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# Application of calixpyrrole modified silica for the removal of 4-chlorophenol from aqueous media

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## RESEARCH ARTICLE



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## ABSTRACT

In this research, calixpyrrole modified silica (III) was synthesized and characterized by Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and scanning electron microscope (SEM) techniques. The synthesized material was used as an extractant for the removal of 4-chlorophenol from aqueous solution. Its efficiency was examined through both batch and column extraction methods. The effects of temperature, pH, initial chlorophenol concentration and mass of the adsorbent were examined using removal efficiencies. Initial concentration and quantity of adsorbent show a noticeable influence on the uptake capacity of the adsorbent. The kinetics and thermodynamics of chlorophenol removal from aqueous media were also investigated. Kinetic studies indicated that the extraction data can be best represented by pseudo second order model. Column extraction data were analyzed through Thomas, Yoon-Nelson and Yan *et al.* models to calculate kinetic coefficients and maximum sorption capacity of the modified silica (III). The adsorbent silica was regenerated by acid treatment without changing its properties.

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## 1. Introduction

Chlorophenols (CPs) are widely used as herbicides, pesticides, fungicides, wood preservatives and as intermediates in the production of pharmaceuticals and dyes [1,2]. CPs present in natural environments [3], and are environmental pollutants, discharged into the environment from many resources such as industrial, agricultural, and domestic activities [4-6]. CPs in water have been classified as priority pollutants by US Environmental Protection Agency (EPA) [7] due to their toxicities and persistence within the environment [8]. Toxicity of CPs is proportional to the number of chlorine substituents on phenol ring [9]. Exposure to CPs in humans may affect muscles, nervous system, heart, liver and kidneys [10,11]. Thus the removal of CPs from wastewater has become a serious challenge to scientists. Different methods with varying degrees of success have been developed to remove CPs from wastewater. These include biological degradation, chemical oxidation, solvent extraction, adsorption, coagulation and

liquid membrane permeation [12-16]. Disadvantages such as high cost, low selectivity and little efficiency are restricting the wide use of some of these treatment methods [17]. Adsorption is considered as a simple and effective method in removing inorganic pollutants from wastewater [18,19]. Many adsorbents such as clays, zeolites, resins and silicates have been investigated for the removal of phenol derivatives [20-23]. Mesoporous silicates are the most preferable adsorbents because they have a large surface area, high selectivity and large pore size [24,25]. The search for low cost and high selective adsorbents has led us to attach calixpyrrole derivative into silica backbone and to investigate the efficiency of the obtained material in removing CPs from aqueous media. Organic groups on the surface of silica create binding sites, which are affinitive to CPs. Calixpyrroles can interact efficiently and selectively with either cations, anions or neutral molecules depending on their pendant arms [26-28].

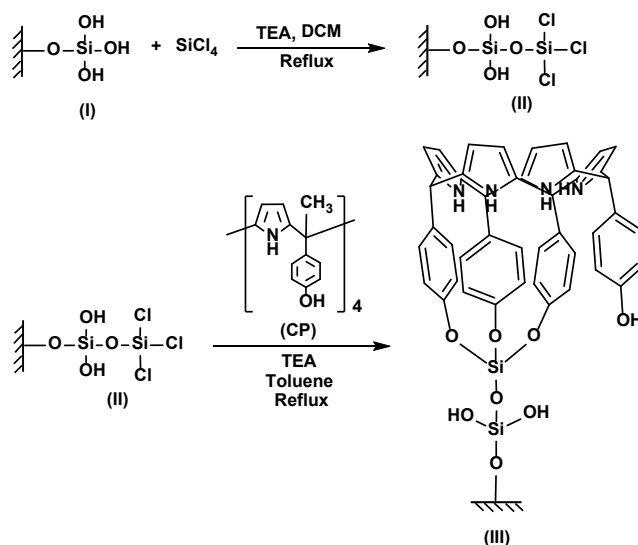


Figure 1. The preparation of silica immobilized calixpyrrole (III).

Therefore, the objective of this study was to evaluate the effectiveness of calixpyrrole modified silica for the removal of CPs from aqueous media. The effects of various operating parameters, such as pH, temperature, sorbent dosage and initial CPs concentration on the uptake capacity have been studied.

## 2. Experimental

### 2.1. Chemicals

Pyrrole (98%), methanesulfonic acid (99.5%), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), sodium hydrogen carbonate (NaHCO<sub>3</sub>), (3-aminopropyl)trimethoxysilan (97%), 18-crown-6 (18-C-6), *p*-hydroxyacetophenone (>98%) and 4-chlorophenol were all purchased from Aldrich and used as received. Silica gel (0.06 mm) was heated at 400 °C for 12 h and then kept in the desiccator over P<sub>4</sub>O<sub>10</sub> to maintain their dryness. Methanol, dichloromethane, hexane, ethanol and acetone (HPLC grade, Fisher) were used without further purification.

