of Gibbs free energy suggests that adsorption of parathion on modified silica is a spontaneous process.

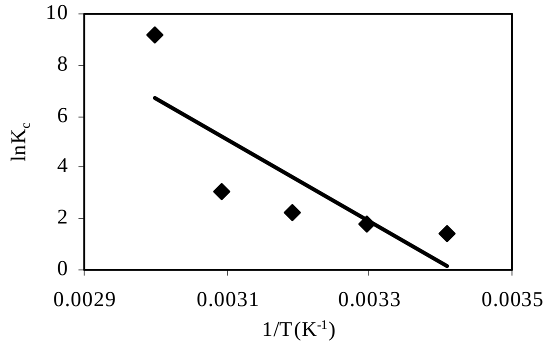


***Figure 9*. Effect of temperature on the % adsorption of parathion**

Adsorbent regeneration

In order to remove parathion from the surface of resin 0.1 g of treated resin was shook in methanol and 1:1 mixture of ethyl acetate. It was observed that the mixture of ethylacetate and n-hexane can remove more then 75%, while methanol can remove only 20% of parathion from the adsorbent surface.

Conclusion

Adsorption of parathion on *p-tert*-butylcalix[4]arene based resin was investigated through batch adsorption procedure. Adsorption isotherm constant values suggest that it is favorable process, while Freundlich isotherm model was found to be best fitted to adsorption data. Kinetic study suggests adsorption of parathion follows pseudo second order kinetic equation. Thermodynamic parameters values show that adsorption of parathion is exothermic and spontaneous. Another advantage of this study is that the adsorbent can be regenerated effectively.

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