Removal of Methyl Green Dye from simulated waste water using Hollow Fiber Ultrafiltration Membrane

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Abstract. Ultrafiltration has been favorably employed for recycling insoluble dyes and high molecular weight, some type of chemicals and water. Despite, ultrafiltration does not remove low molecular weight and soluble dyes (acid, direct, reactive, basic, etc.). The main advantages of the hollow fiber module are very high packing density and low-energy consumption. In this investigation, the performance of a Polyvinyl chloride (18 wt % PVC) hollow fiber ultrafiltration (UF) membrane for methyl green (MG) dye removal from aqueous solution was evaluated by examining the impact of varying the operation conditions (the concentration of dye and volumetric flow rate) to determine their impact on the separation processes (permeate flux and rejection coefficient) at constant pressure, temperature and at neutral pH. two configurations used: Semi-batch filtration and continuous filtration. UF was characterized by scanning electron microscopy. Besides, tests of the UF were carried out with pure water and MG aqueous solutions as feed. Results exhibited a notable influence of flow rate and feed concentration on the permeate flux and rejection, where the highest flux obtained equal to 32.7 l/hr.m² with the highest rejection coefficient value close to 59.46% of the membrane system.

Keywords: Methyl Green, Ultrafiltration, Hollow fiber membrane, Rejection performances,
1. Introduction
The pollution in all its departments is considered as a serious global environmental problem that affects the human environment and health. Therefore, there has been increased interest in wastewater treatment and recycling[1]. One of the most important growing industries is the textile industries, which depend on the use of many toxic chemicals that are used to treat textile products, which in turn increases environmental pollution[2]. There are many methods used to treat wastewater from textile industries for example flocculation, ozonation, irradiation, ion exchange, adsorption, electrochemical degradation, advanced oxidation process, biotechnology method and membranes filtration[3-7]. These mentioned methods can be classified into chemical, physical, and biological methods [8, 9] as shown in Fig. 1:

![Figure 1. Classification of dye removal techniques.](image)

Membrane technology is one of the most important wastewater treatment methods that have witnessed significant development in recent years due to the advantages it possesses with a significant reduction in energy requirement, reduction in the size of equipment, and low capital cost[10]. As it has the ability to bridge the economic gap and sustainability because it does not use chemicals or use them in a very small way, and thus it is the most suitable option for wastewater treatment[11]. Recently, the ultrafiltration membrane is applied in a wider variety of fields, from the chemical industry, like processing of latex[12], recovery of textile[13], dyes removal[14-16] and lubricating oil recovery[17], biotechnology uses, like juice[18], milk
concentration[19], and glue and gelatin[20] and even to the medical uses, like dialysis operations of the kidney[21]. Dyes can be classified in various ways; each group has a structure, very unique chemistry, and particular way of bonding[22]. Cationic triphenylmethane dyes are widespread in industry and biomedical applications as bacterial antigens. Methyl green (MG) \([\text{C}_2\text{H}_3\text{BrClN}_3\cdot\text{ZnCl}_2]\) is a basic triphenylmethane-type dicationic dye, commonly employed to change the color for solutions in biology and medicine plus as a photochromophore to excite the coagulated films[23]. Its Molecular structure is depicted in Figure 2.

![Molecular structure of methyl green dye](image)

**Figure 2. Molecular structure of methyl green dye**

There are several system approaches that one can use to design and lay out a MF or UF plant. They are batch operation; semi-batch filtration, single-pass processing continuous filtration, and multiple recycle operation [24]. The flow of permeate is usually low in Semi-batch filtration because it does not include recycle of the retentate. It is implemented when a large membrane area is handled and it is used mainly for water purification, for example, in reverse osmosis the permeate is pure water whereas the retentate is a concentrated salt solution. The residence time of this configuration is the least when compared to others. Many times, it is used with dead-end mode (zero retentate flow) so that the full feed is transformed into permeate. semi-batch filtration operation is usually limited when the high flow rates are not required and if concentration polarization influences are negligible[25]. The disadvantage of continuous filtration is that the process loop is operating continuously at a concentration factor equivalent to the final concentration of a batch system. The flux, therefore, is lower than the average flux in a batch mode, and the membrane area required is correspondingly higher [25].

