

RESEARCH ARTICLE

Treatment of Methylene Blue and Methyl Orange Dyes in Wastewater by Grafted Titania Pillared Clay Membranes

Nalini Neethu¹ and Tanushree Choudhury^{2*}

¹Environmental Engineering Division, School of Mechanical and Building Sciences, Vellore Institute of Technology, Chennai, India; ²Chemistry Division, School of Advanced Sciences, Vellore Institute of Technology, Chennai, India

Abstract: Background: Amphoteric membranes such as Titania Pillared Clay (TiPILC) membranes exhibit different charges at different pH ranges, subsequently show efficient separation for cationic and anionic organic pollutants in wastewater based on solution pH. The structural properties of such membranes determine their permeability and selectivity to a large extent. The present work is initiated to explore the possibility of enhancing the surface area of TiPILC membranes by grafting with 3-aminopropyltriethoxysilane.

Method: Grafted TiPILC membranes were fabricated by colloidal sol-gel route followed by dip coating, drying and sintering the membranes at 300°C. X-ray diffraction (XRD) spectra of the pillared photocatalyst membranes show the presence of only anatase phase, which exhibits better photocatalytic activity. Fourier Transform Infrared (FT-IR) spectra reveal the formation of delaminated TiPILC material. The specific surface area of TiPILC membrane obtained at pH 3.5 is 183 m²/g.

Results: Literature survey of 47 papers was carried out for the work. 10 papers were based on Patents being dealt on degradation of organic dyes in wastewater by conventional methods, though reports of membrane technology are limited in literature. The rest 37 papers outlined the importance of widespread use of titania photocatalyst powder for degradation studies.

Conclusion: The membrane material thus developed is efficient in complete decolouration of both Methylene Blue and Methyl Orange dyes on account of the high surface charge and high surface area in just one cycle of filtration.

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1. INTRODUCTION

Wastewater which encompasses a wide range of potential contaminants such as toxic species, oxygen-demanding wastes, organic and inorganic chemicals, minerals and sediments, is harmful to the environment and thus augurs for its efficient reuse and recycling to reduce water consumption. Dyes such as Methyl Orange and Methylene Blue (an intensely coloured compound) used in textile, printing, pharmaceuticals, and research laboratories, generate a large volume of wastewater into the environment and cause water pollution even at low concentration [1-3]. These dyes are generally non-biodegradable in nature and are not removed efficiently by the traditional treatment methods such as adsorption on activated C, coagulation, sedimentation, chemical oxidation, and biological digestion [4-6]. Titania, a well-known material in photocatalysis, is generally used for the

degradation of emerging contaminants for its i) no neurological toxicity ii) high chemical stability in organic solvents and caustic soda iii) high material purity iv) small crystallite size v) low cost of crystalline anatase form vi) extreme stability vii) extreme amphoteric character and viii) wide band gap energy [7]. However, its performance requires further enhancement for treating diluted contaminants due to its small surface area and low adsorption ability [8, 9]. The separation of nanoscale titania photocatalyst from water is yet another problem to be solved for its widespread application of the process [10, 11]. Thus, there is a high demand for the development of an intelligent system to remove low concentration contaminant from wastewater [12]. Membrane process integrated with photocatalysis has proven to be a novel water treatment technology and a more sustainable process. Polysulfone membrane was embedded with TiO₂ for studying the degradation of eosin yellow dye under visible light irradiation [13]. Plant-based material laccase as support was tried for immobilization of TiO₂ on it to study the degradation of textile reactive dyes [14]. These polymeric mem-

*Address correspondence to this author at the Chemistry Division, School of Advanced Sciences, Vellore Institute of Technology, Chennai, India; Tel/Fax: +914439931257/+914439932555; E-mail: tanushree.c@vit.ac.in

branes are not stable thermally as well as chemically when compared to inorganic membranes. Thus inorganic membranes have been widely used due to their long life. Among inorganic membranes, porous ceramic membranes have attracted the scientific community due to their numerous benefits such as thermal, chemical, and mechanical resistance and controllable microstructure, but their applications in wastewater treatment are still limited due to high price. Hence, the search is on to develop a low-cost membrane integrated with both adsorption and photocatalysis for novel water treatment technology and for a more sustainable process [15].

