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Binding of Methylene Blue to two types of water soluble polymer and its removal by polyelectrolyte enhanced ultrafiltration

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Abstract. The interactions of water soluble polymers with dye are studied by ultrafiltration using a molecular weight cut off of 10 KDa regenerated cellulose ultrafiltration membrane. Two water-soluble polymers, namely Poly (Sodium-4 Styrenesulfonate) (PSS) and Poly (Vinyl Alcohol) (PVA) were selected for this study. The effects of process parameters, such as, polyelectrolyte concentrations, transmembrane pressure, ionic strength and pH of solution on dye retention and permeation flux were examined. PSS enhanced ultrafiltration achieved dye retention as high as 99% as a result of complexation between polyanion containing aromatic groups and cationic dye. This result was confirmed by the red shift. The retention of dye decreases as the salt concentration increases, a high retention was obtained at pH above 4. However, in case of PVA, relatively low retention (50%) was observed. Ionic strength and pH has no significant effect on the removal of MB. The permeate flux depended slightly on polyelectrolytes concentrations, transmembrane pressure, salt concentration and pH.

Keywords: dye; poly(Sodium-4 Styrenesulfonate) (PSS); poly(Vinyl Alcohol) (PVA); dye retention; polymer enhanced ultrafiltration.

1. Introduction

Dyes are the one of the major constituents of the wastewater produced from many industries related to textile, cosmetics, paper and plastics. The effluent coming out from these industries contains toxic and even carcinogenic dyes, which causes many environmental problems (Safarik *et al.* 2002, Albanis *et al.* 2000, Moreina *et al.* 1998). Consequently, it is important to remove these pollutants from wastewater before their final disposal (Hessel *et al.* 2007) in order to respect guidelines and legislation for dye effluents This dictates the necessity of dye containing water to undergo treatment before disposal to the environment.

The effluents containing methylene blue (MB) may lead to serious problems, which has a harmful influence on human health and environment. Various treatment techniques are currently being employed in an effort to bring about effective removal of dye laden effluents, these wastewater treatment includes coagulation (Lin *et al.* 1996), electrochemical oxidation (Mohan *et al.* 2007), biological treatment (Iqbal *et al.* 2007), advanced oxidation processes (AOPs) that use hydroxyl radicals (Torrades *et al.* 2014, Nidheesh *et al.* 2013) have been applied to remove dyes from wastewater. Wastewaters can be effectively removed by adsorption such as cobalt ferrite nanotubes and porous nanorods can be used as an effective adsorbent for removing polar red dye from aqueous solution (Girgis *et al.* 2015). However these approaches often involve complicated procedures. Membrane based separation processes are becoming attractive for the separation of coloured effluent containing various types of dyes. The membrane processes used to remove dye from the wastewater are reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF). Thus reverse osmosis and nanofiltration are readily recognized as the best available techniques for the separation of several commercial dyes (Srisukphum *et al.* 2009, Purkait *et al.* 2004). In a recent study, Ingole *et al.* (2016) demonstrated that dye rejection enhanced nanofiltration may be a feasible method for the dye wastewater treatment. Whereas, permeability of these membranes is low and thus requires high operating pressure. Ultrafiltration operates at a lower pressure with a higher flux than RO and NF but it has a lower dye rejection. It has been reported that UF combined with other physical and chemical processes could be effectively used for removal of dyes from aqueous solutions (Zaghbani *et al.* 2008). The combination of UF and complexation ability of water soluble polymer may overcome the low retention of UF membrane, while keeping the same performance of flux. One separation technique that can meet the above requirement is complexation ultrafiltration process, also called polymer enhanced ultrafiltration (PEUF) (Kadiogln *et al.* 2010). In PEUF process is based on the complexation of water soluble polymers complexing with dye and form macromolecular species, having a higher molecular weight than the molecular weight cut off of the membrane. PEUF is expected to provide enough permeation flux with removal efficiency (Mondal *et al.* 2012, Tan *et al.* 2006, Ouni *et al.* 2010a).

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Polyelectrolytes having several active anionic groups makes complexes with mono or multivalent metal ions. The complex being larger in size can be removed by ultrafiltration membrane, it is possible to achieve selective separation and recovery of dyes with low energy requirements. 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 dye from aqueous solutions. The binding behaviour and stoichiometry depend on the nature of both dyes and polyelectrolytes and cannot be generalized (Dragan *et al.* 1999).

