CHAPTER 4

PHOTOCATALYTIC REDUCTION OF Cr (VI)

BY POLYSULFONE COMPOSITE MEMBRANES
4.1 POLYSULFONE AND POLYSULFONE/TiO$_2$ COMPOSITE MEMBRANES FOR PHOTOCATALYTIC REDUCTION OF Cr (VI)

For an appropriate water treatment, the sludge released from industries needs to be stored or disposed in a systematic way so that it would not harm the environment. Compared to the conventional water treatment approaches such as reverse osmosis (Mousavi 2009:349), solvent extraction (Hari Haran 2010:6), reduction (Beukes 1999:364), ion exchange (Rafati 2010:147) and electroplating (Dermentzis. 2011), photo catalysis has a number of advantages including high oxidation efficiency and minimal disinfection byproducts. The key drawbacks of suspended process are nano catalyst recovery and its regeneration. Immobilization of the catalyst via a hybrid membrane formation can overcome this drawback. Uniform dispersion of appropriate inorganic particles in polymeric matrix creates reactive surfaces for enhanced purification processes and such hybrid membranes have been used in the field of separation, pervaporation and ultra filtration techniques (Yang. 2006). Incorporation of NPs at low weight percent is an effective way to improve the external as well as internal properties of the membrane (Yang, 2007). Jing Hu et. al., studied both removal and recovery of Cr (VI) present in waste water by using maghemite NPs. The effect of pH, initial concentration, temperature and presence of co-existing ions were studied successfully (Jing Hu 2005:4528-4536). The adsorption and desorption studies revealed that, the maghemite NPs retained their metal removal capacity up to six cycles, the competition between co-existing metal ions were negligible. Another group of researchers prepared PVA-alginate encapsulated ferro photo gels for reduction of Cr (VI) under sunlight (Ani Idris 2012:2151-2156). The superparamagnetic property of photo gels and the robust property of polymer contributed together for the removal of Cr (VI) in 30 mins and use of them for the seven cycles without any pretreatment. Thiocarbamoyl chitosan was prepared and used for the removal of Cr (VI) and Cd (II) by Divya Chauhan et. al. Maximum of 434.8 mg/g adsorption of Cr (VI) was observed (Divya Chauha 2012:670– 675).

PSf/TiO$_2$ membrane is a mixed matrix membrane and the active region on the membrane surface (with semiconductor particles), on bandgap illumination ($\geq 400$ nm) causes electronic transitions from the valence band to conduction band, leaving behind the holes in the former (Gonu Kim 2010:79; Kang Yong 2001:2350). These electrons and holes either migrate to particle surface and become involved in redox reactions or simply liberate
heat. Conduction band electrons are consumed in the reaction to reduce oxidants (Ox $\rightarrow$ Ox$_{\text{red}}$) while, holes are filled via oxidation. In aqueous conditions any dissolved species with reduction potential more than the conduction band of the photocatalyst can in principle consume electrons and Cr (VI) species with a redox potential of 1.3 eV can easily be reduced by TiO$_2$ photocatalyst (Hui Han 2011:11924; Hung-Cuong. 2013:5298). Hydroxyl radicals are generated by oxidation of water at the valence band of TiO$_2$. This occurs at a standard potential of 2.8 eV, and it decreases with increase in pH. To keep the photoreduction process going, it is necessary to avoid the accumulation of holes or hydroxyl radicals in the particles. Addition of hole scavengers/proton donors namely inorganic and organic acids causes a rapid promotion of Cr (VI) reduction and such processes have a potential of simultaneous oxidation of acids and reduction of metal ions.

All the membranes were prepared as reported in Chapter 3. The efficacy of prepared membranes to photocatalytically reduce/reject Cr was investigated. The rate of Cr reduction strongly depends on the pH of reaction and the concentration of NPs incorporated in the membrane. The effect of different acids, catalyst concentration on photocatalytic reduction and surface (membrane)-substrate (Cr) interactions are investigated and reported. The present study gains significance in obtaining a bifunctional hybrid membrane with capability of both metal ion reduction and rejection of metal without any compromise in its native property.

