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# Sorption of 1–Naphthol on β–Cyclodextrin–Poly(ethylene Glycol) hydrogels

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**Abstract:** The sorption behavior of hydrogels prepared by crosslinking β–cyclodextrin with poly(ethylene glycol) modified with isocyanate end groups, is analyzed by using 1–naphthol as a model molecule. Concave sorption isotherms are observed and are well described by the Freundlich isotherm model. The sorption capacity increases as does the concentration of 1–naphthol in the medium and depends on the molar mass of poly(ethylene glycol) used in the synthesis of the hydrogel and on its β–cyclodextrin content.

For hydrogels with the same content of β–cyclodextrin, the sorption capacity decreases with increasing the molar mass of poly(ethylene glycol) used in the synthesis. The higher sorption capacity has been found for the hydrogels prepared from PEG with a molar mass of 400 g/mol and with a β–cyclodextrin content between 9–12 % in weight. The sorption capacity of these samples is close to that reported for other hydrogels based on β–cyclodextrin.

**Keywords:** sorption; β–cyclodextrin; Freundlich isotherm; 1–naphthol, hydrogel.

## Introduction

The networks formed by hydrophilic polymers known as hydrogels, have found important applications in processes involving the release or sorption of different substances[1]. Biomedical applications of hydrogels are perhaps the most usual[2], but also its applications as sorbent for removal of contaminants are becoming important. In this regard, there is great interest in the synthesis of new absorbent materials, particularly those that incorporate components of natural origin. Thus, certain types of biopolymers such as polysaccharides have aroused particular interest in the synthesis of such materials[3].

A class of polysaccharides with a great sorption capacity through the mechanism of inclusion complexation is the family of cyclodextrins[4]. The most important members of this family of polysaccharides are alpha, beta and gamma cyclodextrins. They are obtained by modification of starch.

All of them are molecules that have a toroidal structure with a different number of glucopyranose units. The interior of the cavity formed by these units has a marked hydrophobic character. Substances that have hydrophobic groups can be included in the cavity forming the corresponding complex through host–guest interactions[5]. For example, aromatic compounds produce these types of complexes with cyclodextrins by inclusion of the aromatic ring in the cavity.

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Aromatic compounds are among many of the industrial waste, they are toxic and not easily biodegradable, so its disposal of the environment is a goal of great practical interest. Consequently, the complexation with cyclodextrins can be a suitable procedure to be employed in the separation or extraction of aromatic compounds with applications in environmental protection[6,7].

Considering its current prices the β–cyclodextrin (β–CD) is the most appropriate choice within this family of polysaccharides for use in sorption processes. The solubility of β–CD in water poses a problem in its application to wastewater treatment. A common way to solve this problem is grafting β–CD on suitable organic or inorganic carriers, or crosslinking with different reagents. The latter method is particularly interesting because it allows the obtaining of cyclodextrin hydrogels capable of sorbing pollutants from wastewater and, subsequently, can be easily regenerated.

Recently, our group has developed a new type of hydrogels containing β–CD by using as crosslinking agent a modified Poly(ethylene glycol) (PEG): poly(ethylene glycol) end–capped with a diisocyanate[8,9]. The reaction between the chains of the modified PEG and the hydroxyl groups of cyclodextrin rings leads to the formation of a network with urethane bonds. This paper analyzes the sorption capacity of these hydrogels. We have chosen 1–naphthol as a model sorbate molecule[10]. Other authors[11–14] have studied the sorption of 1–naphthol over several cyclodextrin networks because it can be seen as a model molecule both in terms of aromatic pollutants such as on the formation of inclusion complexes.

In this work we have characterized and quantified by UV–visible spectroscopy the sorption isotherms of 1–naphthol on hydrogels formed by β–CD and PEG. Three different families of hydrogels, differing in the length of the PEG chains that constitute its structure have been used.

Specifically, hydrogels consisting of β–CD crosslinked with PEG of different molar masses (400, 600 and 900 g/mol), have been used, generating materials with different swelling capacities in water. Also, in each of these three families were tested hydrogels with different contents of β–CD. This is very important since it modifies the network topology, being much denser as the percentage of β–CD is reduced (a greater number of PEG chains emerge from each cyclodextrin crosslink). One of the aims of this work is to correlate the sorption capacity of these hydrogels with the network structure.

