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Methylene blue removal from water by Adsorption process on polysulfone (PSf) and polyacrylic acid (PAA) membrane

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Infos	**Abstract - Résumé**

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The present work describes the removal of methylene blue (MB) from water by adsorption process (bach method). This goal was achieved by the synthesis of special membranes from polysulfone (PSf) and poly acrylic acid (PAA) mixtures. The adsorption of MB onto PSf/PAA membrane was studied under different conditions: polymer proportions, pH and concentration of dye solution and contact time. Scanning Electronic Microscopy (SEM) was employed to collect information about membrane morphology which affects adsorption process. Moreover, mechanic and kinetic models were applied to interpret the origin of adsorption. SEM images show that PSf/PAA membranes own a spongeous like-structure which might enhance adsorption of MB along membrane's surface. Both Langmuir and Freundlich models confirm the adsorption of MB on PSf/ PAA membrane. Results lead to values of Langmuir separation factor R_L ranging between 0.38 and 0.08, Freundlich force higher than 1 (n = 1.86) and adsorption capacity Q_m equal to 333 mg/g. The origin of adsorption was assigned to intermolecular interactions between carboxylic groups and dye molecules. Kinetic results demonstrate that the adsorption mechanism follows preferentially pseudo second order than the first pseudo order.

Ce travail présente l'étude de l'élimination du colorant bleu de méthylène (BM) par adsorption sur une membrane synthétique à base de PSf et PAA. L'adsorption de MB sur ce type de membranes a été suivie sous différentes conditions : composition de membrane, le pH et la concentration de la solution du colorant et le temps de contact entre le colorant et la membrane. La microscopie électronique à balayage (MEB) a été utilisée pour collecter des informations sur la morphologie de membrane qui affecte le procédé d'adsorption. A cela s'ajoute l'application des modèles mécaniques et cinétiques pour comprendre le déroulement de ce procédé. Les images de SEM montrent que les membranes utilisées ont une structure spongieuse qui est susceptible d'améliorer la fixation des molécules du colorant sur leur surface active. L'exploitation des résultats des modèles de Langmuir et de celui de Freundlich démontre l'adsorption du BM sur la membrane PSf/PAA. Cette adsorption est caractérisée par un facteur de séparation de Langmuir R_L qui se situent entre 0,38 et 0,08, une force de Freundlich qui est supérieure à l'unité (n = 1,86) et une capacité maximale d'adsorption (Q_m) qui voisine 333 mg/g. Par ailleurs, l'origine de l'adsorption a été attribuée aux interactions intermoléculaires de type électrostatique entre les groupes carboxyles du PAA et les molécules du colorant conformément aux résultats de la cinétique d'adsorption qui suit préférentiellement le pseudo second ordre que le premier pseudo ordre.

1. INTRODUCTION

Dyes are broadly utilized in different fields of human being's needs as food, printing, material, calfskin, plastics, beauty care products, veterinary medication and drug industry and different applications [1]. The accumulation of these compounds in environment disturbs the equilibrium of aquatic systems and increases the water toxicity [2,3]. Therefore, their removal from aquatic ecosystems is very important tto prevent human diseases, especially, when these sources are used in the production of drinking water. Methylene blue (MB) is a cationic dye soluble in water. It is often used in textiles and food industries. Above a certain amount, the consumption of MB provokes a harmful effect on human health such as high blood pressure, abdominal pain, nausea and mental disorder[4].

Several studies were focused on the removal of MB from water[5,6]. In fact, this dye offers particular characteristics: a small molecular weight and positive charges. These properties explain the reasons of its use in many studies to bring to fore the performances of materials in adsorption or filtration processes. Polysulfone (PSf) is hydrophobic polymer which is usually employed to prepare membranes with high mechanical and chemical stability. The hydrophilic polymer as polyacrylic acid (PAA) was added [7–10] to increase the hydrophilic character of membrane, and also to improve significantly the membrane performance in the removal of dye which owns a cationic structure [11].

2. MATERIALS AND METHODS

2.1. Membrane synthesis

Poly sulfone (PSf) was supplied by Rhodia (France) whereas Poly acrylic acid (PAA), methylene blue and dimethyl formamide (DMF) were provided by Sigma-Aldrich (France). PSf was dissolved, 5 wt. %, in dimethyl formamide (DMF) in a glass reactor equipped with a mechanical stirrer and thermostated at 90°C for more than 3 hours. Afterwards, Poly acrylic acid (PAA) was added to the PSf in known proportions, and stirred for 3 hours to form the casting dopes which were cast on a glass plate with a lab-made Gardner knife [12–15]. The obtained membrane will contain anionic carboxylate groups at high pH as illustrated by Fig 1. The cast liquid film was dried in oven at 60°C for 1 hour and finally immersed in a coagulation bath containing a sufficient volume of MilliQ water at 27°C. The membranes were thoroughly washed with water and stored until their use.

