

# Adsorption and recovery of nonylphenol ethoxylate on a crosslinked $\beta$ -cyclodextrin-carboxymethylcellulose polymer

Danielle Bonenfant, Patrick Niquette, Murielle Mimeault and Robert Hausler

## ABSTRACT

A study of adsorption/recovery of nonylphenol 9 mole ethoxylate (NP9EO) on a crosslinked  $\beta$ -cyclodextrin-carboxymethylcellulose ( $\beta$ -CD-CMC) polymer was carried out by ultraviolet-visible (UV-vis) and Fourier transform infrared (FTIR) spectroscopies. The adsorption was performed in mixtures containing 500 mg of the  $\beta$ -CD-CMC polymer and aqueous NP9EO solutions at concentrations 12–82 mg/L, whereas the recovery of NP9EO was effectuated by shaking the  $\beta$ -CD-CMC polymer loaded with methanol. The assays were made at 25°C and atmospheric pressure under agitation. The results have shown that the adsorption is a rapid process and the  $\beta$ -CD-CMC polymer exhibits a high NP9EO adsorption capacity of 83–92 w% (1.1–6.8 mg NP9EO/g  $\beta$ -CD-CMC polymer) dependent of the initial NP9EO concentration in liquid phase. This adsorption may involve the formation of an inclusion complex  $\beta$ -CD-NP9EO and a physical adsorption in the polymer network. The adsorption equilibrium measurements, which were analyzed using the Langmuir isotherm, have indicated a monolayer coverage and the homogeneous distribution of active sites at the surface of the  $\beta$ -CD-CMC polymer. Moreover, the negative value obtained for the free energy change ( $-13.2$  kJ/mol) has indicated that the adsorption process is spontaneous. In parallel, the  $\beta$ -CD-CMC polymer exhibited a high NP9EO recovery efficiency of 97 w% that may occur through a decrease of binding strength between  $\beta$ -CD-CMC polymer and NP9EO. Together, these results suggest that the  $\beta$ -CD-CMC polymer could constitute a good adsorbent for removing nonylphenol ethoxylates from wastewater due to its high adsorption capacity and non-toxic character of  $\beta$ -CD and CMC to environment.

**Key words** | adsorption, crosslinked  $\beta$ -cyclodextrin-carboxymethylcellulose polymer, FTIR spectroscopy, Langmuir isotherm, nonylphenol ethoxylate, recovery, UV-VIS spectroscopy

## INTRODUCTION

Nonylphenol ethoxylates (NPEOs) are lipophilic surfactants considered as an important group of non-ionic industrial compounds that have been extensively used in the manufacture of household detergents, personal-care products, pesticides, wetting and dispersing agents, emulsifiers, and textiles in the last 50 years (Tsuda *et al.* 2000;

Birkett & Lester 2003; Li *et al.* 2004; Yangxin *et al.* 2008). The general structure of NPEOs is shown at the Figure 1 (Bonenfant *et al.* 2009). The annual production of NPEOs in the world has been estimated at approximately 24,000–400,000 tons, of which about 60% enters the aquatic environment (Naylor *et al.* 1992; Naylor *et al.* 1996;

### Danielle Bonenfant

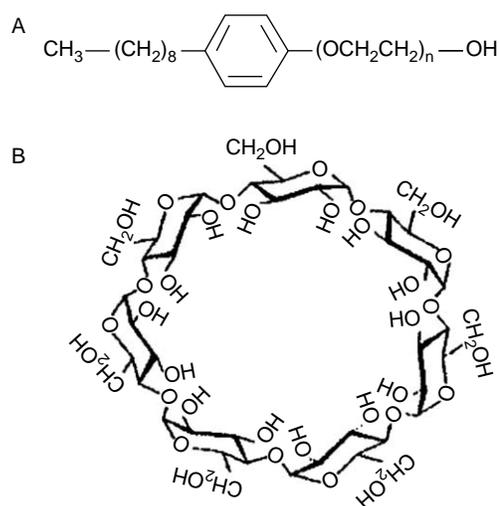
Robert Hausler (corresponding author)  
Département de génie de la construction,  
STEPPE-École de Technologie Supérieure,  
1100, Notre-Dame Ouest,  
Montréal Québec,  
Canada H3C 1K3  
E-mail: [Danielle.Bonenfant@ens.etsmtl.ca](mailto:Danielle.Bonenfant@ens.etsmtl.ca);  
[Robert.Hausler@etsmtl.ca](mailto:Robert.Hausler@etsmtl.ca)

### Patrick Niquette

Dessau inc.—Eau, industries et matières  
résiduelles,  
1220, Lebourgneuf,  
bureau 300,  
Québec Québec,  
Canada G2K 2G4  
E-mail: [Patrick.Niquette@dessau.com](mailto:Patrick.Niquette@dessau.com)

