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# Synthesis and characterization of poly(vinyl-alcohol)-poly(*β*-cyclodextrin) copolymer membranes for aniline extraction

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**Abstract.** In this study, poly(vinyl-alcohol) and water insoluble *β*-cyclodextrin polymer (*β*-CDP) cross-linked with citric acid, have been used as macrocyclic carrier in the preparation of polymer inclusion membranes (PIMs) for aniline (as molecule model) extraction from aqueous media. The obtained membranes were firstly characterized by X-ray diffraction, Fourier transform infrared and water swelling test. The transport of aniline was studied in a two-compartment transport cell under various experimental conditions, such as carrier content in the membranes, stirring rate and initial aniline concentration. The kinetic study was performed and the kinetic parameters were calculated as rate constant (k), permeability coefficient (P) and flux (J). These first results demonstrated the utility of such polymeric membranes for environmental decontamination of toxic organic molecules like aniline. Predictive modeling of transport flux through these materials was then studied using design of experiments; the design chosen was a two level full factorial design $2^k$. An empirical correlation between aniline transport flux and independent variables (Poly *β*-CD membrane content, agitation speed and initial aniline concentration) was successfully obtained. Statistical analysis showed that initial aniline concentration of the solution was the most important parameter in the study domain. The model revealed the existence of a strong interaction between the Poly *β*-CD membrane content and the stirring speed of the source solution. The good agreement between the model and the experimental transport data confirms the model's validity.

**Keywords:** polymer inclusion membranes (PIMs); insoluble *β*-cyclodextrin polymer; aniline; design of experiment; statistical analysis

## 1. Introduction

Cyclodextrins (CDs) are well known typical species of organic compounds receptors in host-guest systems. They are cyclic oligomers composed of six, seven or eight glucopyranosyl units linked together by *α*-1,4- bonds corresponding to *α*- , *β*-, and γ-CD respectively, they possess

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hydrophobic cavity and hydrophilic external surface (Laza-Knoerr *et al*. 2010). Due to their remarkable property to accommodate hydrophobic molecules in their cavity, they have been extensively used as extractants in solvent extraction and as molecular recognition carriers in transport accross liquid and polymeric membranes (Deratani *et al*. 2006, Touil *et al*. 2005, 2006). The inclusion complexation between CD and organic compounds with low polarity have been studied for several decades and much past research has indicated that the process of inclusion complexation between CD and guest is driven by electrostatic forces, Van Der Waals forces, hydrophobic interactions and hydrogen bonding (Laza-Knoerr *et al*. 2010).

However, the excellent water-solubility of CDs limits the use as purification membrane. A useful method is to graft CDs on polymer supports in order to easily reproduce and complexing the subtract (Miyata *et al*. 1996). Polyvinyl alcohol (PVA) is an attractive polymer matrix for water treatment application based on CD-containing membranes because of its very good film forming property and good chemical, thermal and mechanical stability. In order to improve the functionality of the PVA, it is often combined with nanoparticles and with other synthetic and natural polymers, such as polyacrylic acid, polyethylene glycol, poly(N-isopropylacrylamide), poly(vinyl pyrolidone), chitosan, gelatin and cyclodextrins (Paduraru *et al*. 2010). Blending of different polymers is an extremely attractive inexpensive and advantageous method to obtain new structural materials.

Various preparation of PVA/CD membranes have been reported in the literature where CDs have been either physically trapped in PVA or covalently linked to the chain (Eddaoudi *et al*. 2003, Touil *et al*. 2005, Deratani *et al*. 2006, Paduraru *et al*. 2010) using cross-linking reaction. In this study our aim contribution was to synthesis new composite membranes without crosslinker based on poly(vinyl-alcohol) (PVA) blended with water insoluble $\beta$-cyclodextrin polymer (poly $\beta$-CD).

Aniline which is a typical and hazardous pollutant in water was used as a model molecule in our study (Zhao *et al*. 2009). Aniline is an important chemical compound which is well known for its wide applications in the manufacture of dyestuffs, rubbers, pesticides, plastics and paints. However, the aniline-laden wastewater discharged from these industries has become a severe environmental problem as well. It is highly toxic and has harmful influences on human health and aquatic life. Consequently, much attention has been drawn on aniline and its derivatives as environmental pollutants in most countries (Lin *et al*. 2011).

The principal aim of study was to design and evaluate polymer inclusion membranes without plasticizer or cross-linker. Then, the membrane transport efficiency was optimized by designing the aniline transport flux using design of experiment (DOE). The effects of several operating factors affecting the aniline facilitated transport from aqueous solution across polymeric inclusion membranes (PIMs) in two – compartment transport cell were studied by varying experimental conditions using a full factorial design at two levels $2^3$.

## 2. Experimental

### *2.1 Chemicals*

Polyvinyl alcohol (PVA, polymerization degree of about 124, hydrolysis degree of 95%), Dimethyl sulfoxide (DMSO) and sodium hydroxide (NaOH) pellets were purchased from Biochem Chemopharma (Cosne s/ Loire, France). Aniline (99%) was purchased from Merck (Darmstadt, Germany). Native $\beta$-cyclodextrins were obtained from Roquette (Lestrem, France). Citric acid was purchased from Sigma (Saint-Louis, MI, USA).

### *2.2 Synthesis of cyclodextrin polymer*

Water insoluble *β*-cyclodextrin polymer (Poly *β*–CD) was synthesized by In Cyclo, a French start-up, and used without further purification. *β*-Cyclodextrin polymer was synthesized by direct melt copolycondensation, according to their patented process (Skiba 2011). Briefly, a mixture of known amount (w/w) of *β*-cyclodextrin, citric acid and sodium phosphate dibasic was transferred into a reactor which was maintained at temperature ranging between 140 and 150°C for fixed time. The obtained solid form was dissolved in water and dialyzed using polyether sulfate membrane filter with molecular weight cut off of 10,000 Da. After dialysis, the resulted solution was spray dried using Mini Sprayer Dryer B-290® (BÜCHI, Flawil, Switzerland), two fractions were obtained soluble and insoluble polymer. The insoluble polymer was washed with methanol and dried at 60°C (Boukhris *et al*. 2013, Skiba and Lahiani-Skiba 2013). Only the water insoluble polymer fraction was used in this study.

### *2.3 Preparation of copolymer inclusion membranes*

Series of Poly(*β*-cyclodextrin)-poly(vinyl-alcohol) copolymer (Poly *β*-CD/PVA) membranes based on different formulations (Table 1) were synthesized through the same synthesis process as for Poly *β*–CD and at the same conditions. Briefly, an appropriate amount of PVA was dissolved in 6 ml of DMSO at 60°C under stirring for 24 h. A separate DMSO solution containing known amounts of Poly *β*-CD was prepared. These solutions were mixed for 30 minutes (total weight 10 g) until a homogeneous and slight opalescent solution is obtained. The formed gel was then poured into petri-dishes of diameter 9.06 cm and allowed to evaporate in an air oven during 2 days at 80°C. The membranes thickness was controlled by digital micrometer (High-Accuracy Digimatic® , Mitutoyo, Aurora, IL, USA) with 0.1 $\mu$m standard deviation over 10 readings.