4.1.1 Experimental

**Photocatalysis to reduce Cr (VI) to Cr (III) followed by rejection of Cr (VI) to achieve pure water**

All the hybrid membranes were prepared as reported in section 3.1.1.2 and the same were used to reduce Cr (VI) to Cr (III) under sunlight. The detailed experimental setup and the method is explained in section 1.6.4.

4.1.2 Results and Discussions

4.1.2.1 Characterization of NPs and mixed matrix membranes

Figure 4.1 shows the XRD patterns of pure PSf (a), TiO$_2$ NPs (b) and PSf/TiO$_2$ mixed matrix membranes (c, d and e). The pure PSf membrane exhibits a broad and semi crystalline peak at $2\theta = 17.5^\circ$, which corresponds to an amorphous phase. The X-ray patterns for bare TiO$_2$
reveal a 100% peak at $2\theta = 25.3^\circ$, which is indicative of an anatase phase with a d-spacing of 3.4937 Å. The PSf/TiO$_2$ hybrid membrane exhibited a pattern that integrated all of the diffraction peaks of PSf and TiO$_2$ with evidence of the photocatalyst in the polymer matrix. There was complete retention of the TiO$_2$ anatase phase in the hybrid membrane, which was unexpected. The appearance of a rutile phase has been observed during thermal treatment of a hybrid membrane (Behnajady. 2013) because the rutile phase is thermodynamically more stable (Gomati Devi. 2005:919). The absence of peak shifting precludes the existence of long-range internal stresses and/or macroscopic residual stresses. In addition, the lattice parameters and crystal structure remain unaltered, as shown in the Table 4.1. The height of the characteristic peak (intensity) for TiO$_2$ in the hybrid membrane decreases because it depends on the number of crystallites diffracting the X-rays or the amount of the phase exhibiting the reflection. Therefore, M3 shows the highest peak height among its hybrid counterparts. The average crystal diameters of the NPs calculated from Scherrer’s equation are reported in Table 4.1. The crystallite size of the NPs in the hybrid membranes was significantly higher than that of bare TiO$_2$ NPs or the membranes with a lower TiO$_2$ concentration. During membrane preparation, the frequent collisions between NPs over a prolonged period of time can aid the crystal growth or agglomeration depending on the NP load, as shown in the SEM images.

Figure 4.1: XRD patterns of NPs and hybrid membranes
Table 4.1: Catalytic efficiency, crystallite size, lattice parameters and cell volume of TiO$_2$

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Catalytic efficiency$^a$</th>
<th>Crystallite size (nm)$^b$</th>
<th>Lp $\times 10^{12}$ (m/s Pa)$^c$</th>
<th>Lattice Parameters</th>
<th>Cell volume ($\text{Å}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>1.2700</td>
<td>18.0</td>
<td>-</td>
<td>3.7867</td>
<td>9.5010</td>
</tr>
<tr>
<td>M1</td>
<td>4.4871</td>
<td>89</td>
<td>4.68</td>
<td>3.7382</td>
<td>9.3840</td>
</tr>
<tr>
<td>M2</td>
<td>3.3575</td>
<td>37</td>
<td>10.0</td>
<td>3.7684</td>
<td>9.3840</td>
</tr>
<tr>
<td>M3</td>
<td>2.4975</td>
<td>23</td>
<td>1.78</td>
<td>3.7786</td>
<td>9.3847</td>
</tr>
</tbody>
</table>

$^a$ Calculated using slope of Time versus C/C$_0$ graph.

$^b$ Estimated by Debye–Scherrer formula.

$^c$ Hydraulic permeability co-efficient.

Figure 4.2a and 4.2b depict the micrographs of bare TiO$_2$ and the PSf membrane. TiO$_2$ NPs with a particle size of ~25 nm are observed as a block spots with a spherical shape. Figure 4.2b shows the surface image of neat PSf with a pore diameter of ~74.8 nm. Figure 4.2c and 4.2d show the distributed spherical nanoparticle agglomerates on the surface and inner layers of the polymer.

