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The effect of surfactant on dye removal by polyelectrolyte enhanced ultrafiltration

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ABSTRACT

Polyelectrolyte-based separation of toxic dyes is studied to estimate the potential of polyelectrolyte enhanced ultrafiltration (PEUF) using polyethylene glycol (PEG). Removal of methyl orange (MO) an azo dye from aqueous solutions, by continuous polymer enhanced ultrafiltration (PEUF) was investigated. The permeate flux profile and obtained retention of MO were studied as a function of polyelectrolyte concentrations, transmembrane pressure, ionic strength and pH in the absence and in the presence of surfactant (CTAB). The experiments showed that retention of MO in the presence of PEG of different concentrations was 65%. This may be due to that the PEG polyelectrolyte cannot bind MO to form aggregates to enhance UF process. However, when the CTAB was applied at a fixed concentration below CMC, MO decolourization increased and reached a limiting value of 99%. The high rejection for MO dye is due to the formation of H aggregates in the aqueous solution. This result was confirmed by the change of the maximum absorption wavelength. The ionic strength and pH have no effect on the removal of MO in addition of CTAB. The permeate flux depended slightly on polyelectrolyte concentrations, transmembrane pressure, ionic strength and pH.

Keywords: Methyl orange; Polyethylene glycol; Surfactant; Ultrafiltration; PEUF

1. Introduction

A lot of industries like textiles, paper, plastics and leather use dyes to colour their products. Most of the used dyes are toxic and carcinogenic polluting agents, which must be removed from wastewater before rejection in the environment [1].

Removal of these compounds at low concentration is not easy by conventional processes such as coagulation [2], electrochemical oxidation [3], ozonation [4] and biological treatment [5]. Membrane filtration technologies with different types of membranes show great promise for dye removal for their high efficiency and easy operation. Recently, membrane separation processes have been used to treat this kind of effluent and to recycle the dyes. The membrane processes used to remove dye from the wastewater are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Processes involving RO [6] and NF [7] are already recognized as the best available techniques for several commercial dyes. However, permeability of these membranes is low and thus

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requires high operating pressure [8]. Therefore, MF and 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 UF combine with other physical and chemical processes could be effectively used for the removal of dyes from aqueous solution [9,10]. There are two widely used separation techniques: micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF). MEUF and PEUF combine UF 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 UF. Since the pore size of UF membranes is not suitable to separate dyes, water-soluble polymers are used to bind the dyes to form macromolecular complexes rejected by UF. PEUF is expected to provide enough permeation flux with high efficiency.

Polyelectrolytes are particularly useful for the formation of complexes with a variety of molecules ranging from surfactants [11,12], peptides [13], metal counterions [14], dyes [15], etc. Application of polyelectrolyte in the removal of heavy metals by polyelectrolyte enhanced ultrafiltration (PEUF) has a huge potential [16–18]. The mechanism of solute removal in the PEUF process is based on the principle of complexation of the polymer molecule with the charged solute and the complex retention using a relatively open membrane [19,20].

The objectives of this paper are to study the effect of a surfactant on the efficiency of dye–polyelectrolyte solution treatment by UF and the effectiveness of PEUF for the removal of methyl orange (MO). Effects of polyelectrolyte concentration, transmembrane pressure, ionic strength and pH on the removal of MO are investigated.

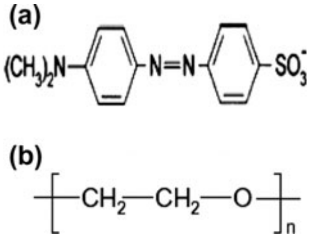

Fig. 1. Molecular structure of (a) MO and (b) PEG.

2. Experimental

2.1. Chemicals

The chemical structures of the molecules used in this work are shown in Fig. 1(a) and (b). MO is a water-soluble azo dye which is widely used in the textile, printing, paper manufacturing and also in research laboratories. MO ($C_{14}H_{14}N_3NaSO_3$, MW 428 Da) was purchased from Fluka. Water-soluble polymer: polyethylene glycol (PEG) (average MW 35,000 Da) was used in this study. This chemical was supplied by Sigma–Aldrich. Octadecyltrimethylammonium bromide (CTAB, MW 392.52 Da) was obtained from Fluka. All the chemicals were used without further purification. Distilled water was used for solution preparation.