Clays have widely been used as support materials due to its low cost, abundance, high porosity and cation exchange property, high surface area, swelling and good binding properties [16]. Immobilization of Titania on such ceramic supports has been carried out by various ways such as in-situ hydrothermal method [17], electrospinning [18], the sol-gel process [19], self-assembly [20], photoassisted deposition, solvent casting and grafting [21]. The sol-gel route for the development of titania pillared clay membrane is the most favoured wet chemical technique as it produces materials in the form of nanosized powders, thin films and fibres which attribute towards a products homogeneity, low-temperature operation and ease of preparation [22]. The membrane reactor thus gains tremendous popularity because of their multi-functions such as i) decomposition of recalcitrant inorganic pollutants ii) destruction of biological toxins iii) inactivation and killing of pathogenic microorganisms iv) physical separation of contaminants and intermediate products, and v) self-anti biofouling action [23-25]. Titania pillared clay membranes (TiPILC) exhibit unique charge characteristics which makes them a good candidate for the removal of charged species such as cationic and anionic dyes, where the membrane exhibits different charge signs at adjustable pH. Generally, for charged substrates, a significant dependency of the photocatalytic degradation efficiency upon pH value had been observed, since overall surface charge and hence the adsorptive properties of titania particles depend strongly on solution pH. The drawbacks that limit the application of such membranes are difficulty in altering the pore size and its low surface area when immobilized on support than powders in suspension [26].

In order to develop highly efficient TiPILC membranes possessing multiple functions of separation and catalysis, a novel chemistry route of grafting the surface of the membrane with an organosilane has been adopted in this work which leads to enhancement in surface area and also exhibits a narrow pore size distribution as revealed from BET surface area studies. The grafting process leads to a monomolecular layer of the organosilane compound on the membrane surface, which is tightly bound and prevents the release of organic molecules in aqueous medium [27]. The pillared membrane thus developed has shown efficiency in removing 99% of MB and MO dyes in just one cycle of filtration. The results are in comparison to reports in literature where decolouration of MB dye solution by TiPILC was achieved 96.5% after twenty hours exposure to UV and a nano-titania ultrafiltration membrane sintered at 750°C was able to degrade 94% of MB dye [28, 29].

1.1. Prior Art

In most of the patents that were surveyed, conventional techniques like flocculation, and adsorption methods were adopted for decolourisation of dyes in wastewater. Heavy oil fly ash based activated C was invented by Vohra [30] for removal of aqueous phase dyes such as Rhodamine B and Methyl Orange. The dye can be removed from wastewater by contacting it with activated C, after which the adsorbent can be separated from wastewater by any filtration process. Though adsorption removal methods using activated C are widely used for dyes, they are ineffective for removal of disperse dyes and vat pigments. Anionic dyes such as fibre reactive dyes require reduction by hydrosulfite before activated C adsorption methods effectively remove colourants. In one of the inventions, colourants were removed from wastewater by first adding a cationic polymer in wastewater to form cationic polymer/colourant complex. An anionic polymer was then added in sufficient quantities to allow further complexation and form a flocculant which is separated by filtration [31]. Though these nano adsorbents are efficient in the removal of dyes, their scope is limited as they need to be separated from wastewater after treatment. Magnetic polymer microspheres comprising a magnetic nanoparticle core surrounded by a polymeric resin was developed for adsorption [32] which could be easily removed from the wastewater by applying an external magnetic field by a local magnet. Johnson and coworkers treated the wastewater with a flocculating agent, after which it was passed through a sand filter to remove any suspended solids [33]. Effluent containing dyes was treated by exposure to NaHSO_3 in combination with an $\text{Al}(\text{OH})_3$ -chloride/ cationic polymer mixture followed by the addition of a flocculant at selected pH conditions for better clarification [34]. In another invention, pH of the wastewater was adjusted in the range 2.0 to 6.9, which was admixed with a cationic flocculant from a quarternary ammonium condensation polymer to form a floc which was then separated by filtration [35]. Colour can be removed from the effluent streams of pulp with plants by adding an effective amount of a decolorizing composition including FeSO_4 and water stable cationic amine polymer in basic pH range [36].

