NEWLY FABRICATED TITANIUM DIOXIDE DOPED POLYMER MEMBRANE FOR DYE REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract: TiO_2 particle doped cross-linked Poly vinyl alcohol- Carboxy methyl cellulose (PVA-CMC membrane was fabricated by solution casting method. These membranes are explored for the purpose of effective removal of methylene blue (MB) and malachite green (MG) dyes from aqueous solutions. Adsorption capacity was measured by UV-Visible spectrophotometer. Optimisation studies were done at different time, pH, initial concentration and temperature. The membranes were characterized by XRD, FTIR, UV and SEM. Kinetic and thermodynamic studies reveal that pseudo second order kinetic model and Langmuir isotherm models are best explained by the mechanism of adsorption of MB and MG dyes onto PVA-CMC-TiO_2 membrane. The regeneration of membranes were effectively done.

Keywords **: Membrane adsorption, Methylene blue, Malachite green, Titanium dioxide, Composite membrane.**

1. Introduction

Removal of toxic chemicals from waste water is the major issue regarding the environmental remediation. The industries such as textile, food, tannery etc uses large amount of water day by day and there by discharging pollutants to water bodies. The disposal of these effluents are of major concern due to their toxicity in low concentration. The treatment of these pollutants extremely low concentration is very difficult. So that we have to take alternative measures to overcome these problems. The removal of toxic dyes become great challenge in day to day life. Membrane adsorption technology is most promising approach to be employed for the removal of pollutants due to their high efficiency, cost effectiveness, and catalytic activities [1]. Our study emphasized on the ability of composite membrane to remove dyes from aqueous solutions. Composite membranes were used because of their co operative effect of both organic as well as inorganic components.

The current study focused on the fabrication of cross-linked PVA-CMC-TiO_2 composite membrane and their effect on the adsorption of Methylene blue (MB) and Malachite green (MG) dyes towards these membranes were explained. CMC is an important derivative of cellulose that combines with PVA to form the material having excellent physico- chemical properties [2]. TiO_2 was used as an inorganic doper for the fabrication of composite membrane because of low cost, non toxicity, strong oxidative properties, chemical and thermal stability [3]. The introduction of TiO_2 particle into PVA-CMC matrix will improve hydrophilic as well as antifouling properties [4].

2. Experimental

2.1. Chemicals

PVA (99% hydrolysed, M.W=115,000, LOBA Chemie, India), Carboxy methyl cellulose sodium salt (M.W=250000, LOBA Chemie, India), Maleic acid (M.W=116.08, Merck), Double distilled water is used as solvent for the preparation of membrane. Methylene blue and Malachite green dyes were commercial grade. Stock solutions of dyes were prepared by dissolving their powder in demineralised water to give 10ppm solution.

2.2. *Preparation of titanium dioxide doped polymer membrane*

Membrane of different compositions were made by mixing Poly vinyl alcohol, Carboxy methyl celluose and Titanium dioxide, in different proportions. Maleic acid was added as a cross-linker. A definite amount of Poly vinyl alcohol dissolved in hot water was boiled with maleic acid in dil.H_2SO_4. To this CMC dissolved in distilled water was added carefully and heated. TiO_2 suspended in distilled water was then slowly added to the above mixture in drop wise manner and homogenized using vortex mixer. Different composition membranes were prepared by mixing different ratios of the components and the slurry obtained was carefully casted on to a Petridish. It was then dried in a hot air oven at 55^{o}C. The resultant membrane was peeled off by soaking it in double distilled water for several hours.

2.2.1. *Physico - chemical characterization*

Crystalline nature of membrane was determined using X-ray diffractometer (Rigaku Miniflex 600) equipped with CuKα radiation (λ= 1.54056A$^\circ$) at 2θ angles between 5° and 80°. FTIR spectra in KBr pellet were recorded using Agilent cary 630 FTIR spectrometer with wave number ranging from 4000-500cm^{-1} was helpful to identify the structure of composite membrane. The surface morphology of the PVA-CMC-TiO_2 membrane was examined using scanning electron microscopy (SEM) operated at an accelerating voltage of 5kV. UV-Visible absorption spectra of PVA-CMC membrane and PVA-CMC-TiO_2 membrane were measured in the wavelength range from 200-800nm using JASCO V-660 UV-visible spectrophotometer. Optical band gap can be determined from tauc plot using kubelka munk equation and evaluated by following equation

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g)$$

Where α is the absorption coefficient and hν is the energy of photon. Since TiO_2 is an indirect transition semiconductor, n is equal to ½. Tauc plot is used to measure optical band gap energy by plotting $(\alpha h\nu)^{1/2}$against energy.

2.2.2. Ion exchange capacity (IEC) measurement

The total ion exchange capacity of the polymer blend membrane and composite membrane was determined as follows. 1.0g of the membrane was taken in H^+ form in a 100 ml beaker. It was then equilibrated with 20 ml 1.0 M NaCl solution for 24 hours. The solution was decanted into conical flask, diluted to 50 ml. The hydrogen ion eluted from the membrane was determined titrimetrically with standard 0.1M NaOH solution using phenolphthalein as indicator. From the titre value the ion exchange capacity of the membrane was determined using the following equation [5],

$$IEC = \frac{Volume\ of\ NaOH\ x\ Molarity\ of\ NaOH}{Weight\ of\ membrane}\ meqg^{-1}$$

Similarly, IEC of TiO_2 particles were also determined.