### 2.2. Apparatus

FTIR spectra were recorded with FTIR-6300, JASCO in wavenumber range of 400-4000 cm<sup>-1</sup> using pressed KBr disks and a spectral resolution of 4.0 cm<sup>-1</sup>. A KBr beam splitter and a sample bench purged with dry air. The FTIR spectra were recorded with pellets obtained by pressing a mixture of 1.0 mg of sample and 100 mg of KBr under reduced pressure. The morphologic characteristics of the modified silica materials before and after modification were determined by scanning electron microscopy (ASC-2100, SERON technology, Korea). The acceleration voltage is 20 kV and the work distance is about 25 mm. Thermogravimetric analysis was conducted by SETARAM-LABSYS Thermal Analyzer in the flow of N<sub>2</sub> within 20-700 °C temperature range, with a heating rate of 3 °C/min. Absorbance spectra measurements were made using computerized double beam UV-Vis Spectrophotometer (Jasco V-530, Serial no A030161150) with wavelength range from 200 to 700 nm, spectral bandwidth 2 nm, time interval 1.0 nm, speed 1200 mm/min, and matched Quartz cell with length 10 mm.

### 2.3. Preparation of modified silica

The synthesis of calixpyrrole modified silica is shown in Figure 1. The two steps procedure is as follow: A mixture of 25 mL of 1.0 M SiCl<sub>4</sub> and 10.0 g of activated silica in 150 mL freshly distilled dry dichloromethane (DCM) was stirred and refluxed under nitrogen gas with 3 mL trimethylamine (TEA) as a catalyst for 24 hrs. The bonded silica (II) was filtered and washed with DCM and toluene. 12.0 g of modified silica (II) was obtained.

A mixture of 5.0 g meso-tetramethyl-*tetrakis*-[4-(2-ethoxy)ethoxyphenyl]calix[4]pyrrole [29], 10.0 g of modified silica (II) and 10 mL of TEA in 150 mL anhydrous toluene was refluxed under an inert atmosphere for 48 hours. The silica immobilized calixpyrrole (III) was filtered and washed in sequence with hot toluene, methanol, distilled water and methanol. Subsequently, the final product (III) was dried under vacuum at 120 °C for 24 hours and kept in desiccator over P<sub>4</sub>O<sub>10</sub>.

### 2.4. Extraction of chlorophenols from aqueous media/batch method

Batch experiments were carried out to investigate the ability of modified silica (III) to extract chlorophenols from aqueous media. Extraction was performed in 100 mL glass stoppered bottles at an adsorbent dose of 0.2 g, chlorophenol concentration of 450 mg/L, temperature of 298 K and contact time of 120 min. This was carried out by mixing 0.2 g of the modified silica (III) with 50 mL of chlorophenol solution. After equilibrium was attained, the solutions were centrifuged and the concentrations of chlorophenols remained in solutions were determined by UV-Vis spectrophotometry. This method was used to study the effect of modified silica (III) dosage, initial chlorophenol concentration, reaction time, solution pH, and temperature on the extraction process. The influence of pH was done at pH values of 2-12 with 0.1 M HCl or 0.1 M NaOH solutions. The effect of initial chlorophenol concentration was done by varying the chlorophenol concentration from 50 to 800 mg/L. Modified silica (III) dose was varied in the range 0.01-0.45 g to determine its effect. The influence of contact time was done by changing the contact time from 0.5 to 180 min. Temperature effect was studied by changing the extraction temperature from 288 to 308 K using a thermostat water bath for temperature control.

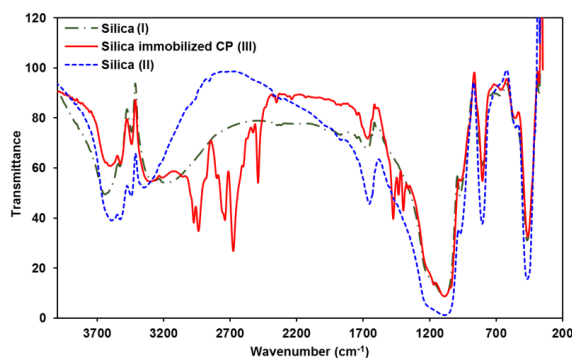


Figure 2. FT-IR spectra of silica (I), silica (II) and silica immobilized calixpyrrole (III).

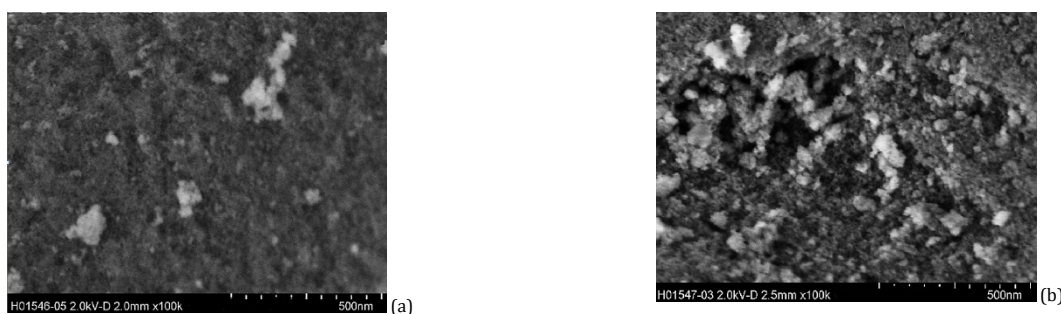


Figure 3. SEM image of the silica (I) (a) and silica immobilized calixpyrrole (III) (b).

