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# Removal of dyes from wastewater using polyelectrolyte enhanced ultrafiltration (PEUF)

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ABSTRACT

Polyelectrolyte-based separation of toxic dyes is studied to estimate the potential of polyelectroyte enhanced ultrafiltration (PEUF) using poly(ammonium-acrylate) as anionic polymer. PEUF experiments are conducted to study the retention characteristics of two model dyes (Safranin T (ST) and Eriochrome Blue Black R (EBBR) in the continuous cross flow system. Effects of the operating conditions, e.g., transmembrane pressure, feed polyelectrolyte concentration, feed dye concentration, ionic strength and pH on the permeate flux profile and observed retention have been investigated. The results show that the highest rejection for ST and EBBR dyes are 99% and 90% respectively. The enhancement is primarily due to the formation of complexes between the anionic polymer and dye molecules. The retention of ST decreases with ionic strength. High retention was obtained at pH range 4–10 in the case of ST; this effect was attributed to the increase of electrostatic interaction. The ionic strength and pH have no effect on the removal of EBBR.

*Keywords*: Safranin T; Eriochrome Blue Black R; Polyelectrolyte; Ultrafiltration

## 1. Introduction

Many industries, such as textile, paper and plastics use dyes in order to colour their products and also consume substantial volumes of water. The effluent coming out from these industries contains toxic and potentially carcinogenic dyes, which causes many environmental problems. Consequently, it is important to remove these pollutants from wastewater before their final disposal [1–3].

Several wastewater treatment technologies have been applied to colour removal, including physical, chemical and biological process [2,4–7]. Biological methods is the most efficient and economic way of reducing the environmental impact of the industrial effluents containing organic pollutants. However, dyed wastewaters cannot be readily degraded by the conventional biological processes, because the structures of most commercial dye compounds are generally very complex and many dyes are non biodegradable [8,9]. On the other hand, the physical methods such as flocculation and precipitation are expensive, difficult for adsorbent regeneration and do not degrade the pollutants. Wastewaters can be effectively removed by wet oxidation [10], electrochemical [11], ozonization and photocatalytic methods [12]. Electrochemical treatment has been successfully tested to treat various industrial wastewaters. The most essential disadvantages of this technique are the large amount of sludge and the low efficiency with respect to some dyes. Therefore, the treatment systems combined with physical, biological and chemical methods become inefficient for the effective treatment of industrial textile wastewater due

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to the variation of wastewater characteristics, besides the costs of these methods are relatively high.

Membrane-based separation processes are becoming attractive for the separation of coloured effluent containing various types of dyes. Processes involving reverse osmosis (RO) and nanofiltration (NF) are already recognized as the best available techniques for several commercial dyes. However, permeability of these membranes is low and thus requires high operating pressure [3]. Therefore, microfiltration (MF) and ultrafiltration (UF) membranes are capable of providing high permeability and the operating pressure requirement is low compared to RO and NF, but not effective to retain the contaminants with small molecules such as dyes. It has been reported that ultrafiltration combined with other physical and chemical processes could be effectively used for the removal of dyes from aqueous solutions [13–16]. There are two widely used separation techniques: micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF). MEUF and PEUF combine ultrafiltration with the presence of water-soluble surfactants and polymers, respectively. In PEUF the macromolecular ligands seem more advantageous since they have a relatively high binding capacity. PEUF is the combination of two phenomena, binding of dyes to a water-soluble natural or synthetic polyelectrolyte, and ultrafiltration. Since the pore size of ultrafiltration membranes is not suitable to separate dyes, water-soluble polymers are used to bind the dyes to form macromolecular complexes rejected by ultrafiltration. PEUF is expected to provide enough permeation flux with high efficiency.

Polyelectrolytes are adsorbed on oppositely charged interfaces, which is a very straightforward and convenient method to create thin layers with defined functionality [15]. The polyelectrolyte functionalization of the inorganic surface could be a simple and suitable method for the surface modified adsorbent and is suggested to be used for the effective removal of acid dye from aqueous solutions. The binding behaviour and stoichiometry depend on the nature of both dyes and polyelectrolytes and cannot be generalized [17].