2.2.3. Determination of percentage water uptake

For the water uptake measurement, dry membranes were weighed and immersed in distilled water for 24 hours, then excess water was removed with absorbent paper and the wet sample was weighed. The water uptake was calculated according to the following equation.

$$\%\ Water\ uptake = \frac{(Ww - Wd)}{Wd} \times 100$$

Where W_w is the wet sample weight and W_d is the dry sample weight.

2.2.4. Chemical stability of the membrane

The chemical stability of PVA-PSSA-ZPS membrane was examined by treating membrane with 20ml different commonly used acids and few organic solvents. Physical change of membranes were noted. UV-Visible spectrophotometer was used to perform the absorbance of the solvents before and after immersion of membrane.

2.2.5. *Dye adsorption studies on the membrane:*

Different dyes were made to adsorb on the membrane and the result was analysed using UV-Visible spectrophotometer. Effect of contact time, initial feed concentration, pH and temperature on adsorption of dyes were studied. Kinetic studies on adsorption were then carried out for the dye that was adsorbed to a greater extend.

2.2.6. *Adsorption of mixture of dyes onto PVA-CMC-TiO_2 membrane*

Prepared PVA-CMC-TiO_2 membrane and PVA-CMC membrane were immersed in the mixture of 20ml 10PPM MB and MG dye solutions and shaken well for 1hour. Adsorption properties were measured by UV-Vis spectrophotometer.

2.2.7. Treatment of textile effluent waste using the membrane

Efficiency of the membrane was tested for the treatment of textile effluent waste collected from the nearby loom unit. The sample dye waste was analyzed on UV- Visible spectrophotometer for its intial concentration.

An effluent treatment column was made, by carefully embedding the membranes in an ion exchange column. Effluent waste was directly poured onto the column and the flow at the outlet was maintained at 0.1ml per minute. After the treatment the eluted waste water was analyzed on UV- Visible spectrophotometer.

2.3. Kinetics of dye adsorption

Kinetics of membrane adsorption was done by adding the prepared membrane in 20ml, 10ppm MB and MG dye solutions. Adsorption at different time intervals were determined. A water bath shaker was used for the purpose. The resulting sample after the removal of membrane was analyzed on UV-Visible spectrophotometer. Theoretical calculations were done as described as follows.

The adsorption capacities for different dyes were calculated by using following equation,

$$qe = \frac{Co - Ce}{M} x\ V$$

C_o and C_e are initial and equilibrium concentration of dyes. V is the volume of dye solution taken in millilitre, M is the mass of membrane or TiO_2 in gram.

Pseudo first order and pseudo second order kinetic models were used to describe the mechanism of MB and MG onto the surface of PVA-CMC-TiO_2 membrane and it can be expressed in equation (1) and (2) respectively [6].

$$\log(q_e - q_t) = \log q_e - \frac{K1t}{2.303} \quad \text{.....(1)}$$

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qt} \quad \text{.....(2)}$$

where q_e and q_t are the amount adsorbed at equilibrium at time 't' in minutes. K_1 and K_2 are the first order and second order rate constant.

2.4. Adsorption isotherm

In the present study Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin isotherm models were used to express the equilibrium data for the adsorption and it can be given in equation (3), (4), (5) and (6).

The Langmuir isotherm focused on monolayer adsorption onto homogeneous surface where as freundlich isotherm on multilayer adsorption onto heterogeneous surface and can be expressed as [7],

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{K_L\, qm} \quad [8] \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad [9] \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

C_e (mg/L), q_e (mg/g), q_m and K_L are the equilibrium concentration and equilibrium adsorption capacity constant related to adsorption capacity (mg/g) and energy of adsorption (L/g) respectively. n and K_F are Freundlich constant. The value of $\frac{1}{n}$ gives the strength of adsorption in the adsorption process [10]. $\frac{1}{n}$ closer to zero for more heterogeneous surface. Value of $\frac{1}{n}$ below 1 for normal adsortpion and $\frac{1}{n}$ above 1 indicates co-operative adsorption.

R_L (separation factor) is the another important parameter used in Langmuir isotherm.

$$R_L = \frac{1}{1 + K_L\, Co}$$

Where C_o (mg/L) is the initial concentration of adsorbate.

The value of R_L corresponding to, R_L>1.0, R_L=1, 01>R_L>0 and R_L=0 for Unfavourable adsorption, Linear adsorption, Favourable adsorption and Irreversible adsorption respectively [1,11,12].