### 2.5. Extraction of chlorophenols from aqueous media/column method

In the column experiments, 2.0 g of modified silica (III) was packed in a Pyrex glass column (20×2.5 cm). Before use, distilled water was passed through the column to equilibrate and clean. Portions of 20 mL of chlorophenol solution (450 ppm) were fed in a down flow manner and effluents were collected at a flow rate of 5 mL/min. The concentration of chlorophenols in the eluent was analyzed by UV-Vis spectrophotometer after 30 min interval. The saturated modified silica was regenerated with 2.0 M HCl solution. This work was repeated many times until the silica material became saturated with chlorophenols.

## 3. Results and discussion

### 3.1. Characterization of silica materials

FTIR analysis was mainly performed to confirm the attachment of calixpyrrole onto silica surface. The characteristic absorption bands of silica and silica immobilized calixpyrrole (III) are displayed in Figure 2. In the spectra of silica (I) and (II), the two characteristic peaks observed at around 801 and 460  $\text{cm}^{-1}$  are corresponding to Si-O vibrations [30]. The band observed at 1076  $\text{cm}^{-1}$  is assigned to Si-O-Si stretching vibration. The presence of adsorption water was reflected by  $\nu(\text{OH})$  vibrations [30] at around 3442 and 1662  $\text{cm}^{-1}$ . The large and broad band near 3600  $\text{cm}^{-1}$  is attributed to O-H stretching vibration. As far as the spectrum of silica (III) is concerned, new strong absorption bands are observed at 2672-2936 and 1419-1471  $\text{cm}^{-1}$  in comparison with that of silica(II). These bands confirm the anchoring of calixpyrrole onto silica surface. The peaks at 1471 and 2936  $\text{cm}^{-1}$  are characteristics of the benzene ring. The absorption band at 1471  $\text{cm}^{-1}$  is associated with C=C stretching vibration of the benzene ring. Peaks at 2936  $\text{cm}^{-1}$  are attributed to C-H stretches. The absorption band

at 1419  $\text{cm}^{-1}$  is attributable to C-N stretching vibration of the pyrrole ring. The band at 2388  $\text{cm}^{-1}$  is related to N-H overtone.

Morphology differences between silica (I) and modified silica (III) are provided by SEM images in Figure 3a-b. SEM micrographs illustrate that particles of silica (I) are relatively homogeneous. Figure 3b clearly illustrates the immobilization of calixpyrroles over the surface of silica particles. In order to get a profound insight into the microscopic structure, EDS elemental mapping is produced and the results are shown in Figure 4. The EDS data of silica immobilized calixpyrrole (III) confirmed the presence of carbon and nitrogen which were primarily absent in activated silica (I) and modified silica (II). This means that the anchoring of calixpyrrole onto silica surface was successful.

Thermogravimetric curves of the activated silica gel (I) and silica immobilized calixpyrrole (III) are shown in Figures 5a-b. TG curves presented an initial mass loss of 6.52% which is attributed to the release of water physically adsorbed on the surface. The second loss of mass of 34.80% is due to the decomposition of the calixpyrrole immobilized on the surface. The last decomposition of 3.65% at 500 K is related to the condensation of the remaining silanol groups. Thermogravimetric analysis reflects the thermal stability of modified silica (III). The above results indicate that silica gel is successfully modified with calixpyrrole.

### 3.2. Effect of mass of silica immobilized calixpyrrole (III)

Different masses (0.01-0.45 g) of calixpyrrole modified silica (III) were added into 200 ppm chlorophenol solutions in 50 mL volumetric flasks. The mixtures were mechanically shaken for 30 minutes to facilitate the interaction of chlorophenol with modified silica (III). The quantity of chlorophenol removed (% E) from the aqueous media was calculated by using the Equation (1).

$$\%E = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

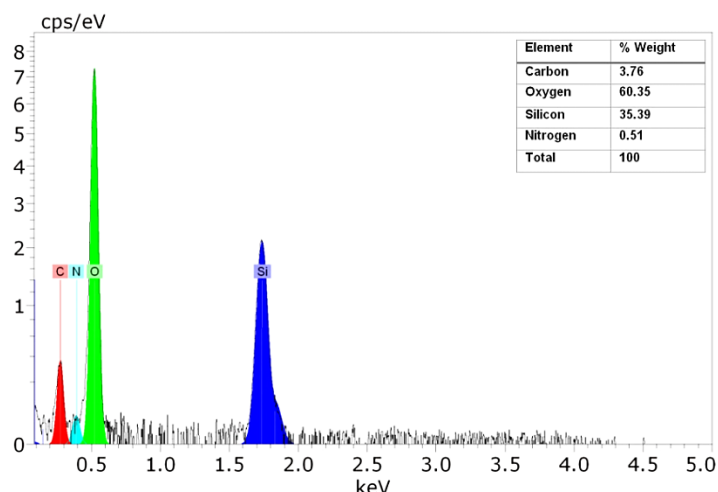


Figure 4. EDX spectrum of silica immobilized calixpyrrole (III).

