Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Dyes from Aqueous Solutions by Low Pressure Batch Ultrafiltration

Ruey-Shin Juang[a]; Ji-Feng Liang[a]; Jiann-Der Jiang[a]
[a] Department of Chemical Engineering, Yuan-Ze Institute of Technology Nei-Li, Taiwan, Republic of China

To cite this Article Juang, Ruey-Shin , Liang, Ji-Feng and Jiang, Jiann-Der(1993) 'Removal of Dyes from Aqueous Solutions by Low Pressure Batch Ultrafiltration', Separation Science and Technology, 28: 11, 2049 — 2059
To link to this Article: DOI: 10.1080/01496399308016733
URL: http://dx.doi.org/10.1080/01496399308016733

SEPARATION SCIENCE AND TECHNOLOGY, **28**(11&12), pp. 2049–2059, 1993

Removal of Dyes from Aqueous Solutions by Low Pressure Batch Ultrafiltration

RUEY-SHIN JUANG,* JI-FENG LIANG, and JIANN-DER JIANG
DEPARTMENT OF CHEMICAL ENGINEERING
YUAN-ZE INSTITUTE OF TECHNOLOGY
NEI-LI, TAOYUAN, 32026, TAIWAN, REPUBLIC OF CHINA

ABSTRACT

The use of a low pressure batch ultrafiltration method to separate dyes from aqueous solutions was investigated at 22°C. Several factors affecting the membrane performance, such as the hydraulic permeability and the rejection coefficient, were examined, including initial dye concentration, the operating pressure, as well as especially the membrane material and the ionic nature of dye molecules.

INTRODUCTION

The removal of hardly-degradable, water-soluble dyes by the conventional chemical (coagulation) or biological (activated sludge) methods was found to be inefficient (1–4). The need for more efficient treatment processes has directed the attention of many researchers to pressure-driven membrane techniques. It is necessary to ensure that the products will be nonabsorbable following ingestion for the removal of all low molecular-weight species as well. Ultrafiltration (UF) is an ideal way to achieve these goals by selection of a membrane with appropriate molecular weight retention characteristics (2, 3). Moreover, the unique ability to modify the selectivity of membranes and to choose the appropriate geometry of the membrane, module, and system configuration make UF not only a separation alternative but also a complement to processes such as adsorption, ion exchange, and reverse osmosis (5, 6).

Seven dye compounds (listed in Table 1) were used in this work. These dyes are generally classified as basic, acidic, and other. While basic dyes possess cationic properties originating from positively charged nitrogen

---

* To whom correspondence should be addressed.

TABLE 1
Characteristics of the Dye Compounds Used in This Study

Name of dye	Color index	pH	Molecular weight	Chemical classification	Ionic nature
Congo Red (CR)	22120	10.10	696.7	Bisazo (direct)	Anionic
Titan Yellow (TY)	19540	6.10	695.7	Monoazo (direct)	Anionic
Amido Black 10B (AB)	20470	6.32	616.5	bisazo (acidic)	Anionic
Indigo Carmine (IC)	73015	6.38	466.4	Indigoid (acidic)	Anionic
Methyl Orange (MO)	13025	5.80	327.3	Monoazo (acidic)	Anionic
Auramine (AM)	41000	9.10	303.8	Diphenylmethane (basic)	Cationic
Nigrosine (NS)	50420	6.10	—	Azine (acidic)	Anionic

or sulfur ions, all acidic and other dyes possess an anionic nature due to negatively charged sulfonate groups. In this regard, all dyes belonging to the last two classes have essentially the same ionic properties (7). It may be noted that basic dyes with positive charges are so named since they have an affinity to basic textile materials with net negative charges, while acidic dyes with negative charges are so named since they have an affinity to acidic textile materials with net positive charges (7).

At present, although many studies on the removal of dyes have been made by either batch (8–10) or continuous UF processes (2–4, 11, 12), the influence of the ionic nature of dye molecules has not been clarified. For example, Majewska-Nowak et al. (2, 3) found that the rejection of dye exceeds 90% for molecular weights greater than 700 $g \cdot mol^{-1}$ when using polysulfone membrane. Moreover, Yoshida et al. (8) studied the influence of chemical structure and other operating parameters, such as pressure, temperature, and solution pH, on the rejection of 28 different dyes.

