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## **Study on the Application of Cucurbit[6]uril as a Nanoporous Adsorbent for the Removal of 2,4-Dinitrophenol from Wastewaters**

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In the present study, cucurbit[6]uril was used as a nanoporous adsorbent for the removal of 2,4-dinitrophenol from aqueous solutions. The experiments were carried out in a batch system to optimize operation variables such as pH of solution, contact time, adsorbent dose and salt concentration. Langmuir, Freundlich and Tempkin isotherms were applied for the explanation of experimental data. The high removal yield was achieved at the real pH, 0.02 g of adsorbent dose and 10 min of contact time. The equilibrium adsorption was best described by the Langmuir isotherm model. The maximum monolayer adsorption capacity was found at 29.85 mg g<sup>-1</sup> for 2,4-dinitrophenol at 25 °C. The kinetics study showed that the adsorption process could be described by pseudo-second order rate equation, and equilibrium was achieved after 10 min. The thermodynamic parameters indicated that the adsorption of 2,4-dinitrophenol on the cucurbit[6]uril is an endothermic and spontaneous process. The results of the present study confirm the applicability of small amount of this adsorbent for efficient removal of 2,4-dinitrophenol from wastewater samples in short reasonable time.

**Keywords:** Cucurbit [6]uril, Nonporous, 2,4-Dinitrophenol, Langmuir, Removal

### **INTRODUCTION**

The presence of the phenol and its derivatives in waste effluent streams is of growing concern due to their high toxicity. Amongst the phenol derivatives, 2,4-dinitrophenol (DNP) is one of the highly toxic compounds and widely used in the production of pesticides, dyes, explosives, and preservatives [1,2]. However, this compound is associated with some undesirable properties like irritation of the eyes, skin and respiratory tract and may cause inflammation of those parts [3]. The United States Environmental Protection Agency (USEPA) listed DNP as one of the toxic pollutants; therefore, treatment of wastewater containing DNP has become inevitable before being discharged into the receiving water bodies. Furthermore, the USEPA

recommends restricting its concentration in natural waters below 10 ng l<sup>-1</sup> [4,5].

In recent years, various technologies have been developed to decrease the concentration of 2,4-dinitrophenol (2,4-DNP), such as, chemical and electrochemical oxidation [6,7], biodegradation and photocatalytic degradation [8-10], membrane filtration [11,12], *etc.* Among all available methods, adsorption is very effective method for treatment of wastewater and is still constantly investigated and developed due to its low initial cost, simplicity of design and ease of operation. Literature reports many research studies/results concerning the removal of 2,4-DNP by activated carbon adsorption, due to high surface area, well-developed pore structure and surface properties of carbon. Nonetheless, its application for wastewater treatment is limited due to economic objectives, namely high cost and need for regeneration [13-15]. Lately,

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Researchers have been interested the preparation of novel adsorbents to replace conventional activated carbon in removal of 2,4-DNP. Hence, many investigations were performed on the applicability of cucurbit[6]uril as an alternative adsorbent for the removal of 2,4-dinitrophenol.

In spite of its first report in 1905, recently, cucurbit[n]urils (CB[n]s) have been widely investigated as novel molecular hosts [16,17]. Similar to cyclodextrins, crown ethers, and calixarenes, CB[n]s have been greatly examined for their binding ability with various guests [18, 19]. CB[n]s can form various complexes *via* H-bonds and  $\pi$ - $\pi$  interactions [20]. Furthermore, self-assemblies based on the “outer-surface interactions of CB[n]s have been attributed to their ability to form weak non-covalent interactions such as hydrogen bonding and  $\pi$ - $\pi$  stacking, as well as C-H $\cdots\pi$  and ion-dipole interactions [21].

Most recently, the synthesis of functionalized derivatives has progressed, and among the manifold applications, cucurbituril-catalyzed reactions are receiving increasing attention [22,23]. Meanwhile, cucurbit[6]uril (CB[6]) is a hexameric macrocyclic compound self-assembled from an acid-catalyzed condensation reaction of glycoluril and formaldehyde (Fig. 1). The rigid structure and capability of forming stable complexes with molecules and ions also make CB[6] attractive as a building block for the construction of supramolecular architectures [16].

The aim of this study is to collect general knowledge about CB[6] concerning its application in water treatment, and, more specifically, to investigate its potential for the treatment of wastewater containing 2,4-dinitrophenol. The effects of various experimental parameters on adsorption process including solution pH, contact time, adsorbent dose and salt concentration are studied. The equilibrium data are analyzed using various adsorption isotherm models. In addition, thermodynamic and kinetics of the adsorption process are studied and discussed in details.

## EXPERIMENTAL

### Apparatus

FT-IR measurements were performed by Fourier transform infrared spectrophotometer (BOMEM MB-Series 1998) using KBr background in the range of 400-4000  $\text{cm}^{-1}$ . Thermal stability of the adsorbent was examined by Bahr,

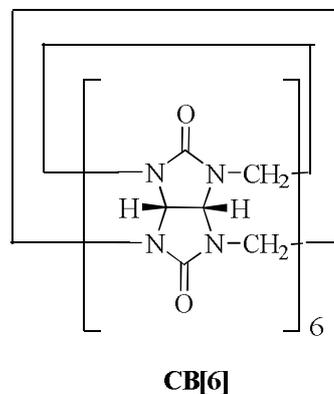


Fig. 1. CB[6] chemical structure.

