Methylene blue elimination from contaminated water solutions using a polyvinyl chloride based polymer inclusion membrane containing bis(2-ethylhexyl)phosphoric Acid

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ABSTRACT

Organic dyes such as methylene blue (MB) are known as important water and environment pollutants. Several techniques have been employed for removing this dye from contaminated aqueous solutions. In this study, polymer inclusion membranes composed of polyvinyl chloride (PVC) and bis(2-ethylhexyl)phosphoric acid (DEHPA), respectively as the base polymer and extractant, without requiring to additional plasticizing reagent are prepared and assessed for the removal of methylene blue from aqueous solutions. The membrane with a composition of 50 wt.% of PVC and 50 wt.% of DEHPA is found to be flexible, physically stable. This PIM shows the best performance for the MB elimination from the solutions. Various techniques including Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy SEM), atomic force microscopy (AFM), contact angle measurements, thermogravimetric analysis (TGA), and stress-strain analysis are employed for characterizing the optimized PIM. The parameters affecting the removal of MB from the solutions are optimized. It is found that a circular disc PIM with 3.5 cm diameter, an average mass of 0.0890 ± 0.0046 g, with a thickness of 72.0 ± 0.8 μm removes quantitatively MB from 50 mL aqueous solution adjusted to pH 3, after 120 min orbital shaking. The PIM is stable for 6 times consecutive cycles. The kinetics of process is obeyed pseudo second-order model, while the Langmuir model interpret well the isotherm of the MB removal.

1. Introduction

Water crisis becomes one of the main world apprehensions, nowadays. This is so serious that, there is even some idea that water may be the cause for some wars between the countries located in regions with poor water sources. Thus, the management of water consumption and their recycling is considered as a solution to overcome the inconveniencies make by water deficit [1].

Industrial [2], agricultural [3], and domestic [4] used waters are polluted by a wide variety of contaminants. Heavy metal ions, residual pesticides and herbicides, dyes, phosphates due to the consumption of detergents, Methylene blue (IUPAC nomenclature: [7-(dimethylamineo) phenothiazine-3-ylidene]

are some chemical pollutants of consumed waters. However, microbiological contaminations should be considered as another main group of pollutants [5].

Synthetic dyes are among the water pollutants which are widely and commonly used in textile, leather, printing, and plastic industries [6, 7]. They are organic substances which are normally toxic, carcinogenic, mutagenic, and non-degradable. Besides, the presence of dyes in water should cause reducing the penetration of sunlight, and thus affect the photosynthetic activity of aquatic life [8].

dimethylazanium chloride) is a member of cationic dyes which are more commonly used to dye textiles [9]. The

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removal of this dye is studied frequently because it may be considered as a pollutant model for cationic dyes [10, 11]. A variety of studies have been performed for the decontamination of waters containing methylene blue (MB). These studies are mainly based on the adsorption

of this pollutant by different biosorbents [12] and synthetic sorbents [13, 14]. Photocatalytic degradation is also among the methods for the removal of MB from water samples [15, 16].
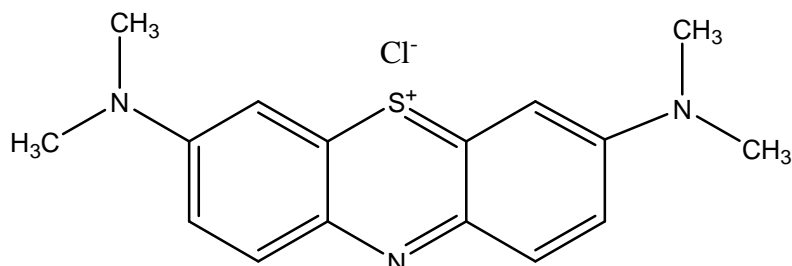
Methylene blue ([7-(dimethylamineo)phenothiazine-3-ylidene]dimethylazanium chloride).

Polymer inclusion membranes (PIMs) are composed mainly of a polymer base and an extractant. However, in some cases an extractant is added to the PIMs composition for achieving to a suitable flexibility and homogeneity of membranes composition. The possibility to tune PIMs characteristics by varying the employed base polymer and/or the extractant for achieving to a desired extraction, separation, or elimination of target species, has made them as important tools for such aims. Nowadays, the potentials of polymer inclusion membranes (PIMs) for the extraction, separation, and elimination of a variety of chemical species including organic [17] and inorganic [18, 19] compounds are well approved. Nevertheless, limited reports are found in the literature for their application in the process of synthetic dyes removal [20].

A few investigations have been attributed to the application of PIMs for the removal of synthetic dyes from contaminated water. Benosmane *et al*. was reported application of polymer inclusion membrane containing cellulose triacetate (CTA) as polymer base, calix [4] resorcin arene (RC8) as a carrier and 2-NPOE as a plasticizer for transporting of 100 mg L^{-1} MB from aqueous solution. The maximum flux value was obtained at pH 11 after 30 h. Their results were consistent with the first-order kinetics [21]. Minhas *et al.* have prepared a polymer inclusion membrane composed of an ester derivative calix [4] arene as the extractant and CTA as the base polymer, for the extraction of the cationic dye methylene blue (MB) from water solutions [22]. Like

other CTA based PIMs, this investigated membrane was also required to a plasticizing agent. This PIM was able to be extract 90% of MB in 4 h with stirring speed 1000 rpm. The manufactured PIM could be used for ten consecutive cycles. Prior to this study, on 2012, Aitali *et al.* reported the application of a PIM included the base polymer cellulose triacetate (CTA), the extractant bis(2-ethylhexyl)phosphoric acid (DEHPA), and the plasticizer 2-nitrophenylhexyloctyl ether (NPOE) for the decontamination of methylene blue from aqueous solutions. By using this PIM, at pH 6 and 350 rpm, 93% of methylene blue was removed [23].

