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The effect of operating conditions on the retention of Toluidine blue by polyelectrolyte-enhanced ultrafiltration

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ABSTRACT

In the present work, we study the effect of experimental conditions on the performance of polyelectrolyte-enhanced ultrafiltration for the removal of Toluidine blue from aqueous solution. The dye solution was processed by ultrafiltration using a regenerate cellulose membrane with pore sizes small enough to block the passage of the polymer and then the complexed dye ions. The experiments showed that retentions as high as 99% and 97% were obtained for PAA and $PANH_4$, respectively, due to the strong electrostatic interaction between anionic polyelectrolytes and cationic dye. The increase of retention was linked to the complexation of the dye by polyelectrolyte while the decrease of the permeate flux was attributed to the accumulated macromolecular complex near the membrane.

Keywords: Poly (acrylic acid); Toluidine blue; Polyelectrolyte-enhanced ultrafiltration; Dye removal

1. Introduction

Dye containing waste stream is one of the major toxic industrial waste. Various types of dyes are used in the process industries like textile, pulp and paper, paints, etc. Several techniques for removal of dye from wastewater, i.e. coagulation/flocculation [1], biological treatment [2], advance oxidation processes [3], adsorption [4,5], and membrane process are the most studied technologies. Among membrane separation technologies, reverse osmosis [6] and nanofiltration (NF) [7] are the best available techniques for the separation of several commercial dyes. However, their major disadvantage is the decline in permeate flux due to adsorption of organic compounds to the surface and pores of the membrane [8]. The use of UF instead of OI or NF reduces the energy cost while the use of polyelectrolyte enhances the retention of the dye by ultrafiltration**.** Polyelectrolyte-enhanced ultrafiltration (PEUF) has been shown to be a promising method for removal of heavy metals [9], anions [10], and dyes [11,12] from aqueous solutions. In PEUF process, contaminant ions are first bound to water-soluble polymer to form macromolecular complex and then retained and concentrated by ultrafiltration membrane. A permeate stream with a low concentration of the target ion is finally produced.

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In the present study, an attempt is made to remove Toluidine blue, a cationic dye, from aqueous solution by PEUF using two polyelectrolytes, poly (acrylic acid) (PAA), and poly (ammonium acrylate) ($PANH_4$). The retention rate and permeate flux were investigated as a function of some parameters such as transmembrane pressure, polyelectrolyte, and NaCl concentrations and pH of solution.

2. Experimental

2.1. Chemicals

The cationic dye Toluidine blue (TB^+) ($C_{15}H_{16}ClN_3S$, $M_W = 305.83$ g mol^{-1}) was purchased from Fluka. Two polyelectrolytes: poly (acrylic acid) (PAA) ($M_W = 100$g mol^{-1}, 35wt%) and poly (ammonium acrylate) ($PANH_4$) ($M_W = 30$ g mol^{-1}, 40wt%) were used in this study. PAA was supplied by Sigma–Aldrich and $PANH_4$ was synthesized in laboratory by radical polymerization of ammonium acrylate monomer [13]. The chemical structures of the three compounds are shown in Fig. 1(a)–(c). Chloride acid, sodium chloride, and sodium hydroxide were provided by Sigma–Aldrich. All chemicals were used without further purification. Distilled water was used for solution preparation.

2.2. Ultrafiltration process and analysis

Ultrafiltration experiments were performed using an Amicon stirred batch cell (model 8050) with effective volume of 50 mL equipped with 10 kDa MWCO regenerated cellulose membrane (Millipore) and connected to a nitrogen-pressurized solution reservoir (Fig. 2). Before use, the virgin membrane was soaked in deionised water for 24 h in order to eliminate preservative products and then the membrane was compacted for 3 h under 5 bar pressure. The value of water permeability Lp obtained from the slope of the flux vs. pressure (Darcy's law, $J = Lp\Delta p$) is found to be 107.28 L h^{-1} m^{-2}. This value was systematically checked after each experiment to ensure that there was no flux decline, otherwise the cleaning procedure would pursue until the reference flux were obtained.