The complete penetration of NPs into the polymer matrix was affected by the concentration of TiO$_2$. As the dosage of NPs increased, the viscosity of the casting solution increased resulting in a larger interaction within the polymer matrix and a decrease in the penetration of NPs into the sublayers. The NPs act as fillers to decrease the void size and improved the interconnectivity between the layers of the membrane (Yilser Devrim. 2009; Teow. 2012). The concentration of NPs affected the nature of the dispersion. Agglomeration was observed in all hybrid membranes as the concentration of TiO$_2$ increased, which contributes to decreased dispersion as well as lower catalytic efficiency and lower water permeability due to plugging of the pores in the membranes with higher concentrations. The membrane surface appears damaged due to high-energy bombardment of electrons, which occurred as the SEM images were recorded.
4.1.2.2 Photocatalytic evaluation

Figure 4.3 represents the photocatalytic reduction of Cr (VI) under different experimental conditions. In addition, the importance of (i) light, (ii) TiO$_2$ NPs, (iii) immobilized TiO$_2$ and (iv) acid for the reduction is shown. The TiO$_2$ NPs catalyze photoreduction only in the presence of acids. Approximately 40% of the reduction was observed immediately after the addition of acid. Enhanced and complete reduction was observed within 2.5 h with the combination of immobilized TiO$_2$, sunlight and an acid.

TiO$_2$ catalyzed photoreactions in aqueous media facilitates the formation of a number of hydroxyl radicals and many reactive oxidizing species. Most of the reported results indicate that oxidation processes are feasible for such photocatalytic degradations. The present study involves reduction, and the probability of reduction is very low unless the holes and hydroxyl radicals, which are potent oxidizing species, are scavenged or converted to reducing species. Acids have been used as hole scavengers. The surface charge properties of TiO$_2$ change with the acidic pH. Adsorption occurs first when TiO$_2$ comes into contacted
with the dissolved metal ions. In a low pH range, Cr (VI) predominantly exists in aqueous solutions as the dichromate anion (CrO$_7^{2-}$). Anions are adsorbed via ligand exchange reactions, which are favored at low pH where the surface is positively charged and site hydration is favorable. Because TiO$_2$ (in acid) has a positive charge, at a pH lower than the isoelectric point of charge, dichromate is most likely electrostatically bonded to the surface of TiO$_2$, and the possible reaction between the active groups on the TiO$_2$ surface and dichromate would occur and favor photocatalytic reduction, as shown in Figure 4.4.

![Figure 4.3: Photocatalytic reduction of chromium in different conditions](image)

The pH of the target solution was adjusted to a pH of 2, and the photocatalytic reductions were studied with respect to different acids. When an acid was added, the concentration of Cr (VI) substantially decreased prior to any catalytic irradiation. At a low pH, HCrO$_4^-$ species formed with a standard electrode potential of 1.33 V, which indicated the probability of the direct reduction with a strong acid. However, this result was only observed at the initial stages, and further reduction was only possible in the presence of a catalyst, as shown in Figure 4.4.
shown in Figure 4.3. Strong acid, such as perchloric acid, which is capable of donating protons directly into the valence band of TiO$_2$, results in a high reduction rate. However, acids that are oxidized by hydroxyl radicals produce lower rates where the holes are scavenged indirectly by the acid via hydroxyl radicals. Perchloric acid is a super acid can easily protonate water to form hydronium ions, which effectively induces proton and charge separation on the NP surface. Electrons from such acids fill valence band holes, which leave more conduction band electrons for Cr (VI) reduction. Therefore, 100 % reduction of Cr (VI) to Cr (III) was observed in perchloric acid within 2.0 h for the M3 membrane.

\[
\text{Cr(VI)} \xrightarrow{e^-} \text{Cr(V)} \xrightarrow{e^-} \text{Cr(IV)} \xrightarrow{e^-} \text{Cr(III)}
\]