### Murielle Mimeault

Department of Biochemistry and Molecular  
Biology,  
College of Medicine,  
Eppley Cancer Institute,  
7052 DRC,  
University of Nebraska Medical Center,  
985870 Nebraska Medical Center,  
Omaha, NE 68198-5870,  
USA  
E-mail: [mmimeault@unmc.edu](mailto:mmimeault@unmc.edu)



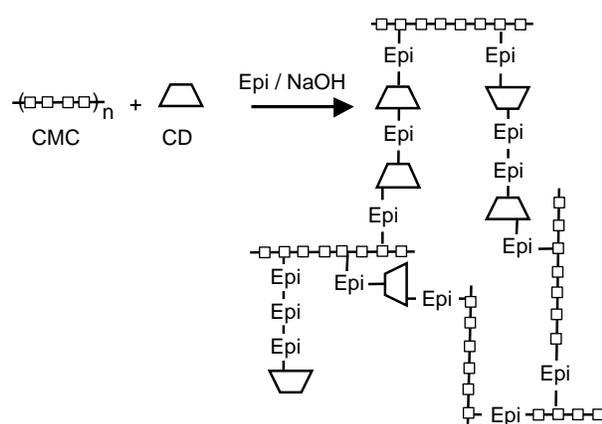
**Figure 1** | Scheme of structures of (A) nonylphenol ethoxylates, and (B)  $\beta$ -cyclodextrin.

Houde *et al.* 2002; Berryman *et al.* 2004). The presence of nonylphenol ethoxylates may cause several problems in the environment due to their incomplete biodegradation by wastewater treatment that results in the transformation of NPEOs to nonylphenol carboxylic acids (NPECs) and nonylphenol (Ahel *et al.* 1994; Soares *et al.* 2008). NPECs and nonylphenol are stable and toxic endocrine disruptors that can induce the prostate cancer and breast tumour cell proliferation, affect the development of testes and reproduction, and cause the feminization of male fish (Giwerzman *et al.* 1993; White *et al.* 1994; Routledge & Sumpter 1996; Blom *et al.* 1998; Brian *et al.* 2005; Sumpter 2007).

NPEOs and nonylphenol are difficult to remove from wastewater. Of particular interest, recent studies have shown that these surfactants may be captured by cyclodextrins (CDs) in aqueous mediums (Kawasaki *et al.* 2001; Bonenfant *et al.* 2009). Cyclodextrins are non-toxic cyclic oligosaccharides characterized by a doughnut-shaped structure including a hydrophobic and non-polar cavity that permit the solubilization of non-polar and low-polarity organic molecules by the formation of water-soluble inclusion complexes (Bender & Komiyama 1978; Bizzigotti *et al.* 1997; McCray & Brusseau 1998; Saenger *et al.* 1998; Szente *et al.* 1999). More specifically, these studies have indicated that the hydrophobicity of nonylphenol 9 mole ethoxylate (NP9EO) and nonylphenol may permit the

formation of water-soluble inclusion complexes with  $\beta$ -cyclodextrin ( $\beta$ -CD) and its derivatives. The formation of van der Waals interactions between the alkyls chains of NP9EO and nonylphenol and the cavity of  $\beta$ -CD may notably contribute to the NP9EO and nonylphenol complexation with  $\beta$ -CD (Bonenfant *et al.* 2009). A better technology using  $\beta$ -CD has also been tested for the adsorption of phenolic compounds in aqueous solution. It has been shown that the use of insoluble crosslinked cyclodextrin-carboxymethylcellulose polymers formed of tridimensional networks containing  $\beta$ -CD, epichlorohydrin (Epi), and carboxymethylcellulose (CMC), may enhance the adsorption capacity of  $\beta$ -CD for the  $\beta$ -naphthol in aqueous mediums (Figure 2) (Crini *et al.* 2002). This phenomenon has been associated with the formation of a very stable inclusion complex  $\beta$ -CD-naphthol which may be favored by the presence of the CMC. In fact, CMC can enhance accessibility and mobility of  $\beta$ -CD following an increase of the swelling of the polymer in water as well as the formation of Epi chains at the surface of the polymer that may favor the interactions between the polymer and  $\beta$ -naphthol.

The present study was undertaken to determine the NP9EO adsorption capacity and recovery efficiency of a crosslinked  $\beta$ -CD-CMC polymer. The adsorption and recovery studies were effectuated in an aqueous NP9EO solution and methanol, and the measures made by UV-vis spectroscopy. The Langmuir isotherm was used to analyse the adsorption equilibrium data. The crosslinked polymer was analyzed by FTIR spectroscopy.



**Figure 2** | Scheme of the reaction of crosslinked CD-CMC polymer (Crini *et al.* 2002).

## MATERIALS AND METHODS

### Materials

$\beta$ -cyclodextrin (98%), epichlorohydrin (99%) and sodium borohydride (98.5%) were purchased from Sigma-Aldrich Canada Ltd (Oakville, Ont.), nonylphenol 9 mole ethoxylate and sodium carboxymethylcellulose from Univar Canada Ltd (Dorval, QC), and methanol optima grade, sodium hydroxide beads, and acetone from Fisher Scientific Co. (Nepean, Ont.). All these products were used without additional purification.