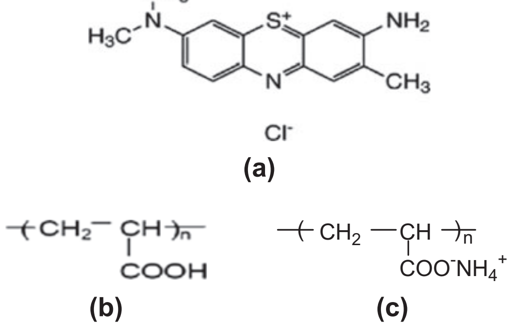

Fig. 1. Molecular structure of (a) Toluidine blue; (b) poly (acrylic acid); and (c) poly (ammonium acrylate).

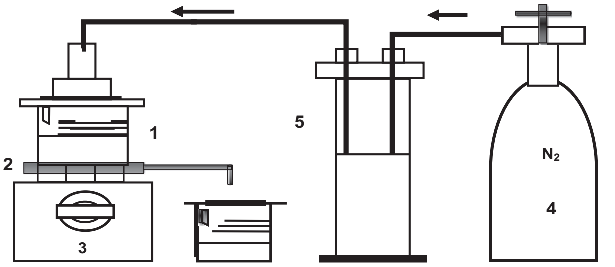

Fig. 2. Ultrafiltration equipment: (1) filtration cell; (2) ultrafiltration membrane; (3) magnetic stirrer; (4) pressure source; (5) reservoir.

The stirred cell and reservoir were then filled with the polyelectrolyte–dye solution and a selected operating pressure was applied. After nearly 30 min a steady state was reached and a permeate of 10 mL was collected and analyzed. After each run, the membrane was thoroughly washed by distilled water and thereafter the water permeability value was checked. All experiments were conducted at room temperature around 25 ± 1°C.

To evaluate the efficiency of ultrafiltration in removing dye, two parameters permeate flux (Jv) and retention rate (R), are determined according to the following equations:

$$J_p = \frac{V}{Sxt} \tag{1}$$

$$R = \left(1 - \frac{C_p}{C_i}\right) \times 100 \tag{2}$$

where R is the retention rate of dye, C_p is the concentration dye in the permeate (mol L^{-1}), C_i is the initial concentration of the dye in the feed solution (mol L^{-1}), J_p is the permeate flux (L h^{-1} m^{-2}), V is the volume of permeate (L), t is the time difference (s), and S is the effective membrane area (m^2).

The concentration of TB in the permeate C_p was measured by a Perkin Elmer Lambda 25 spectrophotometer at 623 nm using a matched pair of glass cuvettes with 1 cm optical lengths.

3. Results and discussion

3.1. Effect of the polyelectrolyte addition on dye removal

The TB retention with and without polyelectrolyte is presented in Fig. 3(a) for different dye concentrations and at 2 bar transmembrane pressure using 4×10^{-4} mol L^{-1} of both polyelectrolytes. We observed from the figure that the retention of TB is negligible in the absence of polyelectrolyte and it is about 11%. Since the TB molecules are much smaller than the membrane pores the retention could be attributed to the adsorption of dye at the surface or in the pores of membrane. In the presence of polyelectrolyte, the retention has been significantly increased to 99% in the case of PAA, and to 97% in the case of $PANH_4$. This suggests that complexes were formed due to binding of cationic TB molecules on anionic polymer through electrostatic interaction resulting in the enhancement of the ultrafiltration process.

The variation of the permeate flux as a function of operation time, with and without polyelectrolyte, is shown in Fig. 3(b). Lower permeate flux is observed during ultrafiltration of dye with polyelectrolyte than that without polyelectrolyte. The flux decline during UF of polyelectrolyte solutions was caused by the accumulation of polymeric molecules at the membrane surface which leads to an increase of total filtration resistance against the solvent flux through the membrane. The flux of TB dye solution in the presence of PAA was higher compared to that in presence of $PANH_4$. This may be related to the effect of the molecular weight of each polymer itself where PAA has higher molecular weight (M_W= 100 g mol^{-1}) compared to $PANH_4$ (M_W= 30 g mol^{-1}).