SPA 503 Thermo-gravimetric Analyzer (TGA) at heating rate of 10  $^{\circ}\text{C min}^{-1}$  over the temperature range of 40-600  $^{\circ}\text{C}$ . TEM images were recorded *via* Zeiss EM900 Transmission Electron Microscope. AFM images were obtained using a Nano Wizard II instrument. Recording the spectra and the absorbance measurements were made by a model Lambda-35 spectrophotometer (Perkin Elmer) with quartz cells. An ultrasonic bath with heating system (LC30H, Sunway Scientific Corporation, Taiwan) at 40 kHz of frequency and 130 W of power was used for the scattering of adsorbent in aqueous or real samples. Jenway pH meter model 3520 was used to measure pH with a combined glass electrode. To separate the phases, an ELE centrifuge (Iecentra-CLD) was used.

### Reagents

All chemicals were of analytical grade and double distilled water was used throughout. 2,4-Dinitrophenol was purchased from Merck (Darmstadt, Germany) and a stock solution of 100  $\mu\text{g ml}^{-1}$  was prepared in water, and working standard solutions were prepared daily by successive dilutions of this stock solution. Cucurbit[6]uril was synthesized according to literature [24]. pH adjustments were performed with 0.001-0.1 M HCl and NaOH (Merck) solutions.

### General Removal Procedure

The adsorption of 2,4-DNP from aqueous solution by CB[6] adsorbent were conducted using the batch method. Briefly, 0.02 g of CB[6] was added to a 10 ml solution of

2,4-DNP ( $10 \mu\text{g ml}^{-1}$ ). This solution was placed under ultrasonic action to reduce the aggregation of nanoparticles for 60 s. Following that, the contents were kept under continuous stirring for 10 min. The resultant suspension was centrifuged and the concentration of remaining 2,4-DNP was determined spectrophotometrically by measuring the absorbance of the supernatant solution at 361 nm. The percentage of 2,4-DNP was calculated using the following equation:

$$\%R = ((C_0 - C_t)/C_0) \times 100 \quad (1)$$

where R is the removal efficiency of the 2,4-DNP,  $C_0$  and  $C_t$  represent the initial and final (after adsorption) analyte concentrations in  $\mu\text{g ml}^{-1}$ , respectively.

## RESULTS AND DISCUSSION

### Characterization of Cucurbit[6]uril

The cucurbit[6]uril nanoporous adsorbent was characterized by FT-IR, TEM, AFM and TGA analyses. The FT-IR spectra of the synthesis CB[6] is shown in Fig. 2. The broad peak located at  $3400 \text{ cm}^{-1}$  is attributed to absorbed water, while peaks at  $2930$  and  $1474 \text{ cm}^{-1}$  correspond to  $-\text{CH}_2$  stretching vibration and bending vibration, respectively.

The TEM image of CB[6] in Fig. 3 shows particles of adsorbent are under 15 nm in size. In addition, this finding is supported by AFM image in relationship with the particle size as well as size distribution of the nanoparticles. As can be seen in Fig. 4, mean size of the particles in a  $2 \mu\text{m} \times 2 \mu\text{m}$  square is 11.9 nm.

Heat stability of CB[6] was appraised *via* TGA analysis. As shown in Fig. 5, the weight loss process is observed in one stage during the range of temperature. This stage occurs from  $400 \text{ }^\circ\text{C}$  to about  $500 \text{ }^\circ\text{C}$ , which is related to the degradation of CB[6]. So, we can utilize CB[6] as adsorbent, under  $400 \text{ }^\circ\text{C}$  without the risk of decomposition.

### Effect of pH

In order to evaluate the influence of pH parameter on the adsorption of 2,4-DNP, the experiments were carried out in the pH range of 2-12. The pH of the solutions was adjusted by NaOH and HCl using a pH meter. The results

indicated that removal of 2,4-DNP is almost constant in the range of 3-9 and is decreased in strong acidic and alkali media. This phenomenon may be assigned to the protonation or deprotonation of the functional groups on the surface of CB[6] in acidic and alkali media. So, in order to mimic potential industrial practice the solutions of 2,4-DNP were not buffered.

