MATHEMATICAL MODELLING AND SIMULATION OF PHOTOCATALYTIC MEMBRANE REACTOR

A thesis submitted towards partial fulfilment of the requirement for the degree

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Under the guidance of

DR. CHIRANJIB BHATTACHARJEE

PROFESSOR

CHEMICAL ENGG DEPARTMENT

JADAVPUR UNIVERSITY

Department of Chemical Engineering, Jadavpur University

Jadavpur, Kolkata-700032

FACULTY OF ENGINEERING AND TECHNOLOGY DEPARTMENT OF CHEMICAL ENGG

JADAVPUR UNIVERSITY

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This is to certify that the thesis entitled "Mathematical Modeling and Simulation of Photo catalytic Membrane Reactor" is a bonafide work carried out by **SUSMIT DUBEY** under my supervision and guidance for partial fulfillment of the requirement of Master of Engineering in Chemical Engineering during the academic session 2014-2016

Dr.Chiranjib Bhattacharjee   Dr. Chandan Guha

Professor   Professor & HOD

Chemical Engineering Dept   Chemical Engineering Dept

Jadavpur University   Jadavpur University

Kolkata-700032   Kolkata-700032

Dean-FET

Jadavpur University

Kolkata-700032

FACULTY OF ENGINEERING AND TECHNOLOGY DEPARTMENT OF CHEMICAL ENGG

JADAVPUR UNIVERSITY

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This foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactorily to warranty its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not endorse or approve any statement made or opinion expressed or conclusion drawn therein but approve the thesis only for purpose for which it has been submitted

Committee for final examination   ....

for evaluation of thesis

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<u>Declaration of Originality and Compliance of original ethics</u>

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Engineering in Chemical Engineering studies during academic session 2014-16.

All information in this documents has been obtained and presented in accordance with ethical rule and academic conduct

I also declare that, as required by the rules and conduct, I have fully cited and referred all material and results that are not original to this work.

NAME: Susmit Dubey

CLASS ROLL NO: 001410302008

EXAM ROLL NO: M2CHE1605

THESIS TITLE: Mathematical Modelling & Simulation of Photo catalytic Membrane Reactor

Signature

(Susmit Dubey)

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I am thankful to all my teachers, my parents and also my colleagues for their support whenever it needed.

Contents

ABSTRACT

Photo catalytic degradation of chlorhexidine digluconate(CHD) solution using nano catalyst (Titanium dioxide,TiO_2) was studied in photo catalytic membrane reactor(PMR). The objective is to develop mathematical model equation for prediction of substrate concentration in permeate stream while changing the initial substrate concentration and reaction time keeping catalyst concentration constant for a set of data resulting a partial differential equation, coupled with other non linear ordinary differential equation has been solved using Runge-kutta fourth order method. Average deviation between theoretical results and experimental data generated in this study found to be remain within $\pm10\%$.

CHAPTER -1

INTRODUCTION

Increasing demand and shortage of clean water sources due to rapid growth of industrialization and population growth has become an issue worldwide. With growing demand various practical strategies has been adopted and out of them rain water harvesting has achieved some popularity. From various studies it has been estimated around 4 billion people worldwide have no or a very little access to clean drinking water and millions of people died of severe waterborne diseases. This statistical figure expected to grow in the short future as increasing water contamination due to overwhelming discharge of micro pollutants and contaminants into natural water cycle. In view to suppress worsening of clean water shortage development of high efficiency & low cost water treatment technologies to treat the waste water is desirable. Processes such as adsorption, coagulation, concentration of pollutants using phase change methodology do not completely eliminate and destroy pollutants. Due to their high operating cost and generation of secondary pollutants other processes like sedimentation, filtration, and chemical waste water treatments are not also well accepted. To overcome the limitation of conventional waste water treatment and make the processes cost effective various advanced treatment technologies has been adopted, optimized and applied. Among recently adopted technologies membrane filtration, advanced oxidation process, UV radiation has have been proven beneficial in removal of various challenging contaminants.

Advanced oxidation process (AOP) is a modern trend of pharmaceutical and municipal waste water treatment. Advanced oxidation process can be categorized as photolysis, electrochemical oxidation, Fenton's oxidation, ozonization, wet air oxidation etc. According to Klavarioti *et a[i]l* ozonization and heterogeneous photo catalysis are the most accepted waste water treatment methodologies. Researchers have observed that ozonization process is more suitable in purifying drinking water than pharmaceutical waste water treatment as latter requires several downstream processing steps. Hence heterogeneous photo catalysis has become more effective in treatment of pharmaceutical waste water. Photo catalysis reactions are more effective where coupled with nano particles used as a catalyst which offer better surface area, higher reaction rate.

Photo catalytic membrane reactor (PMR) is very much effective for heterogeneous photo catalysis reaction and our present study aims at mathematical modelling and simulation of PMR as it can give us a better understanding of the system and helps us getting information about how the reaction will behave while changing design and other parameters without testing it in real life. The model useful for developing a data as the basis for managerial or technical decision making.

1.1. Why Photo catalytic membrane reactor (PMR)?

Photo catalytic reactors is very much efficient in handling heterogeneous oxidation reaction as nanoparticle catalyst can be used effectively using various techniques. Based on usage of catalyst photo catalytic reactors can be divided into two parts

i. Reactor where TiO_2 suspended in a reaction mixture
ii. Reactor where TiO_2 fixed on carrier material.

In case of photo catalyst immobilized on a support, the active surface accessible for components of the solution is significantly reduced what actually results in a loss of photo activity. If the suspension of the catalyst on the active surface is much greater; however; the photo catalytic particle has to separate from the treated water after detoxification. A very well known and promising method for solving problems concerning separation of photo catalyst as well as products and by products of photo decomposition from the reaction mixture is the application of Photo catalytic membrane reactors(PMRs).