### Preparation and characterization of the crosslinked $\beta$ -CD-CMC polymer

The crosslinked  $\beta$ -CD-CMC polymer was prepared at a molar ratio  $\beta$ -CD/CMC of 1/0.75 as following: 20 g of  $\beta$ -CD was mixed with 5 mg of  $\text{NaBH}_4$ , 8.534 g of CMC, 10 g of NaOH and 50 ml of deionized water, in a reactor at 50°C during one hour. After, 26.78 g of epichlorohydrin was added to mixture dropwise at 50°C under vigorous stirring. The  $\beta$ -CD-CMC polymer was washed with 70 ml of acetone at 50°C under stirring during 30 minutes. The polymer was transferred in 200 ml of cold deionized water and stored at 4°C during 24 hours. The polymer was washed with acetone during 24 hours, and washed with deionized water during 24 hours under agitation. Finally, the polymer was collected by filtration, dried at 60°C for 24 hours, and crushed.

The  $\beta$ -CD saturation of  $\beta$ -CD-CMC polymer or amount of  $\beta$ -CD incorporated into the  $\beta$ -CD-CMC polymer was evaluated using an internal standard (Monnier *et al.* 1979). This method has consisted to compare the absorbance of the FTIR bands of  $\beta$ -CD at  $1,024.2\text{ cm}^{-1}$  (mixture) and  $1,031.9\text{ cm}^{-1}$  (polymer) of two FTIR spectra of the dried polymer and a mixture containing 2 g of dried polymer and 430 mg of  $\beta$ -CD (Toma *et al.* 2006; Bonenfant *et al.* 2009). The percentage (%) of  $\beta$ -CD incorporated was calculated as described in Equation (1).

$$\% \beta\text{-CD incorporated} = (A_{\text{polymer}}/A_{\text{mixture}} - A_{\text{polymer}}) \times (C_t \times C_a/C_x) \times 100 \quad (1)$$

In Equation (1),  $C_t$ ,  $C_x$ , and  $C_a$  are the values of the amount of  $\beta$ -CD + Epi + CMC added into the preparation of the  $\beta$ -CD-CMC polymer, and the amounts of polymer (2 g) and  $\beta$ -CD added (430 mg) in the mixture, respectively.

### Preparation of the standard curves

The standard curves were prepared by dilution of NP9EO in deionized water or methanol to obtain the concentration ranges between 6.97–69.7 mg/L (NP9EO–water) and 6.86–68.6 mg/L (NP9EO–methanol). The standard curves were measured by UV-vis spectroscopy at 222 nm (peak associated with detergents) (Pons *et al.* 2004). The standard curves have correlation ( $r^2$ ) of 0.9984 (NP9EO–water) and 0.9993 (NP9EO–methanol).

### NP9EO adsorption experiments

The aqueous NP9EO solution (pollutant) used for the adsorption studies was prepared by dilution of appropriate amounts of NP9EO in deionized water at initial concentrations of 12, 24, 36, 48, 60, and 82 mg/L. The adsorption has been effectuated in a mixture containing 500 mg of crosslinked  $\beta$ -CD-CMC polymer (adsorbent) and 50 ml of pollutant in stopped flasks. The assays with NP9EO at 12–60 mg/L were performed during 1, 2, and 1,440 minutes, whereas the assays with NP9EO at 82 mg/L were effectuated during 1, 2, 5, 10, 15, 30, 60, 120, 180, 240, 480, and 1,440 minutes at  $25 \pm 1^\circ\text{C}$  and atmospheric pressure under a vigorous agitation. All the assays were made in triplicate. After adsorption, the supernatants were filtered using Filtropure cellulose acetate sterile filters (0.45  $\mu\text{m}$  pore size) from Sarstedt Aktengesellschaft & Co., and the amount of NP9EO in liquid phase was analyzed by UV-vis spectroscopy. The polymer loaded during 480 minutes that has been collected after the filtration was washed with two litres of deionized water, and dried at 60°C for 24 hours.

### Determination of the amount of NP9EO adsorbed at equilibrium

The amount of NP9EO adsorbed on the  $\beta$ -CD-CMC polymer at equilibrium,  $q_e$ , has been calculated from the Equation (2).

$$q_e = V(C_i - C_e)/m_a \quad (2)$$

In Equation (2),  $V$  is the volume of aqueous NP9EO solution used for the adsorption (L),  $C_i$  is the initial NP9EO concentration in liquid phase (mg/L),  $C_e$  is the concentration of NP9EO at equilibrium in liquid phase (mg/L), and  $m_a$  is the mass of crosslinked  $\beta$ -CD-CMC polymer used (g).

