

Sorption onto insoluble β -cyclodextrin polymer for 2,4-dinitrophenol

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Abstract The sorption of β -cyclodextrin polymer (β -CDP) towards 2,4-dinitrophenol (2,4-DNP) in aqueous solutions was investigated. The influence of sorption conditions including initial 2,4-DNP concentration, contact time and pH on sorption capability were discussed. The sorption isotherm can be correlated to Freundlich model. The maximum sorption capacity of 2,4-DNP for β -CDP was measured to be 192 mg/g with the initial concentration at 1,000 mg/L at 303 K. The β -CDP was easily recovered by ethanol as washing solvent and they could be used as a kind of recyclable sorbents.

Keywords 2,4-Dinitrophenol · β -Cyclodextrinpolymer · Sorption

Introduction

Removal of pollutants from polluted water has been a challenge for long time and adsorption technique has been proved perfectly to minimize this task [1]. It is now well established that for the wastewater treatment, adsorption is a much better process than other physical techniques, namely, flocculation, froth flotation, etc., because of its efficiency and economy [2]. Moreover, adsorption to remove pollutants without disturbing the quality of water or leaving behind any toxic degraded products has competed with electrochemical, biochemical or photochemical degradation processes. Adsorption process has many extraordinary advantages for recovery of valuable

pollutants from the wastewater [3]. It has been used for the removal of organics from wastewater, primarily focusing on the use of activated carbon as the adsorbent. Regeneration of the spent adsorbent material can be an expensive and intensive process [4]. This has resulted in an interest in developing alternative sorbents for the removal of organic pollutants from aqueous waste streams. These sorbents include clay materials [5], zeolites [6], siliceous materials [7], agricultural wastes [8], industrial by-products [9], biomass [10] as well as natural molecules [11].

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to eight glucose units. The interior cavity of CDs is hydrophobic and can form inclusion complexes with various molecules through host–guest interactions. The practically important, industrially produced CDs are α , β , and γ -CDs, which are made up of six, seven, and eight α -1,4-linked D-glucopyranose units, respectively (Fig. 1). β -CD is the most largely produced cyclodextrin used in many fields including pharmaceuticals, foods, cosmetics, chemical products, and technologies [12].

β -cyclodextrin polymer has been reported to be efficient in adsorption toward organic pollutants and heavy metals in water [13–18]. This kind of polymer is usually synthesized by reacting β -CD with crosslinking agents such as epichlorohydrin [14, 15], diisocyanates [16], polycarboxylic acids [17], and anhydrides [18]. Polycarboxylic acids, such as citric acid [14, 15], are generally of low toxicity and friendly to environment. The condensation between β -CD and citric acid can progress at a temperature not higher than 200 °C and without any organic solvent and harmful additive. It has been found that β -CD polymer crosslinked by citric acid contained carboxyl groups (–COOH) when the polymer is used to adsorb organic molecules. Especially if the target molecules contain

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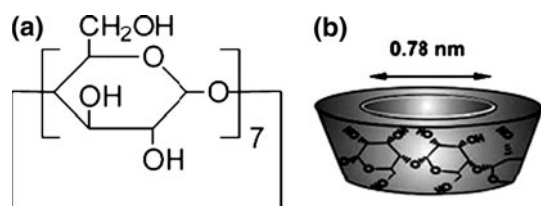


Fig. 1 **a** Chemical structure and **b** shape of β -cyclodextrin

hydrophobic groups (such as phenyl and naphthyl group), the hydrophobic groups should be attracted by β -CDP, and the adsorption would become more interesting. The other interesting advantages of β -CDP were their chemical stability of the polymers and the reproducible values.