It is a hybrid reactor where photo catalysis is coupled with a membrane process. The membrane will play both the role of a simple barrier for the photo catalyst and of a selective barrier for the molecules to be degraded. In PMR similarly as in case of classical photo reactors, the catalyst must be immobilized on a membrane or suspended in the reaction mixture.
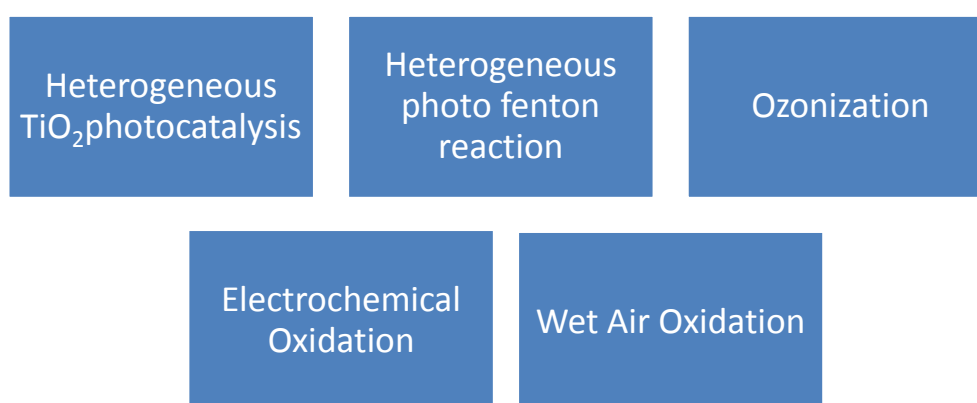
PMRs have some advantage with respect to conventional photo reactors such as

1) Confining of photo catalyst in the reaction environment by means of membrane
2) Proper control of residence time of molecules in the reactor
3) Realization of continuous process with simultaneous catalyst and product separation from reaction environment though in our recent studies we have used batch mode for simplicity of operation
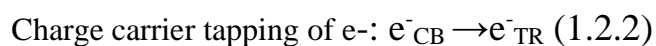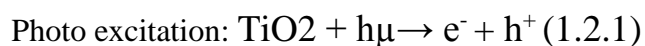
Moreover application of PMR instead of convention photo reactor allows avoiding some additional operation such as coagulation, flocculation, sedimentation which is necessary to remove catalyst from the treated solution. The advantage from this type of reactor is energy saving and reduction in the size of installation. Another one is possibility of reusing the photo catalyst in further runs, what is practically impossible when convention separation system composed of coagulation-flocculation-sedimentation steps is applied.

1.2. Advanced Oxidation Process

As discussed earlier AOP can be of different types

Heterogeneous TiO_2 photocatalysis	Heterogeneous photo fenton reaction	Ozonization
Electrochemical Oxidation	Wet Air Oxidation	

Developments towards heterogeneous photo catalysis(HPC) in presence of nano catalyst are gradually rising and represent highest percentage among AOPs. The fundamentals of photo physics and photo chemistry underlying heterogeneous photo catalysis employing the semiconductor TiO_2 catalyst has been intensively reported in many literature. The semiconductor has been used widely as a photo catalyst for conducting a series of reductive and oxidative reactions on its surface. This is solely contributed by the lone electron characteristics in its outer orbital. When photon energy is greater or equal to band gap energy of TiO_2 illuminated into the surface usually 3.2 eV (anatase) or 3.0 eV (rutile) the lone electron will be photo excited to the empty conduction band. Figure 1 depicts the mechanism of the electron-hole pair formation when TiO_2 particle is irradiated with adequate h. The light wavelength for such photon energy usually corresponds to α<400nm. The photonic excitation causes an empty unfilled valance band and thus creating a electron hole pair (e^-h^+). The series of chain oxidative-reductive reaction that occur at the photon activated surface was widely postulated as follows. According to *S.Mozia* [ii] the following reactions take place in a photo reactor.

Photo excitation: $TiO2 + h\mu \rightarrow e^- + h^+$ (1.2.1)

Charge carrier tapping of e-: $e^-_{CB} \rightarrow e^-_{TR}$ (1.2.2)

Charge carrier tapping of h^+: $h^+_{VB} \rightarrow h^+_{TR}$ (1.2.3)

Electron hole recombination: $e^-_{TR} + h^+_{VB} \rightarrow e^-_{CB} + heat$ (1.2.4)

Photo excited e- scavenging: $(O_2)_{ads} + e^- \rightarrow O2^{\cdot-}$ (1.2.5)

Oxidation of hydrolysis: $OH^- + h^+ \rightarrow OH^{\cdot}$ (1.2.6)

Photo degradation by OH: $R\text{-}H + OH^{\cdot} \rightarrow R^{\cdot} + H_2O$ (1.2.7)

Direct Photo hole: $R + h^+ \rightarrow R^{+\cdot}$(Degraded products) (1.2.8)

Photonation of super oxides: $O_2^{\cdot-} + OH^{\cdot} \rightarrow HOO^{\cdot}$ (1.2.9)

Co – scavenging of e^-: $HOO^{\cdot} + e\text{-} \rightarrow HO_2^-$ (1.2.10)

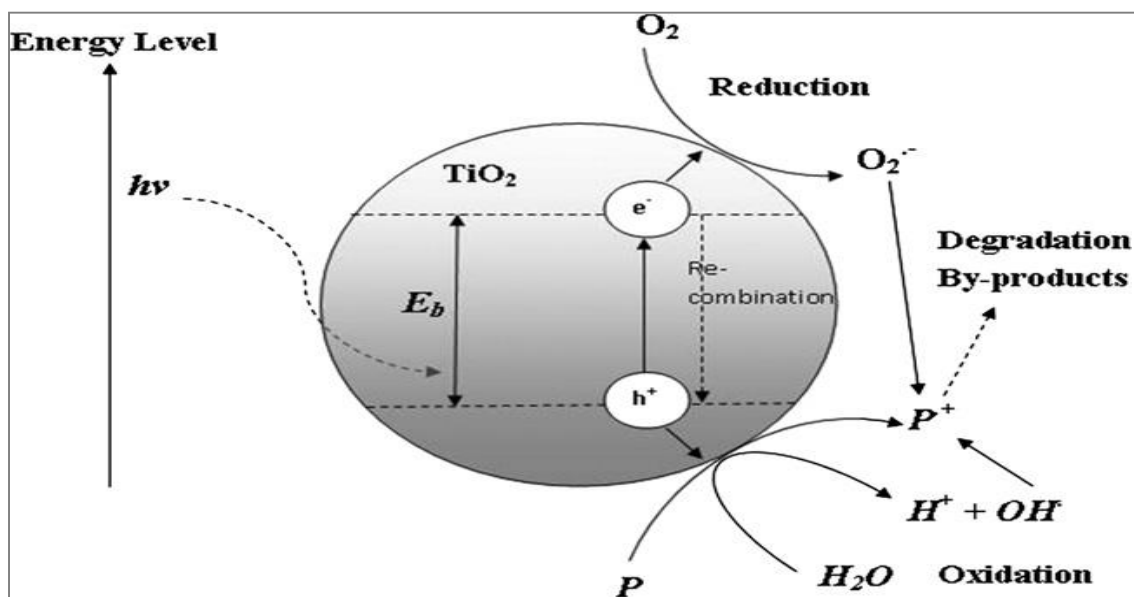Formation of $H_2O_2 \rightarrow HOO^- + H^+ \rightarrow H_2O_2$ (1.2.11)