The metal complex dyes which are in general Cr, Co, Cu, Ni, or Fe complexes of monoazo or disazo dyes were removed from wastewater by means of amines of at least 6 C atoms [37]. These dyes removed from wastewater can be recycled into the dyeing process. Another invention described the use of dry biomass obtained from Eichhoma Solms, a water hyacinth as an adsorbent for maximizing the degree of decolourization and removal of heavy metals. Plant biomass as a base material was selected as it contained a lot of cellulose and yielded high C content to give a specific surface area $621\text{m}^2/\text{g}$ thus providing the material important properties for colour removal [38]. Bentonite clay-based Fe nanocomposite was developed which provided a reactor for treatment of wastewater [39]. It comprised a stainless steel vessel having Fe-Bentonite nanocomposites sprayed to form a layer of inner wall surface; UV light source to irradiate wastewater in the reactor, H_2O_2 source, means for introducing wastewater in the reactor and means for removing wastewater for the reactor after treatment. Clay nanoparticles have been successfully applied in the production of mem-

branes for fuel cells and for gas separation, though its use as a membrane for wastewater treatment is limited in the literature. The present study is thus spurred with an objective to develop a membrane reactor with both adsorptive and separation ability which can effectively degrade dyes in wastewater.

2. EXPERIMENTAL

2.1. Material

The chemicals used in this study such as Montmorillonite K10 with a CEC of 80-100 meq/g, and Cetyl trimethyl ammonium bromide (CTAB) were supplied by Himedia. Titanium isopropoxide and Carboxymethylcellulose (CMC) were brought from Avra chemicals India. Glacial Acetic acid (99%), 2-propanol (99.5%), Methyl orange, Methylene blue and 3-aminopropyltriethoxy silane (APES), and TiO₂ anatase, particle size < 25 nm were bought from Sigma Aldrich.

2.2. Method

2.2.1. Preparation of Grafted Mt with 3-aminopropyltriethoxysilane (APES)

0.1 M APES solution was made in ethanol. 10wt% APES solution was added to Mt dispersion and was stirred for two hours to facilitate the reaction between silane and clay surface to achieve silane modified clay [40]. The product (PS1) was then dried at room temperature.

2.2.2. Preparation of Flat Disk Membrane Support

For the preparation of membrane support, Mt was fabricated into flat disks of 25 mm diameter and 2 mm thickness, sintered at 600°C in a muffle furnace with a heating and cooling rate of 20°C/min and was kept for 30 minutes of hold time [41].

2.2.3. Preparation of TiO₂ sol by Colloidal Sol-gel Method

The precursor for the colloidal sol-gel process was Ti (IV) isopropoxide, common titanium-based organometallic compound, which was hydrolysed by the addition of excess water. The sol was then stirred at room temperature for three hours after which it was peptized by the addition of acetic acid to attain pH2 and pH3.5, respectively.

2.2.4. Preparation of TiPILC Membrane

0.1g of Mt was dispersed in 10 mL of water and was kept for stirring for three hours. 0.1 wt% of cetyl trimethyl ammonium bromide (CTAB) solution was added to the clay sol as an organic modifier. The resulting clay sol was then added dropwise to titania sol prepared at pH2 and pH3.5 respectively and was kept for stirring overnight for complete intercalation of Ti⁴⁺ ions into interlayer spaces of Mt. The supernatant liquid was then drained off and 5wt% of Carboxymethylcellulose (CMC) as a binder was added for coating purpose. The membrane support was immersed in this solution for a certain immersion time. After the desired immersion time, the supports were removed from the sol at a withdrawal rate of 25 mm/sec for uniform coating and dried in air for one hour. The composite membranes at pH2 and

pH3.5 respectively were placed in a programmable muffle furnace for sintering. The temperature was ramped to 300°C at a heating rate of 2°C/min, kept for one hour and then again was ramped back to room temperature at the same rate of cooling (2°C/min). The remaining solution was poured onto a petri dish, dried in air, and was sintered at 300°C (2°C/min) in a muffle furnace. The photocatalyst powders obtained at pH2 (PS2) and pH3.5 (PS3) respectively were used and were depicted through Fourier-Transform Infrared Spectroscopy (FT-IR) Fig. (1), X-Ray Diffraction (XRD) Fig. (2), Zeta potential Analysis Fig. (3), Brunauer-Emmett-Teller (BET) Fig. (4), and Scanning Electron Microscopy (SEM) Fig. (5).