## Results and Discussion

By following the protocol described in the experimental part, the sorption isotherms of 1–naphthol, at 30 ºC, were determined for the hydrogels shown in Table 2. As an example of the general behavior of these systems, the sorption isotherms for the set of hydrogels prepared with a β–CD/PEG molar ratio of 1/4 but with PEG of different molar masses are displayed in Figure 1. As can be seen, all the isotherms show a gentle concavity. Similar results are found for the rest of the studied hydrogels. This type of isotherms are not so frequently encountered, and this behaviour is attributed to that previously sorbed molecules lead to a modification of the sorbent which favours further sorption[15].

Given the nature of the hydrogels studied here, with a structure composed by cyclodextrin rings (with a practically constant interaction energy) and the polymer network linking the cyclodextrin units with a polar (ethylene oxide units) and non polar (hexamethylene units) moieties that also plays a decisive role on the sorption[7,13], the Freundlich isotherm, that

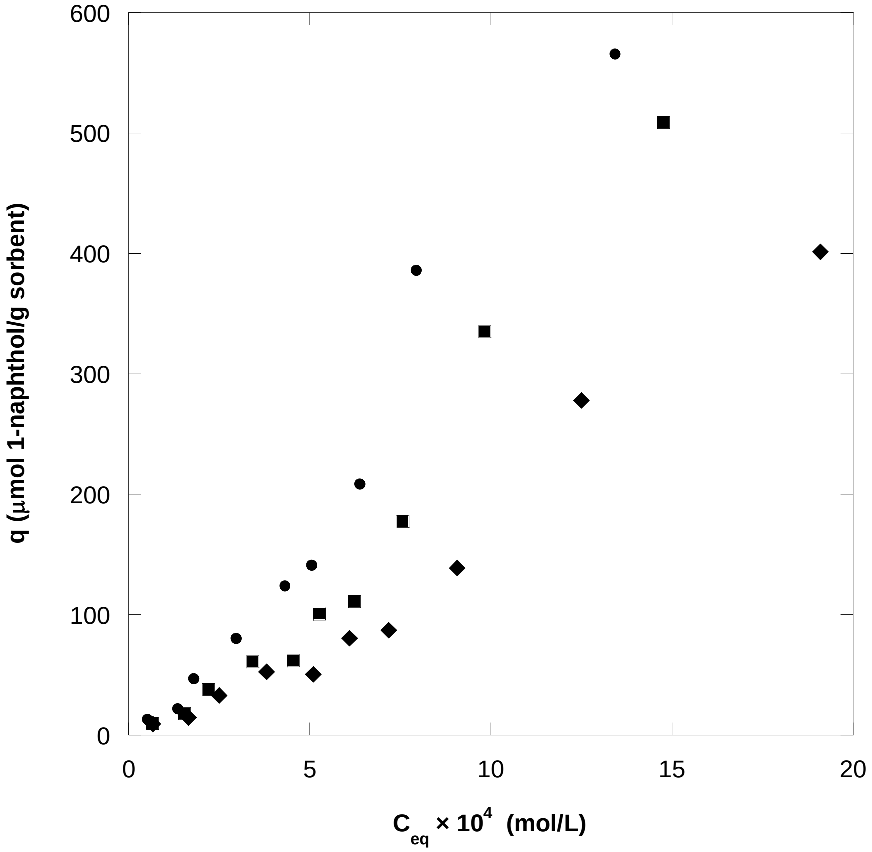

**Figure 1.** Sorption isotherms of 1–naphthol, at 30 ºC, for hydrogels with a β–CD/PEG molar ratio of 1/4: PEG400 (●), PEG600 (■) and PEG900 (♦).

proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between sorbed molecules, should be the most appropriate. The Freundlich equation has the form:

$$q = K_F C_{eq}^{1/n} \quad (1)$$

where q is the uptake of sorbate per unit weight of sorbent, $C_{eq}$ is the concentration of sorbate remaining in solution at equilibrium, and $K_F$ and n the Freundlich parameters representing sorption capacity and sorption intensity, respectively. Although this equation was developed for gas sorption, it is also suitable for sorption in dilute solutions.