2.2. Scanning electronic microscopy

The SEM images were obtained with a Cambridge Instruments Ô model 200 microscope. In order to obtain good membrane cross- section images, the samples were frozen in liquid nitrogen at -190°C, fractured and coated with a thin gold film. The images were obtained at 10 kV voltages and different magnification factors (200X and 2KX).

2.3. pH_{PZC} (point zero charge)

The PZC (point of zero charge) of PSf/PAA membrane was determined using the pH drift method [16,17]. PSf/PAA (0.01 g) was mixed with 50 mL of 0.01 M NaCl solution. The pH of the starting solutions (2.0 to 12.0) was adjusted using HCl and NaOH. After 24 h, the final pH was measured.

2.4. Adsorption of methylene blue

Methylene blue (MB) is an hydrophilic organic compound. It is freely soluble in water and its molecular formula is C16H18N3SCl. It absorbs visible UV light at 663nm wavelength. The hydrophilic polymer PAA is infiltrated easily by water molecules which occupy a part of pores[18].

The adsorption of methylene blue on PSf/PAA 85/15 membrane was carried out in Erlenmeyer flasks containing 100 mL of dye solution. Erlenmeyer's contain was stirred at constant speed 120 rpm for a known time and at ambient temperature (25 ± 1 °C). The range concentration of dye varies between5 and 35 ppm.

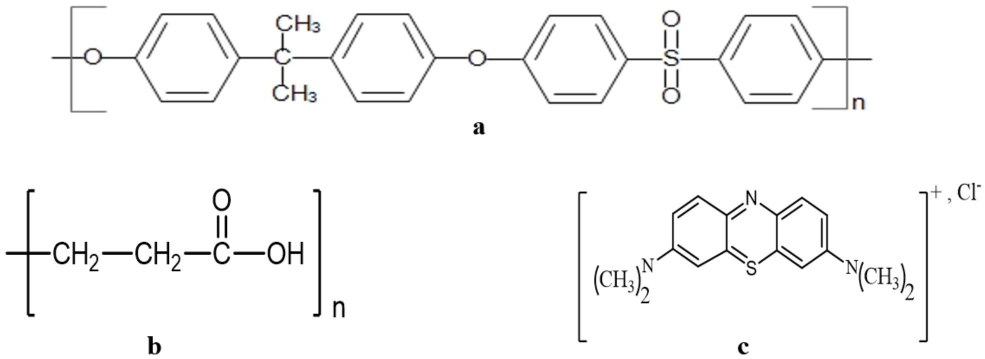

Figure 1 : Chemical structures of PSf (a), PAA (b) and MB dye (c)

The effects of membrane composition, dye concentration, pH and temperature and pH were investigated. The dye absorption was measured using 6705 UV/VIS Spectrophotometer, model JENWAY. The amount of dye adsorbed onto membrane Q_e (mg/g) was calculated using the following equation:

$$Qe = \frac{(C0 - Ce)V}{m} \qquad \text{Eq. 1}$$

Where Q_e is the adsorbed amount of dye (mg/g), C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of dye, respectively, m (g) is the mass of membrane sample and V (L) is the volume of the liquid phase.

3. RESULTS AND DISCUSSION

The adsorption process depends on various parameters as membrane morphology and charges, and the conditions of experiences as pH and adsorbent concentration. Many techniques and experimental attempts were done in order to understand the mechanism of adsorption process of MB onto PSf/PAA membrane.

3.1. Scanning electron microscopy

The scanning electron microscopy was used to collect information regarding membrane morphology. Fig. 2 shows the images of top-surface (a) and cross-section morphologies (b) of PSf/PAA 85/15, respectively.