2.2. UF experiments

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. The inlet flux was held constant (up to 0.5 $m\ s^{-1}$) and a drop in pressure was varied from 0.8 to 2.2 bars by restricting the outlet tube. Organic regenerated cellulose membrane of molecular weight cut-off (MWCO) 10,000 Da, obtained from Millipore was used for all the PEUF experiments.

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

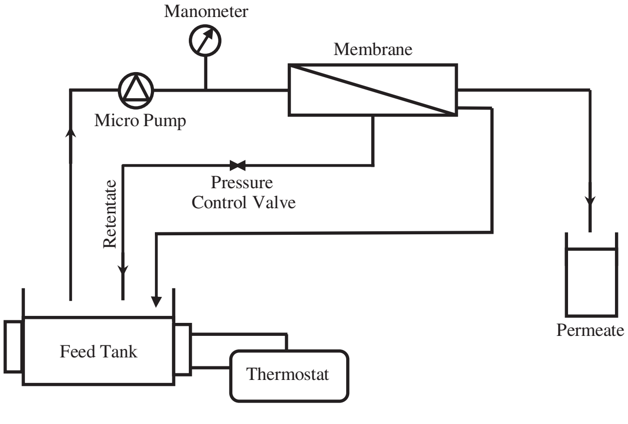

Fig. 2. Schematic diagram of the experimental set-up.

$$J = L_p \Delta P \tag{1}$$

L_p is the permeability of solvent; ΔP is the transmembrane pressure. The value of linear permeability obtained from pure water fluxes was 89.15 L h^{-1} m^{-2} bar^{-1}.

2.3. Methods and analysis

An initial feed volume equal to 200 mL was introduced to the feed tank and was circulated through the module by a micro pump with a variable flow rate was used to feed the solution into the cell. The retentate as well as permeate was recycled into the feed tank. After nearly 30 min, a steady state was reached and permeate of 10 mL was collected and analysed.

After each run, the cell and the membrane were washed thoroughly with pure water for at least 15 min. During compaction of membrane, water flux was measured continuously by a constant flux results. After thoroughly cleaning the system several times with pure water, the membrane permeability was re-evaluated. It was observed that the membrane permeability remained almost constant between successive runs.

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

$$\text{Decolourization } (\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100 \tag{2}$$

where C_0 (mM) is the initial concentration of dye in the feed solution and C_p (mM) 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 is the 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 length. The spectra were scanned in the wavelength region of 400–750 nm. The dye concentration in the absence of CTAB was calculated at 460 nm and in the presence of CTAB at 430 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. Polyelectrolyte concentration varied from 0 to 80 mM, while dye and CTAB concentrations were kept constant at 0.5 and 0.4 mM, respectively, in the effect of polyelectrolyte concentration. For the ionic strength, the MO concentration, PEG concentration and CTAB concentration remained constant at 0.5, 20 and 0.4 mM, respectively, while salt concentration was changed. pH meter (Metrohm 654), equipped with a glass electrode was used for measuring pH solutions. The pH varied from 2 to 12 by adding hydrochloric acid (1 M) or sodium hydroxide (1 M).

3. Results and discussion

3.1. Results obtained from the spectral measurements

3.1.1. The effect of polyelectrolyte concentrations

Azo dyes are well known to form dimers or higher order aggregates in aqueous solution depending on dye structure and media properties [21] and/or the presence of template molecules such as polymers [22], proteins [23] and surfactants [24]. The aggregation of dyes is accompanied by the changes in the absorption or fluorescence spectrum compared to the individual monomeric molecules.

The visible absorption spectra of mixed solutions with a fixed concentration of MO of 4 μM and varying concentrations of the PEG in aqueous media from 0 to 20 mM are shown in Fig. 3(a). In aqueous solution, MO dye exhibits a maximum absorption band at 460 nm. This observation is consistent with literature reports [25]. As PEG concentrations increased gradually, the monomer dye absorbance slightly decreased and the maximum absorption was kept constant at 460 nm. This result confirms the fact that the interaction between MO dye and PEG is not a type of complexation mechanism.