Recently, Tao et al. [18] reported a novel route for the economic and efficient treatment of azo dye pollutant, in which surface-modified organic–inorganic hybrid mesoporous silica spheres were chosen as microreactors for the accumulation and subsequent photodegradation of pollutants in defined regions. They found that dye pollutants can be accumulated inside the polyelectrolyte microshells by the driving force originated from the existence of charged complex within the shell interior.

The objective of the present investigations is to evaluate the efficiency of removal of two types of dyes: Safranin T (ST) cationic and Eriochrome Blue Black R (EBBR) anionic, using PEUF. The poly(ammonium-acrylate) ($PANH_4$) was chosen as a water soluble polymer. The effects of dyes and polyelectrolyte concentrations, transmembrane pressure, ionic strength and pH have been studied.

## 2. Experimental

### *2.1. Chemicals*

Two types of dyes: Safranin T and Eriochrome Blue Black R were used in this study. In aqueous solution the Safranin T (ST) exists in cationic form, while the Eriochrome Blue Black R (EBBR) exists in anionic form. The chemical structures of the two dyes are shown in Figs. 1a,b. These chemicals were obtained from Fluka. The characterisation of the experimental dyes is given in Table 1.

An anionic polyelectrolyte, poly(ammonium-acrylate) ($PA\text{-}NH_4$), with molecular weight $M_w$ 30,000 g.mol$^{-1}$ was synthesised in the laboratory by radical polymerisation, its chemical structure is shown in Fig. 1c.

The measure of the intrinsic viscosity [η] permits to estimate the viscosimetric average molecular weight ($M_w$) of the polyelectrolyte synthesized, this viscosity is determined by Mark-Houwink relation [19]:

$$[\eta] = K.M_w^a \tag{1}$$

The intrinsic viscosity is expressed in dL.g$^{-1}$, *K* and *a* are characteristic constants for every polymeric couple/solvent; in the case of poly(ammonium-acrylate)/water, the expression of $M_w$ becomes [19]:

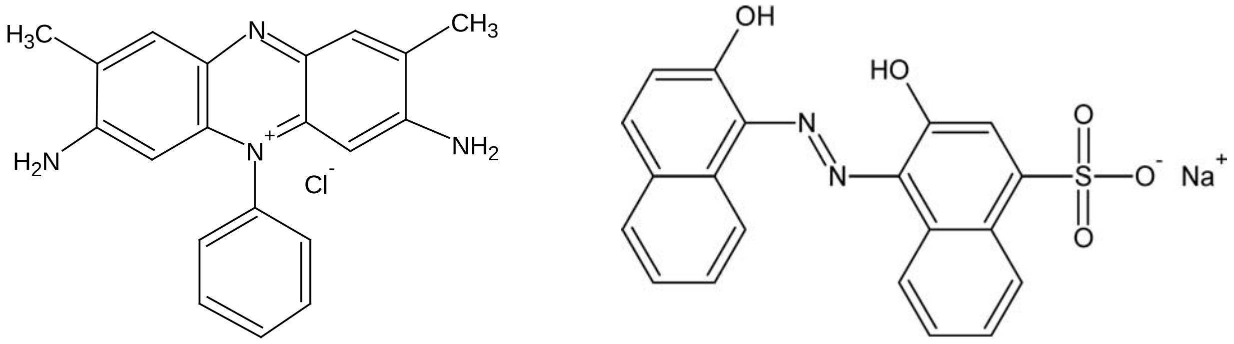
$$M_w = \left(\frac{\eta}{3.75\times10^{-4}}\right)^{\frac{1}{0.7}} \tag{2}$$

All the chemicals were used without further purification. Distilled water was used for the solution preparation.

Table 1
Characterisation of the experimental dyes

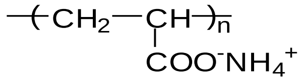
| Dye | Molecular weight (g.mol$^{-1}$) | Dye symbol | $\lambda_{max}{}^{a}$ (nm) |
|---|---|---|---|
| Safranin T ($C_{20}H_{19}ClN_4$) | 350.85 | ST | 525 |
| Eriochrome Blue Black R ($C_{20}H_{13}N_2O_5SNa$) | 416.39 | EBBR | 518 |

[a] Wavelength corresponding to the maximum absorbance of the dye solution



(a) Safranin T

(b) Eriochrome Blue Black R (EBBR)



$$\left(-CH_2-\underset{\displaystyle COO^-NH_4^+}{CH}-\right)_n$$

n: degree of polymerisation

(c) Poly(ammonium-acrylate) ($PANH_4$)

Fig. 1. Chemicals structures of dyes and polyelectrolyte.