**Figure 4.5: Three subsequent one electron transfer processes that result in the formation of stable Cr (III)**

Figure 4.5 shows three subsequent one electron transfer processes that result in the formation of stable Cr (III). The possibility of the formation of Cr (IV) and Cr (V) intermediates during the reduction process does exist. These intermediates are unstable, and the corresponding UV absorption peaks at 510 nm and 520 nm, respectively, could not be traced during the course of the reduction. It is important to note that in all of the reactions involving an acid, a certain amount of Cr (VI) recovery was observed after a particular irradiation time, which indicated the complete consumption of acid or nonavailability of acid resulting in the back reaction of Cr (III) to Cr (VI). Therefore, in addition to the concentration of catalyst and pollutant as well as the irradiation time, the quantity and concentration of acid used were important.

Polysulfone plays an important role as a solid support. Inorganic fillers in porous membranes inhibit macro voids, as shown in the inset of Figure 4.2d. However, these fillers increase the interconnectivity between layers creating a layered nano-macro structural assembly. The interconnectivity of the layers tends to slow down the electron hole recombination process due to the electrons diffusing into the interlayers and interacting prior to returning to the surface of the semiconductor. The improved activity of the TiO$_2$
membrane over the bare TiO$_2$ is also supported by the prediction that the size dependent control to energy gap is simply proportional to $1/R^2$ where R is the particle radius.

![UV-Visible spectra of neat PSf and hybrid membranes](image)

**Figure 4.6: UV-Visible spectra of neat PSf and hybrid membranes**

A drastic increase in the crystallite size of TiO$_2$ in the hybrid membrane, which was calculated from the XRD data, can decrease the band gap energy extending the photon absorption range of the NPs (bare TiO$_2$ has a band gap energy of 3.1 eV) from the UV region to the visible region (sunlight) (Abrams; 2005). Therefore, this membrane can better utilize the visible light and enhance the photoreaction. The UV-visible spectra of the samples shown in Figure 4.6 confirm the extension of the absorption edge in the hybrid samples, and this extension is proportional to the concentration of TiO$_2$ in the membranes.
Figure 4.7: Photocatalytic reduction of Cr (VI) with a) Different hybrid membranes in different acids b) Membrane M1 in different acids with respect to time c) Membrane M2 in different acids with respect to time d) Membrane M3 in different acids with respect to time

The extent of reduction for a series of photoreactions conducted with M1, M2 and M3 in different acids is shown in Figure 4.7. The difference in the catalytic efficiency of these membranes are calculated and reported in Table 4.1. Catalytic efficiency is defined as $k/C_{\text{catalyst}}$ where $k$ is the rate constant of the reaction obtained from the slope of $C/C_o$ as a function of reduction time and $C_{\text{catalyst}}$ is the concentration of the catalyst (Hung-Cuong 2013:5298). M3 depicts the lowest catalytic efficiency, which suggests an adverse factor contributing to the reduction in membranes with a higher concentration. The lower dispersion and higher agglomeration of TiO$_2$ in the membranes with a higher concentration led to fewer surface active sites per overall catalyst mass and an increase in mass transfer.
inhibition, which adversely affected the catalytic activity. However, the complete reduction was not observed in M1 membrane within 2.0 h, and the reduction required an additional 1.0 h for completion, which suggested the deficiency of the catalytic sites for complete reduction. Therefore, the M2 membrane exhibited a complete reduction capacity with a good reduction rate. The experiments were conducted in triplicate, and the results indicated fairly good reproducibility, which confirmed the uniform and equal distribution of NPs in all of the three PSf/TiO$_2$ membranes, as shown in Figure 4.8.

