Chapter 3

INTERACTION OF MODEL EFFLUENTS WITH PAA/CHI AND PAA/PEI MULTILAYERS

Abstract

Composite membranes have been developed from polyamide based microfiltration membranes by self assembly of polyelectrolytes. Polyethyleneimine (PEI), chitosan (CHI) and polyacrylicacid (PAA) were used as polyelectrolytes. The composite membranes were characterized by SEM and FTIR. Model textile effluents based on methylene blue (MB) and coomassie brilliant blue (CBB) were used to investigate their loading and release behavior. The uptake of dye is very much dependent on the type of bilayer. In case of MB, the amount of dye uptake by the multilayer is high with PAA/CHI bilayer and the conformation of dye within the multilayer also has an influence on this. With CHI as the cationic polyelectrolyte, the dye seems to exist in aggregated form within the multilayer. In PAA/PEI multilayers, the dye exists in monomeric and dimeric forms. Dependence of dye loading and release on outermost polyelectrolyte layer, pH of polyelectrolytes and pH of model effluent were investigated with PAA/CHI and PAA/PEI multilayers. Release studies of MB and CBB using 19.5-20 bilayer PAA/PEI and PAA/CHI multilayers show a pH sensitive mechanism. Effective release of MB occurs at low pH (pH 3). But
for CBB the enhanced release takes place at pH 7. The controlled loading and pH sensitive release behavior of multilayers are useful towards drug delivery applications. Analysis of physico-chemical parameters like COD, TDS and TSS of model effluents after the loading reveals that this method is very efficient for reducing both colour and other parameters from effluent stream. This makes the PAA/PEI and PAA/CHI multilayer systems as an effective tool for the effluent treatment.

**Scientific background and motivation**

The effluent treatment in many countries has been focused on industrial wastewater reuse. This reduces the discharge of pollutants and at some instances recovers useful chemicals and byproducts. Wastewater discharged from the dyeing process is the biggest contributor to textile effluent since it carries many auxiliary chemicals and residual dyes. Annual discharge of dye effluent is around 50,000 tones per year. During dyeing process a minimum dye loss of around 10% takes place for all dyes and this value increases up to 60%. Dyeing effluents has high COD, BOD, toxic substances and intense colour. Wide range of structurally diverse dyes is used in textile industry and therefore effluents from the industry are extremely variable in composition. Dye house effluent is very stable to light and air oxidation and the degradation is very difficult because of the presence of complex aromatic molecular structure and synthetic origin. Even though the dye concentration in
Effluents is usually lower than any other chemical found in these wastewaters, but due to their strong color they are visible even at very low concentrations. The synthetic dyes especially methylene blue cause various health issues in human beings [1-6]. It causes adverse effect on functions of cardiovascular, central nervous, gastrointestinal, genitor-urinary systems. Pericardial pain, dizziness, mental confusion, headache, fever, staining of skin, injection site necrosis, fecal discoloration, nausea, vomiting, abdominal pain, discoloration of urine, bladder irritation and anemia can happen due to MB [7].

Several methods including adsorption, ozonation, photocatalytic oxidation, Fenton and photo-Fenton oxidation, ultraviolet (UV) irradiation, electrochemical oxidation electrochemical degradation, coagulation flocculation, biological treatments like bacterial oxidation and flotation are some of the methods used for removal of color, COD and BOD of the effluent [1-15]. Most of these methods suffered from one or other drawbacks. Bacterial oxidation methods are very effective for the removal of BOD but not effective in colour removal. Chemical oxidation methods are very effective for color removal but cause the formation of hazardous byproducts in the stream and thereby inducing high COD values [13,14].

Among these, membrane processes appears to be the most promising methods for textile water reuse. Membrane separation
processes such as microfiltration, ultrafiltration and nanofiltration have been successfully employed at various stages of treatment of effluents. Microfiltration (MF) is suitable for the removal of colloidal dyes where as ultrafiltration (UF) removes particles and macromolecules [15-23]. Nanofiltration is one of the widely used process currently since it aids the separation of low molecular weight compounds [14,15]. Major draw back associated with the membrane filtration is the disposal of concentrated residue.

MB and CBB are having many applications in biological and medicinal fields. MB is used for treating malaria, ifosfamide neurotoxicity, fungal infections, carbon monoxide poisoning etc. In biology methylene blue is used as a dye for a number of different staining procedures and a redox indicator in analytical chemistry. The coomassie dye is a wool dye and it has recently been used in scientific experiments to treat spinal injuries. Coomassie dyes are an integral component of the Bradford method for determining protein concentration in solution. Due to wide range of applications, a method for the concentration of dye molecules from dye effluent and its reuse via release is also very important.