### *2.4 Methods of characterization*

#### *2.4.1 Membrane characterizations*

*Fourier transform infrared spectroscopy*

Attenuated Total Reflection (ATR) – Fourier transform-infrared spectroscopy (FT-IR) measurements were performed on PIMs. Samples were placed on a wedged (Ge-ATR crystal), pressed with a force of 80 N and spectra were then recorded using a Spectrum One® (Perkin-Elmer, Waltham, MA, USA). A freshly cleaned crystal was used as a reference. Each analysis has been conducted in frequency range between 4000 $cm^{-1}$ and 400 $cm^{-1}$, at a resolution of 4$cm^{-1}$ and with 20 scans. All measurements were performed in triplicate.

Table 1 Formulation for the synthesis of Poly *β*-CD/PVA polymer inclusion membranes

| Poly*β*-CD (g) | PVA (g) | Poly*β*-CD (wt%) |
|---|---|---|
| 0 | 1 | 0 |
| 0,2 | 0,8 | 20 |
| 0,3 | 0,7 | 30 |
| 0,4 | 0,6 | 40 |
| 0,5 | 0,5 | 50 |
| 0,6 | 0,4 | 60 |

*Scanning electron microscopy*

A concentrated aqueous dispersion of cyclodextrin/chitosan based polymer was finely spread over a slab and dried under vacuum. The sample was shadowed in a cathodic evaporator with a gold layer (20 nm thick). The surface morphology of the polymer was observed by Scanning electron microscopy (SEM) using 108 a JSM-6031® scanning electron microscope (JEOL, Tokyo, Japan).

*X-ray powder diffractometry analysis*

Sample crystallization was studied by an X-ray powder diffractometry system (Oxpert pro panalytical) operated with Cu K$\alpha$ X radiation at 40 kV and 30 mA. The scans were conducted in the 2$\theta$ range from 0 to 70°. Aniline before and after extraction with Poly $\beta$-CD/PVA as PIM, was carried out by comparing the diffraction pattern of the sample with library data in the powder diffraction files.

*Swelling capacity*

In order to examine the swelling capacity, accurately weighed Poly $\beta$-CD/PVA was immersed in water at room temperature (25 ± 2°C). The granules were removed from the water at different times (until constant mass was achieved), and the surface water of the granules was carefully adsorbed with dry filter paper before they were again weighed (Li *et al*. 2011). The swelling capacity (%), in a sample is defined as the mass loss before and after swelling and it was determined as (Lindqvist *et al*. 2005)

$$S = \frac{W_e - W_0}{W_0} \quad (\%) \tag{1}$$

Where, $W_0$ and $W_e$ are respectively the weight of sample at dry state before and after swelling equilibrium**.**

*2.4.2 Inclusion complex characterization*

The inclusion complex of aniline and $\beta$-CD was confirmed by UV–vis spectrophotometry by comparison of the spectra of native aniline and $\beta$-CD with aniline/$\beta$-CD complexes. The formation of the inclusion complex can be described as follows

$$H + G \Leftrightarrow H - G \tag{2}$$

Where *H* represents the host, $\beta$-CD, *G* the guest, aniline, and *H-G* the inclusion complex

This method was already used to characterize the inclusion of nitrobenzene with $\beta$-CD (Chen *et al*. 2006).

*2.5 Membrane transport experiments*

As illustrated in Fig. 1, chemical transport experiments were performed by using a permeation cell that consists of two identical cylindered Teflon compartments (half-cell volume of 100 ml). The donor and acceptor half-cells were separated by the Poly $\beta$-CD/PVA (the PIM) having active membrane surface area of 7 $cm^2$. Before the ad of determinate amount of aniline (330 $\mu$M) under magnetic agitation (700 rpm), the membrane was equilibrated for 24 h in distilled water. It is worth to note that pH of both half-cell aqueous phases has been kept at 7.5 by adding the required

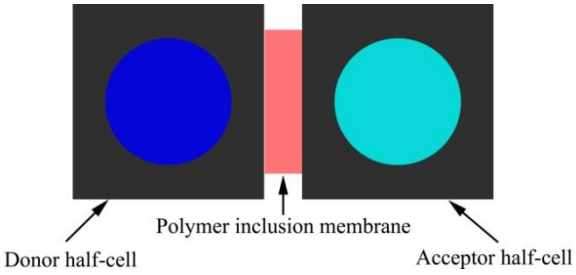



Fig. 1 Experimental setup for aniline extraction with Poly *β*-CD/PVA membrane extraction cell. In donor half-cell, there is initially 100mL of aqueous solution of aniline at 330 μM. Sample for measurements were made from acceptor half-cell

amount of NaOH.

At certain intervals, 800 µl of solution was taken in acceptor half-cell and aniline content was determinated by using an UV/VIS-spectrophotometer 2101PC® (Shimadzu, Kyoto, KYT, Japan). Calibration curve of aniline was prepared by measuring absorbance of samples with predetermine concentrations at 280 nm (corresponding to a maximum absorbency of this chemical).

The removals experiments were conducted at room temperature (25 ± 2°C) with varying the wt% of the P-*β*-CD in the PIM from 0 to 50wt%; beyond 50wt% of poly *β*-CD content, the performances and mechanical strength of the membranes decreased. After each experiment, remaining aniline molecules were removed from membranes by soaking these last in ethanol solution overnight. Each measurement was in triplicate.

### *2.6 Kinetics of transport*

The kinetics of the transport across PIMs was described as a first-order reaction with respect to aniline concentration

$$J_t = -\frac{V}{A}\frac{dC_t}{dt} = PC_t \tag{3}$$

The linear form of the first-order equation is given as follow

$$\ln\frac{C_0}{C_t} = k\,t \tag{4}$$

Where $C_t$ is the aniline concentration at a given time in the feed phase (µmol/L), $C_0$ is the initial aniline concentration in the feed phase (μmol/L), $k$ is the rate constant ($s^{-1}$), t is the transport time (s), $V$ is the volume of the aqueous solution in the feed phase ($V$ = 100 $cm^3$) and $A$ is the area of the effective membrane ($A$ = 7 $cm^2$).

By plotting $\ln\frac{C_0}{C_t}$ versus time, the $k$ values were obtained from the slope of the linear line.

The permeability coefficient ($P$) was calculated as follows

$$P = \frac{V}{A}.k \tag{5}$$

The initial flux ($J_i$) was determined as

$$J_i = P\ C_i \tag{6}$$

### 2.7 Experimental design

In order to evaluate the main effect and interaction of the poly $\beta$-CD content ($Z_1$), the agitation speed of the solution ($Z_2$) and the initial aniline concentration ($Z_3$) on the response (aniline facilitated transport flux) from aqueous solutions, a two level factorial design $2^3$ was used. The original values of each factor and their corresponding levels are presented in Table 2.