Nitrophenols and related compounds are released to the environment from pesticide application and from the effluent of mine processing facilities, foundries, metal finishing plants, refineries, and dye manufacturing plants. Nojima et al. [19] also reported that nitrophenols might be released to the environment from automobile exhaust gas, or as a result of the photochemical reaction of benzene with nitrogen monoxide in highly polluted air. Therefore, nitrophenols are found as contaminants in wastewaters, rivers, groundwater, soil, and in the atmosphere [20]. Nitrophenols are highly toxic to humans and aquatic life and create an oxygen demand in receiving waters. 2,4-dinitrophenol (2,4-DNP) is considered to be the most toxic substance of this group with an LD50 of 30 mg/kg body weight in rats [21]. Most nitrophenols are resistant to biological treatment because of their toxicity. 2,4-DNP interferes with bacterial respiration, so unlike many hard-to-degrade organics, it is inhibitory to bacteria in high concentrations. Therefore, it is not surprising that many investigators have considered the possibility of biodegrading 2,4-DNP either aerobically or anaerobically [22, 23]. A number of bacterial strains have been reported which are capable of using 2,4-DNP as their sole carbon and nitrogen source. These practices need complex and strict control of the operating conditions, as they create excess sludge that requires disposal. There are many methods such as oxidation, precipitation, ion exchange, and solvent extraction to remove phenolic species from aqueous solution. However, in water treatment the most widely used method is adsorption onto the surface of sorbents.

In this article, cross-linked β -cyclodextrin polymer (β -CDP) has been used as sorbents for removal of 2,4-DNP from its aqueous solution. The sorption behavior of the polymer (β -CDP) was compared through experimental investigations. The influence of several operating parameters such as initial concentration, contact time was investigated. Equilibrium isotherms and kinetic models were used to identify the possible mechanism of the sorption process. The recovery of 2,4-DNP from β -CDP and their

recycle use were also studied. The aim of the present work to explore the potential of β -CDP as sorbent.

Materials and methods

Reagents

β -Cyclodextrin (β -CD) was purchased from SD fine chemicals and without any further purification before use. 2,4-DNP (analytical grade, Loba chemicals) has a maximum absorbance at wavelength 361 nm on a UV–vis spectrophotometer. Citric acid monohydrate (CAM, CDH chemicals), Potassium dihydrogen orthophosphate (SRL chemicals), and Polyethylene glycol 400 (PEG-400, SRL chemicals) of molecular weight 370–460. Potassium bromide (KBr) used for FT-IR is a spectrum pure reagent purchased from Merck chemicals. All aqueous solutions were prepared with triple distilled water. The other chemicals were analytical grade.

Instrumentation

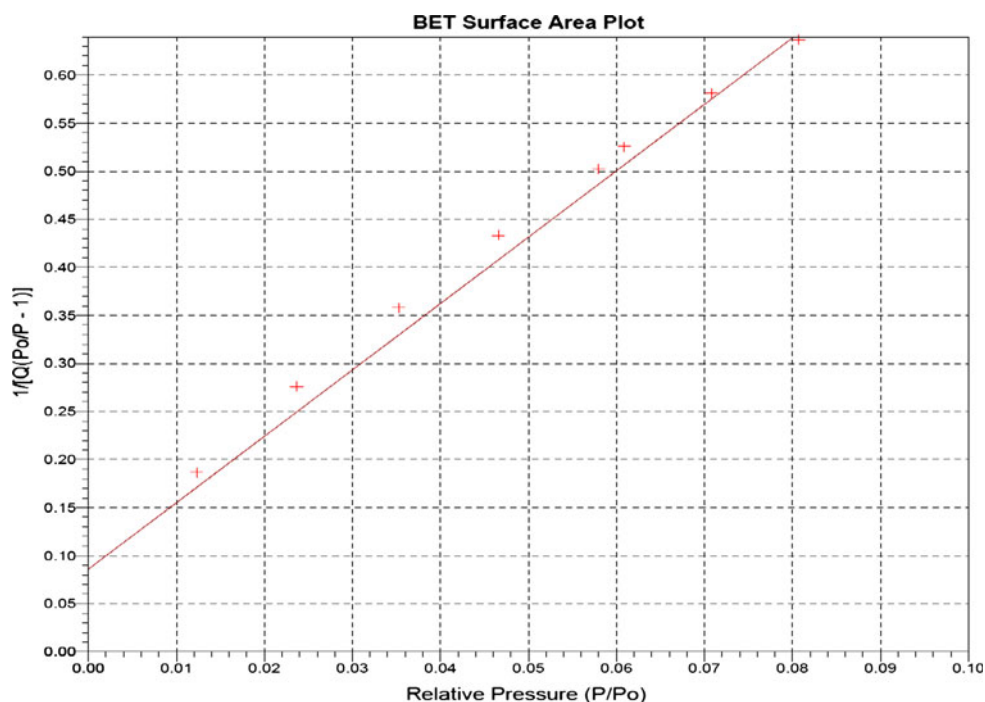
The absorption spectral (UV–vis spectrum) measurements were carried out with Shimadzu UV-2401PC double-beam spectrophotometer. The pH values 3.0, 7.0, and 10.0 were measured using Elico pH meter LI-120. All experiments were carried out at 30 ± 1 °C. Powder X-ray diffraction spectra were taken by XPert PRO PANalytical diffractometer. FT-IR was recorded using Nicolet 380, Thermo Electron Corporation Spectrophotometer and surface morphology was recorded using SEM 111 Hitachi S 3000 H. The solution was stirred on a mechanical shaker (90 times/min). The Brunauer–Emmet–Teller (BET) surface area of the particles was measured by recording nitrogen adsorption/desorption isotherms at 77 K using ASAP 2020 V3.00H analyzer (Fig. 2).