### Effect of Adsorbent Dose

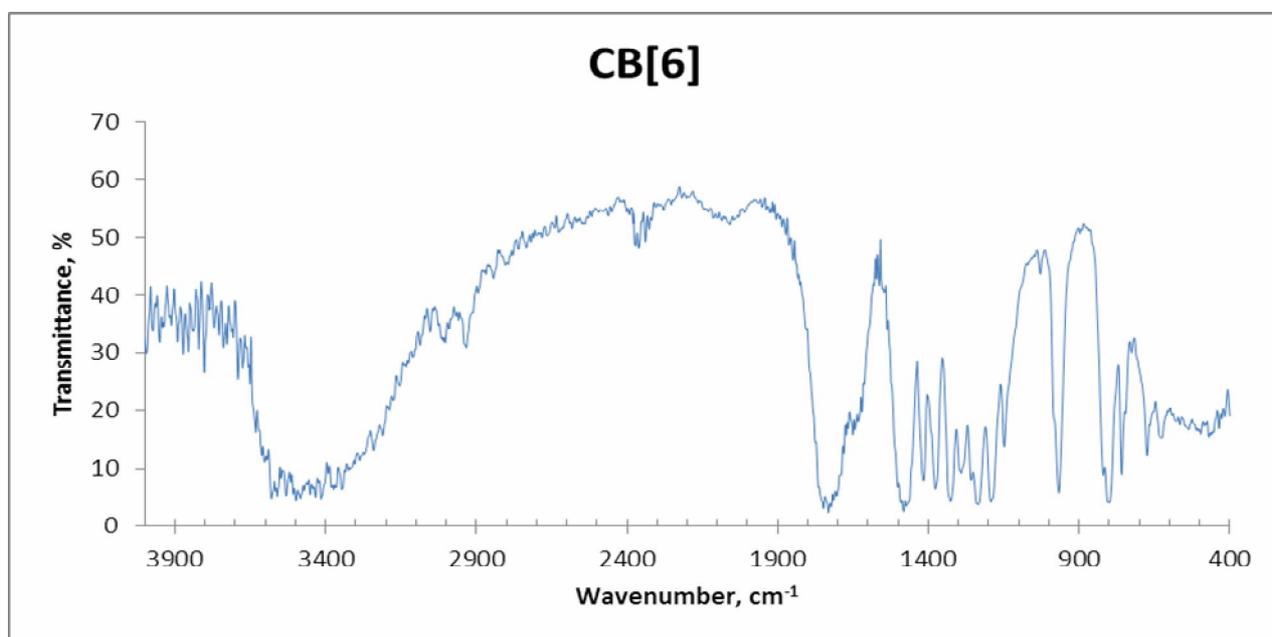
The dependence of the 2,4-DNP adsorption on the CB[6] dose at room temperature was studied. So, the adsorbent amount was varied from 0.0025 g to 0.0250 g per 10 ml, while initial 2,4-DNP concentration was held constant. As expected, the percentage of 2,4-DNP removal increased with increasing adsorbent dosage at the same initial concentration of 2,4-DNP. The experimental results of this investigation are shown in Fig. 6. The increase in analyte removal with the adsorbent dose can be attributed to the increased surface area and the adsorption sites. Thus, 0.02 g of CB[6] was selected as optimum dosage for the subsequent experiments.

### Effect of Salt Concentration

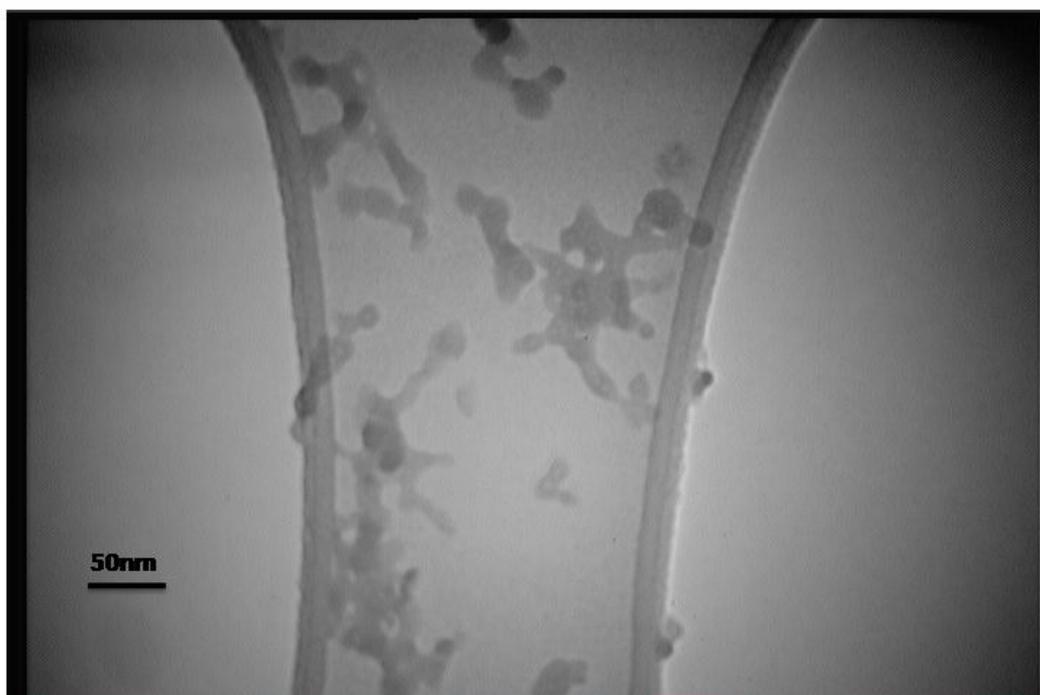
Based on knowledge, ionic strength (salt concentration) influences both electrostatic and non-electrostatic interactions between the adsorbate and the adsorbent surface. Hence, the effect of salt was investigated using standard solution containing NaCl of concentrations ranging from 0.05-0.35 M. It was observed that the removal efficiency was nearly constant by increasing the salt concentration, indicating that the presence of an electrolyte does not have significant effect on the removal process of 2,4-DNP.