The aim of this work was ability to use ultrafiltration to the removal of methyl green dye present in aqueous solutions. The method has the benefit of being able to operate at low pressures, and that means lower energy consumption. To conclude how the process variables influence the
processing of methyl green dye by ultrafiltration, tests were done by varying the flow rate and the dye concentrations of the feed. These parameters were studied to determine their influence on the separation processes (permeate flux and rejection coefficient) at two configurations.

2. Materials and Procedures

I. materials

The physical-chemical characteristic of the MG dye is described in Table 1.

| Dye Name      | Charge | Molecular weight (g/mol) | Molecular volume (Å) | Molecular Shape volume (Å) |
|---------------|--------|--------------------------|----------------------|----------------------------|
| Methyl green  | +2     | 653.240                  | 398.77               | Disc                       |

The feed (MG dye solution) were arranged from the analytical grade chemical products from Sigma-Aldrich. A polyvinyl chloride (PVC) hollow fiber membrane was utilized which was given by the Unit of Membrane Technology Research in the Department of Chemical Engineering at University of Technology, Baghdad-Iraq.

3. Membrane Characterization

I. Scanning Electron Microscope (SEM)

The SEM [Type: VEGA 3 LM, Origin: Germany] provides information about the morphology of surface and cross section. The membrane sample was firstly frozen in liquid N2 for (20 sec) via soaking it and finally dried.

II. Porosity measurements

Porosity (Ε) can be described as the pores volume divided by the membrane total volume. The entire porosity was computed using equation (1), as documented in the literature[26]:

\[ Ε = (1 - \frac{ρ_{\text{fiber}}}{ρ_{\text{PVC}}}) \]  

Where, \( ρ_{\text{fiber}} \) is the density of fiber, and \( ρ_{\text{PVC}} \) is the density of PVC (1.4 gm/cm3) [23].

III. Permeation flux and solute rejection measurements

Permeation module was prepared for testing quantitatively the performance of the hollow-fiber as a function of permeation flux and rejection. The module comprised of (5) fibers with a (25 cm) length. The sides of the shell of the bundles two ends were adhered by glue into double tees of
stainless steel using epoxy resin that sets normally. The module was kept overnight to cure prior its testing and excluding the influence of the left glycerol upon the performance of the module, and this module was run in the test system for (1.5 hr) before any sample collection. The membrane performance experiments were conducted at the trans-membrane pressure (TMP) of (1 bar) at a temperature 25°C. Two configurations of filtration were used:

- Semi-batch filtration (A): The retentate was re-circulated to the feed tank and the permeate solution was collected to calculate the permeation flux as shown in Fig. 3a

- Single-pass continuous filtration (B): The retentate was collected in separated tank and the permeate solution was collected to calculate the permeation flux as shown in Fig. 3b

Also, the dye rejection during the UF experiments was calculated. PVC hollow fiber UF membrane was used with the specifications summarized in Table 2.

| Material                  | PVC   |
|---------------------------|-------|
| Thickness (mm)            | 0.185 |
| Porosity (%)              | 0.35  |
| Effective surface area (m²)| 0.00422 |

![Diagram of filtration system](image)
Figure 3: Schematic diagram of the UF experiments set-up

The permeate flux (J) is described as the flow through membrane per area of membrane and permeation time in L/m².hr (LMH), and it can be computed by this equation[27]:

\[ J = \frac{Q}{\Delta P A} \quad (2) \]

Where, Q is the rate of volumetric flow (L/hr), \( \Delta P \) is the trans-membrane drop of pressure (bar), and (A) is the membrane active surface area (m²). MG with different concentrations (mg/L) was employed to determine the UF membrane rejection (%R). The solute retention is described as the concentration discrepancy across the membrane divided by the bulk concentration on the feed or concentrated side (solute fraction left in the stream of feed)[28] that was computed by this equation[29]:

\[ %R = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \quad (3) \]

Where, \( C_p \) and \( C_f \) are the concentrations of the dye in the permeate solution and the feed, correspondingly. The MG dye concentration was measured at a maximum wavelength of 630 nm by UV-Vis spectrophotometer [Type: U.V-1100, Origin: China].

