4.1 Introduction

Photocatalysis is an efficient process for the degradation and complete mineralization of organic compounds. It plays an important role in the degradation of toxic organic compounds from air and water into components that are nontoxic and safe. The discharge of highly colored synthetic dye effluents from industries can result in serious environmental pollution problems [1]. Moreover wastewater is expected to contain high levels of microorganisms and organic compounds; therefore, water disinfection has been an important and essential technology in biological and biochemical industries [2].

Photocatalytic process using semiconductors appear to be a promising technology under UV radiation that has a number of applications toward air and water purification, water disinfections and hazardous waste remediation. Among the semiconductor-assisted photocatalysts, ZnO plays a vital role due to its high activity towards photocatalytic degradation and mineralization of environmental organic/inorganic pollutants [3-5].

In this chapter, deposited ZnO films are characterized for their structural, morphological, optical and photochemical properties in order to optimize the various preparative parameters such as substrate temperature, solution concentration, quantity of sprayed solution etc. Moreover large area (100 cm²) ZnO thin film was used in photoelectrocatalytic reactor in order to study degradation of Methylene blue (MB) and inactivation of *E.coli*.

4.2 Experimental

4.2.1 Preparation of ZnO film: The preparation of ZnO thin films by SPT has been discussed in section 3.3.2

4.2.2 Photoelectrocatalytic degradation of Methylene Blue: The procedure for degradation of MB has been discussed in section 3.4.2

4.2.3 Photoelectrocatalytic inactivation of *E.coli*: The procedure for photoelectrocatalytic inactivation of *E.coli* has been discussed in section 3.4.3

4.2.4 Characterization of ZnO thin films

Spray deposited ZnO thin films were characterized for their photoelectrochemical, structural, morphological and optical properties by means of photoelectrochemical, X-ray diffraction, scanning electron microscopy and UV-vis spectroscopy techniques. The various deposition parameters such as substrate
temperature, solution concentration and solution quantity have been optimized in order to achieve good quality ZnO thin films.

4.2.4.1 Photoelectrochemical (PEC) characterization

Optimization of preparative parameters of photoactive semiconducting electrode by PEC method is new, reliable and unique technique in thin film technology [6-7]. An appropriate redox electrolyte is chosen and short – circuit current \( (I_{sc}) \) and open circuit voltage \( (V_{oc}) \) of PEC cell formed with photo-electrode is measured with respect to one of the deposition parameters by keeping others at their fixed values. PEC cell was fabricated using a two- electrode configuration, comprising ZnO thin film as photoanode and graphite as a counter electrode. The 0.1 M NaOH was used as electrolyte. The cell was illuminated with 25 W UV OMNILUX lamp for the measurement of short circuit current \( (I_{sc}) \) and open circuit voltage \( (V_{oc}) \).

4.2.4.2 X-ray diffraction (XRD)

Structural properties of ZnO thin films were studied by analyzing the X-ray diffraction patterns obtained using Philips X-ray diffractometer Model PW 3710 for \( \lambda = 1.05406 \) and 2.2897 Å for Cu- \( K_\alpha \) and Cr- \( K_\alpha \) radiation respectively.

4.2.4.3 Scanning electron microscopy

The morphological characterization of the thin films was studied with a JEOL JSM- 6360 Scanning Electron Microscope (SEM).

4.2.4.4 UV-Vis spectroscopy and thickness measurement

Optical absorption studies were carried out in the wavelength range of 300 – 1000 nm using Systronic UV-Vis spectrometer model -119, Bangalore, India. Thickness of the deposited films was calculated by inter- ferometric method.

4.3 Results and Discussion

4.3.1 Optimization of substrate temperature

4.3.1.1 Photoelectrochemical (PEC) characterization

Figure 4.1 shows the variation of short circuit current \( (I_{sc}) \) and open voltage \( (V_{oc}) \) with respect to substrate temperature. Both \( I_{sc} \) and \( V_{oc} \) increases gradually with substrate temperature, attains maximum value \( (I_{sc} = 15 \ \mu A, V_{oc} = 0.47 \ \text{V}) \) at 400 °C substrate temperature and then decreases for higher temperatures. The lower values of \( I_{sc} \) and \( V_{oc} \) at low temperatures are due to partial decomposition of spraying solution. The decreases in \( I_{sc} \) and \( V_{oc} \) after 400 °C temperature is due to fast evaporation rate of spraying solution. Upon illumination of junction in PEC cell, the magnitude of \( V_{oc} \)
increases with negative polarity towards the ZnO thin film indicating cathodic behavior of photo voltage which confirms that the films are n-type. Thus 400 °C substrate temperature is optimized from photoelectrochemical studies.