The layer-by-layer (LbL) assembly of cationic and anionic polyelectrolytes on porous substrates results in novel composite membranes with tunable ultra thin, highly selective separation layer. The possibility to tune their electrostatic nature and thereby
the overall properties by changing the adsorption conditions make PEM useful in many processes. Various applications like gas separation, alcohol-water separation under pervaporation conditions, ion separation, water softening and water desalination under reverse osmosis conditions are possible with polyelectrolyte multilayers [21-31]. Nanoscale level control over each deposited layer makes it a very attractive tools for waste water treatment [26,27]. Since the permeability of PEMs can be well tuned with slight pH adjustments, PEMs can act as a shell that can form open and closed structure at different pH conditions. This property enables the complete recovery of the adsorbed dyes and their reuse after releasing completely under specific pH conditions.

![Chemical structures](image)

**Fig. 3.1:** Structure of (A) methylene blue (MB) and (B) coomassie brilliant blue (CBB)

Loading and release of MB and CBB from model effluent solutions with PAA/CHI and PAA/PEI multilayers by preferential
adsorption method under different adsorption conditions have been investigated. The main objective of the study is to explore the possibility of concentrating and separating the toxic chemicals released into water bodies by a relatively cost effective process. pH controlled release of the loaded dye into water is also studied, which may have relevance in drug release mechanism.

3.1. Characterization of multilayers

The FTIR spectra of PAA/CHI bilayers are given in Fig. 3.2. The absorbance at 1730 cm\(^{-1}\) appears after deposition of PAA/CHI layers, and the peak area and intensity increase with the number of deposited layers. The absorbance at 1730 cm\(^{-1}\) is due to carbonyl stretch of COOH group of PAA [32-34].

![FTIR spectra](image)

**Fig. 3.2:** FTIR spectra of (A) Nylon and PAA/CHI membrane with (B) 5 (C) 9 and (D) 20 bilayers. Deposition pH of PAA and CHI solution are 4 and 2 respectively.
Unlike PAA/CHI, the PAA/PEI FTIR spectra do not show the presence of carbonyl absorbance (1730 cm\(^{-1}\)). Upon deposition of PEI the acid carbonyl groups have completely disappeared, most of the COOH groups are deprotonated during the deposition of PEI (Fig. 3.3).

The broadening and increase of absorption intensity at 1560 cm\(^{-1}\) indicates the increased amount of carboxylate groups in the multilayers. The deposition pH of PEI very much influences the adsorption characteristic of PAA. A 20 bilayer membrane was used for the study and FTIR showed the decrease in the acid carbonyl of PAA with pH (Fig. 3.4).

![FTIR spectra of PAA/PEI membranes](image)

**Fig. 3.3:** FTIR spectra of PAA/PEI membranes with (A) 20 (B) 9 and (C) 5 bilayers. Deposition pH of PAA and PEI solutions was 4 and 6 respectively.
When PEI is deposited from a solution having pH 2, PAA exist mostly in protonated form (~1730 cm$^{-1}$). At pH 4, 70-80% of COOH groups have been converted to COO$^-$ (1500 -1580 cm$^{-1}$). At higher pH, this decrease is even more pronounced. With the increase in pH, broadening is also observed in the COO$^-$ absorption region. So at pH 6 of PEI, most of the adsorbed PAA exist in deprotonated form [32-34]. The SEM images (Fig. 3.5) also show the variation in the molecular architecture with CHI and PEI. When CHI is the cationic polyelectrolyte, pores are visible even after deposition.

![FTIR spectra of PAA/PEI](image)

**Fig. 3.4:** FTIR spectra of PAA/PEI (20 bl). pH of PEI: (A) 2, (B) 4 and (C) 6. Deposition pH of PAA was 4
Fig. 3.5: SEM Images of (A) Bare nylon and 20 bl (B) PAA/CHI (C) PAA/PEI. pH of PAA, CHI and PEI was 4, 2 and 6 respectively
3.2. Effect of number of bilayers on uptake of dye

PAA/PEI and PAA/CHI multilayers were selected for loading of MB and CBB based model effluents. Methylene Blue is a heteroatomic, water soluble cationic dye. UV-visible spectra of methylene blue solution contains a band associated with monomeric units at 665 nm and a shoulder at 605 nm which are attributed to the 0-1 vibronic transition of the monomer [22]. In water, MB cations associate so as to reduce their hydrophobic interactions with water. In the case of heavy loading, MB may agglomerate and gives bands at 560-580 range [22].

The UV-vis absorption spectra of MB loaded PAA/CHI and PAA/PEI multilayers are shown in Figs. 3.6 and 3.7 respectively. Absorption spectra of the film show peaks at 665, 605 and 560-580 nm, which corresponds to monomer, dimer, and agglomerate forms respectively. The uptake of cationic and anionic dye observed to be very much dependent on the type of cationic bilayer. In the case of MB, the amount of dye uptake by the multilayer is high with PAA/CHI layer and the conformation of dye within the multilayer also has an influence on this. With CHI as the cationic polyelectrolyte, the dye seems to exist in aggregated form within the layers. The visible spectra shows broad band at ~ 580 nm together with a shoulder at 655 nm indicative of monomeric form (Fig. 3.6). The dye molecule seems to have diffused into the bulk which facilitates the efficient uptake. CHI
has a number of adsorption sites and in acidic medium the amino group of the chitosan is readily protonated and it becomes highly charged [22].