Synthesis of β -CDP

β -cyclodextrin polymer were synthesized as per the Ref. [24] the few additives are changed and some preparation method was altered. β -CD, PEG-400, CAM potassium dihydrogen phosphate and some triple distilled water were mixed in a round bottom flask and stirred in a boiling water bath. The mixture was transferred into a culture dish and heated in an electric thermostatic oven at 120 °C for 4 h. Because the culture dish was wide open, the water was quickly driven away by heating. Then polymerization started, and the water generated during the reaction was instantly driven away, thus the equilibrium was pushed forward successively.

After naturally cooling, the crude product was weighed (recorded as W_c) and ground finely. The granules were

Fig. 2 Brunauer–Emmet–Teller (BET) surface area of β -CD polymer



purified by soaking and washing with Triple distilled water several times, then suction filtered and dried at 50 °C to constant weight (recorded as W_p). W_p is the weight of the purified β -CDP, i.e., the weight of water insoluble polymer in the product. The yield (Y) of the purified β -CDP was calculated as follows,

$$Y = \frac{W_c - W_p}{W_c} \times 100\% \quad (1)$$

The purified polymer were crushed and sieved into different particles sizes. Studies were focused on a size fraction of below 25 μm . The characteristics of β -CDP were reported in Table 1. These particles have not any hydrogel nature and there is no swelling nature in water.

Characterization of polymer

Fourier transform-infrared red spectroscopy

After purified and dried, polymer was obtained as yellowish crisp granulate with a yield of 9.1 g. Total acidic groups (TA) of Polymer were 8.87 mmol g^{-1} . FT-IR spectra of Polymer

Table 1 Characteristic of β -CD polymer

Properties	Result
Particle size (μm)	<25 μm
Swelling capacity (cm^3/g)	No swelling nature
BET specific surface area (m^2/g)	0.622
Total acid content (mmol/g)	8.8

and native β -CD (a) were shown in Fig. 3. The intensive absorption band appeared at 1,739 cm^{-1} in (b), which was absent in (a), was owed to C=O stretching vibration of carboxyl groups and ester groups. The band at 1,029 cm^{-1} in (b), which was also absent in (a), was owed to C–O–C stretching vibration of ester groups. These two bands observed in (b) indicated that the hydroxyl groups of β -CD had reacted with the carboxyl groups of citric acid. The strong and broad bands at 3,354 cm^{-1} in (a) corresponded to the O–H stretching vibration of the hydroxyl groups of β -CD and 3,417 cm^{-1} in (b) corresponded to the integrated O–H stretching vibration of hydroxyl groups and carboxyl groups. The bands at 2,932 cm^{-1} in (a), 2,924 cm^{-1} in (b), corresponded to the CH_2 asymmetric stretching vibration. C–OH stretching vibration at 1,028 cm^{-1} and C–O–C stretching vibration at 1,156 cm^{-1} of β -CD in (a) also appeared nearly at the same wavenumbers in (b) indicating that the structure characteristics of β -CD were maintained in this polymer. The C–O–C stretching vibration at 1,213 cm^{-1} in polymer its indicated that the hydroxyl groups of PEG had reacted with the carboxyl groups of citric acid.

