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Hollow Fiber Ultrafiltration Membrane for Methyl Green Dye Removal

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Submitted: 28/09/2019 Accepted: 22/12/2019 Published: 25/07/2020 ABSTRACT **KEYWORDS** Hollow fiber membrane. In this study, the behavior of a Polyvinyl chloride (18 wt % PVC) hollow Methyl Green, fiber ultrafiltration (UF) membrane for methyl green (MG) dye removal Ultrafiltration, Rejection from aqueous solution was estimated by studying the influence of varying the operation conditions (the concentration of the dye and volumetric flow performances. rate) to determine their impact on the separation processes (permeate flux and rejection coefficient) at constant pressure and temperature. The PVC membrane was characterized by scanning electron microscopy. Furthermore, tests of the UF were carried out with pure water and MG aqueous solutions as feed. Outcomes explained a notable influence of feed concentration and flow rate on the rejection and permeate flux, with the highest rejection coefficient value close to 75.2% of the membrane system, at neutral pH.

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1. Introduction

Although the two-thirds of the surface of the earth are covered with water, merely (3%) of water is freshwater, and two-thirds of is not usable. That is actually formed via the existence of a diversity of contaminants in raw water, where their mean size changes from the micrometric scale (for example, bacteria) to a few tenths of nanometers (solvated ions) [1]. Textile production is one of the industrial fields that apply a large amount of water and release high quantities of wastewater. The step of dyeing in textile processing is the main source of ecological problems and its streaming must be managed accurately before it is released to the surface water [2]. Many researchers have recognized the significance of the wastewater processing, but the completion of the traditional approach techniques, e.g., biotechnology, coagulation-flocculation, electrochemical oxidation, adsorption, etc. was reportedly incapable to manage the textile wastewater with a broad spectrum of pollutant concentrations [3]. The technologies of a membrane in textile wastewater processing are increasingly expanding and interesting. Membrane separation methods have displayed the most desirable alternative approaches, which can be utilized for a big-scale handling operation due to the benefits,

like economical energy need, huge removal efficiency, environmentally friendly, room temperature operation, low investment, and less pollution, as contrasted with other popular separation systems [4, 5].

Lately, the ultrafiltration membrane is employed in an extended diversity of fields, from the chemical industry, like the recovery of textile [6], processing of latex [7], lubricating oil recovery [8], and dyes removal [9-11], to the medical uses, like dialysis operations of the kidney [12], and even for biotechnology uses, like milk concentration [13], juice [14], protein recovery from cheese whey [15], and glue and gelatin [16].

There are various approaches to the classification of commercial dyes. It can be classified in terms of color, composition, and using means [17]. Cationic triphenylmethane dyes are generally in industrial and biomedical applications as bacterial antigens. Methyl green $[C_{27}H_{35}BrClN_3 \cdot ZnCl_2]$ is a basic triphenylmethane-type dicationic dye, usually using to change the color for solutions in biology and medicine plus as a photochromophore to attract the coagulated films [18]. Its Molecular structure is described in Figure 1.



Figure 1: Molecular structure and shape of Methyl green [19]

Bench-scale systems, if suitably planned, can be an important instrument in assessing fouling and predicting the response of large-scale dead-end UF industries [20]. There are several systems approaches that one can use to design and layout an MF or UF plant. They are batch operation, single-pass processing, feed and bleed, and multiple recycle operation [21].

The aim of this work was the 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).

2. Used Materials and Procedures

I. Used materials

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

Table 1: Physicochemical properties of the MG dye					
Dye Name	Molecular weight (g/mol)	Charge	Shape	Molecular volume (Å)	
Methyl green	653.240	+2	Disc	398.77	

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

3. Membrane Characterization

I. Scanning Electron Microscope (SEM)

The SEM [Type: VEGA 3 LM, Germany] provides information about the morphology of the top surface. The membrane sample was firstly is frozen via soaking it in liquid N_2 for (20 Sec) and finally dried.

II. Porosity measurements

Porosity (E) 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 [22]:

$$\mathcal{E} = \left(1 - \frac{\rho_{fiber}}{\rho_{PVC}}\right) \tag{1}$$

Where, ρ_{fiber} is the density of fiber, and ρ_{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 disintegration performance of the hollow-fiber as a function of flux and rejection. The module comprised of five fibers with a (25 cm) length. The sides of the shell of the bundles' two ends were adhered with glue into double tees of stainless-steel using an 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 h) before any sample gathering. The membrane performance experiments were conducted at the trans-membrane pressure (TMP) of (1 bar) at a temperature of 25°C. The configuration of batch filtration with full recycling of retentate showed that the retentate was recirculated to the tank of feed, whereas the permeate was re-circulated to the tank of feed (Figure 2). Also, the dye rejection during the UF experiments was calculated. Table 2 presented the specifications of the UF membrane was applied.