### Determination of the adsorption rate of NP9EO on the crosslinked $\beta$ -CD-CMC polymer

The adsorption rates of NP9EO at concentrations of 12–82 mg/L on the  $\beta$ -CD-CMC polymer were calculated during the first minute of adsorption, as described in Equation (3).

$$\text{Adsorption rate} = V(C_i - C_t)/m_a t_{\text{ads}} \quad (3)$$

In Equation (3),  $V$ ,  $C_i$ , and  $m_a$  are similar to parameters above described in Equation (2), and  $C_t$  and  $t_{\text{ads}}$  correspond to the NP9EO concentration in liquid phase at 1 minute of adsorption, and time of adsorption (minute), respectively.

### Determination of the Langmuir isotherm constants and parameter

The Langmuir constants  $K_L$  and  $a_L$  were evaluated from the linearisation (Equation (5)) of the Langmuir equation described in Equation (4) (Shoemaker *et al.* 1981; Crini *et al.* 2007).

$$q_e = K_L C_e / (1 + a_L C_e) \quad (4)$$

$$C_e/q_e = (a_L/K_L)C_e + 1/K_L \quad (5)$$

In Equations (4) and (5),  $q_e$ , and  $C_e$  were previously described at Equation (2), and  $K_L$  and  $a_L$  are the Langmuir isotherm constants, respectively. The values of  $K_L$  and  $a_L$  have been obtained from the intercept and slope of the plot  $C_e/q_e$  versus  $C_e$ .

The separation factor,  $R_L$ , was calculated from the Equation (6) (Hall *et al.* 1966; McKay 1982; Crini *et al.* 2007).

$$R_L = 1/1 + a_L C_i \quad (6)$$

In Equation (6),  $a_L$  and  $C_i$  correspond to parameter previously described in Equations (2) and (5).

### Determination of the free energy change of the adsorption of NP9EO on the crosslinked $\beta$ -CD-CMC polymer

The free energy change ( $\Delta G$ ) was calculated from Equation (7) (Crini *et al.* 2007).

$$\Delta G = -RT \ln K_L \quad (7)$$

In Equation (7),  $K_L$ ,  $R$  and  $T$  are the Langmuir constant (L/mol), universal gas constant (J/mol Kelvin), and temperature (Kelvin), respectively.

### NP9EO recovery experiments

The NP9EO recovery assays were effectuated with the crosslinked  $\beta$ -CD-CMC polymer loaded with NP9EO at 82 mg/L that was obtained from the adsorption during 480 minutes. The assays were performed in a mixture containing 504 mg of the crosslinked  $\beta$ -CD-CMC polymer loaded and 50 ml of methanol in stopped flasks that were shaken during 5, 10, 15, 30, 60, 120, 180, 240, 480, 720, 960, 1,200, and 1,440 minutes, at  $25 \pm 1^\circ\text{C}$  and atmospheric pressure. The samples were filtered using Filtropure cellulose acetate sterile filters (0.45  $\mu\text{m}$  pore size) and the supernatants analyzed by UV-vis spectroscopy. All the assays have been made in triplicate.

### Characterization by UV-vis spectroscopy

UV-vis spectra of standard curve samples, pollutant, and aqueous NP9EO and NP9EO-methanol supernatants collected after the assays of NP9EO adsorption and recovery were recorded on a Varian Cary BIO UV-VIS spectrophotometer with a 1 cm quartz cuvette. For each spectrum, covering the 190–800 nm region, a baseline was subtracted. Concentrations of NP9EO contained in the supernatants were evaluated from standard curves established for NP9EO in water and methanol measured at 222 nm (Pons *et al.* 2004).

### Characterization by FTIR spectroscopy

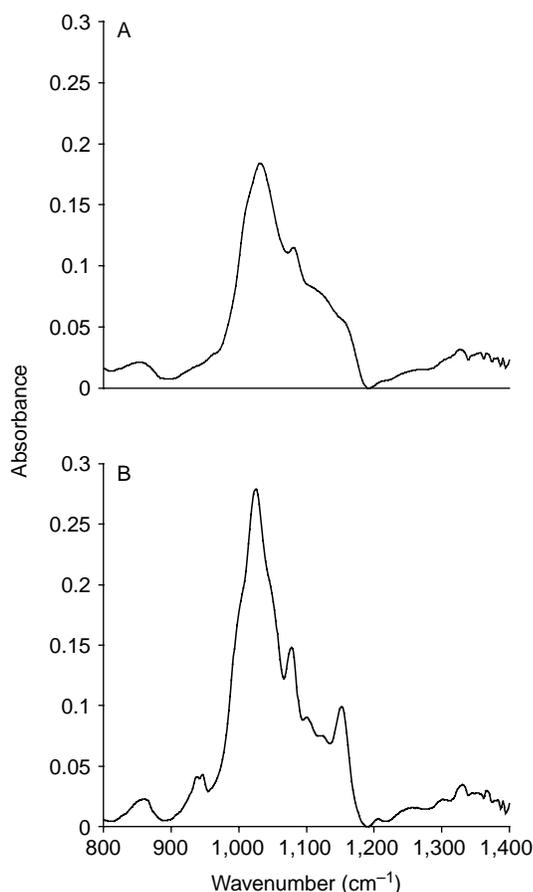
Infrared spectra of dried crosslinked  $\beta$ -CD-CMC polymer, and mixture containing 2 g of crosslinked  $\beta$ -CD-CMC polymer and 430 mg of  $\beta$ -CD were obtained using a Varian