![UV-vis spectra](image)

**Fig. 3.6:** UV-vis spectra of MB loaded PAA/CHI membranes. Number of bilayers 3.5, 4.5, 6.5 and 9.5 respectively in the increasing order. Deposition pH of PAA and CHI was 4 and 2 respectively.

The adsorption of oppositely charged dye molecule to chitosan takes place mainly due to electrostatic interactions. At pH 2, CHI has many cationic centers (NH₃⁺) thus providing many charged sites for binding. In a self assembled system of polyelectrolytes the control over layer thickness and molecular architecture can be achieved by optimizing the deposition pH of the weak polyelectrolyte [25]. PAA at pH 4 was used as the anionic
polyelectrolyte for the LbL assembly along with CHI. pKa value of PAA is 4.3. Above this pH PAA is negatively charged due to deprotonation and at low pH it is chargeless. At pH 4, PAA is partially ionized [25].

The possible electrostatic interaction between PAA and CHI can be represented as follows,

\[
\text{D-COONa} \rightarrow \text{D-COO}^- + \text{Na}^+
\]

\[
\text{R-NH}_2 \rightarrow \text{RNH}_3^+
\]

\[
\text{RNH}_3^+ + \text{D-COO}^- \rightarrow \text{RNH}_3\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{OOC-D}
\]

The degree of ionization of PAA chain is about 20-30-% at pH~2.5 and reaches 100% at pH 6 [28]. The charge density of polyelectrolyte can be controlled by deposition pH and large changes in thickness of the adsorbed layers can be brought about by small changes in pH of deposition [24-25]. A combination of partially ionized/fully ionized polyelectrolyte pair yield thick and interpenetrating bilayers due to non stochiometric pairing of chain segments. Such loopy conformations can swell when the film is placed in contact with aqueous solutions. During uptake, charged dyes are loaded into bulk of the membrane along with the surface [24].

In a multilayer system with PAA as the anionic polyelectrolyte, almost 70% of the bilayer thickness will be contributed by PAA [28]. In a non-stoichiometric pairing condition (as in PAA/CHI bilayers), the loopy, interpenetrating bilayer
contains a large number of uncharged PAA segments not electrostatically bound to cationic polyelectrolyte as can be seen from the FTIR spectra (Fig. 3.2). When such a multilayer is introduced into a solution with high pH (above 4.3, i.e., pKa of PAA), all these uncharged and unbound COOH groups are deprotonated and can attract and bind to oppositely charged ions. Due to 70% bilayer contribution, at higher pHs the multilayer as a whole is negatively charged, which facilitate the uptake of cationic molecule.

The uptake is also increased by hydrogen bonding and van der Waals forces from alternating CHI layers since at higher pH it would deprotonate (effluent pH is 10.5). At this pH, membrane as a whole is negative hence, better loading of MB to surface and inner

Fig. 3.7: UV-vis spectra of MB loaded PAA/PEI membranes. Number of bilayers 3.5, 4.5, 6.5, 14.5 and 19.5 respectively in the increasing order. Deposition pH of PAA and PEI was 4 and 6, respectively
layers of the multilayer takes place. High concentration of charged MB molecules in membrane causes agglomerisation of dye in the membrane surface and bulk [22,28].

Whereas with PAA/PEI combination the dye exist in monomeric/dimeric form as seen from the visible spectra (Fig. 3.7) and the peak position are at 655 nm and 605 nm respectively.

The SEM view of the PAA/CHI and PAA/PEI multilayer shows surface coverage with PEI as the outer layer, while with CHI, the dye molecules have diffused to the inner layers (Fig. 3.8). This also explains the higher proportion of MB uptake by the PAA/CHI bilayers. MB has small molecular size compared with CBB, which can increase the dye -polyelectrolyte ratio in the system. Hence deeper penetration becomes easy. In the presence of H⁺, chitosan has NH₃⁺, cationic centers in the polymer that exist in equilibrium with unprotonated form NH₂. Due to this adsorption can be mainly due to electrostatic forces. At high pH, (effluent has alkaline pH) the unprotonated form is prominent and hence van der Waals forces operate together with electrostatic. In the case of PAA/PEI bilayers, PEI was adsorbed from a solution having pH 6 and PAA from pH 4. Even though partially charged cations and anions are able to form multilayers with appreciable thickness, they are not loopy as much in the case of PAA/CHI multilayers due to the highly branched structure of PEI and comparatively better charge compensation. The multilayers have high degree of cross linking and hence it forms very
dense layers on the surface. Swelling and interpenetration of ions or charged molecules into the bulk is restricted due to this special architecture. So loading is almost surface oriented as seen from the SEM images. FTIR spectra shows the absence of free COOH groups available for deprotonation. Here, PAA is adsorbed to multilayer surface as COO\(^-\) and are bound to positive sites and are not available for binding with dye molecule. Due to these facts PAA/CHI multilayers are more effective for the loading of MB compared with PAA/PEI multilayers.