2.2.5. Photocatalysis and Membrane Separation Experiment

30 ppm of MB and MO dyes solutions were prepared. 0.3 g of photocatalyst samples PS2 and PS3 were added to 30 mL of MB and MO dye solutions respectively and pH was adjusted accordingly. The dispersions were stirred for around one hour in the dark to attain adsorption-desorption equilibrium between dye and catalyst surface. They were then irradiated in sunlight for three hours and change in colour intensity was noted, after which the solution was filtered using uncoated Mt membrane (S2). TiPILC membranes (S1) at pH2 and pH3.5 were irradiated in sunlight for three hours and rejection experiment was carried out for MB and MO dyes respectively. Similarly, same membranes (S5) were used to carry out rejection experiment, but without irradiation. A blank experiment was done by employing only the dyes with uncoated Mt membranes (S4). Model TiO₂ along with the dye solutions was irradiated in sunlight for three hours, was kept in dark for 1 hour and then rejection by TiPILC membranes (S3) was studied. The average flux rate for all separation experiments by TiPILC membranes was 70-110 L/m²/h while with uncoated Mt membrane was 160-170 L/m²/h. The pressure was uniform throughout at 12-17 psi. The percentage removal under different conditions is well depicted through a bar chart in Figs. (6 and 7). The setup of the experiment is shown in Fig. (8).

2.3. Instrumentation

XRD was done using Bruker AXS D8 advance powder diffractometer equipped with Cu-K α generator ($\lambda = 1.5405600 \text{ \AA}$). The generator tension was 35 kV. IR was done on Thermo Nicolet Avatar 370 in the spectral range of 4000-400 cm⁻¹. The contact angle of membranes was analyzed by Contact Angle Meter bearing Model No Kyowa DM501. Zeta potential was measured using Horiba Scientific Nano Partica Nano Particle Analyzer SZ-100. SEM of the cross-section of membranes was taken using High-Resolution Hitachi S-4800 Scanning Electron Microscope. BET surface area of samples was characterized by Nova 1000 Quantachrome Instrument by N₂ sorption at 77.35K. The concentration of the permeate samples from filtration experiment was measured using Thermo Scientific UV-Vis Spectrophotometer in the visible range of 200-800 nm. The membrane filtration unit consisted of a cylindrical chamber with a membrane adapter connected to a pressure gauge of 2 psi and a peristaltic pump Model No RH-P120 VS Contact angle measurement was done by Ses-

sile drop method by KYOWA InterFace Measurement and Analysis System FAMAS.

3. RESULTS AND DISCUSSION

3.1. Membrane Characterization

3.1.1. X-ray Diffraction Analysis

Figure (1) shows the X-ray diffraction patterns of APES treated Mt (PS1) and photocatalyst powder samples PS2 and PS3. PS1 shows characteristic Mt reflection at $2\theta = 5.21^\circ$, which becomes broad and flattened one in PS2 and PS3, indicating complete intercalation of polyoxometalate Ti^{4+} ions into interlayer space leading to an exfoliated and homogenous structure [42]. PS2 and PS3 show only anatase phase (JCDPS No 89-4921) at $2\theta = 25.52^\circ$. Anatase has a lower surface enthalpy and lower surface free energy. Hence, wetting of anatase by water would be less, thus contributes towards hydrophobicity [43]. The result is in correlation with contact angle measurement data.

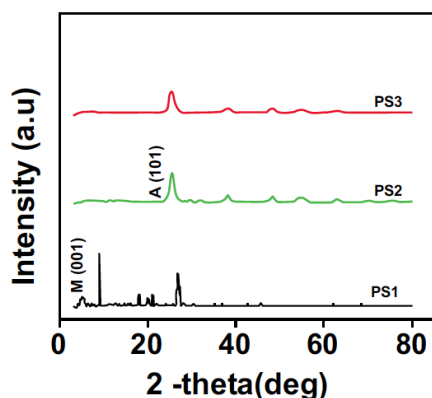


Fig. (1). XRD patterns of grafted Mt (PS1) and photocatalyst powders PS2 and PS3.

3.1.2. FT-IR Analysis

In order to ascertain the formation of grafted TiPILC, FT-IR spectra of PS1, PS2, and PS3 are obtained in Fig. (2). PS1 shows a strong broad band at 3435 cm^{-1} which is the stretching vibration of $-\text{OH}$ group and interlayer water molecules. Bands at 2928 cm^{-1} and 2856.76 cm^{-1} are due to $-\text{CH}$ stretching vibrations that may have happened due to the addition of CTAB as organic modifier. The characteristic Si-O-Si stretch band for Mt is observed at 1049.31 cm^{-1} . Bonded $-\text{OH}$ band at 1628.81 cm^{-1} is observed along with two $-\text{CH}_3$ stretch bands at 1480.61 cm^{-1} and 1392.96 cm^{-1} , thus indicating grafting of APES on the clay surface. Peaks at 523.68 cm^{-1} and 467.05 cm^{-1} respectively correspond to Si-O stretch and Al-OH stretch, which confirms that clay galleries are intact during the grafting process.