The characteristic behaviour of the polymer groups has significant effect on the property of the solution mixture and hence finally affects the ultrafiltration performance. For these reason we plan in the present study to investigate the binding of methylene blue to poly(sodium 4-styrenesulfonate) (PSS) containing aromatic groups and poly(vinyl alcohol) (PVA), as a complexing agents and its removal by polyelectrolyte enhanced ultrafiltration process. Experiments were performed as a function of polyelectrolytes types and concentrations, transmembrane pressure, salt concentration and aqueous pH. Additionally, the UV-visible spectrometry is used to evaluate respective characteristic changes of MB by PSS and PVA, so as to gain a perspective on the interaction between the dye and the complexing polymers.

2. Experimental

2.1 Materials

Methylene Blue (MB) ($C_{16}H_{18}ClN_3S$, (M_W=319.85 g.mol^{-1}) was purchased from Fluka. Two water-soluble polymers: poly(sodium 4-styrenesulfonate) (PSS) (average M_W=70,000 g.mol^{-1}) and poly(vinyl alcohol) (PVA) (average M_W=115,000 g.mol^{-1}) were used as complexing agents in this study. These chemicals were supplied by Sigma–Aldrich. The chemical structures of the three compounds are shown in Fig. 1. Hydrochloride acid, sodium hydroxide were used to adjusted the pH value. All the chemicals were used without further purification. Distilled water was used for solution preparation.

2.2 Ultrafiltration process

2.2.1 Ultrafiltration membrane

Cross-flow membrane filtration was carried out with a tangential cell system Minitan-S purchased from Millipore with an effective filtration area of 30 cm^2. A schematic diagram of the UF system is shown in Fig. 2. Organic regenerated cellulose membrane of molecular weight cut-off (MWCO) 10 kDa obtained from Millipore was used for all the PEUF experiments. The membrane was soaked in deionised water during 24 h in order to eliminate preservative products, then membrane was compacted during 20 min under 2 bars pressure. Pure water flux at various operating pressures was measured and the membrane permeability Lp was determined from the slope of the flux Vs. pressure plot. The value of water

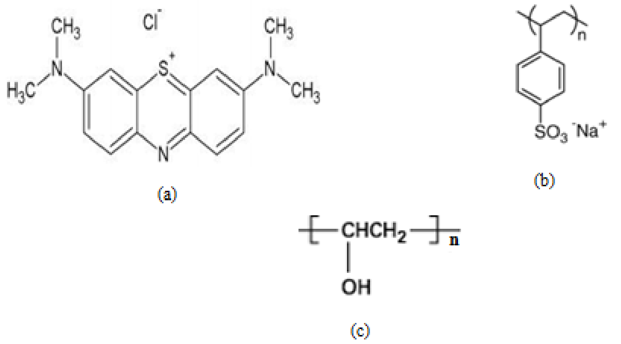


Fig. 1 Molecular structure of (a) methylene blue, (b) poly(sodium 4-styrenesulfonate) and (c) poly(vinyl alcohol)

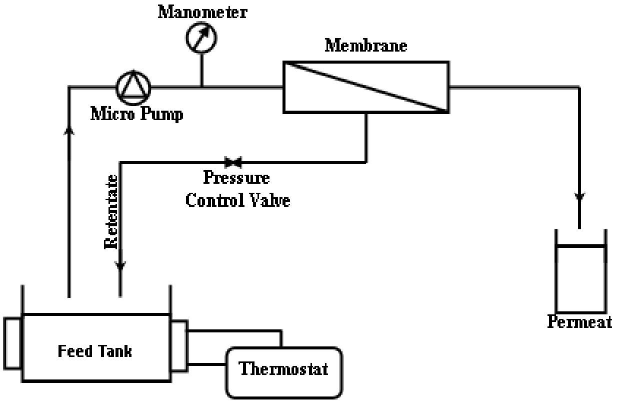


Fig. 2 Schematic of the experimental set-up

permeability determined by using Darcy law

$$J = Lp\Delta p \quad (1)$$

Lp is the permeability of solvent, ΔP is the transmembrane pressure. The value of the membrane permeability was found to be 75.63 L.h^{-1}.m^{-2}.bar^{-1}.

