

Performance of an acidic extractant (D2EHPA) incorporated in IM used for extraction and separation of Methylene Blue and Rhodamin B

S. Aitali^a, O. Kebiche-Senhadji^{*} and M. Benamor^b

Laboratoire des Procédés Membranaires et des Techniques de Séparation et de Récupération (L PMTSR),
Faculté de Technologie-Université de Bejaia, DZ -06000, Bejaia – Algeria

(Received November 24, 2014, Revised February 26, 2016, Accepted August 19, 2016)

Abstract. Laboratory-scale experiments were carried out to investigate the adsorption equilibrium, the adsorption kinetics and facilitated transport of two cationic dyes (Methylene Blue (MB) and Rhodamine B (RB)) on Polymer Inclusion Membrane (D2EHPA-PIM). Different adsorption isotherms (Freundlich, Langmuir and Temkin models) as well as kinetics models indicated that the adsorption process is spontaneous and exothermic. Under the optimal conditions, the adsorption removal efficiencies reach about 93% and 97% for MB and RB respectively. Different extraction values by D2EHPA-PIM were obtained for the two cationic dyes: MB is weakly extracted at pH 2.0 ($E\% = 18.7\%$) whilst $E\% = 82.4\%$ was observed for RB at the same pH. This difference was exploited in a mixture containing both the 2 cationic dyes for the selective extraction of RB at pH 2. Desorption of both dyes was achieved from the membrane by using acidic aqueous solutions and desorption ratio up to 90% was obtained. The formulas of the extracted complexes by the PIMs were, determined by the method of slopes. The dyes transport was elucidated using mass transfer analysis where in it found relatively high values of the initial flux (J_0) as 41.57 and 18.74 $\mu\text{mol.m}^2.\text{s}^{-1}$ for MB and RB respectively.

Keywords: Polymer Inclusion Membrane (PIM); D2EHPA; extraction; cationic dyes; kinetics; equilibrium; facilitated transport

1. Introduction

Colored effluents are widely produced in industries such as textiles, leather, rubber, dye synthesis, printing, pulp mills, food and plastics. Nowadays, their excessive release into the ecosystem represents increasing environmental problem due to their toxicity, mutagenicity, non-biodegradability and undesirable aesthetic aspects (Luo *et al.* 2011).

In particular, in textile industries, the removal of textile dyes from wastewater has been a subject of great interest in the past decades and has been brought to discussion because of new environmental laws, restriction on water availability, and charge for its use (Ueda *et al.* 2011). Once the dye has contaminated the water, its removal by conventional wastewater treatment

*Corresponding author, Ph.D., E-mail: kebiche_anissa@yahoo.fr

^a Ph.D. Student, E-mail: aitalisalima@yahoo.fr

^b Professor, E-mail: mohamedbenamor@yahoo.fr

method is particularly difficult because many dyes are stable to light, oxidizing agent, and are resistant to aerobic bio-oxidation (Ramesh *et al.* 2007).

In last 2-3 decades several decolorization processes have been developed, such as membrane separation (Jiraratananon *et al.* 2000, Treffry-Goatley *et al.* 1983), adsorption (Bhatt *et al.* 2012, Mahmoodi *et al.* 2011), coagulation flocculation (Moghaddam *et al.* 2010, Verma *et al.* 2012), photo-oxidation (Lucas and Peres 2006), biological treatments (Chatha *et al.* 2011, Van der Zee and Villaverde 2005), liquid-liquid extraction (Pandit and Basu 2002, Gungor *et al.* 2008) and others (Djenouhat *et al.* 2008a, Moscofian *et al.* 2012, Bayramoglu *et al.* 2009, Liu *et al.* 2007, Wu *et al.* 2008).

The analysis of recent literature on the topic indicates that the dye removal techniques and processes worth-noting are green and clean, i.e., which meets the requirements of stricter environmental regulations. Unfortunately, cleaner dye wastewater treatment methods generally imply higher energy/operation costs (Mezohegyi *et al.* 2012).

Moreover, a simple, cost effective and safe alternative for color removal and recovery of dyes from textile effluent is required and membrane technology may provide this alternative. Among membrane processes, the extraction by liquid membranes has acquired a prominent role for their use in separation, purification or analytical application in various areas, such as biomedicine, ion selective electrodes, effluent treatment and hydrometallurgy (Muthuraman *et al.* 2010). In this field, some researchers have studied the extraction of anionic and cationic dyes, from aqueous solutions by emulsion liquid membrane (Daas and Hamdaoui 2010, Djenouhat *et al.* 2008b, Das *et al.* 2008).

Supported liquid membranes (SLMs), which employs a porous membrane impregnated with a solvent containing complexing carrier(s) to separate the feed and strip phases, represents one of the most useful types of liquid membrane, as it combines the processes of extraction, diffusion, stripping and regeneration in a single step. Thus having great potential for reducing cost significantly (Yang *et al.* 2001, Drapala *et al.* 2001, Yourd and Tyson 2003). This methodology has been widely applied to study transport of individual species such as metal ions, weak acids and bases, hydrocarbons, biologically important compounds, and gaseous mixtures, as well as the separation of multicomponent mixtures (Yahaya *et al.* 2000).

SLM extraction system was investigated by Nisola *et al.* (2010) in the separation of synthetic dye Rhodamine 6G (R6G) from water. The transport of cationic dyes Methyl Violet and Rhodamine B from aqueous synthetic dye solution through flat type SLM using Di (2-ethyl) phosphoric acid (D2EHPA) as a synthetic carrier, was studied by Hajrabeavi *et al.* (2009). Vegetable oils were also tested as carriers in SLMs for extraction of Rhodamine B (Muthuraman and Teng (2009) and astacryl golden yellow (Muthuraman and Palanivelu 2006).

Recently, a novel type of liquid membrane system, called "polymer inclusion membrane" (PIM) has been developed (Kozlowski *et al.* 2006). PIMs retain most of advantage of SLMs while exhibiting excellent stability and versatility. The lower diffusion coefficient often encountered in PIMs can be easily offset by creating a much thinner membrane in comparison to its traditional SLM (Arous *et al.* 2004, Nghiem *et al.* 2006).