Figure 4.8 Photocatalytic reductions conducted in Perchloric acid in triplicate

4.1.2.3 Kinetic study of photocatalysis

Kinetic study of composite membrane mediated photocatalytic reductions of Cr (VI) to Cr (III) have been investigated as a function of sunlight irradiation. It helped the evaluation of reaction rates, reaction orders, and equilibrium constants, and helped evaluation of a mechanism for the enhanced elimination of Cr. The PSf/TiO$_2$ composite membrane exhibits a very good catalytic activity with respect to reduction of acidified Cr (VI) to Cr (III) in aqueous solution. M2 exhibited better rate of reduction than M1 and M3, because of insufficient catalytic sites in M1 and in M3, because of excess catalytic sites promoting oxidation after the consumption of all the necessary acid (no extra acid has been used because of extra catalyst). The UV-visible absorption spectra for reduction of Cr (VI) after 2
hours of treatment, under various experimental conditions are as shown in Figure 4.9. The curve ‘g’ representing the hybrid membrane with TiO$_2$ and acid, showed a steep decrease (and disappearance) in the height of the characteristic absorbance peak of 350 nm within 2 h of sunlight irradiation indicating the completion of reduction. The higher intensity of only neat PSf membrane, represented by curve ‘a’, than of only Cr (VI) solution, represented by curve ‘b’, is observed because of the evaporation of water caused by exposure to sunlight. In Figure 4.9 there is no evidence for the formation of Cr$^{+3}$ because of the high adsorption tendency of Cr (III) on the membrane.

**Figure 4.9: The UV visible absorption spectra for reduction of Cr (VI) after two hours of treatment, under various experimental conditions.**

The plot of -ln C/C$_o$ against irradiation time for the 100 % photoreduction of Cr (VI) by composite membrane in presence of acid (Figure 4.10) shows a straight line behavior confirming first order reaction kinetics. It can be explained by rate law of first order kinetics for any reactant consumption at concentration C by dC/dt= -k[C], on integration, ln [C]/[C$_o$] = -kt, where C and C$_o$ are substrate concentrations at time t and time 0 in mins, respectively,
and k is first order rate constant. Because the obtained plot was a complete straight line with all the points on it, it indicates the reduction to be a perfect first order reaction.

![Plot of 2.303 log C/C0 versus time of illumination for the photoreduction process by using hybrid membrane (M3) in the presence of acid.](image)

**Figure 4.10:** A plot of -2.303 log C/C0 versus time of illumination for the photoreduction process by using hybrid membrane (M3) in the presence of acid.

For a single substrate reaction on the surface where the catalyst concentration is very low compared to that of substrate, as in this present study, the expression would be the same as Langmiur-Hinshelwood kinetic rate, \( v_{LH} = \frac{kKC}{1 + KC} \), where ‘C’ indicates the concentration of the substrate. In general, photo-oxidation is favored by concentration of solute and oxygen and if the initial oxygen pressure is ambient air (as the present case may be), the equilibrated value of surface coverage by an oxygen molecule and may be regarded as constant. On rearranging the above equation, \( \frac{1}{v} = \frac{1}{k} + \frac{1}{kKC} \), to obtain an equation analogous to linear equation \( y = mx + c \), rate constant k and equilibrium constant K can be obtained. Figure 4.11 gives the plot of \( 1/v \) versus \( 1/C \). All the three membranes showed a straight line trend and the graphically obtained rate constants (min\(^{-1}\)) and equilibrium constants for the corresponding acidified-photocatalytic -membrane -oxidations are as depicted in figure 4.11. Although many photocatalytic reactions show good linearity (Ani Adris 2011:629; Sobczynski 2004:225) in such plots of \( 1/v \) versus \( 1/OD \), unfortunately, this
fit cannot be taken as a definite proof for pre adsorption, as an identical analytical formulation of this rate law is obtained only for reactions occurring entirely within a homogeneous phase (Geetha 2005:919).

Figure 4.11: A plot of $1/v$ versus $1/C$ for the photocatalytic reduction of Cr (VI) using composite membranes with different dosages of TiO$_2$ NPs, in the presence of acid and sunlight.