The responses ($J_i$) were determined from the slope at the steady-state strip solution concentration, according

$$J = \frac{V}{A}\frac{dC}{dt} \tag{7}$$

The correlation of independent variables ($x_1$, $x_2$, $x_3$) and the response (Aniline transport flux) were estimated by a first-order polynomial equation (Hamaidi-Maouche *et al*. 2009, Sado and Sado 1991)

$$y = b_o + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_1x_3 + b_{123}x_1x_2x_3 + \varepsilon \tag{8}$$

Where: $y$ is the aniline transport flux obtained from the slope at the quasi-steady state strip solution, $b_0$ is the average value of the response at the center point of the design, $b_1$, $b_2$, $b_3$, $b_{12}$, $b_{13}$, $b_{23}$, $b_{123}$, are the linear and interaction terms, respectively, $x_1$, $x_2$ and $x_3$, $\varepsilon$ is the random error component which is approximately normally and independently distributed with mean zero and constant variance.

For any factor $Z_j$, the transformation from natural to coded values $x_j$ has been performed by considering the following equations

$$Z_j = x_j \times \Delta Z_j + z_j^o \quad j = 1,\ldots,3; \quad \Delta Z_j = \frac{Z_j^{\max} - Z_j^{\min}}{2}; \quad Z_j^0 = \frac{Z_j^{\max} - Z_j^{\min}}{2} \tag{9}$$

$Z_j^{\max}$ and $Z_j^{\min}$ represent, respectively, the maximum and the minimum level of factor $j$ in natural unit. According to the design chosen, eight experiments of the factorial design and three central points for statistical validity were performed. The eight unknown coefficients of the first-order polynomial equation are estimated by a multi-linear regression based on the least squares criterion.

The matrix B of the coefficients of the model was calculated using the following relation (Kaminari *et al*. 2005), with Excel® software Microsoft (Redmond, WA, USA)

Table 2 Values of operating factors of $2^3$ full factorial model at two levels

| Operating parameters | Level-1 | Level-2 | Level-3 |
|---|---|---|---|
| $Z_1$: Poly $\beta$-CD membrane content $x$ (wt.%) | 30 | 35 | 40 |
| $Z_2$: Agitation speed $w$ (rpm) | 400 | 550 | 700 |
| $Z_3$ : initial aniline concentration $C_0$ ($\mu$M) | 46 | 70 | 94 |

$$B = \frac{1}{N} X^t Y \tag{10}$$

Where: $B$ is the column matrix of estimated coefficients; $X^t$ the transpose matrix of the effects matrix $X$ and $Y$ is the column matrix of observations.

Residuals (difference between the experimental and the predicted values) were then used to evaluate the adequacy of the model; residuals are known to be the variation parts unexplained by the fitted model. It is expected that they occur according to a normal distribution (Goupy 2010).

## 3. Results and discussion

### *3.1 Polymer characterization*

To understand the interaction nature between aniline with Poly *β*-CD/PVA polymer as PIM, some characterizations was performed before and after chemical extraction.

#### *3.1.1 Scanning electron microscopy*

The SEM clearly reveals the nature of the surface of dried Poly *β*-CD/PVA polymer (Fig. 2). Its structure resembled to a sponge with thick, homogenous and smooth cavities. PVA and *β*-cyclodextrins, both porous materials with mesopores and some nanocavities, seems to be the polymer constituents responsible of this polymer porosity.

Besides, the swelling study showed high positive influence of the proportion PVA in Poly *β*-CD/PVA on the swelling property of this polymer membrane (Fig. 3). These results in accordance with whose of Paduraru *et al*. (2010), could be explained by an increase of Poly *β*-CD/PVA porosity due to an higher PVA porosity than native *β*-cyclodextrin one.

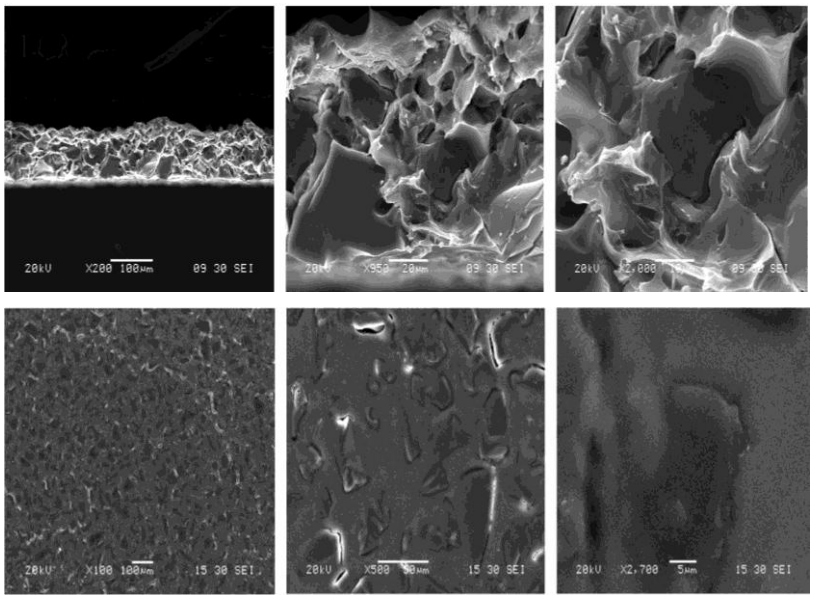


Fig. 2 SEM images of cross section, top surface morphology and bottom surface

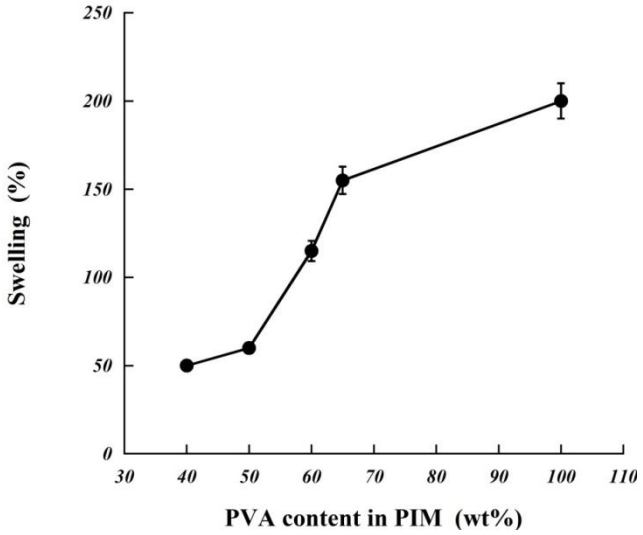



Fig. 3 Swelling curve as a function of PVA content in PVA/ Poly $\beta$-CD PIMs. Each experiment was in triplicate

### *3.1.2 X-ray powder diffractometry*

Fig. 4 illustrates X-ray diffractograms of Poly $\beta$-CD/PVA polymer and its native constituents: PVA and Poly $\beta$–CD polymer. XRPD of native PVA shows an intense peak at $2\theta$ = 20°, while Poly $\beta$–CD polymer has an amorphous structure due to the absence of intense and sharp peak. Nevertheless, Poly $\beta$–CD polymer showed a large peak at $2\theta$ = 18°. With Poly $\beta$-CD/PVA polymers having different proportions of Poly $\beta$–CD, we observed a shift of the PVA peak at 20° to 18° with Poly $\beta$–CD content above 35wt%. We will use therefore for the next experiments, PVA/P $\beta$-CD PIM having P $\beta$-CD content of 30wt% at least.