Powder X-ray diffraction spectrum and Scanning electron microscope

The formation of the β -CDP can be confirmed by X-ray diffractometry. Figure 4 is the powder X-ray diffraction spectrum of β -CD monomer (a) and β -CD-polymer (b). The X-ray spectrum of the polymer shown in Fig. 4b was amorphous and β -CD monomer is semi crystalline in

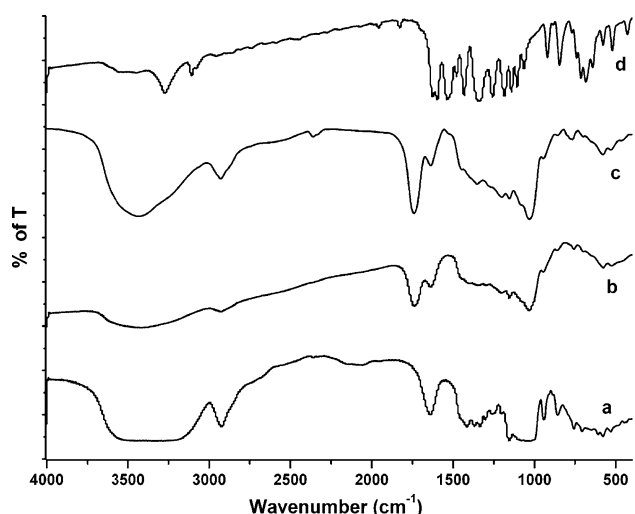


Fig. 3 FT-IR spectra of (a) β -CD, (b) β -CDP (c) β -CDP-2,4-DNP and (d) 2,4-DNP

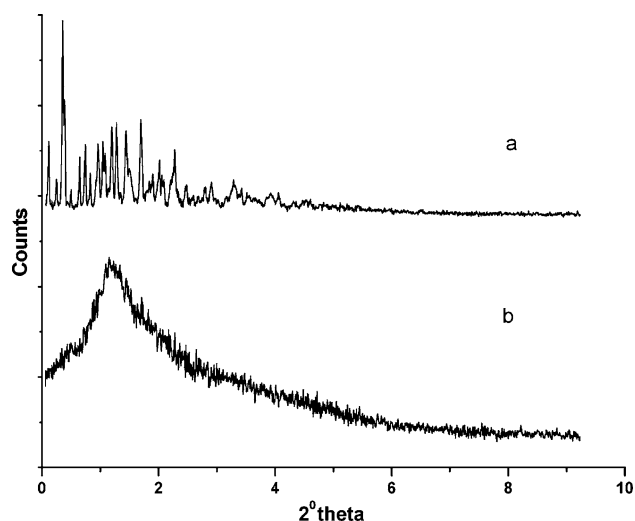


Fig. 4 XRD Pattern of (a) β -CD (b) β -CD polymer

nature. The difference between both spectra of β -CD and polymer is due to the formation of condensation polymer of β -CD with citric acid.

The polymer material was also characterized by SEM analysis. SEM photograph (Fig. 5b) of the polymer formed by β -CD condensation with citric acid. Colloidal like growth showed in SEM image. This is due to the formation of β -CD polymer and it is entirely different from the β -CD. The formation of new structure was confirmed as polymer. The grain size of the material is 5 μ m.

Sorption studies and kinetics

Experimental data were determined by the following batch method: in each experiment, 100 mg dry β -CDP was

mixed with 50 mL aqueous solution (fixed pH 7, unless otherwise specified) of 2,4-DNP at a known concentration in a tightly sealed flask. The sorption temperature is 303 K and the concentration of 2,4-DNP was varied according to experiments. The solution was stirred on a mechanical shaker (90 times/min) for 4 h. The sorbents were removed by centrifugation before measurements. The residual 2,4-DNP concentration in solutions was determined by spectrophotometer and absorbance values were recorded at 361 nm for each solution. These data were used to calculate the sorption capacity of the sorbent by Eq. 2:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

where, q_e is the amount of 2,4-DNP adsorbed at equilibrium (mg/g); C_0 is the initial 2,4-DNP concentration in liquid phase (mg/L); C_e is the liquid phase 2,4-DNP concentration at equilibrium (mg/L); V is the volume of 2,4-DNP solution used in liter (L); and m is the mass of sorbent used in gram (g). Each experiment was done three times under identical conditions. 2,4-DNP initial concentration in the solution varied to investigate its effect on the sorption capacity. Studies were also conducted for various time intervals to determine when sorption equilibrium was reached and the maximum removal of 2,4-DNP was attained.