2.2.2 Procedure

Ultrafiltration experiments were conducted at room temperature and at fixed transmembrane pressure of 2 bars. 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 into the feed tank. After nearly 20 min a steady state was reached and permeates of 10 ml was collected and analysed.

After each run, the cell and the membrane were washed thoroughly with pure water for at least 20 min. During compaction of membrane, water flux is measured continuously until a constant flux results. It was observed that the membrane permeability remained almost constant between successive runs.

Observed dye decolorization percentage and permeate flux can be calculated using Eqs. (2) and (3)

$$Decolorization(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100 \quad (2)$$

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

$$J = \frac{V}{t \times S} \tag{3}$$

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).

Permeate concentrations of the dye 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.

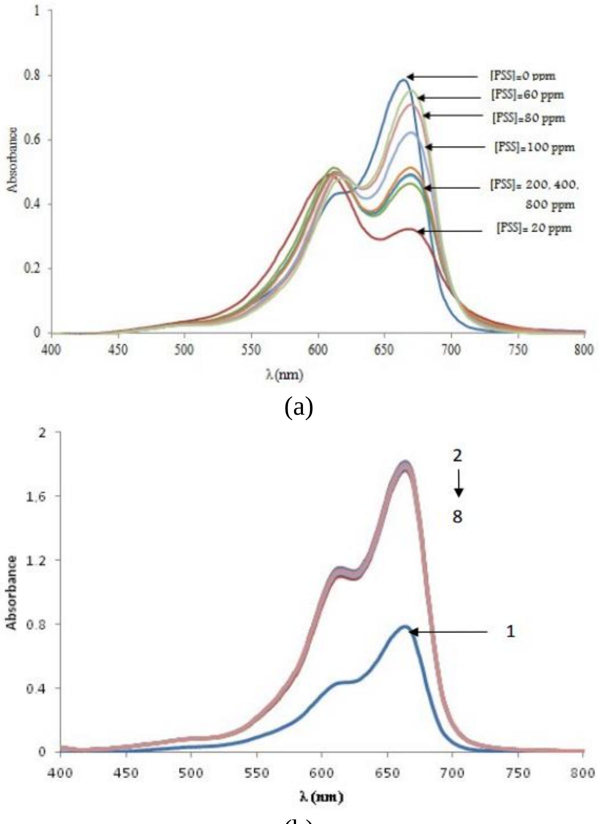
Concentrated stock solutions of the dye and polyelectrolyte were prepared by dissolving weighed amounts in distilled water, the working solutions were then prepared by dilution pH meter (Metrohm 654), equipped with a glass electrode was used for measuring pH solutions.

3. Results and discussion

3.1 UV-Visible study: Effect of polyelectrolytes concentrations

The visible absorption spectra of mixed solution with a fixed concentration of MB of 10 ppm and varying concentrations of the polyelectrolytes in aqueous media from 0 to 800 nm are shown in Fig. 3. In aqueous solution, methylene blue exhibits a band at 665 nm and a shoulder at 612 nm which are assigned to monomeric and dimeric forms, respectively. This observation is consistent with the literature reports **(**Zaghbani *et al.* 2007). The dimerisation is a well-known phenomenon, occurring in concentrated solution of dyes or induced by its preferential adsorption onto solution of dyes or induced by its preferential adsorption onto solid substrate (Shen *et al.* 2006) or in the presence of macromolecules such as DNA (Majewska Nowak *et al.* 2008) and cyclodextrine (Abdullah *et al.* 2007) in the aqueous solution.