### *3.1.3 FTIR spectroscopy*

FTIR is a powerful tool to investigate the nature of chemical interactions between different components of the PIMs. Fig. 5 summarized FTIR of PVA, Poly $\beta$-CD and Poly $\beta$-CD/PVA

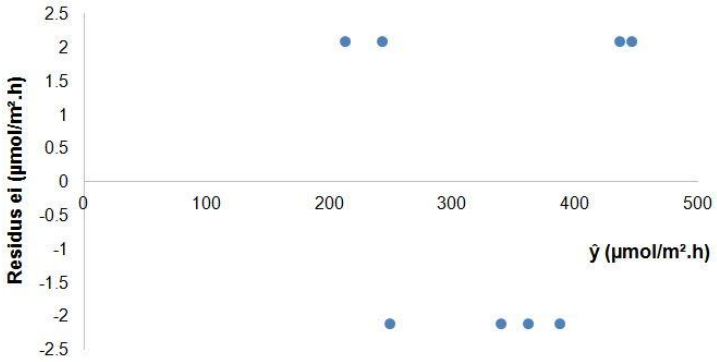



Fig. 4 The XRD diffractograms of the membranes of PVA, Poly $\beta$-CD and their composite membranes

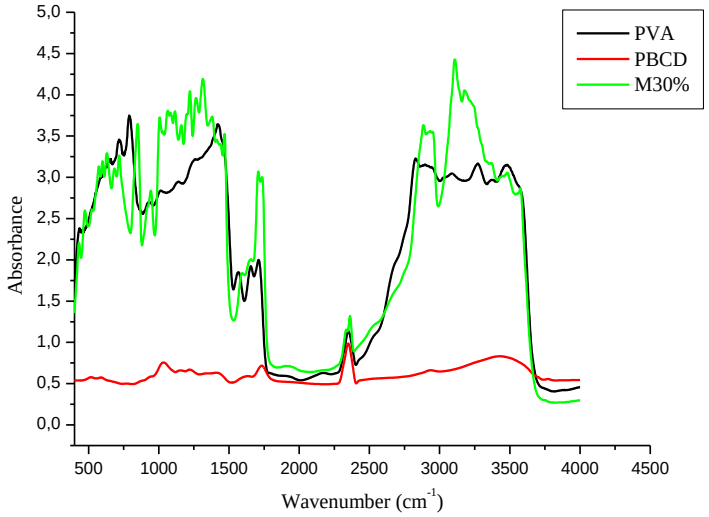



Fig. 5 FTIR spectrums of PVA, P *β*-CD and PIM containing 30wt% of poly *β*-CD

containing 30wt% of Poly *β*-CD.

The PVA spectra shows elongation and deformation of $–CH_2-$ groups respectively at 783 $cm^{-1}$ and 2905 $cm^{-1}$, which shifts respectively to 845 $cm^{-1}$ and 2897 $cm^{-1}$ in the membrane containing 30wt% of poly *β*-CD. The elongation vibrations attributed to the O-H at 3278 $cm^{-1}$ in the PVA membrane and 3452 $cm^{-1}$ in the Poly *β*-CD powder, vibrate at 3103 $cm^{-1}$ in the membrane based on PVA and poly *β*-CD. The groups C-O in the ester of poly*β*-CD vibrates at 1728 $cm^{-1}$ in the poly *β*-CD powder, while it vibrates at 1712 $cm^{-1}$ in the membrane containing PVA and cyclodextrin polymer. All these changes may be explained by the interactions of $-CH_2-$ , O-H and C-O groups in PVA and poly *β*-CD to form hydrogen bindings. Absence of new peaks indicates that the chemical binding between the membrane's components is physical.

### *3.2 Influence of PIM composition on aniline extraction*

In order to optimize the aniline extraction, the influence of PIM membrane composition will be studied. The first experience was to determine the influence of pure PVA membrane (without Poly *β*-CD). We observed (data not shown) the lack of aniline extraction. Besides, Fig. 6 shows that aniline extraction from donor to acceptor half-cell increased with the proportion of the Poly *β*-CD in PIM. These results demonstrate the necessity of Poly *β*-CD in the design of PIM membrane for aniline extraction.

The shape of the permeation curves should show three stages: first, a time lag corresponding to the saturation of PIM in aniline; then, a quasi-steady state representing to regular passage of aniline through the polymeric membrane; and finally, the curve will reach a plateau corresponding to the equalization of aniline in both half-cells. Indeed, for this last step, near to the aniline equalization in both feeding and receiving phases the aniline driving force between the two phases becomes very low see null. On Fig. 6, we can observe the lag time during the first 60 minutes and then the steady-state during at least 5 hours (300 minutes).

The influence of Poly *β*-CD proportion in PIM on aniline extraction could be explained by the solution-diffusion mechanism as proposed by Touil *et al*. (2005). In this hypothesis, *β*-CD is

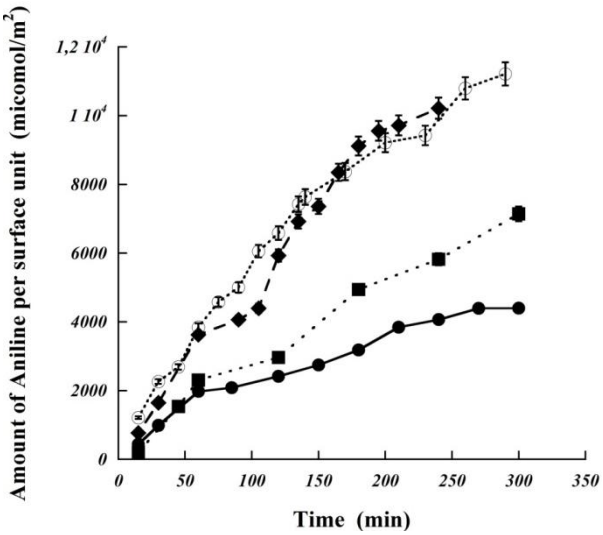



Fig. 6 Evolution versus time of the amount per surface unit of aniline transported into receiving aqueous phase through PVA membranes containing different wt% of the Poly *β*-CD

considered as fixed carriers. First, aniline molecules are adsorbed on the PVA/Poly *β*-CD membrane at the feeding side of the membrane by complex formation between aniline molecules and CD. Then, aniline molecules are transported through the membrane by jumping from one CD to another and diffusing through the polymer network. Finally, the aniline/*β*-CD complex dissociated at the membrane striping interface releasing the chemical in the acceptor half-cell side in our experiment. This proposed diffusion mechanism explained well the absence of extraction with pure PVA membrane and the influence of *β*-CD in PIM, and therefore Poly *β*-CD polymer, on aniline extraction across the composite membrane. Indeed, results can be attributed to the increase of carrier sites (*β*-CD) in the membranes, consequently, the distance between the sites decrease which could reduce the mass transfer resistance and facilitate permeation of aniline.