### Effect of Contact Time

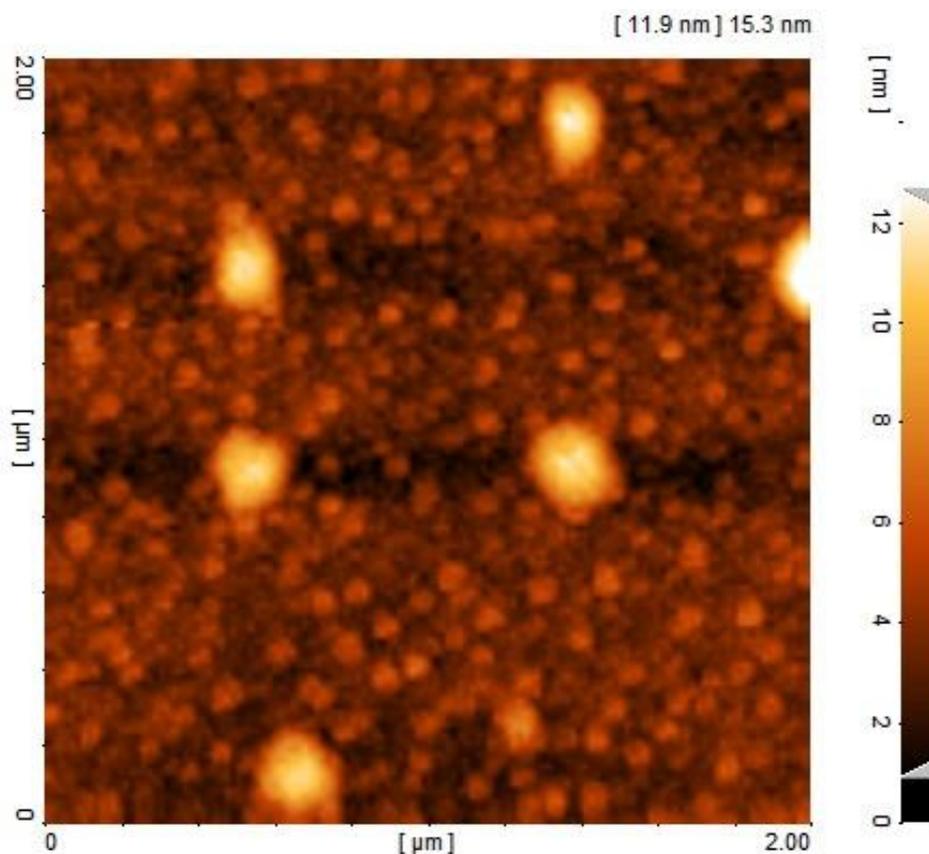
The adsorption is a time-dependent process; therefore, to determine the equilibrium time for maximum 2,4-DNP uptake, a contact time study was carried out. Experiments were performed for different contact times with a fixed adsorbent dose of 0.02 g for CB[6]. A graph of removal percentage versus contact time (Fig. 7) express the rapid adsorption of 2,4-DNP in the first 5 min; thereafter, the adsorption rate decreases gradually and adsorption reaches optimal removal up to 10 min, and it was almost constant



**Fig. 2.** FT-IR spectrum of CB[6].



**Fig. 3.** TEM images of CB[6].



**Fig. 4.** AFM image of CB[6].

after this value. It was found that there are enough adsorption sites in CB[6] for 2,4-DNP to be accommodated in a short time. Therefore, 10 min was selected as optimum contact time.

### Adsorption Isotherms

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The goal of the adsorption isotherms is to correlate the adsorbate concentration in the solution and the adsorbed amount of 2,4-DNP at the adsorbate-adsorbent interface. Several isotherm models are widely used by environmentalists to optimize a design of the adsorption system, such as Langmuir, Freundlich, Redlich-Peterson, Dubinin-Radushkevich, Sips and Temkin [25]. Since the more common models used to investigate

the adsorption isotherm are Langmuir, Freundlich and Temkin equations, the experimental results of this study were fitted with these three models.