The presented report intends to evaluate the potential of a plasticizer free PIM composed the base polymer polyvinyl chloride (PVC), and the cation exchange extracting agent bis(2-ethylhexyl)phosphoric acid for the decontamination of water solutions from methylene blue (basic blue 9). The optimized composition of the PIM with respect to the base polymer/extractant weight percent ratio was investigated. The characteristics of the optimized PIM were studied using FT-infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurements, thermogravimetric analysis (TGA), and stress-strain analysis. The optimized experimental conditions were determined for the removal of MB from water solutions. The investigation of the kinetics and isotherm of the process, for the first time, are also performed.

2. Experimental

2.1. Chemicals and reagents

Polyvinyl chloride, bis(2-ethylhexyl)phosphoric acid (for synthesis), acetone (for analysis), sodium hydroxide (for analysis), acetic acid (glacial), oxalic acid dihydrate (Reag. Ph Eur), and methylene blue (Reag. Ph Eur), were purchased from Merck Chemical Company (Germany). The other chemicals used were tetrahydrofuran (Samchun, Korea), phosphoric acid (85-90 wt%, Fluka, Switzerland), hydrochloric acid (37 wt%, Mojallali, Iran), and sodium sulfate (>99%, Mojallali, Iran).

2.1. Instruments

For the measurement of contact angles, a Goniometer Model CAG-10 was used. The temperature adjustment during the preparation of PIMs was realized by employing the Julabo water bath circulator (model Mp-5, Julabo). The casting solutions was stirred by a magnetic stirrer IKa (Germany). An orbital shaker purchased from Poly Ideal Tajhiz model PIT10 LO was used for extraction and back-extraction processes. The instruments used for the PIM characterization were a Fourier-Transform Infrared Spectrometer (Thermo–Nicolet–is10 FT–IR spectrometer, USA) was used for recording the FT-IR spectra. A Scanning Electron Microscopy (TESCAN, model mira3), an Atomic Force Microscopy (Nano Vac, Ara Research Company), the thermogravimetric analysis by STA 409 PC/PG analyzer (Netzsch), the force digital gauge STM-5 Cap. 5 kN (Santam) for the stress–strain experiments. A glass electrode (Metrohm) connected to a pH meter Metrohm model 780 Herisau was employed for the pH measurements. The analysis of methylene blue in aqueous solutions was carried out by a spectrophotometer Hach model DR5000 at 665 nm. The micrometer SL-M Insize was employed to measure the thickness of prepared PIMs.

2.3. Preparation of PIMs and characterization

To prepare the 50/50 wt.% PVC/DEHPA PIMs, the casting solutions containing 1.2 g of each component (PVC and DEHPA) in 13.2 mL of tetrahydrofurane (i.e. 11 mL of tetrahydrofurane for each 1 g of the PIMs components [24]) were prepared. This solution was firstly stirred magnetically for 2 h (at room temperature), and then was stirred for a further 2 h at 42 °C. Aliquots of 4.4 mL of the casting solution were poured into 75 mm diameter Petri dishes. To slow evaporation of tetrahydrofuran, the petri dishes were covered with a filter paper and a glass plate. evaporate slowly Each Petri dish

was covered with filter paper and a glass plate to reduce the evaporation rate of THF. A circular segment (3.5 cm diameter) of the PIMs formed at the base of petri dishes was cut by a steel punch, after 24 h. the membranes were removed from the Petri dishes, and circular segments (PIM discs) of 3.5 cm in diameter were cut from the middle of the membranes by using a steel punch. All PIM compositions are expressed in weight percentages.

2.4. Extraction and back-extraction experiments

The extraction experiments were carried out by immersing a PIM disc in a plastic jar containing 50 mL of methylene blue (20 mg L^{-1}) adjusted at pH 3, by adding diluted hydrochloric acid or sodium hydroxide solutions. The plastic jar was Shaked on an orbital shaker (200 rpm). To analysis the extracted methylene blue 0.5 mL of the solution was sampled at the end or at predetermined times. The samples were diluted, and the absorbance of the remained methylene blue was calculated spectrophotometrically at 665 nm. The extracted percentage of the dye was calculated by comparing the absorbance of the initial solution and that of the solution after equilibrium. The back-extraction experiments were performed by immersing the PIM discs, used in the extraction experiments, into jars containing 50 mL of the aqueous receiving solution under shaking (200 rpm) on an orbital shaker for a predetermined period of times. The concentrations of the dye back-extracted into the receiving solutions were determined by the procedure described above. It is worth of note that all experiments were realized in triplicate, at room temperature (22±1 °C).

3. Results and Discussion

To design a process for the removal the cationic dye methylene blue (MB), the cationic exchange extractant DEHPA in a polymer inclusion membrane is a potential candidate, because it is presumed that the cation exchange attitude of this extractant may extract MB as its cationic form via the extraction reaction shown in Eq. 1.

$$MB^+_{(aq)} + HP_{(PIM)} \rightleftharpoons MB^+P^-_{(PIM)} + H^+_{(aq)} \qquad (1)$$

where HP denotes DEHPA, "aq" and "PIM" show aqueous and polymer inclusion membrane phases.

The appearance and transparency, non-oily surface, adequate flexibility, and suitable mechanical stability are the primary parameters of the PIMs which may be selected for evaluating their potential as a membrane in removal of a target chemical species from aqueous solutions.

Table 1 Apparent characteristics of the PIMs with different compositions with respect to PVC and DEHPA

PIM No.	PIMs Composition		Apparent characteristics
	PVC	DEHPA	
1	20	80	Oily, No stable mechanically
2	30	70	Oily, No stable mechanically
3	40	60	Oily, No stable mechanically
4	50	50	Transparent, Flexible, Mechanically stable
5	60	40	Transparent, Low flexibility, Mechanically stable
6	70	30	Transparent, Rigid
7	80	20	Transparent, Rigid
8	90	10	Transparent, Rigid

The characteristics of the selected PIM with the acceptable mentioned parameters will be then determined by a variety of techniques. The optimization of parameters affecting the extraction process is required to an efficient removal of the target analyte. Finally, the models for interpreting the kinetics and isotherm of the process in this section are discussed.