To confirm aniline diffusion mechanism through these composite PIMs, two additional experiments were performed.

The first experiment was the study of aniline inclusion in *β*-CD. As seen in Fig. 7, the peak intensity of aniline increased in presence of *β*-CD indicating an inclusion of the chemical in cyclodextrin. This result is comforted by (Chen *et al*. 2006) who has characterized the inclusion complex of nitrobenzene and *β*-CD by UV-vis spectroscopy.

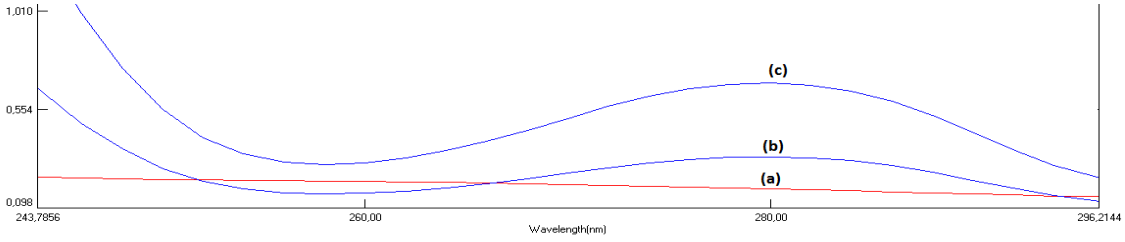



Fig. 7 UV spectra of (a) *β*-CD; (b) aniline; (c) complex *β*-CD/aniline

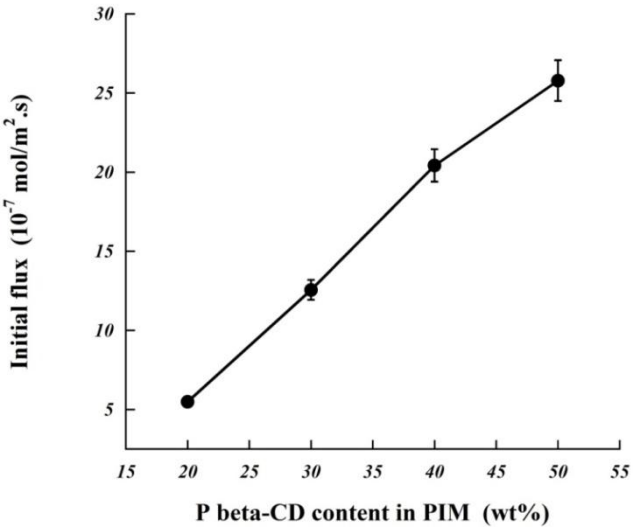



Fig. 8 Plot of initial flux of aniline versus $\beta$-CD polymer content in the membranes. Source phase (330 $\mu$M aniline, pH = 7.5), acceptor phase (distilled water, pH = 7.5), stirring rate of the source phase ($w$ = 700 rpm). Each experient was in triplicate

Table 3 Effect of carrier content on the initial transport flux of aniline molecules across PIMs

| Carrier content $x$ (%) | $k\times10^5$ ($s^{-1}$) | $P\times10^6$ (m/s) | $J_i\times10^7$ (mol/m$^2$.s) |
|---|---|---|---|
| 20 | 1,17 | 1,67 | 5,5 |
| 30 | 2,67 | 3,81 | 12,57 |
| 40 | 4,33 | 6,19 | 20,43 |
| 50 | 5,33 | 7,62 | 25,14 |

The second experience was the study of aniline extraction flux in function of Poly $\beta$-CD content in PIM (Fig. 8). The results indicate that the aniline flux increases with increasing poly $\beta$-CD membrane content, agreeing again our supposition on chemical diffusion process. Besides, Table 3 showed that the best results for flux ($J_i$), permeability ($P$) and constant rate ($k$) were obtained with 50wt% of Poly $\beta$-CD in PIM.

Additional experiments showed that aniline extraction flux can be restored by regenerating the acceptor half-cell phase. Touil *et al*. have observed the same behavior with xylene extraction with cyclodextrin based PIMs (Touil *et al*. 2005)

To summarize, several parameters influenced the aniline extraction by PVA/ poly $\beta$-CD PIMs: the nature and the carrier concentration in PIM; the pH in donor and acceptor phases; nature of the PIM support; the stirring rate; the plasticizer type in PIM; and the concentration of the substrate in the feed phase.

### *3.3 Experimental design methodology*

Although polymer inclusion membrane process is an emerging technology used for the transport and the separation process of hazardous compounds, statistical design of experiments is

Table 4 $2^3$ factorial design matrix and the results

| Run n° | $x_1$ | $x_2$ | $x_3$ | $x$ (wt %) | $w$ (rpm) | Co ($\mu$M) | $y$ ($\mu$mol/m².h) |
|---|---|---|---|---|---|---|---|
| 1 | -1 | -1 | -1 | 30 | 400 | 46 | 251 |
| 2 | 1 | -1 | -1 | 40 | 400 | 46 | 241 |
| 3 | -1 | 1 | -1 | 30 | 700 | 46 | 211 |
| 4 | 1 | 1 | -1 | 40 | 700 | 46 | 390 |
| 5 | -1 | -1 | 1 | 30 | 400 | 94 | 444 |
| 6 | 1 | -1 | 1 | 40 | 400 | 94 | 342 |
| 7 | -1 | 1 | 1 | 30 | 700 | 94 | 364 |
| 8 | 1 | 1 | 1 | 40 | 700 | 94 | 434 |
| 9 | 0 | | 0 | 35 | 550 | 70 | 330 |
| 10 | 0 | | 0 | 35 | 550 | 70 | 327 |
| 11 | 0 | | 0 | 35 | 550 | 70 | 332 |

rarely applied in the membrane processes (Rajasimman and Sangeetha 2009). In order to evaluate the main effect and interaction of the poly $\beta$-CD content ($Z_1$), the agitation speed of the solution ($Z_2$) and the initial aniline concentration ($Z_3$) on the response (aniline facilitated transport flux) from aqueous solutions, a two level factorial design $2^3$ was used.

According to the design chosen, eight experiments of the factorial design and three central points for statistical validity were performed as shown in Table 4.