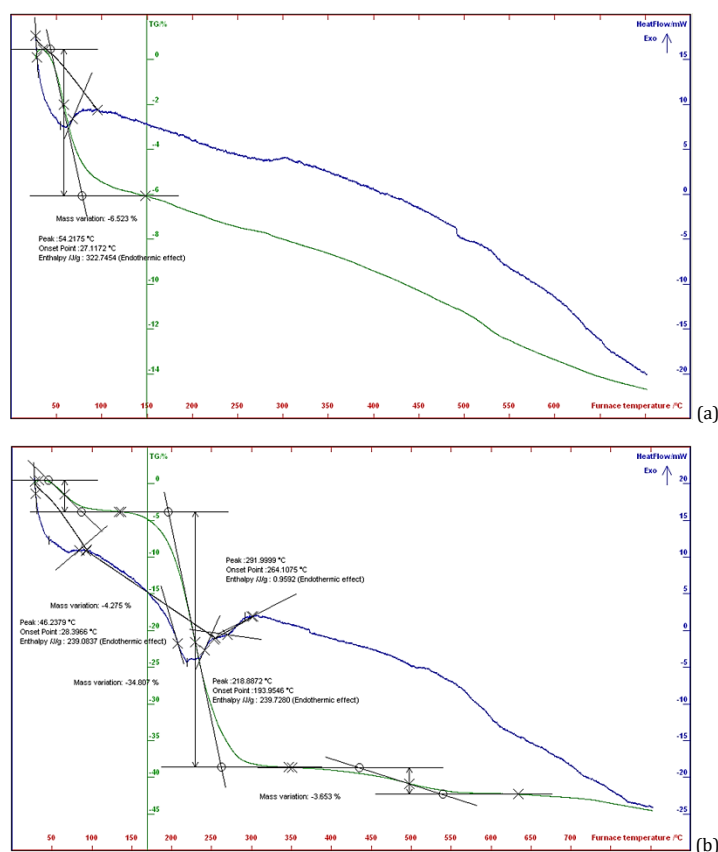


Figure 5. TG curves of (a) silica (I) and (b) silica immobilized calixpyrrole (III).

where  $C_i$  and  $C_e$  represent the initial and equilibrium concentrations of chlorophenol in the aqueous solution. The results are shown in Figure 6. It is evident that the amount of chlorophenol removed from solution increases as the mass of modified silica increases for a given initial concentration. This increase may be attributed to the existence of more binding sites (OH and NH units) for interaction with chlorophenols. The highest quantity of chlorophenol (95.6 %) was extracted by using 0.20 g of modified silica (III). Percent extraction was not changed significantly when the mass of extractant was larger than 0.20 g. So this mass (0.20 g) was used in studying the effects of other parameters (time, temperature, pH and concentration).

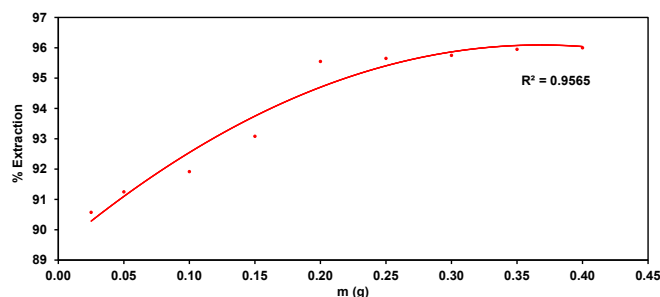
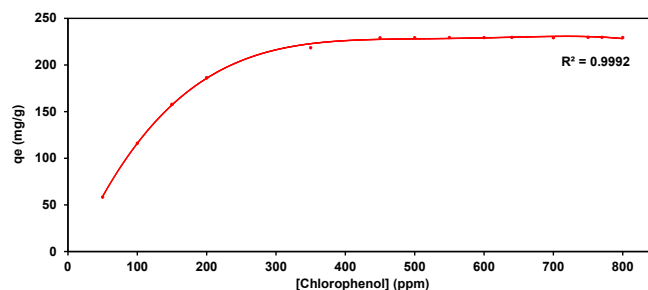
### 3.3. Uptake capacity

Uptake capacity is an important parameter to investigate because it reflects the efficiency of extractant to quantitatively remove contaminants from aqueous media. 0.20 g of modified silica (III) was equilibrated with a series of different concentrations (50-800 ppm) of chlorophenol solutions and the batch method was applied. Uptake capacity ( $q_e$ ) was calculated according to the Equation (2).

$$q = \frac{(C_i - C_e) \times V}{m} \quad (2)$$

**Table 1.** Comparison of various materials for the adsorption of phenol and its derivatives.

Adsorbent	Capacity (mg/g)
Calgon Filtrasorb 400 Carbon [31]	300
Activated carbon [32]	136.2
Amberlite XAD-16 [33]	291.6
Granular Activated Carbon [34]	40
Porous magnetic resin-g-chitosan beads [35]	97
Multiple walled carbon nanotubes (MWNT) [36]	133

**Figure 6.** Effect of modified silica (III) dosage on chlorophenol uptake from aqueous media.**Figure 7.** Variation in capacities of modified silica (III) (mg/g) as a function of chlorophenol initial concentrations (ppm).

where  $V$  is the solvent volume (L),  $m$  is the weight of extractant (g), and  $C_i$  and  $C_e$  are the initial and equilibrium concentrations of chlorophenol in the aqueous solution, respectively.