To our best knowledge, except the first part of our research already available in Procedia Engineering (Aitali *et al.* 2012), no work was published about the use of PIMs for the extraction of industrial dyes from aqueous solution, so, the aim of this study is to investigate the use of polymer inclusion membranes (PIMs) for extraction, facilitated transport and the separation of two cationic dyes (Methylene Blue and Rhodamine B) from diluted aqueous solutions. The PIMs were prepared using cellulose triacetate (CTA) as polymer matrix plasticized with Nitrophenyl Octyl Ether (2-

NPOE) and containing Di (2-ethyl hexyl) phosphoric acid (D2EHPA) as the carrier. The effects of time, pH, stirring speed, concentrations of the D2EHPA and dyes have been optimized.

2. Experimental

2.1 Reagent

Cellulose triacetate (CTA), 2-nitrophenyl octyl ether (2-NPOE), di (2-ethyl hexyl) phosphoric acid (D2EHPA) were obtained from Aldrich. Chloroform (CHCl_3) was acquired from Fluka. Methylene blue (basic blue 9) and Rhodamine B were purchased from Merck. The structures of these dyes are given in Fig. 1.

2.2 Polymer inclusion membrane preparation

PIMs were prepared using the same procedure described in our previous works (Kebiche-Senhadji *et al.* 2008, 2010). CTA was dissolved in chloroform at room temperature and mixed with the plasticizer solution. After vigorous stirring, the carrier (D2EHPA) was added and the solution was stirred to obtain a homogenous solution. The solvent of this mixed solution was allowed to slowly evaporate in a 9.0 cm diameter Petridish, which was covered loosely.

Two samples were cut out from the same piece of the formed film (membrane) for duplicate experiments. The membranes thickness was measured by digital micrometer (Mitutoyo) with 0.1 μm standard deviation over 10 readings. The average thick of the prepared membranes varied from 45 μm to 100 μm .

The results of the characterization study of these membranes were already given in our earlier work (Aitali *et al.* 2012).

2.3 Liquid-solid extraction

The liquid-solid extraction experiments were undertaken at room temperature, stirring the aqueous solution using a magnetic stirrer at 200-500 rpm. Diluted solutions of HNO_3 and NaOH were used to adjust the pH of the aqueous solutions.

The extraction of the dyes was followed by absorbance measurements which were carried out with a UV-visible spectrophotometer (Shimadzu UV-2401 PC). The dyes concentration was calculated from the absorbance, measured at the wavelength of maximum absorption of the two

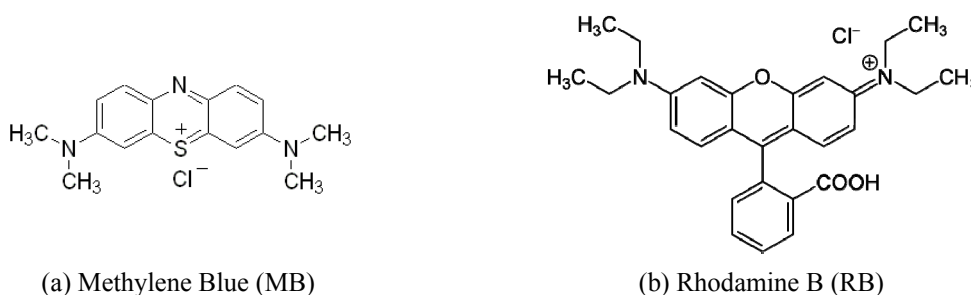


Fig. 1 Chemical structures of Methylene Blue (MB) and Rhodamine B (RB)

dyes (650 nm for MB and 565 nm for RB). The amount of extracted dye (E) and the distribution ratio (D) were calculated using the following equations.

$$E(\%) = \frac{[dye]_{aq0} - [dye]_{aq}}{[dye]_{aq0}} \times 100 \quad (1)$$

$$D = \frac{[dye]_{org}}{[dye]_{aq}} \quad (2)$$

Where:

$[dye]_{aq0}$: initial dye concentration in the aqueous phase (mg/l).

$[dye]_{aq}$: the dye concentration in the aqueous phase after extraction (mg/l).

$[dye]_{sol}$: the dye concentration in the solid phase membrane) (mg/l).

2.4 Membrane transport experiments

The transport experiments of the cationic dyes (BM and RB) were carried out in two compartments Plexiglas cell (100 cm³). The chambers were separated by the PIMs and clamped together (the area of each side of the PIMs in contact with the solution was 4.3 cm²). The source phase was an aqueous dye solution at a concentration of 20 mg/L (pH 6.0). The receiving phase (strip phase) was aqueous solution of HNO₃ (1M) or H₂SO₄ (1M) in the case of the MB or RB transport, respectively. The transport experiments were carried out at room temperature (23–25°C) and both source and strip aqueous phases were stirred at 350 rpm with magnetic stirrers.

For the experiments of dyes separation, a three compartment cell was used (see Fig. 2), wherein the middle compartment (source phase) was filled with the aqueous solution containing a mixture of the two dyes studied here (MB and RB). The other two compartments were filled with aqueous solutions HNO₃ (1M) and H₂SO₄ (1M) which were used as strip phases for MB and RB, respectively.

The dye flux was calculated using the following relationship

$$J = \frac{-V}{A} \frac{dC}{dt} \quad (3)$$

The permeability (P) was evaluated using Eq. (4) as

$$\ln = \frac{dC}{C_0} = \frac{-A}{V} \cdot P \cdot t \quad (4)$$

The initial flux (J_0) was determined as

$$J_0 = P \cdot C_0 \quad (5)$$

where:

V : the volume of the feed solution (m³)

A : the membrane area in contact with the aqueous solutions (m²).