Freundlich parameters are usually determined by fitting the experimental data to the logarithmic form of Equation 1:

$$\ln q = \ln K_F + \left(\frac{1}{n}\right) \ln C_{eq} \quad (2)$$

Figure 2 presents the plot of equation 2 for the sorption isotherms presented in Figure 1. As can be seen, the experimental results are well described by the Freundlich isotherm model. Similar forms of plot are exhibited by the other samples. The suitability of the Freundlich isotherm to describe the sorption behaviour of 1–naphthol on β–CD networks crosslinked with diisocyanates has been also reported by García–Zubiri et al.[13]. Table 1 shows the values of the Freundlich parameters obtained from these representations for all the systems studied in this work.

**Table 1.** Fitting parameters for the Freundlich isotherms ($q = K_F C^{1/n}$).

| Hydrogel | ln $K_F$ | 1/n | r |
|---|---|---|---|
| PEG400–4 | 13.96 | 1.17 | 0.997 |
| PEG400–6 | 15.41 | 1.31 | 0.973 |
| PEG400–10 | 15.54 | 1.32 | 0.997 |
| PEG400–14 | 15.68 | 1.33 | 0.995 |
| PEG600–4 | 14.75 | 1.32 | 0.991 |
| PEG600–6 | 15.24 | 1.35 | 0.982 |
| PEG600–10 | 15.20 | 1.33 | 0.997 |
| PEG600–14 | 15.53 | 1.37 | 0.996 |
| PEG900–4 | 14.33 | 1.33 | 0.994 |
| PEG900–6 | 13.48 | 1.25 | 0.985 |
| PEG900–10 | 15.37 | 1.42 | 0.990 |
| PEG900–14 | 15.79 | 1.48 | 0.994 |

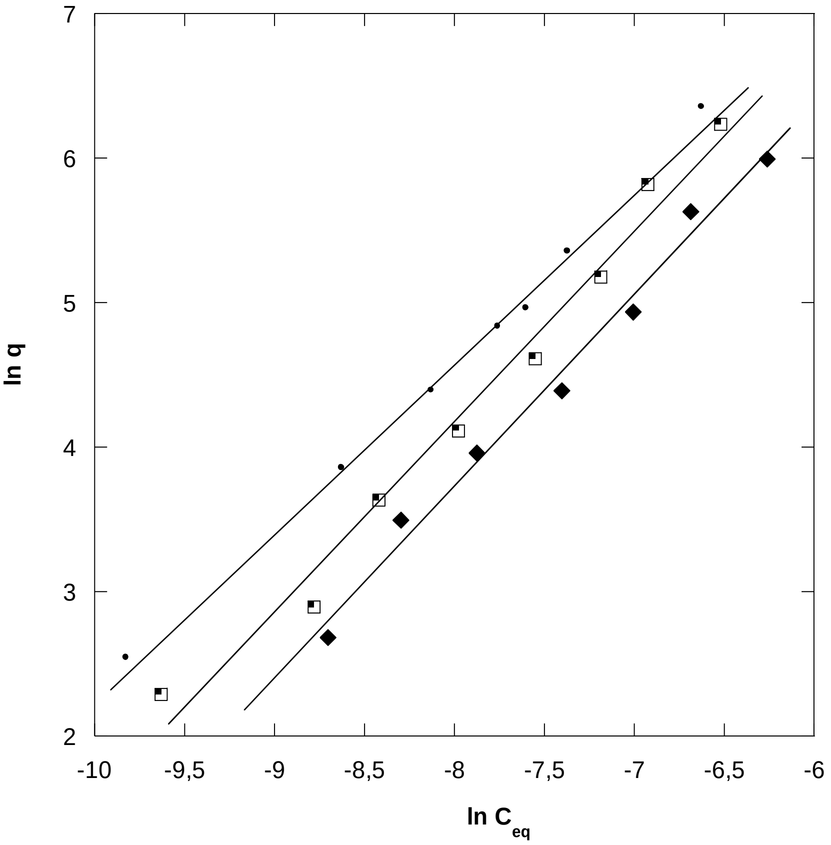

**Figure 2.** Freundlich isotherm plot for the sorption of 1–naphthol on the hydrogels with a β–CD/PEG molar ratio of 1/4: PEG400 (●), PEG600 (■) and PEG900 (♦).