![SEM images](image)

**Fig. 3.8:** SEM images of MB loaded 20 bl (A) PAA/CHI and (B) PAA/PEI. Deposition pH of PAA, PEI and CHI was 4, 6 and 2 respectively.
Similar investigations were carried out for anionic dye molecule CBB. Large CBB molecules do not completely penetrate in to the inner layers, so that dye molecules preferentially get adsorbed near the outer surface [35]. Absorbance spectra after CBB loading shows an increase of absorbance from 0.63 to 0.86 units with PAA/CHI membrane as we increased the number of bilayers from 3 to 20 and in the case of PAA/PEI membrane the absorbance increase from 0.51 to 1.23 units (Figs. 3.9 and 3.10).

Fig. 3.9: UV-vis spectra of CBB loaded PAA/CHI membranes. Number of bilayers 3, 5, 7, 15 and 20 respectively in the increasing order. Deposition pH of PAA and CHI was 4 and 2 respectively
The results clearly indicate the diffusion of dye molecules of model effluent into the bulk of the multilayers even though it has high molecular size. If the loading is associated only with the outer surface there will be no linear increase in loading with number of bilayers. We have already discussed the negative charge of PAA/CHI multilayer under alkaline pHs, which is not suitable for the loading of molecule like CBB. PAA/PEI bilayer shows better loading as expected. Even though the pH selection in the case of PAA/PEI is not suitable for the formation of thick, diffusible bilayers, the highly branched structure of PEI and its positive surface charge density may facilitate the uptake of CBB.

Fig. 3.10: UV-vis spectra of CBB loaded PAA/PEI membranes. Number of bilayers 3, 5, 7, 15 and 20 respectively in the increasing order. Deposition pH of PAA and PEI was 4 and 6 respectively.
loading of CBB near membrane surface and aggregation takes place with PAA/PEI multilayers.

The absorbance study of the effluent solution after loading again shows linear decrease of dye concentration with number of bilayers. The initial CBB concentration of 14.75 mg L\(^{-1}\) decreases to 1.5 mg L\(^{-1}\) and 6.75 mg L\(^{-1}\) with 20 bilayer PAA/PEI and PAA/CHI membrane respectively. MB based effluent shows a decrease from an initial concentration of 14.40 mg L\(^{-1}\) to 6.62 mg L\(^{-1}\) and 9.40 mg L\(^{-1}\) with PAA/CHI and PAA/PEI membranes respectively. These results are shown in Table 3.1.

**Table 3.1:** Dependence of loading with number of bilayers. Membranes used were PAA/CHI and PAA/PEI (Initial concentration of CBB and MB was 14.75 mg L\(^{-1}\) and 14.40 mg L\(^{-1}\) respectively). The value in parenthesis represents the number of bilayers used for CBB, where PAA/CHI and PAA/PEI is terminated with cationic layer. Deposition pH of PAA, PEI and CHI are 4, 6 and 2 respectively.

<table>
<thead>
<tr>
<th>Number of Bilayers</th>
<th>Concentration of CBB after treatment</th>
<th>Concentration of MB after treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAA/CHI</td>
<td>PAA/PEI</td>
</tr>
<tr>
<td>3 (3.5)</td>
<td>10.85</td>
<td>2.75</td>
</tr>
<tr>
<td>5 (4.5)</td>
<td>10.65</td>
<td>2.12</td>
</tr>
<tr>
<td>7 (6.5)</td>
<td>10.5</td>
<td>2.10</td>
</tr>
<tr>
<td>9 (9.5)</td>
<td>9.35</td>
<td>2.08</td>
</tr>
<tr>
<td>15 (15.5)</td>
<td>7.85</td>
<td>2.0</td>
</tr>
<tr>
<td>20 (19.5)</td>
<td>6.75</td>
<td>1.5</td>
</tr>
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</table>
3.3. **Effect of polyelectrolyte pH on loading**

The multilayers with desired properties can be fabricated by varying deposition conditions. Deposition pH and supporting salt concentration are among the most important parameters that can control the charge density along the polymer chain so as to manipulate the molecular architecture of multilayers. pH can be used for the variation of charge density in the case of weak polyelectrolyte whereas ionic strength is the variation factor used for strong polyelectrolytes. Such multilayers have controlled molecular organization and surface properties. It is possible to fabricate molecular scale layers of oppositely charged polymers with different conformations [23,36,37]. The bilayer thickness, degree of interpenetration and surface properties depend on the deposited pH and ionic strength [21,25,35,39]. Loading and release of dye molecules can be controlled by choosing the deposition pH. The possible influences of deposition pH of PEI on the loading of dyes to the bilayers have been analyzed and the results are presented in Fig 3.11 and 3.12. A large variation in loading is not observed however, dyes show pH dependency with respect to the charges present in the dye molecules. Loading is high at pH 6 for CBB and at pH 2 for MB.

