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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

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REMOVAL OF *p*-NITROPHENOL FROM AQUEOUS SOLUTIONS USING AMINOPROPYL SILICA GEL-IMMOBILIZED CALIX[4]ARENE POLYMER (C[4]APS)

ABSTRACT

This study describes the preparation of a new polymeric calix[4]arene derivative and its application as a sorbent material in adsorption of *p*-nitro phenol (PNP). Thus after the preparing of the precursor calixarene derivatives (**1-5**), compound **5** was immobilized onto aminopropyl silica gel supporting material to obtain polymeric calix[4]arene (**6**). All compounds were characterized by using some methods such as FTIR, ^{1}H NMR, elemental analysis, TGA and SEM. Aminopropyl silica gel-immobilized calix[4]arene (C[4]APS) **6** was used as a sorbent in the adsorption studies of PNP and it was examined some parameters such as pH, contact time, initial concentration, process temperature and sorbent dosage. The results showed that pH 6, contact time 1 hour, the concentration of 5.0×10^{-5} M PNP, 0.025 g of sorbent dosage and 25^{o}C of temperature was found as optimum parameters of PNP adsorption by **6**. Also Langmuir and Freundlich isotherms were evaluated to clarify the PNP adsorption mechanism.

Keywords: Aminopropyl silica gel (APS), Adsorption, *p*-nitro phenol (PNP), Polymeric calix[4]arene.

AMİNOPROPİL SİLİKAJEL İMMOBİLİZE KALİKS[4]AREN POLİMERİ (K[4]APS) KULLANILARAK *p*-NİTROFENOLÜN SULU ÇÖZELTİLERDEN GİDERİMİ

ÖZ

Bu çalışma yeni polimerik kaliksaren türevinin hazırlanması ve *p*-nitrofenolün (PNF) adsorpsiyonunda sorbent malzemesi olarak uygulanmasını içermektedir. Kaliksaren türevleri **1-5**'in hazırlanmasından sonra, **5** no'lu moleküle aminopropil silika jel destek maddesi tutturularak polimerik kaliksaren **6** türevi elde edildi. Bütün bileşikler, FTIR, ^{1}H NMR, elemental analizi, TGA ve SEM gibi metotlar kullanılarak karakterize edildi. Aminopropil silika jel immobilize kaliks[4]aren (K[4]APS) **6**, PNF adsorpsiyonu çalışmalarında sorbent olarak kullanılmış ve pH, etkileşim süresi, konsantrasyon, proses sıcaklığı ve sorbent dozajı gibi parametreler çalışıldı. Sonuçlara göre, **6** no'lu molekülün PNF adsorpsiyonu için optimum koşullar pH 6, etkileşim süresi 1 saat, PNF konsantrasyonu 5.0×10^{-5} M, sorbent dozajı 0.025g ve proses sıcaklığı 25^{o}C olarak bulundu. PNF adsorpsiyon mekanizması, Langmuir ve Freundlich izotermleri ile değerlendirildi.

Anahtar Kelimeler: Aminopropil silika jel (APS), Adsorpsiyon, *p*-nitrofenol (PNF), Polimerik kaliks[4]aren.

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1. INTRODUCTION

Many developing in industry has brought to a plenty of new products and services. This advancement causes not only producing useful technology but also more usage of chemicals. As is known to all, many of processes involved chemical which are adequately harmful to the human health and environment when released. Most chemical contaminants are known as organic origin (Nayak and Singh 2006). Among of organic molecules, phenolic compounds are a class of the most contaminants in wastewaters, being generated from petroleum and petrochemical, coal conversion, and phenol-producing industries. Phenols are considered as priority pollutants due to their harmful affect to organisms even at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health (Banat et al. 2000). According to USEPA (US Environmental Protection Agency), phenolic compounds constitute the 11th of the 126 chemicals, which have been designated as priority pollutants (Caturla et al. 1987). The removal of phenol from aqueous solutions can be succeed via many methods such as adsorption, chemical precipitation, ion exchange, membrane processes, etc. (Al-Asheh et al. 2003). Among these methods, adsorption has increasingly received more attention in recent years because the method is simple, relatively low-cost and effective in removing organic contaminant, especially at medium to low metal ion concentrations and from wastewaters (Tabakci and Yilmaz 2008).

Macromolecules are widely used in host-guest chemistry for the construction of various receptors for charged or neutral molecules. Calix[n]arenes (Fig. **1**) are cyclic oligomers composed of phenol units and are very well known as attractive and excellent ionophores because they provide a unique three-dimensional structure with almost unlimited derivatization possibilities (Gutsche 1998; Asfari et al. 2001). A polar lower rim composed of phenolic oxygens has been extensively derivatized to bind and transport ionic species. The upper rim is a shallow bowl lined with aromatic rings that can encapsulate small organic molecules or a polar part of larger compounds (Memon et al. 2003). In the past decade, these compounds have been widely used in supramolecular chemistry as building blocks or molecular scaffolds for the construction of receptors towards ions or neutral molecules (Yilmaz 2009).