*2.2. Ultrafiltration process*

A cross-flow Minitan-S-unit from Millipore was used to determine transport and separation properties of the organic regenerated cellulose membrane (PLGC Millipore).

The effective surface area of the membrane amounted to 30 $cm^2$ and molecular weight cut-off (MWCO) 10 kDa. A schematic diagram of the UF system is shown in Fig. 2.

The membrane was soaked in deionised water during 24 h in order to eliminate preservative products. Then pure water flux at various operating pressures was measured and the membrane permeability $L_p$ was determined from the slope of the flux vs. pressure plot. The pure water flux through membrane at one particular transmembrane pressure is usually expressed with Darcy's law:

$$J = L_p \Delta P \tag{3}$$

$L_p$ is the permeability of solvent; $\Delta P$ is the transmembrane pressure. The value of the membrane permeability was found to be $2.47\times10^{-10}$ $mPa^{-1}s^{-1}$.

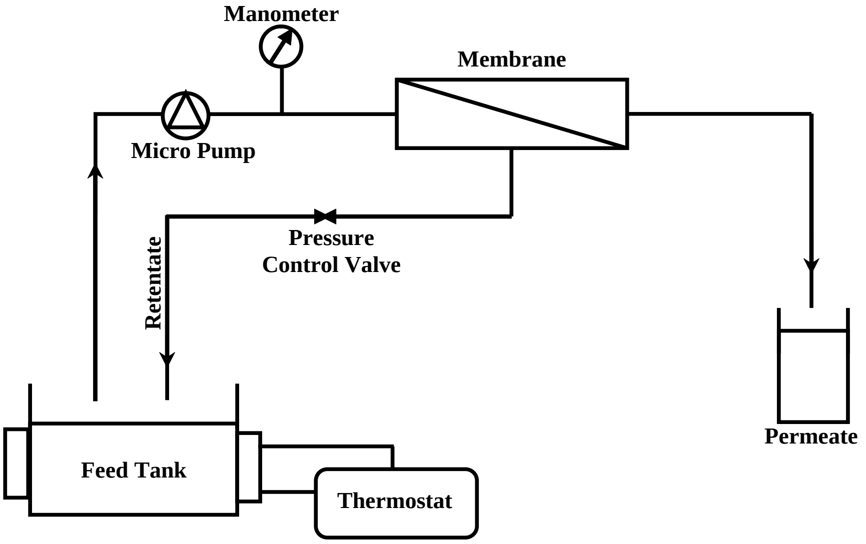


Fig. 2. Schematic of the experimental set-up.

Ultrafiltration experiments were conducted at room temperature and at fixed transmembrane pressure of 1.4 bar. An initial feed volume equal to 200 mL was introduced to the feed tank and was circulated through the module by a volumetric pump. The retentate as well as permeate were recycled to the feed tank. After nearly thirty minutes a steady state was reached and permeate of 10 mL was collected and analysed.

Between the runs the membrane was thoroughly washed with distilled water for at least 15 min and a pressure of 1.4 bar. The membrane permeability was checked to ensure that the permeability remains almost constant between successive runs.

The decolourization percentage of the dyes was expressed as:

$$\text{Decolourization (\%)} = \left(1 - \frac{C_p}{C_0}\right) \times 100 \tag{4}$$

where $C_0$ is the initial concentration of dye in the feed solution and $C_p$ is the dye concentration in permeate.

Permeate volume flux was calculated as follows:

$$J = \frac{V}{t \times S} \tag{5}$$

where $J$ is the permeate flux (L.h$^{-1}$.m$^{-2}$), $V$ denotes volume of the permeate sample collected with time $t$ (h) and $S$ is the effective membrane surface (m$^2$).