Dubinin-Radushkevich model was used to distinguish the nature of adsorption of dyes with its mean free energy and generally focused the Gaussian energy distribution on heterogeneous surface, assumes and Temkin isotherm model assumes heat of adsorption of all molecules that would decrease linearly with coverage [13,14] and their linear form can be expressed as

$$\ln q_e = \ln q_s - K_{ad}\,\varepsilon^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$Qe = \left(\frac{RT}{b}\right) ln(ACe) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5).$$

Where $\frac{RT}{b}$ = B, q_e is the amount of adsorbate (mg/g), q_s is the monolayer adsorption capacity (mg/g), Ɛ is the polanyi potential and can be expressed as,

$$\varepsilon = RTln\left(1 + \frac{1}{Ce}\right)$$

R is the universal gas constant (8.314J/K/mol), T is the temperature at 298K, b is the Temkin isotherm constant, A is the equilibrium binding constant (L/g). B is the constant related to heat of adsorption (J/mol). k_{ad} is the Dubinin-Radushkevich isotherm constant (mol^2/KJ^2) related to mean free energy of adsorption as,

$$E = 1/(\sqrt{-2B})$$

B is the isotherm constant. mechanism of adsorption follows chemical adsorption if E value in between 8 and 16KJ/mol and E<8 KJ/mol for physical adsorption[9,15].

2.5. Adsorption Thermodynamics

Thermodynamic parameters such enthalpy change (ΔH^0), entropy change (ΔS^0) and free energy change (ΔG^0) was used to describe spontaneity of adsorption process. Temperature dependence of equilibrium constant was obtained from Van't Hoff equation can be written as

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

The plot of lnK Vs $\frac{1}{T}$ gives the straight line with slope = $-\frac{\Delta H^\circ}{R}$ and intercept = $\frac{\Delta S^\circ}{R}$. From the slope and intercept, thermodynamic parameters such as ΔH^0 and ΔS^0 can be calculated.

Where R = 8.314J/K/mol (universal gas constant), T is the temperature in Kelvin.

$$K = \frac{Cm}{Ce}$$

C_m is the concentration of dyes on membrane at equilibrium and C_e is the equilibrium concentration of dyes in solution.

3. Results and discussion

Polymer membranes obtained were of different compositions. One sample out of three showed good dye adsoption property. The composition ratio for PVA, CMC and TiO_2 for this membrane was 4.5:4.5:1, (Fig.1). So this membrane was used for further analysis.

(a)

(b)

Fig. 1-(a) Cross-linked PVA-CMC-TiO_2 Membrane; (b) MB adsorbed PVA-CMC-TiO_2 membrane

3.1. *Physico-chemical characterization*

3.1.1. XRD Analysis

XRD pattern of PVA-CMC membrane and TiO_2 doped PVA-CMC membrane was shown in fig.(2). The strong diffraction peak at 27^O, 36^O, 54^O depicts the presence of TiO_2 in rutile phase [16]. PVA-CMC membrane shows diffraction peak around 10^O, 19^O (strong peak), 22^O (shoulder peak) and 40^O corresponds to the semi crystalline nature is due to hydrogen bonding interaction between monomer units [17, 18]. It was also shown that the intensity of polymer blend membrane decreased by the addition of TiO_2 into polymer matrix. It may be due to the

change in structure of polymer blend membrane after addition of TiO_2 particles and there by enhancing amorphous nature of composite membrane.

3.1.2. FTIR

As compared to FTIR spectra of polymer blend with composite membrane, the intensity of blended membrane is slightly changed by the addition of TiO_2 particles into polymer matrix is due to the formation of hydrogen bonding between hydroxyl group of PVA-CMC and TiO_2 particle. Broad intense Peak at 3262cm^{-1} and 2924cm^{-1} is due to hydrogen bonded OH stretching vibration and -CH stretching vibration of CMC. Intense peak at 1632cm^{-1} ascribed to the –C=O stretching vibration. Plane deformation mode of C-H group at 1418-1328cm^{-1} and C=O stretching vibration of aliphatic primary and secondary alcohol in CMC is also shown in IR spectrum. Peak at 913cm^{-1} and 833cm^{-1} corresponds to $–CH_2$ ring vibration and C-C stretching vibration [19] respectively. TiO_2 particles shows major peak around 400cm^{-1} indicates Ti-O stretching and Ti-O-Ti bond stretching vibrations [20].

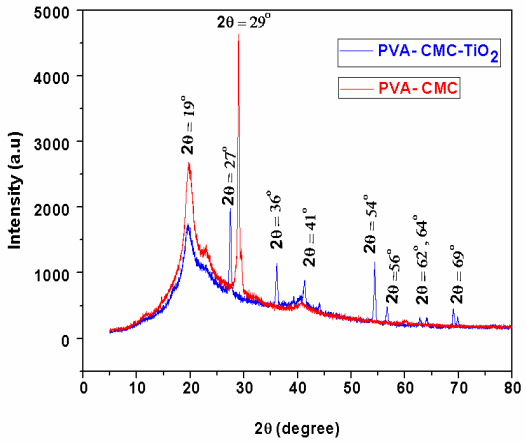

Fig. (2). X-ray diffraction pattern of PVA-CMC membrane and PVA-CMC-TiO_2 membrane

