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Global Challenges in Energy and Environment

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Preface

Global Challenges in Energy and Environment is a proceedings book of the First International Conference on Energy and Environment: Global Challenges (ICEE 2018) held in the Department of Chemical Engineering, NIT Calicut, during 9 and 10 March 2018. National Institute of Technology Calicut (NITC) is one of the premier technical institutions in southern India located in Calicut which is a metropolitan city in the state of Kerala on the Malabar Coast.

Industrial growth, economic development, consumerization and urbanization have resulted in problems of environmental pollution. Environmental engineering is the integration of science and engineering principles to improve the natural environment to provide healthy water, air and land for human habitation and for other organisms and to remediate pollution sites. Similarly, energy is the source of economic growth. Energy consumption reflects the state of the development of the country. Energy engineering is one of the recent engineering disciplines to emerge. It is increasingly seen as a major step forward in meeting carbon reduction targets. In the past two decades, the development in these fields yielded various attractive results that are beneficial for the development of humanity.

This book focuses on the state-of-the-art technologies pertaining to energy and environmental research. This book provides a platform for experts from India and abroad to promote association and knowledge transfer by promising interaction within the wider research community in the fields of chemical and biochemical engineering, wastewater treatment and energy and environmental sustainability using green technologies and industrial applications.

Major areas covered include advanced chemical processes, air pollution and control, biomass conversion, energy policy, planning and management, integrated energy systems, membrane engineering, new perspectives in renewable energy, novel separation processes, nuclear energy applications, photo- and electrochemical engineering, polymeric materials, solid waste management and wastewater treatment.

We expect that this book will be a trigger for further related research and technology improvements in energy and environment.

Kozhikode, India — V. Sivasubramanian
Bengaluru, India — S. Subramanian

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Dr. V. Sivasubramanian is a Professor and Former Head of the Department of Chemical Engineering at NIT Calicut, Kozhikode. After completing his Masters in Petroleum Refining and Petrochemicals, he obtained his M.B.A. from IGNOU and his Ph.D. from Anna University. He has worked as Senior Plant Engineer in Tamil Nadu Industrial Explosives Limited. His research interests include fluidization engineering, wastewater treatment, biofuels, solid waste management and electro-coagulation. He has published several research articles in international journals and conference proceedings. He is a Fellow Member of FICCE and a Life Member of IIChE and GEPRA.

Dr. S. Subramanian is a Professor at the Department of Materials Engineering, Indian Institute of Science, Bangalore. He has a Ph.D. in Metallurgical Engineering from Mysore University. He worked as a postdoctoral researcher at the University of British Columbia, Vancouver, Canada and was a visiting scientist at the Lulea University of Technology, Lulea, Sweden. His research areas include mineral processing and environmental biotechnology. Dr. Subramanian is a Fellow Member of the Indian Institute of Metals and the Geological Society of India. He is a Life Member of the Electrochemical Society of India and the Indian Institute of Mineral Engineers. He is also the present Secretary for Karnataka State Council for Science and Technology.

Chapter 1
Single-Step Electrodeposition of CZTS Thin Film for Solar Cell Application: Effect of Annealing Time

Akanksha Paraye, Arpita Shukla, R. Manivannan and S. Noyel Victoria

Abstract Silicon-based solar cells are widely used solar cells, but it needs a very thick absorber layer. Absorber layers based on cadmium telluride (CdTe), copper indium gallium diselenide (CIGS), copper indium diselenide (CIS), and copper zinc tin sulfide (CZTS) are extensively studied for thin-film solar cells. The use of CdTe for thin-film solar cells is less preferred due to its toxicity. In comparison with CIGS, thin-film solar cells with CZTS absorber layers are preferred since the raw materials are earth-abundant, nontoxic, and inexpensive. The CZTS materials have a high absorption coefficient of 10^4 cm^{-1} and have the band gap energy of 1.4–1.5 eV. In this work, single-step electrodeposition of Cu_2ZnSnS_4 (CZTS) thin-film on gold-coated slide using glycine as a complexing agent was carried out. The effect of different annealing time on surface morphology, crystallite size, and its elemental composition was studied. X-ray diffraction (XRD) analysis reveals the kesterite phase of CZTS. Crystallite size increases with increase in the annealing time. Deposited CZTS thin film annealed for 30 min shows the elemental composition near to the desired stoichiometry (Cu:Zn:Sn:S = 2:1:1:4).