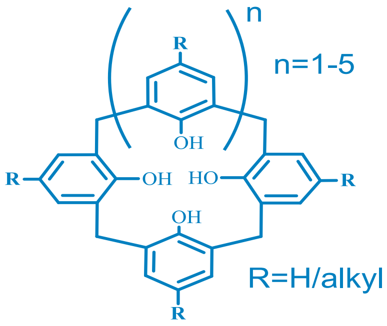


Fig. 1. The general view of calix[4]arenes molecular structure

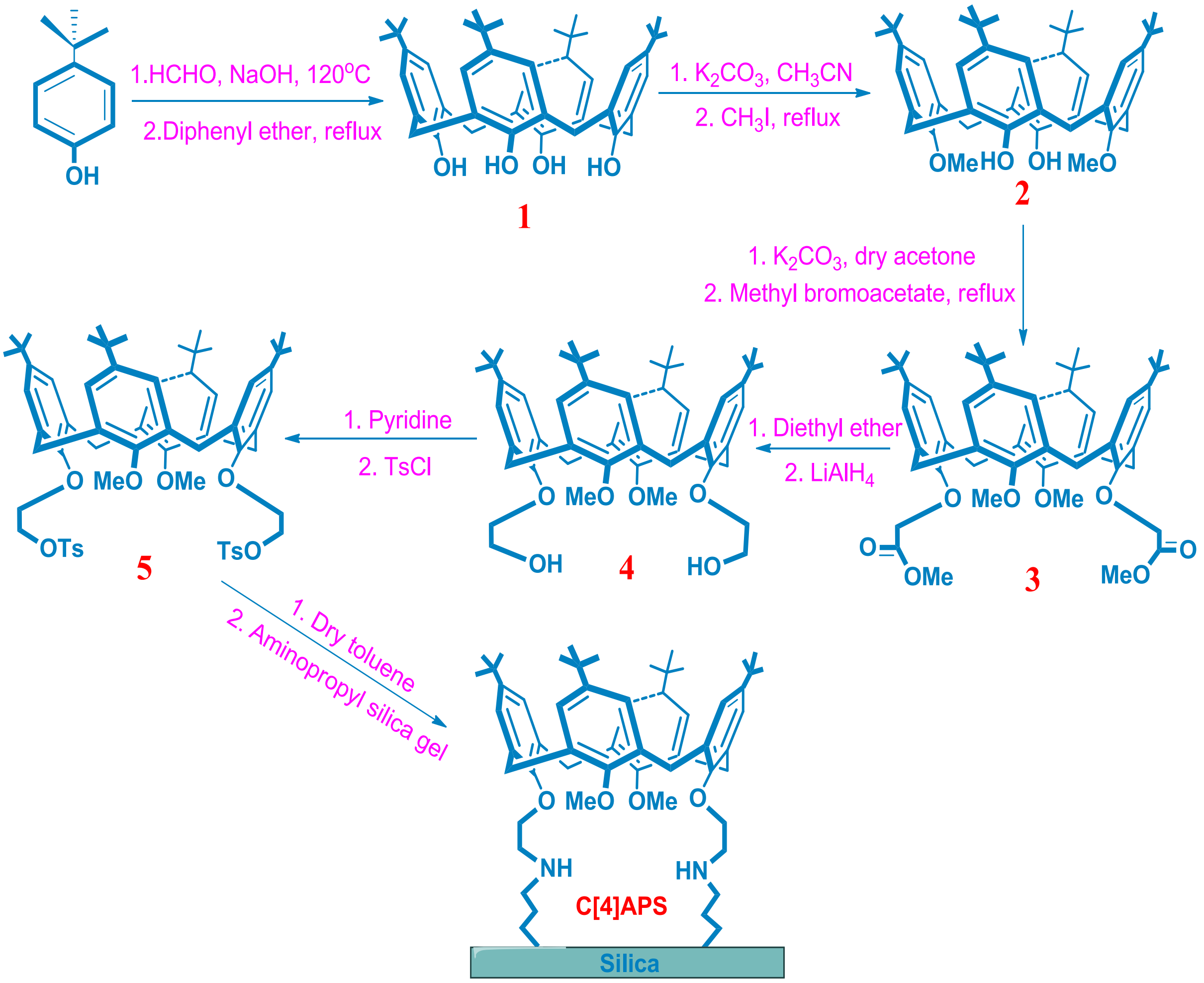
According to our knowledge to immobilize these compounds onto a polymeric support is very useful approach for the ion binding and/or sorption due to their rigid structures (Tabakci 2008). However, among these it was known that calixarenes bearing amide were very effective materials for ions due to capability to form hydrogen bonding. Therefore, an aminopropyl silica gel-immobilized polymer with calix[4]arene (C[4]APS) containing amine was prepared and used as a sorbent for the adsorption of *p*-nitrophenol (PNP) from aqueous solution.