3.2. Stoichiometry and binding constant of polyelectrolyte–dye complexes

The UV-visible spectroscopy is an appropriate method that permits the determination of stoichiometry and constant binding of complexes. The UV-visible spectroscopy study shows (Fig. 4) that maximum wavelength λ_{max} of Toluidine blue in aqueous solution (623 nm) shifted to 550 and 566 nm in the presence of, respectively, $PANH_4$ and PAA. The appearance of blue shifted bands was attributed to the formation of dye H-aggregates [14] which were induced by the complexes formed between cationic dye and polyelectrolytes [15].

The stoichiometry of the polyelectrolyte–dye complexes was determined using the ratio method [16]: a plot of A_{623}/A_{550} and of A_{623}/A_{566} vs. the polyelectrolyte/dye ratio (P/D) was made, respectively, for

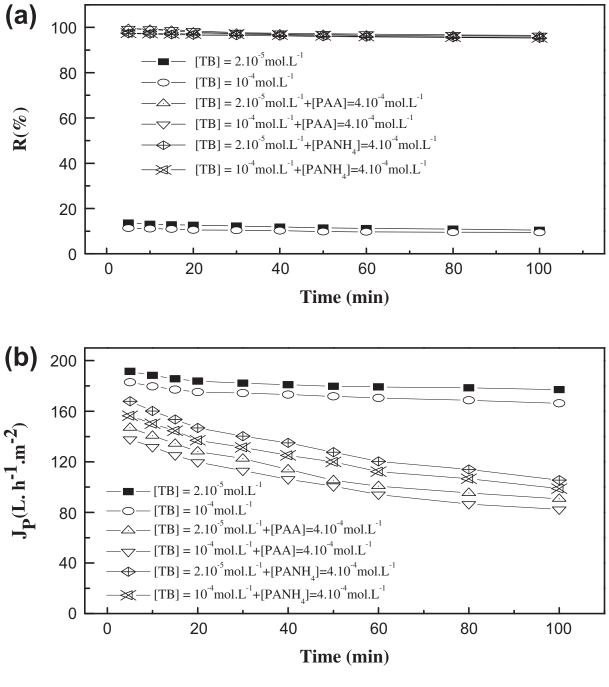

Fig. 3. Variation of (a) retention rate and (b) permeate flux of TB with time at different feed TB concentrations in the absence and in the presence of PAA and $PANH_4$ and Δp = 2 bar.

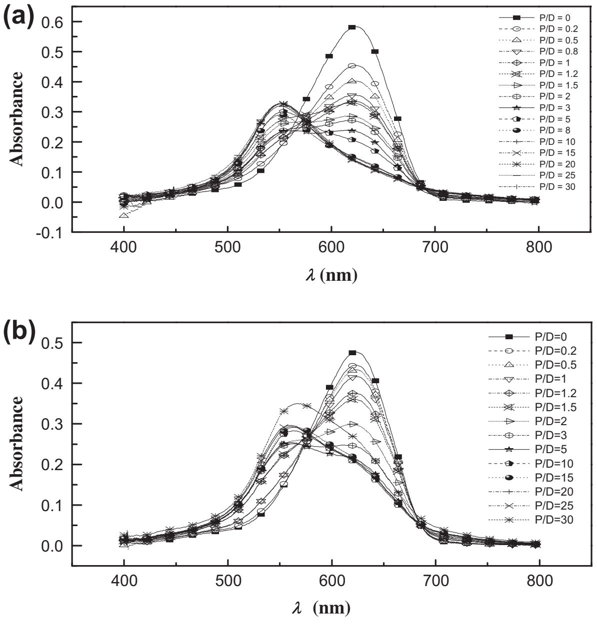

Fig. 4. Absorption spectra of TB in the presence of anionic polyelectrolyte at various P/D ratios, (a) poly (ammonium acrylate) and (b) poly (acrylic acid).