Figure 1

The e_{TR}^- and h_{TR}^+ represents the surface trapped valence band electron and conduction band hole respectively. It was reported that these trapped carriers are usually TiO_2 surface bounded and do not recombine immediately after photon exitation. In the abcense of electron scavenger, the photoexcited electron recombine with the valence band hole in nanoseconds with constant

dissipiation of heat energy.So the presence of electron scavengers is vital for prolonging the recombination and successful functioning of photo catalysis.

Eqn (1.2.5) depicts how the the presence of oxygen prevents the recombination of electron-hole pair and allows the formation of superoxide radical. The superoxide radical furthur protonated to form hydroxyl radicals. The H_2O formed furthur to have scavenging property and thus co existance of these radical species can doubly prolong the recombination time of h^+_{TR} in the entire photocatalysis reaction. However it should be noted that that all occurences in photocatalysis were attributed to the presence of dissolved oxigen and water molecules. Without water molecules the highly reactive hydroxyl radicals could not be formed and impede the photodegradion of liquid phase organics.

The pharmaceutical waste on reaction with hydroxyl radicals converted into carbon dioxide and water with prolonged irradiation time.

So the overall process can be concluded into the following steps:

1. Mass transfer of the organic contaminants in the liquid phase to the TiO_2 surface.
2. Adsorption of the organic contaminants into the photon activated TiO_2 surface.
3. Photo catalysis reaction for the absorbed phase on the TiO_2surface
4. Desorption of intermediate from the TiO_2 surface
5. Mass transfer of the intermediate from the interface region to bulk fluid

Rate determining step of the overall rate of reaction is the slowest step. When mass transfer rate is very fast compared with the reaction steps the organic concentration the immediate vicinity of the active sites are indistinguishable from those in bulk liquid phase. When mass transfer rate are limiting the change in the aeration or liquid flow condition past the titanium dioxide photo catalyst may alter the overall reaction rate.

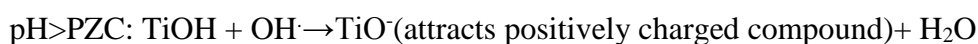## 1.3. Operational Parameters of Photo catalytic Reactor

After the integration of the semiconductor catalyst with a photo reactor, the oxidation rates and efficiency of the photo catalytic system are highly dependent on a number of operation parameters that govern the kinetics of photo mineralization and photo-disinfection. The

followings outline a range of photo reactor operating parameters that affects the photo catalytic performance of TiO$_2$ photocatalysts in water treatment.

1. ***TiO$_2$ Loading***: The rate of degradation of pharmaceutical wastes directly depends upon the catalyst loading, as available active surface area increases with concentration and thus surface reactions also enhanced. Some researcher has found that degradation rate not always directly proportional to catalyst loading and they explained that this was due to decrease in no of photons or increase in the UV scattering from the catalyst surface with an increase in catalyst loading. Actually the excess catalyst particle can create a light screenings effect that reduces the effective surface area of TiO$_2$ being exposed to light illumination and photo catalytic efficiency decreases. So the screening effect of UV responsible for decrement in the rate of photo catalysis for catalyst loading is higher than the threshold value. Though catalyst loading is directly proportional to substrate concentration an excess of catalyst provides an obstacle for light penetration on active surface. Thus proper ratio of initial substrate and catalyst concentration should be maintained. The decrease in reaction rate due higher concentration of catalyst was explained by some researcher as due to agglomeration and sedimentation of TiO$_2$. So a optimum value for catalyst loading is required for photo catalytic degradation of pharmaceutical waste so that UV light can penetrate the catalyst suspension and provide active sites with necessary energy for activation.

2. ***Effect of PH of solution***: In heterogeneous photo catalysis pH is one of the most important parameter. Variation of pH means alteration of concentration of H$^+$and OH$^-$ ion in reaction mixture. The concentration of hydroxyl radical plays a vital role in photo catalytic degradation as OH radical is a key species for oxidation. Again photo catalytic reaction is a surface phenomenon; the rate of degradation depends on the attachment rate of substrate on active site of catalyst. That attachment is really depends on the pH medium and can be explained with the help of point zero charges (PZC) TiO$_2$ at pH 6.25. Thus the catalyst particles are positively charged in acidic media and on the other hand it is negatively charged in alkaline media. If the surface is negatively charged an acidic matrix is favorable for adsorption whereas positively charged matrix shows better adsorption in alkaline medium. The above can described with the help of logarithmic acid dissociation constant (pK$_a$) of the substrate. Acid

medium is favorable for lower pK_a values and alkaline medium is for substrate with higher pK_a values. When pH increased the formation of hydroxyl radicals increased thus oxidation process enhanced up to pH 7 after that it decreased up to pH value 10 due to formation of phenoxide ion from oestradiol which compete with hydroxyl radical for adsorption. In the range of pH 10-12 the phenoxide ions were neutralized by unprotonated hydroxyl radical and form neutral phenoxide radical which could react at the TiO_2surface and thus rate increased. So in general degradation depends on the pK_a value of reactants or the surface charge of the pollutant and pH f the media should be adjusted accordingly.