The deposition pH of PEI was varied from 2-6 for the fabrication of PAA/PEI multilayers. Since PEI is a weak polyelectrolyte, as already discussed it is possible to vary charge
density along the polymer chains by changing the pH. pKa value of PEI is 6.3. Above this pH PEI is weakly charged due to deprotonation of NH$_3^+$ group. The charge density increases with decrease in pH of solution. The deposition pH of PAA is 4, so that it is partially charged.

The pH of deposited PEI in fact determines the ionization of carboxyl group of PAA (Fig. 3.4). At pH 2 of PEI, PAA shows the presence of free COOH groups within the multilayers as can be seen from FTIR spectra (Fig. 3.4). A non stochiometric ion pairing is expected due to fully charged/partially charged polyelectrolyte combination at low pH region (below pKa) that will result in thick and loopy (open) layers so as to facilitate more uptake of dyes. Most of the carboxyl groups have been converted to COO$^-$ as pH is changed to 4. Further at pH 6, both the polyelectrolytes are partially charged leading to stochiometric charge pairing and the bilayers formed are dense and less swollen [33-35].

Even though the dye uptake is expected to be on the higher side at lower pH, CBB uptake is maximum at pH 6. This may be due to the low diffusion of larger CBB molecules to the inner layers. The presence of COOH groups at low pH repels the negatively charged CBB molecules (effluent pH 10.5), but at high pH the number of COOH groups have been decreased and this may decrease the repulsive force between the dye molecule and
multilayer. This together with the larger size of CBB results in the slightly larger uptake at pH 6 (Fig. 3.4).

![Absorbance vs Wavelength](image)

**Fig. 3.11:** UV-vis spectra of CBB loaded PAA/PEI (20 bl). Deposition pH of PEI (A) 6 (B) 4 and (C) 2. pH of PAA is 4

MB being a cationic dye the uptake is high at low pH as expected. When PAA/PEI (pH 4/2) multilayer was exposed to a solution of MB at pH 10.5, all the available free sites (carboxyl groups) are deprotonated and can attract positively charged MB molecule. But the lack of uncompensated charged groups (COOH) inside the polymer matrix at high pHs (4 and 6) makes them less effective for the loading of cationic molecules like MB [24,28]. The absorbance at 580 nm represents that the MB molecules are in aggregated state and the shoulder at 605 nm represents the MB dimers.
The absorbance studies of effluent after membrane treatments also showed similar trend.

The comparatively higher uptake of MB can also be explained on the basis of multilayer thickness. Due to its small size it can travel more distance within the bilayer. As the total film thickness increases, the loading capacity of the multilayer also increases due to diffusion of molecules into multilayers. The conformation and charge density of PEI, changes with pH of the solution which in turn influences the conformational state of PEI during adsorption to multilayers. At low pH, PEI assumes flat conformation due to high intramolecular repulsion. The highest

Fig. 3.12: UV-vis spectra of PAA/PEI (19.5 bl) after MB loading. Deposition pH of PEI: (A) 2 (B) 4 and (C) 6. pH of PAA is 4
loading capacity is achieved by films that are thickest and with a low ionic and covalent cross linking density [28,40,41,42].

3.4. **Dependence of pH of effluent solution on loading**

PAA/PEI and PAA/CHI membranes with outermost PAA layer was used for the pH dependent loading studies of MB. UV-vis spectra (Fig. 3.13) show loading of methylene blue to 20 bilayer PAA/CHI multilayer at varying pH (3, 7 and 10.5). The absorption maxima of MB are at 605 nm (dimers) and 655 nm (monomers) for pH 7 and 3. But for pH 10.5, absorption maxima are shifted towards 580-590 nm and 655 nm. The shift in absorption wavelength towards 580-590 nm regions indicates the aggregation of methylene blue molecule in the multilayer [18,25].

With PAA/PEI multilayers, the bands were obtained at 655 nm and 605 nm, except for loading at pH 10.5. At this pH, the absorption maxima obtained at 580-605 nm region shows the presence of dimmers and aggregates in the multilayers (Fig. 3.14).

Dye molecules generally have a significant hydrophilic or hydrophobic character. Such molecules are having the ability to aggregate when in close proximity to each other. During uptake, the dye molecules are in close proximity and they form aggregates [42]. The aggregation can be characterized by shift in absorption wavelength. The pH, that promotes the electrostatic attraction between dye molecules and functional groups of multilayers, the
dye molecules are closer to each other and thus they are more likely to aggregate.