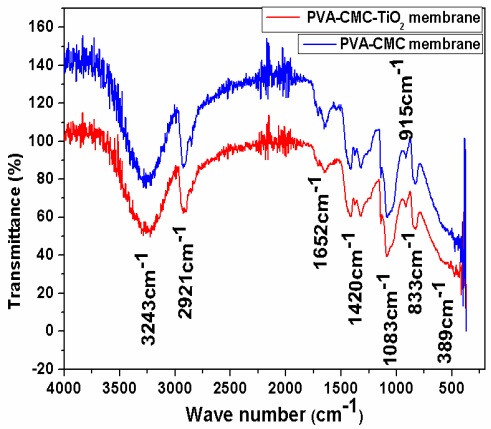

Fig. (3). FTIR spectra of PVA-CMC membrane and PVA CMC-TiO_2 membrane

3.1.3. UV-Vis spectroscopy

Optical property of membrane were studied using UV- Vis spectrophotometer. Fig.(4) shows blue shift for PVA-CMC-TiO_2 membrane PVA-CMC membrane, TiO_2 particles. The spectra exhibit between 200-800nm were studied. The results shows that TiO_2 particle shows peak at 349nm due to charge transfer from oxygen to Ti(IV) [21] with absorbance of 0.8824 and the band at higher wavelength (λ> 240nm) attributed to charge transfer from oxygen to octahedral Ti(IV) sites [22]. PVA-CMC- TiO_2 shows peak at 343nm with absorbance of 0.9172, which indicates that both polymer membrane as well as inorganic material exhibits good absorbance in the UV region. The TiO_2 shows visible light absorbance and band gap energy of 3.5530eV and that of polymer membrane was 3.6152eV. When TiO_2 was introduced into the polymer matrix, the band gap energy increased, which inturn decrease the conductivity while adding TiO_2 particle into polymer matrix.

3.1.4. SEM

The SEM micrographs of PVA-CMC-TiO_2 composite membrane is depicted in Fig.(6). Heterogeneous surface is observed which indicates good interfacial adhesion between TiO_2 and polymer matrix. Aggregation of TiO_2 particle on the surface of polymer matrix was also observed.

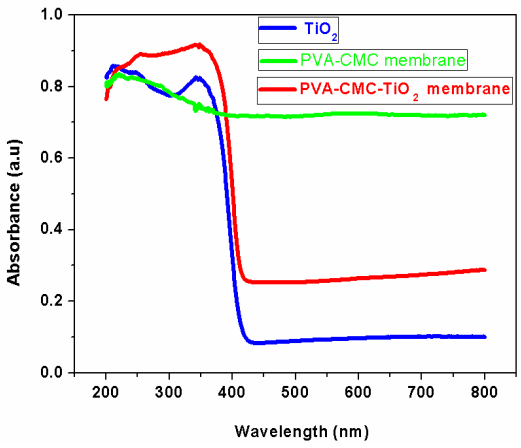

Fig.(4). UV- Visible absorbance

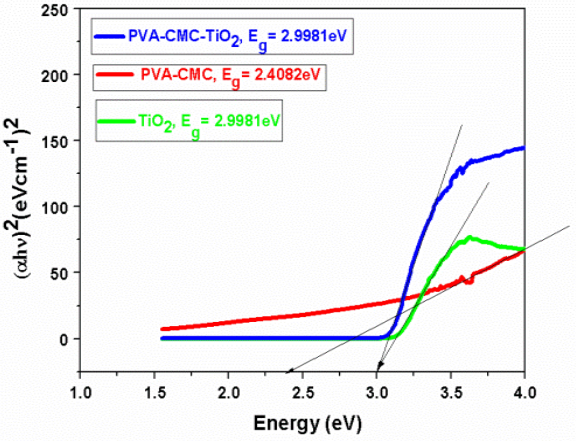

Fig.(5). Tauc plot for optical band gap energy determination

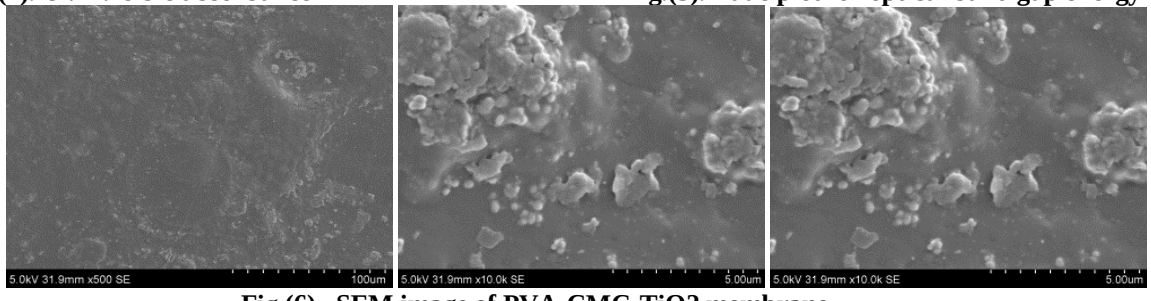

Fig.(6). SEM image of PVA-CMC-TiO2 membrane

3.2. Ion exchange capacity of TiO_2 *particles and* PVA-CMC-TiO_2 *membrane*

It was observed that IEC value of TiO_2 was 3.2meqg^{-1} and that of PVA-CMC-TiO_2 membrane was found to be 6.436meqg^{-1}. Results show

that composite membrane has high capacity to exchange H^+ ions than the inorganic counterpart. It may be due to large number of movable H^+ ions as well as high water uptake of polymer matrix.

