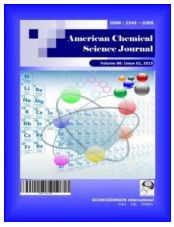

American Chemical Science Journal
16(4): 1-10, 2016, Article no.ACSJ.29198
ISSN: 2249-0205

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Synthesis of β-Cyclodextrin-Epichlorohydrin Nanospheres: Its Application for Removal of *p*-nitrophenol

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Authors' contributions

This work was carried out in collaboration between all authors. Author SS designed and directed the study. Author US managed the analyses and the literature searches. Author MA carried out the experimental work. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/29198
Editor(s):
(1) Anonymous.
Reviewers:
(1) Maurizio D'Auria, Università della Basilicata, Potenza, Italy.
(2) Xiaoquan Lu, Northwest Normal University, Lanzhou, China.
(3) Silvia Álvarez Torrellas, Complutense University, Madrid, Spain.
Complete Peer review History: http://www.sciencedomain.org/review-history/16281

Original Research Article

Received 28th August 2016
Accepted 17th September 2016
Published 21st September 2016

ABSTRACT

The aim of this work is to investigate synthesis conditions of water insoluble β-cyclodextrin (β-CD) nanospheres that could be useful as an adsorbent to remove very low concentration of *p*-nitrophenol (*p*-NP) from water. The effect of several parameters on β-CD polymer synthesis such as β-CD/epichlorohydrin (EPI) mole ratio, reaction temperature and NaOH concentration was investigated. The FTIR-ATR analysis confirmed the formation of β-CD polymer structure with the addition of EPI by preserving the basic β-CD structural units. To determine the optimal synthesis conditions, performances of the synthesized β-CD nanospheres were determined by measuring the adsorption efficiencies of *p*-NP. On the basis of these results, the optimal synthesis conditions of β-CD nanospheres were 65°C, 40% NaOH (w/w) concentration and β-CD/EPI=1/55 mole ratio. Langmuir and Freundlich isotherm models were fitted on experimental data. It was found that Langmuir model described best for adsorption of *p*-NP onto β-CD nanospheres. On the basis of the Langmuir analysis, the maximum adsorption capacities were determined to be 17.203 mg *p*-NP per gram of β-CD nanospheres. The β-CD nanospheres at predetermined optimum reaction conditions

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were also characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Brunauer-Emmet-Teller (BET) analysis. The combination of results from SEM,TEM and BET indicated that the synthesized β-CD nanospheres have a porous and sponge-like structure and 1.54 m^2/g specific surface area.

Keywords: β-cyclodextrin nanosphere; epichlorohydrin; p-nitrofenol; adsorption.

1. INTRODUCTION

Water is an essential, indispensable and unprotected resource for all the living beings on earth. Apart from domestic and agricultural uses, in the industrial facilities developed with the efforts of humankind to advance the technology, inarguably requires the use of water. As a result of these advancements, organic compounds such as pesticides, by-products of disinfecting agents, monocyclic aromatic hydrocarbons, methyl tertiary butyl ether, toluene, phenol and *p*-NP are widely present in potable water supplies [1-4]. It is known that these substances are carcinogenic and pose a serious threat to human lives even at very low concentrations. Technologies such as the use of activated carbon, zeolites and reverse osmosis are currently being used to treat water before consumption. However, activated carbon fails to remove many organic pollutants at concentration levels of nanograms per liter. Zeolites also show low affinity for organic compounds and reverse osmosis requires high pressure and is, therefore, energy-inefficient, and it does not remove all small molecules from water as the membranes are not perfectly semipermeable [4-6]. Thus, new water treatment processes to remove these organic pollutants are required. CD based polymers are candidate for the separation organic pollutants from water.

Cyclodextrins (CDs) have characteristic toroidal shapes that form well-defined cylindrical cone-shaped cavities. The inside of cavity is hydrophobic, while the outside of the truncated cone is highly hydrophilic [7]. The most characteristic feature of CDs is the ability to form inclusion complexes through host-guest interactions [8]. These interactions depend mostly on hydrophobic interactions between the host cyclodextrin and the guest organic molecules [9]. Native cylodextrins are soluble in water, therefore native CDs cannot directly be used in removing organic pollutants from water [7]. To overcome the solubility issues, CDs are used after being linked with various crosslinkers (EPI, hexamethylene diisocyanate, toluene-2,6-diisocyanate, isophorone diisocyanate etc.) and forming water insoluble β-CD polymers. β-CD polymers have been successfully applied to the removal of organic pollutants, dye and heavy metal from water [3,10-15]. EPI is the most frequently used crosslinker in polysaccharide chemistry. Bifunctional EPI contains two reactive functional groups: An epoxide group and a chloroalkyl moiety which can react with the hydroxyl groups of CDs in alkaline medium. The resulting product is a heterogeneous mixture of various CD glyceryl ethers. The synthesized CD polymers are purified before applications and the presence of free/unreacted EPI can be discarded [16-18]. Stoichiometric ratio of substrates, temperature and base concentration are the most important parameters affecting the polymerization reaction.