4.1.2.4 Recycling study of photocatalysis process

Many sets of experiments were repeated with the same PSf/TiO$_2$ composite membranes of different concentrations of NPs to check the efficiency, reproducibility, and reusability of solid supported catalyst. Figure 4.12 (b, c, and d) shows the durability of prepared composite membranes for photocatalytic reactions. It evidently illustrates the recycling of membrane up to six cycles without any pretreatment. Membrane M1 causes a reduction of 97% for the first use and its capacity reduces to 91% at the sixth use. 100% reduction for M2 was achieved because of the increased availability of the active sites. Exposure of the membrane to sunlight increases the surface roughness showing a slight damage on the membrane surface which allows exposure of more number of NPs to sunlight and hence an increased activity is observed. The reduction reaches 95% after six cycles within 2.5 h which describes the
reusability of the membrane M2. M3 membrane of higher catalyst concentration showed an enhanced and complete reduction within 2 h up to six recycles. All the three membranes showed an enhanced and efficient reduction of hexavalent Cr to trivalent Cr indicating the no-loss of TiO$_2$ NPs on repeated usage and it is supported by XRD patterns. The reductions were conducted in controlled parameters such as concentration of TiO$_2$, hybridization, and acid presence as represented in figure 4.12a. As expected catalyst failed to cause any reduction in dark. It was observed that TiO$_2$ NPs catalyze the photoreduction on illumination. The lone membrane remained inept for reduction of Cr. With bare NPs, a small reduction of about 36% was observed. The photocatalyst with a bandgap of 3.1 eV responds to the light of solar spectrum to produce the electron hole pair and cause redox reactions under the illumination of sunlight. However, the produced electrons and holes remain insufficient/ineffective to cause complete reduction. The percent of recombination of electrons and holes affects photocatalytic efficiency significantly (Sahu 2008:154).

When considering a nanoparticle, the concept of deep traps and defects may not be applicable. The defects or the irregularities are only with the surface states. The polymer matrix for the TiO$_2$ allows easy induction of electrons thus maximizing the charge separation time and acts as carrier traps, avoiding recombination, which later detraps the same to the NP’s surface leading to a good interfacial charge transfer. Thus, the importance of polymer matrix on to which the nano-TiO$_2$ has been immobilized contributes to charge carrier separation (Sayo 1999:937) and effectively causes redox reactions. The holes that cause oxidative reactions have very strong oxidizing power and they directly oxidize water to produce highly reactive species (OH$^-$) as shown in Figure 4.13. When oxidative tendency increases, possibility of h$^+$ being used in the reaction also increases and the rate of recombination decreases. When the positive holes are sufficiently consumed, the process of electrons transferring to oxygen molecules on the reduction site enhances the rate of photocatalytic reduction. Acids were used as hole scavengers and promote necessary reduction. The pH of target solution is maintained at 2 using perchloric acid, which is a strong acid and has a very high dissociation constant. The release of H$^+$ ions is further responsible for the reduction of hexavalent Cr. At low pH, the formed HCrO$_4^-$ specie has a standard electrode potential of 1.33 V and this is indicative of the chances of direct reduction (39 %) with a strong acid.
Figure 4.12: Extent of Cr (VI) reduction in sunlight under different experimental conditions

However, this was only at the initial stages and further reduction was possible only in the presence of a catalyst, and plots in Figure 4.12a are clearly indicative of this situation. The photocatalytic reduction conducted in dark showed zero reduction. Although sunlight is one of the important parameters, sunlight fails to cause reduction in the absence of a catalyst. The required criteria such as illumination of light on anatase TiO$_2$ catalyst, immobilization of catalyst on PSf polymer matrix as solid support, and use of acid as proton donor is responsible for 100% reduction of Cr (VI) within 2 h.
Figure 4.13: Representation of a) electron hole formation, b) hole scavenging c) reduction process.

The adsorption properties of a catalyst vary greatly with the pH (Petten. 2002). In this study, reduction reaction predominates because of the presence of perchloric acid. TiO$_2$ will have a large surface proton exchange capacity in acidic environment as H$^+$ ions are adsorbed onto TiO$_2$ surface. The adsorbed H$^+$ ions also capture photogenerated electrons to form H$_{abs}^-$ to reduce Cr (VI).