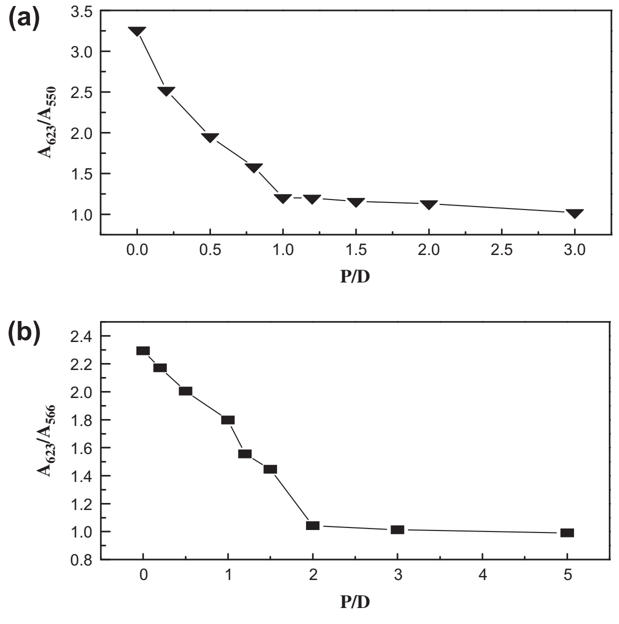

Fig. 5. Stoichiometry of (a) TB–PANH$_4$ complex and (b) TB–PAA complex.

TB–PANH$_4$ and TB–PAA system as shown in Fig. 5. According to this figure, plots of A_{623}/A_{550} and A_{623}/A_{566} decreased with the increase in P/D. The stoichiometry of TB–PANH$_4$ complex was found to be 1:1, which indicates that the binding is at adjacent anionic sites. This stoichiometry indicates that every potential anionic site of the polymer was associated with the dye cation. This result was similar to that reported for interaction between Toluidine blue and cyclodextrin [17]. In the case of TB–PAA complex the stoichiometry is 2:1, which indicates that the binding take place on alternate anionic sites. Similar results were reported in the case of binding of pinacyanol chloride on poly (methacrylic acid) [18].

The binding constant of dye–polymer complex can be determined using the Rose–Drago equation [19]:

$$\frac{C_D C_{PE}}{A - A_0} = \frac{1}{K_c L(\varepsilon_{DP} - \varepsilon_D)} + \frac{C_{PE}}{L(\varepsilon_{DP} - \varepsilon_D)} \quad (3)$$

where A is the absorbance of the complex measured at 550 nm using different set of solutions containing varying amounts of polyelectrolyte solution (C_{PE}) in a fixed dye concentration (C_D), L is the optical path length of the solution, ε_D and ε_{DP} are the respective molar extinction of TB and TB bound to polymer, and K_c is the binding constant. The value of binding constant K_c was then obtained from the slope and intercept of the plot of $C_D C_{PE}/(A - A_0)$ against C_{PE} was shown in Fig. 6. The value of the binding constant of TB–PAA complex is found to be 4,358 dm^3 mol^{-1} [20] and it is higher compared to that of TB–PANH$_4$ complex which is 3,878 dm^3 mol^{-1}.

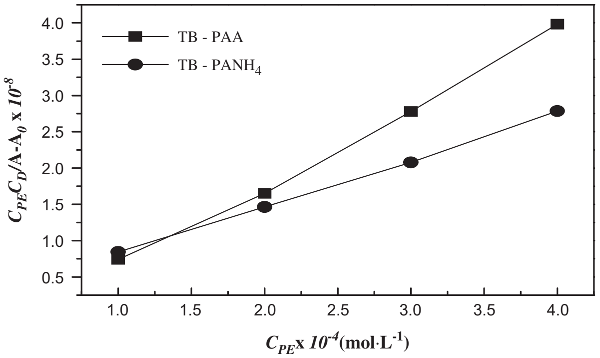

Fig. 6. Plots of $C_D{\cdot}C_{PE}/A - A_0$ against C_{PE} for both complexes TB–PAA and TB–PANH$_4$.

3.3. Effect of transmembrane pressure

The effect of transmembrane pressure on the TB retention and permeate flux was studied with Δp ranging from 0.6 to 2.6 bars. The dye and polyelectrolyte concentrations were fixed at 10^{-4} and 4×10^{-4} mol L^{-1}, respectively. From Fig. 7(a), it is observed that the retention of TB dye remains independent of pressure. This observation indicates that the retention of dye by PEUF is solely favored by the complexation of dye molecules by polyelectrolyte. Similar behavior is observed in the literature [21]. On the other hand, Fig. 7(b) shows that the permeate flux increases with pressure Δp ranging from 0.6 to 2.0 bar. With increase in pressure, the effective driving force for the solvent transport is higher for a fixed feed concentration [22].