The Langmuir isotherm assumes that intermolecular forces are decreased rapidly with distance and this leads to the prediction that the maximum adsorption capacity consists of a mono-layer type adsorption, where all sorption sites are identical and energetically equivalent [26]. The linear form of the Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (2)$$

where  $q_e$  is the amount of 2,4-DNP adsorbed per unit mass of adsorbent ( $\text{mg g}^{-1}$ ) and  $C_e$  is the equilibrium concentration of 2,4-DNP in solution ( $\text{mg l}^{-1}$ ),  $q_m$  is the maximum adsorption amount of 2,4-DNP per gram of

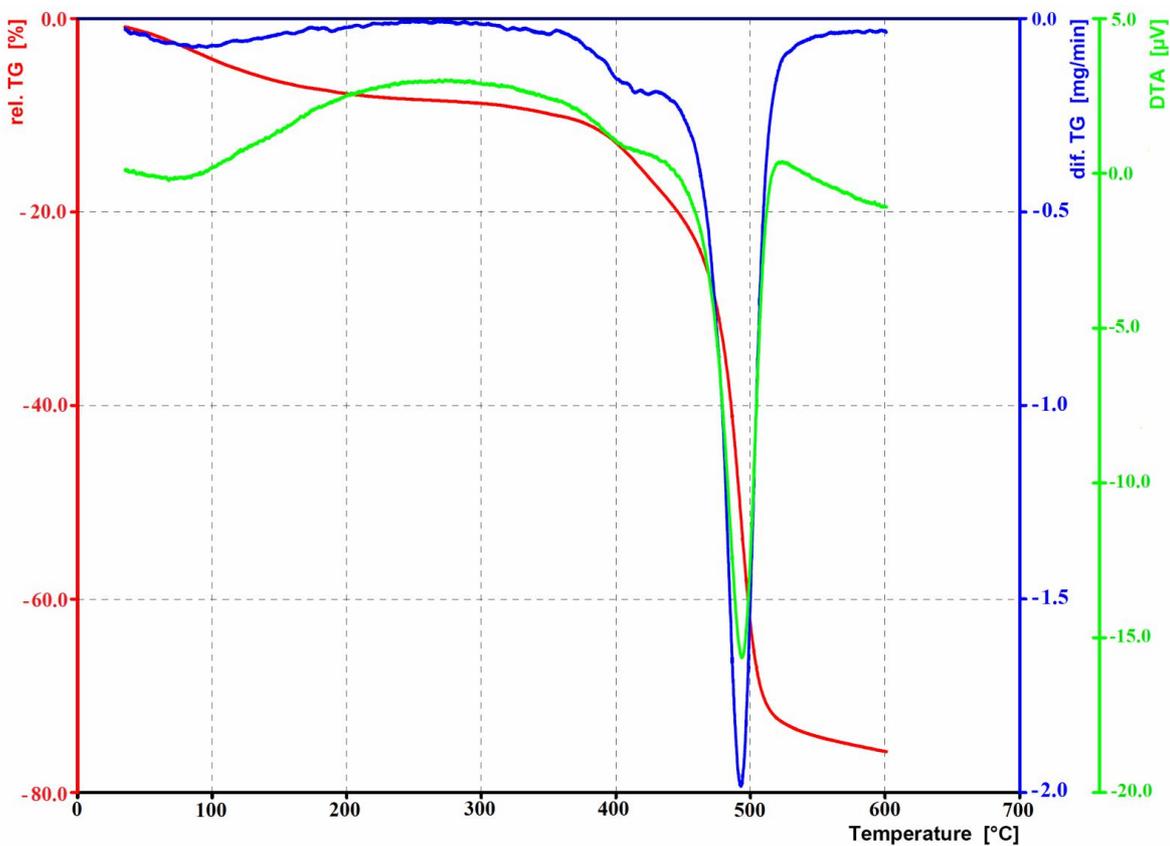


Fig. 5. Thermo-Gravimetric Analysis (TGA) of CB[6].

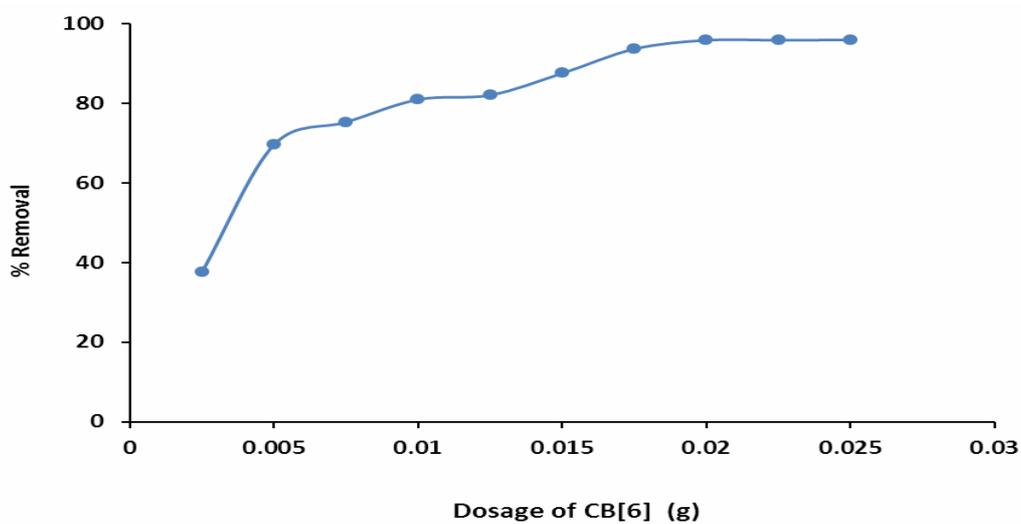


Fig. 6. Effect of adsorbent dose on the removal of 2,4-DNP.