Fig. 3(a) represents the visible spectra of aqueous MB solutions at 10 ppm for several poly(sodium 4-styrenesulfonate) (PSS) concentrations. The monomer dye absorbance decreased and absorbance at the shoulder increased weakly. This figure show also that in the presence of small amounts of PSS, the aggregation of MB is also induced in the environment of the polymer, as can be seen in the case of [PSS]=20 ppm by the disappearance of the monomer band. But, as the concentration of PSS increases up to 20 ppm, the maximum absorption wavelength of MB solution increased from 665 to 672 nm. This red shifted band is typical for J aggregates (Ouni *et al.* 2010a). J-aggregates are spectroscopic entities that are characterized by a red-shifted adsorption with respect to monomer absorption whereas H-aggregates present a blue-shifted band. In J- aggregate the molecular alignment is edge to edge, while in H aggregate the molecules are aligned in face to face arrangement (Yao *et al.* 2007). The change of maximum absorption is believed to be due to formation of J- aggregate in the aqueous solution. Such a behavior can be explained by the change of absorption which is due to the formation of some complexes between the polyelectrolyte and the dye molecules in the aqueous solution by electrostatic interaction. PSS induced bathochromic shift in the absorption spectra of MB. The initial red shift in the absorption band can be essentially ascribed to the transition of the monomeric dye molecules from the free or unbound state to the bound state, and the concomitant conformational changes in the dye molecules and the polymer (Quadrifoglio *et al.* 1971, Antonov *et al.* 1999).



(a)

(b)

Fig. 3 The visible absorption spectra of MB at 10 ppm in the presence of (a) PSS and (b) PVA at various concentrations (ppm) (1):0, (2):20, (3):60, (4):80, (5):100, (6):200,(7):400 and (8): 800

Moreno-Villoslada *et al.* (2009) investigated the binding of MB to polyelectrolytes containing sulfonates groups such as poly(sodium 4-styrenesulfonate) (PSS) poly (sodium vinylsulfonate) (PVS) and the more hydrophobic poly[sodium2-(N-acrylamido) 2-methyl-propanesulfonate] (PAMPS). They concluded that MB in the presence of PSS, the main driving forces for the interaction with PSS are short range aromatic/aromatic interactions, which result in stronger binding (smaller dissociation constants). MB molecules may distribute randomly on the polymeric binding sites, and the self-aggregation of the MB is prevented at a moderate excess of the polymer. The Fig. 4 explain the aromatic/aromatic interaction between MB and PSS

The absorption spectra of MB in aqueous solution at various concentrations of PVA were also investigated. It is observed from Fig. 3(b) that in the presence of increasing PVA concentrations the absorbance is increased and the absorption wavelength does not change and kept constant at 664 nm. This result confirms the fact that the interaction between MB and PVA is not a type of complexation mechanism.

The same trends were observed by Tan *et al.* (2006) in the case of the decolorization of dyes in the presence of polyelectrolytes through the ultrafiltration process using the hollow fiber membrane module. They mentioned that the addition of PVA does not interfere with the absorption spectra of three cationic dyes used, measurement of the UV-spectroscopy of the dye solution indicated that no complexes were formed. However, when the PSS was added the UV- absorption spectrum is shifted from 553 nm for the pure new fuchsin (NF) solution to 503 nm for the PSS containing NF solution, this shift is due to the formation of complexes by electrostatic attraction.

3.2 Ultrafiltration study

3.2.1 Effect of the polyelectrolyte concentration

The removal of Methylene Blue with two types of polyelectrolytes as a function of polyelectrolyte concentration in feed solution is shown in Fig. 5(a). It is observed from this figure that in the absence of polyelectrolytes, the dye retention was 26%. This can be attributed to the adsorption of dye particles on the pore walls or on the membrane surface. In our previous study Fraj *et al.* (2014), the ultrafiltration of MB at different concentrations was studied, we observed that the retention of MB reaches constant values in the order of 13%, when concentration of MB increases from 0.02 to 0.5 mM. Since the MB 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. Zaghbani *et al.* (2008) observed the same behavior. Whereas, in the presence of the PSS solutions, the decolourisation is increased and then reaches a limiting value of 99%. The increasing MB retention trajectory can be explained by the fact that the number of available binding sites increases, following the increment in polymer loading; the proliferated binding sites thus contribute to the enhanced complexation of dye molecules with the chelating polymers, thereby leading to increased dye retention (Chakraborty *et al.* 2014). The further increase in retention can be assumed due to the complex formation between the cationic MB molecules on anionic polymer through electrostatic interaction resulting in the enhancement of the ultrafiltration process, water soluble polymers with sulfonated groups favor the electrostatic polymer-dye interaction. The increasing of the concentration of polyelectrolyte increases the amount of complexed dye and as a consequence increases MB retention. When the equilibrium of complexation is attained the excess of polymer will have no effect on the retention efficiency.