On the other hand, Kukushkina et al. (9) studied the separation of azo dyes by using cellulose acetate membranes with average diameters ranging from 4.8 to 9.8 nm, and concluded that high separations of dye solutes are favored by the aggregation of dye solutes in the aqueous solution, which is facilitated by the sorption of dye molecules on cellulose acetate material. Although they found that the affinity of dye solutes to cellulose acetate material depends on the chemical nature of the dye molecules, they gave no further information on the effect of such an affinity. In addition, Zuk et al. (12) found that the aggregation of dye particles facilitated water recovery and the concentration of dyes using a polyacrylonitrile hollow-fiber.

As seen in the work of Matsuura et al. (13, 14) in the separation of various organic and inorganic solutes using cellulose acetate reverse osmosis membranes, the cellulose acetate membrane is basic and consequently should exhibit a stronger affinity to basic dyes than to acidic dyes. In this paper the effect of several factors, including the ionic nature of dye molecules and the membrane material, on membrane performance by low pressure batch UF was examined using Amicon Diaflo YM (slightly negative charged, i.e., basic in nature) and PM (slightly positive charged, i.e., acidic in nature) membranes (15).

EXPERIMENTAL

Apparatus and Membrane

All batch UF experiments were carried out in an Amican Model 8200 stirred cell. It had a maximum operating pressure of 0.53 MPa, an effective membrane area of 28.7 cm^2, and a cell volume of 200 cm^3. To reduce the concentration change in the retentate during UF, a reservoir with a volume of about 200 cm^3 was directly connected to the stirred cell. The cell stirrer speed was controlled by a magnetic motor on which the cell was placed. The stirring speed was fixed at 300 rpm to prevent the formation of a serious vortex in the cell. The applied pressure varied from 0.1 to 0.4 MPa gauge, and was controlled by nitrogen gas.

The membranes used in this study were the Amicon Diaflo hydrophilic YM10 and hydrophobic PM10 ultrafilters. They had the same molecular weight cutoff of 10,000, which corresponds to a mean membrane pore radius of 3.8 nm. The clean water fluxes (J_w) given by the manufacturer were 90–120 and 900–1800 L·m^{-2}·h^{-1}, respectively, at 0.39 MPa and 25°C after 5 minutes of operation. It should be noted that only membranes, whether YM or PM, with a J_w deviation smaller than 2% were used in this study. The tolerable operating pressures and temperatures for both ultrafilters were 0.47 MPa and 100°C. All experiments were performed at 22 ± 1°C.

Reagents and Procedure

Table 1 lists the dye compounds employed in this work, together with their chemical structure, Color Index, molecular weight, solution pH, and ionic nature. All dyes were supplied by Merck Co. The initial concentration of dye was changed from 25 to 300 g·m^{-3}.

The separation properties of the membranes were determined by measuring the rejection coefficient R, defined as (1–4, 8–12):

$$R = 1 - (C_p/C_f) \tag{1}$$

where C_p and C_f are the dye concentrations in the permeate and feed, respectively. For each run, the first 20 cm^3 of the permeate was discarded.

This corresponds to a volume ratio of permeate to feed of less than 0.05. The rejection coefficient was thus calculated by analyzing the following 20 cm^3 of the permeate because the permeate composition was found to be invariably during UF.

On the other hand, the transport properties of the membranes were determined by measuring the permeate flux of a dye solution (J_v) at a given pressure. In this case the first 20 cm^3 of the permeate was also discarded, and an average permeate flux was obtained by analyzing the following 100 cm^3 of the permeate. The hydraulic permeability L_p (in m^3·N^{-1}s^{-1}) was calculated from the following equation (1–3):

$$L_p = J_v/\Delta P \tag{2}$$

where ΔP is the pressure difference (MPa).

The pH values in the feed, retentate, and permeate were measured with a pH meter (Radiometer Model PHM82). The concentration of dye was analyzed with a UV-visible spectrophotometer (Hitachi Model U-3410) at each appropriate wavelength. The final concentration of dye in the retentate was also determined to check whether the mass balance was fulfilled or not. The clean water flux was measured both before and after UF of each sample to verify the absence of fouling phenomena.