Excalibur 3100 FTIR spectrometer equipped with a reflexion ATR module, and continuously purged with dry air. For each spectrum, covering the  $500\text{--}7,900\text{ cm}^{-1}$  region, 200 interferograms were coadded, apodized and Fourier transformed to give a resolution of  $2\text{ cm}^{-1}$ . Moreover, each spectrum was corrected by the subtraction of a linear baseline in the  $800\text{--}1,400\text{ cm}^{-1}$  region.

## RESULTS AND DISCUSSION

### Characterization of the crosslinked $\beta$ -CD-CMC polymer

The results obtained from the FTIR measurements have indicated a  $\beta$ -CD saturation percentage of crosslinked  $\beta$ -CD-CMC polymer of 91 w% of the  $\beta$ -CD (added during the preparation) (Figure 3). This result indicates that an amount of 18.2 g of  $\beta$ -CD could be incorporated in the

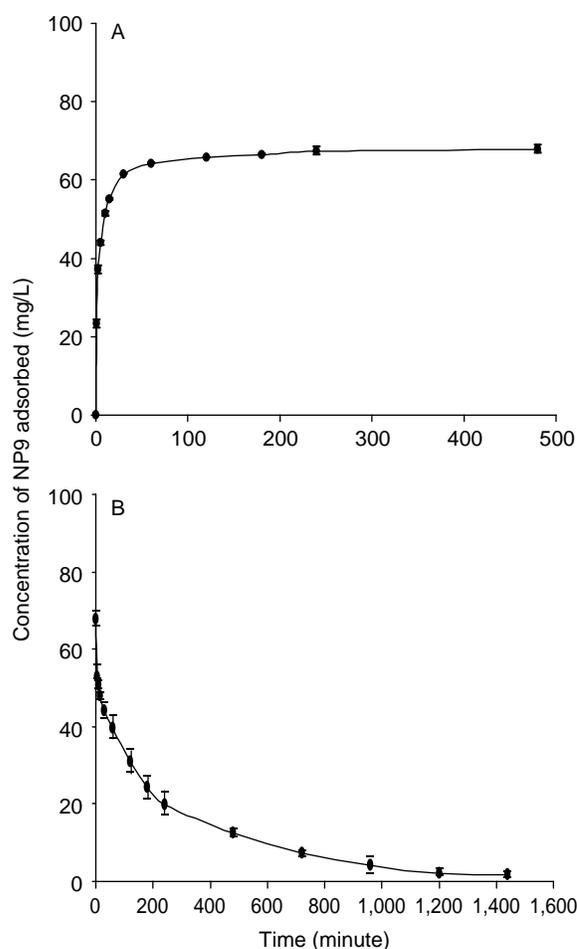


**Figure 3** | FTIR spectra of the  $800\text{--}1,400\text{ cm}^{-1}$  region of dried (A) crosslinked  $\beta$ -CD-CMC polymer, and (B) mixture containing 2 g crosslinked  $\beta$ -CD-CMC polymer and 430 mg  $\beta$ -CD. FTIR spectra were measured at  $25 \pm 1^\circ\text{C}$ .