![Graph](image)

**Figure 4.1** Variation of $I_{sc}$ and $V_{oc}$ against substrate temperature for ZnO thin films deposited onto FTO glass substrate.

### 4.3.1.2 Structural Analysis

XRD pattern of deposited ZnO thin films are shown in fig. 4.2. From XRD data, it is seen that the films exhibit hexagonal crystal structure with preferential growth along the (002) plane. The intensity of the (002) diffraction is relatively highest at the substrate temperature of 400 °C, indicating an improvement of the film crystallinity. The reason for relatively lower peak intensities is the lower film thickness. The analogous results were reported for spray deposited ZnO films, deposited through aqueous medium [8]. All the peaks in the diffraction pattern were indexed using JCPDS data card No. 05 – 0664. The crystallite size of the ZnO thin films was evaluated using Scherrer’s formula,

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (4.1)

where $\lambda$, $\theta$, and $\beta$ are X-ray wavelength, Bragg diffraction angle and FWHM respectively. It is found that as substrate temperature increases, the crystallite size increases; it becomes maximum at 400 °C and then decreases further with in substrate
An increase in crystallinity with substrate temperature is due to the optimum rate of supply of thermal energy for crystallization with substrate temperature. The decrease in crystallite size above 400 °C may be due to the drying up of the droplets before reaching the substrate.

Figure 4.2 XRD patterns of ZnO thin films deposited onto glass substrates for different substrate temperatures

The dislocation density \( \delta \) which represents the amount of defects in the film, was determined using the formula [9].

\[
\delta = \frac{1}{D^2} \tag{4.2}
\]

The dislocation density exhibit decreasing trend with increasing deposition temperature which leads decrease in lattice imperfections with deposition temperature.

Lattice constants \( a \) and \( c \) are calculated by using well known analytical method. Zn – O bond length \( L \) is given by formula [10]

\[
L = \sqrt{\frac{a^3}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \tag{4.3}
\]

where the \( u \) parameter in the Wurtzite structure is given by,

\[
u = \frac{a^2}{3c^2} + 0.25 \tag{4.4}
\]
Zn-O bond lengths is given table 1. It is observed that bond length is minimum at 400 °C.

**Table 1: Variation of structural properties with respect to temperature**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Crystallite size (nm)</th>
<th>( \delta(10^4) ) (nm(^{-2}))</th>
<th>a/c</th>
<th>Zn-O bond length (Å)</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>35</td>
<td>1.863</td>
<td>0.6296</td>
<td>1.9699</td>
<td>156</td>
</tr>
<tr>
<td>350</td>
<td>36</td>
<td>1.175</td>
<td>0.6223</td>
<td>1.9756</td>
<td>204</td>
</tr>
<tr>
<td>400</td>
<td>53</td>
<td>1.175</td>
<td>0.6294</td>
<td>1.9655</td>
<td>252</td>
</tr>
<tr>
<td>450</td>
<td>46</td>
<td>0.9032</td>
<td>0.6236</td>
<td>1.9725</td>
<td>205</td>
</tr>
</tbody>
</table>

Quantitative information concerning the preferential crystal orientation can be obtained from the texture coefficient, \( TC \) defined as,

\[
TC(hkl) = \frac{I(hkl)}{\frac{1}{n} \sum \frac{I(hkl)}{I_0(hkl)}}
\]

where \( TC (hkl) \) is the texture coefficient, \( I(hkl) \) is the XRD intensity and \( n \) is number of diffraction peaks considered, \( I_0 (hkl) \) is the intensity of the XRD reference of randomly oriented grains [11].