C_0 : the initial concentration of the dye (mol/m³)

C : the concentration of dye at time t (mol/m³)

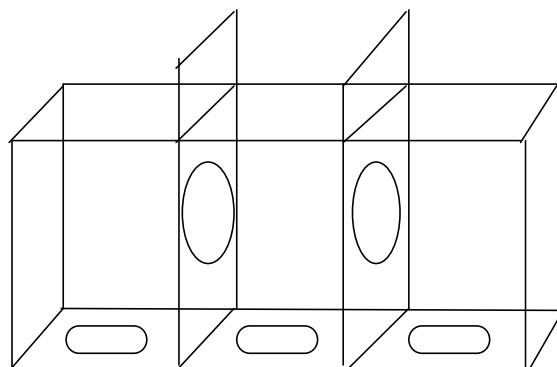


Fig. 2 Representation of the three compartment transport cell

2.5 Adsorption isotherms

The adsorption isotherm is fundamental in understanding the adsorption mechanism. Important information about how the adsorbate molecules are distributed between the liquid phase and the solid phase once steady state is reached and can be interpreted based on the adsorption isotherm. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of a substance in the system conditions. Langmuir, Freundlich and Temkin models were used in this study to describe the equilibrium adsorption of MB and RB on the PIM. The expression of the Langmuir model is given by

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max}} K_L + \frac{C_e}{Q_{\max}} \quad (6)$$

where Q_e ($\text{mg}\cdot\text{g}^{-1}$) is the equilibrium amount of the dye adsorbed by the membrane, C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium dye concentration in the solution, Q_{\max} ($\text{mg}\cdot\text{g}^{-1}$) is the maximum uptake of the dye and K_L ($\text{L}\cdot\text{mg}^{-1}$) is the Langmuir constant. Q_{\max} and K_L constants are calculated from the slope and intercept of the plot of C_e/Q_e versus C_e .

The Freundlich isotherm is commonly given as

$$\text{Log}Q_e = \frac{1}{n}\text{Log}C_e + \text{Log}K_F \quad (7)$$

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Higher value for K_F indicates higher affinity for adsorbate and the values of the empirical parameter $1/n$ lie between $0.1 < 1/n < 1$, indicating favorable adsorption. K_F and $1/n$ can be determined from the linear plot of $\text{Log} Q_e$ versus $\text{Log} C_e$.

Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. The Temkin isotherm is given as

$$Q_e = B \text{Ln} C_e + B \text{Ln} A \quad (8)$$

where A (L/g) is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B is related to the heat of adsorption. A plot of Q_e versus $\ln C_e$ enables the determination of the isotherm constants B and A from the slope and intercept of the straight line plot (Oladoja *et al.* 2008).

2.6 Thermodynamic study

In order to evaluate better the feasibility and the temperature effect, for dye adsorption onto the D2EHPA-PIM, thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were evaluated.

The Gibbs free energy change ΔG° (kJ/mol) is related to the equilibrium constant K_c by Van't Hoff equation

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

It is also related to the change in entropy ΔS° (J/mol.K) and the heat of extraction ΔH° (kJ/mol), at constant temperature T as follows

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

Where: R is the universal gas constant (8.314 J/mol.K)

Equilibrium constant K_c can be calculated as

$$K_c = C_0 / C_e \quad (11)$$

So, we can write

$$-RT \ln K_c = \Delta H^\circ - T \Delta S^\circ \quad (12)$$

And finally

$$\ln K_c = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (13)$$

3. Results and discussion

3.1 Liquid-solid extraction

3.1.1 Effect of contact time

The equilibrium adsorption time of the two basic dyes (MB and RB) on the PIM was investigated for a period of 360 min. A high initial slope of the adsorption curves can be observed in Fig. 3, indicating that the initial uptake is fast. This phenomenon could be explained considering that at the beginning of the sorption process all the reaction sites are unoccupied and consequently the extraction is high. After the initial uptake (60 min), there was a transitional phase (from 60 to 120 min) and then the *plateau* (Fig. 3). So, 120 min is sufficient to reach the equilibrium for both MB and RB and this period was employed for all the subsequent experiments.

3.1.2 Effect of stirring speed

Table 1 shows the influence of stirring speed on the extraction of MB and RB. The results

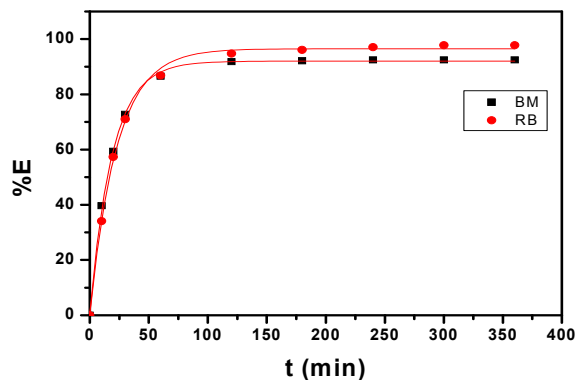


Fig. 3 Effect of the contact time on adsorption of BM and RB dyes on PIM

Table 1 Effect of the stirring speed on the extraction efficiency of the cationic dye by D₂EHPA-PIMs

Stirring speed	Methylene blue	Rhadamine B
200	90.64	95.21
300	90.76	95.12
350	92.46	97.82
400	91.99	97.38
450	90.96	95.40
500	89.54	95.20

indicate that extraction efficiency increases by increasing stirring speed, the maximum was obtained at 350 rpm. The decrease of the efficiency, when the speed is upper than 350 rpm, is caused by the turbulence created by stirring. A comparable result was obtained by Muturaman and Teng (2009).

3.1.3 Effect of the carrier concentration

The dependence of dye adsorption on the quantity of the extractant (D2EHPA) in the membrane was examined by varying the amount of D2EHPA in the membrane matrix from 5 to 30 $\mu\text{mol}/\text{cm}^2$ (quantity of D2EHPA/unit surface of the membrane). While keeping other parameters such as initial concentration of dyes (50 mg/L), stirring rate 350 rpm, pH 6.0 and contact time 120 min, constant.

The extraction efficiency increases with the carrier loading in the membrane (up to 15 $\mu\text{mol}/\text{cm}^2$) then is stabilized for high concentrations (Fig. 4). This trend can be easily explained in terms of number of available extraction sites for the cation dyes.