Result and discussion

Influence of the initial 2,4-DNP concentration

The influence of various initial 2,4-DNP concentration on sorption was investigated (Fig. 6). The quantity of β -CD Polymer was kept constant while the concentration of 2,4-DNP varied between 100 and 1,000 mg/L. The results showed an increase in the sorption capacity with the initial concentration of 2,4-DNP increase. The sorption capacity of β -CDP was due to the BET specific surface area, the content of β -CD units in the Polymer, and inclusion effect between the sorbent and the sorbate. The BET specific surface area of β -CDP is given in Table 1; however, the BET specific surface area does not play an important role. In previous works [25, 26], it was reported that the sorption mechanism of β -CDP was complex, probably simultaneously dominated by surface sorption (physical adsorption, hydrogen bonding) and diffusion into the polymer network, chemisorptions via the formation of an inclusion complex due to the presence of the CD sites. β -CD molecules have a remarkable capacity to form inclusion complexes, and the β -CDP retains the inclusion properties of CD molecules.

Fig. 5 Scanning electron microscope photographs (Pt. coated) of (a) β -CD and (b) β -CD polymer

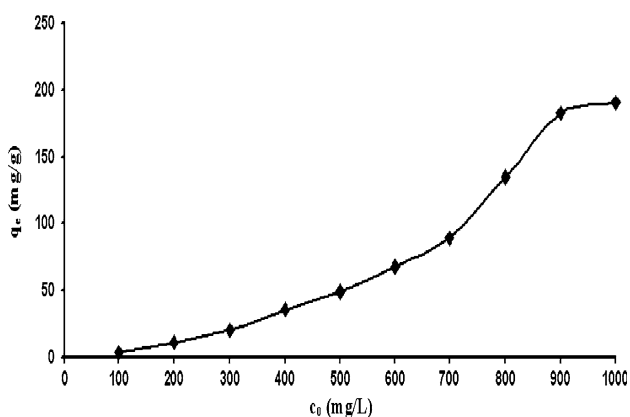
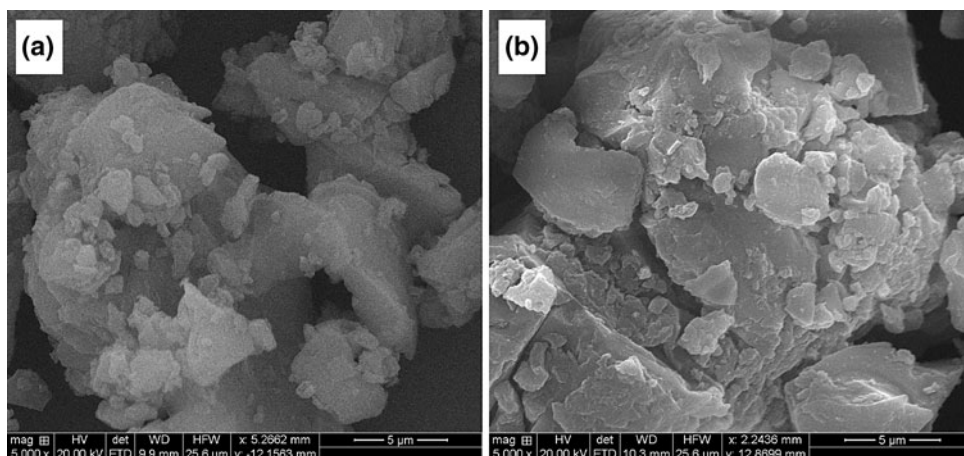


Fig. 6 Effect of initial concentration on 2,4-DNP sorption (conditions: sorbent: 0.1 g β -CD polymer, volume: 50 mL, temperature: 303 K)

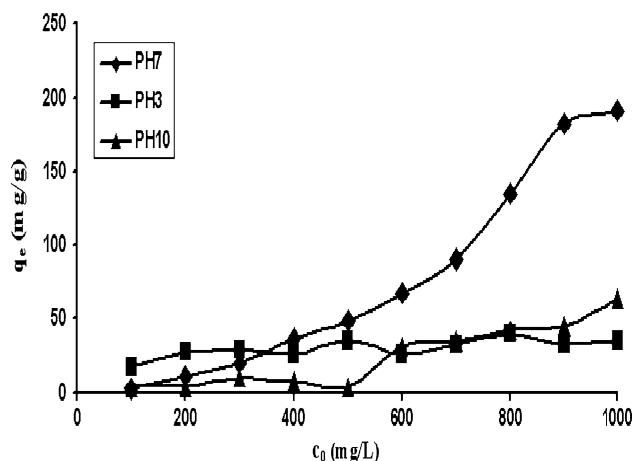


Fig. 7 Effect of pH on 2,4-DNP sorption (conditions: sorbent: 0.1 g β -CD polymer volume: 50 mL, temperature: 303 K)