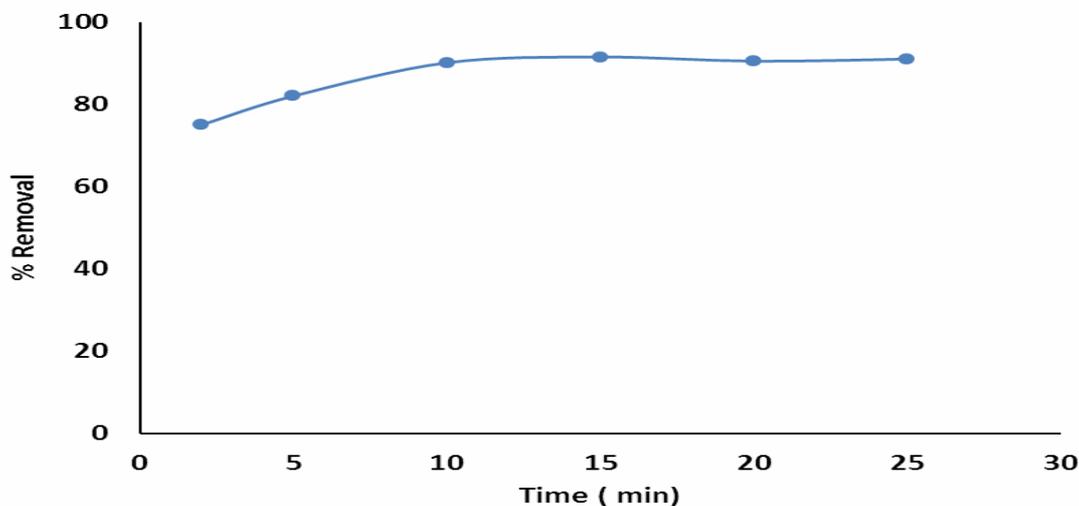


Fig. 7. Effect of contact time between 2,4-DNP and CB[6] .

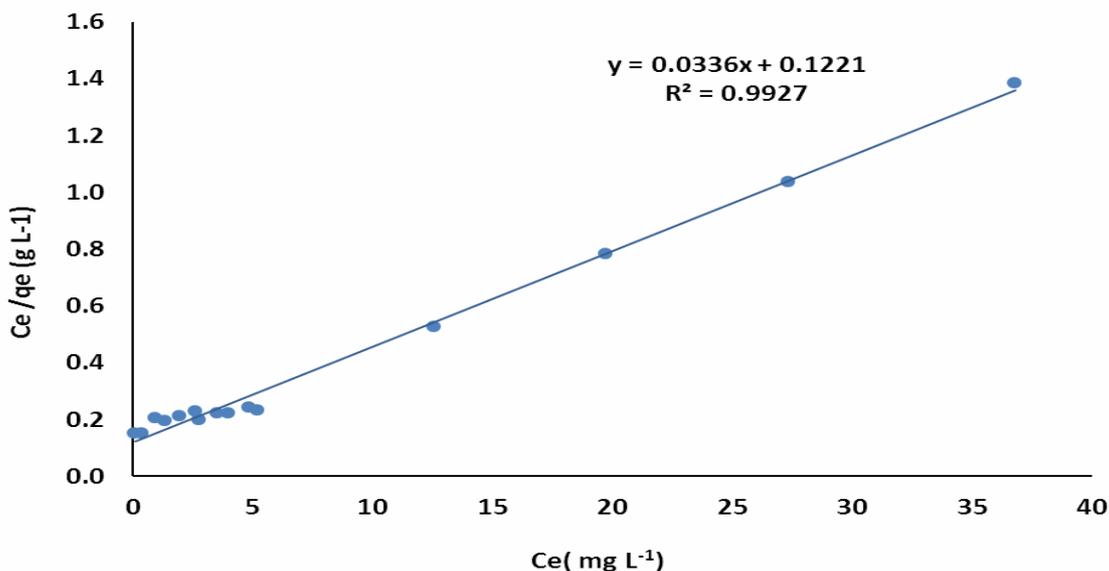


Fig. 8. The Langmuir isotherm for removal of 2,4-DNP.

adsorbent ( $\text{mg g}^{-1}$ ) and  $K_L$  is the Langmuir adsorption equilibrium constant ( $\text{l mg}^{-1}$ ). The Langmuir constants  $K_L$  and  $q_m$  are calculated from the slope and intercept of the plot of  $C_e/q_e$  versus  $C_e$ . The parameters of the Langmuir equation were calculated and are given in Table 1 indicating that the maximum adsorption capacity of CB[6] is 29.85

$\text{mg g}^{-1}$  for 2,4-DNP.