In this study, we focussed on the synthesis of water insoluble β-CD-EPI polymer nanospheres in order to remove the model organic pollutant *p*-NP from water. Moreover, we have investigated the relationship between reaction conditions and adsorption capacities of the end products. Furthermore, the obtained β-CD nanospheres were characterized by FTIR-ATR meas urements and their morphologies and were determined through SEM and TEM analyses.

2. MATERIALS AND METHODS

2.1 Materials

In the experiments, β-cyclodextrin (≥97%), NaOH, epichlorohydrin, acetone (≥99.5%) and *p*-nitrophenol (spectrophotometric grade) were used. To prepare all the aqueous solutions, deionized water with a conductivity of 18.2 MΩ.cm (Milli–Q Gradient, Millipore) was used. All the chemicals were provided by Sigma-Aldrich company.

2.2 Synthesis of Water Insoluble β-CD Nanospheres

The synthesis procedure of β-CD nanospheres has already been described by Jiang et al. [19].

A typical procedure for preparing β-CD nanospheres was described as follows: β-CD was mixed with NaOH solution and magnetically stirred for 20 min untill β-CD was dissolved completely. Then, EPI was added in dropwise as the mixture was heated gently up to predetermined temperature. The reaction mixture was polymerized under vigorous stirring. After stirring for about 2 h, precipitate could be observed, and the viscosity of the solution was also increased. The solution was mixed with 100 mL acetone, and the insoluble polymers were poured into water. The resultant product was filtrated, and further washed with acetone in a Soxhlet extractor for 12 h. After drying in vacuum oven at 60°C and 70 kPa for 6h, the nanospheres were crushed and granulated to 150-250 μm in diameter. A series of β-CD nanospheres were prepared with different mole ratios of β-CD/EPI (1/33, 1/44, 1/55 ve 1/66), reaction temperature (55, 65 and 75°C) and NaOH concentrations (30%, 40% ve 50% (w/w)).

2.3 Adsorption toward *p*-NP by β-CD Nanospheres

Adsorption experiments of β-CD nanospheres (0.3 g) were carried out by using an orbital shaker (Max Q4000 Barnstead, Lab-line) operating at 200 rpm and 25°C in batch systems with 50 mL solution volume. Nanospheres were brought into contact with *p*-NP solution until equilibrium was reached. *p*-NP concentration in the solution was determined with a UV-spectrophotometer (Shimadzu UV-1601A) at λ=318 nm. By using the determined equilibrium concentrations (C*) and initial *p*-NP concentrations (C_o ~5 ppm), adsorption efficiencies were calculated with Equation 1.

$$\%\ Adsorption\ efficiency = \frac{C_O - C^*}{C_O} \times 100 \quad (1)$$

The amount of adsorbed *p*-NP per unit β-CD nanosphere mass (q) was calculated by the mass balance (Equation 2).

$$q = \frac{C_o - C^*}{m} \times V \quad (2)$$

Where m is β-CD nanosphere mass and V is the solution volume.

Under predetermined optimal reaction conditions, the adsorption experiments of β-CD nanosphere were carried out in different *p*-NP concentration ranges (1-10 ppm) and adsorption isotherms for *p*-NP were determined.

In this study, Langmuir and Freundlich isotherms were applied to fit the equilibrium data of adsorption of *p*-NP onto β-CD nanosphere. The adsorption data were the mean values of three replicate determinations. The parameters and correlation coefficients of Freundlich and Langmuir isotherm models (Eq. 3 and Eq. 4, respectively) were determined by a nonlinear regression program.

$$q = K_F C^{*1/n} \quad (3)$$

$$q = \frac{Q^o b C^*}{1 + bC^*} \quad (4)$$

Where Q° is maximum amount of the *p*-NP per unit mass of β-CD nanosphere to form a complete monolayer on the surface bound at high C* and *b* is a constant reflecting the affinity of β-CD nanosphere for the *p*-NP and related to the free energy of adsorption; K_F and *n* are indicators of adsorption capacity and adsorption intensity or surface heterogeneity, respectively [20].