The permeate concentrations of dyes were measured by a Perkin-Elmer Lambda 20 spectrophotometer using a matched pair of glass cuvettes with 1 cm optical lengths. The spectra were scanned in the wavelength region of 400–800 nm. Concentrated stock solutions of the dye and polyelectrolyte were prepared by dissolving weighed amounts in distilled water, the working solutions were then prepared by dilution. The concentration of polyelectrolyte was varied while the concentration of dye was varied and vice versa. For dye filtration a feed concentrations of 10, 20 and 30 mg.L$^{-1}$ were selected and the feed polymer concentration was kept constant at 20 mg.L$^{-1}$. Dye concentration was kept constant at 20 mg.L$^{-1}$ and PANH$_4$ concentrations were varied from 5 to 40 mg.L$^{-1}$ in the effect of the polyelectrolyte concentration. For the effect of ionic strength, the dye concentration remained constant at 10 mg.L$^{-1}$, while the concentration of PANH$_4$ and the concentration of NaCl were varied. The pH was varied from 2 to 12 by adding chloride acid or sodium hydroxide. pH meter (Metrohm 654), equipped with a glass electrode was used for measuring pH solutions.

## 3. Results and discussion

### 3.1. Results obtained from the spectral measurements

Studies on binding of cationic dye to different synthetic and natural polymer by absorbance, fluorescence and circular dichroism experiments during the last few decades yielded significant contributions [20–25]. In those results the importance of both electrostatic and hydrophobic interactions is strongly emphasized.

The visible absorption spectra of mixed solutions with a fixed concentration of dyes of 5 mg.L$^{-1}$ and varying concentrations of the polyelectrolyte in aqueous media from 0 to 100 mg.L$^{-1}$ are shown in Fig. 3. The cationic dye ST (Fig. 3a) exhibits a maximum absorption at 520 nm in water. This observation is consistent with literature reports [26,27]. As PANH4 concentrations increased gradually, the monomer dye absorbance decreased and the maximum absorption was shifted to 475 nm. Usually, such kinds of interactions are initiated by the electrostatic interactions among oppositely charged polyelectrolyte and dye.

The change in the maximum absorption may be attributed to dimerisation leading to H-type aggregation of the dye molecules assisted by the polyelectrolyte chain. H aggregates are spectroscopic entities that are characterised by a blue-shifted adsorption with respect to monomer absorption. Whereas J aggregates present a red-shifted band. The dimerisation is a well known phenomenon, occurring in concentrated solution of dyes or induced by its preferential adsorption onto solid substrate [23] or in

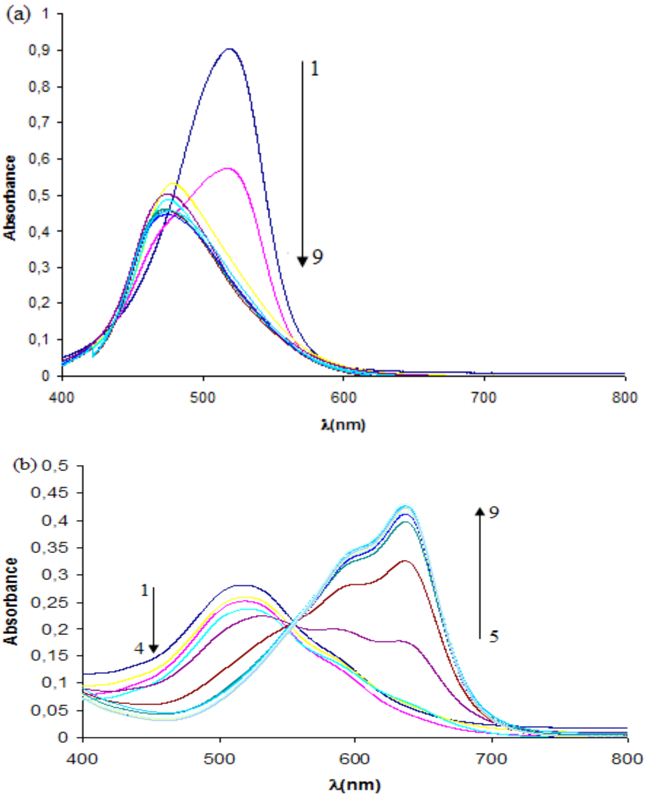


Fig. 3. The visible absorption spectra of ST (a) and EBBR (b) at 5 mg.L$^{-1}$ in the presence of PANH$_4$ at variables concentrations (mg.L–1): (1) : 0; (2) : 1; (3) : 5 ; (4) : 10 ; (5) : 30 ; (6) : 50 ; (7) : 65 ; (8) : 80 ; (9) : 100.

the presence of macromolecules such as DNA [24] and cyclodextrine [26].