3.1.4 Effect of the initial dye concentration

The effect of the initial dye concentration on the percentage of dye removal was studied by varying the dye concentration in the range of 0.25 to 1.5 mmol/L. As shown in Fig. 5, the removal capacity of the membranes, decreases with the increase in the initial dye concentration. In the case of low dye concentrations, the ratio of initial number of dye moles to the available functional sites is low. At high concentrations, the number of these sites becomes lesser and subsequently the

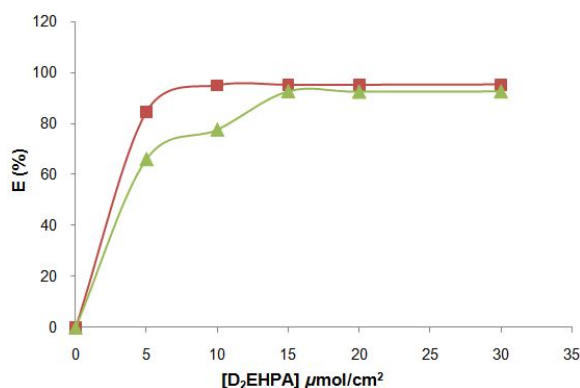


Fig. 4 Influence of D2EHPA concentration on the extraction efficiency of BM and RB dyes by PIM

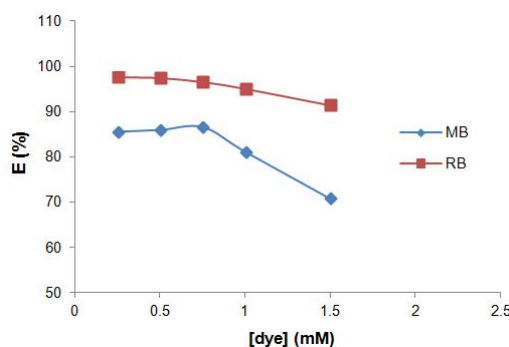


Fig. 5 Effect of concentration dyes on the extraction efficiency of BM and RB dyes by PIM

removal of dyes depends on the initial concentration. This behaviour has also been shown in other different metal carrier polymer membrane systems (Kebiche-Senhadji *et al.* 2010, Kozlowski *et al.* 2002).

3.1.5 Effect of the the aqueous solution pH

The pH of the aqueous phase has a significant influence on the extraction behaviour. The effect of pH on the retention capacity of the D2EHPA-PIMs was tested with the two basic dyes (MB and RB) in the pH range of 1.0–12.0, the D2EHPA concentration in PIM and dye in aqueous phase were kept constant. As shown in Fig. 6, the extraction efficiency of MB and RB dyes increase up to pH 6.0 and then remain almost constant at higher value of pH. The extraction is weak at pH 2.0 in the case of the MB, and its maximum extraction is achieved at pH 6.0. However, the D2EHPA-PIM shows a good retention for RB at pH 2.0 ($E\% = 82.4\%$) and the extraction efficiency increases slightly up to 97% at pH = 6.0. These results can be explained taking into account that the cationic exchange becomes more difficult when the acidity increases, because of the weak dissociation of the acidic extractant (D2EHPA) in relatively low pH solution. Moreover, the difference in the chemical structure of MB and RB (Fig. 2) is at the basis of their different retentions.

More details on this issue are reported in the next section on the determination of the complex structure.

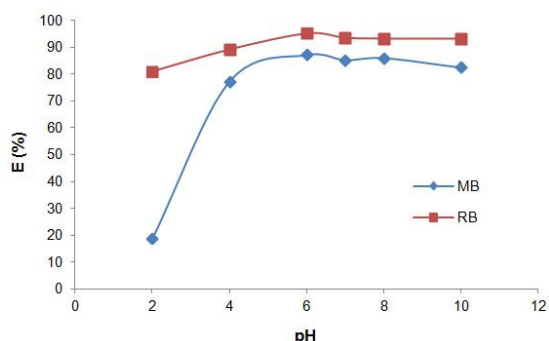


Fig. 6 Influence of pH on the D2EHPA-PIMs adsorption capacity of MB and RB

3.2 Determination of the complex structure

As reported in our previous research paper (Aitali *et al.* 2012) using the curves of $\log D = f(\text{pH}_f)$ and $\log D = f([\text{HL}])$ (Figs. 7-8), we have established the composition of the formed complex Methylene Blue-D2EHPA *via* the linear curves forms as

$$\text{Log}D = m \text{pH}_f + (m + n) \log[\text{D2EGOA}]_{org} + \log K_{m,n} \quad (14)$$

From the slope of the linear curves $\text{Log} D = f(\text{pH}_f)$ ($m = 1$ (exactly 0.958)) and $\text{Log} D = f([\text{HL}])$ ($m + n = 1$ (exactly 1.088)) where D2EHPA is noted HL (acidic extractant), we have determined the formula of the formed complex, and then we have proposed the mechanism given by the following equation



with: $m = 1$ and $n = 0$.

The result suggests that MB is extracted by the matrix (CTA-NPOE-D2EHPA) in the form: MB-L.

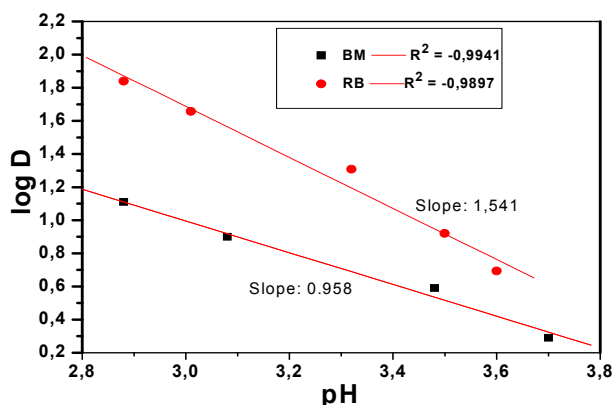


Fig. 7 Determination of extraction stoichiometry of the cationic dyes with D2EHPA (Plots of $\log D$ vs the equilibrium pH)

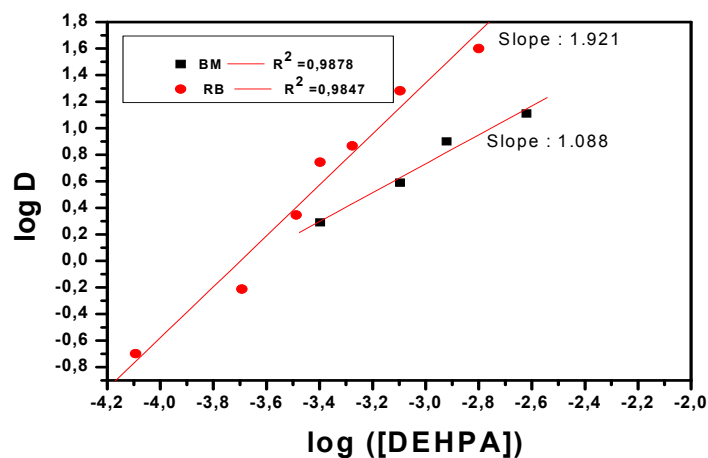
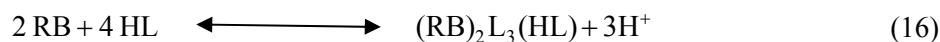


Fig. 8 Determination of extraction stoichiometry of the cationic dyes with D2EHPA (Plots of $\log D$ vs $\log [D2EHPA]$)

Using the same method, in the case of the RB extraction we have found $m = 1.541$ (see Fig. 7) and $n + m$ is determined to be 2 (exactly 1.921 see Fig. 8) and the value of n thus becomes nearly 0.5. The composition of the extracted species in the membrane matrix is then given as $RBL_{1.5} \cdot 0.5 HL$, which can be also writing: $(RB)_2L_3 \cdot HL$. Thus, in the RB extraction, one molecule of the cationic dye is carried into the organic phase by two D2EHPA molecules.