It was observed that the uptake capacity of modified silica (III) increases as the initial concentration of chlorophenol increases till it reaches maximum at 450 ppm (Figure 7). This trend indicates that the binding sites of modified silica (III) are incapable to interact any further with free chlorophenol molecules in solution. The maximum uptake capacity of modified silica (III) is 229 mg/g. It is worth mentioning that chlorophenols were not extracted with activated silica (I) and modified silica (II). The results show that modified silica (III) has a high uptake capacity for chlorophenol which is bigger or similar to the other materials reported in the literature (Table 1).

### 3.4. Effect of pH

A series of 450 ppm chlorophenol solutions were transferred into glass stoppered bottles and the pH was adjusted to the desired value (2-12) with 0.1 M HCl or 0.1 M NaOH solutions. 0.20 g of modified silica (III) was added into each bottle and the mixtures were stirred for 30 minutes. An inspection of Figure 8 indicates that the removal of chlorophenols by modified silica (III) slightly increased when the pH of solution increased from 2.0 to 10.0. Further increase in pH of the media shows a minor decrease in the percentage of removal of chlorophenols. This may be attributed to the competition between hydroxide ions and chlorophenols.

### 3.5. Effect of temperature

Extraction experiments are conducted at various temperatures in the range of 288 to 308 K. The uptake capacities of modified silica (III) for the chlorophenols at different temperatures are shown in Figure 9. The results show that the capacity for chlorophenols rises by increasing the temperature of the solution.

This method was also used to study the thermodynamics of the extraction process. Gibbs free energy ( $\Delta G^\circ$ ) was calculated using the Equation (3).

$$\Delta G^\circ = -RT \ln K_d \quad (3)$$

where,  $R$  is the universal gas constant (8.314 J/mol.K),  $T$  is the temperature (K) and  $K_d$  is defined by the equation:

$$K_d = C_a/C_e \quad (4)$$

where  $C_a$  is the chlorophenol ion concentration removed from solution at equilibrium and  $C_e$  is the equilibrium chlorophenol concentration in solution. Furthermore, the enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) parameters were calculated from the slope and intercept of the plot of  $\ln K_d$  vs.  $1/T$  respectively by using Van't Hoff equation [37]:

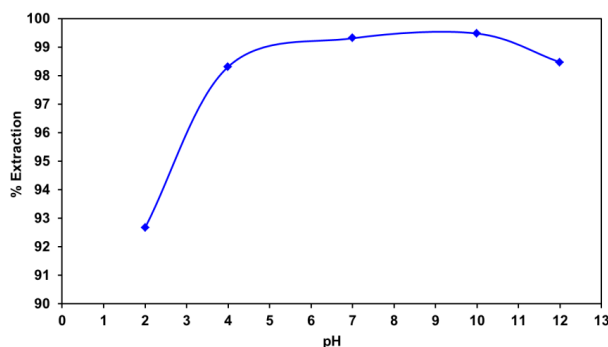
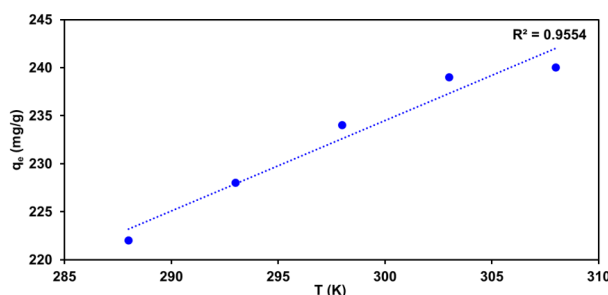
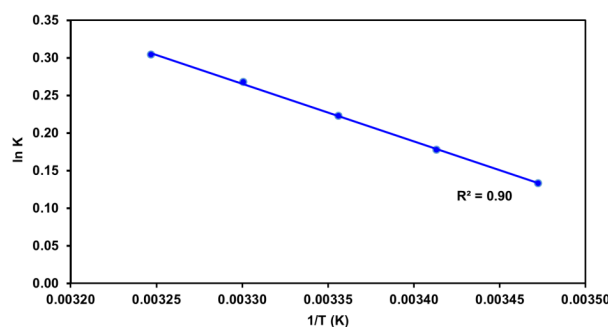
$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

The results obtained are presented in Figure 10 and Table 2.

The positive value of standard enthalpy (6.375 kJ/mol) indicates that the uptake of chlorophenol by modified silica (III) is an endothermic process which explains the fact that uptake efficiency increases with increase in temperature.