As \( TC (hkl) \) increase, the preferential growth of the crystallites in the direction perpendicular to the \((hkl)\) plane is the higher. The variation of \( TC (002) \) of films with respect to temperature is shown in Fig. 4.3. It can be seen that at 300 °C deposition temperature there is no orientation of grains along c-axis, as temperature increases c-axis orientation increases. \( TC (002) \) has its maximum value of about 4.5 at 400 °C.

After structural analysis, it has been found that the films prepared at 400 °C have relatively higher crystallinity than deposited at lower and higher temperatures. Thus 400 °C is fixed as the optimize temperature for further film depositions.
Fig 4.3 Texture coefficient of various planes at different substrate temperatures

4.3.1.3 Morphological properties

Scanning electron micrograph (SEM) images of zinc oxide thin films deposited at different substrate temperatures are shown in Fig. 4.4 (a-d). The micrographs show that substrate is well covered with compactly organized large number of grains.

Figure 4.4 Scanning Electron micrographs of ZnO thin films deposited at a) 300, b) 350, c) 400, d) 450 °C substrate temperatures
As we increase temperature the overgrown particles disappears due to complete decomposition of precursor solution. At higher temperature (400 °C), films become more rough, loose and grains are randomly grown on surface of substrate. The film surface becomes relatively smooth, dense and mixtures of large and small platelets are seen in Fig. 4.4 (c) for film deposited at 400 °C temperature. It is observed that the grain size (≈125-200 nm) observed by SEM images is larger than the value determined by XRD, which may be due to the discrepancy between the mean dimension of the crystallites perpendicular to diffracting planes by XRD and the observable aggregates in SEM images. For higher temperatures, these platelets are clustered forming large grains as seen in Fig 4.4 (d). Therefore, it can be concluded that the morphology of particles changes and their size reduces by increasing the substrate temperature [12].

4.3.1.4 Optical properties

Optical transmission spectra of ZnO thin films are shown in Fig. 4.5. As temperature increases the transmittance goes no increasing attains maximum at 400 °C then decreases for further increase in temperature [8]. The films show moderate optical transmittance between 82 to 94 % at 550 nm. At lower temperatures, relatively lower transmission is due to the formation of whites milky films due to incomplete decomposition of the sprayed droplets. The amplitude of interference fringes decreased for higher temperatures indicated the loss in surface smoothness, leading to light scattering loss. These interferences fringes are used to determine to the film thickness by fitting observed and calculated transmittance data. It is seen that the film thickness increases with increasing substrate temperature attains maximum value at 400 °C (~252 nm), beyond which it decreases. This can be explained as follows: initially, at lower substrate temperature eg. 300 °C, the temperature may not be sufficient to decompose the sprayed droplets therefore, results in low thickness. At a particular substrate temperature of 400 °C, decomposition occurs at the optimum rate resulting maximum thickness. The decrease in film thickness at higher substrate temperature may be due to a higher evaporation rate of the initial ingredients of the solution [13]. Similar kind of variation is already observed [14].
Figure 4.5 Transmittance spectra of ZnO thin films deposited at different temperatures

Figure 4.6 plot of $(\alpha h \nu)^2$ vs $h \nu$ for the typical ZnO thin film deposited at 400 °C

For the direct transition, the optical band gap energy of ZnO thin film was determined by using the equation,

$$\alpha = \text{Const.} \left( \frac{\nu - E_g}{h \nu} \right)^{1/2}$$

(4.6)

where $h \nu$ is the photon energy and $E_g$ is the optical band gap. By extrapolating the linear part of the plot of $(\alpha h \nu)^2$ vs $h \nu$ to $\alpha = 0$, optical band gap was estimated. The
band gap value of films increases from 3.10 to 3.24 eV, up to 400 °C. The band gap energy decreases for higher substrate temperature due to the relaxation of the built in strain. It is well known that the ZnO band gap is particularly sensitive to small changes in carrier concentration, grain boundary configuration and film stress [15]. The decrease of band gap with the increase of substrate temperature is attributed to an increase of crystallite size and a modification of the grain boundary configuration during growth [16].