The feed solution was prepared by dissolving 10, 20, 30, 40, and 50 mg of MG in 1 L of distilled water. The operating conditions were as follows: concentration (10–50) mg/L, feed flow rates (100, 150 and 200) ml/min, operating pressure 1 bar and temperature 25°C.
4. Results and Discussion

I. Scanning Electron Microscopy

Scanning electron microscopy analyses were carried out to discover the morphology on the surface of the membranes. Figure 4 presents the cross-section of the PVC hollow fiber. It could be remarked that there was a large, fingerlike structural layer at the outer edge; furthermore, a large, fingerlike macro void layer was located at the inner edge of the cross-section of the PVC hollow fiber with a very small sponge structure situated between them.

![Figure 4. SEM image of the PVC hollow fiber membrane](image)

II. The Effect of Feed Flow Rate

Fig. 5 and Fig. 6 show the effects of feed flow rate on the permeate flux and MG rejection of hollow fiber membrane as a function of time for the second design lay out of the membrane system where the permeate collected to calculate the permeation flux. It can be noticed that increasing feed flow rate from 100 to 200 ml/min results in increasing the permeate flux of the hollow fiber membranes from 29.5 to 31.85 (L/m² hr) as shown in Fig. 5. The flow rate or turbulence, whether produced by stirring or pumping the fluid, or moving the membrane, has a noticeable effect on permeate flux. In addition, agitation and mixing of the fluid near the membrane surface ‘‘sweep’’ away the accumulated solute, reducing the hydraulic resistance of the ‘‘cake’’ and reducing thickness of the boundary layer. It is also believed that extremely high shear, such as that obtained with thin channel and rotary devices, actually reduces the thickness of the ‘‘gel’’ layer. In any case, this is one of the simplest methods of controlling the effect of concentration polarization. Therefore product rate increase with the increase of the feed flow rate[30]. Whereas the flux decreased gradually with time for the three flow rates, the flux through the membrane decreases over time which is the typical flux-time behavior [31], so the
concentration polarization influenced solution was less significant and for the same reason, there is less rejection for MG dye with the time as shown in Fig. 6.

**Figure 5.** Effect of feed flow rate on the permeate flux of hollow fiber membranes (TMP=1bar, feed concentration=20mg/L).

**Figure 6.** Effect of feed flow rate on the rejection of MG dye (TMP=1bar, feed concentration=20mg/L).

**III. The Effect of MG concentration**

Fig.7 and Fig.8 show the influence of concentration in feed solution on the permeate flux and rejection of hollow fiber UF membrane. By increasing the concentration of the feed, both the permeate and the rejection rate decrease at a higher rate than the first design, and the reason for
this trend is due to the design configuration of this experiments, so the concentration polarization influenced solution was less effect. Furthermore flux decline can be caused by several factors, such as plugging of the membrane pores, adsorption inside the membrane pores, concentration polarization, and gel layer formation. Additional resistance on the feed side to transport across the membrane is found due to these factors [32].

![Figure 7](Effect of feed concentration on the permeate flux of hollow fiber membranes (TMP=1bar, feed flow =100mL/min).)

![Figure 8](Effect of feed concentration on rejection of hollow fiber membrane (TMP=1bar, feed flow =100mL/min).)
• Single-pass continuous filtration (B):

It was evaluated the effect of permeate flux and rejection behavior under best conditions which were obtained from the previous filtration process (i.e. Semi-batch filtration (A)) as present in Figure 9. It can be noted that the permeate flux reduced with time and it was less than the previous filtration lay out and the same noted for rejection behavior. A primary reason for flux decline during the initial period of a membrane separation process is concentration polarization of solute at the membrane surface this can occur in conjunction with irreversible fouling of the membrane as well as reversible gel layer formation [33].

![Figure 9. Permeate flux and Rejection behaviors of MG dye for continuous filtration (feed concentration=20mg/L, TMP=1bar, feed flow =100mL/min).](image)

5. Conclusion

The results explained that methyl green is removed with the PVC membrane, with the highest rejection coefficient value close to 59.46% for the membrane system, at neutral pH. This may be described because the separation by ultrafiltration membrane is not only due to the size of the molecular cut-off of the membrane (MWCO) but also due to the negative charge on the molecules, which have an enlarging influence, increasing the rejection coefficient of the membrane. The shape of the molecules is also significant when the molecules have a disc or
globular shape (such as methyl green), and the charge reduces the volume so that the molecules readily pass through the pores of the membrane.

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