Figure 2: Schematic diagrams of the UF experiments set-up

(Material)	Thickness (mm)	Porosity (%)	I.D &O. D* (mm)	Effective surface is (m^2) (Å)
PVC	0.185	0.35	0. 7& 1.07	0.00422

Table 2: Hollow fiber UF membrane Specifications

* O.D: outside diameter & I.D : inside diameter

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 [24]: (2)

$$J = \frac{Q}{\Delta P A}$$

Where Q is the rate of volumetric flow (L/h), ΔP is the trans-membrane drop of pressure (bar), and (A) is the membrane active surface area (m^2) . 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 of the feed or concentrated side (solute fraction left in the stream of feed) [25] that was computed by this equation [26]:

$$\%R = \left(1 - \frac{cp}{cf}\right) * 100 \tag{(°)}$$

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

The feed solution was prepared by dissolving 10, 20, 30, 40, and 50 mg of MG in 1000 ml of (distilled water). The working conditions: feed flow rates (100,150 and 200) ml/min, concentration (10–50) mg/L, 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 3 presents the cross-section of the PVC hollow fiber. It could be remarked 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 located between them.



Figure 3: SEM image of the PVC membrane

II. The Effect of Feed Flow Rate

The mass transfer is improved as the linear velocity of flow across the membrane is raised. The coefficient value of the mass transfer is influenced by the velocity of flow through the reliance of Sh (Sherwood number) on Re (Reynolds number). Therefore, the permeate flux is improved significantly via the turbulence increment. The turbulent flow helps remove the attached material from the surface of the membrane, decreases the concentration boundary layer thickness, and hence decreases the permeate flux resistance. Higher linear velocities of flow across the membrane could be done by increasing the rate of the volumetric flow or by decreasing the flow channels' diameter or height [27].

Figures 4 and 5 present the impacts of feed flow rate upon the (MG) rejection and permeate flux of a membrane as a function of time for the membrane system, where the permeate re-circulated to the feed tank. It can be notified that the growing feed flow rate from 100 to 200 ml/min led to improving the permeate flux within (32-35.54) L/m².hr, as presented in Figure 4. Usually, raising the flow rate of the liquid effects in improving the disturbance of the liquid on the membrane surface, and that leads to sweeping away the attached solute and enhancing the permeation flux [21], whereas the flux reduced gradually with time for the three flow rates tested in this work. This means that the concentration polarization was influenced because the existence of MG in the solution was notable and for the same reason, there is less rejection for MG dye with the time, as shown in Figure 5.



Figure 4: Effect of feed flow rate on the permeate flux of PVC membrane (TMP=1bar, feed concentration=⁴0mg/L)



Figure 5: Effect of feed flow rate on the rejection of MG dye (TMP=1bar, feed concentration=*0mg/L)

III. The Effect of MG concentration

In common, around (10-20%) of textile dyes are dropped through the dyeing operation and consequently, the released effluent distinctively includes within (10-1000) ppm of the components of the dye [28, 29].

Figures 6 and 7 reveal the impact of concentration in feed on the rejection and permeate flux of (UF). It can be observed that the rising of the feed concentration from 10 to 50 mg/L led to a decline in the permeate flux from 34.12 to 29.32 (L/m².hr), as displayed in Figure 6. And, the dye rejection reduced from 75.2% to 16.7% as presented in Figure 7, the decrease of the permeate flux and the rejection of dye at a high concentration of the dye solution is probably owing to the attachment of the particles of dye particles upon the surface of the membrane which causes either a partial or an entire blockage of pore [30]. Moreover, the layer that deposited from the dye could be formed which highly decreases the effective area of the surface and influences the quantity of permeate. Additionally, raising the concentration of feed would also enhance the viscosity of the feed and the thickness of the boundary layer that improves the resistance to mass transfer [31].



Figure 6: Effect of feed concentration on the permeate flux of PVC membrane (TMP=1bar, feed flow =100mL/min)



Figure 7: Effect of feed concentration on the rejection of the hollow fiber membrane (TMP=1bar, feed flow =100mL/min)

5. Conclusion

The results explained that methyl green is removed with the PVC membrane, with the highest rejection coefficient value close to 75.2% of the membrane system, at neutral pH. This may be described because the separation by ultrafiltration membranes is not only due to the size of the molecular cutoff 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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