The sorption capacity of a hydrogel is usually defined as the micromoles of sorbate sorbed per gram of polymer. The sorption capacity of our hydrogels can be easily determined from the values of q reported in the sorption isotherms. In Figure 3 are shown the sorption capacities for the whole set of hydrogels containing PEG400 while in Figure 4 are plotted the sorption capacities for hydrogels containing the same β–CD/PEG molar ratio (1/4) but have been prepared using PEG samples with different molar masses (chain lengths). For all the samples, an increase in the sorption capacity is observed with increasing the initial concentration of 1–naphtol in solution, a behaviour that has been found previously in β–CD–containing hydrogels[11–13].

On the other hand, as shown in Figure 3, for hydrogels prepared with PEG presenting an identical molar mass there is a small increase in the sorption capacity of the hydrogels when decreasing the ratio β–CD/PEG and this increase is more notorious as the initial concentration of 1–naphthol increases.

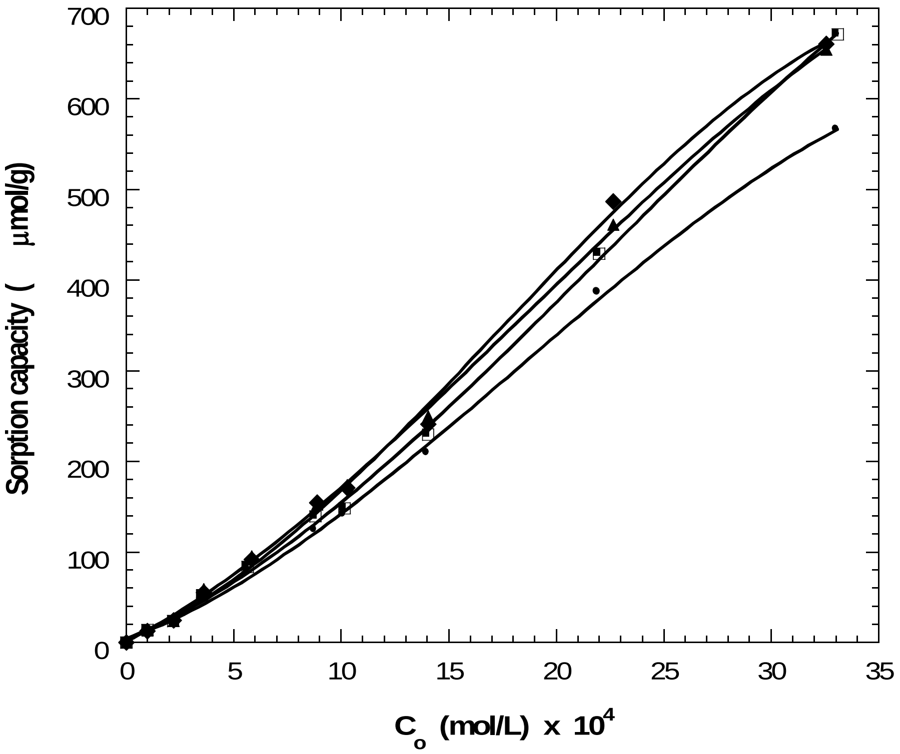

**Figure 3.** Sorption capacity of hydrogels prepared from PEG400 versus starting concentration of 1–naphthol in water at 30ºC: PEG400–4 (●), PEG400–6 (■) PEG400–10 (▲) and PEG400–14 (♦).

It can be clearly seen that while the shape of the curves is similar in all cases, the sorption capacity decreases as the molar mass of PEG increases, this result may seem surprising since it was found that when the molar mass of PEG is constant, the sorption capacity of the hydrogels decreases as the β–CD content does (Figure 3).

In addition, it can be clearly seen while the shape of the curves is similar in all cases (Figure 4), the sorption capacity of the hydrogels decreases as the molar mass of PEG increases. It is clear that the structure and/or the chemical composition of the network also play an important role in the sorption behavior in these classes of hydrogels.