In contrast, the Freundlich isotherm is an empirical equation which is used to describe adsorption at multi layers and adsorption on a heterogeneous surface. It is suitable for high and middle range of solute concentration but not for low concentrations [27]. The Freundlich model in linear

**Table 1.** Isotherm Parameters for the Adsorption of 2,4-DNP onto CB[6]

Isotherm model	Parameter	Value
Langmuir isotherm	$q_m$ (mg g <sup>-1</sup> )	29.85
	$K_L$ (l mg <sup>-1</sup> )	0.275
	$R^2$	0.9927
Freundlich isotherm	$K_F$ [(mg g <sup>-1</sup> )/(mg l <sup>-1</sup> ) <sup>1/n</sup> ]	5.07
	$1/n$	0.6371
	$R^2$	0.8861
Tempkin isotherm	$K_T$ (l mg <sup>-1</sup> )	5.1
	$B$ (J mol <sup>-1</sup> )	5.29
	$R^2$	0.8701

**Table 2.** Kinetic Parameters of 2,4-DNP Adsorption onto CB[6]

Pseudo-first order			Pseudo-second order		
$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mg g <sup>-1</sup> )	$k_2$ [(g mg <sup>-1</sup> min <sup>-1</sup> )]	$R^2$
4.34	$7.4 \times 10^{-3}$	0.162	0.84	0.9974	

**Table 3.** Thermodynamic Parameters for the Adsorption of 2,4-DNP onto CB[6]

Sample	Temp. (K)	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (KJ mol <sup>-1</sup> )
2,4-Dinitrophenol	293	-108.7		
	298	-110.7		
	303	-112.7		
	308	-114.7	+9.4	+40.28
	313	-116.7		
	318	-118.7		
	323	-120.8		

form is given as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where  $C_e$  is the equilibrium concentration of 2,4-DNP solution ( $\text{mg l}^{-1}$ ),  $q_e$  is the equilibrium capacity of 2,4-DNP on the CB[6] adsorbent ( $\text{mg g}^{-1}$ ),  $K_F$  is a Freundlich constant related to adsorption capacity ( $\text{mg}^{1-(1/n)} \text{g}^{-1} \text{l}^{1/n}$ ) and  $1/n$  is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of material. The values of  $K_F$  and  $1/n$  calculated from the intercept and slope of the plot of  $\log q_e$  versus  $\log C_e$  are listed in Table 1. The correlation coefficient was found to be 0.8861.

The Tempkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage of the adsorbate molecules over adsorbent surface [27] and is expressed by the following equation:

$$q_e = B \ln K_T + B \ln C_e \quad (4)$$

where in  $B = RT/b$ ,  $T$  is the absolute temperature ( $K$ ),  $R$  is the universal gas constant,  $8.314 \text{ (J mol}^{-1} \text{ K}^{-1})$ ,  $K_T$  is the equilibrium binding constant ( $\text{l mg}^{-1}$ ) and  $B$  is related to the heat of adsorption. The constants obtained for Tempkin isotherm are shown in Table 1. As the results in Table 1 shows, the correlation coefficients for three isotherm models including: Langmuir ( $R^2 = 0.9927$ ), Freundlich ( $R^2 = 0.8861$ ) and tempkin ( $R^2 = 0.8701$ ) indicates that the data have a better fit with the Langmuir model. It was observed that the Langmuir isotherm provides a better model of the system for the adsorption of 2,4-DNP on CB[6].

### Adsorption Kinetics Study

The kinetic models were used to predict the variation of adsorbed analyte with time using adsorbent. To further study the adsorption behavior of 2,4-DNP onto CB[6], two well-known adsorption models, pseudo-first order and pseudo-second order adsorptions are adopted to study the adsorption kinetics [26]. The pseudo-first order model is defined by the equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2} \times 303t \quad (5)$$

where  $k_1$  is the pseudo-first order rate constant ( $\text{min}^{-1}$ ),  $q_e$  is the adsorption equilibrium capacity ( $\text{mg g}^{-1}$ ), and  $q_t$  is the amount of 2,4-DNP adsorbed ( $\text{mg g}^{-1}$ ) at various times ( $t$ ). The rate constant  $k_1$  and  $q_e$  were obtained from the slope and intercept of the linear plots of  $\log(q_e - q_t)$  against  $t$ , respectively.

The following equation stands for the linear form of the pseudo-second order model [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where  $q_e$  and  $q_t$  represent the amount of 2,4-DNP adsorbed per unit mass of the adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium at any time, and  $k_2$  is the rate constant of the pseudo-second order equation ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). The rate constant  $k_2$  and  $q_e$  were obtained from the slope and intercept of the linear plots of  $t/q_t$  against  $t$ , respectively. The resulting kinetic parameters, rate constants, and the adsorption at equilibrium for 2,4-DNP are listed in Table 2. As can be seen, the correlation coefficients of the pseudo-second-order kinetic model ( $R^2 = 0.9974$ ) were greater than that of the pseudo-first-order model ( $R^2 < 0.1$ ). However, it can be said that the adsorption fits to the pseudo-second-order better than the pseudo-first order kinetic model.