In a recent study, Dasgupta *et al.* (2015) investigated the Reactive red (RR) retention through ultrafiltration enhanced by synthetic and natural polyelectrolytes. They concluded that the increasing dye retention due to the complexation of the dye molecules with the polyelectrolyte had attained a dynamic equilibrium, wherein, any further increase in polymer loading could only lead to redundancy or a marginal increase in dye retention at the most.

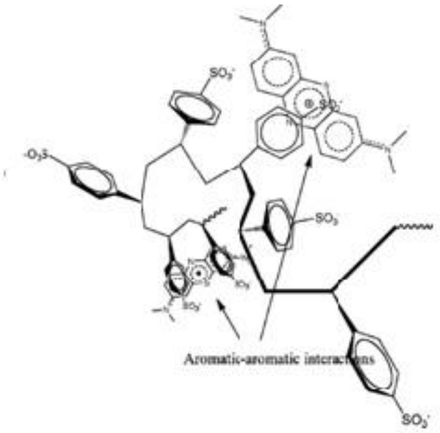
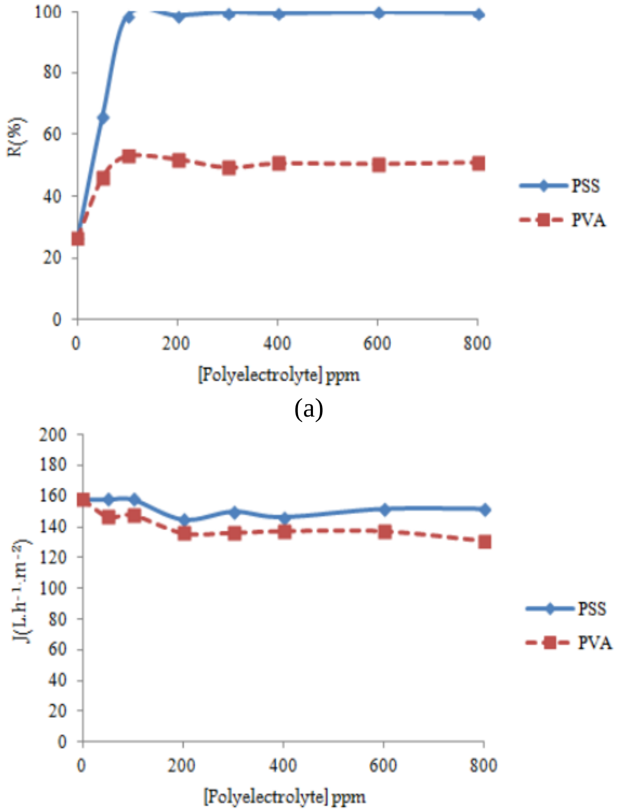


Fig. 4 Schematic representation of aromatic-aromatic interaction between MB-PSS

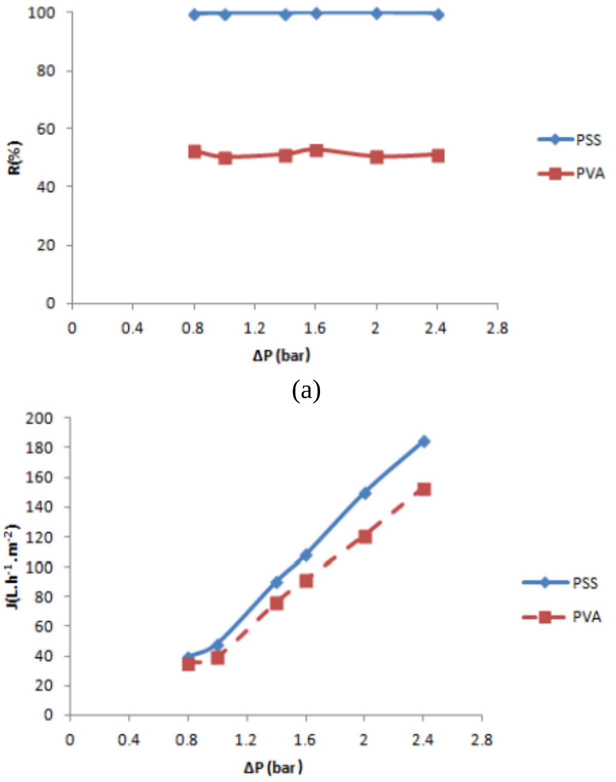


(a)

(b)