Keywords Thin film · Electrodeposition · CZTS · Annealing time · XRD · Crystallite size

1.1 Introduction

The enhancement of the world population, the consumption of conventional energy, and its harmful side effects on environment are also increased. It is expected that demand of energy to be twice that of today's energy demand, i.e., approximately 30 TW. The consumption and demand of this energy for next few years will be very challenging [1]. The present energy demand is fulfilled by fossil fuel such as oil,

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coal, and gasses which emits toxic gasses after its consumption, and on the other hand, they are not promising, since their quantity will be not sufficient to fulfill the future energy demand. Therefore, the world is focusing on renewable energy sources to fulfill this energy demand with the least side effect on environment. Solar energy is found to be an alternative and promising way to fulfill the present and future energy demand, and it is also known as one of the green and clean energy. One of the best applications of solar energy is solar cell or photovoltaic cell. Solar cell is an electric device which converts the solar energy directly into the electricity due to photovoltaic effect which is a physical and chemical phenomenon. Solar cell can be broadly divided into three generations. The first generation solar cells are also known as a conventional, traditional, or wafer-based cell which is made of crystalline silicon. Silicon-based solar cell is widely in use. But there are many demerits of silicon—such as it has an indirect band gap material, with low absorption coefficient, it needs thick absorber layer, and it losses its efficiency at higher temperature, i.e., in hot sunny days. Second-generation solar cells are basically thin-film solar cells, which include amorphous silicon; cadmium telluride (CdTe); and copper indium gallium diselenide (CIGS). Materials used in second-generation solar cells as an absorber material are rare, expensive, and toxic. The availability of indium (In) and selenium (Se) makes them expensive, whereas cadmium (Cd) is toxic to environment [2]. Third-generation solar cells include a number of thin-film technologies often described as emerging photovoltaic. These solar cells are made of organic-based materials. Most of them have not yet been commercially applied and are still in the research or development phase. These solar cells are not promising cells as they loss their efficiency with very short time period. In last ten years, thin-film solar cells have attracted the researchers most due to its requirement of less absorber material which reduces the cost of thin films; absorber materials for thin film can be flexibly deposited on substrates such as glass, stainless steel, and plastic, especially suitable for solar building integration [1]. Inorganic absorber materials presently in use are copper indium gallium diselenide (CIGS), copper indium diselenide (CIS), and cadmium telluride (CdTe). Elements of these absorber materials also have some demerits, such as availability of indium (In) and selenium (Se) which makes them expensive and cadmium (Cd) which is toxic [3]. Absorber materials for thin-film technology with desirable requirements such as being inexpensive and environmental-friendly with direct band gap are under study. Compared to commercialized absorber materials, CZTS have the benchmark characteristics such as it is composed of only earth abundant, inexpensive, and non-toxic elements. Cu_2ZnSnS_4 (CZTS) is a promising absorber material, with direct band gap of 1.4–1.7 eV and high absorbance coefficient of 10^4 cm^{-1} for thin-film solar cell, which is expected to become the ideal absorber layer material for next-generation thin-film solar cell [4]. There are various routes for the preparation of CZTS nanoparticles and thin films for the solar cell application. Techniques such as thermal evaporation [5], atom beam sputtering [6], pulsed laser deposition [7], hybrid sputtering [8], etc., are well-established routes for the deposition of CZTS thin films. But on the other hand, they are very expensive and require high energy to operate, with very high vacuum pressure. However, there are other techniques also which demands low energy such as successive ionic layer adsorption and reaction (SILAR)

[9], chemical bath deposition [10], spray pyrolysis [11], and electrochemical deposition [12]. Electrochemical deposition is one of the well-known low energy demand technique as it provides scalable deposition of the desired film at room temperature. In this present work, the electrodeposition of CZTS thin film on gold-coated substrate under potentiostatic mode was carried out. Glycine was used as a complexing agent in this study. The deposited sample was then annealed for different time periods at constant temperature. The effect of annealing time on its surface morphology, crystallite size, and its elemental composition was studied.