PS2 and PS3 show the presence of strong bands at 3399.03 cm^{-1} and 1621.55 cm^{-1} due to bonded $-\text{OH}$ stretching and bending vibrations of water thus indicating the formation of anatase phase. Characteristic bands at 1049.31 cm^{-1} and 523.68 cm^{-1} which correspond to Si-O-Si stretch and Si-O stretch respectively are lost completely, indicating complete intercalation of Ti^{4+} ions into interlayer space resulting

in formation of a delaminated and homogenous TiPILC material. Absorption bands at 1621.55 cm^{-1} and 1445 cm^{-1} are assigned respectively to the asymmetric $>\text{COO}$ and symmetric $>\text{COO}$ stretching vibrations. The presence of these two bands suggests a bidentate bridging coordination for the acid group. The band at 1410.10 cm^{-1} corresponds to deformation mode of $-\text{CH}$ stretch of alcohol groups for alkoxide and band at 461.93 cm^{-1} is due to $\nu(\text{Ti-O-Ti})$ vibration.

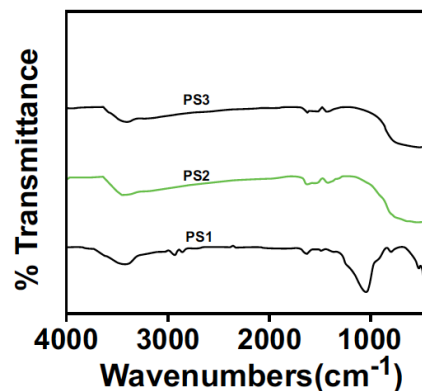


Fig. (2). FT-IR spectra of grafted Mt (PS1) and photocatalyst powders PS2 and PS3.

3.1.3. Zeta Potential Analysis

Zeta potential is measured as a potential at the slipping plane position. The slipping plane is located outside of the outer Helmholtz layer near the solid surface. It locates at 1.5nm distant from the surface in water. Therefore, strictly speaking, the zeta potential is not the surface potential, but in absence of specific adsorption of ions, may be considered to be approximately equivalent to the surface potential. When the surface charge is large, the electrostatic repulsion among particles takes place, and dispersibility in the suspension is enhanced for the powder system.

The zeta potential of TiO_2 nanoparticles in suspension is controlled by the pH through the following process:



Figure (3) shows the results for the zeta potential of powder suspensions PS1, PS2, and model TiO_2 obtained from measurements of the electrophoretic mobility in an aqueous medium. PS2, PS3 and model TiO_2 have zeta potential $< -25\text{ mV}$, hence exhibit better stability of dispersion in an aqueous medium. The results are in agreement with XRD analysis, where sintering of TiPILC materials at lower temperature 300°C produces anatase phase, which has a negative potential as it has more OH^- groups on its surface available for H-bonding [44]. Thus the adsorption of cationic pollutants is enhanced leading to better photocatalysis.

3.1.4. Specific Surface Area Analysis

Table 1 summarizes the specific surface area of PS2 and PS3 calculated by the BET equation (S_{BET}) and the results are compared with that of Mt whose specific surface area being reported is $31\text{ m}^2/\text{g}$ [45]. As evident, PS3 has the large-

est specific surface area ($183\text{m}^2/\text{g}$) amongst the three, which is an important parameter for enhanced photocatalytic activity. Fig. (4) represents a narrow pore size distribution pattern for PS2 and PS3, necessary for rejection of microcontaminants like MB and MO dyes with a molecular weight of less than 500. Pure Titania membranes on the other hand exhibit greater pores and a wider pore size distribution [46].

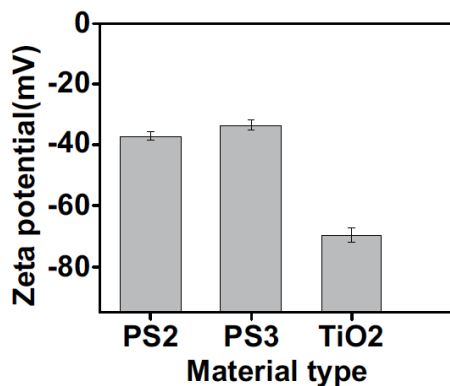


Fig. (3). Zeta Potential of Model TiO₂ and photocatalyst powders PS2 and PS3.