3.4. Effect of polyelectrolyte concentration

The effect of polyelectrolyte concentration, on the TB retention and permeate flux was studied at fixed dye concentration of 10^{-4} mol L^{-1}, with polyelectrolyte concentration ranging from 10^{-4} to 10^{-3} mol L^{-1} as shown in Fig. 8(a).

When the anionic polyelectrolyte, PAA and PANH$_4$, were added in the TB solution, the decolorization increased slightly and then reached a limiting value of 99% in the case of PAA and 97% in the case of PANH$_4$. This suggests that, electrostatic interaction is considered to be important in the enhancement of the ultrafiltration process. Increasing the concentration of polyelectrolyte increases the amount of dye complexed and as a consequence increases TB retention. Tan et al. [11] investigated the decolorization of three cationic

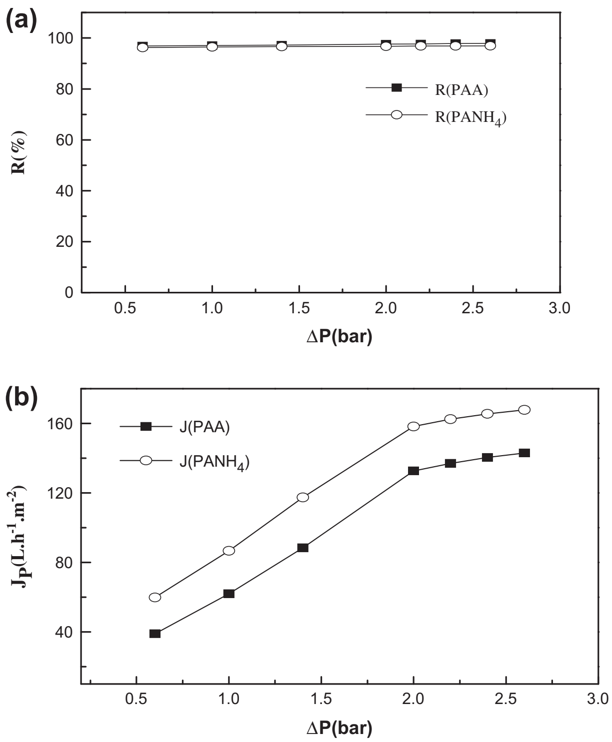

Fig. 7. Effect of transmembrane pressure on (a) TB retention and (b) permeate flux of TB at polyelectrolyte concentration of 4×10^{-4} mol L^{-1}. Feed TB concentration is 10^{-4} mol L^{-1}, Δp ranging from 0.6 to 2.6 bars.

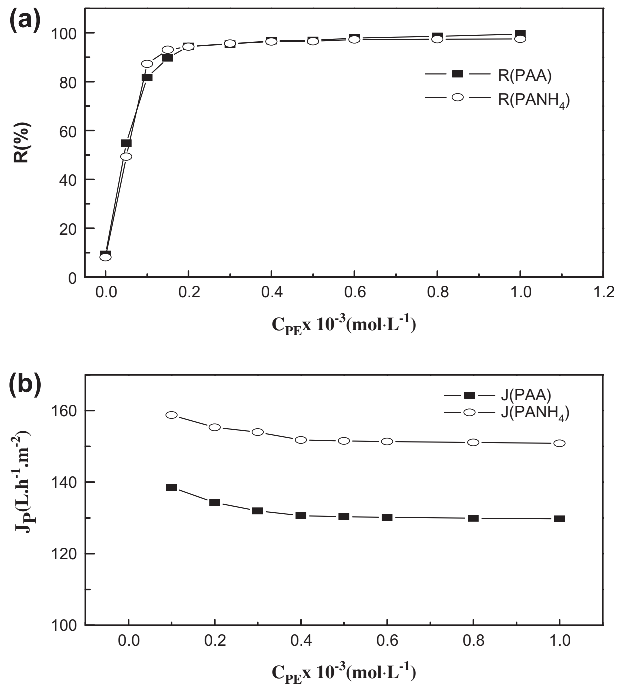

Fig. 8. Variation of (a) TB retention and (b) permeate flux as a function of feed polyelectrolyte concentration. Feed TB concentration is 10^{-4} mol L^{-1}, Δp = 2 bar.