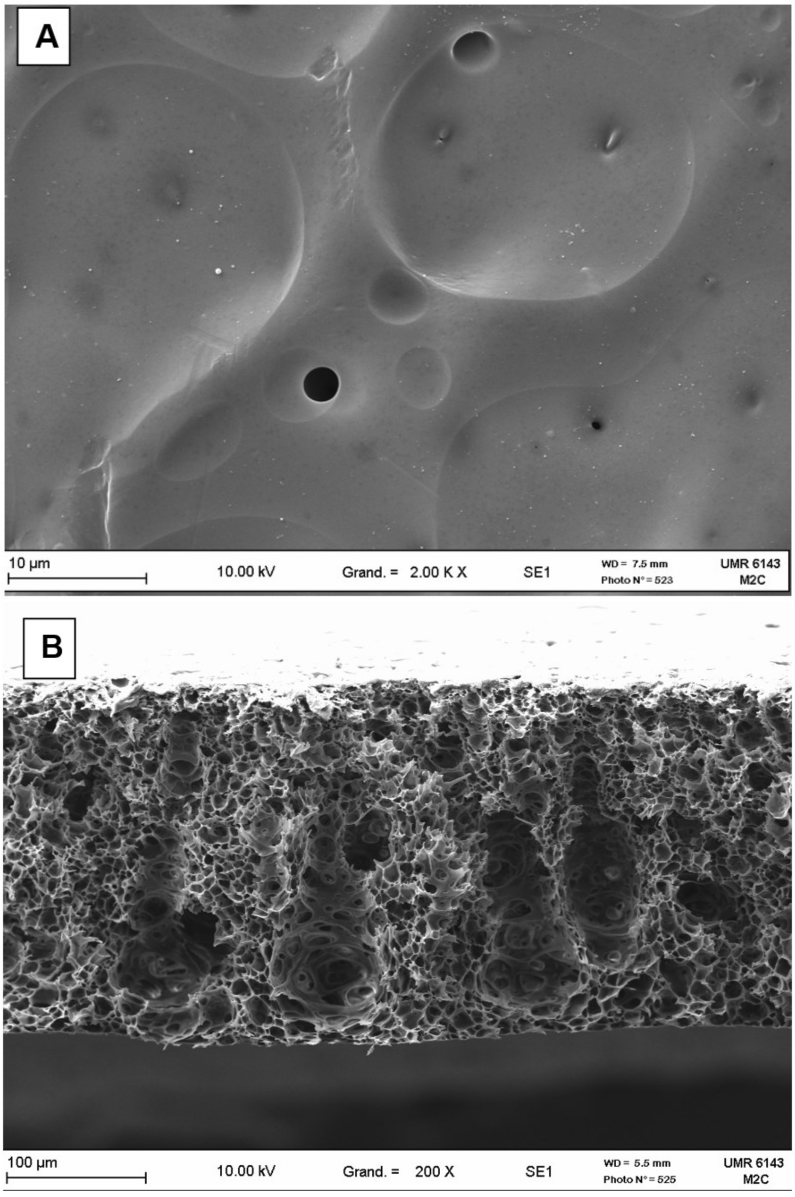

Figure 2 : SEM top-surface (A) and cross-section (B) of PSf/PAA 85/15 membrane

SEM images of membrane surface reveal that membranes contain inter-connected or dead-ended pores with different densities and sizes. It was also observed that the outer-surface pores contain sub-open pores and fine pores inner the sub-pores [19].

The distribution pores observed in the image of membrane cross section demonstrates the high level of PSf/PAA membrane porosity. This porosity would have a benefit effect on the adsorption process. It increases the specific surface of contact between membrane and pollutant.

3.2. pH_{PZC} (point zero charge)

The pH_{PZL} parameter is usually used to evaluate the ionic exchange capacity in acidic and basic medium. Therefore, PSf/PAA samples were exposed to pH variation from 2 to 12 by adding HCl or NaOH as shown in figure 3.

The behavior of pH_{PZL} curve as illustrated in Figure 3 shows that the density of surface charge of PSf/PAA membrane is near to zero at low pH and decreases to negative values when the pH increases more than 5. The trend observed about pH = 5 is due to the passage of carboxylic groups from molecular form (-COOH) in acid medium to ionic form ($-COO^-$) in basic medium. These results confirm the presence of carboxylic groups into membrane structure.

3.3. Methylene blue adsorption

3.3.1. Effect of pH

The pH of dye solution plays an important role in the whole sorption process especially on the adsorption capacity. To study the effect of pH on MB adsorption onto PSf/PAA membrane, experiments were carried out by varying the pH of dye solution.