Fig. 5 Variation of (a) MB retention and (b) permeate flux as a function of feed polyelectrolyte concentration. Feed MB concentration is 100 ppm

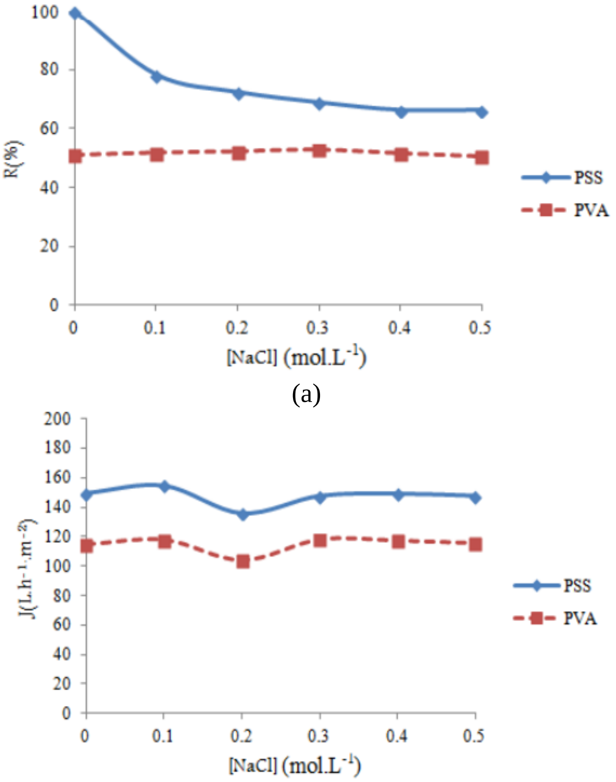
However, when the PVA was applied in the MB solution, the decolourisation reaches 40-50%. The slightly increase in retention can be attributed to the adsorption of PVA molecules to the surface of membrane, the polyelectrolyte molecules non-coordinate with MB dye will provoke problems of fouling. In addition, this may be due to that the PVA polyelectrolyte cannot bind MB to form aggregates in enhacing the UF process. This result was further confirmed by the measurement of λ_{max} indicates in Fig. 3(b), PVA produces no perturbation in the visible spectra of the dye and any new band was observed. It means that no complex could be formed in the solution.



(a)

(b)

Fig. 6 Effect of transmembrane pressure on (a) MB retention and (b) permeate flux of MB at polyelectrolyte concentration of 300 ppm



(a)

(b)

Fig. 7 Effect of NaCl concentration on (a) MB retention and (b) permeate flux at polyelectrolyte concentration of 300 ppm. Feed MB concentration is 100 ppm

Fig. 5(b) depicts the effect of polyelectrolytes concentrations on the permeate flux of MB. The permeate flux observed during ultrafiltration process of dye with polyelectrolyte is lower than that without polyelectrolyte. The decline of flux is attributed to the effect of concentration polarisation at the membrane surface, when the polyelectrolyte concentration increased more complexes entities were formed. 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. In the presence of PSS; the flux is higher compared to with the PVA. This may be related to the fact that molecular weight PSS (M_W = 70,000 g.mol^{-1}) is lower compared to that of PVA (M_W = 115,000 g. mol^{-1}). Similar results were obtained in the case of the retention of the Crystal Violet in the presence of polyacrylic acid and polyethylenenimine by ultrafiltration (Ouni *et al.* 2010b).

3.2.2 Effect of transmembrane pressure

The effect of transmembrane pressure on the UF dye rejection at a fixed MB and polyelectrolytes concentrations of 100 and 300 ppm, respectively, is depicted in Fig. 6(a). It can be noticed from this figure, that the retention of MB 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 (Ouni *et al.* 2010a, b).

The effect of operating transmembrane pressure on the permeate flux for fixed dye, and polyelectrolyte concentrations is presented in Fig. 6(b). It is evident from this figure that the flux increases with pressure. This is a typical behavior of driven pressure process. With increase in pressure, the effective driving force for the solvent transport is higher for a fixed feed concentration. In addition, this results can be interpreted with the help of Darcy's law, which states that solvent flux is indirect proportion to the pressure difference applied a cross the UF membrane.