3.3. Water uptake capacity

The results show that swelling degree of membrane is less as compared to polymer matrix without TiO_2. The percentage degree of swelling of PVA-CMC membrane was found to be 215% and the TiO_2 doped membrane was found to be 186.22 ± 5%. Cross-linking decreased the swelling degree. When cross-linking agent, maleic acid was added to PVA matrix, esterification reaction occured within the matrix. Addition of TiO_2 to the polymer matrix, reduced the free volume in the blend and this also decreased the water uptake capacity of the membrane

3.4. *Chemical stability of the membrane*

Chemical stability of PVA-CMC-TiO_2 membrane was investigated by soaking the membrane into different solvents and dilute acid solution for 24 hours at room temperature. Sample did not show any physical change and there was also no noticeable weight change.

*3.5. **Factors affecting adsorption***

The membrane was found to adsorb malachite green (MG) and methylene blue (MB) in a very efficient manner. The Fig.(20) and (21) show that the dye content before and after adsorption on the membrane. Almost complete removal can be noticed distinctly from the UV-Visible spectrum. So further studies were carried out for the adsorption of these two dyes.

3.5.1. *Effect of Contact time*

The effect of time on adsorption was investigated. The adsorption of dyes onto the membrane at different time interval ranging from 10min to 90minute is shown in (Fig.7) Adsorption initially increased and then equilibrium was attained. Dye adsorption onto the membrane increased with increase in time. Observation shows that equilibrium was reached just after 90min for MB and 80min for MG by using 10ppm dye solution. A rapid decolourisation occurred after 50 minutes for MB and after 30min for MG. Percentage of dye removal using PVA-CMC-TiO_2 membrane is in the order of MG > MB.

3.5.2. Effect of temperature

The effect of temperature on dye adsorption on the membrane was studied at 318K, 328K and 338K using 10ppm dye solutions. Adsorption capacity increased with increase in temperature. (Fig.8) The temperature dependence on adsorption was measured using Van't Hoff plot. From the slope and intercept, spontaneous nature of the process was confirmed.

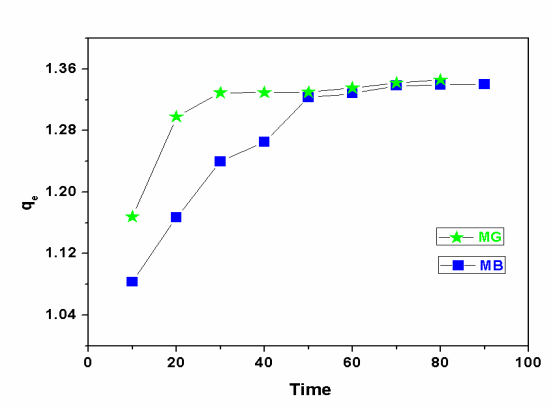

Fig.(7). Effect of time

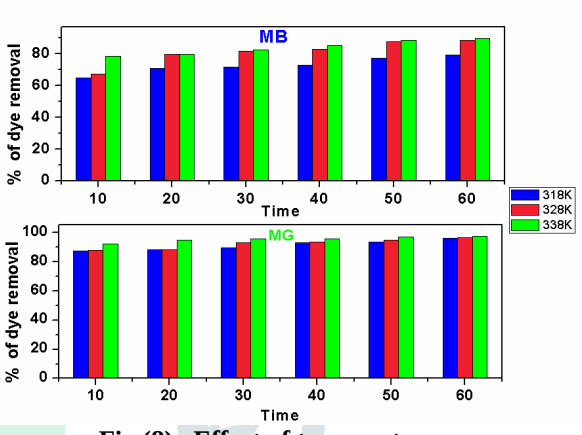

Fig.(8). Effect of temperature

3.5.3. *Effect of Initial concentration*

Initial concentration is an important factor in dye adsorption process. Optimisation studies were done with initial concentration ranging 20ppm to 100ppm. Observations show that as the initial concentration increased, the dye adsorption also increased, (Fig.9).

3.5.4. *Effect of pH*

pH dependence is also an important parameter in membrane adsorption studies. The effect of pH on adsorption was studied at pH ranging from 3 to 10. Maximum adsorption capacity has been observed at pH 6 for MB and pH 10 for MG. In the case of MB, percentage of dye removal increased initially upto pH 6 and then decreased, (Fig.10).