The adsorption percentage of dye amount was calculated using the following mathematical equation:

$$R\,\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad \text{Eq. 2}$$

Fig. 4 shows that the MB removal increases with the increase of pH of dye solution. At low pH (pH = 3) the carboxylic groups are in molecules form as noted previously. Then, the intermolecular interactions between dye molecules and membrane surface are very weak. Higher retention is observed at higher pH values where carboxylic groups are in ionic forms. In fact, at pH higher than 5, carboxylic groups embedded by PSf/PAA membranes develop strong ionic intermolecular interactions with positive groups embedded by MB. Similar behavior was observed between hydrogel grafted and methylene dye (MB) [19,20].

3.3.2. Effect of membrane composition

Three membrane sheets with different composition PSf/PAA 95/05, 90/10 and 85/15 were used to study the adsorption process of MB.

The comparison of three curves depicted by Fig. 5 show clearly the improvement of MB adsorption with the increase of PAA fraction. The values of maximum adsorption capacity deduced from these curves reached 49.9, 67.04 and 87.82 mg/g for PSf/PAA 95/05, 90/10 and 85/15 membranes, respectively.

Of course, the origin of this improvement is due the increase of carboxylic groups embedded by PAA polymer. These groups establish ion–ion interactions with positive dye charges [21].

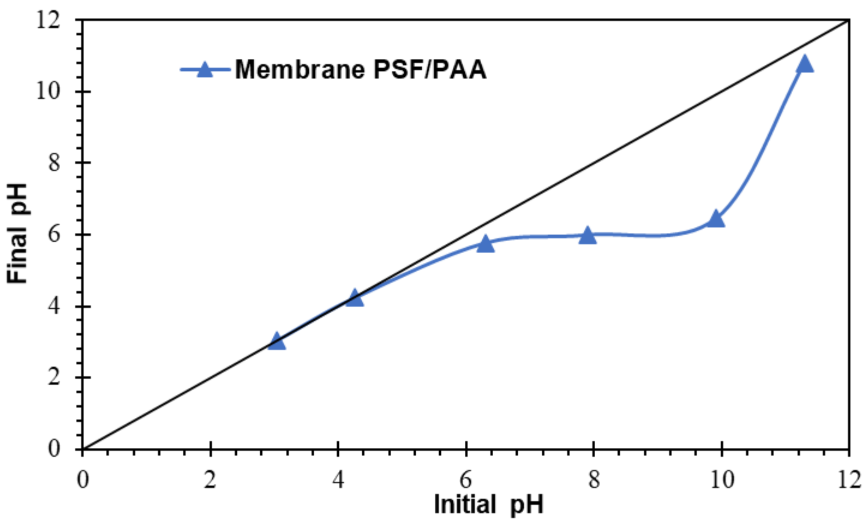

Figure 3 : pH_{PZC} (point zero charge) of PSf/PAA 85/15

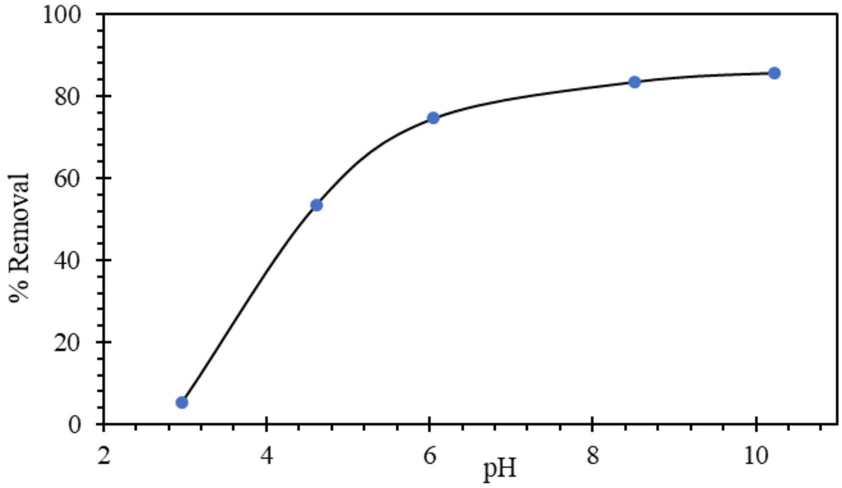

Figure 4 : Effect of pH on MB adsorption Onto PSf/PAA membranes.
C_0 = 10 mg/L, V = 50 mL, m = 10 mg, agitation speed = 120 rpm and T = 24 ± 1 °C)

Similar results were obtained by other authors [12, 22] who assigned the adsorption of different cationic dyes on negative charged polyelectrolytes to the establishment of electrostatic interactions between the positives charges of dye molecules and the negative sulfonate groups of polyelectrolytes

3.3.3. Effect of initial concentration of MB solution

Several experiments were carried out at different dye concentrations. Due to its higher adsorption capacity PSf/PAA 85/15 membrane was selected to study the effect of MB initial concentration on MB adsorption. Then, three concentrations 10, 25 and 35 mg/L were prepared to achieve this aim.

