Cationic dye (MB) removal using polymer inclusion membrane (PIMs)

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Abstract

Studies were carried out to remove a basic dye (Methylene Blue; MB) from their aqueous solutions using polymer inclusion membranes (PIMs) consisting of Cellulose Triacetate (CTA) as the base polymer, 2-Nitrophenyl octyl ether (2-NPOE) as the plasticizer and Di-(- Ethyl hexyl) phosphoric acid (D2EHPA) as the carrier. The manufactured membranes have been characterized by Scanning Electron Microscopy (SEM) (morphology), Fourier Transform Infrared Spectroscopy (FTIR) (chemical structure) and TGA (thermal analysis). The membranes thickness was measured by digital micrometer. The fractions of base polymers and of the carrier D2EHPA were varied to determine the optimum composition with respect to extraction capability of the membranes. After optimization of the pH of the aqueous solution, the concentration of D2EHPA in the membrane, the concentration of the MB and the stirring speed, more than 93% extraction efficiency has been reached at pH = 6.0. The chemical formula of the complex (D2EHPA-MB) extracted by the PIMs was determined by the method of slopes.

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Keywords: Polymer Inclusion Membrane (PIM); D2EHPA; Extraction; cationic dye, Methylene Blue (MB).

1- Introduction:

Dyes are widely used in various industries, such as textiles, paper, plastics, cosmetics and leather, for coloring their final products [1]. It is recognized that public perception of water is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater [2]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [3]. Once the dye has contaminated the water, its removal by conventional wastewater treatment method is particularly difficult because many dyes are stable to light and oxidizing agent and are resistant to aerobic bio-oxidation [4].

In recent years several physico-chemical decolorization processes have been developed, such as membrane separation, electrochemical, flocculation–coagulation, reverse osmosis, ozone oxidation, biological treatments, etc. [5]. Ultimately, 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 technologies, liquid membranes have 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 [6].
Muthuraman et al. [7,8] and Hu et al. [9] reported the recovery of dyes by liquid-liquid extraction. Membrane liquid have been developed for the extraction of dyes from wastewater. Some workers have studied the extraction of anionic and cationic dyes, from aqueous solutions by emulsion liquid membrane [10-12]. Removal of anionic reactive dyes from water using anion exchange membranes as adsorbers was reported by Liu et al [13], Wu et al. [14] have also used a cation exchange membranes for treating a water containing a cationic dye methyl violet 2B.

Supported liquid membranes (SLM) have the advantage of achieving selective removal and concentration in single step. Thus having great potential for reducing cost significantly [15-17].

The separation of synthetic dye Rhodamine 6G (R6G) and water was investigated using blended organic liquids in a supported liquid membrane (SLM) extraction system [18]. 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 carrier was studied by Hajrabeavi et al [19]. Vegetable oils were used such as carried natural in SLM for extraction of Rhodamine B [20] and astacryl golden yellow [21].

Supported Liquid Membranes (SLMs) are considered as an attractive alternative to conventional liquid–liquid extraction, especially in the treatment of dilute solutions, because they combine the extraction and stripping processes in a single step. However, lack of long-term stability is the main drawback of the SLM process, although it has been reported that this stability can be reduced by the proper composition choice of the membrane phase [6].

Recently, a novel type of liquid membrane system, called a polymer inclusion membrane (PIM) has developed; PIMs are formed by casting cellulose triacetate (CTA) from an organic solution to form a thin stable film [22]. Polymer inclusion membranes (PIMs) retain most of advantage of SLM 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 [23, 24].

Ozmen and Yilmaz have synthesized a membrane polymer using a B cyclodextrin and starch for the sorption of Congo red from aqueous solution. It was found that, the pH effects of the adsorption capacity and the effective pH range for the sorption is better at pH equal 4 to 8 [25]. Kyzas et al. [26] used the molecularly imprinted polymer (MIP) for the adsorption of a Reactive Red (RR) and basic red dye, MIPs were applied in four sequential cycles of adsorption-desorption with a limited loss of adsorption capacity only 10%.

The aim of this study is to investigate polymer inclusion membranes (PIMs) consisting of plasticizer cellulose triacetate (CTA) and Di (2-ethyl) phosphoric acid (D2EHPA) as the carrier, for removing the cationic dye methylene blue from aqueous solution. The effects of time, pH, the stirring speed, concentration of the D2EHPA and dyes have been optimized.

1- Experimental

2-1- Reagent

Cellulose triacetate (CTA), 2- Nitrophenyloctyl ether (2NPOE), Di(2-ethyl hexyl) phosphoric acid (D2EHPA) were obtained from Aldrich. Chloroform (CHCl₃) was acquired from Fluka.