So if pH<PZC and pH >PZC the following reaction can take place

pH<PZC : $TiOH + H^+ \rightarrow TiOH_2^+$(Attracts negatively charged compound)

pH>PZC: $TiOH + OH^- \rightarrow TiO^-$(attracts positively charged compound)+ H_2O

3. ***Effect of Temp***: Various studies have been conducted on the dependence of photo catalytic reaction on reaction temp. Heterogeneous photo catalysis in the presence of TiO_2 nano particle is combination of diffusion and reaction phenomena, and then they are degraded inside the active pores of TiO_2. The change of temp does not affect the reaction rate; it affects the rate of diffusion of the substrate molecule on the catalyst surface. Generally heterogeneous photo catalysis is very less sensitive to temperature. According to *Nakasima et al[iii]* surface reaction rate reaction rate increased with temp as substrate diffusion constant increased with temp. Some other researcher observed that reaction rate increased up to 45°c and after that it decreased. They attributed that to the fact that after 45°c, dissolved O_2 which is one of the major parameters disappeared from the system. Though from various research works it has been concluded ambient temp is favorable for photo catalysis.

4. ***Effect of energy source***: Like other parameters, light intensity plays an important role in photo catalytic reaction. The band gap energy of 3.2eV for TiO_2 nanoparticle is supplied from the light energy of UV radiation or sunlight. In some instances visible light fails to provide this amount of energy for photo catalysis. The photo chemical effect of light sources with different wavelength will have a profound consequence on photo catalytic reaction rate depending on the type of photo catalyst used – crystalline phase, anatase-to-rutile phase or any other. The crystalline phase

has smaller band gap energy compared to anatase, so it can be activated with light wavelength up to 400 nm. UV ray is divided into A, B, and C type. UV-A provides light photon sufficient for photonic activation of the catalyst. For lamp driven photo reactor system uses UV-C artificially for photonic activation of catalyst and reduction of variable micro organisms. Light intensity also affects the degree of photo catalytic reaction on organic substrate. To achieve higher reaction rate particularly in water treatment, a relatively high intensity of light source is required to adequately provide each TiO_2 with sufficient photon energy required. However whenever using the nominal TiO_2 particles without modification the surface reaction restricted to photons with wavelength shorter than the absorption edge of approx 400nm. *Magrini et al[iv]* also discovered decomposition rate increases with radiation intensity. Again at high intensities the dependency of photo catalytic reaction rate on radiant flux reduced to zero. This was explained by saturated surface coverage of the catalyst, resulting in mass transfer limitation in adsorption and desorption thus preventing the effect of the light intensity to set in. *Sarkar et al* also reported that degradation of chlorhexidine increases up to light intensity 80 μW cm^{-2} but later decreases due to increase in hole-electron recombination rate. Thus the wavelength and intensity of irradiation are target specific and these should be adjusted very rationally.

CHAPTER-2

LITERATURE REVIEW

1. Many researchers have studied that variation of rate with initial concentration of pharmaceutical waste. Among them *Coleman Et al*[v] reported that the degradation of 17-β oestradiol was linearly dependent on initial substrate concentration. Again *Hu et al*[vi] observerd that rate of reaction increases with increasing aqueous concentration of sulphonamides up to a certain level.

2. *Calza et a*[vii] observed that with catalyst loading pharmaceutical degradation increased up to a certain level and determined the value approximately 600 mg L^{-1} TiO$_2$concentration. Sarkar et al made the same observation. *Hu et al*[viii] determined that degradation rate is not always directly proportional to catalyst loading and they explained that this was due to   decrease in no of photons or increase in the UV scattering from catalyst surface with an increase in catalyst loading.

3. For paracetamol Yang et al[ix] observed that upto .8 gm/l degradation increases and decreased beyond 5 gm/l.

4. *Coleman et al*[x] that variation of reaction rate within the range of 1-12. They explained that when the pH increased, the formation of hydroxyl radical   increased and thus the oxidation process also enhanced upto pH 7, after that rate decreased up to pH10 due formation of large amount of phenoxide ion oestradiol which competed with hydroxyl ion for adsorption

5. *Giraldo et al*[xi] observed that degradation of oxolinic acid was favoured at pH > 7.5 but less than 11 as at pH > 11 the repulsion between oxolinic acid and catalytic surface increasesd.

6. *Coleman et al*[xii] studied the dependency of the rate of reaction rate on light intensity. They found that rate of degradation of 17-β oestradiol was proportional to the square root of UV intensity. *Abellan et al*[xiii] carried out experiment in UV intensity range of 240-310 nm and *Yang et al* performed the photo catalysis in presence of UVC(254 nm) but not in UVA(365 nm) as paracetamol showed negligible absorbance above wavelength of 350 nm.

7. Recently *Ho et al* analysed photo catalytic degradation of chlorhexidine on UV intensity and it was observed that with increasing intensity the rate increased up to 80μW cm^{-2} but the rate decreased after intensity. They reported that this was because the hole electron recombination rate increased at a higher intensity; therefore; the hole electron availability for photo oxidation was reduced after a certain range of UV intensity

8. *Chatzitakis et al*[xiv] studied the temperature effect on photo catalytic degradation of chloramphenicol in the temp range of 3°c to 57°c. They observer that degradation rate increased up to $40°c$ and after that it deceased

9. *Liang et al*[xv] found that in the range of 4-60°c the rate of reaction increased with increase in temp. They stated that with increase in temp the rate of diffusion of substrate molecules on the catalyst surface increased and hence the photo catalysis increased.

10. *Bhattacharjee et al*[xvi] found that at the initial stage of membrane separation process boundary layer first forms over the membrane within very short time and it is very insignificant. After that concentration polarization layer starts and flux decline soon.

11. *Sarkar et al*[xvii] considered a transient diffusive mass transfer due to concentration gradient prevailing across the membrane and convective transfer resulting due to existing trans membrane pressure over the membrane and mathematical model developed accordingly

CHAPTER-3

MATERIALS AND METHODS

1.1. Materials

The catalyst system used was aeroxideP25(mixture of rutile and anatase) of particle size 21nm with surface area 35-65 m^2 g^{-1} from sigma-aldrich were used as received. Chlorhexidine digluconate(20% W/V) solution was purchased from sigma-aldrich to prepare simulated solutions for experimental purpose. Polyether sulfone membrane was used. The solvent was n-methyl-2-pyrrolidinone and polyvinylpyrrolidone was used as the hydrophilic and pore formation additive. All experiments with ultrapure water from Arium Pro VF having resistivity of 18.2MΩ-cm.