As shown in Fig 6, the maximum adsorption capacity of MB increases from 85 to 227 mg/g when the concentration moves from 10 to 35 mg/L, respectively. The equilibrium is reached quickly for low concentrations contrary to high ones.

The obtained results prove clearly that there is a relationship between the capacity of adsorption and the dye concentration [23]. It might be proposed that with the increase of dye molecules, in the surrounding of membrane sites, novel layers might be formed enhancing dye adsorption [10,12,24].

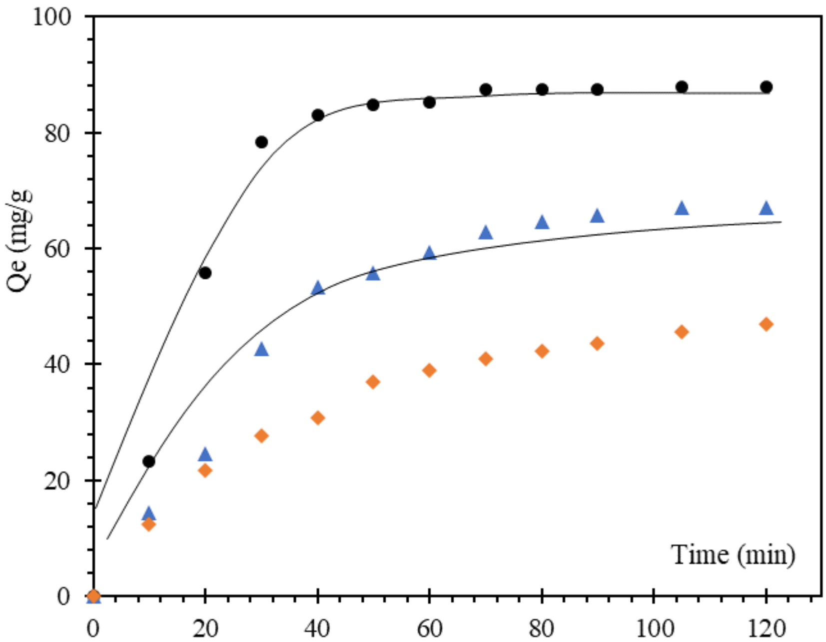

Figure 5 : Effect of membrane composition on MB adsorption
C_0 = 10 mg/L, m = 10 mg, V = 100 mL, 120 rpm, T = 24 ± 1 °C and pH = 10.5
(♦) PSf/PAA 95/05; (▲) PSf/PAA 90/10 and (●) PSf/PAA 85/15

3.3.4. Adsorption kinetics

In this study, the two most-widely used models, pseudo first order (PFO) model proposed by Lagergreen and pseudo second order (PSO) model proposed by Mc Kay and Ho, were selected to describe the adsorption kinetic of MB onto PSf/PAA 85/15 membranes. Four concentrations 10, 25 and 35 mg/L were chosen to realize this aim [25,26].

The linearized form of the pseudo-first-order(PFO) and the pseudo second order (PSO) models are respectively represented by the following equations [27]:

$$\mathrm{Ln}\,(Q_e - Q_t) = \ln Q_e - K_1 t \qquad \text{Eq. 3}$$

$$\frac{t}{Q_t} = \frac{1}{(K_2\, Q_e^2)} + \frac{t}{Q_e} \qquad \text{Eq. 4}$$

Where:

- Q_e(mg/g) and Q_t(mg/g) are the adsorbed amounts at equilibrium and at time t (min), respectively.
- K_1(min^{-1}) and K_2(mg g^{-1}min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

Fig. 7 and fig. 8 represent respectively the curves of the pseudo-first order and pseudo second order at different concentrations. The exploration of kinetic results according to both models, showed that the large values of correlation coefficient (R^2) at different concentrations are close to unity for pseudo-second order model, which confirms that, the sorption kinetics of MB onto PSf/PAA membrane follows preferentially the pseudo-second-order process [28]. This tendency is confirmed by the difference between the experimental and theoretical adsorption capacity, which is lesser for the SPO than FPO as demonstrated in table 1.