4.3.2 Optimization of solution concentration

4.3.2.1 Photoelectrochemical (PEC) characterization

![Figure 4.7 Variation of $I_{sc}$ and $V_{oc}$ against concentration for ZnO thin films deposited onto FTO glass substrate](image)

The variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) as a function of solution concentration is shown in fig. 4.7. It shows that $I_{sc}$ and $V_{oc}$ increases with increasing in solution concentration and attains maximum values ($I_{sc} = 27 \mu A$, $V_{oc} = 0.56 V$) for the films deposited at 0.2 M concentration. The lower values of $I_{sc}$ and $V_{oc}$ at low concentration are due to decreased absorption of incident light owing to low film thickness. The corresponding lower values for higher solution concentration are due to incomplete growth of compound and showing powdery nature of films [17-18].
4.3.2.2 Structural Analysis

Fig. 4.8 show x-ray diffraction patterns of ZnO thin films with different solution concentrations in spraying solution prepared at optimized substrate temperature of 400 °C. The crystallinity of the films increases up to 0.2 M concentration and then decreases for higher concentrations. A matching of observed and standard ‘d’ values of ZnO using JCPDS card No. 05-0664 confirms that the deposited films fit well with the hexagonal crystal structure having preferred orientation along (002) plane. As the solution concentration increases, the intensity of planes increases evidently up to 0.2 M and then decreases [19]. Some weak reflections such as (100), (101) and (110) have also been observed with smaller intensities.

![XRD patterns of ZnO thin films deposited at various solution concentrations](image)

**Figure 4.8 XRD patterns of ZnO thin films deposited at various solution concentrations**

The variation of TC (002) of films with respect to concentration is shown in Fig. 4.9. As concentration increases intensity of (002) plane increases and other planes disappears which shows ZnO films are highly oriented along [002] direction at 0.2 M concentration.

The average crystallite size of ZnO thin films is calculated using the Scherrer’s relation 4.1. The average crystallite size of the ZnO thin films increases up to 0.2 M concentration and then increases. Average crystallite varies from 42-55 nm.
4.3.2.3 Morphological properties

Fig. 4.10(a-d) shows the scanning electron micrographs of ZnO thin films deposited at various solution concentrations. It is seen that films are uniform, smooth, compact, adherent, densely packed and well covered by large number small and big grains. As the
concentration increases the roughness and grain size increases without overgrowth up to 0.2 M concentration and then decreases for higher concentrations with overgrowth. Average grain size varies from 142–333 nm at different concentrations. Films deposited at 0.2 M concentration (Fig. 4.10 b) shows densely organized mixture of large small grains.

### 4.3.2.4 Optical properties

The optical transmission spectra of ZnO films over spectral range 350–1000 nm for all the films deposited at various solution concentrations are as shown in Fig. 4.11. As the concentration increases the transmittance goes on increasing attains maximum at 0.2 M, then decreases for further increase in concentration. The films show moderate optical transmittance between 74 and 94 % at 550 nm. The increase in transmittance might be attributed to uniform, adherent and well-crystallized films on surface of substrate. The well-developed interference pattern is observed for all deposited films showing specular to great extent. Thickness of the film varies from 252–850 nm, with 400 nm being optimum at 0.2 M concentration. Direct band gap (Fig. 4.12) of ZnO thin films decreases from 3.26–3.25 eV up to 0.2 M and further increases for higher solution concentrations.

![Figure 4.11 Transmittance spectra of ZnO thin films deposited at various solution concentrations](image-url)

Figure 4.11 Transmittance spectra of ZnO thin films deposited at various solution concentrations
Figure 4.12 Plot of $(\alpha h \nu)^2$ vs $h \nu$ for ZnO thin films deposited at different concentrations

4.3.3 Optimization of quantity of sprayed solution

4.3.3.1 Photoelectrochemical (PEC) characterization

Figure 4.13 Variation of $I_{sc}$ and $V_{oc}$ against quantity of spraying solution for ZnO thin films deposited onto FTO glass substrate

The variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) as a function of concentration has been shown in Fig. 4.13. It shows that $I_{sc}$ and $V_{oc}$ increases with increasing in solution quantity and attains maximum values ($I_{sc} = 52 \, \mu A$, $V_{oc} = $
0.58 V) for the films deposited at 100 ml. The lower values of $I_{sc}$ and $V_{oc}$ at 50 ml solution quantity are due to decreased absorption of incident light owing to low film thickness. The corresponding lower values of $I_{sc}$ and $V_{oc}$ for the film deposited at 100 ml solution quantity due to incomplete growth of compound.