2.4 Characterizations of β-CD Nano-spheres

Structural characterizations of β-CD nanospheres before and after adsorption experiments were done through FTIR-ATR spectroscopy (Spectrum 100, Perkin Elmer) for each reaction condition. FTIR spectra were recorded at room temperature with a resolution of 4 cm^{-1} over the range of 400-4000 cm^{-1}. The ATR accessory of the FTIR contained a ZnSe crystal. Morphologies and specific surface area of synthesized β-CD nanospheres at optimum reaction conditions were determined through SEM (Evo 40, Zeiss), TEM (G2 S-Twin, Fei Tecnai) and BET (Micromeritics Gemini VII) analyses, respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of β-CD /EPI Mole Ratio

A series of β-CD nanosphere was prepared with different mole ratios of β-CD/EPI (1/33, 1/44, 1/55 and 1/66) at 50 % (w/w) NaOH concentration and 65°C reaction temperature. FTIR-ATR spectra of the synthesized β-CD nanosphere are shown in Fig. 1a. The peaks of O-H stretching vibration (3400 cm^{-1}), C-H

stretching (2890–2870cm^{-1}) and bending vibration (1443 cm^{-1}) from normal alkanes, C-O-C stretching vibration (1032 cm^{-1}) were observed. FTIR spectrum of β-CD in Fig. 1b shows O-H stretching vibration at 3275 cm^{-1}, C-H stretching vibration at 2925 cm^{-1}, C-H deformation vibration at 1412.8 cm^{-1} and 1334.66 cm^{-1}, C-C stretching vibration at 1152 cm^{-1}, C-O stretching vibration at 1077 cm^{-1}, C-H deformation vibrations and glucopyranose stretching vibrations at 938 cm^{-1}, 851 cm^{-1}, 754 cm^{-1} [17,21-23]. The similarities between the spectra of β-CD and β-CD nanosphere also indicate that the basic structural units are preserved in β-CD nanosphere, in good agreement with other reports [17,19,24,25].