3.3.5. Adsorption isotherms

In this study, the most known isotherm models, Langmuir and Freundlich, were applied to get more information about PAA and MB interactions.

Langmuir's model

Equation 5 represents the mathematical expression of Langmuir's model where as Equation 6 the linearization equation of this model [29, 30]:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad \text{Eq. 5}$$

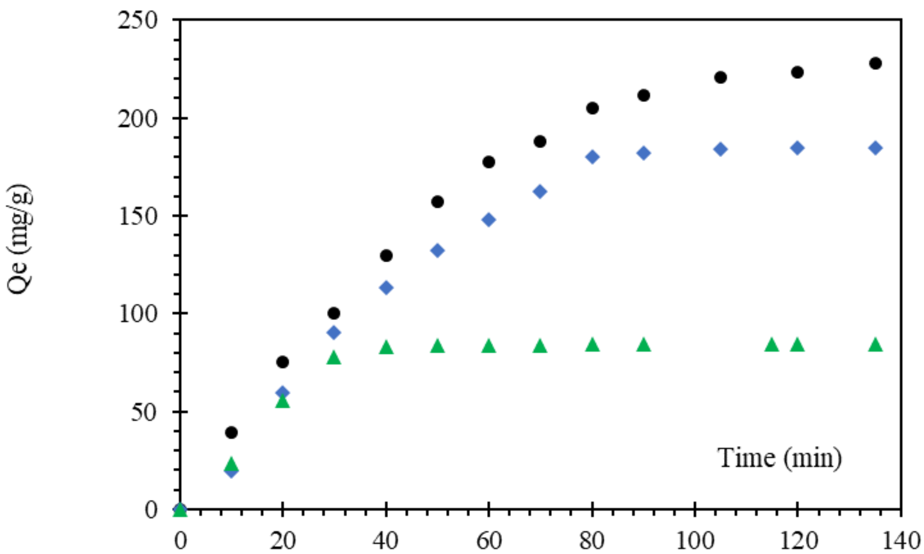

Figure 6 : Effect of dye concentration on MB adsorption onto PSf/PAA 85/15;
(▲) 10, (♦) 25 and (●) 35 mg/L
m = 10 mg, V = 100 mL, agitation speed = 120 rpm, T = 24 ± 1 °C and pH = 10.5

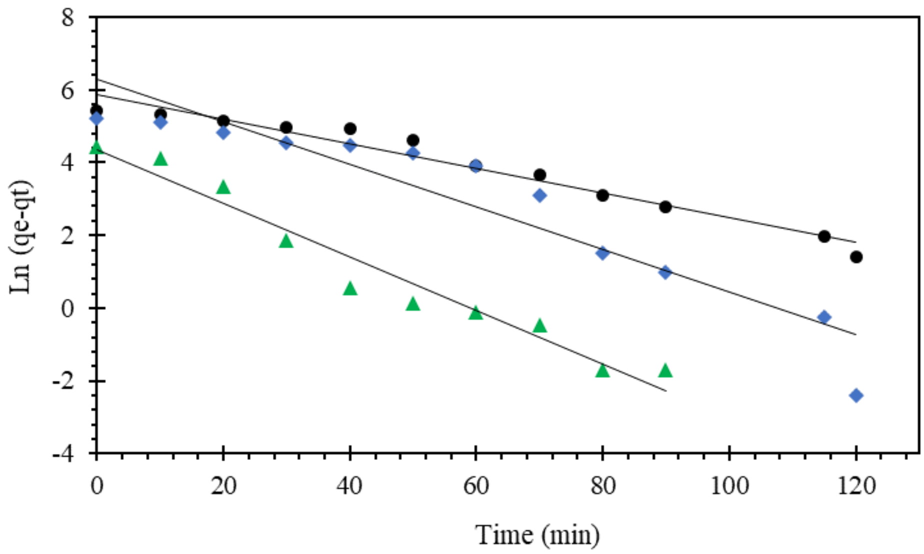

Figure 7 : PFO curves of the kinetics of MB adsorption onto PSf/PAA membrane at m = 10 mg, V = 100 mL, agitation speed = 120 rpm, T = 25 ± 1 °C and pH = 10.5.
(▲) 10, (♦) 25 and (●) 35 mg/L