4.3.3.2 Structural Analysis

The XRD patterns for the ZnO thin films grown on glass substrates a studied in the 2θ range of 10–100° are shown in Fig. 4.14. It is seen that the material deposited is polycrystalline irrespective to the quantity of spraying solution. It is found that, the film tends to grow in specific (002) crystallographic directions. However, as quantity of solution is increased, the intensity of (002) peak increases up to 100 ml spraying quantity and decreases for higher quantity. The variation of preferred orientation with respect to quantity of spraying solution may be attributed to the change in film thickness [20].

Above 100 ml, milky and powdery films are resulted. It is seen that the crystallite size increases with increase in spraying solution. The analysis reveals that the quantities of spraying solution strongly influence the crystallite size (38 – 63 nm) as well as thickness of the thin films (Fig. 4.15).

![XRD patterns of ZnO thin films deposited at different quantities of spraying solution](image)

**Figure 4.14** XRD patterns of ZnO thin films deposited at different quantities of spraying solution
4.3.3.3 Morphological properties

Figure 4.15 Variation of thickness with quantities of spraying solution

Figure 4.16 Scanning electron micrographs of ZnO thin films deposited at (a) 50 ml, (b) 100 ml, (c) 150 ml and (d) 200 ml quantities of spraying solution
Fig. 4.16(a-d) show SEM images of ZnO thin films deposited with different quantities of spraying solution. It is observed that the surface morphology of the films is strongly dependent upon the quantity of spraying solution. It is seen that films are uniform, smooth, compact, adherent, densely packed and well covered by large number small and big grains, at lower concentration the layers are made up of mixture of small grains and big grains. This is due to incomplete decomposition of initial ingredient of the solution. The average grain size varies from 266 – 540 nm.

4.3.3.4 Optical properties

Fig. 4.17 shows the spectral transmittance as a function of wavelength for ZnO thin films deposited with solution quantity between 50 ml to 200 ml at a fixed substrate temperature of $T_s=400 \, ^\circ C$. It is seen that transmittance decreases with increase in solution quantity.

The low transmittance is attributed to increase in thickness, which causes surface darkening. At higher solution quantity $> 100$ ml films prepared with this solution are thicker and consequently less transparent. At higher thickness, the films tend to be powdery in nature and whitish in appearance. However, there is a slight shift in the absorption band edge. The shift in the absorption edge can be accounted for the increase in carrier concentration and blocking of low energy transitions. Band gap energy decreases with increasing quantity of spraying solution from 3.25 to 3.20 eV due to increase in particle size.
4.4 Photoelectrocatalytic degradation of Methylene Blue (MB) by ZnO Photoelectrode

Photoelectrochemical studies of ZnO thin film

Especially the wavelength of 365 nm was selected in view of later application of the ZnO layers in water purification, as 365 nm are readily available, making photochemical processes convenient to be carried out. In Fig. 4.1, a typical current–potential curve in the dark and under illumination in 0.1N NaOH is shown for optimized ZnO film deposited on FTO. The plateau photocurrents reached a few millivolts above the photocurrent onset potential, showing the semiconducting properties of the n-ZnO [21].

![Figure 4.18. i–E curve for a glass/FTO/ZnO electrode; with electrolyte 0.1M NaOH under UVA illumination (Active area 64 cm²)](image)

Photoelectrocatalytic degradation of Methylene blue

Sulfur dyes are the most commonly used dyes manufactured for cotton in terms of volume. They are cheap, generally have good wash-fastness and are easy to apply. The dyes are absorbed by cotton from a bath containing sodium sulfide or sodium hydrosulfite and are made insoluble within the fiber by oxidation. In the present work, methylene blue is selected as a model of dye pollutant with which the degradation efficiency of the as-prepared ZnO thin film catalysts are to be investigated. Methylene blue (MB), C₁₆H₁₈ClN₃S, is a brightly blue in colour (Fig. 4.18). It has many uses in a
range of different fields such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder, which yields a blue solution when dissolved in water \cite{22}.