From absorption spectra of dye loaded bilayers (Figs. 3.13 and 3.14) and from Table. 3.2, it is clear that pH 10.5 is suitable for the loading of cationic MB to PAA/CHI and PAA /PEI multilayers. With PAA/CHI multilayer, 82.4% dye is removed from the effluent solution at pH 10.5. The loading percentage value decreases to 79.5% and 35% when the pH of effluent is 7 and 3 respectively. Compared with PAA/CHI, PAA /PEI bilayers show less loading as already discussed in section 3.2. The loading profile is similar to that of PAA/CHI membranes and at pH 10.5, PAA/PEI show almost 2.5 times better uptake of MB (53.2%) compared with other pH (21.9 and 23.4%, Table 3.2).

![Absorption Spectra](image)

**Fig. 3.13:** UV-vis spectra of MB loaded PAA/CHI (19.5 bil). pH of MB: (A) 10.5 (B) 7 and (C) 3. Deposition pH of PAA and CHI was 4 and 2 respectively.
The factors which affect the loading profile at different effluent pH are, electrostatic interaction between dye molecules and charge probes in multilayers and swelling of multilayers.

Electrostatic interactions play an important role in the heavy uptake of MB molecules at high pH. Methylene blue is a cationic dye and is highly charged in ordinary pH conditions. It is clear that at pH 10.5, PAA is having maximum charge density due to the deprotonation of carboxylic acid groups, and this leads to higher uptake of cationic MB molecules [28]. The repulsion from amino groups of cationic dye is very weak at this pH. This enhances the rate of loading of MB to both PAA/PEI and PAA/CHI multilayers at higher pH.

Fig. 3.14: UV-vis spectra of MB loaded PAA/PEI (20 bl) pH of MB: (A) 7 (B) 10.5 and (C) 3. Deposition pH of PAA and PEI was 4 and 6 respectively
Table 3.2: Dependence of pH of effluent on dye loading and removal, PAA/CHI and PAA/PEI multilayers with 19.5 and 20bl were used for the study. Deposition pH of PAA, CHI and PEI was 4, 2 and 6 respectively.

<table>
<thead>
<tr>
<th>pH of effluent</th>
<th>Removal of CBB (%)</th>
<th>Removal of MB (%)</th>
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<tbody>
<tr>
<td></td>
<td>PAA/CHI</td>
<td>PAA/PEI</td>
</tr>
<tr>
<td>3</td>
<td>74.3</td>
<td>76.3</td>
</tr>
<tr>
<td>7</td>
<td>81.7</td>
<td>82.3</td>
</tr>
<tr>
<td>10.5</td>
<td>44.0</td>
<td>90.0</td>
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</table>

Another factor that affects the loading of dye molecules to multilayers is the swelling upon exposure to aqueous solution. The ability of a multilayer to swell depends on degree of ionic cross linking, dynamic nature of the bonds, degree of hydrophilicity and the electrostatic forces operating in the hydrated film [42]. All these factors are directly related to the charge density of the free functional groups in the multilayers.

At alkaline pH, PAA/CHI and PAA/PEI multilayers undergo deprotonation of carboxyl group. The surface charge density of polymer strands increases and chain extension takes place for stability. This in turn enhances the possibility of swelling in PAA/PEI and PAA/CHI multilayers.

Deprotonation of amino groups at high pH and uptake of counter ions and water molecules for charge compensation is possible in the case of PEI and CHI [43]. This phenomena cause additional swelling at high pH.
Furthermore, the ionic cross links of PAA/PEI and PAA/CHI multilayers are dynamic and sensitive to external pH conditions. This allows the chains to undergo some reorganization during the swelling process due to breaking and deforming of ionic cross links that holds the film together and hence further swelling of the multilayer results. Swelling improves the free voids and sites inside the multilayer which again leads to increased uptake of small molecular size MB on the film [42].

Similar swelling of PAA/PEI and PAA/CHI multilayers is possible at low pH due to the protonation of amino group [42]. The low loading profile of MB molecules at low pH shows the predominance of electrostatic interactions over swelling and diffusion. The positively charged dye molecules get repelled at low pH.

The overall negative charge of PAA/CHI layer is another factor that control loading. As we already discussed, the alkaline environment makes PAA/CHI multilayer more negative and therefore enhanced MB uptake. As fig. 3.14 shows, maximum loading at pH 7 was observed but the absorbance measurement of effluent solution after loading shows a better loading at pH 10.5 (Table 3.2). This may be due to the aggregation of dye on the multilayer surface and thereafter sedimentation into the solution due to large size of the aggregates at pH 10.5.

Figs. 3.15 and 3.16 represent the pH dependent loading of CBB on PAA/CHI and PAA/PEI multilayers with 19.5 bilayers
respectively. PAA/CHI membranes show the absorbance maxima at 610 nm for CBB and showed efficient loading at pH 7. UV-visible spectra clearly indicate the availability of membrane surface near support for loading even after coating 19.5 bilayers of CHI/PSS. More compact and dense PEI/CHI multilayers shows less absorption at substrate surface compared with former system (Figs. 3.15 and 3.16).