1.2. Photo catalyst Immobilization and support

Catalyst can be used in a reactor system in three forms

1. **In suspension mode**: where catalyst nano particles remained suspended in a solution.
2. **Dip coating Technique**: In this process membrane is coated with semiconductor nano particle by dipping the membrane in nano particle suspension and radiated under UV radiation. According to *Sarkar et a[xviii]l* during dip coating process concentration of TiO_2, dipping time, and irradiation time were varied. After trial experiments, the dipping and irradiation time was fixed at 30mins. The concentration of TiO_2 varied in three different ways .05wt%, 01wt%, .15wt%. The formation of TiO_2 coated layer could be single or multiple. After 30mins of dipping the coated membrane was irradiated for 30mins. The nano particle was completely stirred with water to form a stable suspension before coating operation. Finally the membrane is washed with distilled water to remove excess TiO_2 deposited on membrane surface.
3. **Impregnation**: Impregnation method used to seal porosity in membrane in different process like dry vacuum & pressure, wet vacuum & pressure, internal impregnation method.
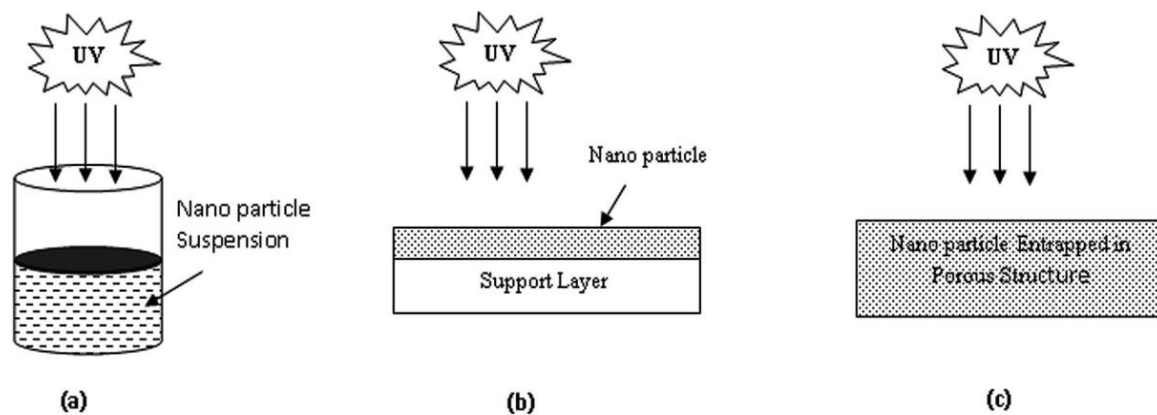
Figure 2

Different modes of application of TiO$_2$ nano particles 1) suspension mode 2) surface immobilization 3) entrapped in porous structure.

CHAPTER-4

MODEL DEVELOPMENT

The membrane separation process can be conducted in two ways, either in a dead end mode or in a cross flow mode. In dead end mode the entire feed is made to pass through a membrane to become a filtrate. As a result the concentration of separated substrate increases what eventually leads to the formation of filter cake on a membrane surface. The cake can clog membrane and is responsible for reduction in the filtration performance. Therefore the dead end process is not suitable for industrial application on a large scale. In the cross flow mode the feed solution moves parallel to the membrane surface on the upstream side of membrane and the permeate on the downstream side of the membrane moves away from membrane in the direction normal to the surface. The unfiltered portion of the feed called retentate can be wasted or recycled to the reactor. The main advantage of the membrane surface is limited since the feed flowing tangentially to the membrane partially removes the deposited molecules. At the initial stage of the membrane separation process a boundary layer form over the membrane within very short time. After that concentration polarization starts and decrease in the flux occur. This happened due build up of extra resistance caused by deposition of solute over the membrane surface. So now the membrane resistance is the sum of membrane hydraulic resistance and that due to polarized layer formation over the membrane. Diffusive mass transfer occurs due to concentration gradient prevailing across the membrane due to concentration polarization and convective mass transfer resulting due to trans membrane pressure over the membrane.

$$\partial c / \partial t = D \, \partial 2c / \partial y2 + j \, \partial c / \partial y \quad (2.1)$$

Where j, d, c represents volumetric flux, diffusivity, the concentration along the boundary layer respectively. The term c is a function of both vertical distance from the membrane surface(y) and time (t). The above equation no 2.1 is partial differential equation. The partial differential equation need to change into a ordinary differential equation using the three following boundary conditions.

B.c.-1 at y=0 $D\frac{\partial c}{\partial y} + J(c-c_p) = kc(\frac{Q}{A})$ (2.2)

B.C.-2 at y=∂ C=C_b

B.C.-3 at t=0 C=C_b

Where Q is the mass permeate laving the membrane from discharge side and A is effective surface area available for permeation.

In the present study concentration boundary layer formed by CHD molecules on membrane surface. At the membrane surface the concentration of CHD decreases due to adsorption & photo catalytic reaction. Under fully developed condition the on the periphery of the boundary layer concentration of CHD is same as the bulk phase concentration (i.e at y=∂

where ∂= boundary layer thickness under fully developed boundary condition.)

Again the above equation (2.1) is valid for constant density and diffusivity, though it is very likely that the value of these two parameters will change during the operation. Therefore the change in density and diffusivity should be considered in such a way so that the effectiveness of the model remains unaltered. As the present model is dealing with catalytic membrane system, effect of concentration buildup on the membrane surface will be somewhat different compared to conventional non reacting pressure driven membrane separation process. Once the molecules of the contaminant reach the membrane surface it will get adsorbed and subsequently degraded by photo catalytic reaction. So in this case there will be drop of concentration of reactant instead of typical build up of solute concentration on the polarized layer.

The Kozeny-Carmen equation is used to calculate the pressure drop of fluid when crossing the medium that typically consist of porous bed the membrane can be assumed as porous structure thus modified Kozeny-Carmen equation has been used in prediction of pore length in terms of trans membrane pressure(p), pore dia(d_p), thickness of the membrane (l) and membrane hydraulic resistance(R_m).

$$\frac{\Delta p}{l} = \frac{180\mu(1-\epsilon)2}{dp2 \in 3}$$

The first derivative of equation with respect to time have been represented below

$$\frac{\partial l}{dt} = \frac{360J}{A\mu Rmdp2}K1 - \frac{180}{A\mu Rmdp2}K2 \ (2.2)$$

Where K_1 and K_2 is function of $\in$. This is useful as it I assumed the length of polarized layer is gradually increasing. Thus due formation of polarized layer the effective thickness of membrane increases as well as resultant resistance of membrane increases.

