Separation of Crystal Violet Dye from Wastewaters by Using Supported Liquid Membrane Technology

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The current study enumerates the use of supported liquid membrane (SLM) technology to remove and recover crystal violet dye from wastewaters. The management of textile industry waste effluents is one of the main concerns of environmental health experts due to having excessive concentrations of dyes and resistance to biodegradation. Liquid membranes offer an affordable and green method for the selective removal of dyes from aqueous solutions. To create a liquid membrane, refined and edible vegetable oils were supported on microporous polymeric films of polypropylene (PP1E). Various parameters influencing transport, such as pH range in the feed solution, initial dye concentration, acid concentration in the strip solution, oil viscosities, and membrane lifetime, have been studied. The maximum flux value ($1.7 \times 10^{-5}$ mg/cm²/s) for crystal violet dye was obtained with sunflower oil-supported membrane at a pH of 12 in the feed solution and a concentration of 0.3 M hydrochloric acid in the strip solution. Under ideal conditions, the maximum amount of dye was transported within 6 hours. Studies on membrane stability and morphology revealed that the flux remained constant up to about 24 hours and then decreased gradually. Morphological studies showed that this may be attributed to deformation of pores shape and gradual clogging.

1. Introduction

The significant increase in the world’s population, unplanned industrialization, and urbanization caused by the excessive use of chemicals has resulted in a massive increase in environmental pollution caused by the toxic contaminants of these processes. Any colored organic compound with one carboxylic group and one nitro or azo group can be regarded as a dye. The majority of wastewaters oozing out of textile and printing industries are colored, and they are usually accompanied by other pollutants as well. Color removal from industrial wastewater is a difficult problem for waste management technicians and environmental scientists. Chemical species in textile industry wastewaters belong to a wide variety of active groups, but the color is due to the dyes used in different processes; thus, colored wastewater cannot be easily treated by usual chemical, physical, and biological treatment methods [1, 2]. This is because wastewaters from the textile industries contain complex and synthetic organic compounds that are extremely resistant to degradation. The pH, color, salts, suspended solids, and chemical oxygen demand of dye effluents are all high. The presence of these colorants in water is not only unsightly but also harmful to the environment, human health, and ecological and biological organisms. Contaminations caused by dye wastewater impede the proper functioning of ecosystems, which is required for a healthy and sustainable environment.

The majority of the techniques used to remove dye from aqueous solutions are based on the various processes of nanofiltration, adsorption, photodegradation, electrolytic methods, and flocculation. Recently, membrane separation
and membrane-based processes have achieved practical and marketable significance in industrial and environmental applications.

A number of researchers have expressed an interest in these immobilized liquid layer techniques involving supported liquid membranes (SLM) [3–5]. The separation of chemical species using SLMs has been extensively mentioned in the literature. Membrane-based separation methods have been widely used in diverse industrial processes (such as dehydration of organic compounds, desalination, and wastewater treatment facilities) for the treatment of toxic pollutants like heavy metals, phenolic compounds, and dyes. Currently, membrane-based separation methods have been extensively applied to industrial separation of different compounds in both gaseous and aqueous phases. These methods have advantages against other separation methods such as their greener production (i.e., negligible generation of secondary pollution) with the least installation complexity for existing facilities and low energy consumption for reduced capital investment. Currently, membrane-based separation methods have been extensively applied to industrial separation of different compounds in both gaseous and aqueous phases. Despite many benefits, however, extensive application of membrane-based methods is restricted by certain barriers. For instance, in terms of stability and reusability, these membranes are subject to short lifetimes because of fouling by particulate matter present in aqueous streams [6, 7]. Furthermore, the reported literature on the use of LMs is based on the use of toxic synthetic solvents and chemicals [(8–10). As a result, edible nontoxic vegetable oils free of additives were used as membrane liquids. Vegetable oils are fatty acid glycerides that have recently been used in industry to produce biofuel and biodiesel [11, 12]. According to a recent literature review, the use of liquid membranes (LM) for the removal of dyes from waste effluents is uncommon. [13] reported a study to remove the reactive black 5 dye from synthetic textile wastewaters using agricultural wastes and determination of adsorption isotherm. [14] have reported the effect of chloride ion on the degradation of sulfadiazine using reduced graphene oxide modified with sodium anthraquinone-2-sulfonate photocatalyst. [15] investigated the Fenton and photo-Fenton processes for textile dye degradation and sludge production. Other researchers used vegetable oil as LMs to selectively remove phenols and cationic dyes [16, 17]. [18] described the use of colloidal gas aphrons for organic dye separation from wastewater. For the removal of solvent yellow dye from aqueous solutions, [19] tried a predispersed solvent extraction technique. Traditional liquid-liquid extraction processes have also been used to remove and recover various dyes [17].