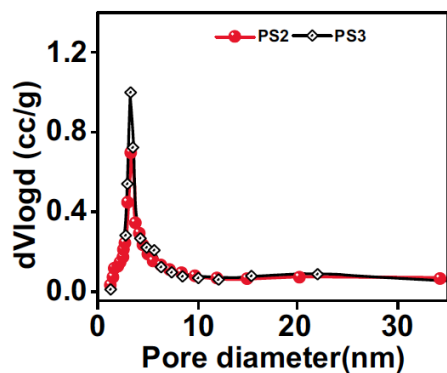


Fig. (4). Pore size distribution pattern of photocatalyst powders PS2 and PS3.

Table 1. Showing Specific surface area calculated for photocatalyst powders PS2 and PS3.

Nature of Material	Specific Surface Area (m^2/g)
PS2	167.79
PS3	183.71

3.1.5. SEM

Fig. (5) shows SEM images of cross section of TiO₂ and TiPILC membranes. The TiO₂ micrographs a (i) and (ii) reveal formation of aggregates, while that of TiPILC membranes at pH2 and pH3 show the formation of homogeneous and dispersed structures, a result of delamination, which is in agreement with XRD analysis. Presence of a bond is also seen in c (ii) which may have taken place due to the grafting process on the surface of the membrane.

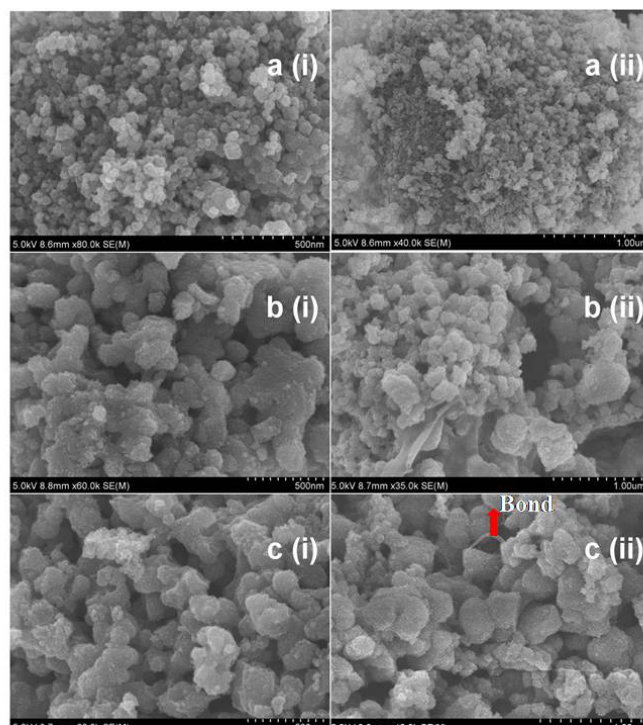


Fig. (5). a(i) and (ii) Anatase phase of Model TiO₂ b (i) and (ii) cross section of TiPILC membrane at pH2 c (i) and (ii) cross section of TiPILC membrane at pH3.5.

3.1.6. Contact Angle Measurement

The average contact angle value of titania pillared clay membrane was reported to be $107 \pm 1^\circ$ as compared to $85 \pm 1^\circ$ for only titania coated membrane. Thus titania pillared clay membrane exhibited hydrophobicity.

3.2. Membrane Rejection Analysis

Permeates from the separation experiments carried in section 2.2.5 were collected and their concentrations were measured by UV-Vis Spectrophotometer using the equation below [47].

$$\% \text{ Removal} = (C_0 - C_t / C_0) \times 100$$

Where C₀= initial concentration of dye in ppm

C_t= final concentration of dye in ppm

Figure (6a) (i) shows the maximum absorption peak of Methylene Blue (MB⁺) dye in solution at 559 nm whereas Fig. (7a) (i) shows maximum absorption peak for Methyl Orange dye in solution at 464 nm. The subsequent decrease in the peaks corresponded to decrease in concentration level of the dye when different membranes were used as described in section 2.2.5. Isoelectric potential (IEP) of TiPILC is -0.8 and that of Mt is -11.9 [45]. Thus at pH2 and pH 3.5, their surfaces are negatively charged. Methylene Blue (MB) is a cationic dye which is strongly acidic at pH 2 and pH 3.5. MB dye was completely removed (100%) at pH 3.5 due to an increased electrostatic attraction between charged TiPILC membrane surface and dye solution. The enhanced surface