Ouyang et al. [26] found that, when high molecular weight PEG such as PEG 800, 2,000 and 20,000 are added to the orange I aqueous solution, no obvious red shifts of $\lambda_{\max}$ are observed at different PEG concentrations, whereas we report that the J- aggregates of anionic azo dye orange I can be induced by addition of PEG oligomers (PEG 200, 400, 600) in aqueous solutions, the self-association of the dye is reflected by the large red shift of the absorption band. The aggregation of the dye is strongly affected by the PEG molecular weight, PEG concentration and the ionic strength of the solution.

The same behaviour has been reported in the case of the absorption spectra of crystal violet [27] in the presence of polyethylenimine (PEI) at various concentrations. When the PEI concentrations increased the

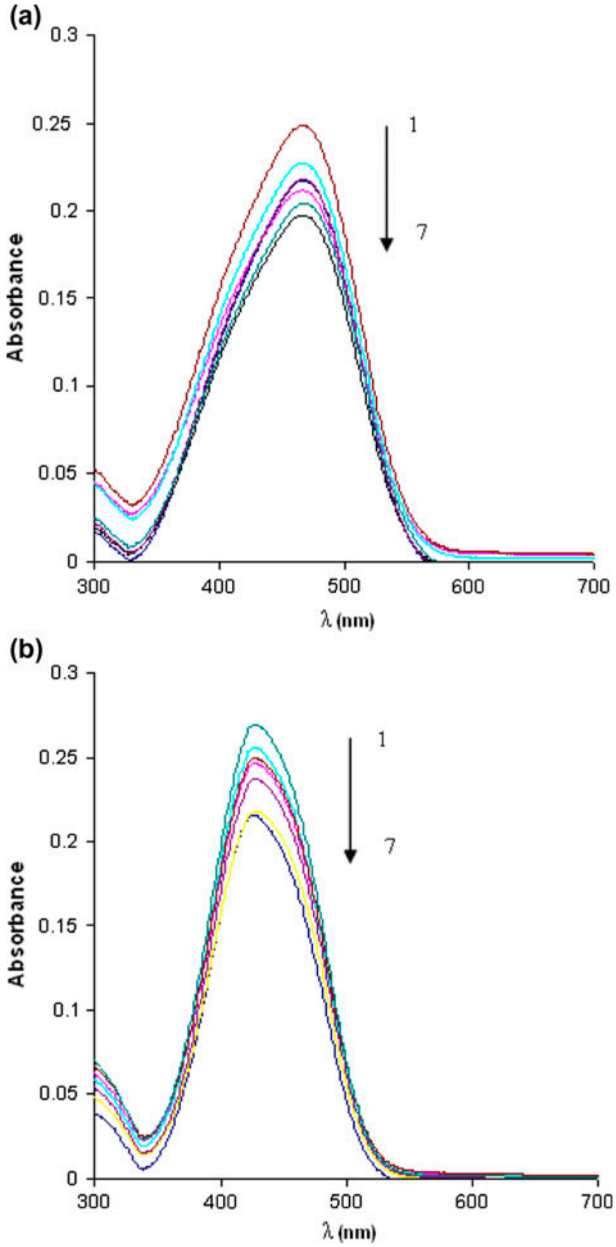

Fig. 3. The visible absorption spectra of MO at (4 μM) in presence of (a) PEG at variables concentrations (mM): (1): 0; (2): 1; (3): 2; (4): 5; (5): 8; (6): 10; (7): 20; (b) and in presence of CTAB (0.2 mM).

absorption wavelength does not change. PEI produces no perturbation in the visible spectra of the CV dye. It means that no complex could be formed in the solutions.

Fig. 3(b) presents the visible spectra of aqueous MO solution at 4 μM for several polyelectrolyte concentrations ranging from 0 to 20 mM in the presence of CTAB at concentration 0.2 mM lower than its critical micelle concentration (CMC). The CMC of CTAB is 0.65 mM [28]. It can be noticed from this figure that the addition of CTAB at a fixed concentration below the CMC shift the λ_{max} from 460 to 430 nm. At low surfactant concentrations (below the CMC), the observed changes can be ascribed to the formation of dye–surfactant ion pairs and large aggregates containing the dye in a dimeric or higher aggregation state [29].