Methylene blue (basic blue 9) was purchased from Merck; the structure of this dye is given in Fig.1. The aqueous phases were prepared by dissolving the different reagents in distilled water.

\[ M= 319.852 \text{g/mol} \]

![Fig. 1: The structure of methylene blue.](image)
2-2- Polymer inclusion membrane preparation

PIMs were prepared using the same procedure described by Kebiche-Senhadji et al. [27, 28]. A chloroform solution of CTA (200mg) in 20ml, the appropriate plasticizer (0.3ml) and the carrier (D2EHPA) in variable amounts were poured into a 9.0 cm diameter flat bottom glass Petri disk. The solvent was allowed to evaporate slowly overnight to obtain a polymer film. A small quantity of distilled water was deposited on the film to help its unstitching of the glass support.

2-3- Membrane characterization

FTIR spectra were obtained using FTIR-8400S of Shimadzu spectrophotometer; measures were taken in the range 4000-400 cm\(^{-1}\) with 4cm\(^{-1}\) resolution and 80 scans.

Scanning electronic microscopy image and micro analyze of PIMs were acquired using a HITACHI S4500 microscope that can reach a resolution of 1.5nm.

Thermogravimetric analyses were achieved using an apparatus of thermogravimetry of high resolution, TGA2350 (MT instruments) with a temperature going from ambient until 1000 °C.

2-4- Membrane solid-liquid extraction

Solid liquid extraction experiments were undertaken at fixed temperature and with stirred solution using a magnetic stirrer in rang of [200-500rpm]. Dilute HNO\(_3\) and NaOH were used to adjust pH of aqueous solution.

The wavelength of maximum adsorption \(\lambda_{\text{max}}\) of methylene blue was 650nm. The percentage extraction (E) and the distribution ratio (D) were calculated as per the following equation.

\[
E \% = \frac{[\text{dye}]_{\text{aq}0} - [\text{dye}]_{\text{aq}}}{[\text{dye}]_{\text{aq}0}} \times 100 \quad (1)
\]

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

Where

- \([\text{dye}]_{\text{aq}0}\): initial dye concentration in the aqueous phase (mg/l).
- \([\text{dye}]_{\text{aq}}\): dye concentration aqueous phase after extraction (mg/l).
- \([\text{dye}]_{\text{org}}\): dye concentration in the organic phase (membrane (mg/l)).

3- Results and discussion

3-1- Membrane characterization

Several techniques were investigated to characterize the PIMs such as: FTIR, SEM and ATG.

3-1-1- FTIR

Table 1 selects the peak values of the reference CTA, CTA+2NPOE and CTA+2NPOE+D2EHPA membranes. The obtained results showed the absorption bands located around 1740cm\(^{-1}\), which is attributed to stretching vibration of the carbonyl group. The IR spectra of the CTA exhibit weak bands at 2930 cm\(^{-1}\) attributed to the stretching modes of aliphatic CH groups. In addition, the absorption band at 1370 cm\(^{-1}\) is due to CH deformation of CH\(_3\). The absorption band at 1740 cm\(^{-1}\) correspond to C=O (acetate) stretching. Two absorption bands at 1030 and 1210 cm\(^{-1}\) attributed to C–O stretching mode are also observed.

The peaks at 1525 and 1350 cm\(^{-1}\) correspond respectively to the stretching modes of \(\text{N=O}\) and C-N of 2NPOE. The bands at 1240 and 1020 cm\(^{-1}\) correspond respectively to the stretching modes of P=O and P-O bond of D2EHPA. This indicates that only weak interactions occur between constituents of the PIMs such as Van der Waals or hydrogen bonds.
Table 1: Peak values and the corresponding radical in different membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Peak value (cm⁻¹)</th>
<th>Corresponding radical</th>
</tr>
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<tbody>
<tr>
<td>CTA</td>
<td>2950</td>
<td>C-H</td>
</tr>
<tr>
<td></td>
<td>1740</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>1370</td>
<td>C-H (deformation of CH₃)</td>
</tr>
<tr>
<td></td>
<td>1210 and 1030</td>
<td>C-O</td>
</tr>
<tr>
<td>CTA+2NPOE</td>
<td>2960-2850</td>
<td>C-H</td>
</tr>
<tr>
<td></td>
<td>1740</td>
<td>C=O (CTA)</td>
</tr>
<tr>
<td></td>
<td>1525</td>
<td>NO₂</td>
</tr>
<tr>
<td></td>
<td>1465</td>
<td>-CH₃</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>C-N</td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>-CH₂</td>
</tr>
<tr>
<td>CTA+2NPOE+D2EHPA</td>
<td>Same bands in addition to</td>
<td>P=O</td>
</tr>
<tr>
<td></td>
<td>1230</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1035</td>
<td></td>
</tr>
</tbody>
</table>

3.1.1. SEM

The SEM images of all membranes (Fig. 2) show uniform surfaces and appear dense with no apparent pores.