The recovery of crystal violet dye from aqueous solutions was investigated in this work using the supported liquid membrane (SLM) technique. The treatment of textile industry wastewaters is one of the main concerns of environmental health experts due to having excessive dyes and pollution. Therefore, there is need to develop techniques that utilize nontoxic and degradable materials with high efficiency. Crystal violet dye is used in a variety of manufacturing applications, including paper dyeing, printing inks such as navy blue and black ballpoint pens and inkjet printers, and the textile industry. It is also used to color a wide range of products, including fertilizers, antifreeze, detergents, and leather. It is the active ingredient in Gram’s stain, a technique used to classify bacteria in the medical community. Crystal violet is a cationic, triphenylmethane dye and is responsible for causing eyes, skin, and digestive tract irritation. It is a mitotic poisoning agent which is carcinogenic and therefore is regarded as a potential biohazard. It is considered as highly hazardous as its exposure may cause permanent blindness and respiratory and kidney failure.

The method described for the selective removal of dye utilizes nontoxic vegetable oils as membrane liquids and presents a thorough study on membrane stability and morphology. The transport of crystal violet dye is found to be controlled and influenced by a variety of factors. These variables comprise of pH range in the feed solution, acid concentrations in the strip solution, membrane lifetime, initial quantity of dye, and types of vegetable oils.

1.1. Theoretical Principles. Fick’s law governs the phenomena of continuum mass transport through porous membranes by a diffusion mechanism and therefore adequately describes the situation being treated here. It takes the general form

\[
J = \frac{1}{A} \frac{d}{dt} m(t). \tag{1}
\]

We also have the gradient form

\[
J = D \frac{\partial}{\partial x} C(x, t). \tag{2}
\]

Here, the time dependent flux \( J(t) \) is defined as the rate of flow of a property, per unit area \( A \) of the membrane, per unit time, in units of \([\text{quantity}]\,[cm^{-2}s^{-1}], \) and \( D \) is the standard diffusion coefficient.

In general the partition coefficient \( P \), which is directly proportional to a permeability coefficient \( P_c \), relates a solute concentration \( C_1 \) in the membrane at the donor side and the solute concentration \( C_2 \) in the membrane at the receptor side. We have

\[
P = \frac{C_1}{C_d} = \frac{C_2}{C_r}, \tag{3}
\]

where \( P \) is experimentally determined, as described in this paper for a given fluid at a given temperature.

In a very simple interpretation of the gradient equation, we see

\[
\frac{dm(t)}{dt} = DA \frac{\partial C}{\partial x} = \frac{DA}{\Delta x} [C_2 - C_1] = \frac{DAP}{\Delta x} [C_d - C_l], \tag{4}
\]

where \( \Delta x \) is the membrane thickness, and we label the ratio \( D\Delta P/\Delta x \) as the membrane permeability coefficient \( P_c \).

By Fick’s law, the rate of change of mass \( m(t) \), which can be directly associated with a molar quantity, in the aqueous feed control volume \( V \), is directly proportional to the area
A of the permeable membrane and the concentration of the solute $C(t)$ at time $t$, in this control volume:

$$\frac{dm(t)}{dt} \propto A.C(t). \quad (5)$$

The concentrate $C(t)$ is a molecular density so that $m(t) = V.C(t)$, and furthermore, the initial concentrate is given by $C(0) = C_0$. The constant of proportionality in this simple first-order differential equation is the partition coefficient $P$, so that is now

$$\frac{d}{dt} V.C(t) = -PA.C(t) \implies \frac{dC(t)}{dt} = -\frac{PA}{V} C(t). \quad (6)$$

Note: by definition flux, $J(t) \equiv (-dm(t)/dt)/A$, and the negative sign indicates the rate of decrease of solute concentration $C(t)$ as flux solute diffuses systematically from high-concentration regions to low-concentration regions.

Integrating this simple initial value problem yields

$$C(t) = C_0 e^{(-PA/V)t} \text{ or } \ln \frac{C(t)}{C_0} = -\frac{AP}{V}. \quad (7)$$

We can see that equilibrium is eventually achieved when $C(t) = C_0$.