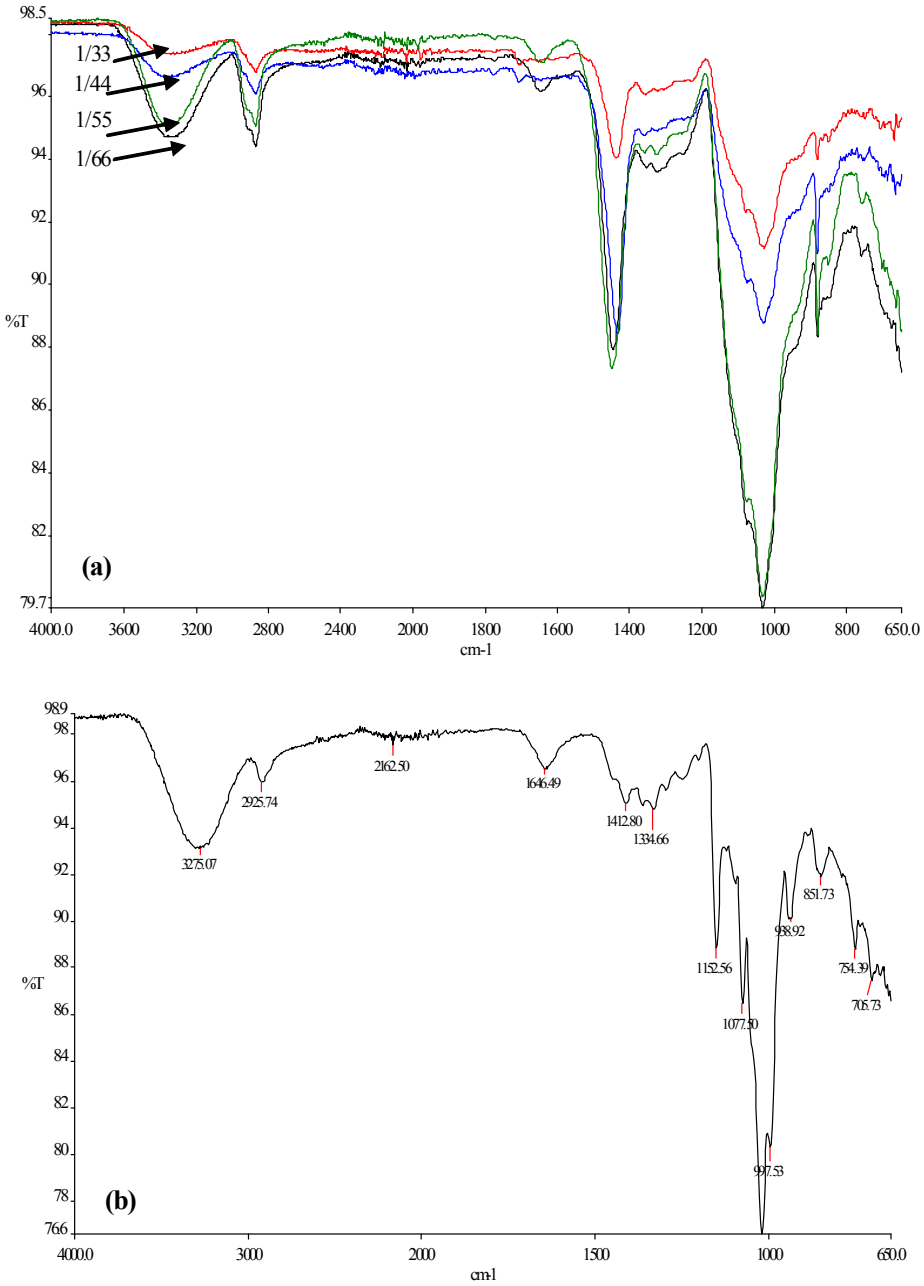

Fig. 1. FTIR-ATR spectra of β-CD nanosphere with β-CD/EPI=1/33, 1/44, 1/55 and 1/66 mole ratios (a) and β-CD (b)

One mole β-CD possesses 21 hydroxyl groups which could partly react with EPI. These numerous hydroxyl groups are able to form a number of linkages with EPI [26,27]. The produced new hydroxyl groups during the reaction could further react with EPI [27]. With increasing EPI concentration, the intensity of O-H (3400 cm^{-1}) band increased which indicated the formation of new O-H groups during the crosslinking reaction and the intensities of C-H (2870 and 1443 cm^{-1}) and C-O-C (1032 cm^{-1}) bands also increased. The stretching vibration of C-O-C at 1032 cm^{-1} indicated the occurrence of the cross-linked β-CD nanospheres [19]. In addition, the intensity of the C-H vibration (1443 cm^{-1}) increased with the crosslinking reaction according to the introduction of the glyceryl bridges [28]. There are no peaks appearing at 1288 cm^{-1} (CH_2Cl rocking band) and 1249.79 cm^{-1} (CH_2Cl wagging band) in the synthesized β-CD nanosphere under different mole ratios. It is concluded that EPI reacted almost completely with β-CD in according to the initial mole ratios [17].

Adsorption efficiencies of β-CD nanospheres were determined through adsorption experiments where liquid phase *p*-NP concentrations with time were followed. In these experiments, equilibrium was reached after approximately 30 min. The adsorption efficiencies of β-CD nanospheres for *p*-NP at β-CD/EPI = 1/33, 1/44, 1/55 and 1/66 mole ratios were calculated as 51.54, 68.46, 82.87 and 46.24 %, respectively. It is well-known that the adsorption capacity decreases with increases in the extent of cross-linking [29]. The cross-linking degree indicates the mean amounts of EPI per β-CD unit [30]. It is concluded that an increase of EPI amount formed dense β-CD nanosphere structure and adsorption efficiency of nanospheres decreased due to the mass transfer limitations. FTIR-ATR spectra of β-CD nanospheres before and after *p*-NP adsorption are given in Fig. 2. The most important change of β-CD nanospheres was the appearance of N-O asymmetric and symmetric stretching vibrations (~1282-1288 cm^{-1}) that could be explained by the adsorption of *p*-NP.