RESULTS AND DISCUSSION

Effect of Molecular Weight of Dye on Membrane Performance

Figure 1 shows the effect of the molecular weight of dye on the rejection coefficient and hydraulic permeability of YM10 membranes. Evidently the rejection coefficient of a dye exceeds 99% for a molecular weight greater than 700 g·mol^{-1}. This is largely attributed to the fact that in aqueous solutions the direct dyes (TY and CR) tend to dissociate to colored anions and to form ionic micelles which are readily aggregatable (1, 8–10). In this case, the maximum sizes of the created dye aggregates can vary from 1 to 100 nm (9). Although the present results are in good agreement with those obtained by Majewska-Nowak et al. (1–3) using polysulfone membranes, such a comparison is groundless because the polymer material as well as the pore size and the pore size distribution of the membranes used are different.

It has also been reported that the rejection coefficient increases in the sequence from monoazo to triazo dyes, while with the same number of azo groups the rejection coefficient increases with the molecular weight of dyes (9). Such a tendency, however, is somewhat inconsistent with the present findings (dye AB versus TY). The predominant factor is still

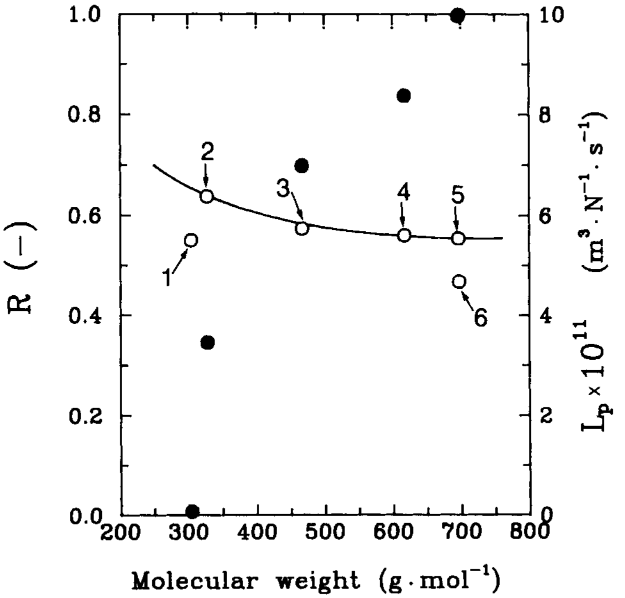

FIG. 1 Effect of the molecular weight of dye on the rejection coefficient (●) and hydraulic permeability (○) of YM10 membrane. Dye concentration = 100 g·m^{-3}, ΔP = 0.4 MPa. Dye: (1) AM, (2) MO, (3) IC, (4) AB, (5) TY, and (6) CR.

believed to be the aggregatability of dye molecules in the aqueous solutions because the molecular weight of dyes is comparable.

Of the dyes investigated in this work, nigrosine (NS) is not shown in this figure since the molecular weight is unavailable. The measured values of R and L_p are 0.99 and 5.64 × 10^{-11} m^3·N^{-1}·s^{-1}, respectively, under the described conditions. Presumably, the molecular weight is more than 700 g·mol^{-1} on the basis of the very high rejection coefficient.

As shown in Fig. 1, the hydraulic permeability gradually decreases with the increasing molecular weight of dyes, except for dyes AM and CR. The smaller values of L_p for dyes with higher molecular weights can be explained by the high retention of these dyes by membranes (1). Hence, the dye concentration in the solution layer at the membrane surface (which is attributed to concentration polarization) is much higher than that in an analogous layer formed during UF of low-molecular-weight dyes (which, to a considerable degree, passed through the membranes). For the direct dye CR, it may be inferred that the aggregatability is higher than for another direct dye TY as reflected by the solution pH (7). The dye AM will be further discussed in the following section.