In general, studies of polyelectrolyte/surfactant complexes (PSCs) have shown that surfactants with charge opposite to that of the polyelectrolyte can aggregate with the polyelectrolyte in solution to form a PSCs due to both an electrostatic attraction of the oppositely charged species and the cooperative hydrophobic attraction of the tail groups of the surfactant molecules that results in the formation of polyelectrolyte/surfactant aggregate [30]. This aggregation of the polyelectrolyte and surfactant can occur up to several orders of magnitude below the CMC of the surfactant and is often referred to as the critical aggregation concentration.

This blue shifted may be attributed also to the formation of aggregates in the aqueous solution. H aggregates are spectroscopic entities that are characterized by a blue-shifted adsorption with respect to monomer absorption. The H aggregate is formed with face-to-face stacking with the molecules adopting a slipped parallel structure due to the neighbouring weak π–π intramolecular interaction [31].

Zaghbani et al. [28] found that in the presence of CTAB (below CMC), the spectrum of EBBR shift from 530 to 672 nm. The increase in λ_{max} values can be assumed due to some sort of association or complex formation between dye and surfactant. The complex formation of the dye surfactant is a consequence of the mutual influences of electrostatic and hydrophobic interactions. The formation of ion pair EBBR–CTAB reduced the electrostatic interaction between anionic dye molecules and thus, enhanced dimerization by London dispersion and hydrophobic forces.

No spectral changes are observed on addition of the PEG at varying concentrations.

3.2. *Dye decolourization*

3.2.1. *Effect of the polyelectrolyte concentrations in absence and in presence of CTAB*

UF experiments were conducted at room temperature (25˚C) and at a fixed transmembrane pressure of 2 bars. The effect of the polyelectrolyte concentrations is carried out of MO. PEG concentrations varied from 0 to 80 mM, while the concentration of the dye and surfactant was kept constant at a value of 0.5 and 0.4 mM, respectively. Fig. 4(a) and (b) shows the retention rate of MO and flux permeates as a function of PEG concentrations. As shown in Fig. 4(a), in the absence of polyelectrolyte, the retention of MO was about 19%. 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 from this figure that in the absence of CTAB, the retention of MO reaches 60–70%. This increase in retention can be attributed to the adsorption of PEG molecules to the surface of the membrane; the polyelectrolyte molecules non-coordinated with MO dye will provoke problems of fouling.

Vela et al. [32] found that despite the MW of PEG (35,000 Da) being much greater than the membrane MWCO (10,000 Da); measured membrane PEG retention confirmed that some PEG molecules passed through the membrane. An explanation for this can be found in the fact that PEG molecules are not spherical but have an elongated morphology and a non-rigid chemical structure. Another reason for this may be the influence of MW distribution of the PEG used in the experiments.

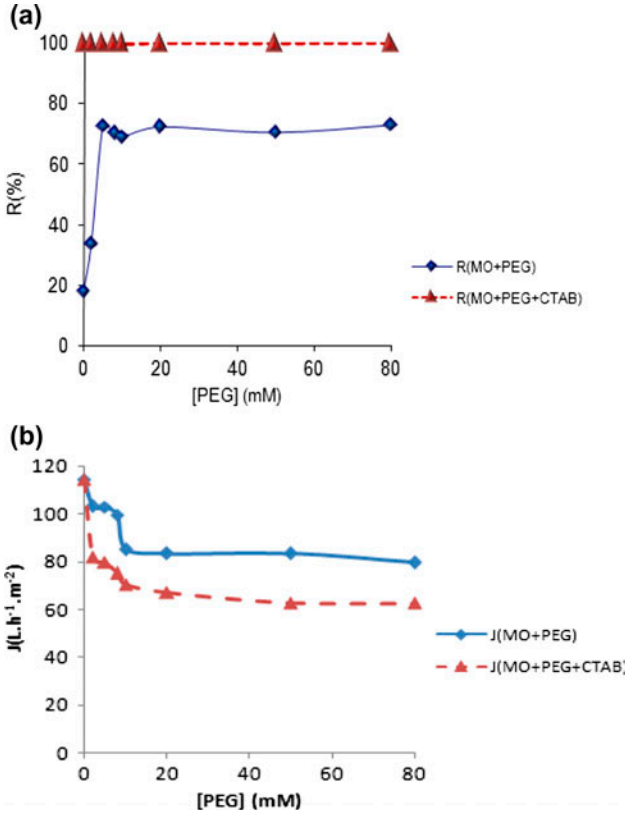

Fig. 4. Effect of polyelectrolyte concentrations on the retention (a) and permeate flux (b) of MO. [MO] = 0.5 mM, [CTAB] = 0.4 mM, $\Delta p = 2$ bar.