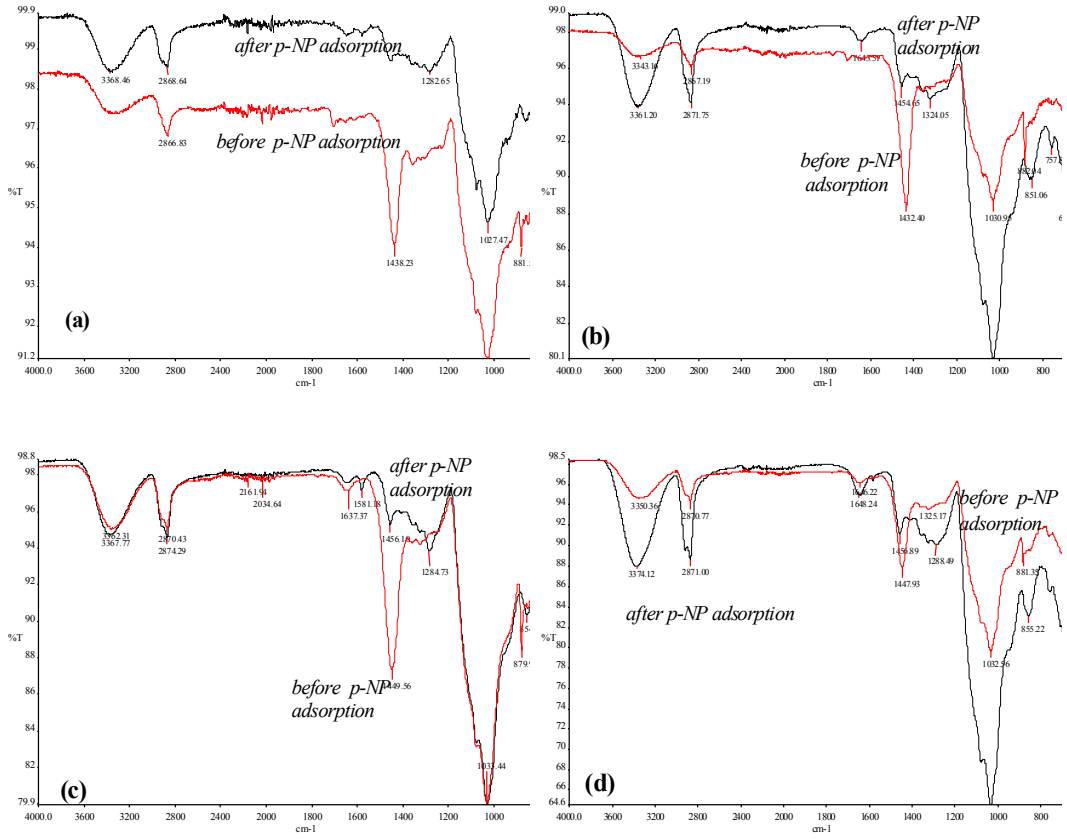

Fig. 2. Comparative spectrums of β-CD nanospheres showing before and after *p*-NP adsorption at different mole ratio of β-CD/EPI a) 1/33, b) 1/44, c) 1/55 and d) 1/66.

The variation in the intensity of N-O stretching vibrations with the synthesized β-CD nanospheres under different the mole ratio of β-CD/EPI was in agreement with the variation in the degree of adsorption. The highest intensity of N-O stretching vibrations was observed at β-CD/EPI=1/55 mole ratio, where the adsorption efficiency was also the highest.

3.2 Effect of Temperature on β-CD Nanosphere Synthesis

Effect of reaction temperature on β-CD nanosphere synthesis was studied with β-CD/EPI= 1/55 mole ratio and 50% (w/w) NaOH concentration at 55, 65 and 75°C. Changes in structures of β-CD nanospheres were determined through FTIR-ATR analyses and the comparative results are given in Fig. 3.

The characteristic IR peaks of the produced β-CD nanospheres at different temperature are similar to each other, as discussed above in Section 3.1. The intensity of C-H (1443 -1449 cm^{-1}) and C-O-C (1030-1034 cm^{-1}) bands increased with increasing temperature. The lower intensity of O-H bands was observed at 75 °C. At this temperature, the new hydroxyl group could be less produced due to the volatility of EPI. The time required to complete the reaction decreased from 110 min to 30 min while the reaction temperature increased from 55°C to 75°C. The adsorption efficiencies of β-CD nanospheres for *p*-NP at T=55, 65 and 75°C were calculated as 82.49, 82.87 and 26.85%, respectively. In terms of adsorption efficiency, there was no significant difference between the produced β-CD nanosphere at 55 and 65°C. However, from the viewpoint of reaction time, the optimal reaction temperature is 65°C.

3.3 Effect of Base Concentration on β-CD Nanosphere Synthesis

Effect of base concentration on β-CD nanosphere synthesis was studied with 30, 40 and 50% (w/w) NaOH concentration at β-CD/EPI=1/55 mole ratio and 65°C. Changes in structures of β-CD nanosphere were determined through FTIR-ATR analyses and the comparative results are given in Fig. 4.