### Adsorption Thermodynamic

Adsorption thermodynamics can provide information on the inherent energy change of adsorbent after adsorption and also the mechanism involved in the adsorption process. So, we investigate the effect of temperature on the adsorption behavior of 2,4-DNP onto CB[6], by calculating the Gibbs free energy ( $\Delta G$ ), entropy change ( $\Delta S$ ) and enthalpy change ( $\Delta H$ ) using the Eqs. (7) and (8):

$$\ln \frac{q_{e2}}{q_{e1}} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

where  $q_e$  is the equilibrium adsorption capacity of CB[6] for 2,4-DNP ( $\text{mg l}^{-1}$ ),  $C_e$  is the equilibrium concentration of adsorbate in solution ( $\text{mg l}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  represents the temperature ( $K$ ).

**Table 4.** Comparison of the Adsorption Capacities of 2,4-DNP onto CB[6] with Different Adsorbents

Adsorbents	Maximum adsorption capacity (mg g <sup>-1</sup> )	Adsorbent dose (g)	Time	Ref.
Yellow bentonite	9.62	0.30	-	[13]
Carbon nanospheres	32.9	0.01	5 h	[28]
MIP-SiO <sub>2</sub>	15.7	0.02	12 h	[29]
Olive wood	5.80	0.05	24 h	[30]
Cotton cellulose C <sub>2</sub>	11.23	0.05	48 h	[31]
SilprImCl <sup>a</sup>	33.32	-	4 h	[32]
SilprM <sub>4</sub> ImCl <sup>b</sup>	35.90	-	4 h	[32]
SilprM <sub>1</sub> M <sub>2</sub> ImCl <sup>c</sup>	37.00	-	4 h	[32]
CB[6]	29.85	0.02	10 min	This work

<sup>a</sup>Imidazole-modified silica. <sup>b</sup>4-Methylimidazole-modified silica. <sup>c</sup>1,2-Dimethylimidazole,-modified silica.

**Table 5.** Recovery Tests for Removal of Spiked 2,4-DNP in Real Water Samples by CB[6]

Sample	Added 2,4-dinitrophenol (mg l <sup>-1</sup> )	Recovery (%)
Mino Island water	0.5	79.0
Arvand River wate	0.5	97.8
Abadan refinery wastewater	0.5	98.3

The calculated values for the changes of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are shown in Table 3. The negative values of  $\Delta G$  and increasingly negative values with increasing temperature confirm the spontaneous nature and feasibility of adsorption reactions at higher temperature. Positive values of  $\Delta H$  reflect the endothermic nature of adsorption of 2,4-DNP on CB[6]. The positive values of  $\Delta S$  shows the increased disorderness and randomness at the solid-liquid interface of 2,4-DNP with CB[6] that bring about some structural changes in 2,4-DNP and CB[6]. The improvement of adsorption capacity of CB[6] at higher temperatures was

attributed to the expansion of pore size and activation of the adsorbent surface.

### Comparison with other Methods

The performance of the proposed method was compared with other methods. Adsorption capacities of 2,4-DNP on various adsorbents were summarized in Table 4. It can be concluded that the contact time, adsorbent amount and adsorption capacity of cucurbit[6]uril nonporous adsorbent in comparison with the reported adsorbents in the literature are preferable and superior, and shows satisfactory

removal performance for 2,4-DNP.

### Removal of 2,4-Dinitrophenol from Aqueous Solutions

To evaluate the accuracy and applicability of the proposed method, the removal procedure of 2,4-dinitrophenol in real samples were examined using Mino Island water, Arvand River water and Abadan refinery wastewater. The analytical results, along with the recoveries for the spiked samples, are given in Table 5. It is seen that under optimized conditions above 92% of the 2,4-DNP can be removed from the solutions.

Therefore, it could be concluded that cucurbit[6]uril could effectively remove 2,4-dinitrophenol from water and wastewater samples.

### CONCLUSIONS

In the present study, cucurbit[6]uril was considered as a novel, effective and low cost nonporous adsorbent for the removal of 2,4-dinitrophenol from aqueous solutions. The experimental factors such as solution pH, contact time, adsorbent dose, salt concentration, adsorption kinetic and isotherm models were investigated to study the adsorption process.

The kinetic studies showed that the 2,4-DNP adsorption process followed pseudo-second order kinetics models. The isotherm adsorption data were well fitted by the Langmuir model. The experimental data fitted to Langmuir isotherm showed that the adsorption capacity is 29.85 mg of analyte per gram of adsorbent which is comparable or better than some of the previously reported adsorbents for removal of 2,4-DNP. Furthermore, thermodynamic analysis reveals that the removal of 2,4-DNP from aqueous solution by CB[6] was a spontaneous and endothermic process over the temperature range considered. Finally, utilizing of this system could be a promising candidate for the successful removal of 2,4-DNP from water and wastewater samples.

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