![Figure 4.18 The structure of Methylene Blue $C_{16}H_{18}ClN_3S$ (MW 319.85 gm)](image)

During the course of the degradation experiments, the concentration of MB decreases due to decomposition (photoelectrochemical oxidation). Blank experiments (no light or no bias, not shown) showed the total absence of degradation. First, MB degradation was studied under broadband UVA illumination. A dilute solution of MB in 10 mM Na$_2$SO$_4$ was circulated at a flow rate of 12.2 l h$^{-1}$ through the single electrochemical cell. After equal interval of time 4 ml MB solution was withdrawn with help by syringe for spectroscopic and COD analysis. The photocurrent at a fixed bias voltage of 1.5 V vs. steel was passed through the cell, the average photocurrent in 0.004 A.

Figure 4.19(a) shows the variation in the extinction spectra of MB collected at various intervals during its photocatalytic detoxification recorded in the wavelength range from 400 to 800 nm. During the course of the degradation experiments, the concentration of MB decreases due to its decomposition (photochemical oxidation). It is further used to plot variation in ln($C/C_0$) as a function of reaction time as shown in figure 4.20 (b) that shows degradation kinetics (extinction taken at 665 nm). The linear integral transform ln($C/C_0$) as a function of degradation time reveals the apparent first order reaction kinetics. The linear portion in this plot has a slope of rate constant (-$k$). As illustrated in Fig. 4.19 (b), the photocatalytic activities (kinetic fit for the degradation of MB) of nanocrystalline ZnO are investigated on the photodegradation of MB under UVA light illumination. Figure 4.19 (c) shows that 48 % reduction of COD values during degradation of MB. The decrease of photocurrent in later stages of the experiment is due oxidation of organic species as well as photocorrossion of ZnO photoelectrode.

In the lower part of Fig. 4.19(b) the variations in ln($C/C_0$) as a function of illumination time are plotted. The linear section in this can be taken as the apparent first order rate constant of the degradation reaction:
\[
\ln \left( \frac{C}{C_0} \right) = -kt 
\]  
(4.8)

where \( C \) is the concentration of MB remaining in the solution at time \( t \) and \( C_0 \) is the initial concentration at \( t = 0 \).

The rate constant in a batch reactor of given electrode size is inversely proportional to the volume. Moreover, \( k \) is proportional to the area of the electrode if a sufficiently well collimated light source is used and to its intensity and therefore to the photocurrent. In order to intangible from these external parameters and to make comparison of experimental data obtained under various conditions possible, it is useful to define,

\[
k' = kV 
\]  
(4.9)

\[
k'' = \frac{k'}{A} 
\]  
(4.10)

\[
k''' = \frac{kVF}{i_{ph}} 
\]  
(4.11)

\[
p = \frac{1}{k'''} 
\]  
(4.11)

where \( F \) is Faraday’s constant (96,500 mol\(^{-1}\)), \( V \) the volume, \( A \) the area of electrode, \( k'' \) the rate constant or kinetic parameter, which is independent of total photocurrent \( (i_{ph}) \) and total volume of solution. The \( p \) reflects the efficiency of oxidative degradation of the solute (when extinction is used) or of the amount of oxidizable atoms in the solution (in the case of COD).
Figure 4.19 Detoxification of MB with ZnO under UVA light illumination a) extinction spectra with reaction time and b) kinetics of detoxification (extinction taken at 665 nm) c) normalized COD with reaction time

It is generally accepted that, when semiconductor photocatalyst are irradiated by light with energy higher than or equal to the band gap, an electron (e\(^{-}\)) in the valence band (VB) can be excited to the conduction band (CB) with the simultaneous generation of a hole (h\(^{+}\)) in the VB. The photoelectron can be easily trapped by electronic acceptors like adsorbed O\(_{2}\) to produce a superoxide radical anion (O\(_{2}^{-}\)), whereas the photo-induced holes can be easily trapped by electronic donors, such as organic pollutants, to oxidize organic pollutants [23]. However, if the photo-generated electrons recombined with the photo-induced holes, the photocatalytic activity would be decreased. In general, oxygen vacancies in ZnO catalyst can act as the active centers to capture photo-induced electrons and the recombination of photo-induced electrons and holes can be effectively inhibited, so that the photocatalytic activity can be greatly improved [24]. The values of the parameters \(k, k', k'', k'''\) and \(p\) are found to be 1.2 \(\times\) 10\(^{-3}\) s\(^{-1}\), 2.4 \(\times\) 10\(^{-3}\) cm\(^3\)s\(^{-1}\), 3.75\(\times\) 10\(^{-5}\) cm.s\(^{-1}\), 57900 M\(^{-1}\) and 1.72 \(\times\) 10\(^{-5}\) M respectively. The unlikely higher values of \(k''\) and \(k'''\) can be explained by an improvement of the photoanode surface by prolonged illumination and interfacial electron transfer. In this experiment, it is possible to degrade MB with a ZnO photocatalyst to about 56 % in 180 min. reaction time. Photocatalytic activity of ZnO is attributed to the donor states caused by the large number of defect sites such as oxygen vacancies and interstitial zinc atom and the acceptor states which arise from zinc vacancies and interstitial oxygen atoms [25].
Figure 4.20 FTIR spectra of methylene blue (a) before and (b) after degradation