2. METHODS

2.1. Materials and Equipments

High-purity aminopropyl silica gel (APS) was purchased from Fluka and used as support material for the immobilization of a *p-tert*-butylcalix[4]arene ditosiletoksi dimetoksi derivative. In the synthesis of monomeric calix[4]arenes, analytical thin layer chromatography was used for monitoring of the reactions on precoated silica gel plates (SiO_2, Merck PF254). All chemicals were purchased from Merck or Aldrich. Aqueous solutions were prepared with deionized water (Millipore Milli-Q Plus water purification system). IR spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrometer. UV–Visible spectra were obtained on a PG Instruments T80+ UV–visible spectrophotometer. Elemental analyses were performed on a Leco CHNS-932 analyzer. Melting point analyses of calix[4]arene molecules were performed on a Buchi B-540 analyzer. ^{1}H-NMR spectrums were recorded by 400 MHz Varian 6105 spectrophotometer. SEM images were taken by JSM-5600 analyzer. pH adjustments were performed by Orion 420A pH meter.

Compounds **1–5** were prepared according to previously described procedures (Gutsche 1990; Erdemir et al. 2006; Unob et al. 1998; Kerdpaiboon et al. 2005; Knoblauch et al. 2000), while aminopropyl silica gel immobilized calix[4]arene polymer (C[4]APS) employed in this work. The synthetic route for these compounds was illustrated in Scheme **1**.



Scheme 1. The synthetic route of preparation of C[4]APS

Immobilization of compound 5 onto APS (C[4]APS)

A mixture of compound **5** (1.0 g; 0.932 mmol), APS (2 g), and dry toluene (100 mL) was stirred at room temperature for 5 days under nitrogen atmosphere. The cooled mixture was filtered and the solid was washed with toluene, dichloromethane, methanol and distilled water, respectively. The product was dried at 45°C under vacuum for 3 h to give 2.41 g of C[4]APS.

Adsorption studies

In adsorption experiments, 0.025 g of C[4]APS was shaken with 10 mL of aqueous solution containing PNP solution ($5x10^{-5}$ M) at 200 rpm in a 50 mL-closed glass flask at 25°C for 1 h and centrifuged. The concentration of the PNP remaining in aqueous phase after the adsorption was then determined spectrophotometrically (at 317 nm and 401 nm for pH 1-7 and pH 8-10, respectively). The percent adsorption (%A) was calculated as:

$$A\% = [(A_o - A)/A_o] \times 100 \quad (1)$$

where A_o and A are initial and final concentrations of PNP before and after adsorption, respectively.

3. RESULTS and DISCUSSION

3.1. Preparation and Characterization of C[4]APS

Calixarenes have been widely used as three-dimensional building blocks for the construction of artificial molecular receptors capable of recognizing neutral molecules, cations and more recently anions (Yilmaz et al. 2006; Tabakci et al. 2006; Memon et al. 2006). Thus, having chosen the *p-tert*-butylcalix[4]arene (**1**) as the basis for derivatives, synthetic scheme had to be developed to enable the derivatization of the molecule. The syntheses of compounds **1–5** were based on the previously published procedures (Gutsche 1990; Erdemir et al. 2006; Unob et al. 1998; Kerdpaiboon et al. 2005; Knoblauch et al. 2000), while the reaction step leading to C[4]APS (Scheme **1**) were reported for the first time.

From the FTIR results of C[4]APS, it was revealed that compound **5** was immobilized onto APS, due to appearing at 3200 cm^{-1}, 3400 cm^{-1} and 1047 cm^{-1} bands in its FTIR spectra corresponding to O-H, N-H and Si–O, respectively.

Elemental analysis data given in Table **1** showed that the loading of calix[4]arene moiety was 0.757 mmol g^{-1} on C[4]APS. From the Table **1**, successfully immobilization of calix[4]arene derivative on APS was clearly observed.

Table 1 Results of elemental analysis for C[4]APS

	C%	H%	N%	Bonded amount (mmol g^{-1})[a]
Calix[4]arene derivative[b]	76.55	7.67	3.59	-
APS	5.48	1.23	2.09	-
C[4]APS	42.17	3.24	1.59	0.757

[a] Calculated according to the C and N content
[b] Tabakci and Yilmaz (2008)

SEM images of APS and C[4]APS were taken to evaluate its surface morphology and displayed in Fig. **2**. Images of APS show distinct flake and lumpish structure because of the strong intra-molecular hydrogen bonds. However, the porous SEM images of C[4]APS indicated that the adding calix[4]arene units into APS units blocked the formation of the intra-molecular hydrogen bonds. This kind of loose and porous structures was favorable for producing good sorption properties.