Fig. 2: SEM views of CTA membrane (a), CTA + 2-NPOE membrane (b) and PIM containing D2EHPA (c) (surface morphology).
3-1-1- TGA

We used thermogravimetric analyses (TGA) to link specific temperature and height of mass changes to the degradation of a specific compound or fragment of it. Fig.3 shows thermogram (% weight loss vs. temperature) for the PIM (CTA+2-NPOE+D2EHPA). The thermogram of the PIM containing D2EHPA was somewhat different of the general trend; it was observed an absence of actual separation of the degradation steps attributed to individual components.

The feature of the thermogram seems to indicate peculiar interactions between the components in the membrane; more details were given in a previous work [27].

![TGA](image)

Fig. 3: Thermogram of PIM (CTA + 2-NPOE + D2EHPA)

3-2- Solid-liquid extraction

3-2-1- Effect of the carrier concentration

D2EHPA in the membrane is varying in this range of (5-30 µmol/cm²). The results of different carrier concentration are given in Fig. 4. The percentage of extraction increase with increase of carrier concentration up to 15 µmol/cm² then stabilized for the concentration higher.

![Effect of D2EHPA concentration onto the extraction efficiency](image)

Fig. 4: Effect of D2EHPA concentration onto the extraction efficiency.
3-2-2- Effect of the pH in aqueous solution

pH of the aqueous solution is one of important parameter which controls the process of extraction of dyes. To study the effect of pH on the extraction percentage of dye from the aqueous solution, pH is varied between 1 and 12, whereas D2EHPA concentration in PIM and dye in aqueous phase were kept constant. The relationship between the extraction efficiency and the pH is given in Fig. 5. The results show that the extraction of MB is highest at pH= 6±0.2. These results indicate that the dye is extracted in cationic form, across the hydrophobic membrane with high value of the extraction efficiency.

The measure of the final pH shows a decrease of two unite, which confirm that we have an exchange between H⁺ of the D2EHPA and the of BM⁺ (the cationic dye species form neutral ion pairs with the anionic carrier)

\[
\text{Dye}^+_{\text{aq}} + [\text{RH}_2]_{\text{org}} \leftrightarrow [\text{dye(RHR)}]_{\text{org}} + \text{H}^+_{\text{aq}}
\]

This result is comparable to that obtained by Drapala and Hajarabeevi [16, 19]

![Fig. 5: Effect of the pH of the aqueous solution onto the extraction efficiency](image)

3-2-3- Effect of stirring speed

Fig.6 shows the influence of stirring speed on the extraction of the MB. The result indicates that extraction efficiency increase by increasing of speed, the optimum was obtained at 350 rpm. For the speed faster than 350 rpm the decrease of permeability is the consequence of the turbulence caused by stirring. The same result is obtained by Muturaman and Teng who studied the transport of RhodamineB (cationic dye) cross supported liquid membrane using vegetable oil as carrier [20]. Further research studies were done at 350 rpm.
3.2.4 Effect of initial dye concentration

The variation of the dye concentration at the optimum condition have been done over the rang [30 - 300 ppm]. It’s shown in Fig. 7 that the extraction of the cationic dye is constant in the interval [30 – 250 ppm] the efficiency of extraction is average 67 %, after this value (250 ppm) a decrease of the extraction efficiency is noticed with the increase of the dye concentration. This may be due to membrane saturation and lower effective membrane area. This behavior has also been shown in several studies concerning a number of different metal carrier polymer membrane systems [28-30].

3.4 Determination of the complex form

The curves of log D = f (pH) (Fig.8) and log D = f ([HR]) (Fig.9), give the composition and the complex formed methylene blue-D2EHPA, the curves have linear forms and show that the distribution coefficient (D) increase with increasing pH and D2EHPA concentration:
Log (D) = m pHf + (m=n) log [D2EHPA]org + log K_{m,n}........(11)

From the slope of the functions Log D = f (pHf) and Log D = f ([HR]) we can determine directly the complex form extraction of dye with the PIM, then we can write:

\[ \text{MB}^+ + (m + n) (\text{HR}) \leftrightarrow \text{MBR}_m (\text{HR})_n \]

With: m = 1 and n = 0.

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

4- Conclusion:

A simple and efficient method is presented for the recovery of a cationic (MB). The method is based on the use of a polymer inclusion membrane (PIM) containing Di(2-ethyl hexyl) phosphoric acid as extractant which transfers quantitatively MB species from an aqueous feed phase into a solid organic phase (PIM). The efficiency of the method 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, an almost quantitative (93%) recovery of methylene blue is achieved. The cationic dye is extracted by the matrix (CTA-NPOE-D2EHPA) in the form: MB-R. The characterization of membrane resumes that only weak interactions between constituents of the PIMs such as Van der Waals or hydrogen bonds.

These results are very promising and we are also complete the study by the facilitated transport operation.

References

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