3.1. Selection of the PIM's composition

To select an optimum wt.% of PVC and DEHPA for preparing the suitable PIM in terms of flexibility, mechanical stability and transparency, eight compositions including a series of PIM containing 10 to 80 wt.% of DEHPA and correspondingly 90 to 20 wt.% PVC were prepared and their apparent characteristics were evaluated. The results are given in Table 1. Based on the apparent flexibility it was decided to select the PIM with the 50/50 wt.% of PVC/DEHPA (PIM No. 4) for following the study. As it is seen this PIM was transparent which reflects the good homogeneity of the PIM constituents. It has the advantage of flexibility without requiring an additional plasticizer. In fact, it seems the extractant itself plays the role of a plasticizer. Furthermore, the apparent mechanical stability allows to select this composition as an appropriate PVC/DEHPA ratio for following the experiments. A circular segment of the PIMs (3.5 cm diameter) with the selected composition has an average mass of 0.0890±0.0046 g. The thickness of these PIMs was 72.0±0.8 μm.

3.2. Selected PIM characterization

A series of tests were carried out for the characterization of the selected 50/50 wt.% PIM. These tests included the contact angle determination, preparation of Field Emission Scanning Electron Microscopy (FESEM) images of the surface and cross-section, roughness determination of the PIM's surface by Atomic Force Microscopy (AFM) technique, Thermal Gravimetric Analysis (TGA), tensile test, and FT-IR spectroscopy. The images and data of these tests are given in supplementary file (Supplementary File, Figures S1 to S5). The measured contact angles of the PVC-film and the PIM 50/50 wt.% PVC/DEHPA were found to be 99.8 (±1.5) deg and 66.5 (±3.7) deg, respectively. The observed reduced contact angle for the evaluated PIM with respect to the extractant free PVC-film is attributed to the presence of the polar molecules DEHPA in the former.

The acquired FESEM images (Supplementary File, Figure, S1) confirmed a smooth surface for the PVC-film, whereas that of the selected PIM was wrinkled. The obtained images of the PIM's cross-section revealed the presence of DEHPA in channels of the PIM. The AFM 3D-images of the PVC-film and the PVC/DEHPA PIM (Supplementary File, Figure S2) confirmed more roughness of the PIM (1.6 mm) with respect to that of the PVC-film (0.7 mm). This shows the presence of DEHPA results in wrinkled surface of the PIM.

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analysis allowed evaluating and comparing the thermal stability of the PVC-film and the 50/50 wt.% PVC/DEHPA PIM (Fig. S3). The TGA profile of the PVC-film demonstrated a weight loss, corresponding to the loss of surface water molecules, at 70-190 ℃. Dehydrochlorination of PVC and then decomposition of the polymer to carbon dioxide and volatile hydrocarbons were observed at 240 ℃ and 400 ℃, respectively. The TGA profile for the 50/50 wt.% PVC/DEHPA PIM reveals the evidence for the surface water loss as a weight loss was observed in the temperature range 110-180 ℃. Dehydrochlorination of PVC can be attributed to the weight loss observed at 230-390 ℃, while at higher temperature than 400 ℃, the decomposition of the PIM is approved.

Tensile test and the stress-strain curves of PIMs allows investigating the elasticity and mechanical characteristics of such membranes (Supplementary File, Figure S4). The comparison of the stress-strain curves of the PVC-film

and that of the investigated PIM clearly demonstrated that the presence of DEHPA affects the mechanical properties of the membrane. In fact, the determined tensile strength of the PVC-film was 137 MPa and that for the PIM was 18.9 MPa, while the corresponding values of the elongation at break were 368% *vs*. 110.8%.

The FT-IR spectra of DEHPA, PVC, and the studied PIM were recorded to elucidate the probable interactions between the PIM's constituents (Supplementary File, Figure S5). The main absorption peaks appeared in the spectrum of PVC included the CH cis and trans bending vibrations at 616.05 cm^{-1} and 965.30 cm^{-1}, the C-Cl stretching band at 695 cm^{-1} and 834.38 cm^{-1}, bending vibration of the CH_2 moieties bonded to Cl at 1261.20 cm^{-1}, bending vibrations of other CH_2 groups at 1334.97 cm^{-1} and 1426.21 cm^{-1} and the stretching vibration of these moieties at 2977.51 cm^{-1} and 2921.54 cm^{-1}. The significant absorption peaks appeared on the FT-IR spectrum of DEHPA were that attributed to P-O-C and P-O-H groups at 1000.46 cm^{-1}, the absorption peak at 1247.46 cm^{-1} which denoted the presence of P=O bond, the peak observed for O-H group at 1687.50 cm^{-1} (significantly far from that suggested for such groups, due to the hydrogen bonding in DEHPA), and three peaks at 1380.79 cm^{-1}, 1463.56 cm^{-1}, and 2969.10 cm^{-1} which were interpreted by considering the bending and stretching vibrations of CH_2 groups. The absorption peaks on the spectrum of the PIM, i.e. 638.20 cm^{-1}, 696.53 cm^{-1}, 1331.13 cm^{-1}, 1436.10 cm^{-1} (close to those observed for

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PVC), and 100.97 cm^{-1}, 1384.73 cm^{-1}, 1466.55 cm^{-1}, 1670.11 cm^{-1} (nearly the same appeared on the DEHPA spectrum), reveals the absence of specific interactions between PVC and DEHPA. However, the stability of the membrane may be attributed to the electrostatic interactions of the PIM constituents.