Effect of pH

To evaluate the influence of the pH on the sorption of the 2,4-DNP, tests were carried out in neutral (pH ~ 7), acidic (pH ~ 3), and alkali (pH ~ 10) solutions with concentration between 100 and 1,000 mg/L of 2,4-DNP solution at 303 K. pH of these working solutions were adjusted by using NaOH and H₃PO₄ from the range of pH 3, 7, and 10. The values of the sorption capacity for 2,4-DNP on β -CDP in pH 7 is higher than other two pH solutions (Fig. 7) because the some of β -CDP may get hydrolyzed and dissociated into β -CD and citric acid. So that the 2,4-DNP molecule formed inclusion complex with β -CD and it could not be separated by centrifuge method, because it soluble in this solution itself and absorption value also increased. Due to this reason the sorption capacity is increase in pH ~ 7. The sorption capacity of this polymer towards 2,4-DNP is 192 mg/g. Thus, all the studies were performed at pH 7.

Kinetics of adsorption capacity

The β -CD polymer was applied to adsorption toward 2, 4-DNP of which the initial concentration was 1,000 mg/L as shown in Fig. 8. In less than 60 min, the concentration (C) of 2,4-DNP was decreased to 671 mg/L and the equilibrium attain after 60 min. The adsorption capacities (q) were calculated according to Eq. 1. As shown in Fig. 8 (Inset), the maximum adsorption capacities of the polymer toward 2,4-DNP: $q_{max} = 192$ mg/g it's indicating that the polymer adsorbed 2,4-DNP considerably. In several authors have been reported the different verities of materials (carbon) AP-32 carbon (apricot stone shell) [27], Prolabo (Charcoal activated powder) [27], GAC (granular activated carbon) [28], PHEMA microbeads [29], Bentonite [30], Paper mill sludge [31], Phanerochaete chrysosporium biomass [32], Palm pith carbon [33], Coir pith carbon [34], Fly Ash [35], Coal Fly Ash [36], Aged—refuse in biofilter [37] are able to adsorb the 2,4-DNP.

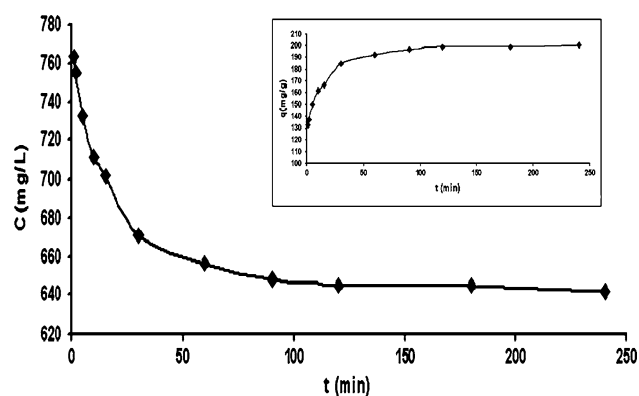


Fig. 8 Effect of contact time on 2,4-DNP sorption. Kinetics of adsorption (Inset) capacity of β -CD polymer (conditions: sorbent: 0.1 g β -CD polymer, 2,4-DNP initial concentration: 1,000 mg/L, volume: 50 mL, temperature: 303 K)

Table 2 Comparison of 2,4-DNP adsorption on various adsorbents

S. No.	Adsorbent	Adsorbability (mg/g)	References
1	AP-32	162	[27]
2	Prolabo (Charcoal activated powder)	187	[27]
3	GAC (Granular activated powder)	33	[28]
4	PHEMA microbeads	16.2	[29]
5	β -CD polymer	192	In this study
6	Bentonite	3.92	[30]
7	Paper mill sludge	4.49	[31]
8	Phanerochaete chrysosporium biomass	4.09	[32]
9	Palm pith carbon	19.16	[33]
10	Coir pith carbon	19.12	[34]
11	Fly Ash	22.0	[35]
12	Coal Fly Ash	1.5–1.7	[36]
13	Aged—refuse in biofilter	1.53	[37]