Effect of Membrane Material on Membrane Performance

From Table 2 it is clear that the rejection coefficient of acidic dye AB by the YM10 membrane is higher than that by the PM10 membrane, which is consistent with the basic nature of the YM membrane and the acidic nature of the PM membrane (15). As also indicated previously in the separation of dyes by reverse osmosis (7), the stronger the affinity of a membrane material to dyes (cellulose acetate material versus basic dye or aromatic polyamidohydrzide material versus acidic and other dyes), the lower the rejection coefficient of the dyes. This can be interpreted by the higher equilibrium distribution constant obtained for cellulose acetate membrane material when the dye compounds are more positively charged (basic dyes) (7). It is worth noting that this constant is defined as the ratio of solute concentration of the interfacial solution to that of the bulk solution phase, which is calculated from chromatography data on the retention volume while the dye solution stream is injected through the column packed with membrane material powder.

On the other hand, the rejection coefficients of basic dye AM by both membranes are negligibly small but nearly equal. This is mainly due to the very low molecular weight of this dye (303.8 $g \cdot mol^{-1}$). In this regard, the influence of the ionic nature of this dye on the rejection coefficient is accordingly not as evident.

Interestingly, as shown in Table 2, the permeate flux ratio J_v/J_w of the YM10 membrane due to the presence of acidic dye AB is larger than that of the PM10 membrane, while the trend is reversed with respect to the presence of basic dye AM. This can be explained by the strong affinity between the PM membrane and acidic dyes or between the YM membrane and basic dyes. This means that in these cases, concentration polarization occurs more readily (due to the higher adsorptivity of membrane material

TABLE 2
Comparison of the Rejection Coefficient and Hydraulic Permeability of Dyes AB and AM by YM10 and PM10 Membranes[a]

Dye	Color index	YM10		PM10	
		R	J_v/J_w	R	J_v/J_w
AB (acidic dye)	20470	0.87	0.84	0.48	0.70
AM (basic dye)	41000	0.02	0.78	0.01	0.98

[a] Operating pressure = 0.2 MPa, dye concentration = 100 $g \cdot m^{-3}$, and temperature = 22°C. In this case the clean water fluxes J_w for YM10 and PM10 were found to be 53.2 and 480.1 $L \cdot m^{-2} \cdot h^{-1}$, respectively, after 30 minutes of operation.

to dye molecules) at the membrane surface (1, 7, 9, 15, 16). Practically, it is also observed from experiments that coloration of the membranes is serious for dyes with stronger affinities. Consequently, the hydraulic permeability decreases when the dye concentration increases, since the degree of concentration polarization also increases.

Effect of Initial Dye Concentration on Membrane Performance

The relationship between the rejection coefficient and the initial concentration of dye in the aqueous solution is shown in Fig. 2. Apparently the rejection coefficients of dyes AB and IC by the YM10 membrane decrease with increasing dye concentration. This effect becomes more pronounced for dyes with a lower molecular weight (IC). The decrease of the rejection coefficient with an increase in dye concentration can be explained by assuming the sorptive–capillary hypothesis (1, 9), which is based on the statement that a thin layer of solvent (water) is formed on the surface of a membrane immersed in the aqueous solution. The thickness of the solvent layer decreases with increasing dye concentration. The number of

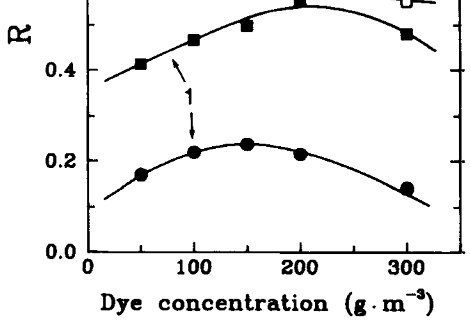

FIG. 2 Dependence of the rejection coefficient on the initial concentration of dye in the aqueous solution by YM (open symbols) and PM (filled symbols) membranes. Dye: (1) AB, (2) IC. ΔP = 0.1 (▲), 0.2 (■, ◇, ○), 0.3 (●), and 0.4 MPa (△, □).

pores accessible to the dye particles increases, leading to a decrease of the rejection coefficient.

The weak dependence of the rejection coefficient of dye AB by the YM10 membrane and the dye concentration becomes clear if we assume that particles of dye have a much greater size than the pore diameters in the membrane. This assumption is supported by the high rejection coefficient (>80%).