3.3. Optimization of the MB removal by the selected PIM
3.3.1. Selected of aqueous phase pH

Considering that MB is a cationic dye and DEHPA is a cationic exchange extractant, it can be assumed that the extraction equilibrium equation may be followed via the equation 1. Thus, the aqueous phase pH affects the process. To investigate the influence of this parameter on the removal process of MB from aqueous solutions by the selected 50/50 wt.% PVC/DEHPA PIM, a series of extraction experiments of MB under the selected experimental conditions given in the caption of Figure 1 has been performed.

The results revealed that an enhancement in pH value in the range of 1-3 accompanied with an augmentation of the extraction percentage of MB. This may be attributed to the deprotonation dependency of DEHPA to the aqueous phase pH. Beyond pH 3 the extraction of methylene blue did not vary by pH values. This investigation convinced us to select pH 3 as an optimum value for continuing the experiments.
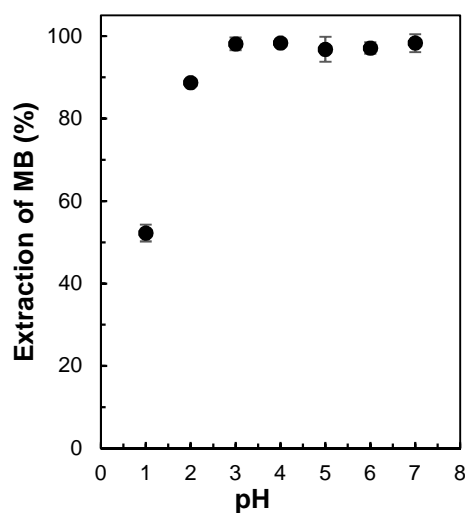

Fig. 1. Variation of the extraction percentage of MB from 50 mL aqueous solution adjusted to various pH by using a 3.5 cm circular PIM (50/50 wt.% PVC/DEHPA). Other experimental conditions: initial MB concentration 20 mg L^{-1}, shaking time 150 minutes (200 rpm), room temperature (22±1 ℃).
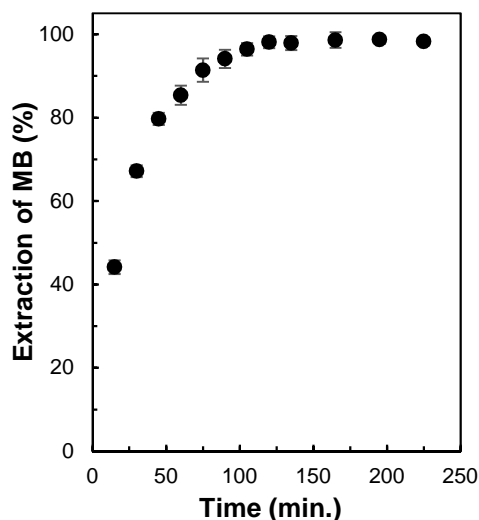
Fig. 2. Variation of the extraction percentage of MB from 50 mL aqueous solution adjusted to various pH 3 by using a 3.5 cm circular PIM (50/50 wt.% PVC/DEHPA). Other experimental conditions: see the caption of Figure 1.

3.3.2. Time dependency of the process

The time dependency of the MB extraction by the selected PIM was verified by the extraction of MB as a function of time. Figure 2 demonstrates the results of this investigation. It seems that the extraction percentage of MB by the investigated PIM increases the extraction time. An equilibrium is reached beyond 120 minutes. The results allowed performing the experiments using this extraction time.

3.3.3. Ionic strength and extraction efficiency

Industrial effluents are conventionally accompanied with significant amount of salts. Thus, the investigation of the ionic strength of solutions containing MB lets to evaluate the capability of the extraction system for the removal of the analyte from such media.

To investigate the effect of this parameter on the efficiency of the investigated PIM for removal of MB from aqueous solutions, the extraction of MB from the solutions adjusted to pH 3 and containing Na_2SO_4 in the range 0.05-0.5 mol L^{-1} was performed. The results (Figure 3) confirmed that the extraction of MB does not depend on the salt concentration up to 0.2 mol L^{-1}. By increasing the salt concentration, the extraction efficiency was significantly diminished. This may be attributed to the ionic interactions between the salt's ions and the dye.
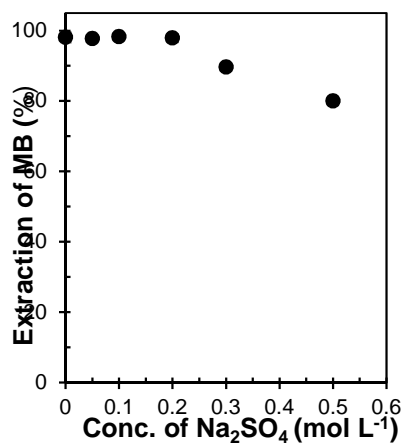

Fig. 3. Variation of the extraction percentage of MB from 50 mL aqueous solution adjusted to pH 3 and contained various amount of Na_2SO_4 (0-0.5 mol L^{-1}) by using a 3.5 cm circular PIM (50/50 wt.% PVC/DEHPA). Other experimental conditions: see the caption of Figure 2.
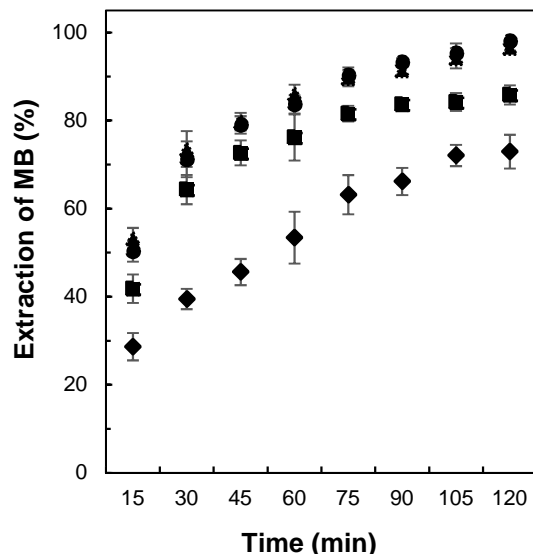
Fig. 4. Variation of the extraction percentage of MB from 50 mL aqueous solution adjusted to pH 3 by using a 3.5 cm circular PIM (50/50 wt.% PVC/DEHPA), as function of time using different shaking rate (⊔ 100 rpm, ⊓ 150 rpm, ⏐ 200 rpm, and ▲ 250 rpm). Other experimental conditions: see the caption of Figure 2.