The mechanism of the reaction is proposed as



The difference between the complexes formed with the two cationic dyes can be attributed to the difference in the chemical structures of the two dyes (Fig. 2).

3.3 Adsorption isotherms study

Langmuir, Freundlich and Temkin models were used in this study to describe the equilibrium adsorption of MB and RB on the PIM.

Parameters and correlation coefficients obtained from Freundlich, Langmuir and Temkin models are summarized in Table 2.

The fitting of the sorption data of MB and RB onto DEHPA-PIM, to the 3 isotherm models showed that the linearity of the Langmuir and Temkin isotherm models were higher than that of

Table 2 Parameters of Model-fitting to the Experimental MB and RB Adsorption Data obtained from Freundlich, Langmuir and Temkin models

Dye	Freundlich			Langmuir				Temkin		
	n	K_F	R^2	Q_{\max} (mmol/g)	K_L	R_L	R^2	A	B	R^2
BM	3.98	7.53	0.940	6.06	16.50	0.056	0.950	36.41	2.273	0.978
RB	5.95	4.37	0.900	3.40	3.68	0.305	0.930	123.64	1.002	0.927

the Freundlich isotherm model (Table 2). This suggests that the sorption of MB and RB on PIM is more probably a monolayer sorption rather than sorption on a surface having heterogeneous energy distribution.

In particular, according to the results of the Langmuir model (Table 2), the maximum adsorption capacity of the membranes (DEHPA-PIM) is 6.06 mmol/g and 3.40 mmol/g for MB and RB respectively. As known, the adsorption process can be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Mahmoodi *et al.* 2011).

The value of R_L is less than 1 but greater than 0 for the two dyes studied (Table 2) confirming that the adsorption process is favorable.

3.4 Thermodynamic study

The temperature effect on the adsorption rate of RB on the D2EHPA-PIM was investigated at five different temperatures (20, 30, 35, 40, and 50°C) using an initial concentration of RB of 0.605 mmol/L. The obtained results showed that the adsorption capacity slightly decreases with the increasing of the temperature i.e., an exothermic adsorption process.

ΔH° and ΔS° were calculated from the slope and intercept of Van't Hoff plots, respectively (Fig. 9). The values of ΔH° , ΔS° and ΔG° are given in Table 3. The negative value of ΔH° (-37.33 kJ/mol) means that the adsorption process was carried out as exothermic at 20–50°C. Based on the apparent enthalpy changes of adsorption (< 45 kJ/mol), the uptake of RB on D2EHPA-PIM can be considered an adsorption type intermediate between physical and chemical adsorption (Bilgili 2006).

The positive value of ΔS° for RB dye adsorption process indicates an irregular increase of the randomness at the membrane–solution interface during the adsorption process. The adsorption process of the cationic dye (RB) on the D2EHPA-PIM is feasible and spontaneous thermodynamically as the negative values of ΔG indicate. More negative values of ΔG at higher temperatures as observed in this study (Table 3), imply greater driving force for adsorption at high temperature as indicated by Ngah and Fatinathan (2010). The results of the measurement of the thermodynamic parameters indicate that the dye–PIM interaction equilibrium could be explored for practical application (Al-Rashed and Al-Gaid 2012).

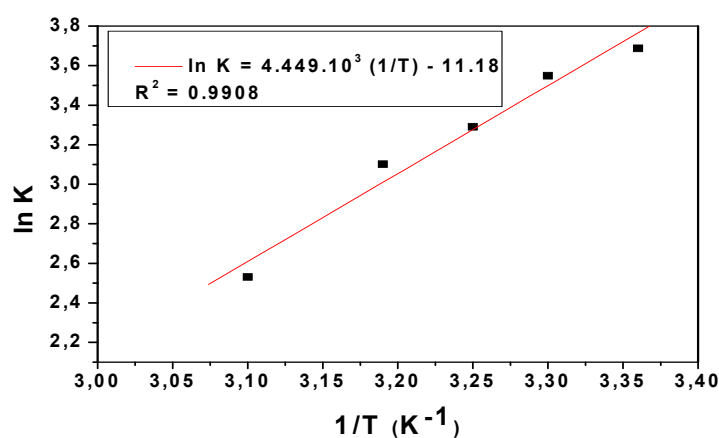


Fig. 9 $\ln(K_c)$ vs $(1/T)$

Table 3 Thermodynamic parameters for Rhodamine B adsorption on D2EHPA-PIM at different temperature

T (K)	ΔH (kJ/mol)	ΔS (j/mol.K)	ΔG (kJ/mol)
293			-64.89
303			-65.83
308	-37.33	+94.05	-66.30
313			-66.77
323			-67.71

Table 4 Sorption kinetic models constants of MB and RB for the system D2EHPA-PIMs

Dye	Pseudo first ordre		Pseudo second ordre	
	K_1 (min ⁻¹)	R^2	K_2 (g.mg ⁻¹ .min ⁻¹)	R^2
MB	0.039	0.994	0.060	0.999
RB	0.025	0.956	0.146	0.998

3.5 Sorption kinetics study

To determine the adsorption kinetic of MB and RB on the membranes, the pseudo first-order and pseudo second-order kinetic models were applied as indicated by Eqs. (17)-(18), respectively

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2,302} \times t \quad (17)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (18)$$

where q_e (mg/g) and q_t (mg/g) are the amount of the adsorbed dye at equilibrium and at time t (min), respectively. K_1 (1/min) is the pseudo first-order rate constant and K_2 (g/(mg·min)) is the pseudo second-order rate constant. The pseudo first-order model assumes that the rate of adsorption is proportional to the number of free adsorption sites.

The straight-line plots of $\text{Log}(q_e - q_t)$ and t/q_t versus t were used to determine the rate constant (k_1), which can be obtained from the slope of the plots.