Thermogravimetric analysis (TGA) of C[4]APS was determined and its TG and DTG curves presented in Fig. **3**. As it seen in Fig. **3**, the weight-loss of C[4]APS occurred at two main regions. At range of this temperature the remaining of the 86% of material without decomposed. First weight-loss of C[4]APS occurred between 47-96^{o}C about 0.5% due to leaving of water inside C[4]APS. After that, second weight-loss was observed between 397-516^{o}C about 10% due to leaving of organic molecules. There were Si-O units when C[4]APS was heated up to higher temperature. These data revealed that C[4]APS shows strong grafting polymer property under to highly heat conditions although its preparation process requires slightly a long synthetic route leading to cost.

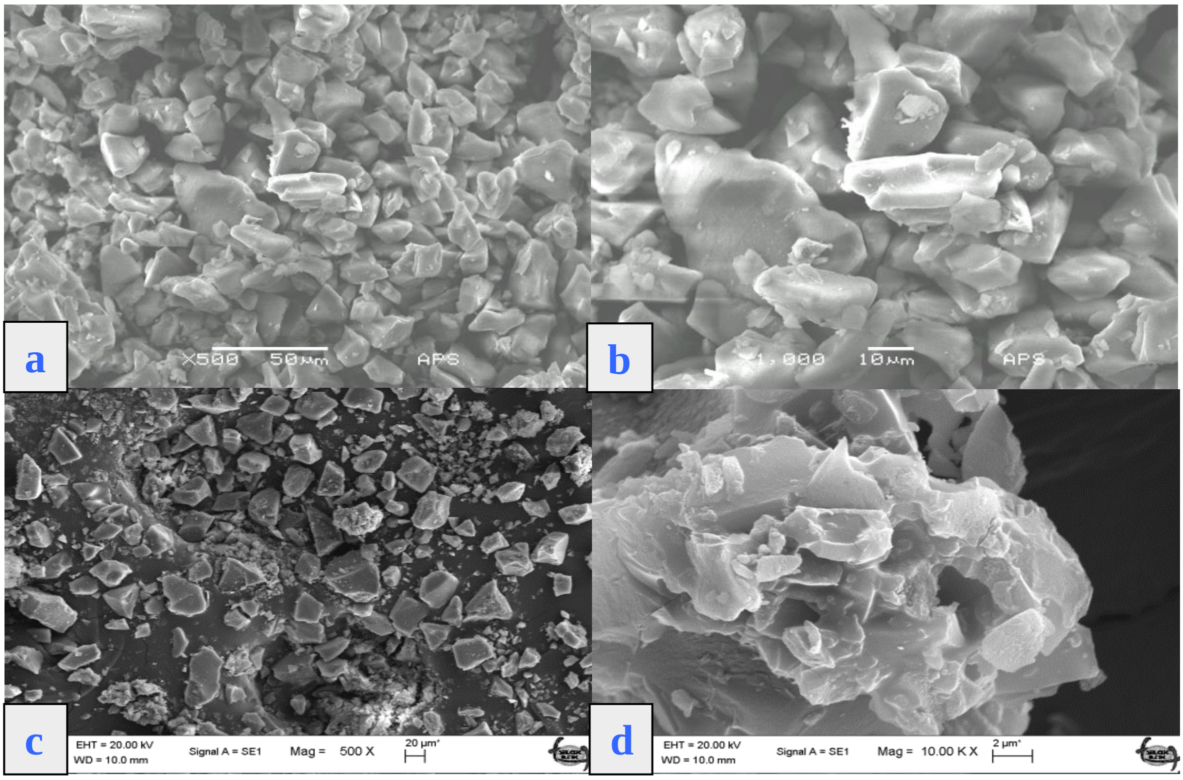


Fig. 2. SEM images (a): 50µm, (b): 10 µm for APS, (c): 20µm, (d): 2µm for C[4]APS