FTIR analysis of control MB showed presence of N-H stretch at 3433.19 cm\(^{-1}\), alkanes at 2862.31-2913.04 cm\(^{-1}\), presence of azo bond (N=N stretch) at 1632.90 cm\(^{-1}\), aromatic ether at 1378.55 cm\(^{-1}\), S=O stretch at 1150.93 cm\(^{-1}\) provides the evidence for sulfonated bond present in MB, primary alcohol (C-OH stretch) at 1021-cm\(^{-1}\) confirms the MB dye with phenolic group, (Fig. 4.20 a), whereas metabolite formed after degradation of MB showed N-H stretch at 3149 cm\(^{-1}\), presence of azo bond (N=N stretch) at 1633.88 cm\(^{-1}\), C-H deformation at 601.43 - 872.72 and 1400.52 cm\(^{-1}\) respectively, peak at 1191.48 cm\(^{-1}\) showed presence of aliphatic ether, a peak at 1056.99 cm\(^{-1}\) showed presence of C-OH stretch (Fig. 4.20 b). Absence of peak at 1150.93 cm\(^{-1}\) for sulfonated bond in formed metabolites obtained after degradation confirms the cleavage of sulfonated bond by photoelectrocatalytic degradation.
Photocorrosion of ZnO photoelectrode was examined by measuring zinc by atomic absorption spectroscopy in degraded sample. During the course of degradation of MB 24 % ZnO thin film was dissolve due to photocorrosion.

4.5 Photocatalytic inactivation of E. coli

A number of mechanisms have been proposed to interpret the antibacterial behavior of metal oxides. Moos et al.[26] attributed the antibacterial behavior of MgO to several mechanisms including the production of active oxygen species, interaction between metal oxide particles and membrane cell walls, penetration of individual metal oxide particles into cells. Sawai et al. measured the active oxygen species generated in ZnO slurries by using chemiluminescence and oxygen electrochemical analysis and found that H$_2$O$_2$ was produced in ZnO slurries and the concentration of produced H$_2$O$_2$ was linearly proportional to the ZnO particle concentration. H$_2$O$_2$ was also detected by Matsunaga et al. [27] with a spectrophotofluorometer. Stevenson et al. [28] suggested that electrostatic interactions between the bacteria surface and nanoparticles could be involved. We shall start the discussion by looking at the structure of the cell envelope of E. coli.

E. coli is a Gram-negative bacterium and has a membrane structure as shown in Fig. 2.1. E. coli cells have a rod-like morphology with a length of approximately 1–3 µm and a diameter of 0.5–1 µm. The cell envelope of E. coli consists of an inner membrane (~8 nm thick), a periplasm containing the peptidoglycan (cell wall) and an outer membrane (~10–15 nm thick). The inner and other membranes have a lipid bilayer structure. The outer layer of the outer membrane (OM) bilayer consists of lipopolysaccharide (LPS) and the inner layer of the OM bilayer consists of phospholipids. The OM also contains proteins such as porins that act as passive diffusion channels for hydrophilic molecules. The inner membrane consists of ~ 40 % phospholipids and ~ 60 % protein.