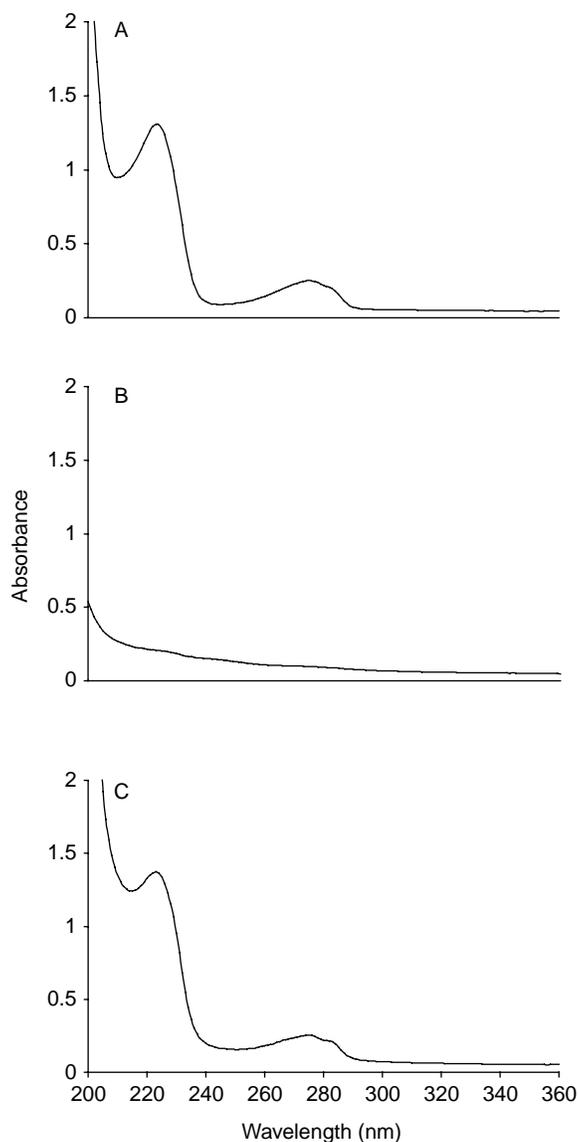
53.2 g of polymer and formed tridimensional networks with Epi and CMC. This high  $\beta$ -CD content of the polymer provides it with a great adsorption capacity for the NP9EO.

### Determination of the NP9EO adsorption capacity of the crosslinked $\beta$ -CD-CMC polymer

The results shown in Figure 4 have revealed that the values of the adsorption of NP9EO in the crosslinked  $\beta$ -CD-CMC polymer rapidly increase during the first 60 minutes and reach a saturation adsorption capacity value of  $68 \pm 1\text{ mg/L}$  ( $6.8 \pm 0.1\text{ mg}$  of NP9EO/g of  $\beta$ -CD-CMC polymer) after 480 minutes. This maximum value of absorption corresponds to 83 w% of the amount of NP9EO contained in the



**Figure 4** | Variation of (A) NP9EO adsorption in the crosslinked  $\beta$ -CD-CMC polymer, and (B) NP9EO recovery in the methanol. The assays of adsorption were effectuated with an aqueous solution at an initial NP9EO concentration of 82 mg/L. All the assays were performed at  $25 \pm 1^\circ\text{C}$  and atmospheric pressure under agitation.



**Figure 5** | UV-vis spectra of (A) pollutant, (B) supernatant after the adsorption of an aqueous solution of NP9EO at 82 g/L during 480 minutes, and (C) supernatant after a NP9EO recovery of 1,440 minutes. The absorbance values were measured at 222 nm. The assays were effectuated at  $25 \pm 1^\circ\text{C}$  and atmospheric pressure under agitation.

pollutant. This result is in agreement with those of Murai *et al.* (1996) that have indicated that about 85 w% of an other non ionic alkylphenol ethoxylate (APE) was adsorbed on  $\beta$ -CD-Epi polymer at  $25^\circ\text{C}$ . This high adsorption capacity can be associated with the formation of a very stable inclusion complex  $\beta$ -CD-NP9EO, as suggested by Crini *et al.* (2002). The inclusion complex  $\beta$ -CD-NP9EO may be stabilized by the presence of hydrophobic interactions of van der Waals formed between the cavity of  $\beta$ -CD

and the alkyl chains of the NP9EO as previously proposed (Bonenfant *et al.* 2009). The formation of this complex can be favoured by the presence of CMC that may enhance accessibility and mobility of the  $\beta$ -CD in the polymer by promoting the swelling of the polymer in water. Moreover, Epi can also enhance the adsorption through the generation of chains at the surface of the polymer, that can contribute to increase the interactions between the polymer and NP9EO. The results of adsorption are in agreement with the disappearance of the peak at 222 nm (associated with NP9EO) that was observed in the UV-vis spectrum of the supernatant measured after the adsorption of 480 minutes (Figure 5).

The results showed in Table 1 indicate that the NP9EO adsorption capacity of  $\beta$ -CD-CMC polymer increases with the initial NP9EO concentration in liquid phase. However, the percentage of NP9EO adsorbed decreases with the initial concentration. This data indicates that the adsorption of NP9EO on the  $\beta$ -CD-CMC polymer is highly concentration dependent, and the polymer can adsorb much more NP9EO at low concentration.

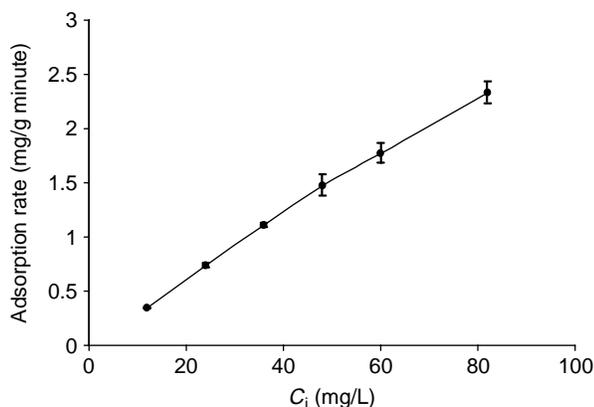
#### Determination of the adsorption rate of NP9EO on the crosslinked $\beta$ -CD-CMC polymer

Figure 6 shows that the adsorption rate of NP9EO measured at the beginning of the adsorption (first minute) linearly increases when the initial NP9EO concentration rises. These results indicate that the adsorption rate of NP9EO is proportional to the initial NP9EO concentration in liquid phase at the beginning of the adsorption.