Fig. 3 shows the visible spectra of aqueous EBBR solution at 5 mg.L$^{-1}$ for several PANH$_4$ concentrations ranging from 0 to 100 mg.L$^{-1}$. The experimental results indicate that in the absence of PANH$_4$, EBBR presents a maximum absorption at 518 nm. In the presence of polyelectrolyte at concentration lower than 10 mg.L$^{-1}$, the maximum absorption was kept constant at 518 nm and the absorbance decreases. As the concentration of polyelectrolyte increased from 10 to 100 mg.L$^{-1}$, the absorption band at 518 nm vanished and a new broad absorption band centred at 640 nm was formed. This large red-shifted band is typical for J aggregates [23]. Appearance of an isosbestic point suggests the formation of 1:1 stoichiometric complex between the dye molecule and polyelectrolyte. The change of maximum absorption is believed to be due to formation of J-aggregates in the aqueous solutions.

### 3.2. *Effect of transmembrane pressure and feed polymer concentration on dye decolourization*

Fig. 4 shows the variation of retention and permeates flux of ST for different concentrations from 10 to 30 mg.L$^{-1}$ with and without PANH4 (initial concentration, 20 mg.L$^{-1}$). It is observed from Fig. 4a that in the absence of polyelectrolyte the dye retention was in the range 20–40%. Whereas, in the presence of the polyelectrolyte solutions; the decolourization has been significantly increased to 99%.

This confirms that in the presence of PANH$_4$ some complexes were formed due to binding of anionic polymer with ST molecules through electrostatic interaction, resulting in the enhancement of the ultrafiltration process. Changes in absorption spectra of dyes upon binding indicate the aggregation of neighbouring bound dye molecules on the polymer chain. Electrostatic interactions and hydrophobic interactions are considered to be important in binding process. Increasing the concentration of polyelectrolyte, the aggregation increases as a consequence augmentation of ST retention.

The variation of the permeate flux with time in absence and in presence of polymer is presented in Fig. 4b. As shown in this figure the permeate flux depends slightly on the polyelectrolyte concentration.

Fig. 5 shows the influence of transmembrane pressure and polymer concentration on the ST retention and permeates flux, when transmembrane pressure varied from 0.8 to 2 bar and concentration of PANH$_4$ from 0 to 40 mg.L$^{-1}$. Fig. 5a depicts that at concentration of polyelectrolyte values lower than 10 mgL$^{-1}$, the retention of ST increase with increasing the concentration of PANH$_4$ and transmembrane pressure. When PANH$_4$ concentration is above 10 mg.L$^{-1}$, the dye removal reaches around 99.5%. The cationic polymer demonstrated its strong effectiveness in enhancing the UF for decolourization of ST solution.

The effect of applied pressure on the permeate flux is presented in Fig. 5b. The increase in the permeate flux is not surprising, since the pressure difference between retentate and permeate is the driving force for the process.

### 3.3. *Effect of the polyelectrolyte concentration*

The effect of the polyelectrolyte concentration is carried out for ST and EBBR. The concentration of PANH$_4$ was varied from 0 to 40 mg.L$^{-1}$, while the concentration of dye was kept constant at a value of 10 mg.L$^{-1}$.

Figs. 6a and 6b show, respectively, the retention rate of two dyes and flux of permeate as a function of polyelectrolyte concentrations. As shown in Fig. 6a, in the absence of PANH$_4$, the retention of ST was about 21%. This can be attributed to the adsorption of dye particles on the pore walls or on the membrane surface. In addition, it is clearly seen that the ST dye retention is slightly higher compared to EBBR dye retention in the presence of