To better understand the influence of the hydrogel β–CD content on the sorption of 1–naphthol, in Figure 5 the sorption capacity has been plotted as a function of the β–CD weight % in the hydrogel, when using 1–naphthol solutions with concentrations close to 150 mg/L. Similar results were obtained using other initial concentrations of 1–naphthol from 14 to 470 mg·L$^{-1}$.

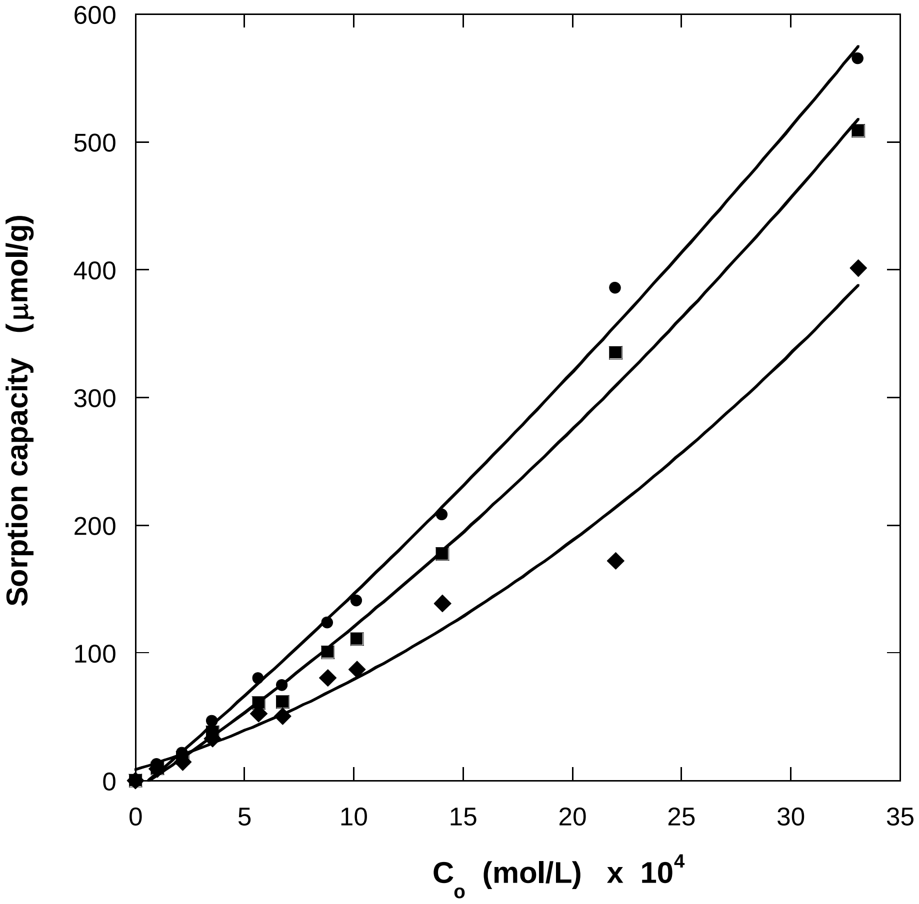

**Figure 4.** Sorption capacities for hydrogels prepared from PEG samples with different molar masses but with the same β–CD/PEG molar ratio (1/4) versus starting concentration of 1–naphthol in water at 30ºC: PEG400 (●), PEG600 (■) and PEG900 (♦).

Figure 5 indicates that the chemical structure of the network, in this case determined by the PEG chain length, plays a decisive role in the sorption process. It seems that the β–CD cavities are not the only elements that act as sorbents but also the network cavities (secondary cavities) formed by the PEG chains linked by urethane groups plays an important role in the trapping of 1–naphthol molecules.

The data presented in Figure 5 also show that for hydrogels prepared from PEG with a fixed molar mass, the sorption capacity progressively decreases as the β–CD content in the hydrogel increases. As the β–CD content decreases, the number of PEG chains linked by each cyclodextrin unit on the network must be greater, resulting in an increasingly denser network where the 1–naphthol molecules can be trapped more easily.