Equations (6) and (7) are used to predict the permeation pattern of SLM’s when the feed solutions are relatively dilute in metal species (Danesi, 1984).

The partition coefficient $P$ is an important indicator in the vegetable oil screening analysis and is used to evaluate the extraction performance of different oils; in this analysis,

$$P = \frac{C_{or}}{C_{aq}}, \quad (8)$$

where $C_{or}$ is the concentration of dye in the oil phase (mg/L) and $C_{aq}$ is the concentration of the remaining dye in the feed phase after reaching equilibrium.

### Table 1: Investigated vegetable oils along with their values for partition coefficients, density, and viscosity.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Type of oil</th>
<th>Partition coefficient</th>
<th>Viscosity (cP)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sunflower oil</td>
<td>10.4</td>
<td>65.4</td>
<td>0.91</td>
</tr>
<tr>
<td>2</td>
<td>Olive oil (virgin)</td>
<td>9.98</td>
<td>78.5</td>
<td>0.93</td>
</tr>
<tr>
<td>3</td>
<td>Coconut oil</td>
<td>8.1</td>
<td>59.8</td>
<td>0.87</td>
</tr>
<tr>
<td>4</td>
<td>Palm oil</td>
<td>7.6</td>
<td>98</td>
<td>0.98</td>
</tr>
<tr>
<td>5</td>
<td>Mustard oil</td>
<td>7.7</td>
<td>97</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The rate of separation $S$ reflects the extent of separation of dye through the membrane.

$$S = \frac{C_0 - C(t)}{C_0} \times 100, \quad (9)$$

where $C_0$ is the initial concentration of dye in the feed phase and $C(t)$ is the concentration of dye at time $t$ (mg/L).

### 2. Experimental

#### 2.1. Materials.

Edible vegetable oils were procured from the local markets. All other chemicals were of AR-grade, except for crystal violet (MW 408.9 g/mol) (Alrich). The organic phase was supported by an Accural PP1E microporous film (Akzo F, GMBH). This film has a porosity of 64%, a thickness of 92.5 m, a pore diameter of 0.11 m, and a tortuosity of 1.6. The film was soaked in the vegetable oil for 24 hours to impregnate the carrier in the film by capillary action. A Shimadzu UV/Vis spectrophotometer (5301PC, $\lambda_{max}$ 590 nm) was used to analyze the dye samples. The Brookfield (BII+) system was used to measure viscosities.

#### 2.2. Measurements of Partition Coefficients.

Partition coefficients in glass vials were determined by varying the ratios of aqueous dye solution to oils. Initially, all of the organic solute was in the aqueous phase. To disperse the two liquids,
the vials were vigorously mixed on a mixer for one day before being allowed to equilibrate. After that, the samples from both phases were taken. The dye concentration in the aqueous phase was directly analyzed, whereas the oil phase was dissolved in appropriate organic solvent and back extracted via pH change for analysis. Only the aqueous phase was analyzed, with the exception of a few initial measurements of the oil phase to establish mass balance, and the solute concentration in the polymer phase was obtained by difference. The concentration of dye was determined using a UV-Vis spectrophotometer.

2.3. The Permeation Cell. Perspex was used to make the apparatus used for permeation studies. The permeation cell is depicted in Figure 1. It is made up of two identically sized and shaped compartments. Each cell has a volume of 140.0 mL, and a membrane cut into an effective surface area of 14.2 cm² could be fixed between feed (Figure 1(c)) and strip (Figure 1(d)) chambers. These chambers have two openings, one for the stirrer (Figure 1(a)) to undo the resistance of the boundary layer and the other for sample withdrawal (Figure 1(e)). An adjustable power supply was used to regulate the speed of the stirrers.

3. Results

Five varieties of vegetable oils were investigated to check their suitability to be used as membrane liquids. The relevant data, along with the values for partition coefficients, density, and viscosity, are presented in Table 1. Based upon the results of its partition coefficient \( P \), sunflower oil has more affinity for crystal violet dye. This might be attributed to
Figure 3: Continued.
viscosity differences in the oils used. The magnitude of viscosity is directly related to resistance to flow and boundary layer thickness; therefore, sunflower oil was chosen as the membrane liquid.