However, when the CTAB was applied in the MO–PEG solution, the decolourization is increased and then reaches a limiting value of 99%. The further increase in retention can be assumed due to the complex formation. The efficiency of the separation of the system dye–polyelectrolyte by the process of UF can be improved by the addition of a surfactant, which can act as a complexing agent. The result was further confirmed by the measurement of $\lambda_{\max}$ indicates in Fig. 3(b). The same behaviour was observed in the effect of PEG on Cu^{2+} removal in micellar enhanced UF. As SDS is an anionic surfactant and PEG is a nonionic polymer, there is a great tendency of interaction of hydrophobic character [33].

Katarzyna [34] investigated the effect of a cationic polyelectrolyte on the dye and surfactant removal from aqueous mixtures by low-pressure membrane process. It was found that when a cationic polyelectrolyte was present in the dye–surfactant mixture, this was concomitant with a decrease in membrane permeability and an increase in dye and surfactant retention.

Petzold et al. [35] found that polyelectrolyte–surfactant complexes can remove dyes due to triple complex formation. They concluded that the dyes with positive charge were effectively removed with complexes with an excess of polyelectrolyte and they found that complexing agents with hydrophobic parts and positive or negative charge are able to bind the dye via hydrophobic as well as electrostatic interaction forces.

Fig. 4(b) depicts the effect of polyelectrolyte concentrations on the permeate flux of MO, this figure shows that the permeate flux of dye depended slightly on the PEG concentrations. In addition, it can be observed from this figure that the permeate flux was higher for the dye solution as compared to the presence of polyelectrolyte. In the case of UF process, the cake formation was less noticeable since the dye particle could easily pass through the membrane, thus, reducing the resistance against the solvent flux through the membrane. Furthermore, it was also found that the permeate flux of MO–PEG system was a little bit higher compared to MO–PEG–CTAB system. This trend may be explained by the formation of some aggregates in the presence of CTAB. This generates a deposited layer over the membrane surface and a consequently increased the resistance against the solvent flux through the membrane. In addition, the flux decline caused by the accumulation of molecules on the nearby membrane surface, known as concentration polarization, may lead to membrane fouling. 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.

3.2.2. Effect of transmembrane pressure

The effect of transmembrane pressure on UF dye rejection at a fixed PEG, MO and CTAB concentration of 20, 0.5 and 0.4 mM, respectively, is depicted in Fig. 5(a). It can be noticed from this figure that the retention of MO remains independent of pressure. This observation indicates that the retention of the dye in the presence of polyelectrolyte by the membrane governs overall dye retention. Similar behaviour is observed in the literature [36].