Romo et al.[7] found that using different crosslinking agents of the β–CD, the networks prepared with 1,6–diisocyanatohexane (HDMI) (the same diisocyanate that has been used in the synthesis of hydrogels prepared in this work), had a higher sorption capacity than those crosslinked with epichlorohydrin, succinyl chloride or toluene diisocyanate. It therefore appears that urethane units generated by the reaction with HDMI can establish favorable interactions (probably by hydrogen bonding) with the 1–naphthol molecules. This could also explain the higher sorption in gels with smaller PEG chain length, in which the urethane groups are present in a higher relative proportion on the network.

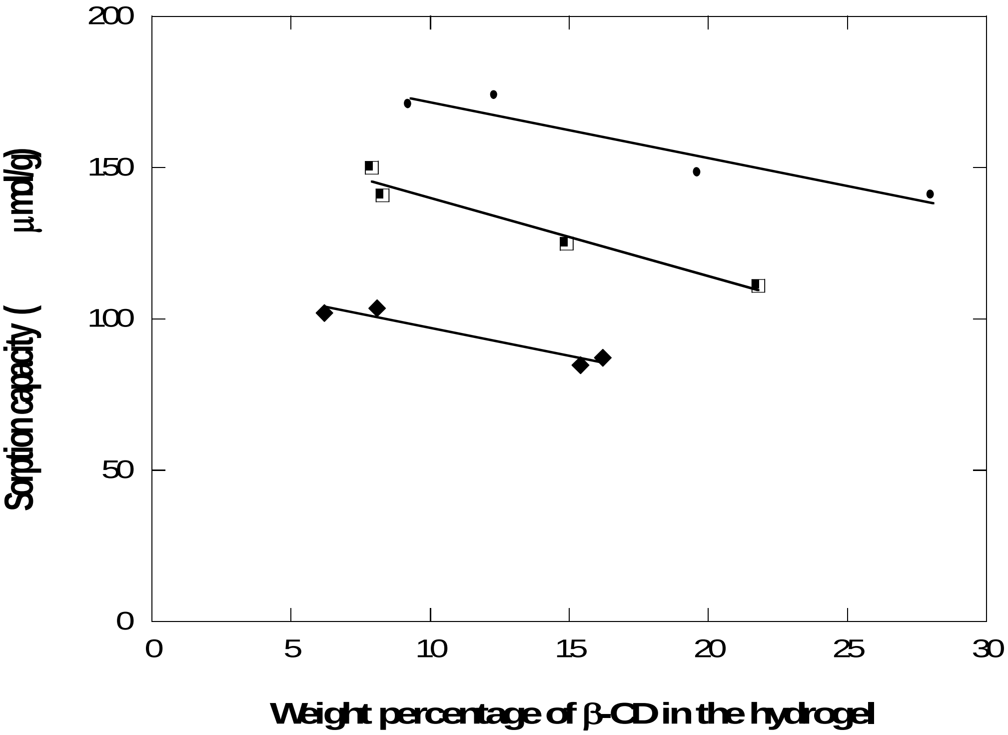

**Figure 5.** Sorption capacity of the hydrogels vs. β–CD content, at 30ºC, for 1–naphthol solutions with a starting concentration close to 150 mg/L: PEG400 (●), PEG600 (■) and PEG900 (♦).

There are several works that take the 1–naphthol as a model molecule to study the sorption on other cyclodextrin networks. In particular, García–Zubiri et al.[10] studied the sorption of this compound in β–CD hydrogels crosslinked with different reagents. The most similar samples to those studied here are the prepared with 1, 6–hexamethylene diisocyanate as crosslinking agent. A value of 103.7 μmol/g is reported in this study, for the sorption capacity of this network by using a solution of 1–naphthol in water with a concentration of $5.2\cdot10^{-5}$ mol/L. This is a higher value than the best obtained with our hydrogels to this concentration of 1–naphthol (95 μmol/g for PEG400 hydrogels), although their network have a significantly higher content of cyclodextrin (42.6% vs. 12%).

Crini et al.[11] studied the sorption of 2–naphthol on β–CD hydrogels (20–31% of β–CD) crosslinked with epichlorohydrin. The values reported for the sorption capacity of these networks are ranging between 105 and 106 μmol/g at similar concentrations of 2–naphthol ($5\cdot10^{-4}$ mol/L) in water, although 2–naphthol forms more stable inclusion complexes with β–CD than 1–naphthol[16] and the sorption behavior can be affected.