On the other hand, the rejection coefficient of acidic dye AB by the PM10 membrane increases with increasing dye concentration up to a value of about 150 g·m^{-3}, thereafter it decreases. This effect is slightly pronounced at higher pressures. Since the particles of this bisazo dye can aggregate in aqueous solutions (10), the increase in the size of penetrating particles (due to dye aggregates) increases the rejection coefficient in the initial range of concentrations. Moreover, the layer of bound water on the membrane is thick in this case, the penetration of dye molecules by diffusion through the membrane is not large, and the capillary flow of water under the influence of the pressure gradient is dominant. At higher dye concentrations the thickness of the water layer at the membrane surface decreases, and membrane rejection is worse (1).

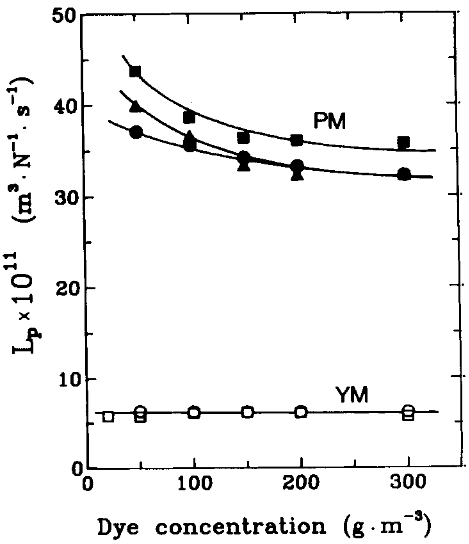

FIG. 3 Dependence of the hydraulic permeability and the initial concentration of dye AB in the aqueous solution by YM (open symbols) and PM (filled symbols) membranes. ΔP = 0.1 (■), 0.2 (▲, ○), 0.3 (●), and 0.4 MPa (□).

Figure 3 illustrates the dependence of hydraulic permeability on the initial concentration of dye AB in the aqueous solution. It was found that the hydraulic permeability for the YM10 membrane is almost independent of dye concentration, but for the PM10 membrane it decreases slightly with increasing dye concentration. It is worth noting that the hydraulic permeability for dye IC by the YM10 membrane is nearly the same as that for dye AB (not shown) in the concentration range studied.

It has been reported that the hydraulic permeability to solutions of most of the dyes varies little in the concentration range 2–500 $g \cdot m^{-3}$, but for solutions of equal concentration, the hydraulic permeability depends on the type of dye (9). The decrease of hydraulic permeability with increasing dye concentration for a PM membrane is due to an increase in the degree of concentration polarization, since dye AB has a strong affinity for this membrane material.

Effect of Operating Pressure on Membrane Performance

Figure 4 shows the dependence of hydraulic permeability on operating pressure. It is also observed that, under the conditions studied, the hydraulic permeability of the YM10 membrane is almost independent of the

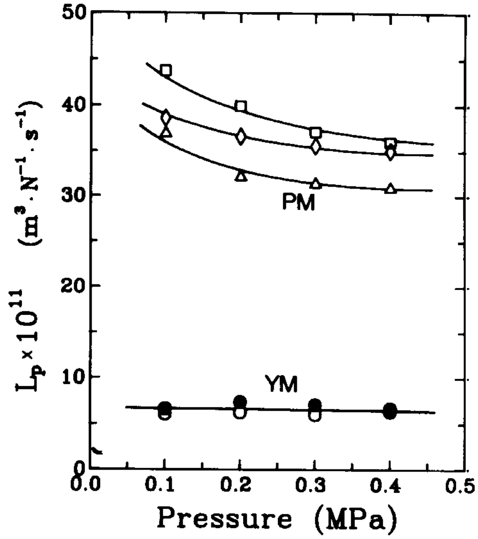

FIG. 4 Dependence of the hydraulic permeability on the operating pressure. Dye AB (open symbols) and IC (filled symbols). Dye concentration = 50 (□), 100 (◇), and 200 $g \cdot m^{-3}$ (△, ○, ●).

operating pressure. However, for the PM10 membrane it decreases with increasing operating pressure; this effect also depends on the dye concentration. The causes of the differences of membrane performance between YM and PM are the same as described above.