3.1. Permeation Studies. The optimal pH range in the feed solution was determined by running permeation experiments at various pH levels. Figure 2(a) depicts the results as well as the experimental conditions. The percentage of dye transported increased with increasing pH, reaching a maximum around pH 12. It is noteworthy that transport efficiency decreased at higher pH values (>13). At significantly higher pH values, the dye solubility in oil gradually decreases; so, additional experiments were conducted by keeping the pH on the feed side at 12.0. [20] have reported the impact of pH-responsive magnetic Janus particle catalysts on pharmaceuticals performance of high-efficiency adsorption and degradation. Muthuraman and Palanivelu [16] discovered that at high pH levels, hydroxyl group dissociation is inhibited, resulting in decreased solubility. [21] have reported that the removal of extracellular polymeric substances protein depended on the combined effect of sludge conditioning agent tannic acid and pH regulations.

The concentration of hydrochloric acid in the strip solution is critical for improving and facilitating the transport process. To achieve maximum dye transport, different HCl concentrations in the strip solution were tried, ranging from 0.1 M to 0.4 M. Figure 2(b) depicts the results as well as the experimental conditions. It is established that hydrochloric acid helps permeation and that

Figure 3: Scanning electron micrograph at magnifications 10x (a) unused and (b) used; 50x (c) unused and (d) used; 100x (e) unused and (f) used; and 200x (g) unused and (h) used.
transport increases linearly with concentration until a maximum is reached at 0.3 M. This demonstrates that at higher acid concentrations, the dissociation of the oil-dye cluster is reduced.

Constant stirring of solutions on the feed and strip sides is needed to undo the formation of boundary layers at the solution-membrane interface. Figure 2(c) depicts that with stirring speeds of up to 550 rpm, the flux value increased but decreased with higher speeds. This can be attributed to vigorous stirring causing membrane liquid (oil) to leak through the membrane openings. Therefore, the stirring speed was set to 450 rpm for further experiments.

Figure 2(d) depicts the flux variation as the quantity of dye in the feed side increases. This parameter was studied using a wide range of dye concentrations. Flux and dye concentration were found to have a direct proportional relationship up to 300 mg/L. Any additional increment in dye concentration has no effect on the flux. This could be due to the membrane’s small surface area (14.2 cm²), which caused flux saturation. Similar results have been reported for various metalloorganic SLM systems [22].

3.2. Membrane Lifetime. The lifetime of oil-membrane system is critical to ensure continuity of the process. Lifetime usually depends upon the loss of oil from micropores of the polymer film. The loss of membrane liquid can be attributed to multiple factors, such as pressure difference, deterioration of polymeric film, and solubility of the membrane liquid in strip or feed solutions. All these factors lead to flux reduction gradually; therefore, aging experiments were conducted to study the membrane stability.

Experiments show that the flux remained constant up to about 24 hours and then decreased gradually (Figure 2(e)). Six experiments were run in total. Initial concentration, 100 mg/L, of the dye was transported to strip solution within the duration of 8 hours. After every 5-hour duration, strip and feed solutions were changed while keeping the same membrane. The factors contributing towards membranes instability include Marangoni effect, Bernard instability, membrane preparation procedure, shear surface forces, and changes in polymeric support pores morphology ([23]; Ashraf and Almamak 2005). If the membrane morphology does not change, the membrane lifetime can be increased by reimpregnation of the support with vegetable oil after regular intervals of time.

The morphology of used and unused membrane was studied by using scanning electron microscopy. Figure 3 depicts the surface structures of membranes at different magnifications. There is a clear difference in the texture of used and unused films. The original PP film is shown in Figures 3(a)-3(g) whereas used membrane is shown in Figures 3(h). It can be observed that PP1E film has pores with well-defined boundaries. This becomes clearer with increased magnification. Clogging of pores with solid particulate matter can also be seen at higher magnification. Prolonged use of the membrane also caused a decrease in porosity per unit area of the membrane as shown in Figures 3(g) and 3(h).

4. Conclusions

Vegetable oils were discovered to be active membrane liquid in the selective recovery of crystal violet dye from aqueous solutions. A variety of parameters influence dye transport, including pH in feed side, type, and basicity of the acid in the strip solution, appropriate viscosity of oils, dye quantity in the wastewater, etc. By increasing the stirring speeds, the transportation rate through the membrane increases until it becomes linear. The dye permeation rate increases with initial concentration but becomes linear at higher concentrations.

Data Availability

Data is available on request in the form of excel sheets.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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