**Table 2.** Thermodynamic parameters for chlorophenol uptake using modified silica (III) at different temperatures.

Parameter	T (K)				
	288	293	298	303	308
$K_d$	1.142	1.195	1.250	1.307	1.350
$\Delta G^\circ$ (KJ/mol)	-0.319	-0.434	-0.552	-0.675	-0.779
$\Delta H^\circ$ (kJ/mol)			6.375		
$\Delta S^\circ_{\text{calculated}}$ (J/mol.K)			23.25		
$\Delta S^\circ_{\text{experimental}}$ (J/mol.K)			23.23		

**Figure 8.** Effect of solution pH on the % extraction of chlorophenol from aqueous media.**Figure 9.** Effect of temperature on the removal of chlorophenol from aqueous media.**Figure 10.** Van't Hoff plot of chlorophenol extraction with modified silica (III) from aqueous medium.

The positive standard entropy change (23.23 J/mol.K) suggests the increase in randomness at the solid-liquid interface.

### 3.6. Effect of contact time and uptake kinetics

Modified silica (III) (0.20 g) were equilibrated with 50 mL samples of 450 ppm chlorophenol solution in glass-stoppered bottles for a fixed period of time (0.5-60 minutes). It can be observed that the rate of uptake of chlorophenols from aqueous media is fast at the beginning (first 5 minutes) and then diminished gradually with time until equilibrium is reached after 15 minutes (Figure 11). The concentration difference between the chlorophenol solution and the surface of modified silica (III) accelerates the diffusion process of these molecules from the liquid-phase to solid, causing the fast increase of uptake in initial stage [38]. The initial fast uptake

rate may be also attributed to the availability of accessible binding sites on the surface of modified silica (III). The slow uptake in the later stages is probably due to the less availability of binding sites for interaction with chlorophenols.

The mechanism of chlorophenol uptake by modified silica (III) was analyzed by fitting experimental data to the pseudo-first-order (Equation 6) [39], and the pseudo-second-order (Equation 7) [40] kinetic models.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

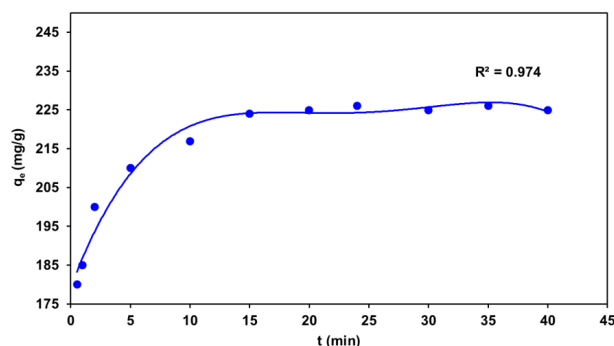
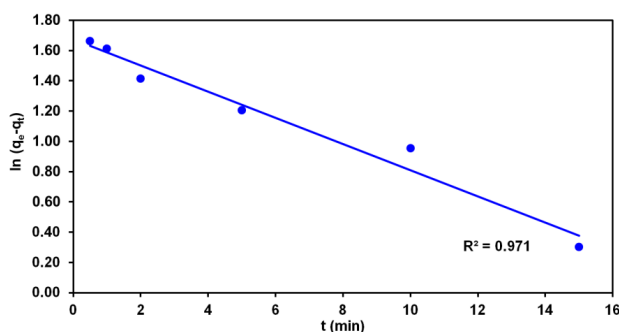
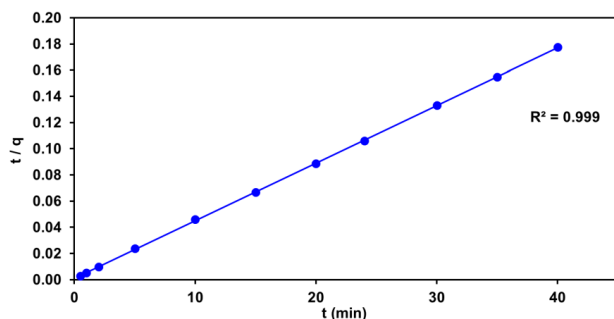
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where  $q_e$  and  $q_t$  are the amounts of chlorophenol removed (mg/g) at equilibrium and at time  $t$  (min), respectively.



**Table 3.** Pseudo-first order and second order constants for chlorophenol uptake by modified silica (III) at 298 K. (cal. = Calculated; exp. = Experimental).

$C_i$ (ppm)	$q_e$ , exp. (mg/g)	Pseudo-first order rate constants			Pseudo-second order rate constant		
		$k_1$ (1/min)	$q_e$ , cal. (mg/g)	$r^2$	$k_2$ (g/min.mg)	$q_e$ , cal. (mg/g)	$r^2$
450.0	229.16	0.0866	5.338	0.971	0.016	227.27	0.999

**Figure 11.** Effect of contact time on chlorophenol removal from aqueous media by modified silica (III) at 298 K.**Figure 12.** Pseudo-first order kinetics for chlorophenol uptake by modified silica (III) at 298 K.**Figure 13.** Pseudo-second order kinetics for chlorophenol uptake by modified silica (III) at 298 K.

$k_1$  (1/min) is the pseudo-first-order rate constant and  $k_2$  (g/mg min) is the pseudo-second-order rate constant; The values of  $k_1$  and  $q_e$  were calculated from the slope and intercept of the plot of  $\ln(q_e - q_t)$  vs.  $t$ , respectively. Likewise, the values of  $q_e$  and  $k_2$  were calculated from the slope and intercept of the plot of  $(t/q_t)$  vs.  $t$ , respectively.