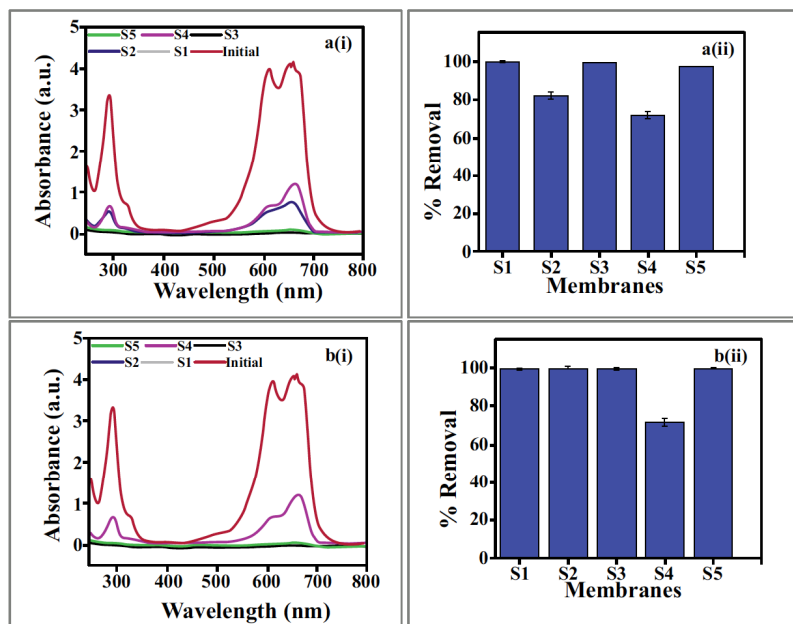


Fig. (6). a(i) UV-vis absorption spectra of MB dye with different membranes at solution pH2 (ii) % Removal of MB dye at pH2, b (i) UV-vis absorption spectra of MB dye with different membranes at pH3.5, b (ii) % Removal of MB dye at pH3.5.

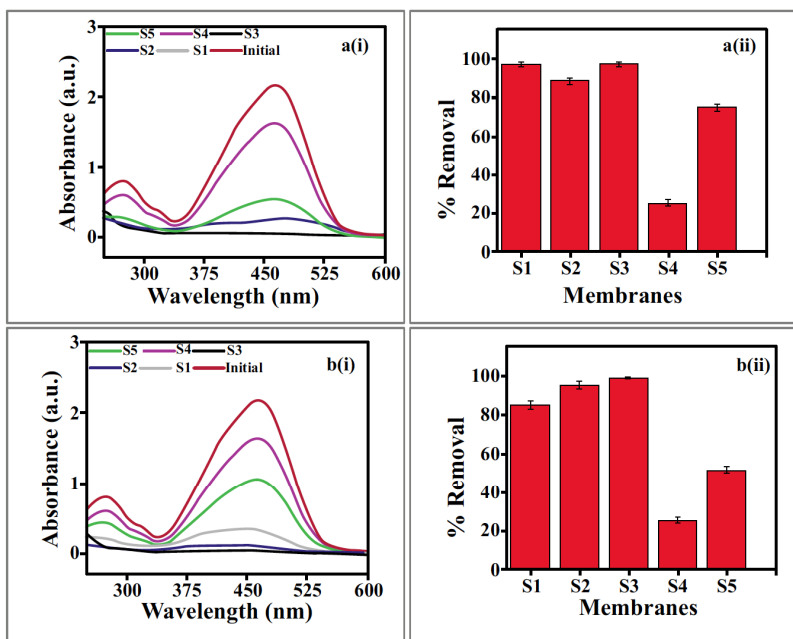


Fig. (7). a(i) UV-vis absorption spectra of MO dye with different membranes at solution pH2 (ii) % Removal of MO dye at pH2, b (i) UV-vis absorption spectra of MO dye with different membranes at pH3.5, b (ii) % Removal of MO dye at pH3.5.

area is another factor behind the complete removal of the dye. Fig. (6a) (ii) showed % removal of MB dye in the order S1~S3~S5>S2>S4 for solution pH 2 whereas in Fig. (6b) (ii) the order was S1~S2~S3~S5>S4 for solution pH 3.5.