So, in order to calculate concentration profile with time we have first converted the partial differential equation (2.1) into ordinary differential equation and later solved using Runge-Kutta 4th order method used in discretization for the approximate solution of ordinary differential equation with the help of Matlab R2010b. The concentration profile has been depicted in Figure 6 under next chapter (Page 28). The resultant concentration has been tallied with practical result available under ***experimental data(page 25)***

1. $\quad \partial c / \partial t = \mathrm{D} \partial 2c / \partial y 2 + \mathrm{j} \, \partial c / \partial y$ (2.1)

With the help of second equation (2.2) we can calculate polarized layer thickness change over time. But in recent paper we have not calculated the change of polarized layer thickness. But can be used for explaining how resistance changes with time as resistance is a vital parameter to determine how rate of reaction changes over time.

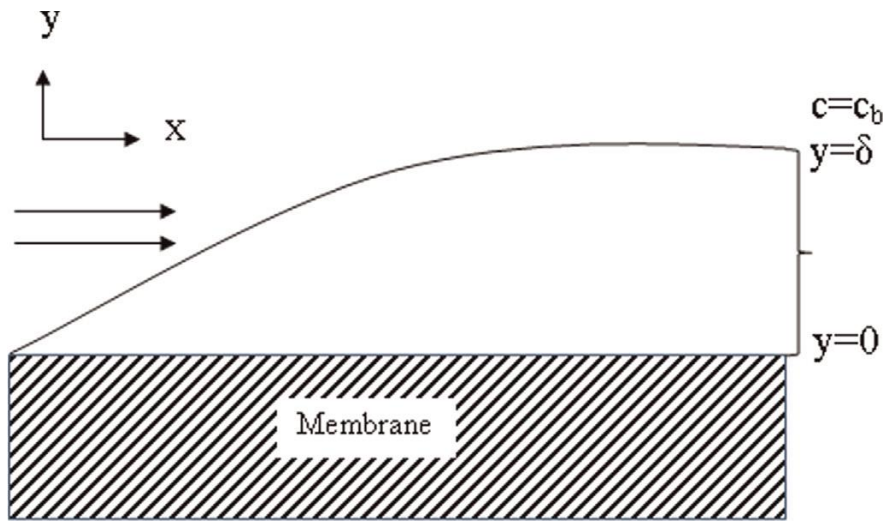2. $\quad \dfrac{\partial l}{dt} = \dfrac{360J}{A\mu Rmdp2} K1 - \dfrac{180}{A\mu Rmdp2} K2$ (2.2)

Figure 3: Schematic representation of concentration boundary layer on the membrane surface

CHAPTER-5

RESULT AND DISCUSSION

The below photo reactor (figure 2) was used to carry out photo catalytic degradation of CHD(chlorhexidine digluconate)which is as a pharmaceutical waste. The working principle of experimental set up was very simple. Being a batch mode operation during the experiment the pressure stream was recycled back to the feed tank for further photo catalytic reaction. The Trans membrane pressure was generated by controlling the flow rate of the flow rate of the retentate stream. At constant time interval aliquot sample was collected from the permeate line to analyze the degradation of CHD using PMR.
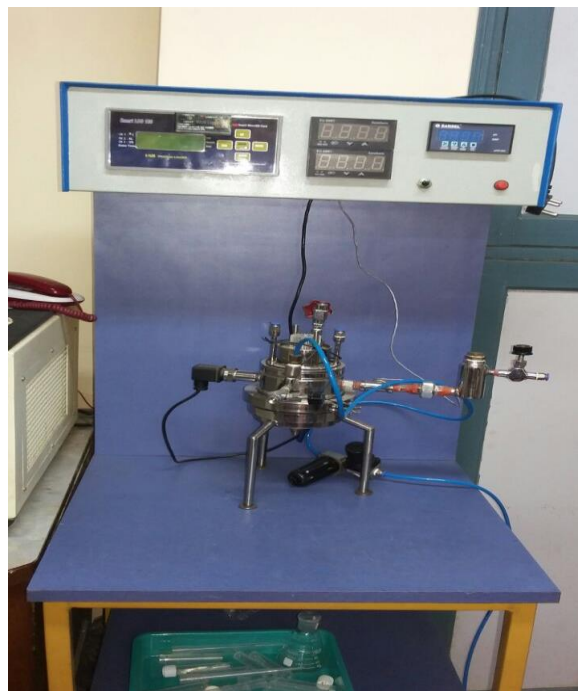

Figure 4

4.1. Experimental Data:

Time(min)	Conc of TiO_2	Initial Conc of CHD gm/l	% conversion	Final Conc of CHD gm/l
0	.02	.1	63.47	.036
15	.02	.1	67.32	.032
30	.02	.1	68.70	.031
Set 2				
0	.02	.5	53.21	.233
15	.02	.5	55.47	.222
30	.02	.5	57.74	.211
Set 3				
0	.04	.1	72.24	.027
15	.04	.1	73.21	.026
30	.04	.1	75.27	.024