The application of the statistical test of Student (Oughlis-Hammache *et al*. 2010) for the determined coefficients, allowed us to estimate their significance and eliminate those whose influence is not significant. After eliminating insignificant coefficients, the model equation becomes

$$\hat{y} = 334{,}65 + 17{,}25\,x_1 + 15{,}15\,x_2 + 61{,}50\,x_3 + 45{,}15\,x_1x_2 - 25{,}20\,x_1x_3 - 12{,}00\,x_2x_3 \qquad (11)$$

The test of reliability for the predicting equation has been carried out by the Fisher's test (Kafarov 1974, Oughlis-Hammache *et al*. 2010), it compared the residual variance with the replication variance. Table 5 gives the results of the variance analysis. The tabulated $F$ value for the 5 % significance level and degrees of freedom $f_1$ and $f_2$ ($f_1 = N - p = 1$ and $f_2 = N_0 - 1 = 2$) is 18, 5. It was found that the estimated value of $F$ is much less than this value. The two variances are then statistically equal: the adjustment error between the real model and the postulated model is negligible in front of the experimental error. Hence, it can be concluded that the established predicting equation gives an excellent fit to the observed data.

The obtained regression equation shows that the initial aniline concentration of the solution ($x_3$) has the strongest and positive effect on the aniline transport flux, since the corresponding

Table 5 Analysis of variance for the first-order model

| Source of variations | SS | f | MS | $F$-value |
|---|---|---|---|---|
| Residual error | 35.28 | 1 | 35.28 | 5.57 |
| Experimental error | 12.67 | 1 | 6.33 | |

coefficient ($b_1$ = +61.5) is positive and the most important of the others investigated factors. The stirring speed also affects positively the transport flux of aniline through the PIM since his effect is positive ($b_2$ = +15, 15) on the response. The positive sign of this coefficient indicates that an increase in the stirring rate improves the transport flux. This effect is explained by the decrease of the thickness of the diffusion boundary layers at the membrane interfaces. poly $\beta$-CD content of membranes ($x_1$) has a positive effect ($b_3$) on the aniline transport flux since that the increase of $\beta$-CD carrier in the membranes decrease the distance between the sites and therefore the aniline molecules could jumped easily between the sites. These results were in complete agreement with those obtained in the kinetic study previously performed.

The significance interactions found by the design of experiments for aniline transport flux are essentially between poly $\beta$-CD content and agitation speed of the source ($x_1x_2$), poly $\beta$-CD content and initial aniline concentration ($x_1x_3$) and between agitation speed and initial aniline concentration ($x_2x_3$).

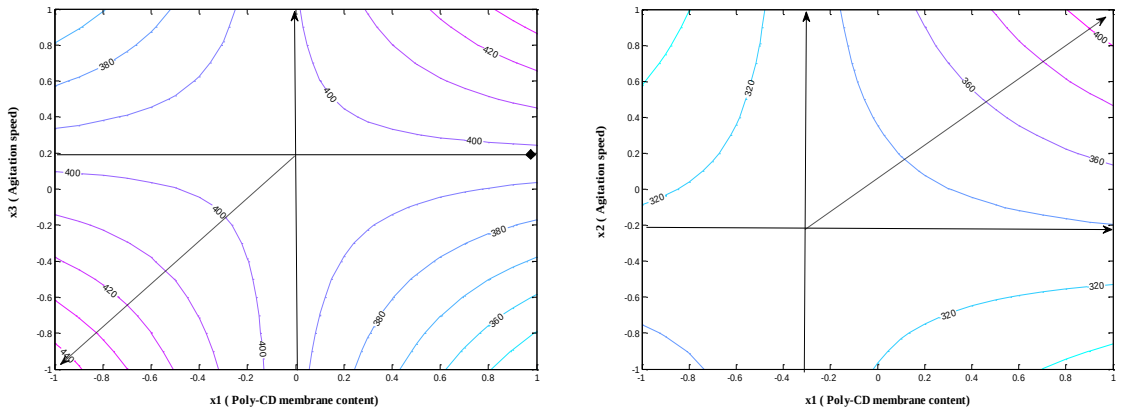
The MEP has also demonstrated the existence of a strong interaction between the poly $\beta$-CD content and agitation speed of the source phase since his coefficient is strong and positive in front of other interactions factors.

### *3.3.1 Interaction diagrams*

The response contour curves are plotted to visualize the interaction between the variables and to determine the direction in which the variables should be changed in order to optimize aniline transport flux.

#### *3.3.1.1 Interactions in Plane of Poly β-CD membrane content / agitation speed of the source phase ($x_1$-$x_2$)*

The Fig. 9 gives the response contour plots for poly $\beta$-CD membrane content and stirring speed of the source phase for two concentrations of aniline (70 $\mu$M and 94 $\mu$M). Fig. 9(a) shows that in the case of the high concentration of aniline, the best transport fluxes were obtained with low agitation rate and low $\beta$-CD content in the membranes, whereas in the case of medium aniline




(a) Interaction in the plane Poly-CD membrane content-agitation speed ($Co$ = 94 $\mu$M)

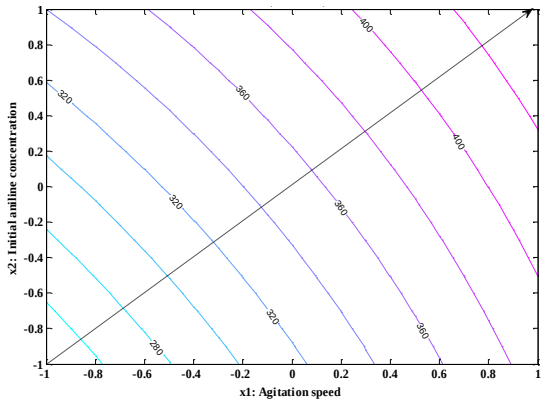
(b) Interaction in the plane Poly-CD membrane content-agitation speed ($Co$ = 70 $\mu$M)

Fig. 9 Surface contour plots in the plane poly $\beta$-CD membrane content / agitation speed of the source phase ($x_1$-$x_2$), (a) $C_o$ = 94 $\mu$M; and (b) $C_o$ = 70 $\mu$M

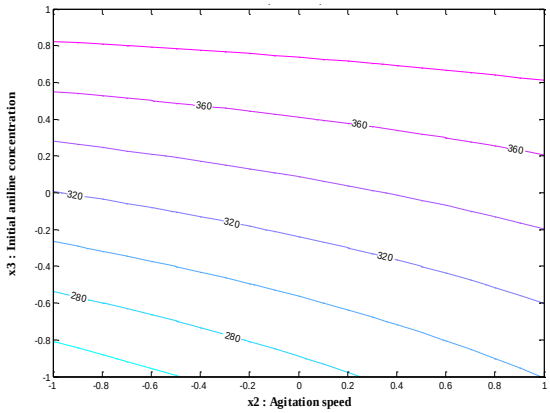
concentration ($C_o$ = 70 $\mu$M), a strong agitation and high concentration of poly $\beta$-CD in the membranes were required to achieve high fluxes. The results explain well the influence of the initial aniline concentration on the transport flux.