In an inactivation of E.coli bacteria in this work, the initial population of E.coli count was around $10^{10}$ CFU/ml in 10 mM Na$_2$SO$_4$. In all experiments, the solution was circulated through the photoelectrochemical cell. Photocatalytic antibacterial activity of the ZnO films against E. coli was investigated under various conditions (Fig 4.21). Also it is observed that BOD reduction is 60 % during the inactivation of the E.coli.
Figure 4.21 Normalized inactivation count of E. coli with reaction time

i. In one of the blank experiments (no ZnO film present on the FTO substrate, application of 1.5 V to the cell) there was no noticeable decrease of bacterial count after 150 min.

ii. In another blank experiment, the influence of the presence of Zn\(^{2+}\) ions was tested, by dispersing the bacteria in a solution of 0.096 mM Zn\(^{2+}\), 10 mM Na\(_2\)SO\(_4\). This is the zinc ion concentration, originating from photocorrosion, which was found in the middle of an experiment where a ZnO electrode was illuminated under a bias of 1.5 V for 2 h (Fig. 4.21). After the 150 min. degradation experiment, in the absence of light and electrical bias, the bacterial count was decreased by 1%.

iii. In an experiment with direct UVA illumination, the bacterial count was decreased to less than 1 percent. In this experiment the ZnO covered glass/FTO plate was replaced by a glass plate.

iv. A dramatic effect was noticed when a UVA illuminated ZnO electrode was used. This corresponds to the photoelectrochemical mode under open circuit. Direct absorption of UV light by the bacteria was excluded as light was almost entirely absorbed by the backside illuminated ZnO layer before entering the solution. In the open circuit mode, both light induced
charge carriers (e\(^-\), h\(^+\)) are available at the surface of the semiconducting electrode but the rate of recombination is high. At the end of the experiment, the bacterial count was decreased by a factor of 10\(^7\). Similar results on bacterial photokilling have been obtained earlier. A.G. Rincon et al. reported an *E.coli* count decrease from 10\(^7\) to 10\(^3\) CFU/ml due to only UV light after 4 h illumination and a decrease from 10\(^7\) to 10 CFU/ml due to light and TiO\(_2\) suspended particles after 1.25 h [29]. In another report the antibacterial activity of nanorods based ZnO thin films synthesized by a hydrothermal process against *E.coli* bacteria was investigated under UV irradiation and showed strong antibacterial activity with an apparent first order degradation rate constant of 0.0015 s\(^{-1}\) in a drop of 100 µl [30].

An even larger effect was noticed when the ZnO layer was electrically biased in order to suppress charge carrier recombination. In this case, conduction band electrons were not present at the interface and recombination is suppressed. As expected, the bacterial count was further reduced, killing practically all the bacteria initially present. From the initial slope, a first order rate constant of 0.0115 s\(^{-1}\) was found. Such high rate constants cannot be explained on the basis of a single attack of a cell by a valence band hole or a surface bound •OH radical, based on the measured electrical currents during the reaction (around 4 mA). It is well known that dead bacterial cells and their contents, spilling out once the wall is damaged, is toxic for living cells. This effect and the accessibility of iron for the Fenton reaction, after wall destruction, may be responsible for the observed high rate constants. However, since the strongly oxidizing reactants (h\(^+\), •OH) and other potentially toxic intermediates (•O\(_2\), H\(_2\)O\(_2\)) are only available at the electrode surface, reactions involving these species are confined to the electrode surfaces.

ZnO nanoparticles exhibit strong antibacterial activities on a broad spectrum of bacteria. The antibacterial mechanism of ZnO is still under investigation. The photocatalytic generation of hydrogen peroxide was suggested to be one of the primary mechanisms. In addition, penetration of the cell envelope and disorganization of the bacterial membrane upon contact with ZnO nanoparticles were also indicated to inhibit bacterial growth. However, in the photoelectrochemical mode, hydrogen peroxide is an...
intermediary product of the electrode processes water oxidation / oxygen reduction and is therefore not present in the bulk of the solution. As to the role of Zn$^{2+}$ ions released through photocorrosion, the binding of Zn$^{2+}$ ions to the membranes may have some effect. In fact, prolongation of the lag phase of the microbial growth cycle has been suggested [31]. However, chemical interactions between ZnO and the components of the cell envelope (lipid bilayer, peptidoglycan, membrane proteins, lipopolysaccharides) and physical interactions between ZnO and the cell envelope structure causes to final death of the cell.
References