![Graph showing UV-vis spectra of CBB loaded PAA/CHI (19.5 bl). pH of CBB: (A) 7 (B) 3 and (C)10.5. Deposition pH of PAA and CHI was 4 and 2 respectively.](image)

**Fig. 3.15:** UV-vis spectra of CBB loaded PAA/CHI (19.5 bl). pH of CBB: (A) 7 (B) 3 and (C)10.5. Deposition pH of PAA and CHI was 4 and 2 respectively.

The above results show that swelling of multilayers has no effective role in the loading of CBB. High swelling of PAA/CHI and comparatively low swelling of PAA/PEI multilayers at pH 10.5 and pH 3 shows no effective changes in loading. Here the surface charge density and overall membrane charges are the
predominant factors which affect the loading of CBB on to multilayer [11]. As we already discussed, it may be due to the large molecular size of CBB compared with MB. Large size of CBB molecule makes the diffusion very difficult in to the multilayer matrix.

CBB is an anionic dye and it shows maximum ionization at higher pHs. Therefore we expect maximum loading at pH 10.5, but CBB shows maximum at pH 7 to PAA/CHI multilayer. At pH 10.5 the outermost CHI layers are weakly charged due to deprotonation hence loading is not efficient at alkaline pH. Moreover the repelling carboxylate groups are very active at this pH and the multilayer as a whole is negatively charged. At low pH (pH 3), as we already explained the cationic centers are fully charged but the CBB is weakly charged. This restricts the CBB molecule to get adsorbed in to multilayers.

At pH 7 (near pKa) PEI and CHI are partially charged and CBB is almost completely deprotonated. These factors enhance the loading of CBB to multilayers. Therefore we got a better loading at pH 7. Due to thick and non loopy structure of PAA/PEI layers the effect of pH on swelling is negligible compared to the former system. The low absorbance of loaded CBB molecules at pH 10.5 supports this observation (Fig. 3.16)

PAA/PEI membrane shows the maximum at 610 nm for pH 3 and 10.5 system, but at pH 7 the maximum is at 570 nm (Fig.
3.16). Shift in absorption maximum at pH 7 may be due to the heavy loading and molecular rearrangements like dimerisation or agglomerisation near membrane surface or bulk [11,44,45].

Table 3.2 shows the percentage of dye removal after membrane treatment as a function of pH of effluent, (dye concentrations are given in bracket after the treatment and were calculated from calibration graph after the treatment). It is evident that both these bilayers are effective for dye removal and the maximum loading in the case of PAA/PEI multilayers at pH 10.5 is due to the aggregation of dye near membrane surface and sedimentation in to solution due to its large size. These aggregates can be easily removed by filtration. With PAA/PEI membrane it is

![UV-vis spectra of CBB loaded PAA/PEI (19.5 bl). pH of CBB: (A) 7 (B) 3 and (C) 10.5. Deposition pH of PAA and PEI was are 4 and 6 respectively](image)
possible to remove 90% dye molecule from pH 10.5 effluent solutions. Low absorbance in the absorption spectra is due to the sedimentation of dye molecule to solution from membrane surface.

3.5. **Dependence of pH on Release**

Industries consume a lot of fresh water during dyeing fabrics and in due course consume lot of non degradable molecules which affect the quality fresh water supplies. Waste water reuse at different stages of dyeing is an important application as far as water conservation is concerned [3]. Textile industry is the larger consumer of fresh water.

Since we have an assembly of CHI, PEI and PAA, which are considered as weak polyelectrolytes, their permeation characteristics can be articulated by controlling pH of the polyelectrolytes during deposition and pH of the filtered solution. This also provides an important platform for loading and release of dyes. So that the used chemicals can be concentrated and release from water. This has a particular advantage of recycling the costliest dyes.

In membrane based textile effluent treatment, microfiltration is used for the removal of colloidal material and the ultrafiltration for macromolecules and other particles. We have already reported that CHI/PSS system can be tuned for the separation and concentration of macromolecules, salts and other small molecules [24]. The dye stuffs can be concentrated and
auxiliary chemicals can be reused since the pH dependent release is possible. This kind of studies can be used to explore the possibility of concentrating dye molecules from water streams with a relatively cost effective process.

Concentration of dye molecules from water streams and its pH controlled release is possible by multilayer treatment. This is possible due to the open and closed structure of bilayers at different pH [46,47]. All these results, reveals the usefulness of pH controlled trigger for changes in polyelectrolyte multilayers.