3.3.4. Effect of shaking rate on the extraction efficiency

Considering the diffusion-controlled mechanism for the extraction of MB by the studied PIM, the thickness of the stagnant layer at the solution/PIM interface affects the rate of the extraction of the analyte, as it is mentioned in the first Fick's law. This thickness may decrease by increasing the shaking rate. To elucidate the mechanism of the uptake of MB by the PIM and determine the optimum shaking rate a series of extraction of MB by the investigated PIM were performed. The shaking rate was changed in the range of 100-250 rpm. The results are presented in Figure 4. An increase in the shaking rate from 100-200 rpm an increase in the extraction percentage observes; a consequence of the diminish in the thickness of the interface stagnant layer. Beyond this region (i.e. 250 rpm), the extraction percentage remained practically invariant. The turbulence created at higher shaking rate prohibit us to study the shaking rates higher than 250 rpm. To continue the experiments, the shaking rate of 200 rpm was chosen.
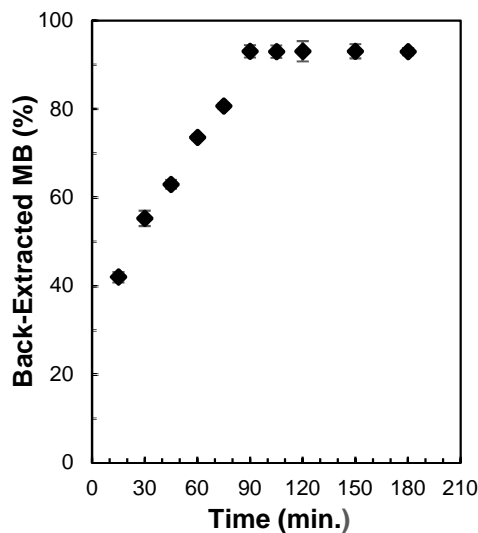
3.3.5. Back-extraction study

hydrochloric acid and sulfuric acid showed efficient stripping reagents, the best back-extraction results were obtained by using oxalic acid. The higher efficiency of oxalic acid with respect to the other investigated acids as

The study of MB recovery from the loaded PIMs allowed us to find out the back-extraction step conditions. This investigation is important because the ultimate application of PIMs is their use in transport process, where the extraction and stripping are taking place simultaneously. To perform this investigation, the PIMs loaded by MB under optimized extraction conditions (pH 3, extraction time 120 minutes, and shaking rate 200 rpm) were contacted with 50 mL solution of different reagents as stripping solution. The MB content of the loaded PIMs was 97±1 % of it is initial amount. The employed solutions were a series of acid solutions (hydrochloric acid, sulfuric caid, acetic acid, and oxalic acid) in the concentration range of $0.05 – 0.5$ mol L^{-1} (except for oxalic acid which was in the range of $0.05 – 0.2$ mol L^{-1}). The loaded PIMs were contacted for 2 h, at 200 rpm, with the investigated stripping solutions. The percentages of recovered MB by using the studied solution are given in Table 2.

The selection of acids for the back-extraction process was based on the reaction of the extraction step, shown in Eq. 1. In fact, the reverse reaction is assumed in acidic media. Acetic acid could not be considered as a suitable candidate for the back-extraction process. Although back-extraction reagent may be attributed to protonation of anionic form of the extractant and thus the release of the cationic form of methylene blue, besides the reduction of methylene blue in the presence of this acid [25].

Table 2 Back-extraction percentage of MB from loaded PIMs by using different stripping reagents

Acid	Concentration (mol L^{-1})	Recovered MB (%)
HCl	0.05	60.0±0.8
	0.1	68.2±1.4
	0.2	68.7±1.7
	0.3	74.9±1.1
	0.5	84.6±0.7
H_2SO_4	0.05	75.7±0.05
	0.1	77.1±1.4
	0.2	84.7±1.8
	0.3	85.5±1.6
	0.5	87.6±0.4
CH_3COOH	0.05	7.3±0.6
	0.1	8.1±0.8
	0.2	16.1±0.9
	0.3	17.9±1.1
	0.5	18.2±0.9
$H_2C_2O_4$	0.05	59.8±0.7
	0.1	93.8±1.8
	0.15	94.1±1.8
	0.2	94.5±0.9

Fig. 5. Time dependency of the back-extraction process of MB from loaded 50/50 wt.% PVC/DEHPA PIM (obtained under optimal conditions) by using 0.15 mol L^{-1} oxalic acid, at room temperature (22±1 ºC) and shaking rate 200 rpm.

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The results allowed us by employing 0.15 mol L^{-1} of oxalic acid as appropriate reagent for the back-extraction of MB from loaded PIMs. The time dependency of the back-extraction process of MB was studied by contacting a loaded PIM with the optimized back-extraction reagent and following the concentration of MB in the solution at given intervals. The results are presented in Figure 5. The results revealed that the back-extraction increases with time in the range of 20-90 minutes, where a quantitative stripping is taken place at 90 min. Thereafter, the back-extraction was not dependent on time. However, we use a time of 120 minutes for the back-extraction process.