Table 4 displays the rate constants K_1 and K_2 and the correlation coefficients (R^2) for the pseudo first-order and pseudo second-order models for the cationic dyes sorption on D2EHPA-membranes, considered in this work.

It can be seen that the correlation coefficient of pseudo-second-order kinetics (≥ 0.998) is greater than that of pseudo-first-order kinetics, so it can be concluded that the sorption of the two dyes MB and RB on the CTA-D2EHPA membranes obeys the pseudo-second-order kinetic model.

The pseudo second-order kinetic model relies on the assumption that the rate-limiting step may be adsorption, involving valence forces through the sharing or exchanging of electrons between adsorbent and adsorbate (Hanafiah *et al.* 2012).

This confirms that adsorption of dyes takes place via surface exchange reactions until the surface functional sites are fully occupied; thereafter, dye molecules diffuse into the membrane network *via* further interactions.

Table 5 Efficiency removal of MB by PIM regenerated with 1M HNO₃

N_{cycle}	E (%)
1	92.13
2	91.67
3	91.66

3.6 Desorption study

Desorption of the filled adsorbents is essential as the adsorbent can be reused in another cycle. In this work, desorption experiments of the membranes saturated with dyes, were conducted using HNO₃, H₂SO₄ and CH₃COOH solutions. After several tests (varying the acids concentrations) HNO₃ (1M) H₂SO₄ (1M) solutions were selected as stripping solutions giving the best desorption percentage for MB and RB (desorption ratio up to 90%). The MB adsorption capacities by regenerated PIM remains unvaried in three consecutive cycles.

Indeed, these tests on desorption were also very useful for the selection of the stripping solution in the transport study (see below).

3.7 Facilitated transport study of the dyes

The methods of membrane transport process are reported in Section 2.4. Flux experiment using the PIM without carrier showed that no transport of dyes from the source phase to the strip phase occurred. From this result it can be established that the PIM without carrier acts as an effective barrier to dyes species permeation.

3.7.1 Concentration profiles versus time (Individual Transport of MB and RB)

Fig. 10 shows the concentration profiles of dyes in the feed and stripping solutions. The curves shows that the concentration in the source phase decreased of 91.53% for MB and 85.63% for RB and this loss of concentration is not fully recovered in the receiving phases, mainly in the case of

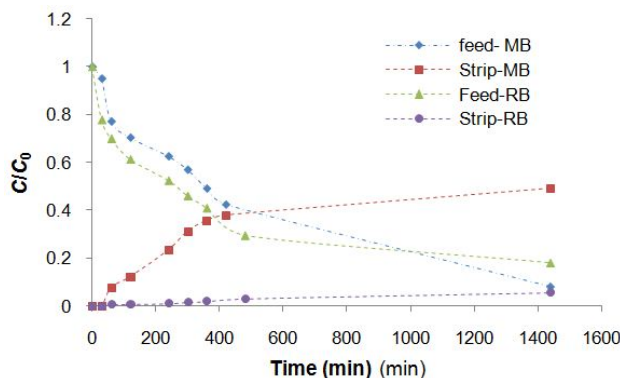


Fig. 10 Concentration profile vs time (in individual dyes transport) with D2EHPA CTA/PIM from a feed solution of BM or RB dyes : 30 mg/l; receiving solution: 1M HNO₃ (MB transport) or 1M H₂SO₄ (RB transport)

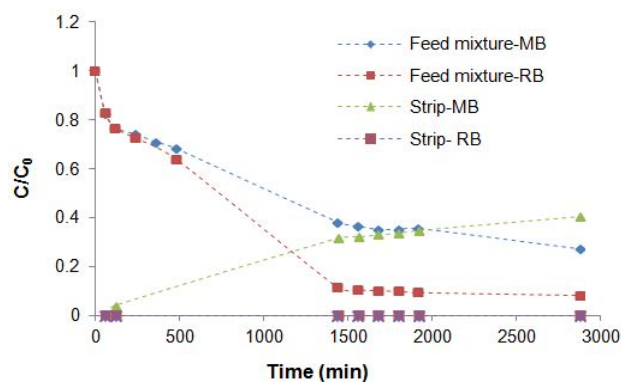


Fig. 11 Concentration profile vs. time for the system D2EHPA CTA/PIM using a mixture dyes (MB+RB) as source solution

RB which is fairly transported in the stripping compartment. This can be explained by the highly accumulation of RB on the membrane surface.

The initial flux (J_0) calculated using the Eq. (5) (on the basis of the linear plot of $\ln C/C_0$ versus time) gives the values of $41.57 \mu\text{mol.m}^2.\text{s}^{-1}$ and $18.74 \mu\text{mol.m}^2.\text{s}^{-1}$ for MB and RB, respectively. The difference in initial flux for MB and RB can be related to the difference in the mechanism of the association of the two dyes with the carrier (D2EHPA) as discussed above (Section 3.2).

The Fluxes obtained in this study are much higher than those found by Yang *et al.* (2013) ($J_{\text{max}} = 30.0 \cdot 10^{-3} \text{ mol.m}^2.\text{h}^{-1} = 8.41 \mu\text{mol.m}^2.\text{s}^{-1}$) in their recent research on facilitated transport of dyes by bulk liquid membranes containing Calix[4]arene-linked Triphenylene dimers as carriers.

3.7.2 Selectivity study

The separation study of a solution mixture containing MB and RB which represents one of the main differences compared to our previous study (Aitali *et al.* 2012) was carried out in a three compartment cell as described above (Section 2.4). The results reported in Fig. 11 show that the dyes concentrations decrease of 72.91% and 94.72% for MB and RB, respectively. However, MB is transferred to the stripping solution (1M HNO_3) while RB is simply accumulated on the membrane at the interface feed solution -strip solution (1M H_2SO_4).

4. Conclusions

PIM containing D2HEPA as extractant was successfully tested for the removal of cationic dyes (MB and RB) from aqueous solutions.

The efficiency of the process depends on various parameters, i.e., the pH of the aqueous phase, the quantity of the extractant in the membrane, the initial dye concentration and the stirring speed. Under optimum conditions, the extraction efficiencies are of ca 93% and 97% for MB and RB, respectively. MB is weakly extracted at pH 2.0 ($E\% = 18.7\%$), and its maximum extraction was achieved at pH 6.0. However, the D2EHPA-PIM shows a good retention for RB at pH 2.0 ($E\% = 82.4\%$) and the extraction efficiency increases slightly up to 97% at pH= 6.0. This difference can be exploited to extract selectively RB in mixture with MB at pH 2.0.