The characteristic peaks of β-CD nanospheres were observed in all NaOH concentrations. With increasing NaOH concentration, the intensities of O-H (3400 cm^{-1}), C-H (2870 and 1443 cm^{-1}) and C-O-C (1032 cm^{-1}) bands relatively increased. *p*-NP adsorption efficiencies with 30, 40 and 50% NaOH concentration were calculated as 58.26, 85.61 and 82.87%, respectively. In terms of

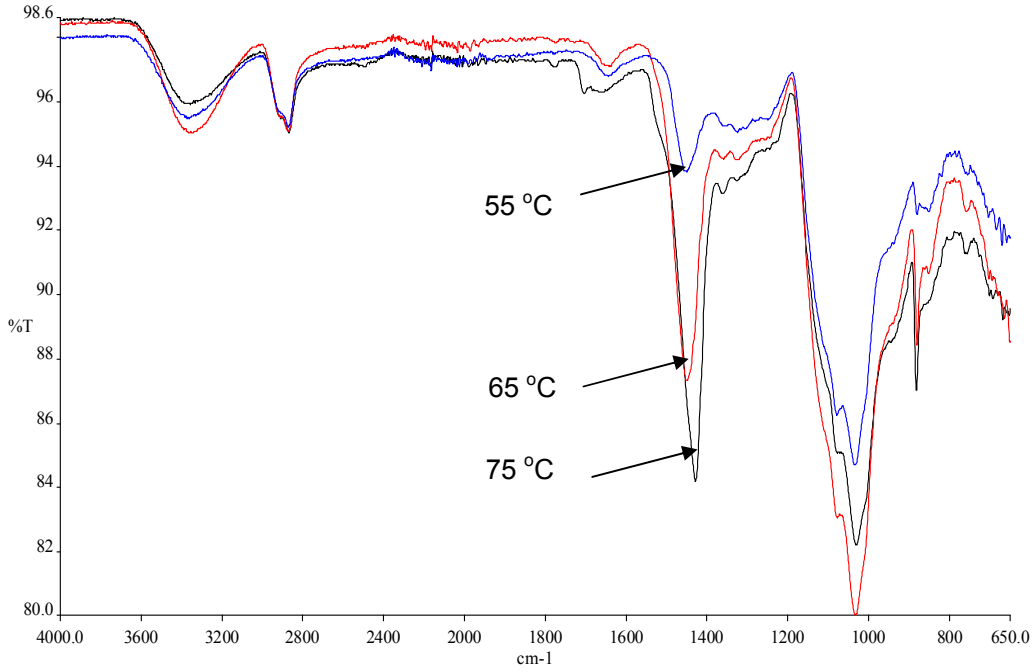

Fig. 3. FTIR-ATR spectra of the synthesized β-CD nanospheres at different temperatures

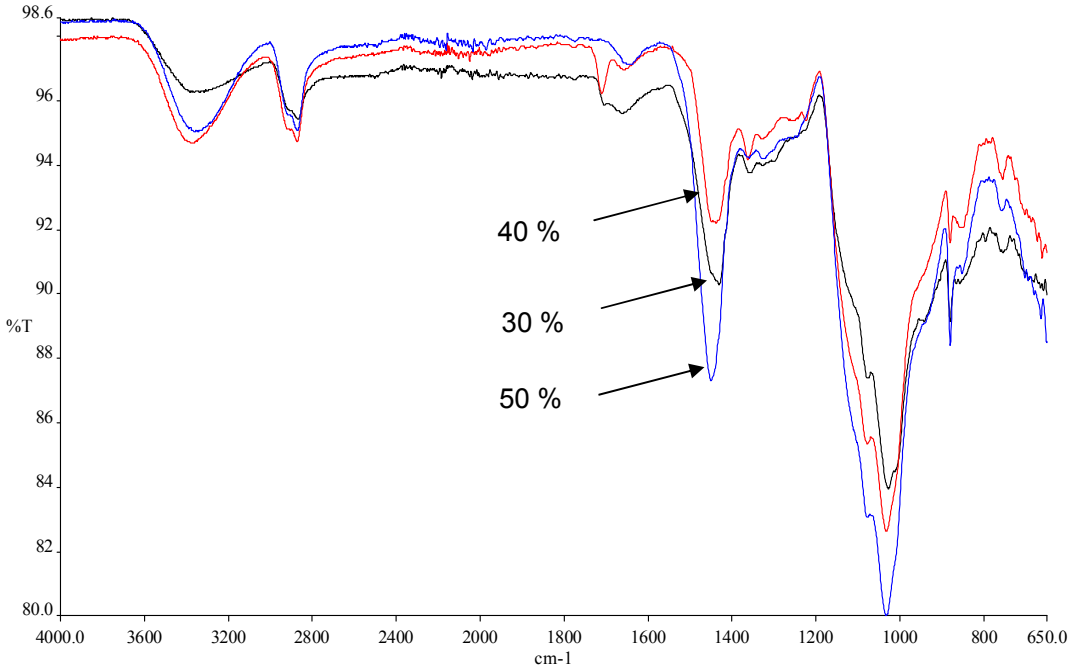

Fig. 4. FTIR-ATR spectra of the synthesized β-CD nanospheres at different base concentration