Methyl Orange (MO), an anionic dye, is characterized by the presence of NH group which easily interacted with the grafted membrane bearing hydroxyl groups thus forming H-bond. It is due to the formation of this bond that the anionic dye was adsorbed on the surface of the membrane. The extent of removal depended on the surface charge of the membrane material as being clearly shown in Fig. (7a) (ii) where

% removal was in the order S1~S3>S2>S5>S4 for solution pH2 and in Fig. (7b) (ii) the % removal was in the order S3>S2>S1>S5>S4 for solution pH3.5. S1 and S3 showed the highest removal (~100%) at pH2 and pH3.5 respectively.

It can thus be concluded that effective separation of MB and MO dyes by TiPILC membranes can take place in one cycle of filtration by just adjusting the pH of the solution with that of the surface charge of the membrane. TiPILC membranes thus exhibit an integration of photocatalysis with separation on account of high surface charge and enhanced surface area.

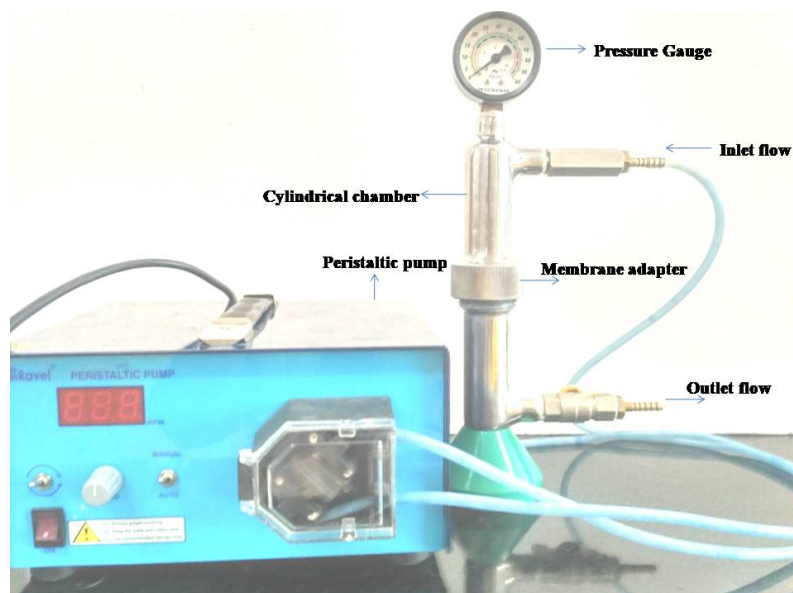


Fig. (8). Filtration set up showing peristaltic pump and membrane adapter unit fitted with a pressure gauge.

CONCLUSION

An attempt has been made to fabricate low-cost amphoteric titania pillared clay membranes by sol-gel process being sintered at 300°C. Grafting of the surface of clay by 3-aminopropyltriethoxysilane (APES) rendered the surface hydrophobic thus enhancing the surface area to 183m²/g which aided in better adsorption and separation of micro-organic contaminants. The surface charge of such amphoteric membranes can be easily altered by variation in pH which thus leads to selective adsorption of cationic and anionic pollutants. Titania pillared clay membranes exhibit negative surface charge at pH2 and pH3.5. MB dye, a cationic pollutant gets easily adsorbed (~99%) on the membrane material prepared at pH3.5. On the other hand, MO being an anionic dye shows ~90% retention for membrane material prepared at pH2, whose surface exhibits less negative charge as compared to the one prepared at pH3.5. Zeta potential studies testify to this fact. Production of only anatase phase at a lower temperature (300°C) enhanced dye degradability, though concerns of fouling remain which may be taken as future work.

LIST OF ABBREVIATIONS

TiPILC	=	Titania Pillared Clay
Mt	=	Montmorillonite
CTAB	=	Cetyl Trimethyl Ammonium Bromide
CMC	=	Carboxymethylcellulose
APES	=	3-Aminopropyltriethoxy Silane
IEP	=	Isoelectric Potential
MB	=	Methylene Blue
MO	=	Methyl Orange

NOMENCLATURE

PS1	=	APES Treated Clay
PS2	=	TiPILC Photocatalyst powder at pH2

PS3	=	TiPILC photocatalyst powder at pH3.5
S1	=	TiPILC membrane with 3 hour irradiation in sunlight
S2	=	TiPILC photocatalyst treated dye solution filtered using uncoated Mt membrane
S3	=	Titania photocatalyst treated dye solution filtered with TiPILC membrane
S4	=	Control experiment involving dye with uncoated Mt membrane
S5	=	TiPILC membrane without irradiation

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are the basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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