3.2.3 Effect of salt concentration

Wastewaters from textile manufacturing or dye producing industries contain various types of suspended and dissolved compounds apart from the dyes which can be considered as impurities in the dye removal process. These impurities could be salts, acids, alkalis. For this reason, an investigation was carried out on the effect of salt concentrations on the removal of MB by PEUF process.

The influence of the salt concentrations on dye removal was studied under identical conditions for the two types of polyelectrolytes chosen for this study. The effect of added NaCl concentrations on the retention of MB in presence of PSS is shown in Fig. 7(a), where it can be seen that MB retention decreases from 99.9% to 66% upon increasing the salt concentrations from 10^{-4} to 510^{-1} mol.L^{-1}. As NaCl concentrations increases, there is a competitive inhibition occurs between the binding of dye molecule and the salt to the monomer, the formation of complexes in solution is decreased. Seeing that, ions present in solution mask the charge of PSS and MB and this confirms the electrostatic nature of the complexes formed. The increase in salt concentration leads to the camouflaging of charges along the polyelectrolyte chain as well as the dye molecules. This, in turn, reduces the electrostatic interaction between the chelating polyelectrolyte and the dye ions, thereby resulting in relatively depreciated dye retention efficiency owing to the unhindered passage of the unbound dye molecules through the UF membrane (Dasgupta *et al.* 2015).

This trend may also be explained in the fact that salt causes an increase in ionic strength, which results in a shielding effect of surface charge and a notable reduction in Donnan effect. A weakly charged polyelectrolyte experiences less segment to segment repulsion and the formation of loops and tails of largely uncharged sections is favored. As a result, the unbound dye in the stream passes thought the UF membrane leading to poor retention (Shen *et al.* 2006, Ouni *et al.* 2010b).

This behavior may be also explained by the fact that when the feeds of high ionic strength are treated, the positive ions (i.e., Na^+) in the solution can shield the negative membrane groups, as well as neutralize the negative charges of polyelectrolyte. Hence, the electrostatic interaction between cationic dye, anionic polyelectrolyte and membrane ionic groups is markedly weakened. As a result the molecular sieve effect can be dominant and membrane selectivity decreases.

As the salt concentration greater than 0.4 $mol.L^{-1}$, the retention does not decrease further. This can be explained by the fact that at a critical salt concentration, the attachment sites are completely saturated and there is no further scope of attachment of either the dye or the co-ion. Since, the salts completely dissociate in the solution, there is a dynamic equilibrium between the relative attachment of dye molecules, salts and dissociation of dye molecules and polymer.

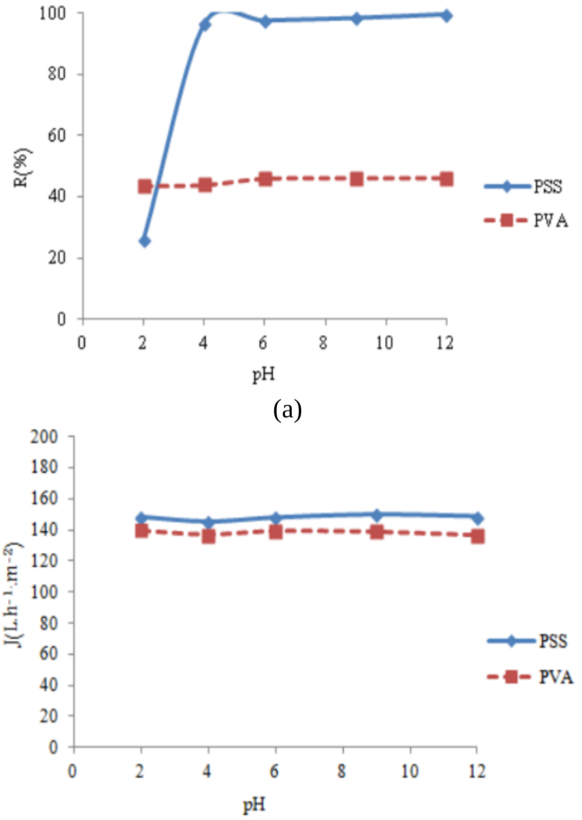
When the PVA was applied in the MB solution (Fig. 7(a)), it should be mentioned from this figure that MB retention kept constant upon increasing the salt concentrations. This result confirms the fact that the complex formed in this case is not of electrostatic interaction.