adsorption efficiency, there was no significant difference between the produced β-CD nanosphere at 40 and 50% NaOH concentration. The role of NaOH in the reaction is to provide the alcoholate sites to β-CD and EPI for the polymerization. Jiang et al. reported that insoluble polymers could be produced when the concentration of NaOH was over 30% [19]. It was reported that the favorable deprotonation of C-2 or C-3 carbon atoms in β-CD glucopyranose units increased with increasing NaOH concentration which resulted in an easy reaction between EPI and β-CD. Therefore, high NaOH concentration is suitable for production of water insoluble β-CD nanospheres.

3.4 SEM, TEM and BET Analysis

SEM and TEM images of the synthesized β-CD nanospheres under optimal reaction conditions (65°C, 40% NaOH (w/w) and β-CD/EPI=1/55 mole ratio) are given in Fig. 5. Through SEM images (Fig. 5a), it has been determined that β-CD nanospheres have a porous, sponge-like structure. This porous structure provides more surface area for adsorption. Through TEM images (Fig. 5b), it can be seen that β-CD-EPI polymers have a spherical shape. The BET surface area of the synthesized β-CD nanospheres under optimal conditions was measured by recording nitrogen adsorption/desorption isotherms at 77°K and the surface area was 1.54 m^2/g.

3.5 Equilibrium Models

In order to determine the isotherm of *p*-NP adsorption onto β-CD nanospheres which is produced under optimal conditions (65°C, 40% NaOH (w/w) and β-CD/EPI=1/55 mole ratio), adsorption experiments (N=200 rpm and T=25 °C) were carried out in different initial *p*-NP concentrations (1-10 ppm) (Fig. 6). The obtained equilibrium data from the adsorption experiments fit the Freundlich and Langmuir isotherm models. The parameters and correlation coefficients of the isotherms, which were determined by a nonlinear regression program, are presented in Table 1.

The favourability and the nature of adsorption process can be identified from the value of °*n.* The value of Freundlich exponent n=1.835 in the range 1-10, indicates the favorable adsorption [13]. The Freundlich model does not describe the saturation behavior of the surface as well as Langmuir model. Langmuir constants Q^o and *b* correspond to the monolayer capacity at equilibrium and the affinity for the binding of *p*-NP molecules, respectively. Langmuir isotherm model is very suitable for describing adsorption equilibrium of *p*-NP by β-CD nanosphere due to

high regression coefficients. The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of *p*-NP onto β-CD nanosphere and also the homogenous distribution of active sites on the material, since the Langmuir equation assumes that the surface is homogenous [13,20].

Adsorption efficiencies of β-CD nanosphere for *p*-NP concentrations of 1, 3, 6, 7, 8 and 10 ppm are 82.9, 83.47, 85, 85, 85 and 85% respectively. This result indicates that β-CD nanosphere can be even more effective in removal of *p*-NP at very low concentrations. Some existing adsorbents such as activated carbon and zeolite have some affinity to organic compounds, but fail to remove contaminants to a suitable degree of very low concentration. It can be expected that these β-CD nanosphere will adsorb organic pollutants to low concentrations levels, making them suitable for USEPA limits. The USEPA recommends a maximum level of 1 μg mL^{-1} of total phenolic compounds in water supplies [31].