**Table 1** | NP9EO adsorption capacity of the crosslinked  $\beta$ -CD-CMC polymer

Initial NP9EO concentration (mg/L)	NP9EO adsorption capacity* (mg NP9EO/g $\beta$ -CD-CMC polymer)	Percentage of NP9EO adsorbed (%)
12	$1.10 \pm 0.01$	92
24	$2.18 \pm 0.02$	91
36	$3.22 \pm 0.02$	89
48	$4.22 \pm 0.05$	88
60	$5.18 \pm 0.08$	86
82	$6.8 \pm 0.1$	83

\* The NP9EO adsorption capacity was determined at 1,440 minutes of adsorption (dynamic equilibrium). The adsorption of NP9EO was performed at  $25 \pm 1^\circ\text{C}$  and atmospheric pressure under agitation.



**Figure 6** | Variation of the adsorption rate of NP9EO on the crosslinked  $\beta$ -CD-CMC polymer versus initial concentration of NP9EO in liquid phase. The adsorption rate was evaluated at the first minute of adsorption,  $25 \pm 1^\circ\text{C}$  and atmospheric pressure.

#### Determination of the adsorption isotherm of NP9EO on the crosslinked $\beta$ -CD-CMC polymer

The adsorption isotherm and plot of  $C_e/q_e$  versus  $C_e$  are shown at Figure 7. The curve of Figure 7(B) gives a straight line with a high linear correlation coefficient ( $R^2 = 0.9976$ ), indicating that the experimental adsorption results at equilibrium fit the Langmuir adsorption isotherm. The  $K_L$  and  $a_L$  calculated from the curve shown in Figure 7(B) and Equation (5) were found to be 1.23 L/g (202.2 L/mol) and 0.11 L/mg, respectively. The fact that the experimental results fit the Langmuir isotherm indicates a monolayer coverage of NP9EO molecules and the homogeneous distribution of active sites at the surface of the crosslinked  $\beta$ -CD-CMC polymer (Shoemaker *et al.* 1981; Crini *et al.* 2007). These data support the results from Murai *et al.* (1996) that have indicated that the adsorption equilibrium of another APE on a  $\beta$ -CD-Epi polymer also fitted the Langmuir isotherm.

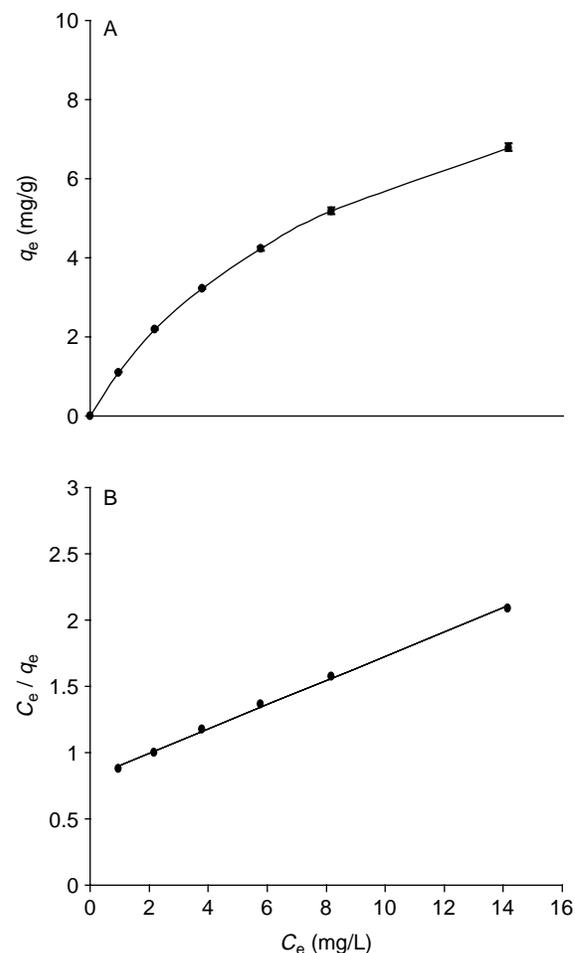
The values of the separation factor  $R_L$  that were calculated from the Equation (6) and experimental values of  $a_L$  obtained from Figure 7 are presented in Figure 8. The separation factor indicates if the isotherm shape can be favourable or unfavourable to the adsorption. In the case of the adsorption of NP9EO on the  $\beta$ -CD-CMC polymer, the data in the Figure 8 show  $0 < R_L < 1$ , indicating that the isotherm shape is favourable to the adsorption of NP9EO (Weber & Chakravorti 1974; Crini *et al.* 2007).