Fig. 7(b) depicts the effect of salt concentration on the permeate flux. It is obvious from this figure that permeate flux remained relatively unperturbed in the presence of salt. Thus due to that the effect of ionic strength on the conformation of the chelating polyelectrolyte was negligible. Furthermore, it was also found that permeate flux in the case of PSS is higher than PVA. This could be the cause of the increase of the charge at the surface of membrane in the case of PVA.

3.2.4 Effect of pH on the removal of MB

Dye wastewater is discharged at different pH. Therefore, it is important to study the role of pH in the removal of MB. The pH of the solution was maintained by adding chloride acid or sodium hydroxide solutions. These experiments were conducted in polyelectrolyte and dye concentration of 100 and 300 ppm, respectively.

Fig. 8(a) presents the influence of pH on the removal of MB. It can be seen from this figure, in the case of PSS, maximum retention of MB was noticed as 99% for pH above 4, in the acidic region, the removal of MB increases by increasing the pH of the feed solutions. This increase is related to the variation of the charge of dye and that of the polyelectrolyte. The change of the retention as a function of the pH may be due to the increase of the concentration of H^+ ions that competes with the functional groups MB that is positively charged to attach to the PSS, which is negatively charged. The same trends have been reported in our previous research in the case of the Methylene Blue retention assisted by ultrafiltration of polyacrylic acid and ammonium polyacrylate (Fradj *et al.* 2014). We concluded that the increase in pH leads to an increase of deprotonated carboxylic groups which favors the formation of dye-polyelectrolyte complex by electrostatic interaction between MB^+ and PAA^-.



(a)

(b)

Fig. 8 Effect of pH on (a) MB retention and (b) permeate flux. Concentrations of MB and polyelectrolytes are 100 and 300 ppm, respectively

Dasgupta *et al.* (2015) stated that the high dye retention for polyethyleneimine and chitosan were achieved in acidic media. However, in both the instances, the dye retention encountred steep drop at pH levels chose to the mean acidity constants of the respective chelating polyelectrolyte and traced declining trajectories in alkaline media. The retention profile can hence be viewed as the trademark of the dominant electrostatic interaction between the chelating polyelectrolyte and the target dye molecules, which decreased progressively, as the solution pH was raised. The quantum drop witnessed in the retention profile thus essentially marks a prominent reduction in dye retention efficiency, following complete deprotonation of the chelating polymer.

Ku *et al.* (2005) stated that solution pH level plays a very important role on the surface charge of the membrane and the species distribution of the acidic dye stuff. For experiments conducted in solutions of pH levels greater than pKa of specific acidic dyestuff, the permeability and rejections were roughly kept constant because most dyestuff molecules were neutral even though the charge of the membrane was negative. The rejection of dyestuffs by the nanomembrane system was slightly lower for most experiments operated at acidic solutions than at alkaline solutions, which could also be contributing to the increase of electrostatic attraction between the positively charged membrane and negatively charged dyestuff species.

This figures shows that practically there is no significant effect on the retention of MB in the presence of PVA and this result confirms the non-electrostatic aspect of the complexes formed in this case.

Fig. 8(b) shows the variation of permeate flux with pH for fixed dye and polyelectrolyte concentrations. It can be observed from this figure that the pH has no significant effect on permeate flux of MB by PEUF.

4. Conclusions

This study demonstrated the competence of PEUF in regard to separation of methylene blue from its aqueous solution. The interaction between MB and two water soluble polyelectrolytes has been investigated.

Spectroscopic results show that the binding of MB to the polyanion containing aromatic groups (PSS) affected the MB spectra, a red shift was obtained and confirmed the nature complexes.

PSS enhanced ultrafiltration was able to demonstrate high MB rejection over 99%. This was due to the strong electrostatic interaction and aromatic/aromatic interaction between MB and PSS. The decolourization of MB depends of the ionic strength and the pH of the feed solution in the case of PSS. Methylene blue presents high retention ability at pH above 4. However, in case of PVA, the MB rejection level offered by PVA enhanced ultrafiltration under no circumstances exceeded 50%. The pH and the ionic strength have no significant effect for the removal of MB. Based on the results it can be concluded that the PVA is not suitable for the decolourization of MB. The use of PSS was more advocated, as the most appropriate complexing agent, rather than PVA.

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