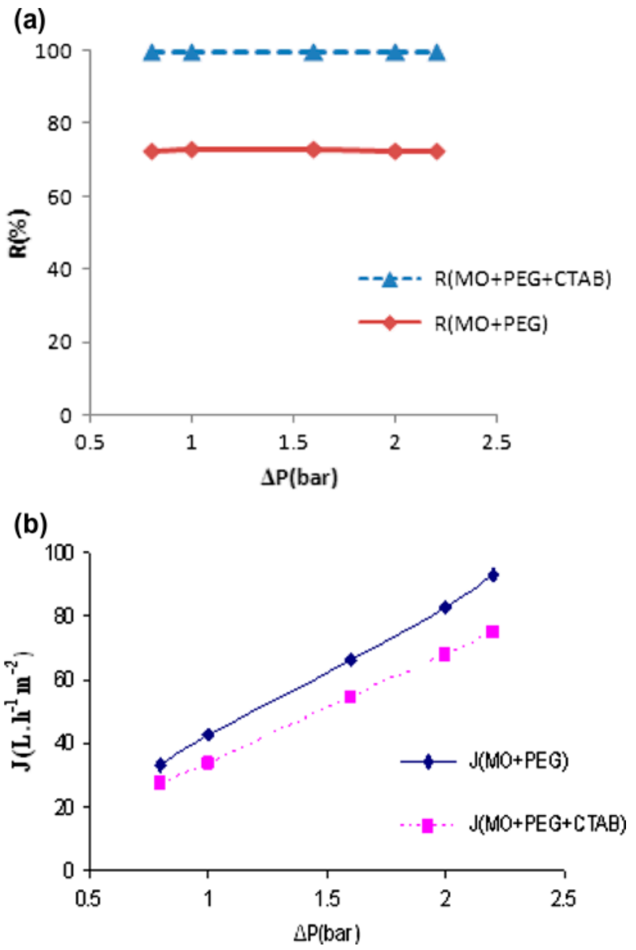

Fig. 5. Effect of transmembrane pressure on (a) MO retention and (b) permeate flux of MO. [PEG] = 20 mM, [MO] = 0.5 mM, [CTAB] = 0.4 mM, $\Delta p = 0.8$, 1, 1.6, 2 and 2.2 bars.

The effect of operating transmembrane pressure (ΔP) on the permeate flux for fixed dye, polyelectrolyte and CTAB concentration is presented in Fig. 5(b). It is evident from this figure that the flux increases with pressure. This results in an increase in the permeate flux due to an increase in the effective driving force. With increase in pressure, the effective driving force for the solvent transport is higher for a fixed feed concentration [37].

3.2.3. Effect of salt concentrations

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 ionic strength on the removal of MO by a PEUF process.

The effect of added salt concentrations on the retentions of MO is shown in Fig. 6, where it can be seen that increase in salt concentrations decreased the dye removal in the absence of CTAB. For example, in the case of Na_2SO_4, retention decreases from 53 to 31%. As salt concentration increases, there is a competitive inhibition occurs between the binding of dye molecule and the salt to the monomer. 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 [38]. However, beyond a certain salt concentration, 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, in order to maintain electroneutrality of the solution, there is a dynamic equilibrium between the relative attachment of dye molecules, salts and dissociation of dye molecules and the polymer. At high salt concentration, the polymer dissociation is affected by the local development of the charged layer near the monomer attachment sites owing to distortion of the electric field attraction of the free counter ions [39].

However, when the CTAB was applied in the MO solution, it should be mentioned from this figure that MO retention kept constant upon increasing the salt concentrations. The addition of CTAB at a fixed concentration to the solution did not influence the removal of MO It also noticed from this figure that the retention of MO was not affected by various types of salts present in the solution.

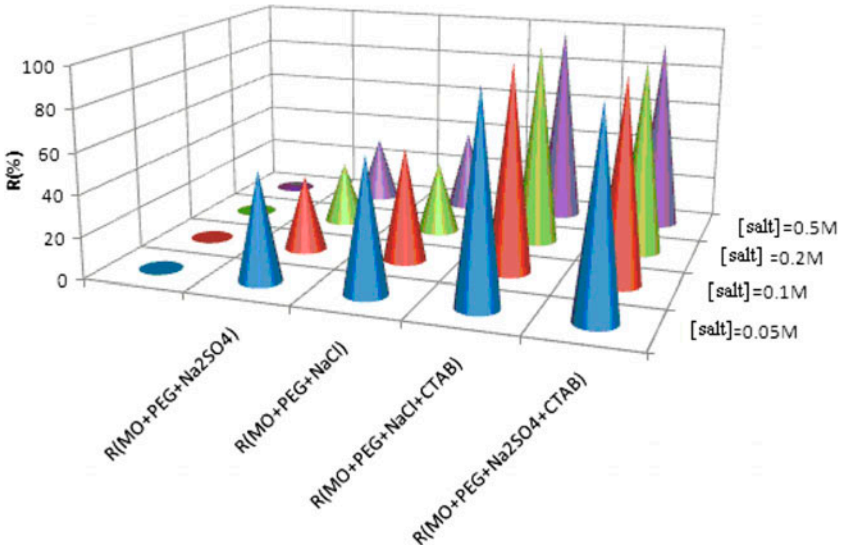

Fig. 6. Effect of salt concentrations on the MO retention. Concentration of MO, PEG and CTAB are 0.5, 20 and 0.4 mM, respectively. $\Delta p = 2$ bar.