Our work shows that an increase in the operating pressure decreases the rejection coefficient of dyes AB and IC (not shown). This effect also becomes more pronounced for membranes with a higher permeate flux (PM10) and slightly pronounced for a dye with a lower molecular weight (IC). In the former case, increasing pressure is followed by an increase in the permeate flux of the membrane. Accordingly, the dye concentration in the solution layer at the membrane surface increases and the rejection coefficient decreases. For the high-molecular-weight dye AB (bisazo) the pressure has a relatively slight effect on the extent of rejection (1) because the aggregates of this dye may be greater or comparable in size to the pore diameters in the membrane.

CONCLUSIONS

The removal of the dyes from aqueous solutions by the low pressure batch UF method has been studied at 22°C. The following results are obtained.

1. The rejection coefficient of dye by YM10 membrane exceeds 99% for molecular weights greater than 700 $g \cdot mol^{-1}$, which is due to the aggregability of these dyes in aqueous solutions. The hydraulic permeability of dyes decreases with increasing molecular weight, especially for dyes with higher aggregabilities.
2. The affinity of membrane materials to dye molecules plays an important role in the membrane performance of the UF of dye solutions. In general, the stronger the affinity of membrane materials to dyes (YM versus basic dyes or PM versus acidic and other dyes), the lower the rejection coefficient of dyes and the hydraulic permeability of membranes, as shown in Table 2.
3. The dependence of the rejection coefficient and the dye concentration can be satisfactorily explained by assuming the sorptive–capillary hypothesis.

NOTATIONS

C_f	dye concentration in the feed ($g \cdot m^{-3}$)
C_p	dye concentration in the permeate ($g \cdot m^{-3}$)
J_v	permeate flux in the presence of dye ($L \cdot m^{-2} \cdot h^{-1}$)

J_w clean water flux ($L \cdot m^{-2} \cdot h^{-1}$)
L_p hydraulic permeability defined in Eq. (2) ($m^3 \cdot N^{-1} s^{-1}$)
ΔP pressure difference (MPa)
R rejection coefficient defined in Eq. (1) (—)

ACKNOWLEDGMENT

This work was supported by the ROC National Science Council under Grant NSC82-0402-E155-025, which is greatly appreciated.

REFERENCES

1. K. Majewska-Nowak and T. Winnicki, *Environ. Prot. Eng.*, *9*(4), 81 (1983).
2. K. Majewska-Nowak and T. Winnicki, *Desalination*, *60*, 59 (1986).
3. K. Majewska-Nowak, T. Winnicki, and J. Wisniewski, *Ibid.*, *71*, 127 (1989).
4. J. C. Watters, E. Biagtan, and O. Senler, *Sep. Sci. Technol.*, *26*(10&11), 1295 (1991).
5. I. Bemberis and K. Neely, *Chem. Eng. Prog.*, p. 29 (November 1986).
6. A. S. Jonsson and G. Tragardh, *Desalination*, *77*(1/2/3), 135 (1990).
7. T. Liu, T. Matsuura, and S. Sourirajan, *Ind. Eng. Chem., Prod. Res. Dev.*, *22*(1), 77 (1983).
8. T. Yoshida, M. Asai, Y. Uedo, and J. Koshitani, *Maku*, *4*(6), 407 (1979).
9. L. Y. Kukushkina, E. V. Migalatil, A. F. Nikiforov, and V. V. Pushkarev, *Zh. Prikl. Khim.*, *50*(8), 1847 (1977).
10. T. Hori, M. Mizuno, and T. Shimizu, *Colloid Polym. Sci.*, *258*(9), 1070 (1980).
11. A. R. Cooper and R. G. Booth, *J. Appl. Polym. Sci.*, *23*, 1373 (1979).
12. J. S. Zuk, M. Rucka, and J. Rak, *Chem. Eng. Commun.*, *19*, 67 (1982).
13. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, *15*, 2905 (1971).
14. T. Matsuura, L. Pageau, and S. Sourirajan, *Ibid.*, *19*, 179 (1975).
15. R. Singh, *Chem. Eng. Prog.*, p. 59 (June 1989).
16. G. B. van den Berg and C. A. Smolders, *Desalination*, *77*(1/2/3), 101 (1990).

Received by editor December 14, 1992