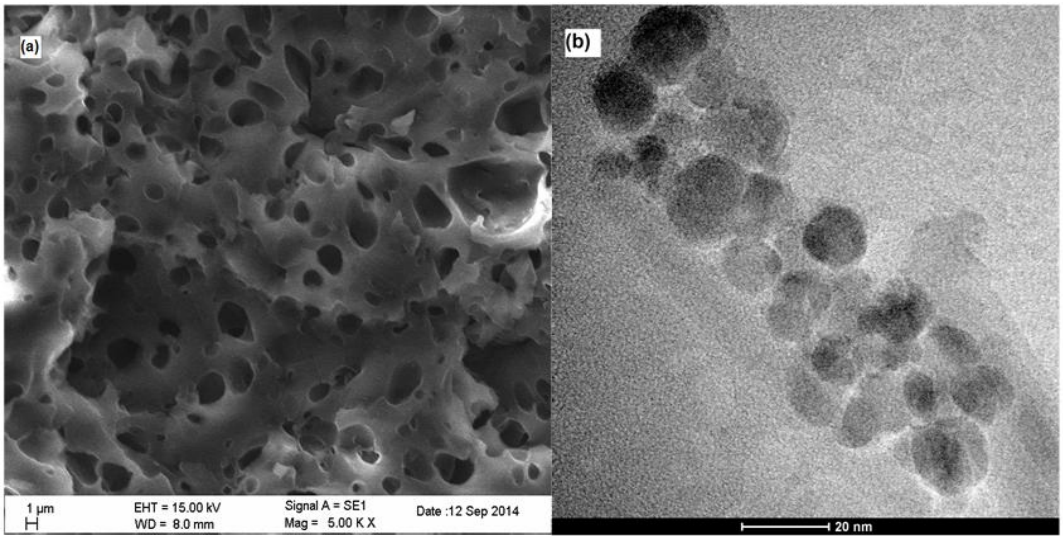

Fig. 5. SEM and TEM images of the synthesized β-CD nanospheres under optimal reaction conditions

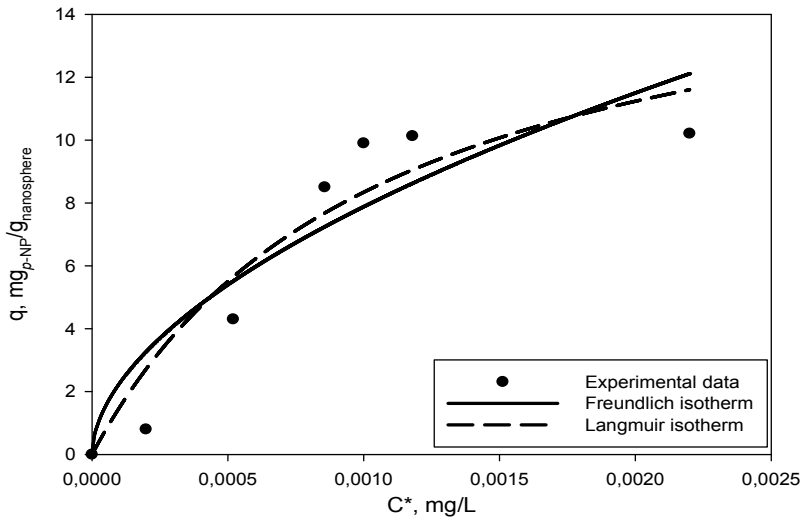

Fig. 6. Adsorption isotherms for *p*-NP on β-CD nanospheres: experimental points and fitted points of Langmuir and Freundlich isotherms

Table 1. Equilibrium models and their calculated parameters

Equilibrium models	Parameters	Values
Freundlich isotherm	K_F (L/mg)	0.339
	n	1.835
	r^2	0.843
Langmuir isotherm	Q^o (mg/g)	17.20
	b (L/mg)	0.942
	r^2	0.910

4. CONCLUSION

In this study, β-CD nanospheres were synthesized with β-CD and EPI polymerization reaction, for the removal of *p*-NP from aqueous solutions. Effects of β-CD/EPI mole ratio, temperature and NaOH concentration on β-CD nanosphere synthesis were studied. It was found that the optimal synthesis conditions for β-CD nanosphere were as follows; reaction temperature 65 ^{o}C, β-CD/EPI=1/55 mole ratio and 40 % NaOH concentration. Adsorption equilibrium was studied with both the Langmuir and Freundlich isotherm models. The adsorption process followed the Langmuir isotherm with an adsorption capacity of 17.20 mg g^{-1}. The chemical and morphological properties of the β-CD nanospheres were assessed by FTIR, SEM and TEM analyses. Most important parameters affecting the adsorption efficiencies of β-CD nanospheres are β-CD/EPI mole ratio, reaction temperature and base concentration. The obtained spherical and sponge-like β-CD nanospheres exhibited high adsorption capacities and short equilibrium time toward *p*-NP. The experimental results imply that the β-CD nanospheres are expected to have very promising adsorption application for organic pollutants at very low concentration.

ACKNOWLEDGEMENTS

This study was financially supported by Cumhuriyet University Scientific Research Projects with the project number M-540.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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