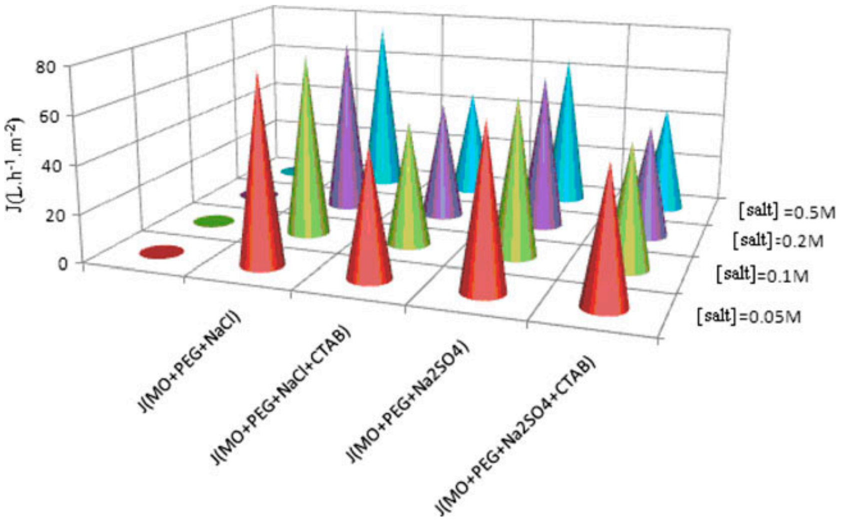

Fig. 7. Effect of salt concentrations on the permeate flux. Concentrations of MO, PEG and CTAB are 0.5, 20 and 0.4 mM, respectively. $\Delta p = 2$ bar.

Fig. 7 illustrates the variation of permeate flux as a function of salt concentrations. It is obvious from this figure that permeates flux remains independent of ionic strength. It was also found that the permeate flux in the case of NaCl is higher than Na_2SO_4. Low permeability in the presence of salt could be ascribed to the rise in osmotic pressure caused by the decrease in the driving force.

3.2.4. Effect of pH

Dye wastewater is discharged at different pH. Therefore, it is important to study the role of pH in the decolourization of MO. The pH of the solutions was maintained by adding hydrochloric acid (1 M) or sodium hydroxide (1 M) solutions. Aqueous solutions of different concentrations were carried out in the range of pH 2–12 to study dye removal. These experi-