3.3.6. Extraction/back-extraction cycles and reusability of the studied PIM

The reusability of a PIM signifies its possible practical application. To assess this characteristic of the studied PIM, the consecutive extraction/back-extraction cycles
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(10 cycles) were realized. The results (Figure 6) demonstrate the potential of the 50/50 wt.% PVC/DEHPA PIMs for using in 6 extraction/back-extraction cycles. The observed decrease in the stability of the PIM may be attributed to the possible leakage of DEHPA from the membrane
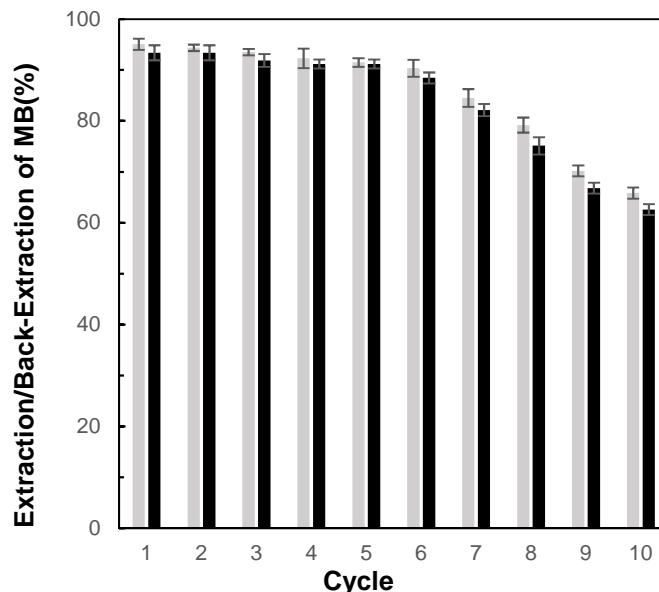

Fig. 6. Reusability of the 50/50 wt.% PVC/DEHPA PIMs in consecutive extraction/back-extraction of MB.

3.3.7. PIM's capacity and the extracted species characterization

To determine the capacity of the 50/50 wt.% PVC/DEHPA PIM toward MB, the extraction of this analyte from aqueous solutions (50 mL) containing different concentration of MB (5-200 mg L^{-1}) adjusted to pH 3 by the 14 mm diameter PIMs was followed. The calculated capacity of the PIM (q) increases by the MB concentration (Figure 7-a). However, a level off, corresponding to the saturation of PIM, was observed beyond initial concentration of 100 mg L^{-1} of MB. The

maximum capacity of the studied PIM was calculated to be 61.5 mg MB per each gram of the membrane.
The obtained data in this investigation was employed for the plotting of the mole ratio of MB to the extractant (mmol MB/mmol DEHPA), as a function of the initial concentration of MB in the aqueous phase (Figure 7-b). As it is seen, the variation of MB/DEHPA mole ratio as a function of the initial MB concentration has an inflection at the ratio equals to about 1. This investigation confirms that the stoichiometry of MB to DEHPA is that previously considered in Eq. 1.
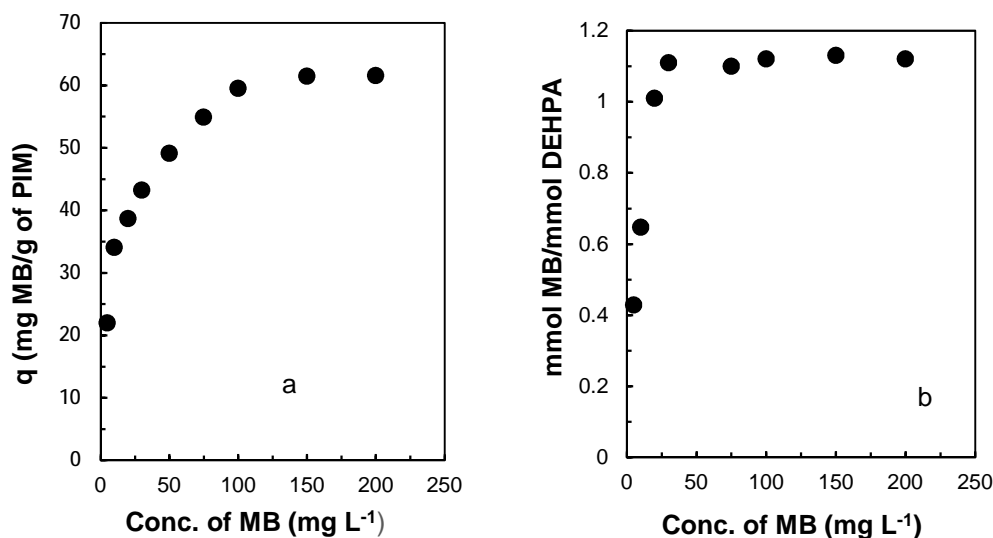
Fig. 7. Variation of the studied PIM's capacity **(a)** and, Variation of the MB/DEHPA mole ratio in the studied PIM **(b)** as a function of the methylene blue concentration in aqueous phase.

3.4. Kinetics and isotherms of the MB removal process

the kinetics of the MB removal by the studied PIM four models including pseudo-first order, pseudo-second order, intraparticle diffusion, and Elovich models were tested. Mathematical Eqs. (2-5) were used to represent linear versions of these models, respectively [27].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$
$$q_t = k_{int}\sqrt{t} + C \qquad (4)$$
$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \qquad (5)$$

in these equations k_1 in min^{-1}, k_2 in g mg^{-1} min^{-1} and k_{int} in mg g^{-1} min$^{-0.5}$ are the rate constant in the corresponding equations. The terms q_t and q_e are respectively the amounts of MB adsorbed in mg per 1 g of PIM in each of the tested time and at equilibrium condition. The parameter c in mg g^{-1} is a constant in intra–particle diffusion equation, related to the thickness of the boundary layer, a in mg g^{-1} min^{-1} in the Elovich equation shows initial rate of the adsorption and b (g mg^{-1}) denotes the constant of desorption which relates the surface

min$^{-0.5}$).