The experimental data for adsorption of the two dyes on PIMs used as adsorbent were well

fitted by the Langmuir isotherm model obtaining a maximum adsorption capacities of 6.06 mmol/g and 3.40 mmol/g for the adsorption of MB and RB, respectively.

Kinetic studies showed that the adsorption process obeyed to the pseudo-second-order rate model, thereby suggesting that the rate-limiting step may be the adsorption, involving valence forces through the sharing or exchanging of electrons between adsorbent and adsorbate. The negative value of ΔH° reflected the exothermic nature and the negative values of ΔG° confirmed the spontaneity of the adsorption of the cationic dye (RB).

The initial flux (J_0) values ($41.57 \mu\text{mol.m}^2.\text{s}^{-1}$ and $18.74 \mu\text{mol.m}^2.\text{s}^{-1}$ for MB and RB respectively) obtained in the transport study are relatively high compared to similar studies reported in literature. The good separation of the two dyes is a very interesting result but it will be optimized by the investigation of other stripping agents for the RB recovery.

Moreover, further experiments with real textile effluents evaluating the total costs will be carried-out for making the full-scale implementations possible.

Acknowledgments

The authors would like to acknowledge funding from the Ministry of The Ministry of Higher Education and Scientific Research of Algeria, through CNEPRU Project No. J0100620090016.

References

- Aitali, S., Kebiche-Senhadji, O., Mansouri, L. and Benamor, M. (2012), "Cationic dye (MB) removal using polymer inclusion membrane (PIMs)", *Procedia Eng.*, **33**(1), 38-46.
- Al-Rashed, S.M. and Al-Gaid, A.A. (2012), "Kinetic and thermodynamic studies on the adsorption behavior of Rhodamine B dye on Duolite C-20 resin", *J. Saudi Chem. Soc.*, **16**(2), 209-216.
- Arous, O., Kerdjoudj, H. and Seta, P. (2004), "Comparison of carrier facilitated silver (II) and Copper (II) ions transport mechanisms, in a supported liquid membrane and in a plasticized cellulose triacetate membrane", *J. Membr. Sci.*, **241**(2), 177-186.
- Bayramoglu, G., Altintas, B. and Arica, M.Y. (2009), "Adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation-exchange resin", *Chem. Eng. J.*, **152**(2), 339-346.
- Bhatt, A.S., Sakaria, P.L., Vasudevan, M., Pawar, R.R., Sudheesh, N., Bajaj, H.C. and Mody, H.M. (2012), "Adsorption of an anionic dye from aqueous medium by organoclays: equilibrium modeling, kinetic and thermodynamic exploration", *RSC Adv.*, **2**(23), 8663-8671.
- Bilgili, M.S. (2006), "Adsorption of 4-chlorophenol from aqueous solutions by xad-4 resin: Isotherm, kinetic, and thermodynamic analysis", *J. Hazard. Mater.*, **B137**(1), 157-164.
- Chatha, S.A.S., Asgher, M., Ali, S. and Hussain, A.I. (2012), "Microbial color stripping: A novel technology for removal of dye from cellulose fibers", *Carbohydr. Polym.*, **87**(2), 1476-1481.
- Daas, A. and Hamdaoui, O. (2010), "Extraction of anionic dye from aqueous solution by emulsion liquid membrane", *J. Hazard. Mater.*, **178**(1-3), 973- 981.
- Das, C., Rungta, M., Arya, G., Gupta, S.D. and De, S. (2008), "Removal of dyes and their mixture from aqueous solution using liquid emulsion membrane", *J. Hazard. Mater.*, **159**(2-3), 365-371.
- Djenouhat, M., Hamdaoui, O., Chiha, M. and Samar, M.H. (2008a), "Ultrasound-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane: Part 1: Membrane stability", *Sep. Purif. Technol.*, **62**(2), 636-641.
- Djenouhat, M., Hamdaoui, O., Chiha, M. and Samar, M. (2008b), "Ultrasound-assisted preparation of water-in oil emulsion and application to the removal of cationic dyes from water by emulsion liquid