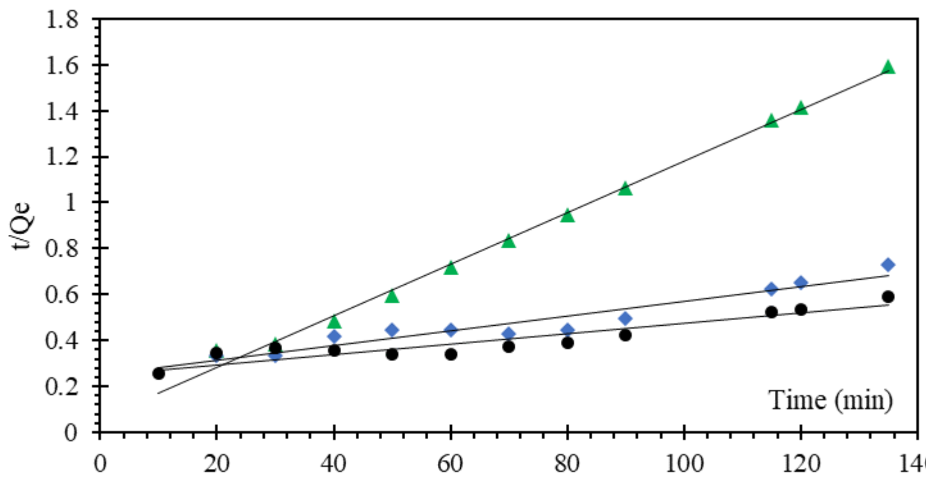

Figure 8 : PSO curves of the kinetics of MB adsorption onto PSf/PAA membrane at m = 10 mg, V = 100 mL, agitation speed = 120 rpm, T = 25 ± 1 °C and pH = 10.5.
(▲) 10, (♦) 25 and (●) 35 mg/L

Table 1 : PFO and PSO parameters for adsorption of BM onto membrane PSf/PAA85/15

		Pseudo-first order			Pseudo-second order		
C_0 (mg/L)	$Q_{e.\ exp}$	$Q_{e.\ cal}$	K_1	R^2	$Q_{e.\ cal}$	K_2	R^2
10	85	78	73.6	0.955	89.28	21	0.995
25	184	534	58.5	0.883	312.5	0.411	0.917
35	227	357	34	0.959	434.78	0.212	0.869

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_L\, Q_m\, C_e} \qquad \text{Eq. 6}$$

Where:

- Q_e is the amount of MB adsorbed per gram of PSf/PAA at equilibrium (mg/g),
- C_e is the equilibrium concentration of MB (mg/L),
- Q_m is the maximum monolayer coverage capacity (mg/g), K_L is Langmuir isotherm constant (L/mg).

The plot of $1/Q_e$ versus $1/C_e$ as shown in Fig.8, leads to deduce the values of Q_m and K_L. The Langmuir isotherm constant might be used to calculate the Langmuir separation factor R_L from the following Equation:

$$R_L = \frac{1}{1+K_L\, C_0} \qquad \text{Eq. 7}$$

The adsorption is considered favorable when the value of R_L is between 0 and 1, linear if $R_L = 0$ and, no favorable when the R_L values are greater than 1 [30].
The exploitation of results obtained from Langmuir' model, shown in Fig. 9, allows the deduction of the Langmuir isotherm constant $K_L = 0.313$, and the Langmuir separation factor R_L which values are ranging between 0.38 and 0.08. Values of both parameters indicate that the adsorption of MB on PSf/PAA membrane is favorable. This analysis is reinforced by the value of correlation coefficient which is close to unit $R^2 = 0.992$.

Freundlich's model

The empirical model of Freundlich [31] is expressed by the following Equation:

$$Q_e = K_f\, C_e^{1/n}$$

Where:

- Q_e is the amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g),
- C_e is the equilibrium concentration of adsorbate (mg/L),
- K_f is the adsorption capacity at unit concentration and 1/n is the adsorption intensity. Freundlich's parameters can be deduced from the linearization of the above Equation:

The plot of LnQe as a function of LnCe leads to the values of n, K_f and R^2. Their values, deduced from fig 10, were n = 1.86, $K_f = 66.75$ and $R^2 = 0.972$, respectively. Adsorption is considered favorable when the value of n is higher than 1 [30].
The analysis of these parameter summarized in Table 2 leads to admit that the adsorption of MB on PSf/ PAA is favorable (n > 1) and Langmuir model describes better this adsorption process than Freundlich model ($R^2_L = 0.992 > R^2_f = 0.972$).