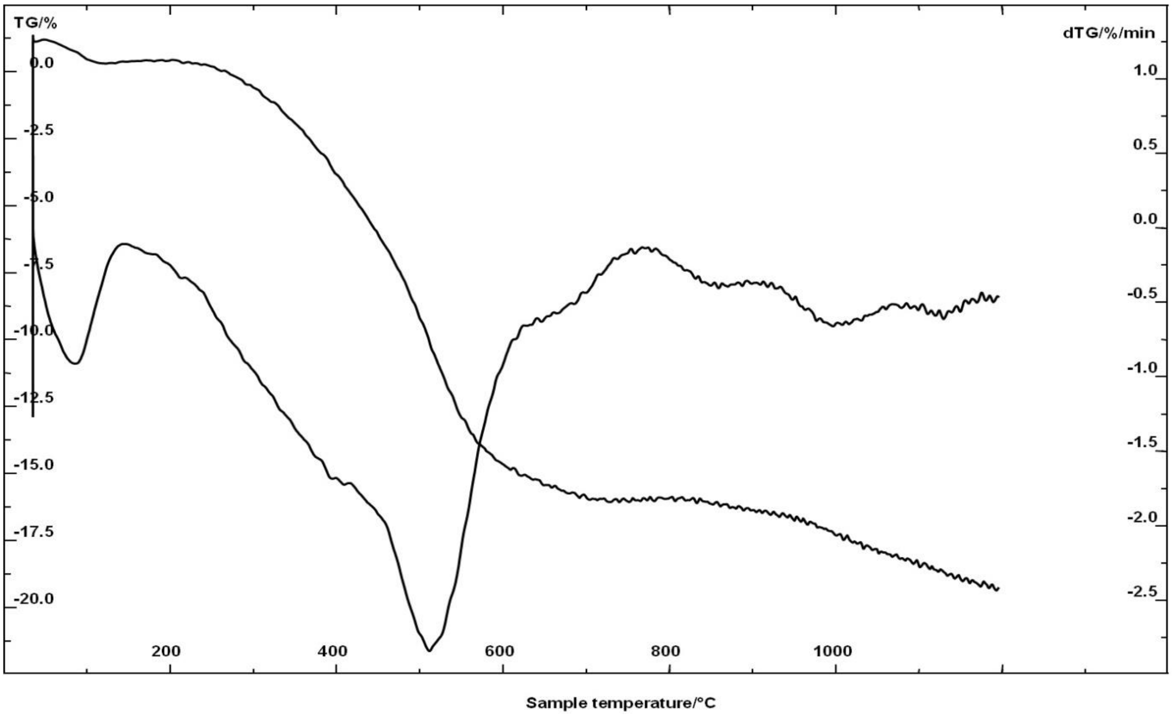


Fig. 3. TG and DTG curves of C[4]APS

Effect of pH

The pH is one of the most important factors for adsorption process. The effect of pH on the sorption of PNP was studied as follows: 250 mL of 5x10^{-5}M PNP solution was prepared and taken about 40 mL in a beaker. The pH of solution was adjusted by adding diluted hydrochloric acid or sodium hydroxide. Ten milliliters of PNP solution was taken in a conical flask and treated with 0.025 g of sorbent (C[4]APS) over the range of pH 2-10, the final concentration of PNP was determined spectrophotometrically. As it seen in Fig. **4**, maximum uptake of PNP took place about 76% at pH 6. When the pH of solution goes beyond the pK$_a$ of PNPs, PNPs chiefly exist as phenolate anions, while they are molecules below pK$_a$. Therefore, we consider that phenol forms of PNP effectively sorbed onto C[4]APS are molecules not its phenolate anion forms. Thus, the molecular interactions including hydrogen bonding, hydrophobic interaction and Van der Waals forces are the possible factors for the adsorption of phenols.

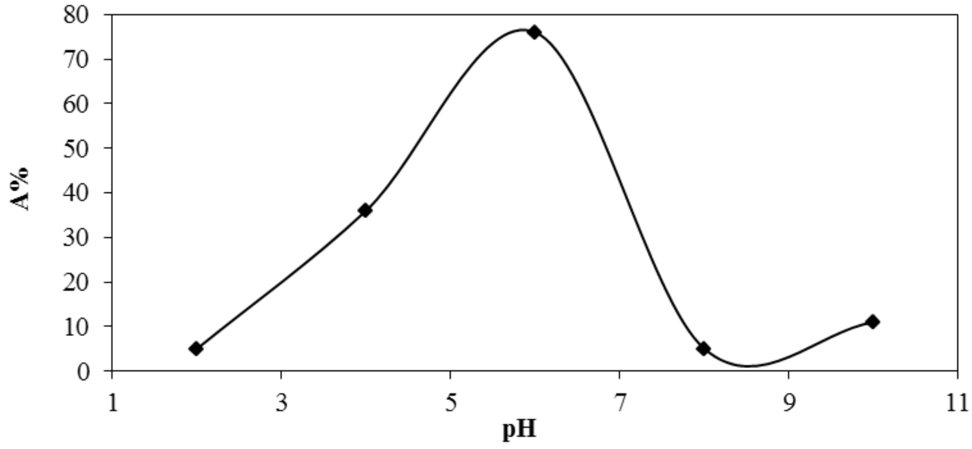


Fig. 4. Effect of pH for the sorption of PNP on C[4]APS

Effect of contact time

The effect of time on the sorption of PNP by C[4]APS was studied by taking 0.025 g sorbent with 10.0 mL of PNP solution (in $5x10^{-5}$ M concentration) in different conical flasks at pH 6 and 25°C for different time intervals such as 30, 60, 90, 120, 150, 180 min. Fig. **5** shows the effect of contact time on the sorption of PNP using this sorbent. The results indicate that the percent adsorption of PNP by C[4]APS increased with increasing time of equilibration and it reached the constant plateau at about 60 min for PNP.