dye solutions in the presence of different polymers and concluded that only anionic polymer poly (sodium-4-styrenesulfonate) (PSS) was suitable for the decolorization of cationic dyes from aqueous solutions. Thereafter, 0.4 mM remains constant. The flux decreases from 138.549 to 129.723 L h^{-1} m^{-2} in the case of PAA and from 158.749 to 150.858 L h^{-1} m^{-2} in the case of $PANH_4$. This result may be attributed to the fact that by adding PAA and $PANH_4$ polyelectrolytes, TB–PAA and TB–$PANH_4$ complexes were formed. This generates a deposited layer on the membrane surface and consequently increases the resistance against the solvent flux through the membrane.

3.5. Effect of salt concentration

Wastewaters from textile-manufacturing contain various auxiliary compounds such as salts, acids, and alkalis that may affect PEUF performance. Here, we limited the study to the effect NaCl chosen as salt model. The effect of added NaCl concentration on the retention rate of TB in the presence of polyelectrolyte was studied at fixed dye and polyelectrolyte concentration equal to 10^{-4} mol L^{-1} and 4×10^{-4} mol L^{-1}, respectively, with NaCl concentration ranged from 10^{-3} to 0.5 mol L^{-1} (Fig. 9(a)) shows that the retention of TB decreases upon increasing the NaCl concentration up to 0.1 mol L^{-1} for both polyelectrolyte (PAA and PA NH_4). At NaCl concentration above 0.1 mol L^{-1}, the retention of TB reaches constant values equal to 67 and 63% for PAA and $PANH_4$, respectively. The addition of salt is likely to reduce the electrostatic interaction between the dye molecule and polyelectrolyte and as a result the unbound dyes molecules pass through the ultrafiltration membrane leading to poor retention. In another way when NaCl concentration increases, the Na^+ ions progressively replace TB^+ dye, but beyond 0.1 mol L^{-1} of NaCl equilibrium is reached between the two cations and polyelectrolyte counter-ions.

Fig. 9(b) depicts the effect of salt concentration on the permeate flux**.** It can be seen that the permeate flux increased slightly with increasing NaCl concentrations for both polyelectrolyte. The increase of the flux is about 9.07 and 4.85% in presence of PAA and $PANH_4$, respectively.

3.6. Effect of pH on TB removal

The pH value may affect the binding of TB on polyelectrolyte. The pH of the dye solutions was

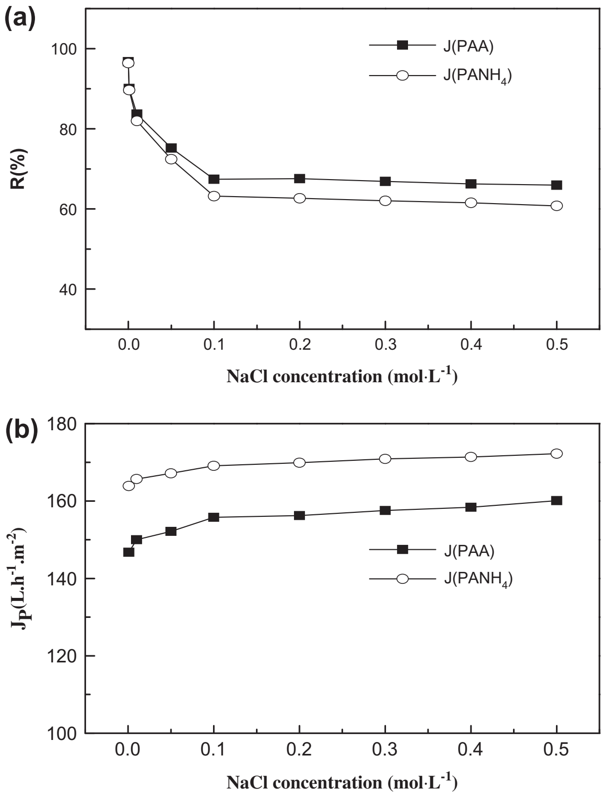

Fig. 9. Effect of NaCl concentration on (a) TB retention and (b) permeate flux. Concentrations of TB and polyelectrolytes are 10^{-4} mol L^{-1} and 4×10^{-4} mol L^{-1}, respectively, Δp = 2 bar.