Our group[17] has studied de sorption of 1–naphthol on β–CD hydrogels prepared by reaction with acylated poly(ethylene glycol) with a molar mass of 600 g/mol. These networks, linked by ester groups, and with different β–CD/poly(ethylene glycol) ratios: 1/4, 1/6, 1/8 and 1/10; show a maximum sorption capacity of 82.8 μmol/g for concentrations de $5.2\cdot10^{-5}$ mol/L of 1–naphthol. This value is very similar to the reported here (79.7 μmol/g) for networks prepared with from PEG600. Consequently, the linkage of β–CD moieties with urethane or esther groups have a similar influence on the sorption behavior of these hydrogels based on PEG.

## Conclusion

In short, the hydrogels synthesized here based on PEG400 and β–CD bonded by urethane–type links, have a good sorption behavior, at least comparable to others β–CD–based hydrogels studied by other research groups. This fact, coupled with its chemical and thermal stability, and good mechanical properties, as has been reported in previous works[8, 9] makes them interesting materials for removing organic contaminants from water.

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## Experimental Section

1–naphthol (99%) was purchased from Sigma–Aldrich and was used as received. Ultra pure Milli–Q deionized water was employed in all the experiments.

Synthesis and characterization of the cyclodextrin hydrogels used as sorbent materials have been described in a previous paper[9]. Briefly, commercial samples of poly(ethylene glycol) (PEG) (Aldrich) with different molar masses (400, 600 and 900 g/mol) are end–caped with isocyanate groups by using a diisocyanate reagent (hexamethylene diisocyanate) in N,N–dimethylformamide as solvent at 328 K and dibutyltin dilaurate as catalyst. The end–capping reaction is monitored by FTIR spectroscopy and when the process conclude a solution of β–CD (99.5% of purity, was kindly supplied by Roquette Laisa España S.A.) in DMF (16.5 wt.–%) was injected. After 30 min of stirring, the mixture is transferred into appropriate moulds.
Finally, the gelation process is completed in an oven for 7 days at 348 K. All the gels were washed for 4 days with DMF and for two weeks with distilled water; the solvent being replaced every day. Finally, the gels were dried at vacuum.
Following this protocol, we have prepared from every PEG sample four networks with different β–CD/PEG molar ratios in the feed: 1/4; 1/6; 1/10 and 1/14. These samples are denoted as PEGA–b, where A indicates the molar mass of the original PEG precursor and b; their molar contribution in the feed. So, a gel denoted as PEG400_10 is formed by PEG with a molar mass of 400 g/mol with a β–CD/PEG molar ratio of 1/10.

As previously reported, the composition of these materials was determined by elemental analysis; their values are shown in Table 2.

**Table 2.** Hydrogel compositions, expressed as β–CD mass percentage, obtained by elemental analysis.

| **β–CD/PEG Molar ratio** | **PEG400** w % β–CD | **PEG600** w % β–CD | **PEG900** w % β–CD |
|---|---|---|---|
| 1/4 | 28.1 | 21.8 | 16.2 |
| 1/6 | 19.7 | 14.9 | 15.4 |
| 1/10 | 12.4 | 8.3 | 8.1 |
| 1/14 | 9.3 | 7.9 | 6.2[a] |

[a]) β–CD/PEG molar ratio in the feed

1–naphthol sorption capacity of the hydrogels was determined as follows: finely divided dry gels (≈ 500 nm) weighting approximately 28 mg were mixed with 8 mL of an aqueous solution of 1–naphthol, of known concentration in a capped amber vial. The mixture is stirred for 48 h maintaining the temperature at 30 ºC by using a thermostated bath. The amount of remaining 1–naphthol in the aqueous phase was determined by filtering the solution (Millipore Millex–HV 0.45 μm) and then analysed by UV spectroscopy (Kontron Instruments UVIKON 932) using the peak at 321 nm. For each sample, sorption experiments were carried out using ten different 1–naphthol concentrations ranging between $9.71 \cdot 10^{-5}$ and $3.31 \cdot 10^{-3}$ mol/L, and repeated twice. A dilution method was used for samples with the highest concentration.

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