XRD patterns of TiO$_2$ NPs and composite membranes of different concentrations of NPs (1.5/2.0/2.5 wt %), before and after the reductions are as represented in figure 1.14. The XRD patterns were expressed as simple mixed patterns of different components present in the hybrid (Dong. 2007:1787). The 100% peak observed at $\theta = 25.30$ indicated the pure anatase form of prepared TiO$_2$ NPs, with no trace of rutile peaks. The same peak can be observed in all composite membranes suggesting the incorporation of NPs into the polymer matrix with an evidence of d-spacing at 3.4937 Å. The height of the peaks (intensity) depends on the number of crystallites diffracting the X-rays or the amount of phase exhibiting the reflection and hence BM3 shows highest peak height for TiO$_2$. But the absence of peak shifting excludes the existence of long-range internal stresses and/or macroscopic residual stresses.

In addition, the lattice parameters and crystal structure remains unaltered. The prominent decrease in intensity of the characteristic peak in AM3 can be attributed to decrease in amount of phase/crystallinity that may have been caused due to turbulence created via repeated stirring during subsequent reductions. The crystallite size of the NPs incorporated into the polymer matrix before and after the recycling process is calculated and tabulated in Table 4.2. As observed, the crystallite size decreases substantially in lower concentrated membranes after the recycling. Size decrease should be because of crystallite size refinement. Crystallite size refinement is achieved via repeated brittle fracture that
occurs during repeated recycling. This also causes membrane damage and can be evidenced from SEM images. However, the presence of NPs after recycling evidences the reliability of the hybrid membrane for such degradations.

Figure 4.14: XRD patterns of (a) bare TiO$_2$ NPs and neat PSf, (b) M1 membrane before reduction process (BM1) and after recycling (AM1), (c) M2 membrane before reduction process (BM2) and after recycling (AM2), (d) M3 membrane before reduction process (BM3) and after recycling (AM3)
Figure 4.15: SEM images for (a) TiO$_2$ NPs, (b) neat PSf membrane, (c) BM1, (d) BM2, (e) BM3, (f) AM1, (g) AM2, and (h) AM3 six recycles of photocatalytic reaction

Figure 4.15 shows surface images of PSf/TiO$_2$ mixed matrix membranes for the membranes before and after the photoreduction obtained by SEM. With the increase in TiO$_2$ concentration, the deposition of NPs increases and is seen as different sizes of flaks indicating agglomeration. Viscosity of the casting solution increases with concentration of TiO$_2$ leading to a higher interaction between polymer matrices, troubling the penetration of NPs into the sublayers of polymer leading to agglomerates on surface. The illumination of titania with light allows the electrons in 2p valence band of oxygen to jump to 3d conduction band of titanium. As the holes are continuously scavenged by either adsorbed water and/or acid, the electrons emitted during the process causes the surface damage of the membrane.
leading to an increase in roughness (evidenced by AFM images). Figure 4.15 clearly depicts the membrane damage, the damage being proportional to dosage of TiO$_2$ and number of cycles. Roughness facilitates better adsorption of Cr ions and hence enhances photoreduction. It is also important to mention that the third and fourth cycles gave better percent of reduction because of the above-mentioned fact. But, the damage beyond a particular point (6 cycles for 500 mg of TiO$_2$) adversely affected the reduction capacity of the membrane. This was however dependent on concentration of TiO$_2$ in the membrane.

Table 4.2: Crystallite size and roughness of the membranes before and after recycling for six times to carry out reduction of Cr (VI)

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Before reduction process</th>
<th>After recycling process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average Crystallite Size (nm)</td>
<td>Roughness (nm)</td>
</tr>
<tr>
<td>M1</td>
<td>89</td>
<td>8.8</td>
</tr>
<tr>
<td>M2</td>
<td>53</td>
<td>6.6</td>
</tr>
<tr>
<td>M3</td>
<td>50</td>
<td>7.61</td>
</tr>
</tbody>
</table>