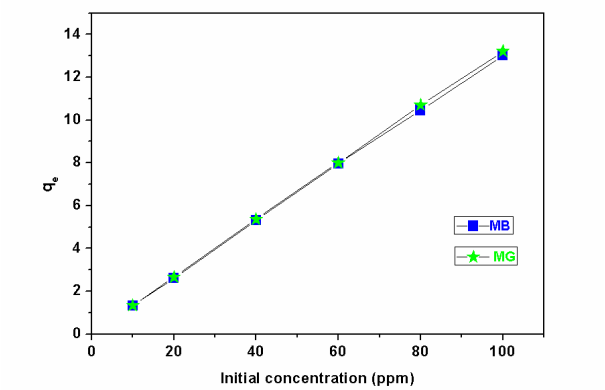

Fig.(9). Effect of initial concentration

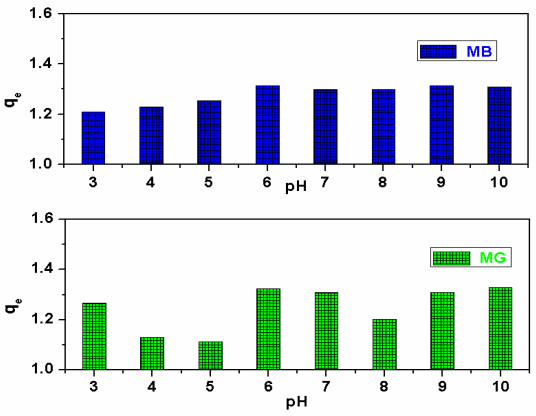

Fig.(10). Effect of pH on dye adsorption

3.6. Adsorption of mixture of dyes onto PVA-CMC-TiO_2 membrane

The intensity of absorbance was given in Fig.(11). The results shows that when TiO_2 particle was introduced into polymer matrix, adsorption capacity will be increases.

3.7. Treatment of textile effluent using membrane

The investigation shows that, the efficient removal of effluent from loom unit was done by PVA-CMC-TiO_2 membrane. These membrane shows the removal efficiency of around 95%.

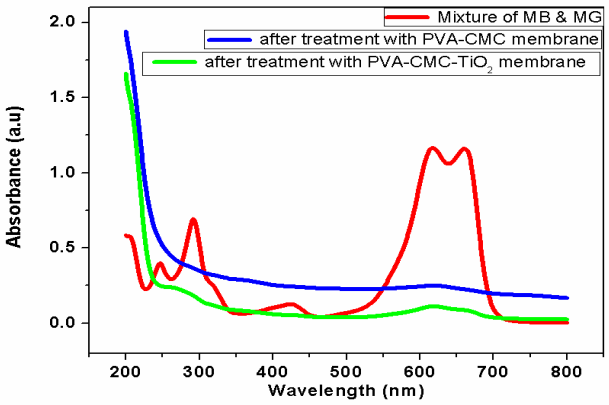

Fig.(11). Adsorption of mixture of MB and MG dyes onto the membrane

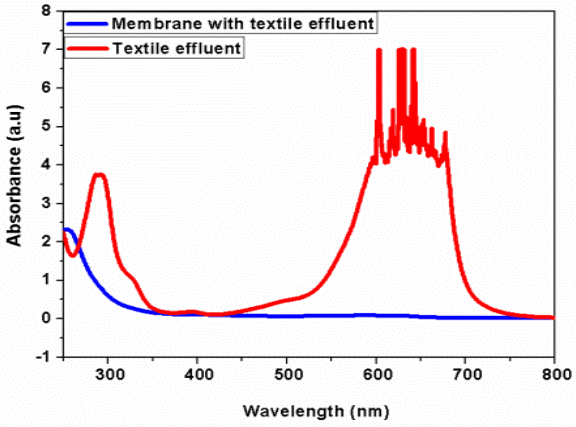

Fig.(12). Treatment of textile effluent using membrane

3.8. Kinetics of adsorption

Kinetics of membrane adsorption was done by adding the prepared membrane in 20ml 10ppm MB and MG dye solutions. Then it is kept in water bath shaker for different time intervals. After that membrane removed from dye solution and amount of dye adsorbed on the membrane was measured by UV-Visible spectrophotometer.

Results reveal that the linear regression coefficient of second order is higher than that of first order. In pseudo second order model, the experimental and calculated values are more agreeable to each other for both MB and MG dyes. This indicates that second order kinetic model is best model to explain the mechanism of adsorption process.

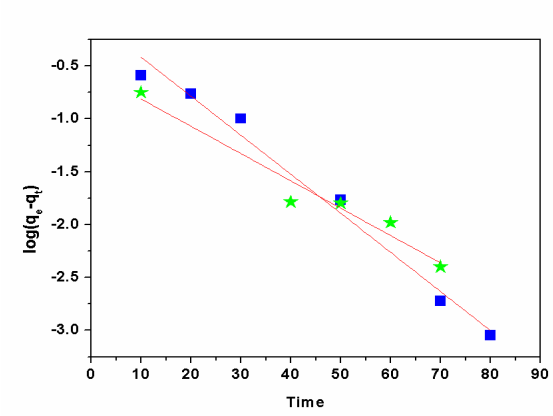

Fig.(13). Lagergren's pseudo first order kinetic model

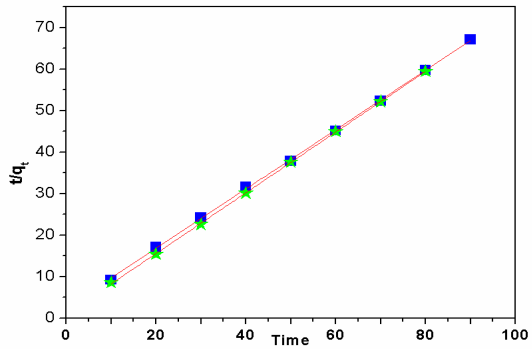

Fig.(14). Ho's pseudo second order kinetic model

Table (1) Pseudo first order and second order kinetic parameters

DYES	First order kinetics (lagergren's)				Second order kinetics (Ho's)			
	q_e (exp) (mg/l)	q_e (calc) (mg/l)	K_1 (min^{-1})	R^2	q_e (exp) (mg/l)	q_e (calc) (mg/l)	K_2 (g/mg.min)	R^2
MB	1.2693	0.8991	0.0849	0.9811	1.2693	1.3978	0.2055	0.9996
MG	1.3097	0.0594	0.2796	0.9435	1.3097	1.3671	0.5774	0.9999