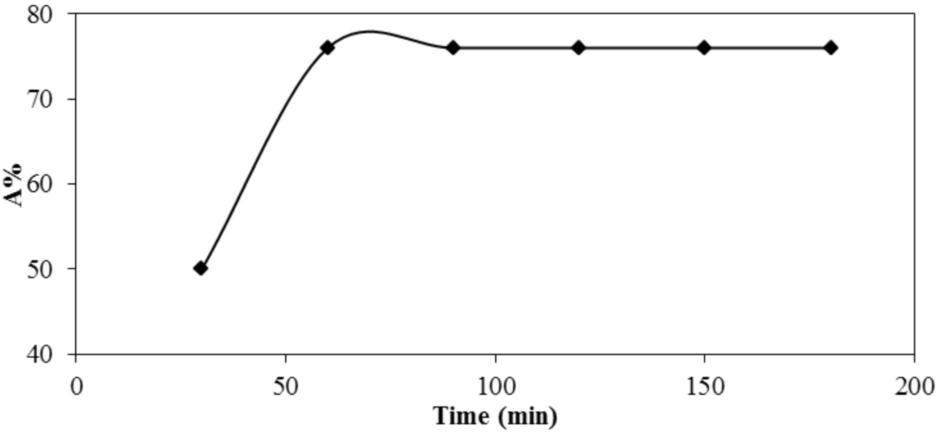


Fig. 5. Effect of time for the sorption of PNP on C[4]APS

Effect of PNP concentration

Solutions of different PNP concentrations ($2.5x10^{-5}$, $5x10^{-5}$, $7.5x10^{-5}$, $1x10^{-4}$ M) were used to investigate the effect of concentration on the removal of PNP by 0.025 g sorbent at pH 6 and 25°C. Percent adsorption was calculated for mentioned concentration value from Eq.**1**. As it seen in Fig. **6**, percent adsorption increase with increase of PNP concentration up to $5x10^{-5}$M while it decrease after that concentration. This finding may be explained with the high driving force for mass transfer.

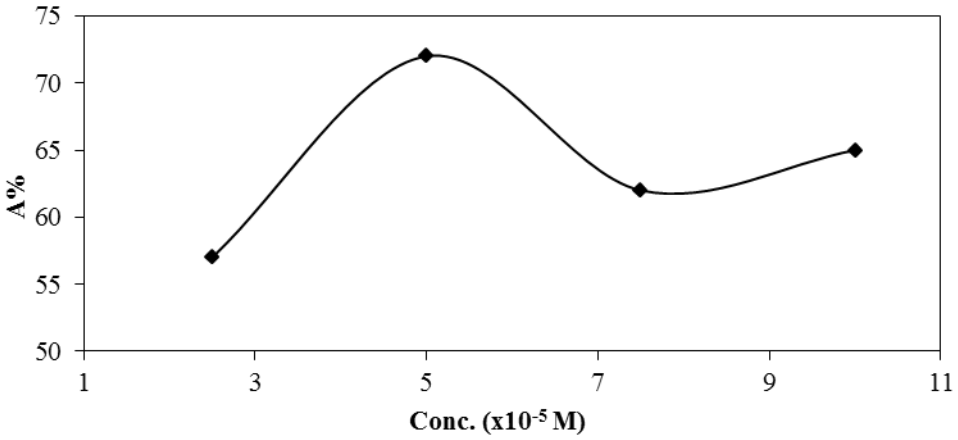


Fig. 6. Effect of PNP concentrations for sorption of PNP on C[4]APS.

Effect of sorbent dosage

The effect amount of sorbent dosage on the sorption of PNP by C[4]APS was studied with 10.0 mL of PNP solution (in 5x10^{-5} M concentration) at pH 6 and 25°C for different sorbent dosage such as 15, 25, 50, 75, 100 mg. Percent adsorptions were calculated Eq.**1**. The percent adsorptions were increased (from 50 to 76%) with increasing of the amount of sorbent from 15 to 25 mg (contact time 1 h; 25°C; pH 6). As it seen in Fig. **7**, sorbent dosage increased from 25 to 100 mg there was no change about adsorption efficiency. The reason for that is the availability of more binding sites sorption of PNP.