#### *3.3.1.2 Interactions in plane of agitation speed of the source phase / Initial aniline concentration ($x_2$-$x_3$)*

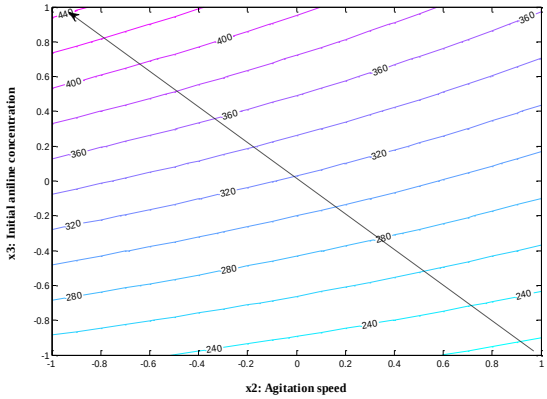
Fig. 10 gives the response contour plots for agitation speed of the source phase and initial aniline concentration for three concentrations of poly $\beta$-CD polymer (30, 35 and 40%) in the membranes. Fig. 10(a) shows that at high concentration of $\beta$-CD, important fluxes are achieved at both at, high concentration of aniline solution and agitation speed of the source phase. For the intermediate concentration of $\beta$-CD in the membranes, Fig. 10(b) shows that important fluxes can be achieved at high initial concentration of aniline whatever the agitation speed of the source phase. In the case of low concentration of poly $\beta$-CD polymer in the membranes Fig. 10(c), important fluxes can be achieved at low agitation speed of the source solution and high initial concentration of the aniline. This result shows well the interactions effects between parameters on transport flux.




(a) Interaction in the plane agiation speed-initial aniline concentration ($x$ = 40%)




(b) Interaction in the plane agiation speed-initial aniline concentration ($x$ = 30%)




(c) Interaction in the plane agiation speed-initial aniline concentration ($x$ = 35%)

Fig. 10 Surface contour plots in the plane agitation speed of the source phase / initial concentration of aniline ($x_2$-$x_3$): (a) $x$ = 40%; (b) $x$ = 35%; and (c) $x$ = 30%

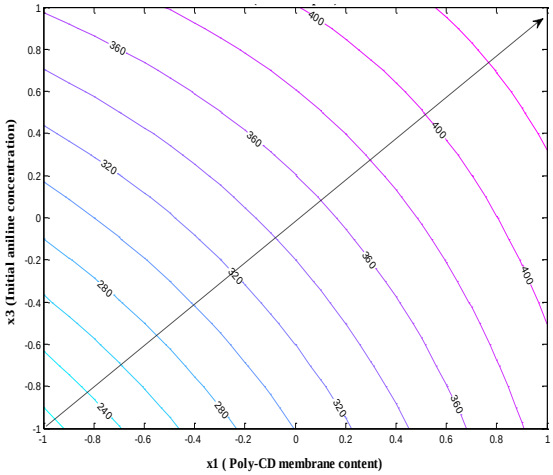



Fig. 11 Surface contour plot in the plane poly $\beta$-CD membrane content / initial aniline concentration. ($x_1 - x_3$), ($x_2 = +1$)

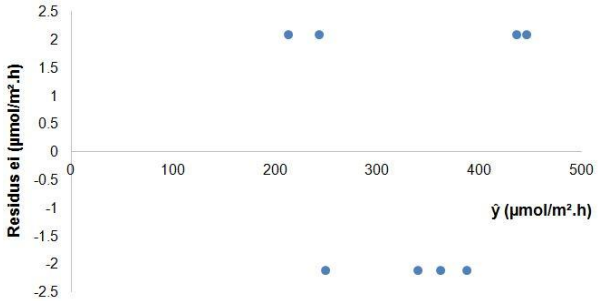



Fig. 12 Diagram of residues

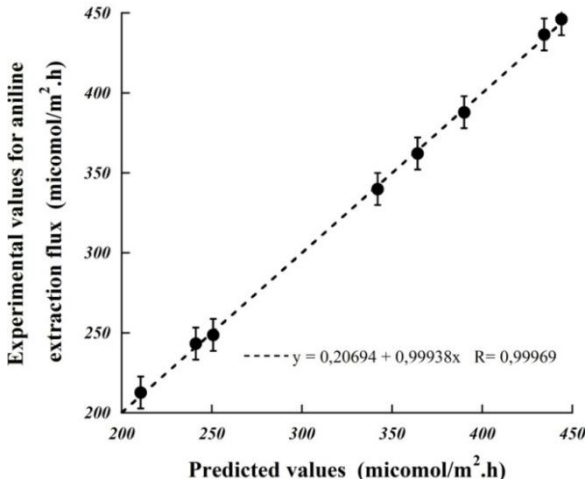



Fig. 13 Plot of experimental versus predicted values for the aniline extraction flux by a PVA/ poly $\beta$-CD PIM with 30 wt% of poly $\beta$-CD. Each experiment was in triplicate

Table 6 Optimum values of the process parameters for high transport flux

| | Optimal values | |
|---|---|---|
| Parameters | Coded units ($x_i$) | Actual units ($Z_i$) |
| Poly $\beta$-CD membrane content | 1.14 | 41% |
| Agitation speed | 2.72 | 958 rpm |
| Initial aniline concentration | 5.56 | 203 $\mu$M |

#### *3.3.2.3 Interaction in plane of Poly β-CD membrane content/ initial aniline concentration ($x_1$-$x_3$)*

Fig. 11 gives the response contour plot for poly $\beta$-CD polymer and initial aniline concentration at optimal agitation speed of the source phase ($w$ = 700 rpm), as seen, high fluxes can be achieved at high poly $\beta$-CD membrane content and at high initial aniline concentration.

### *3.4 Residual analysis*

The plot of the residuals (Fig. 12) revealed that they have no obvious pattern and unusual structure. This implies that the model proposed is adequate because there is no apparent relation between the predicted and residues values; the points are randomly arranged.

In addition, Fig. 13 demonstrates the strong correlation between $\hat{y}$ (predicted values) and $y$ (experimental values), which is very good for the quality of fit. All these results confirmed that the obtained model explains well the experimental results.

## 4. Optimization

In this study, the obtained regression equation is used to find the optimal conditions in which the operational variables should be adjusted in order to optimize the aniline transport flux. Optimal values of the process parameters were first calculated in coded units using Matlab 07® software (Natick, MA, USA) and then converted to actual units. The results are shown in Table 6

The optimum values for the stirring speed and the initial concentration of aniline are outside the domain of study, however, we can bring them to the highest levels of the area of interest because the model obtained is valid, only in the chosen interest domain. In these conditions, the optimal transport flux obtained by the model reaches about 536 $\mu$mol/m².h.