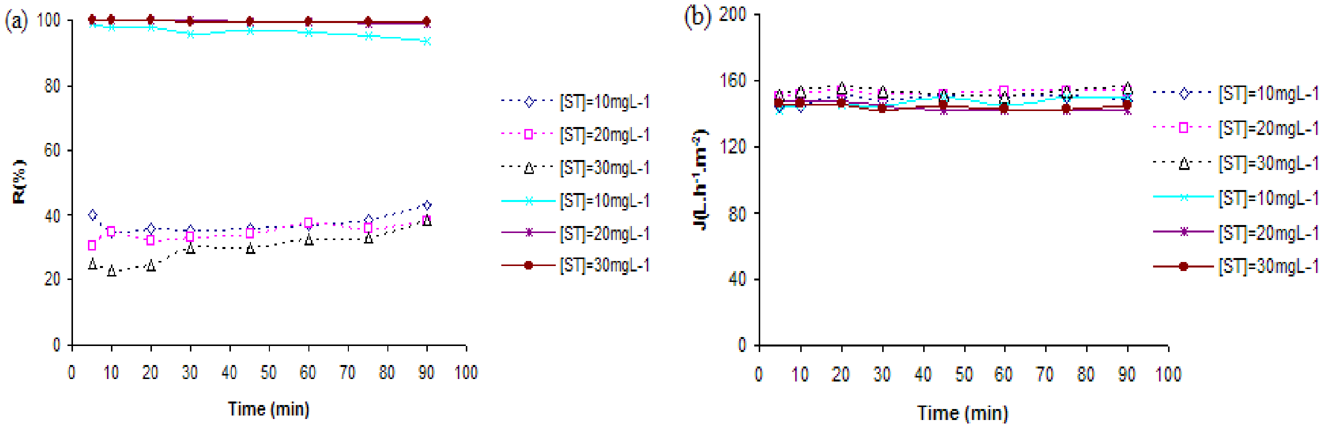


Fig. 4. Variation of retention of ST (a) and permeate flux (b) with time in the absence (-------) and in the presence of PANH$_4$ (20 mg.L$^{-1}$), $\Delta P$ = 1.4 bar.

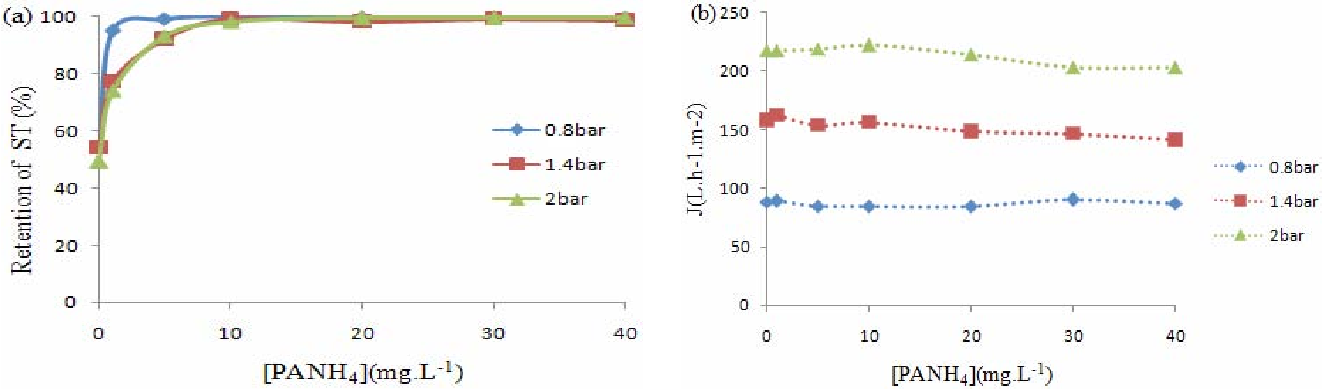


Fig. 5. Effect of polyelectrolyte concentration and transmembrane pressure on the retention (a) and the permeate flux (b) of ST. [ST] = 20 mg.L$^{-1}$.