The experimental value of  $q_e$  obtained from pseudo-first-order kinetic (Figure 12) is different from the calculated  $q_e$  value. In contrast, pseudo-second-order plot fitted data very well (Figure 13). The constants of pseudo first-order and pseudo second order models are given in Table 3. The correlation coefficients ( $R^2$ ) indicate that the uptake processes could be well defined by pseudo-second-order model under the experimental conditions. In addition, there is a high agreement between the calculated and experimental capacity values obtained from the pseudo-second-order kinetic model. This shows that chemical interaction is the rate-controlling step [41]. This also suggests that the number of binding sites on the silica surface and the number of chlorophenol

molecules in the liquid phase together determine the rate of uptake [42].

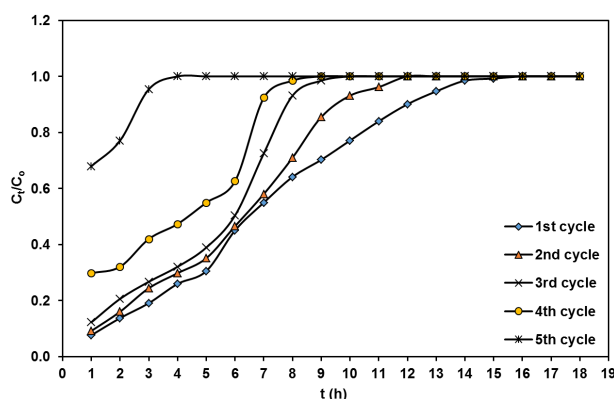
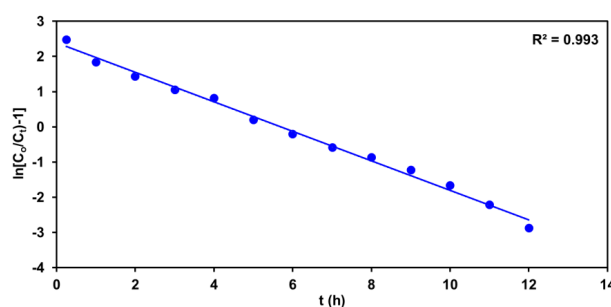
### 3.7. Column studies

Modified silica (III) was practically tested *via* column uptake studies. The plot  $C_t/C_0$  vs  $t$  produced the breakthrough curve (Figure 14). The breakthrough time and exhaustion time was found to be 5 and 14 hr, respectively. The maximum column capacity,  $q_{total}$  (mg/g) for a given flow rate and inlet concentration is equal to the area under the plot of the adsorbed chlorophenol concentration,  $C_{ad}$  (mg/L) vs time ( $t$ , min) and is determined from Equation 8 [43]:

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ads} dt = \frac{QA}{1000} \quad (8)$$

**Table 4.** Calculated column kinetic parameters for chlorophenol uptake on modified silica (III).

Model	Parameter		
Thomas	$r$	$q_t$ (mg/g)	$r^2$
	0.932	6.411	0.993
Yoon-Nelson	$k_{YN}$ (1/h)	$\tau_{YN}$ (h)	$r^2$
	0.416	6.68	0.994
Yan et al. [44]	$k_y$ (mL/h.mg)	$q_y$ (mg/g)	$r^2$
	23.63	0.40	0.985

**Figure 14.** Column breakthrough curve for the uptake of chlorophenol onto modified silica (III).**Figure 15.** Linear plot of the Thomas model for the removal of chlorophenol by modified silica (III).

where  $Q$ ,  $A$  and  $t_{total}$ , are the volumetric flow rate (ml/min), the area under the breakthrough curve and the total flow time (min) respectively. The capacity of the modified silica (III) column for chlorophenol was found to be 7.8 mg/g. The uptake capacity of removal of chlorophenols by column technique is lower than that obtained by batch uptake studies. This may be attributed to the fact that the extraction of chlorophenols by column technique depends on several factors such as the flow rate of the mobile phase and the type and amount of mobile and stationary phases [28].

In this study, three models (Thomas, Yoon and Nelson and Yan *et al.*) were applied to describe kinetic studies. The linearized form of Thomas mode [44] is expressed as follows:

$$\ln\left[\left(\frac{C_0}{C_e}\right)-1\right] = \left(\frac{K_t q_T M}{Q}\right) - (K_t C_0 t) \quad (9)$$

where  $q_T$  is the maximum capacity of uptake (mg/g),  $C_0$  and  $C_e$  are the inlet and outlet concentrations (mg/L) of chlorophenol respectively,  $Q$  is the volumetric flow rate (mL/min),  $K_t$  is the Thomas rate constant (mL/g.h), and  $M$  is the total mass of adsorbent.  $k_T$  (0.932 mL/mg.hr) and  $q_T$  (6.41 mg/g) were calculated from the slope and intercept of linear plot of  $\ln[(C_0/C_e)-1]$  vs  $t$  at a given flow rate (Figure 15). The results are given in Table 4. Thomas model indicates that the rate driving force obeys 2<sup>nd</sup> order reversible reaction kinetics.