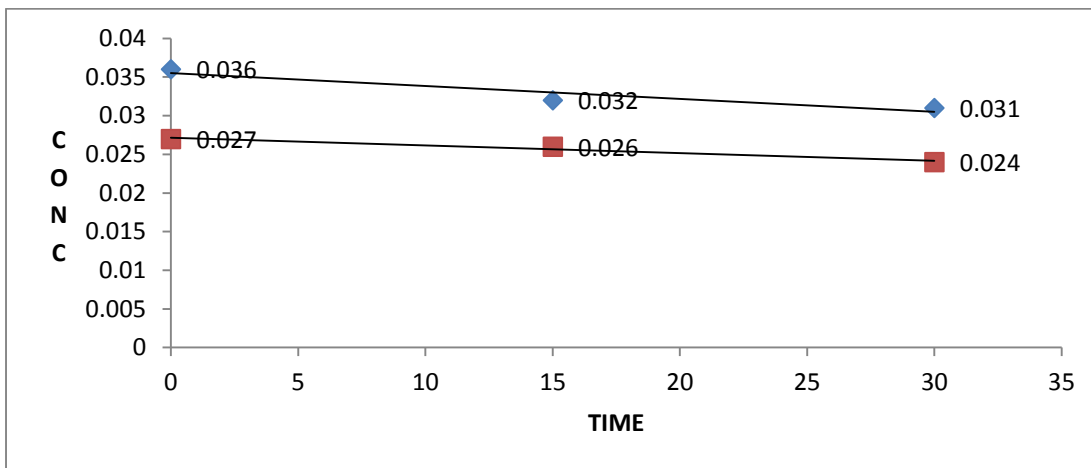| Set 4				
0	.04	.5	65.49	.327
15	.04	.5	66.58	.332
30	.04	.5	68.35	.341
Set 5				
0	.04	1	52.14	.521
15	.04	1	54.69	.457
30	.04	1	56.67	.433
Set 6				
0	.01	.5	32.46	.337
15	.01	.5	35.28	.323
30	.01	.5	31.58	.342

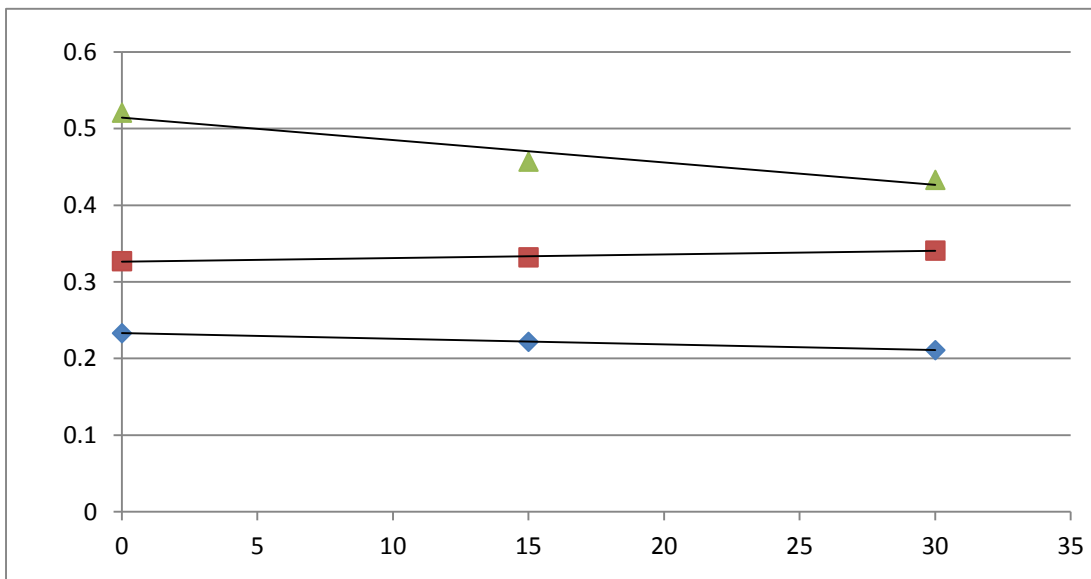**Figure 4** *Concentration Vs Time plot for data set 1 & 3*

Figure 5 *Concentration Vs Time plot for data set 2, 4&6*

4.2. Measurement of kinetic parameter

In general, a photo catalysis reaction process in presence of nano particle follows pseudo first order reaction kinetics but when adsorption plays a important role during photo catalysis process the reaction started following Langmuir- Hinselwood kinetics. During the first 10 min experimental data shows a good agreement with the model equation for pseudo first order reaction and we can show it through curve fitting. Model adopted for pseudo first order reaction has been shown below:

$$-r = \frac{dc}{dt} = k_{obs} C$$

Where r and k_{obs} is pseudo first order reaction rate and arte constant respectively. The above equation can be written as $-\ln(C/C_0) = K_{obs}t$. Initial concentration of pharmaceutical waste was represented as C_0 and corresponding concentration C. The rate constant was calculated from the slope of the plot and calculated values are $.0394 min^{-1}$, $.0759 min^{-1}$. After 10 minutes Langmuir – Hinselwood has been adopted in current study. The equation is given below

$$\frac{1}{Kobs} = \frac{1}{Kchdg\ Kr} + Co/Kr$$

Where Kchdg is equilibrium adsorption constant of CHD on catalyst surface and Kr is the rate of photo catalytic reaction. From plot of 1/Kobs Vs Co Kr and Kchdg has been calculated as .134 g/min and 5.43 g^{-1} respectively

4.3. Simulation method for output parameters for PMR

The simulation of CHD concentration in permeate stream and the polarized layer thickness on the membrane surface at the different inlet concentration of CHD simulated so far using developed mathematical model. During the simulation initial substrate concentration varies in three different ways as .1, .5 ,1 mg/l. During the first 10 minutes of simulation the pseudo first order and after that L-H kinetic rate constant was provided along with respective input substrate concentration as input parameters of the model. The simulator predicted the above