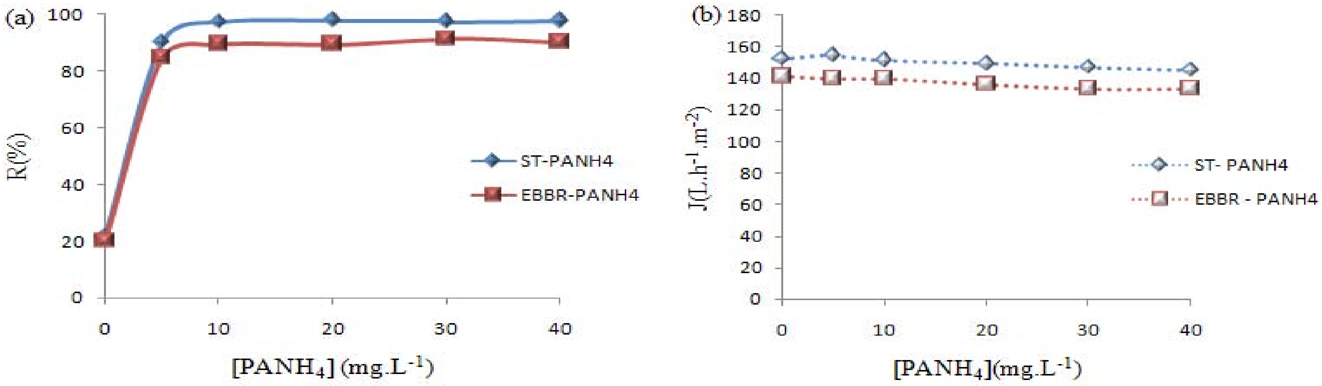


Fig. 6. Variation of retention (a) and permeate flux (b) of dyes as a function of feed polyelectrolyte concentration. Feed ST and EBBR concentration is 10 mg.L$^{-1}$, $\Delta P$ = 1.4 bar.

PANH$_4$. This result is due to the formation of some complexes through electrostatic attraction between anionic polymer and cationic ST dye. In a recent study, Tan et al. [16] investigated the decolourization of three cationic dyes solutions in the presence of different polymers and concluded that cationic dyes -anionic polymers was suitable for the decolourization of dye aqueous solutions. Whereas the retention of EBBR reaches 80–90%. This suggests that J aggregates were formed. This result was further confirmed by the measurement of $\lambda_{max}$ indicated in Fig. 3b.

Fig. 6b depicts the effect of polyelectrolyte concentration on the permeate flux of ST and EBBR. This figure shows that the permeate flux of ST solution is higher than the permeate flux of EBBR solution. In general, the worsening of membrane permeability during UF of model solution containing various organic components can be attributed to adsorptive fouling. This statement can be supported by hydrophilic/hydrophobic proprieties of membranes and retained substances. This effect is more pronounced for high molecular weight dyes [28].

### 3.4. *Effect of ionic strength*

The influence of the ionic strength of the solution on the UF efficiency was also studied. In reality, effluents from textile and dyeing industries would contain a high concentration of salts which may affect the removal of dye solution.

The effect of added NaCl concentration on ST retention is shown in Fig. 7a, where it can be seen that ST retention decreased from 99.9% to 20% upon increasing the sodium chloride concentration from $10^{-4}$ to $10^{-1}$ M. This decrease may be due to the fact that at higher ionic strength, the formation of complexes in solution is decreased.

An increase in salt concentration leads to a screening of the charges along the PANH$_4$ chain and positively charged of ST, for this reason, the importance of electrostatic attraction or repulsion decreases. A weakly charged polyelectrolyte experiences less segment to segment repulsion and the formation of loops and tails of largely uncharged sections is favoured. As a result, the unbound dye in the stream passes thought the ultrafiltra-

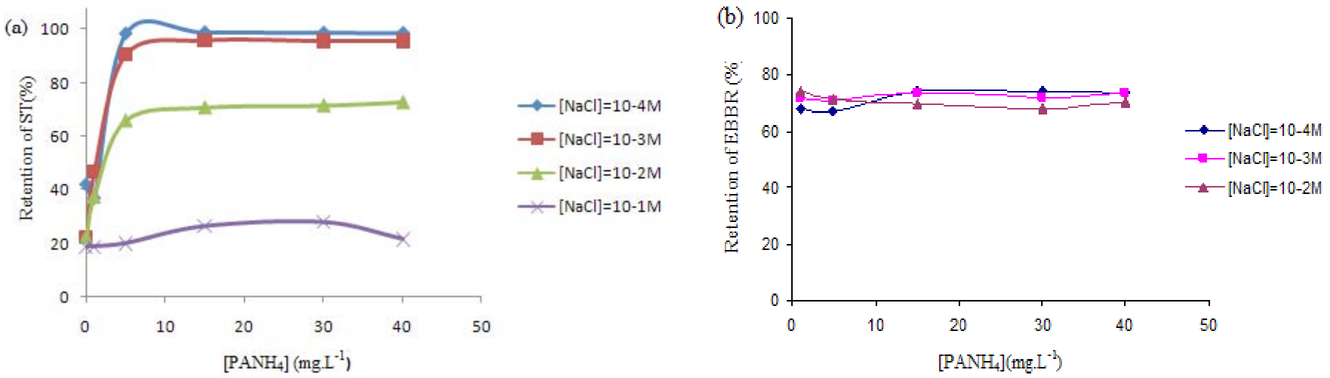


Fig. 7. Effect of ionic strength on the retention of ST (a) and EBBR (b) as a function of feed PANH$_4$. Feed dye concentration = 10 mg.L$^{-1}$, Δ$P$ = 1.4 bar.