The linearized form of Yoon-Nelson model is represented as follows:

$$\ln\left(\frac{C_e}{C_0 - C_e}\right) = K_{YN}t - \tau K_{YN} \quad (10)$$

where  $C_e$  and  $C_0$  are the effluent and influent concentrations,  $\tau$  is the time required for 50% adsorbate breakthrough (min),  $K_{YN}$  is Yoon-Nelson constant and  $t$  is the time (min). A plot of  $\ln[C_e/(C_0-C_e)]$  versus  $t$  provides a straight line with a slope of  $K_{YN}$ , and intercept of  $-\tau K_{YN}$  (Figure 16). The results are listed in Table 4. The High value of  $R^2$  indicates that Yoon-Nelson model also fits well to the experimental data.

The linearized form of Yan et al. model is expressed by the Equation (11) [44]

$$\ln\left[\left(\frac{C_e}{C_0 - C_e}\right)\right] = \left(\frac{K_y C_0}{Q}\right) \ln\left(\frac{Q^2}{K_y q_y m}\right) + \left(\frac{K_y C_0}{Q}\right) \ln t \quad (11)$$

where  $q_y$  is the maximum uptake capacity (mg/g) of adsorbent and  $k_y$  is the kinetic rate constant (mL/min.mg).  $k_y$  and  $q_y$  were calculated from the slope and intercept of the plot of  $\ln[C_e/(C_0-C_e)]$  vs.  $\ln t$  (Figure 17).

Both Thomas ( $R^2 = 0.993$ ) and Yoon-Nelson ( $R^2 = 0.994$ ) models show better fitting than Yan's model ( $R^2 = 0.985$ ). The highest sorbent capacity given by Thomas model is 6.41 mg/g which is consistent with that's calculated by integrated area method. The highest breakthrough time for 50% removal estimated by Yoon-Nelson model is around 6.68 h (Table 4).



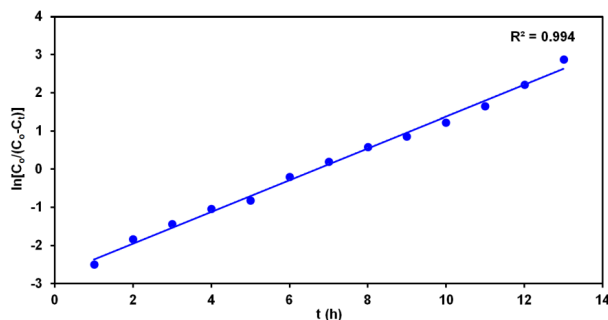


Figure 16. Linear plot of the Yoon-Nelson model for the removal of chlorophenol by modified silica (III).

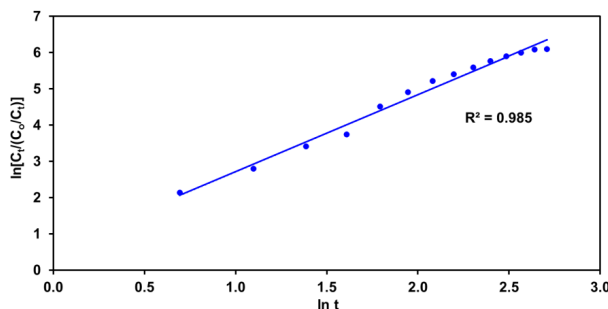


Figure 17. Linear plot of the Yan et al. model for the removal of chlorophenol by modified silica (III).

A useful extractant in wastewater treatment should have high uptake capacity for toxic pollutants and a good regeneration property. Regeneration of utilized modified silica (III) was done with 2.0 M HCl to desorb the attached chlorophenols followed by washing with distilled water [28]. Recycled silica (III) was used for consecutive five cycles for the removal of chlorophenols (Figure 14). The integration method was applied to calculate the maximum uptake capacity after first regeneration and it is determined to be 7.3 mg/g. This implies that modified silica (III) may be suitable adsorbent for chlorophenol removal from wastewater. The uptake capacity of regenerated modified silica (III) was not significantly reduced in the first four cycles. Then in the fifth cycle, capacity significantly decreased (0.32 mg/g), the breakthrough curve became steeper and the breakthrough happened faster.

#### 4. Conclusion

Based on the results obtained in this study, calixpyrrole modified silica(III) was confirmed as an effective extractant for 4-chlorophenols. The removal efficiency was dependent on experimental parameters such as the amount of extractant, contact time, pH, initial concentration of chlorophenol and temperature. This material showed high uptake capacity (229 mg/g) for chlorophenol in aqueous solution which suggests the possibility of using this material in wastewater treatment. Thermodynamic studies indicated that the extraction process is endothermic and has a spontaneous nature. The uptake rate for chlorophenol was obtained to be conforming to the pseudo-second order kinetic model. The chemical stability of the modified silica (III) in acidic media, as well as the regeneration by washing with 2.0 M HCl, allowed the reuse of this material for many cycles.

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#### Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Author contributions: All authors contributed equally to this work.

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

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