- membrane: Part 2: Permeation and stripping”, *Sep. Purif. Technol.*, **63**(1), 231-238.
- Drapala, A., Dzygiel, P., Jonsson, J.A. and Wieczorek, P. (2001), “Supported liquid membrane extraction of peptides”, *Acta Biochim. Polnia*, **48**(4), 1113-1116.
- Gungor, O., Yilmaz, A., Memon, S. and Yilmaz, M. (2008), “Evaluation of the performance of calix[8]arene derivatives as liquid phase extraction material for the removal of azo dyes”, *J. Hazard. Mater.*, **158**(1), 202-207.
- Hajrabeavi, N., Bilal, L.M., Easwramoorthy, D. and Palanivelu, K. (2009), “Facilitated transport of cationic dyes through a supported liquid membrane with D2EHPA as carrier”, *Desalination*, **245**(1-3), 19-27.
- Hanafiah, M.A.M., Ngah, W.S.W., Zolkafly, S.H., Teong, L.C. and Abdul Majid, Z.A. (2012), “Acid blue 25 adsorption on base treated *Shorea dasyphylla* sawdust: Kinetic, isotherm, thermodynamic and spectroscopic analysis”, *J. Environ. Sci.*, **24**(2), 261-268.
- Jiraratananon, R., Sungpet, A. and Luangsowan, P. (2000), “Performance evaluation of nanofiltration membranes for treatment of effluents containing reactive dye and salt”, *Desalination*, **130**(2), 2177-2183.
- Kebiche-Senhadji, O., Mansouri, L., Tingry, S., Seta, P. and Benamor, M. (2008), “Facilitated Cd(II) transport across CTA polymer inclusion membrane using anion Aliquat 336 and cation D2EHPA metal carrier”, *J. Membr. Sci.*, **310**(1-2), 438-445.
- Kebiche-Senhadji, O., Tingry, S., Seta, P. and Benamor, M. (2010), “Selective extraction of Cr(VI) over metallic species by polymer inclusion membrane (PIM) using anion (Aliquat 336) as carrier”, *Desalination*, **258**(1-3), 59-65.
- Kozłowski, C.A. and Walkowiak, W. (2002), “Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes”, *Water Res.*, **36**(19), 4870-4876.
- Kozłowski, C.A., Kozłowska, J., Pellowski, W. and Walkowiak, W. (2006), “Separation of Cobalt 60, Strontium 90, and Cesium-137 radioisotopes by competitive transport across polymer inclusion membranes with organo phosphorous acids”, *Desalination*, **198**(1-3), 141-148.
- Liu, C.-H., Wu, J.-S., Chiu, H.-C., Suen, S.-Y. and Chu, K.H. (2007), “Removal of anionic reactive dyes from water using anion exchange membranes, as adsorbers”, *Water Res.*, **41**(7), 1491-1500.
- Lucas, M.S. and Peres, J.A. (2006), “Decolorization of the azo dye reactive black 5 by Fenton and photo-Fenton oxidation”, *Dyes Pig.*, **71**(3), 236-244.
- Luo, P., Zhang, B., Zhao, Y., Wang, J., Zhang, H. and Liu, J. (2011), “Removal of methylene blue from aqueous solutions by adsorption onto chemically activated halloysite nanotubes”, *Korean J. Chem. Eng.*, **28**(3), 800-807.
- Mahmoodi, N.M., Salehi, R. and Arami, M. (2011), “Binary system dye removal from colored textile wastewater using activated carbon: Kinetic and isotherm studies”, *Desalination*, **272**(1-3), 187-195.
- Mezohegyi, G., Van der Zee, F.P., Font, J., Fortuny, A. and Fabregat, A. (2012), “Towards advanced aqueous dye removal processes: A short review on the versatile role of activated carbon”, *J. Environ. Manag.*, **102**(49), 148-164.
- Moghaddam, S.S., Moghaddam, M.R.A. and Arami, M. (2010), “Coagulation/flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology”, *J. Hazard. Mater.*, **175**(1), 651-657.
- Moscofian, A.S.O., Pires, C.T.G.V.M.T., Vieira, A.P. and Airoidi, C. (2012), “Organofunctionalized magnesium phyllosilicates as mono- or bifunctional entities for industrial dyes removal”, *RSC Adv.*, **2**(8), 3502-3511.
- Muthuraman, G. and Palanivelu, K. (2006), “Transport of textile dye in vegetable oil based supported liquid membrane”, *Dye Pig.*, **70**(2), 99-104.
- Muthuraman, G. and Teng, T.T. (2009), “Use of vegetable oil in supported liquid membrane for the transport of Rhodamine B”, *Desalination*, **249**(3), 1062-1066.
- Muthuraman, G., Palanivelu, K. and Teng, T.T. (2010), “Transport of cationic dye by supported liquid membrane using D2EHPA as the carrier”, *Coloration Technol.*, **126**(2), 97-102.
- Nghiem, L.D., Mornane, P., Potter, I.D. and Perera, J.M. (2006), “Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs)”, *J. Membr. Sci.*, **281**(1-2), 7-41.
- Ngah, W.S.W. and Fatinathan, S. (2010), “Adsorption characterization of Pb(II) and Cu(II) ions onto

- chitosan-tripolyphosphate beads: Kinetic, equilibrium and thermodynamic studies”, *J. Environ. Manag.*, **91**(4), 958-969.
- Nisola, G.M., Cho, E., Belton, A.B., Han, M., Kim, Y. and Chung, W.-J. (2010), “Dye/water separation through supported liquid membrane extraction”, *Chemosphere*, **80**(8), 894-900.
- Oladoja, N.A., Aboluwoye, C.O. and Oladimeji, Y.B. (2008), “Kinetics and isotherm studies on methylene blue adsorption onto ground palm kernel coat”, *Turkish J. Eng. Environ. Sci.*, **32**(5), 303-312.
- Pandit, P. and Basu, S. (2002), “Removal of organic dyes from water by liquid–liquid extraction using reverse micelles”, *J. Coll. Interf. Sci.*, **245**(14), 208-214.
- Ramesh, B., Parande, A.K., Raghu, S. and Kumar, T.P. (2007), “Textile technology. Cotton textile pressing: Waste generation and effluent treatment”, *J. Cotton Sci.*, **11**(3), 141-153.
- Treffry-Goatley, K., Buckley, C.A. and Groves, G.R. (1983), “Reverse osmosis treatment and reuse of textile dye house effluents”, *Desalination*, **47**(1-3), 313-320.
- Ueda, A.C., Oliveira, L.H., Hioka, N. and Aznar, M. (2011), “Liquid–liquid extraction of basic yellow 28, basic blue 41, and basic red 46 dyes from aqueous solutions with reverse micelles”, *J. Chem. Eng. Data*, **56**(3), 652-657.
- Van der Zee, F.P. and Villaverde, S. (2005), “Combined anaerobic–aerobic treatment of azo dyes-A short review of bioreactor studies”, *Water Res.*, **39**(8), 1425-1440.
- Verma, A.K., Dash, R.R. and Bhunia, P. (2012), “A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters”, *J. Environ. Manag.*, **93**(1), 154-168.
- Wu, J.-S., Liu, C.-H., Chu, K.H. and Suen, S.-Y. (2008), “Removal of cationic dye methyl violet 2B from water by cationic exchange membranes”, *J. Membr. Sci.*, **309**(1-2), 239- 245.
- Yahaya, G.O., Brisdon, B.J., England, R. and Hamad, E.Z. (2000), “Analysis of carrier-mediated transport through supported liquid membranes using functionalized polyorganosiloxanes as integrated mobile/fixed-site carrier systems”, *J. Membr. Sci.*, **172**(1-2), 253-268.
- Yang, X.J., Fane, A.G. and Naughtan, M. (2001), “Removal and recovery of heavy metals from wastewater by supported liquid membrane”, *Water Sci. Technol.*, **43**(2), 341-348.
- Yang, F., Zhang, Y., Guo, H. and Wei, X. (2013), “Highly efficient liquid membrane transport of dyes using calix[4]arene-linked triphenylene dimers as carriers”, *Separ. Sci. Technol.*, **48**(10), 1565-1571.
- Yourd, E.R. and Tyson, J.F. (2003), “Comparison of supported liquid membranes and solid phase extraction for quantitative removal of lead from aqueous solutions”, *Can. J. Chem.*, **81**(10), 1061-1069.