Moreover, the  $R_L$  values show that the adsorption of NP9EO is more favourable at lower concentration.

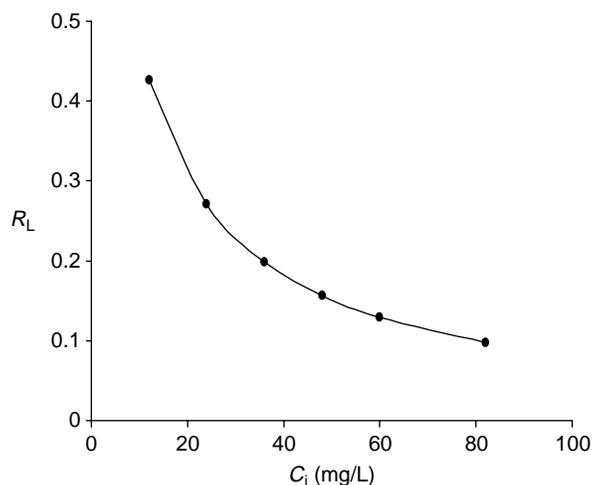
The value of free energy change calculated from Equation (7) and experimental value of  $K_L$  (L/mol) was found to be  $-13.2$  kJ/mol. The negative value of free energy change indicates that the adsorption of NP9EO on the  $\beta$ -CD-CMC polymer is a spontaneous process (Crini *et al.* 2007).

#### Determination of the NP9EO recovery efficiency of the crosslinked $\beta$ -CD-CMC polymer

The NP9EO recovery pattern shown in Figure 4 indicates that the NP9EO is rapidly released from crosslinked  $\beta$ -CD-CMC polymer to methanol and reaches a minimum



**Figure 7** | Curves of adsorption isotherm of NP9EO on the crosslinked  $\beta$ -CD-CMC polymer at  $25^\circ\text{C}$ . The measurements were effectuated with 500 mg of  $\beta$ -CD-CMC polymer at atmospheric pressure.



**Figure 8** | Variation of the separation factor versus initial NP9EO concentration in liquid phase for the adsorption of NP9EO on the  $\beta$ -CD-CMC polymer at 25°C.

concentration value of NP9EO of  $1.7 \pm 0.6$  mg/L, corresponding to a maximal NP9EO recovery efficiency of 97 w%. This result is consistent with the UV-vis spectrum of the supernatant after NP9EO recovery during 1440 minutes that shows a peak with an absorbance at 222 nm comparable to spectrum of the pollutant (Figure 5). The high NP9EO recovery efficiency can be explained by a decrease of the binding force between  $\beta$ -CD-CMC polymer and NP9EO in the presence of methanol as compared to the binding force occurring in the aqueous complex  $\beta$ -CD-NP9EO (Murai *et al.* 1998). This phenomenon can be due to the formation of a strongest interaction between methanol and  $\beta$ -CD-CMC polymer.

## CONCLUSIONS

The results from the present study have shown that the crosslinked  $\beta$ -CD-CMC polymer possesses a high NP9EO adsorption capacity of 83–92 w% (1.1–6.8 mg of NP9EO/g of  $\beta$ -CD-CMC polymer) of the initial NP9EO concentration between 12–82 mg/L present in liquid phase. This adsorption capacity is dependent of adsorption time and initial NP9EO concentration. The adsorption of NP9EO in the polymer can be associated with the formation of a very stable inclusion complex  $\beta$ -CD-NP9EO that can be favoured by the polymer network. The stability of this inclusion complex can be due to the presence of

hydrophobic interactions of van der Waals formed between  $\beta$ -CD-CMC polymer and NP9EO. The adsorption equilibrium measurements have revealed that the adsorption of NP9EO fit the Langmuir isotherm indicating that this adsorption process involves a monolayer coverage of NP9EO molecules and the homogeneous distribution of active sites at the surface of the  $\beta$ -CD-CMC polymer. Moreover, the kinetics measurements and negative value of free energy change have shown that the adsorption of NP9EO was a rapid and spontaneous process.

In contrast, the high NP9EO recovery efficiency of 97 w% in methanol may be due to a decrease of the binding force between  $\beta$ -CD-CMC polymer and NP9EO consequently to formation of strongest interaction among methanol and  $\beta$ -CD-CMC polymer.

The adsorption of NP9EO in crosslinked  $\beta$ -CD-CMC polymers could constitute an advantageous technology for removing NP9EO from wastewater due to the high adsorption capacity of these polymers and non-toxic character of  $\beta$ -CD and CMC to environment.

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