## 5. Conclusions

To conclude, in the first part of our work, PVA/ poly $\beta$-CD polymer used as PIM showed its ability to extract aniline by solution-diffusion mechanism. In such PIMs, $\beta$-CD is considered as fixed carriers allowing aniline to "jump" from one cyclodextrin to the next by diffusing through the polymer network. This explained why more PIM contained poly $\beta$-CD, more aniline flux through PIM was high reaching thus more than $25.10^{-7}$ $\mu$mol/m$^2$.h with a poly $\beta$-CD content of 50wt%. In addition, PVA containing no $\beta$-cyclodextrin, that's why this polymer had no influence on aniline extraction flux. Besides, we showed that PVA content in our PIMs should be less than 50wt% in order to limit the PIM swelling property.

In the second part of our work, the experimental designs methodology was used successfully to develop a reliable mathematical model between the aniline transport flux across polymer inclusion membrane in a two-compartment cell and the three main parameters affecting the transport flux. Statistical analysis showed that initial aniline concentration of the solution was the most influent parameter, with a positive effect ($b_3$ = +61, 50) in the chosen study domain. The increase in the stirring rate has a positive effect on the transport flux of aniline, and its optimal value is 956 rpm. In the optimal conditions, the transport flux obtained by the model reaches about 536 $\mu$mol/m².h. The model revealed the existence of a strong interaction between the poly $\beta$-cyclodextrin membrane content and the stirring speed of the source solution. The observation of surface contour plots allows choosing the favorable and economical conditions driving to a satisfactory aniline transport flux across PIMs and therefore condition for optimal aniline extraction in aqueous media like wastewaters.

## References


Boukhris, T., Lahiani-Skiba, M., Martin, D. and Skiba, M. (2013), "Pre-formulation of an oral cyclosporine free of surfactant", *J. Incl. Phenom. Macrocycl. Chem.*, **75**(3), 323-332.

Chen, M., Diao, G. and Zhang, E. (2006), "Study of inclusion complex of $\beta$-cyclodextrin and nitrobenzene", *Chemosphere*, **63**(3), 522-529.

Deratani, A., Touil, S., Palmeri, J., Tingry, S. and Bouchtalla, S. (2006), "Pertraction of xylene isomers using cyclodextrin-containing membranes: mass transport mechanism and modelling", *Desalination*, **200**(1), 103-105.

Eddaoudi, H., Deratani, A., Tingry, S., Sinan, F. and Seta, P. (2003), "Fullerene membrane transport mediated by $\gamma$-cyclodextrin immobilised in poly(vinyl alcohol) films", *Polym Int.*, **52**(8), 1390-1395.

Goupy, J. 2010), "Modélisation par les plans d'expériences - Plans pour surfaces de réponse", *Tech. Ing.*, Ref No. 42419210.

Hamaidi-Maouche, N., Bourouina-Bacha, S. and Oughlis-Hammache, F. (2009), "Design of experiments for the modeling of the phenol adsorption process", *Chem. Eng. Data*, **54**(10), 2874-2880.

Kafarov, V.V.I. (1974), "Méthodes cybernétiques et technologie chimique", - Traduit du russe par C. Sinolecka. Editions Mir, Moscou, Technique Soviétique.

Kaminari, N.M.S., Ponte, M.J.J.S., Ponte, H.A. and Neto, A.C. (2005), "Study of the operational parameters involved in designing a particle bed reactor for the removal of lead from industrial wastewater — central composite design methodology", *Chem. Eng. J.*, **105**(3), 111-115. DOI: 10.1016/j.cej.2004.07.011

Laza-Knoerr, A.L., Gref, R. and Couvreur, P. (2010), "Cyclodextrins for drug delivery", *J. Drug Target*, **18**(9), 645-656.

Li, N., Wei, X., Mei, Z., Xiong, X., Chen, S., Ye, M. and Ding, S. (2011), "Synthesis and characterization of a novel polyamidoamine–cyclodextrin crosslinked copolymer", *Carbohydr. Polym.*, **346**(13), 1721-1727.

Lin, X., Zhang, J., Luo, X., Zhang, C. and Zhou, Y. (2011), "Removal of aniline using lignin grafted acrylic acid from aqueous solution", *Chem. Eng. J.*, **172**(2-3), 856-863. DOI: 10.1016/j.cej.2011.06.073

Lindqvist, N., Tuhkanen, T. and Kronberg, L. (2005), "Occurrence of acidic pharmaceuticals in raw and treated sewages and in receiving waters", *Water Res.*, **39**(11), 2219-2228.

Miyata, T., Iwamoto, T. and Uragami, T. (1996), "Characteristics of permeation and separation of xylene isomers through poly(vinyl alcohol) membranes containing cyclodextrin", *Macromo. Chem. Phys.*, **197**(9), 2909-2921.

Oughlis-Hammache, F., Hamaidi-Maouche, N., Aissani-Benissad, F. and Bourouina-Bacha, S. (2010), "Central composite design for the modeling of the phenol adsorption process in a fixed-bed reactor", *J. Chem. Eng. Data*, **55**(7), 2489-2494. DOI: 10.1021/je900868v

Paduraru, O.M., Vasile, C., Patachia, S., Grigoras, C. and Oprea, A.M. (2010), "Membranes based on poly(vinyl alcohol)/beta-cyclodextrin blends", *Polymery*, **10**(6), 473-484.

Rajasimman, M. and Sangeetha, R. (2009), "Optimization of process parameters for the extraction of chromium (VI) by emulsion liquid membrane using response surface methodology", *J. Hazard. Mater.*, **168**(1), 291-297. DOI: 10.1016/j.jhazmat.2009.02.044

Sado, G. and Sado, Mz.-C. (1991), "Les plans d'expériences. De l'expérimentation à l'assurance qualité", AFNOR, Paris La Défense.

Skiba, M. (2011), "Nouveau procédé de synthèse de copolymères, terpolymères et tetrapolymères de cyclodextrines et leurs utilisations", Brevet FR2954770.

Skiba, M. and Lahiani-Skiba, M. (2013), "Novel method for preparation of cyclodextrin polymers: Physico-chemical characterization and cytotoxicity", *J. Incl. Phenom. Macrocycl. Chem.*, **75**(3), 341-349.

Touil, S., Tingry, S., Palmeri, J., Bouchtalla, S. and Deratani, A. (2005), "Preparation and characterization of $\alpha$-cyclodextrin-containing membranes—application to the selective extraction of xylene isomers", *Polymer*, **46**(23), 9615-9625.

Touil, S., Tingry, S., Bouchtalla, S. and Deratani, A. (2006), "Selective pertraction of isomers using membranes having fixed cyclodextrin as molecular recognition sites", *Desalination*, **193**(1-3), 291-298.

Zhao, D., Zhao, L., Zhu, C., Tian, Z. and Shen, X. (2009), "Synthesis and properties of water-insoluble $\beta$-cyclodextrin polymer crosslinked by citric acid with PEG-400 as modifier", *Carbohydr. Polym.*, **78**(1), 125-130

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