Kinetics and isotherms investigation of the extraction processes are important for the plant designing and optimization of the MB removal process [26]. To assess coverage degree, and the activation energy for a chemical process. The evaluated variables of the studied models by using the experimental data are regrouped in Table 3.

To select the best model for describing the kinetics of the process the correlation coefficient of the experimental and those predicted by the models (R^2), and the closeness of the experimental adsorption capacity ($q_{e,Exp}$) and the corresponding calculated value ($q_{e,Cal}$) were considered. This comparison led to select the pseudo-second order model for describing the kinetics of the adsorption process of MB by the selected PIM. This confirm also that the chemical nature of the adsorption of MB on the PIM. Figure 8-a depicts the variation of t/q_t as a function of time by employing the mathematical equation of the pseudo-second order model (Eq. 3).

The application of the intraparticle diffusion model on the extraction of MB by the examined PIM revealed a two-step process for the uptake of MB by the PIM (Figure 8-b). These steps may be described by a fast adsorption process of the analyte on the PIM, with a relatively high k_{int} (7.270 mg g^{-1} min$^{-0.5}$), and then the diffusion of MB into the pores of this membrane with a lower kinetic constant k_{int} (2.414 mg g^{-1}

Table 3. Evaluated kinetic variables by employing the examined pseudo-first order, pseudo-second order, intraparticle diffusion, and Elovich kinetic models for the extraction of MB by the 50/50 wt.% PVC/DEHPA PIM

Kinetic model	Evaluated parameter	Corresponding value
	$q_{e,Exp}$ (mg g^{-1})	76.92
Pseudo-first order	$q_{e,Cal}$ (mg g^{-1})	66.27
	k_1 (min^{-1})	0.028
	R^2	0.885
Pseudo-second order	$q_{e,Cal}$ (mg g^{-1})	83.33
	k_2 (g mg^{-1} min^{-1})	0.0007
	R^2	0.968
Intraparticle diffusion	k_{int} (mg g^{-1} min$^{-0.5}$)	7.270[a]
		2.414[b]
	c (mg g^{-1})	3.609[a]
		51.987[b]
	R^2	0.917[a]
		0.903[b]
Elovich	a (mg g^{-1} min^{-1})	0.0938
	b^{-1} (mg g^{-1})	19.826
	R^2	0.918

[a]First step, including the adsorption of MB on the PIM. [b]Diffusion process of MB into the PIM pores.
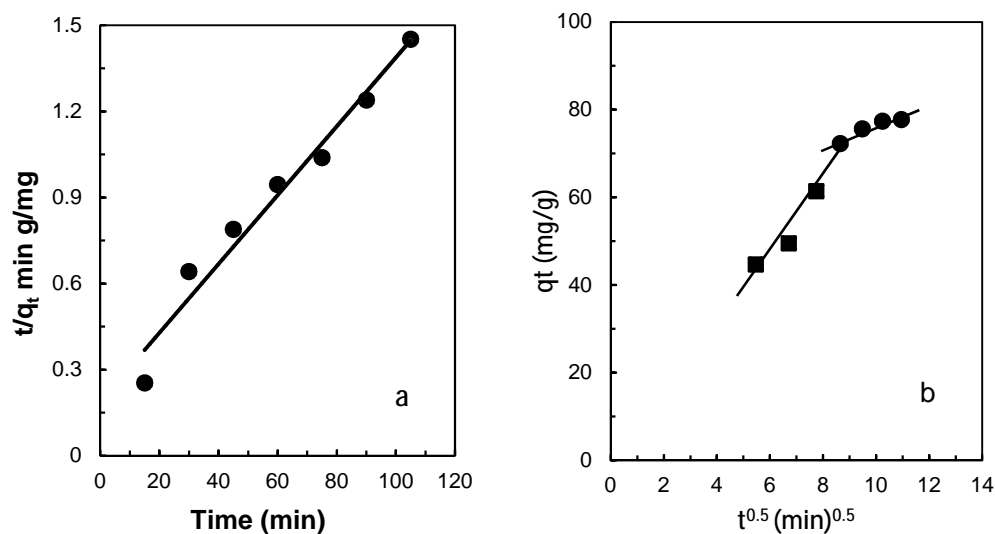
Fig. 8. Least square linear plot of (a) pseudo second-order and (b) intraparticle diffusion kinetic model for the extraction of MB by the 50/50 wt.% PVC/DEHPA PIM.

The isotherm model describing the experimental data in an adsorption experiment leads to deduce the analyte/adsorbent interactions. To this end, the data obtained through the removal study of MB by the 50/50 wt.% PVC/DEHPA PIM, were treated by using four conventional models Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R).

The Langmuir isotherm is mathematically presented by Eq. 6:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (6)$$

in this equation C_e and q_e are the analyte concentration and capacity of the adsorbent at equilibrium, respectively, q_{max} (mg g^{-1}) is the maximum capacity of the PIM and b (L mg^{-1}) is a constant which is related to the energy of adsorption process. In this model it is assumed that the monolayer adsorbed species is formed, without any interaction between these species. The separation factor (R_L) has no dimension and is defined by Eq. 7. The evaluated R_L indicates a process is favorable (0 <R_L<1), unfavorable ($R_L > 1.0$ and < 0), or irreversible ($R_L = 0$).

$$R_L = \frac{1}{1+bC_0} \qquad (7)$$

The Freundlich isotherm describes the multilayer adsorption with energetically heterogeneous distribution of active sites. It is mathematically described by Eq. 8, in which K_F ((mg g^{-1})(mg L^{-1})) $^{1/n}$ and the dimensionless parameter n denote the adsorption capacity and adsorption intensity, respectively. The slope (1/n), ranges between 0 and 1. 1/n close to zero shows more heterogeneity of the surface, 1/n lower < 1 reveals a chemisorption process, and 1/n > 1 indicates a cooperative adsorption.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (8)$$

In Temkin isotherm model, it is assumed that the adsorption heat is linearly decrease by the progress of the process. This model is described by Eq. 9, where R is the gas constant (0.0083 kJ mol^{-1} K^{-1}), T is temperature (K), b is a constant related to heat of adsorption (kJ mol^{-1}) and K_T is the Temkin isotherm constant (L g^{-1}). The plot of q_e versus ln C_e allows estimating K_T and b.