3.9. Adsorption isotherm

Langmuir, Freundlich, Dubinin and Temkin isotherm models were used to study the adsorption properties of prepared membrane. From linear regression coefficient values, it is observed that Langmuir isotherm was the best fitted model for explaining adsorption of both MB and MG dyes on the surface of PVA-CMC-TiO_2 membrane. From slope and intercept obtained from graph, monolayer adsorption capacity (qm), separation factor (R_L), energy of adsorption (K_L) were calculated. Malachite green showed high adsorption capacity than MB. The negative RL values indicates that the adsorption of dyes on to the membrane is a favourable one. R^2 value 0.99 for both dyes proved that adsorption data was best fitted to Langmuir isotherm model.

Negative value of Freundlich isotherm constant 1/n indicates that sorption of MB and MG dyes onto the membrane follows normal adsorption and their R^2 value is 0.87 for MB and MG dyes. Mean free energy of adsorption of MB is 3.9223KJ/mol and MG is 5.1164KJ/mol, indicates the physisorption process.

Temkin constant related to heat of adsorption (b) obtained from graph is negative for MB and MG dyes reveals that the adsorption of MB and MG dye on to the membrane was endothermic in nature and their R^2 value is greater than that of Dubinin isotherm model.

Table (2) Langmuir, Freundlich, Dubinin, Temkin isotherm parameters

Dyes	Langmuir constants				Freundlich constants		
	q_m(mg/g)	K_L	R_L	R^2	$\frac{1}{n}$	K_F	R^2
MB	1.0965	-25.4743	$-3.9409x10^{-3}$	0.9960	-0.0424	1.2167	0.8739
MG	1.1578	-53.9817	$-1.8559x10^{-3}$	0.9992	-0.0202	1.2788	0.8732

Dyes	Dubinin isotherm constants				Temkin isotherm constants			
	q_s	K_{ad}	E	R^2	A (l/g)	B	B	R^2
MB	1.1118	-0.0325	3.9223	0.7966	$5.9774x10^{-8}$	-0.0716	$-3.4602x10^{4}$	0.8441
MG	1.1877	-0.0191	5.1164	0.6477	$1.7851x10^{-11}$	-0.0494	$-5.0153x10^{4}$	0.7716