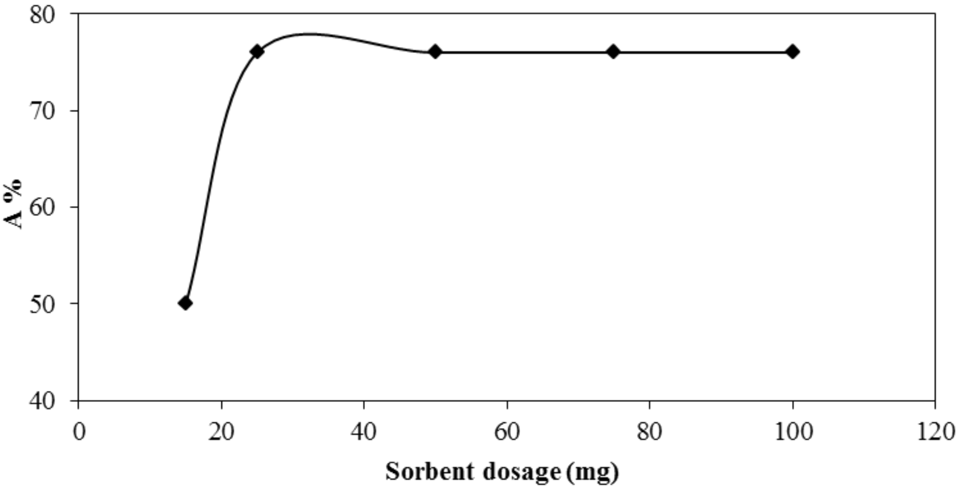


Fig. 7. Effect of sorbent dosage for sorption of PNP on C[4]APS

Effect of temperature

Different temperatures such as 25, 35, 45 and 55°C were applied during adsorption of 0.025g PNP in order to investigate the effect of temperature at pH 6 and 1 h. Percent adsorption was calculated for above mentioned temperature values from Eq.**1**. As it seen in Fig. **8**, percent adsorption decreases with increase temperature of adsorption medium. With increasing temperature from 25°C to 55°C, the sorption capacities of PNP decrease, which is agreement with the literature (Garcia-Araya et al., 2003). This result also implies that the low temperature is favorable for the adsorption of PNP.

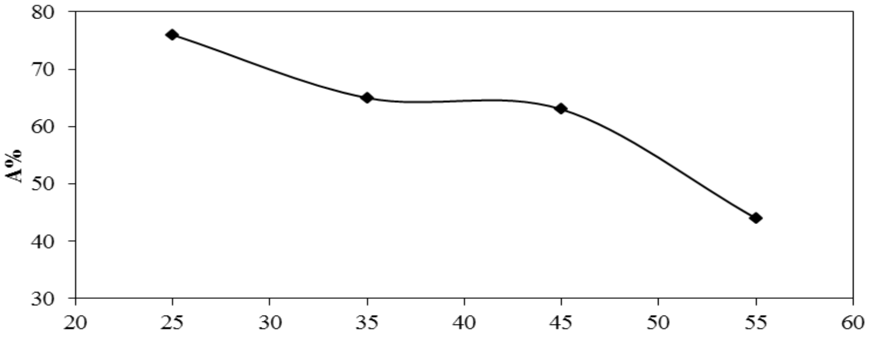


Fig. 8. Effect of temperature for sorption of PNP on C[4]APS

Sorption isotherms

Several models have been published in the literature to describe experimental data of sorption isotherms. Among them, the Langmuir and Freundlich models are the most frequently used models. In this study, both models were used to describe the relationship between the amount of adsorbed PNP and its equilibrium concentration in solution.

Langmuir isotherm is represented by the following equation (Weber 1972):

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \qquad (2)$$

where C_e is equilibrium concentration (M) in solution, q_e is sorption capacity (mmol g^{-1}) at equilibrium, the constant q_0 signifies the sorption capacity (mmol g^{-1}) and b is related to the energy of sorption (L $mmol^{-1}$).

The linear plot of C_e/q_e versus C_e shows that sorption follows a Langmuir isotherm (Fig. **9**). Values of q_0 and b were calculated from the slope and intercept of the linear plots and are presented in Table **2**. The applicability of the Langmuir isotherm suggests the monolayer coverage of the PNP sorption onto C[4]APS (Weber 1972).

To determine if the PNP sorption process by C[4]APS is favorable or unfavorable for the Langmuir type sorption process, the isotherm shape can be classified by a term ''R_L'' a dimensionless constant separation factor, which is defined below (Hamdaoui 2006):

$$R_L = 1/(1 + bC_0) \qquad (3)$$

where b is Langmuir constant (L $mmol^{-1}$). The parameter RL indicates the shape of the isotherm accordingly: $R_L>1$, unfavorable; $R_L=1$, linear; $1>R_L>0$, favorable; $R_L=0$, irreversible.