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e \qquad (9)$$

The adsorption of ionic species in two-step mechanism; i.e., initially by the adsorption of the analyte on the most energetically favorable sites and then the multilayer adsorption process is taken place This type of the adsorption may be described by the Dubinin–Radushkevich (D–R) isotherm (Eq. 10).

$$\ln q_e = \ln q_{max} - \beta \varepsilon^2 \qquad (10)$$

β in mol^2 kJ^{-2} is the activity coefficient attributed to the energy of the adsorption process, and ε is the Polanyi potential. Polanyi potential is defined by Eq. 11:

$$\varepsilon = RT\ln(1 + \frac{1}{C_e}) \qquad (11)$$

The parameter E (adsorption energy) allows describing the nature of the adsorption process. In fact, an estimated value of E (Eq. 12) between 8 and 16 kJ mol^{-1} denotes a chemisorption process, while a particle diffusion model is assumed for the process with E values > 16 kJ mol^{-1}.

$$E = \frac{1}{\sqrt{2\beta}} \qquad (12)$$

The experimental data were used by employing the above-mentioned isotherm models and the corresponding parameters have been evaluated. These estimated values are regrouped in Table 4.

The obtained correlation coefficients (R^2) allowed concluding the Langmuir isotherm as the most suitable model for describing the process of the MB removal by the studied PIM. Moreover, this conclusion was reconfirmed by the closeness of the experimental value of q_{max} and that predicted by the Langmuir model. The appraised R_L (*i.e.,* 0.142, greater than zero and lower than 1) demonstrates the process is favorable and shows highly tendency of MB to the adsorbent sites.

Based on the kinetic study of the process (see the above kinetics study), it was concluded that the process is chemically controlled. This conclusion has been reconfirmed by considering the evaluated 1/n parameter based on the Freundlich model. This value was calculated to be 0.061, which is lower than 1, and thus the chemisorption process is concluded. Moreover, the estimated E value by using the Dubinin-Radushkevich model (14.744 kJ mol^{-1}), allowed also to consider a chemisorption process for the removal of MB by the 50/50 wt.% PVC/DEHPA PIM.

Table 4 Evaluated parameters of the removal process of MB by the 50/50 wt.% PVC/DEHPA PIM

Isotherm model	Parameter	Evaluated value
	$q_{max, Exp}$ (mg g^{-1})	61.513
Langmuir	$q_{max, Cal}$ (mg g^{-1})	67.114
	b (L mg^{-1})	0.120
	R_L	0.142
	R^2	0.938
Freundlich	K_F ((mg g^{-1})/(mg L^{-1})$^{1/n}$)	32.681
	1/n	0.061
	R^2	0.911
Temkin	a (L g^{-1})	15.255
	b (kJ mol^{-1})	1.138
	R^2	0.895
Dubinin-Radushkevich	b (mol^2 kJ^{-2})	0.002
	$q_{max, Cal}$ (mmol g^{-1})	0.002
	E (kJ mol^{-1})	14.744
	R^2	0.917

4. Conclusion

The 50/50 wt.% of PVC/DEHPA PIM showed the apparent suitable characteristics required for using a PIM for separation and extraction process. It was transparent, homogeneous, mechanically stable, and flexible. A 3.5 cm circular segment of this PIM was used for following the extraction experiments by this type of PIM; with an average mass of 0.0890±0.0046 g and a thickness of these PIMs was 72.0±0.8 μm. This PIM was able to extract quantitatively MB as its cationic species (20 mg L^{-1}) from 50 mL of aqueous solutions adjusted to pH 3, after 120 min of shaking (200 rpm). A volume of 50 mL solution of oxalic acid 0.15 mol L^{-1} was used for the complete back-extraction of MB from loaded PIMs, beyond 90 min. The maximum capacity of the studied PIM was calculated to be 61.5 mg MB per gram of the membrane. The variation of MB/DEHPA mole ratio as a function of the initial MB concentration has an inflection at the ratio equals to about 1; confirming that the extraction process proceeds based on the following equation:

$$MB^+_{(aq)} + HP_{(PIM)} \rightleftharpoons MB^+P^-_{(PIM)} + H^+_{(aq)}$$
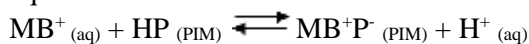
A comparison of this study with other investigated PIMs used for the extraction or removal of MB revealed that the developed PIM is a plasticizer-free PIM which is simple and cost effective than the compared PIMs. Also, the studied PIM able to extract MB faster than others. In this paper, for the first time the kinetics and isotherm of the MB extraction by used the PIMs was assessed and indicated that the pseudo-second order model was suitable for describing the kinetics of the adsorption process of MB by the selected PIM. This confirms also that the chemical nature of the adsorption of MB on the PIM. The application of the intraparticle diffusion model on the extraction of MB by the examined PIM revealed a two-step process; these steps may be described by a fast adsorption process of the analyte on the PIM, and then the diffusion of MB into the pores of this membrane with a lower kinetic constant.

It was confirmed that the Langmuir model interprets suitably the process of the MB removal by the studied PIM. The appraised R_L revealed that the process is favorable and shows highly tendency of MB to the adsorbent sites.

The evaluated 1/n parameter of the Freundlich model. was lower than 1, indicating that process is chemisorption. Moreover, the estimated E value by using the Dubinin-Radushkevich model, allowed also to consider a chemisorption process for the removal of MB by the 50/50 wt.% PVC/DEHPA PIM.

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