Figure 4.16 represents the AFM images of the membranes before and after the photoreduction process. In the images, the darker areas belong to the lower points and micrometric valleys of the membranes structure and brighter areas show the points on the membranes with more height. The presence of TiO$_2$ particles in the membrane matrix created some superficial disorders on the membrane surface causing the surface roughness. The mean roughness (Ra) of the membrane is as tabulated in Table 4.2. It depicts the roughness to be inversely proportional to the concentration of the catalyst. Overall, the roughness of the membrane increases with treatment. Hence, photoreduction process damages the surface and causes more roughness.
Figure 4.16: 3D images of AFM for PSf TiO$_2$ composites before the reduction and after the recycling process.
4.2 SULFONATED AND AMINATED POLYSULFONE BLEND MEMBRANES FOR PHOTOCATALYTIC REDUCTION OF Cr (VI)

4.2.1 Results and discussions

The results of photocatalytic experiments for bare sPSf/PSf membrane and sPSf/PSf/TiO$_2$ composites are described in Figure 4.17. We could observe with an average of 100 % reduction of Cr (VI) within 3 h in all the three composite membranes in which TiO$_2$ NPs are embedded, whereas the reduction is not observed in control membrane. Even though the initial concentration ($C_0$) was 10 ppm, the value of $C/C_0$ is reduced in the earlier stage itself for all the membranes. And the same trend is observed for the reduction reaction plots for aPSf/PSf and aPSf/PSf/TiO$_2$ membranes as shown in Figure 4.18.

![Figure 4.17: Normalized concentration depletion curve for photocatalytic reduction of Cr (VI) using composite membranes made of sulfonated polysulfone](image)

The initial reduction is credited to acidic nature of the membranes. The chemical modification performed in the present study will induce an acidic nature to the polysulfone with the pendant groups to its backbone. When an acidic polymer/TiO$_2$ system is illuminated with sun light, both TiO$_2$ and polymer absorb the photons at their interface, followed by the charge separation at the interface. This is because the conduction band of TiO$_2$ and the lowest unoccupied molecular orbital
Figure 4.18: Normalized concentration depletion curve for photocatalytic reduction of Cr (VI) using composite membranes made of aminated polysulfone

Figure 4.19: Schematic representation of electron hole charger in composite membranes
level of the polymer are well matched for the charge transfer. The electrons generated by polymer will be initiated to the conduction band of TiO$_2$, which enhances the charge separation and consequently promote the photocatalytic activity. Simultaneously, a positively charged hole might be formed by electrons migrating from TiO$_2$ valence band to the polymer. The schematic representation of electron hole charge transfer system of immobilized NPs on conductive polymer is represented in Figure 4.19.

4.3 CONCLUSIONS
Prepared PSf/TiO$_2$ composite membranes responded well for solar light-mediated photocatalytic reduction of Cr (VI) with acid being a hole scavenger for the promotion of reduction. Both micro and macro changes were observed with respect to surface morphology and crystallite size of TiO$_2$ within the membranes due to recyclability. The investigations reveal membrane damage (because of electron transitions) to be proportional to dosage of TiO$_2$ and number of recycles. The membrane with 500 mg of TiO$_2$ retained its reduction capacity up to a maximum of six cycles. The study reveals the significance of using the reliable membrane repeatedly in batches to treat chromium contaminated water. The Langmiur-Hinshelwood kinetic model for 100% reduction of Cr (VI) showed a first-order rate equation, where the rate of the reaction was dependent on concentration of Cr (VI). The necessity of an acid for the reduction of Cr (VI) encouraged us to think on the method/material to avoid the utilization of acid and hence the reduction experiments were performed with the modified polymers (sPSf and aPSf).

It can be concluded that the role of acidic polymer to inject electrons into TiO$_2$ conduction band under visible light radiation caused enhanced photoreduction. The electrons cause reduction of Cr (VI) to Cr (III). The main advantage of immobilization of TiO$_2$ photocatalyst is its application in continuous treatment of contaminated water. This procedure of immobilization will guarantee the long-term stability and avoid possible leaching of TiO$_2$ particles into the solution. It can also allow easy regeneration of TiO$_2$ in case of adsorption.