The calculating of R_L value as 0.022 indicated that sorption of PNP on C[4]APS was favorable at $5x10^{-5}$ M PNP concentration at 25°C and pH 6.

The Freundlich isotherm was also applied for the PNP removal by sorption. Freundlich isotherm model is given by the following equation (Rao et al. 2002):

$$ln q_e = ln K_f + \left(\frac{1}{n}\right) ln C_e \qquad (4)$$

where K_f and n are Freundlich sorption isotherm constants, being indicative of the sorption capacity and intensity of sorption. The values of K_f and n were calculated from the intercept and slope of the plots of ln q_e versus ln C_e (Fig. **10**). Freundlich isotherm data are also given in Table **2**. On the comparison of the R^2 values given Table **2**, we can conclude that in sorption of PNP on C[4]APS Langmuir equation represents much better fit to the experimental data than the Freundlich equation.

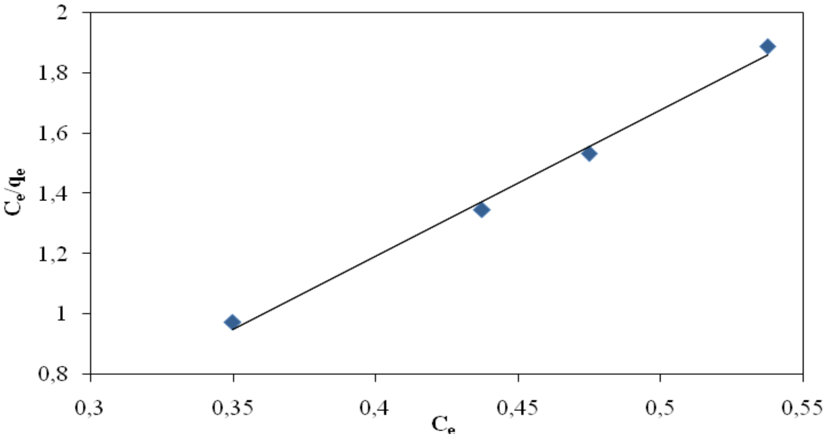


Fig. 9. Langmuir plot for the removal of PNP (at pH 6)

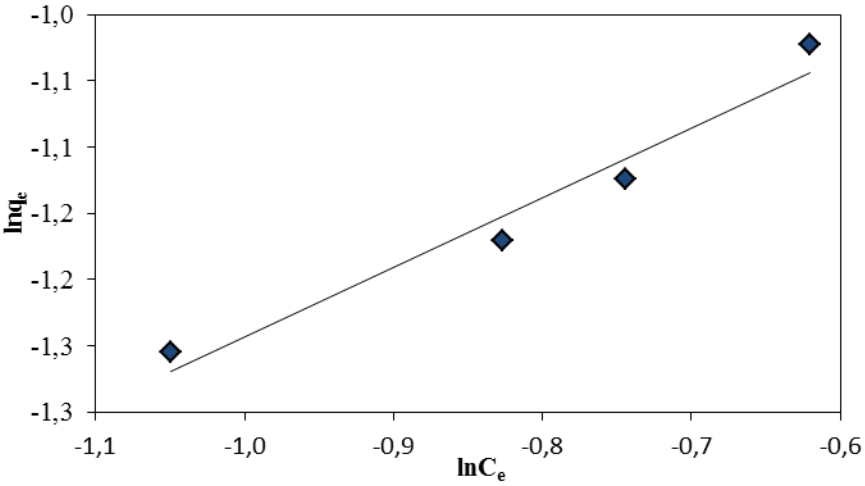


Fig. 10. Freundlich plot for the removal of PNP (at pH 6)

Table 2 Langmuir and Freundlich isotherm parameters

Langmuir isotherm parameters				Freundlich isotherm parameters		
q_0 (mmol/g)	b (L/mmol)	R^2	R_L	K_f	n	R^2
0.206	6.49	0.994	0.022	0.191	1.9	0.955

CONCLUSION

The preparation and characterization of an aminopropyl silica gel-immobilized *p-tert* butylcalix[4]arene polymer (C[4]APS) was successfully achieved. The sorption studies of PNP were performed by C[4]APS as sorbent material and the results appeared that 0.025 g of C[4]APS was effective sorbent in high yields at pH 6 and 25°C in 5×10^{-5} M initial concentration for 1 h with 76% percent adsorption. In the isotherm studies, it was determined that the experimental data follow better Langmuir isotherm model than Freundlich. Batch sorption capacity (q_0) was calculated as 28.7 mg g^{-1}. Consequently, the immobilization of a *p-tert*-butylcalix[4]arene derivative bearing toluene sulfonyl groups onto APS became useful approach for PNP removal from aqueous media by sorption.

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