mention two parameters. In the process simulation the precession level for each iteration was maintained at .01% which is most significant aspect of whole simulation process.
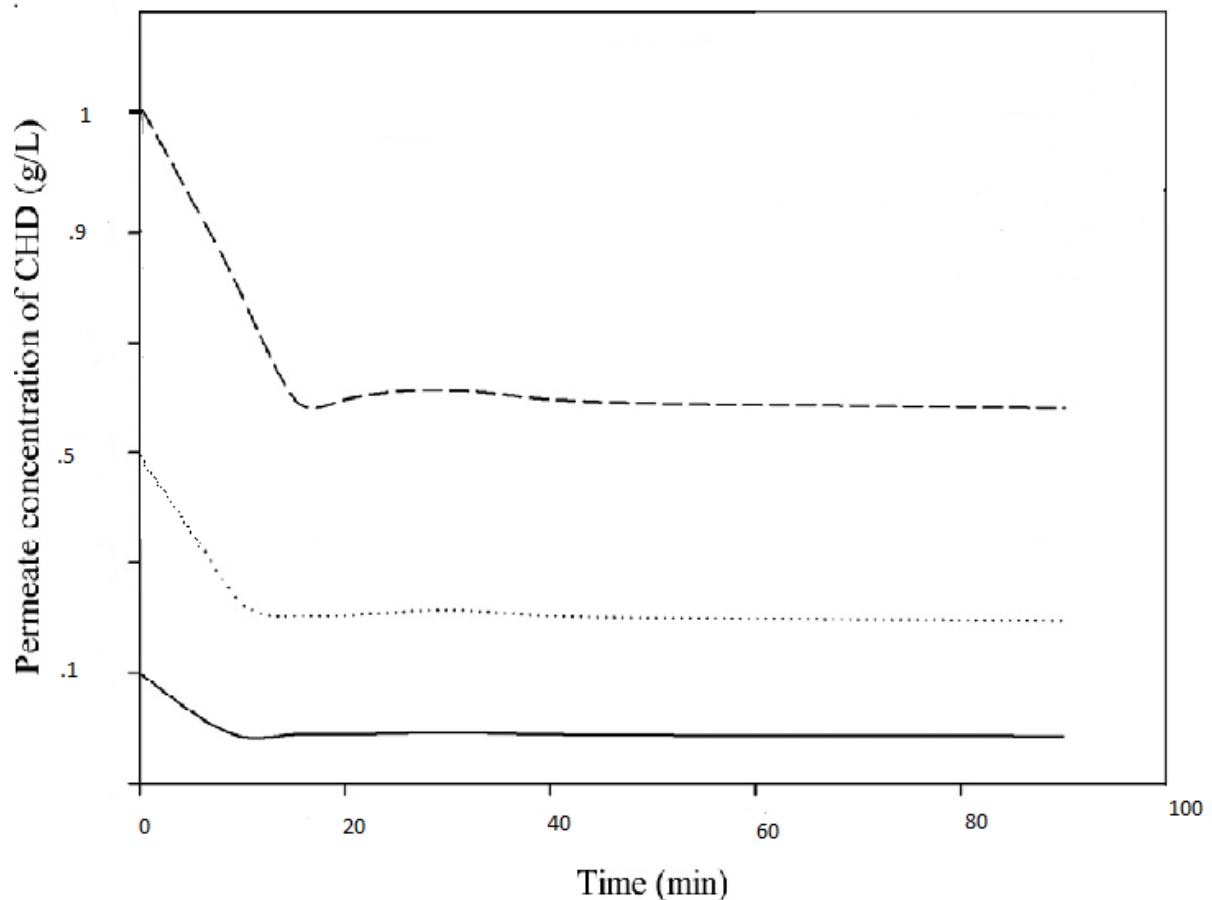

Figure 6: Simulated CHD concentration in permeate stream

1.(------) represents initial concentration of CHD 1 gm/l

2.(……) represents initial concentration of CHD .5 gm/l

3.(____) represents initial concentration of CHD .1 gm/l

From the above graph it the final concentration for each cases (1,2,3) comes approximately .625, .200 & .4, whereas from experimental result it can be seen final concentration are .470, .222 & 0 .334. By comparison these two data we can conclude that the assume equation for photo-catalytic reaction quite perfectly justify the practical result.

4.4. Assessment of process permeate concentration

The substrate concentration in permeate stream is an important parameter to predict the performance of the photo catalytic membrane. In general membrane separation process it is always expected that substrate will pass less through the membrane surface and the present

case is no different. The main difference between common membrane separation with the photo catalytic membrane separation is that in first case membrane separate different types of molecules by working as a selective barrier whereas in latter case catalytic membrane surface degrades the molecule which is needed to be separated. In the present study CHD concentration in the permeate stream should be lower than the initial concentration as CHD molecules are degraded by photo catalytic action of the membrane under UV irradiation. The only fatal of CHD exposure would get reduced as much as possible. The above simulated plot has been shown for different feed concentration and it clearly depicts the CHD decreases up to 10 minutes then it starts to increase up to certain level again it falls at steady state value. It may be happened because the target particle would instantly react with catalyst particle on the membrane surface initially for first 10 minutes. During photo catalysis process target molecules are absorbed on the catalyst surface first then it degraded under photo catalytic action of TiO_2 nanoparticle. According to that at initial stage of reaction fresh nano particles fresh nano particles on the membrane absorb more CHD molecules and eventually those are degraded but after 10 minutes there are no such catalytic particles are left for further degradation. As a result the membrane showed a poor catalytic performance which encouraged for permeation of target molecules through membrane under constant TMP. After several interval the catalytic surface regain its activity by absorbing by products generated from CHD during photo catalysis and hence, the nano particle take part in photochemical reaction as well as the CHD concentration started to fall again in permeate line. The above mentioned possible explanation may be helpful to understand the working principle of photo catalytic membrane.

CHAPTER -6

CONCLUSION

Considering the impact of pharmaceutical wastes on the aquatic environment, it is desirable to take necessary action against the alarming threat posed by discharged pharmaceutical waste. Among all other treatment methodologies, heterogeneous photo catalysis has already been established as a future trend for the treatment of pharmaceutical waste, and by this process, maximum removal of drug components can be achieved with the production of no secondary pollutants. Several process parameters are involved in AOP using nano particles, and these need to be optimized. To make the process more economic as well as more acceptable to researchers and industries, the recycling and reuse of nano particles should be investigated. Moreover, optimization of the process parameters and kinetic studies are required for better understanding of the degradation process. In most cases, researchers have used batch processes; very few literature reports are available regarding the continuous oxidation process, though the latter can enhance the performance of the system, making the continuous process more acceptable for large scale wastewater treatment.

In most of the reviewed literature, the immense potential of the photo catalytic degradation approach is well accepted but further improvements are still needed for better exploitation by pharmaceutical industries. Above all, the recycling and reuse of the photo catalyst in a continuous wastewater treatment process is the main area which must be developed in future for large scale implementation of heterogeneous photo catalysis. Moreover, the impact of the photo catalyst on the environment has not yet been studied according to the available literature, and that will be another area of exploration. In our project we are doing modelling and simulation of PMR reactor that will very handy in future as we can get information of reactor behaviour for different types of solution, different types of membrane, different types of reactor design, for different modes(batch/continuous) without actually testing it in real life.

CHAPTER-7

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