tion membrane leading to poor retention [28]. Seeing that ions present in the solution mask the charge of PANH4 and ST and this confirms the electrostatic nature of the complexes formed.

The effect of ionic strength on the retention of EBBR is presented in Fig. 7b, where it can be seen that EBBR retention decreases slightly upon increasing the NaCl concentration. The low decrease of retention upon increasing the salt concentration confirms the fact that the complex formed in this case is not of electrostatic nature.

### *3.5. Effect of pH*

One of the most important factors in the interaction of dye with binding polymer is pH. The pH was varied from 1 to 10 by adding chloride acid or sodium hydroxide, when the concentrations of dyes and PANH$_4$ were kept constant at 10 mg.L$^{-1}$ and 30 mg.L$^{-1}$, respectively.

Fig. 8 presents the influence of pH on the retention of ST and EBBR. It can be seen from this figure, in the acidic region, the removal of ST increases by increasing the pH of the feed solutions. This can be explained on the basis of the competition of H$^+$ with ST to be bound to the polymer, as a result of protonation of the carboxylate groups. ST presents high retention ability at pH above 4 and the removal of ST reaches a limiting value of 99%.

The same behaviour has been reported in the case of the retention of cations such as Cd$^{2+}$ [29] by PEUF in presence of PANH4. It has been often reported that when interactions between water soluble polymers and metal-ions in solution take place by according bonds, the nature of the metal ions and the effect of pH may induce differences in the retention profiles and selectivity of equally charged metal ions [30]. The carboxylic groups PANH4 are expected to exhibit unlike acid strength. During the dissociation of PANH$_4$, the ionized carboxylic groups of the polyacid attract the protons. As a consequence, the deprotonation of a functional group depends of the dissociation degree of all the other groups.

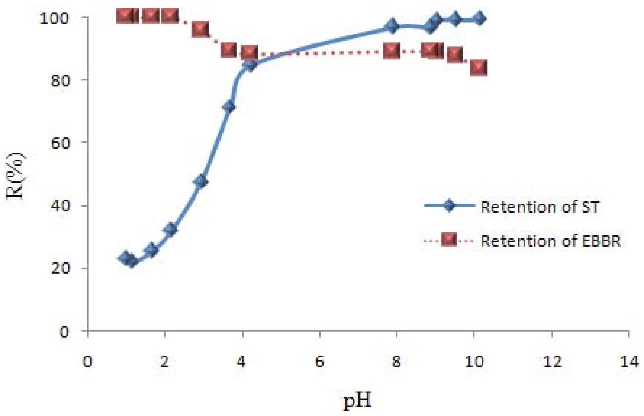


Fig. 8. Effect of pH on the retention of ST and EBBR ([dye] = 10 mg.L$^{-1}$, [PANH4] = 30 mg.L$^{-1}$), Δ$P$ = 1.4 bar.

This figure shows that practically there was a notable effect of pH on the retention of EBBR dye and this result confirms the non electrostatic aspect of the complexes formed in this case.

## 4. Conclusion

Decolourization of ST and EBBR aqueous solution by the polyelectrolyte enhanced ultrafiltration (PEUF) was undertaking in the presence of anionic polyelectrolyte.

The retention of ST and EBBR was in the order of 99 and 97%, respectively. For polyelectrolyte concentration above 10 mg.L$^{-1}$, the decolourization of ST solution depends of the ionic strength and the pH of the feed solution. Whereas, a slightly effect was noted in the case of EBBR. These experimental results were attributed to the formation of complexes through electrostatic attraction for ST and J-aggregates for EBBR.

The UV-Vis spectrophotometry showed that the anionic polyelectrolyte affected the ST and EBBR spectra.

Hypsochromic and batochromic effect was noted and confirmed the nature of complexes.

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