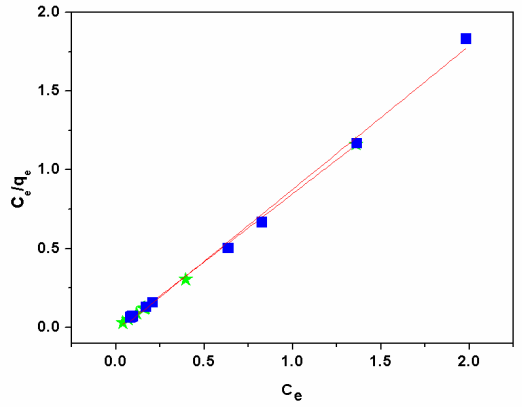

Fig.(15). Langmuir isotherm

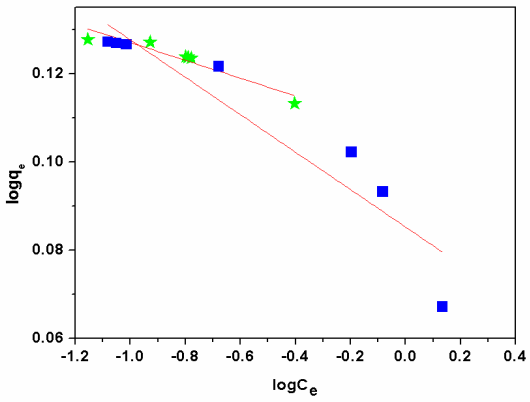

Fig.(16). Freundlich isotherm

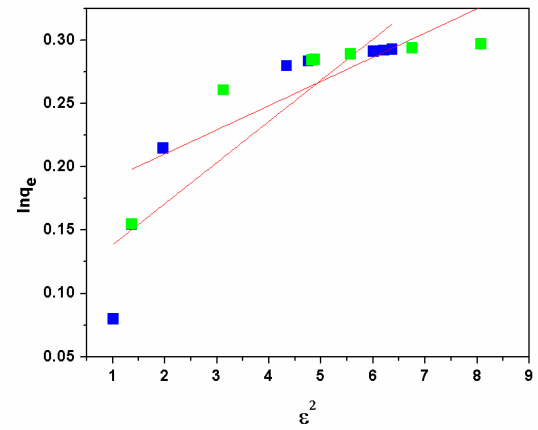

Fig.(17). Dubinin isotherm

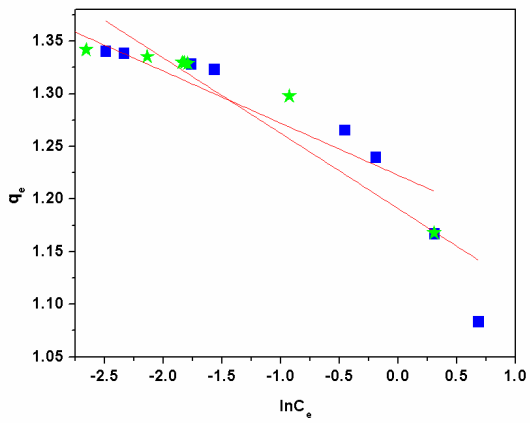

Fig.(18). Temkin isotherm

3.10. Adsorption thermodynamics

The spontaneous nature of adsorption onto the membrane was proved by adsorption thermodynamics. Adsorption studies were carried out at different temperatures such as 318K, 328K and 338K using 10ppm MB and MG solutions. Temperature dependence on adsorption constant was obtained from Van't Hoff plot, which is given in Fig.(19). Table.8 shows the thermodynamic parameters like ΔH°, ΔS° and ΔG° for adsorption. From the results, it is clear that the positive value of ΔH° indicates that the adsorption of dyes onto the PVA-CMC-TiO_2 membrane is endothermic. The positive value of ΔS° indicates that the dye molecules adsorbed onto the membrane surface are organised. The ΔG° values were obtained by substituting the values of ΔH° and ΔS° in Gibbs free energy equation. Here negative value of ΔG° indicates that adsorption of MB and MG dyes onto the membrane is spontaneous in nature.

Table(3). Thermodynamic parameters for the adsorption of dyes onto the membrane

DYES	ΔH^0 (J/mol)	ΔS^0 (J/mol.K)	ΔG^0 (KJ/mol)
MB	37.0197	128.3416	-3.8208×10^4
MG	20.9829	83.8284	-2.4959×10^4

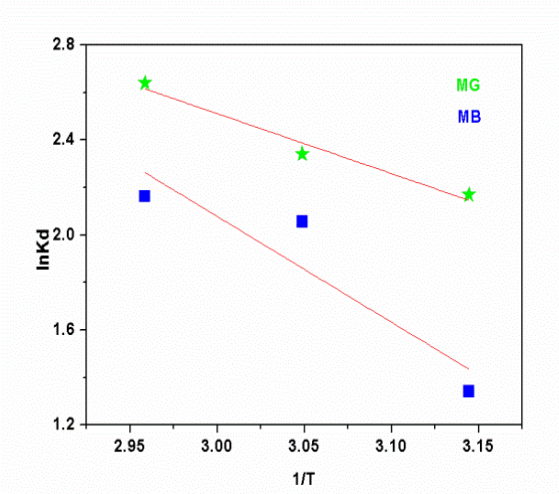

Fig.(19). Van't Hoff plot

3.11. *Regeneration of membranes*

Regeneration of membrane is an important figure of merit in adsorption process. Reusablity will save time, cost of production and also reduce wastes. MB adsorbed membrane was regenerated by adding the mixture of 1M HCl and 1M HNO_3 solution and it was shaken well for 30minutes and finally washed with distilled water. After recycling, the membrane could be regenerated and used again. Eight cycles of adsorption-desorption process were carried out. Similarly MG adsorbed membrane were regenerated by using the eluent such as 1M HCl. After 8th regeneration cycle, the removal rate of MB decreased upto 81.48% and MG decreased upto 92.26%. It was observed that the removal efficiency decreased slightly with increasing adsorption-desorption cycle.

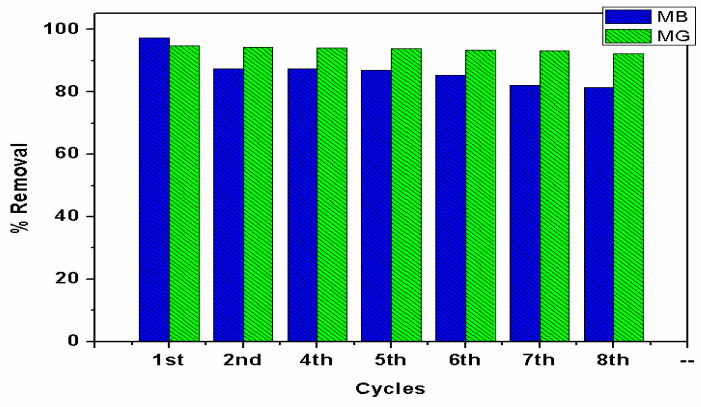

Fig.(20). Regeneration of MB and MG adsorbed membrane

4. Conclusion

Cross-linked membrane was used as promising candidate for the effective removal of toxic MB and MG dyes from aqueous solutions. XRD and UV characterization results that the addition of TiO_2 particle to the polymer matrix enhanced not only the amorphous nature but also band gap energy. Studies show that it was also used as an efficient adsorbent for the removal of textile effluent and MB-MG dye mixture. Mechanism of adsorption follows Langmuir isotherm and pseudo second order model. Thermodynamic studies results that adsorption of dyes onto the membrane was feasible, endothermic and spontaneous in nature. Desorption study shows that around 81% and 92% removal efficiency shown by MB and MG dyes after 8th regeneration cycle confirms that membrane can be used as effective catalyst.

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