These data are listed in Table 2 and from the Table 2, the β -CD polymer having very good adsorption capacity. Even though it having low surface area (0.622 m²/g) when compared to AP-32 (BET surface area is 129 m²/g)

Adsorption isotherm

The Freundlich model was used to model experimentally obtained isotherms. The operating conditions that produced the best response for the percentage of 2,4-DNP removal were used in isotherm studies. The Freundlich equation is applicable to adsorption on heterogeneous surfaces, i.e., surfaces with non-energetically equivalent sites [26]. The adsorption curves obtained were applied to the Freundlich

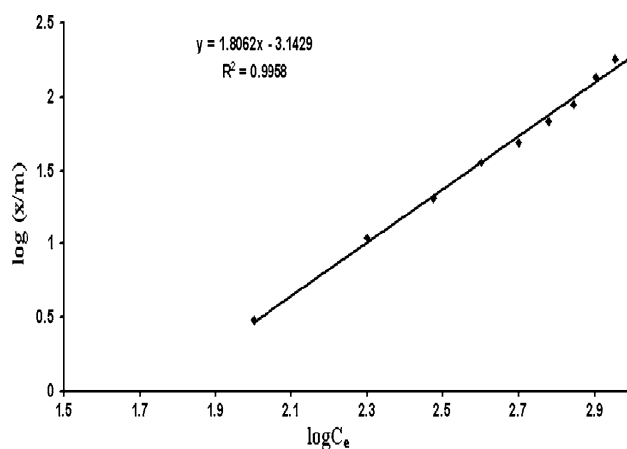


Fig. 9 Freundlich adsorption isotherms of β -CD polymer with 2,4-DNP

equation, the linearised Freundlich isotherm equation given by:

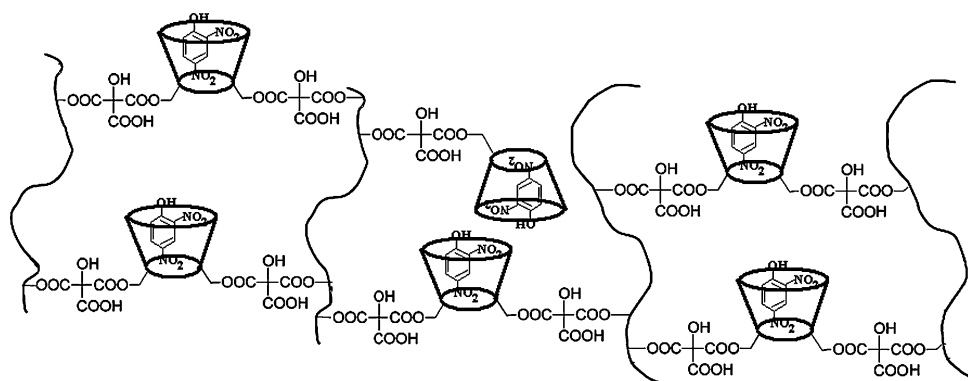
$$\log\left(\frac{x}{m}\right) = \log K + \left(\frac{1}{n}\right) \log(C_e) \quad (3)$$

where x/m is the amount of solute absorbed per unit weight of adsorbent (mg/g) and C_e is the concentration of solute remaining in solution at equilibrium (mg/L). The model provides a representation of the adsorption equilibrium between an adsorbate in solution and the surface of the adsorbent. Freundlich parameters K and $1/n$ are empirical constants and indicate of the extent of adsorption and adsorption effectiveness, respectively. As can be seen from Fig. 9, the isotherm model fit the β -CD polymer, since they were in the linear region. Examination of the plot suggests that the linear Freundlich isotherm provided a good model for the sorption of 2,4-DNP, thus, signifying the heterogeneous surface or pores for the adsorption of 2,4-DNP onto the β -CD polymer. Figure 9 shows the linear Freundlich sorption isotherm constants K and n , and the coefficients of determination R^2 . Based on the R^2 values, the linear form of the Freundlich isotherm appeared to produce a practical model for estimating sorption for concentration range 0–1,000 mg/g. The Freundlich expression Eq. 4 is an exponential equation and, therefore,

$$q_e = K[\text{DNP}_e]^{1/n} \quad (4)$$

Assumes that as the adsorbate concentration increases, so too does the concentration of adsorbate on the adsorbent surface. This expression is characterized by the extent of the adsorption (K) and the heterogeneity factor (n), and so the Freundlich isotherm may be used to describe heterogeneous systems. This suggests that some heterogeneity in the surface or pores of the β -CD polymer will play a key role in 2,4-DNP adsorption, and that the heterogeneous adsorption model will be better for isotherm simulation. Results in Fig. 9 show that