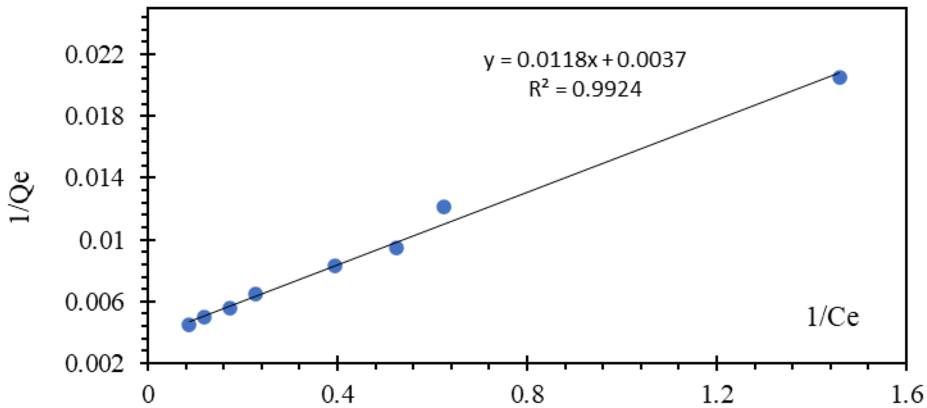

Figure 9 : Langmuir model for membrane PSf/PAA85/15
at C_0 = 5 – 35 mg/L, V = 100 mL, m = 10 mg, 120 rpm, pH = 10.5 and T = 25 ± 1 °C.

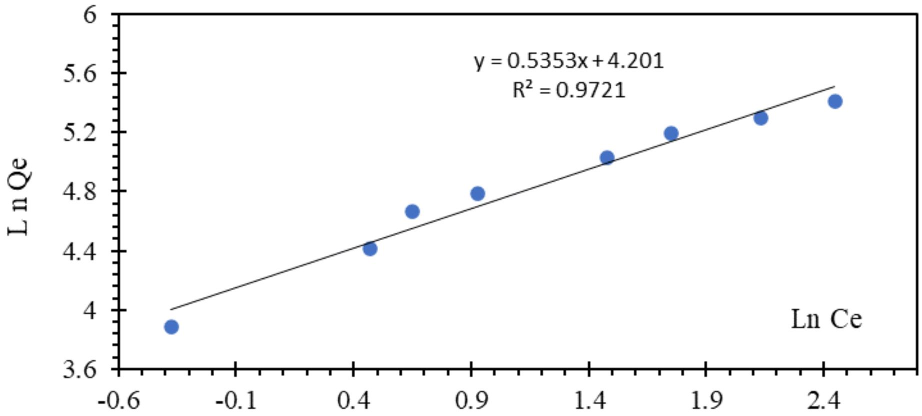

Figure 10 : Freundlich model for membrane PSf/PAA 85/15 at C_0 = 5 – 35 mg/L, V = 100 mL, m = 10 mg, 120 rpm, pH = 10.5 and T = 25 ± 1 °C.

Table 2. The parameters of Langmuir and Freundlich

Langmuir				**Freundlich**		
Q_m	K_L	R_L	R^2	n	K_F	R^2
333	0.313	0.38 and 0.08	0.992	1.86	66.75	0.972

Q_m(mg/g), K_L(L/mg), K_F (mg/g) $(L/mg)^{1/n}$, K_t(J/mol), b (J/mol)

4. CONCLUSION

Novel synthetic membrane composed of poly sulfone (PSf) and Poly acrylic acid (PAA) mixture were used in the removal of methylene blue (MB) from aqueous solution. Membrane's morphology was studied by Scanning Electronic Microscopy (SEM) which brings to fore the presence of superficial pores and various kinds of inter communicative pores in the membrane core. Globally, membrane structure seems to be like spongeous structure. Such a structure might have a benefit quality in water treatment either in adsorption or in filtration processes.

Under various conditions: membrane composition, initial concentration and pH, the adsorption tests of MB on PSf/PAA membranes show an excellent performance of dye removal. The results prove that the adsorption capacity increases with pH value which affects the ionization of functional groups responsible of inter molecular interactions between carboxylic groups embedded by membrane and positive dye molecules. The adsorption capacity reaches 333 mg/g at pH 10.

Based on the value of correlation coefficient, the adsorption of MB follows perfectly Langmuir's model (R^2=0.992) and the kinetic was well described by the pseudo-second-order (R^2= 0.995). Such results are the consequence of strong ions - ions interactions whose involved membrane and dye molecules.

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