The release studies were carried out using dye loaded PAA/CHI and PAA/PEI (19.5 and 20 bl). pH of MB and CBB are selected as 10.5 and 7, respectively, for the study. Fig. 3.17 shows the release of MB molecules into the surrounding solution. The MB molecules exist predominantly as dimers in solution after release. The release of MB from PAA/PAH system into water showed that, the released MB is in monomeric state predominantly with trace amount of dimer in the solution [28]. In the present system the existence of MB as dimer in solution indicates the high dye loading efficiency of PAA/CHI and PAA/PEI compared to PAA/PAH.
The release of MB from PAA/CHI and PAA/PEI multilayers is studied and the maximum release rate is observed at pH 3. The amount of dye released at pH 3 is 100%. At pH 5 and 7, percentage release is 52.2% and 28% with PAA/CHI multilayer and 22.27% and 26.3% with PAA/PEI multilayers respectively (Figs. 3.18 and 3.19).

The factors affecting the high release rate at lower pH is the difference in concentration gradient between film and surrounding solution as well as the ineffectiveness of PAA bilayers to bind MB molecules diffused throughout the film surface and bulk.

As pH of the surrounding solution decreases, PAA becomes protonated and less charged. A reduction in the attractive force and accompanying increase in the repulsive interactions between
the dye molecules and the film leads to a disruption of aggregates and promotes the release of dye molecules. The electrostatic bonds between MB and carboxylate groups break. Hence MB is diffused into the surroundings. MB molecule within the film repels each other at lower pH due to large diffusion rate which further enhances the release rate [28].

The total amount of MB deposited on PAA/CHI and PAA/PEI multilayers is 3.02 mg and 3.00 mg respectively. The study shows the loaded dye molecules can be completely released under suitable pH control and could be reused. At pH 3, 100% release of loaded MB molecule is possible as is clear from Figs. 3.18 and 3.19.

![Fig. 3.18: Absorbance of MB (605 nm) released from PAA/CHI (19.5 bl) to water at pH (▲) 3 (●) 5 and (▼) 7. Deposition pH of PAA and CHI was 4 and 2 respectively](image-url)
PAA/PEI and PAA/CHI membranes (19.5 bl) were used for the loading as well as release studies of CBB. 3, 5 and 7 were the pH of surrounding environment selected for the release studies. The release study of CBB shows the change in release rate with the change in substrate. Here PAA/PEI membrane shows negligible release compared with PAA/CHI membrane. At lower pH, there is no release from PAA/PEI membrane (Figs. 3.20 and 3.21)

The relatively low release at pH 3 is due to the high charge density of cationic polyelectrolytes at lower pHs. The loaded CBB molecules are strongly captured within the multilayers due to this high charge density. At pH 7, concentration gradient plays an
important role in the release. But at other pHs both charge density of polyelectrolyte and dye effluent affect the results.

![Graph showing absorbance vs. time](image)

**Fig. 3.20**: Release of CBB (600 nm) from PAA/CHI (20 bl) to water at pH (▲) 7 (●) 5 and (▼) 3. Deposition pH of PAA and CHI was 4 and 2 respectively

CBB shows slow release from multilayers when compared to MB due to low diffusion rate connected with molecular size. The release rate is almost 10 times lower than the MB release. Almost 100% of MB is released to pH 3 within 30 minutes. But such saturation is not seen in the case of CBB after 600 min. Almost 30-40% dye is retained in the film even after 600 min. This shows the strong electrostatic interaction between cationic polyelectrolyte (PEI and CHI) and CBB than PAA and MB. Slow release after 10 hours makes these systems potentially applicable for controlled drug delivery.
The COD values show tremendous decrease after the treatment with polyelectrolyte multilayers. The initial COD of MB is considerably reduced after treatment with 20 bl PAA/PEI and PAA/CHI membranes. COD value got reduced from 4300 mgO$_2$ L$^{-1}$ to 200 mgO$_2$ L$^{-1}$ (95.35 %) after treatment with PAA/CHI bilayer and similarly PAA/PEI shows a 88.4% removal. The 95.35% COD removal is comparable with COD removal by thermo chemical treatment done by S. Mahesh and co-workers [48]. The results obtained for CBB based effluent shows less efficient COD removal from the dye effluent. Here the reduction percentage is in between 45-60. These values are well under ISI standards for
industrial dye effluent for surface water and irrigation purpose [6,31,48,49].

![Graph showing COD values before and after treatment]

**Fig. 3.22:** Comparison of the COD values before and after treatment with bare nylon, PAA/PEI and PAA/CHI (19.5 and 20 bl).

**Conclusions**

The present results lead to the conclusion that, self-assembled multilayers can be successfully used for the treatment of colored effluents. The loading and release can be controlled by controlling the molecular architecture of the multilayers, which in turn depend upon a number of parameters such as type of polyelectrolyte, number of bilayers, pH of polyelectrolyte and pH of effluent. The binding sites on the surface layer and the charge on the dye molecules determine the efficiency of dye uptake. PAA/PEI and PAA/CHI multilayers are particularly superior in
colored effluent treatment, since the quantity of polyelectrolyte used for coating is less (in micrograms). The complete recovery of the dyes from the system is also possible. The system is completely free of fouling and can be used for further treatments. Another important aspect with the present multilayers is that they can be used for the considerable reduction of chemical oxygen demand (COD).
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