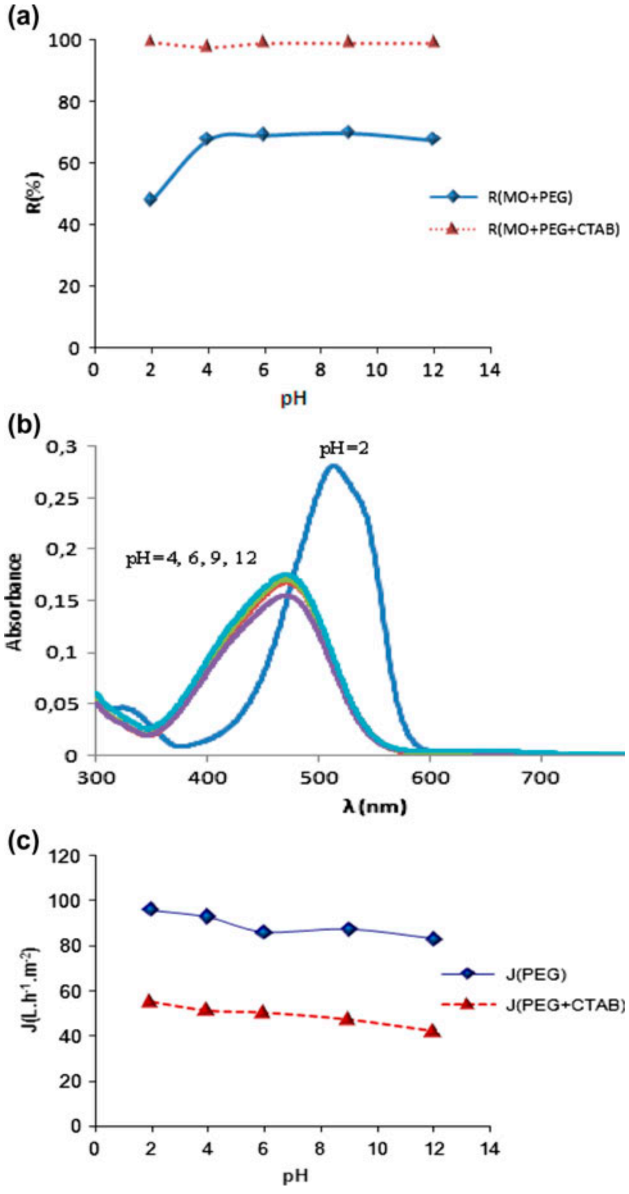

Fig. 8. Effect of pH on (a) MO retention, (b) visible absorption spectra of MO (4 μM) and (c) permeate flux.

ments were conducted in polyelectrolyte and dye concentration of 20 and 0.5 mM, respectively. Fig. 8(a) presents the results of the influence of the solution pH on the MO removal. It can be seen from this figure, maximum retention of MO was noticed as follow 70% for pH above 4, in the acidic region, the removal of MO increases by increasing the pH of the feed solutions. According to Fig. 8(b), from pH 2 to 12, the absorption intensities of MO increased with its position red shifted from 465 to 508 nm. Meanwhile, intense absorption band of MO at 465 nm which was replaced by an intense band at 508 nm in acidic solutions was assigned to the (n–Π^*) transition [40]. MO is red coloured below pH 3 and appears yellow above 4 (pKa = 3.7) and the colour depends upon the concentration of H^+ and OH^- ions. This is due to that in acid medium; the structure of MO is quinoid (Fig. 9), which is more stable than azo form. Therefore, the strong acidic condition blocks MO retention.

The same behaviour has been reported in the case of the retention of crystal violet [27] by PEUF in presence of PEI. The sharp increase obtained in the retention of CV might be explained that at higher pH, CV becomes colourless and the colour could be again retrieved by adding acids. The reaction of CV with the hydroxide ion brings about fading of the colour of the CV and results in the formation of the colourless carbinol.

Ku et al. [41] stated that solution pH level plays a very important role on the surface charge of the membrane and the species distribution of the acidic dyestuff. For experiments conducted in solutions of pH levels greater than the pKa of specific acidic dyestuff, the permeability and rejections of dyestuffs 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 the electrostatic attraction between the positively charged membrane and negatively charged dyestuff species.

Whereas, when CTAB (0.4 mM) was applied, it seems that there is no significant effect of pH on the retention of MO dye. The decolourization is near 99% in the whole range of pH. The increase in decolourization has been linked to complex forms.

Fig. 8(c) represents the variation of permeate flux with pH for fixed dye and polyelectrolyte concentrations. From this figure, it can be observed that the pH

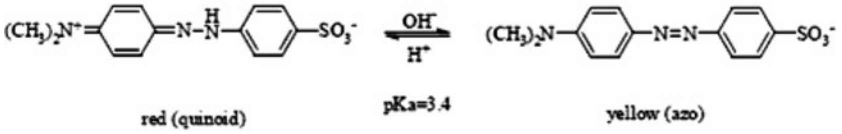

Fig. 9. Effect of pH on the structure of MO.

did not have any significant effect on permeate flux of MO by PEUF in absence and in the presence of CTAB.

4. Conclusion

The study of the effect of adding a surfactant (CTAB) to a concentration below the CMC on the retention of MO showed a high retention about 99%. This was due to the formation of some aggregates in the aqueous solutions. In the presence of CTAB, the pH and the ionic strength have no significant effect on the removal of MO. Spectroscopic results show that the surfactant affected the MO spectra; a blue shift was noted and confirmed the nature complexes. The UV–visible spectrometry further confirmed the above results of the PEUF. These results demonstrate the potential of the PEUF for effective removal of organic pollutants such as MO.

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