Fig. 10 Adsorption product of 2,4-DNP with β -CD polymer as inclusion complex



there is a steady increase in the extent of adsorption (K) with an increase of initial concentration of 2,4-DNP, indicating that increasing the bulk liquid concentration increases the driving force of 2,4-DNP from bulk solution onto and into the solid particle. The values Freundlich constants, K and $1/n$, were found to 3.141 and 1.806 respectively on the β -CD polymer at 30 °C.

In addition, the Freundlich constant ' n ' can measure the deviation from linearity of the adsorption. If $n = 1$ the adsorption is linear; this represents that the adsorption sites are homogeneous in energy and no interaction takes place between the adsorbed species. If $n < 1$ this entails that increased adsorption alters the sorbent in a manner that increases the sorption capacity, such as forming new adsorption sites. When $n > 1$, or becomes larger yet, the adsorption bond becomes weak, and the value of x/m changes significantly with small changes in C_e . As the n value of the β -CD polymer is less than unity, this would seem to suggest that the 2,4-DNP inclusion complex is formed rather than physical adsorption is prevailing [38]. The kinetic results showed that the β -CD polymer can eliminate high concentration of 2,4-DNP from aqueous solution by adsorption. The uptake of 2,4-DNP was higher at high initial 2,4-DNP concentration. An effort was also made to infer the data using the Langmuir equation. Nevertheless, the fit was typically found to be very poor.

Characterization of adsorption-product

The solid complex formation may be confirmed by FT-IR spectroscopy (Fig. 3c) because the bands resulting from the included part of the guest molecule are generally shifted or their intensities altered. In 2,4-DNP the two peaks are observed at 1,540.6 and 1,348.0 cm^{-1} due to the characteristics stretching of aromatic nitro group. In the adsorption product shows the stretching peaks of aromatic nitro group intensities are reduced and shifted to 1,352 cm^{-1} this is due to the nitro groups are included into the β -CD cavity. The N=O stretching frequency appeared at 1,626 cm^{-1} in 2,4-DNP but it shifted to 1,637 cm^{-1} and intensities are

reduced in the adsorption product this is due to the nitro groups are included into the β -CD cavity. The intensive absorption band appeared at 1,740 cm^{-1} this is due to C=O stretching vibration of carboxyl group so that the acid group does involve in the bond formation. The band at 1,200 cm^{-1} in adsorption product so that the ester group does not affected during the adsorption process. From the above discussion the 2,4-DNP is adsorbed by inclusion complex formation on β -CD polymer (Fig. 10).

Recovery of 2,4-DNP and recycle use of β -CD polymer

To recover the adsorbed 2,4-DNP and to reuse the β -CD Polymer, 0.3 g β -CDP with previously adsorbed equilibrium 2,4-DNP, was shaken for 2 h at 40 °C with 10 mL absolute alcohol. The recovery ratio was defined as the ratio of the 2,4-DNP amount in alcohol to the amount previously adsorbed on β -CDP. The recovery ratio (first time) of 2,4-DNP on 90% on β -CDP. It was observed that the sorption capacity was not changed after this treatment. Even after five times regeneration tests were performed, the β -CDP has almost the same sorption ability in contrast to original β -CDP. This suggested that recyclable values of the β -CDP were more advantageous than activated carbon in practical use. Compared with some recent data in the literatures [25, 26, 39] the result also revealed the potential of β -CDP to be effective sorbents for removing pollutants in the water.

Conclusion

Results of sorption showed that the β -CDP exhibited good sorption behavior and acceptable sorption time towards 2,4-DNP. Equilibrium isotherm data were consistent with the Freundlich equation for β -CDP. Adsorption of 2,4-DNP on β -CDP was found to be inclusion complex formation and it conformed with FT-IR spectra. Furthermore, the regeneration of β -CDP was so easy that β -CDP could be used as a kind of recyclable sorbents.

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