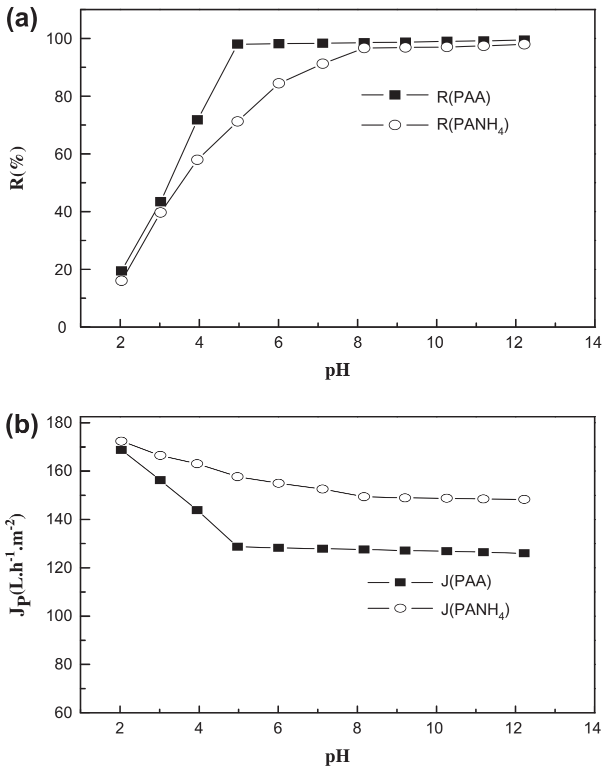

Fig. 10. Effect of pH on (a) TB retention and (b) permeate flux. Concentrations of TB and polyelectrolytes are 10^{-4} mol L^{-1} and 4×10^{-4} mol L^{-1}, respectively, Δp = 2 bar.

varied from 2 to 12 by adding chloride acid or sodium hydroxide. UF experiments were conducted at dye and polyelectrolyte concentrations of 10^{-4} and 4×10^{-4} mol L^{-1}, respectively. We observed from Fig. 10(a) a sharp increase of dye retention when pH increases from 2 to 5 for PAA and from 2 to 8 for $PANH_4$ and, thereafter, the dye retention reach a plateau at 98% and 97% for PAA and $PANH_4$, respectively.

At lower pH, in the case of poly (acrylic acid), the hydrogen ion concentration increases, dissociation of the dye, and the COOH group of PAA are prevented which is responsible for lower retention. Since, the pKa value of PAA is in the acidic range, there is complete retention of the dye at the neutral pH. The sharp transition of dye retention takes place when pH is increased from 2 to 5, which is also observed in another study [23]. The dissociation of the polyelectrolyte ($PANH_4$) reaches maximum at pH greater than 8. As the solution alkalinity increases, the ammonium groups detach from the amide functional form and forms ammonium hydroxide in the solution resulting in an increase in the dissociation of the polymer. Similar behavior was also observed in the case of removal of safranin T with $PANH_4$ [24].

The effect of pH on the flux permeate is also determined and depicted in Fig. 10(b). From this figure, it is observed that the flux in an opposite trend to the retention decreased when pH increased from 2 to 5 in the case of PAA and from 2 to 8 in the case of $PANH_4$. This can be attributed to the change of polyelectrolyte conformation from linear to globular as a result of neutralization of polymer charge by cationic dye. This polymer configuration can produce a fouling phenomenon by pore blocking, which caused the observed decrease in permeate flux [25].

4. Conclusion

The study of removal of TB using polyelectrolyte-enhanced ultrafiltration has been performed using a frontal ultrafiltration cell demonstrated the potentiality of this method. The PEUF experiments showed that high-dye retention of 99% in the case of PAA and 97% in the case of $PANH_4$ were obtained. This was due to the strong electrostatic interaction between TB and anionic polyelectrolytes. The complex dye–polyelectrolyte formed were 2:1 and 1.1 for PAA and $PANH_4$, respectively. The decolorization of TB solutions depends on the ionic strength and the pH of the feed solution for both polyelectrolytes. The optimum TB retention was obtained at pH 5 for PAA and at pH 8 for $PANH_4$. This study was conducted on model solutions. As perspective of this work, an industrial application in textile dyes can be considered.

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