1.2 Experimental

Gold-coated microscopic slide having thickness of 100 Å (Sigma-Aldrich, 99.99% Au) was used as a substrate for electrodeposition of CZTS. Precursors of analytical grades (Merck) were used for the deposition of CZTS thin film. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was used as a copper precursor, zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) was used as a zinc precursor, tin chloride ($SnCl_2$) was used as a tin precursor, and sodium thiosulfate ($Na_2S_2O_3$) was used as a sulfur precursor. Glycine as a complexing agent was used in this study to narrow down the differences in the cathodic potential. Electrolyte was prepared by using deionized water. The electrolyte contained 10, 20, 5, 80, and 100 mM of Cu, Zn, Sn, S, and glycine, respectively. HNO_3 or KOH solutions were used to adjust the pH at 2.5. CZTS deposition was performed under potentiostatic mode.

Deposition studies of CZTS were performed in an electrochemical workstation, CHI 660E, CH Instruments, USA. Experiment for CZTS deposition was carried out using three electrode configurations (counter, reference, and working). Platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference. The working electrode was prepared by using gold-coated microscopic slide, having dimensions of 10 mm × 10 mm × 1.1 mm. Cyclic voltammetry (CV) runs for the electrolyte having all the precursors with and without complexing agent were carried out to find out the suitable deposition potential of CZTS. CV runs were carried out with scan rate of 0.5 v/sec. Deposition of CZTS was done for 20 min under potentiostatic mode. The obtained deposition was then washed using deionized water, dried, and annealed at 300 °C for different time periods 30, 45, 60, and 75 min in inert environment. Scanning electron microscope (SEM) (Zeiss Evo-Model EVO 18) was used to study the morphology of the deposits. Energy-dispersive X-ray analysis (EDX) (INCA 250 EDS with X-MAX 20 mm detector) was also done for elemental composition. X-ray diffraction (XRD) (PANalytical 3 kW X'pert) was used to analyze the crystalline nature of the deposits at different annealing conditions. The energy band gap was calculated by using absorption spectra obtained by Shimadzu UV-1800, UV–visible spectrophotometer (UV–vis).

1.3 Results and Discussion

1.3.1 Cyclic Voltammetry

The cyclic voltagrams obtained for CZTS in the presence and absence of complexing agent are shown in Fig. 1.1. Elements such as copper, zinc, tin, and sulfide have different deposition/reduction potentials, due to which it is very hard to co-electrodeposit from a single electrolyte [13]. In order to narrow down this reduction potential gap between all the elements, glycine was used as a complexing agent to an electrolyte and reduction potential was optimized [14]. The effect of complexing agent can be clearly seen by obtained cyclic voltagrams shown in Fig. 1.1. In the absence of glycine, the cathodic sweep presents two peaks. After addition of glycine, both the reduction potential shifted to the negative direction and a well-defined peak was observed at −0.86 V (Vs. Ag/AgCl). Moreover, the current density increases with addition of glycine which is due to the complexing action of the same.

1.3.2 Scanning Electron Microscopy

In order to analyze the effect of annealing time on surface morphology and elemental composition (Table 1.1) of the CZTS thin films, SEM measurement was carried out. Figure 1.2 shows the SEM images of the deposits annealed for different durations at 300 °C. Morphological study for all the samples annealed for different time duration shows agglomeration of particles in nature, and this helps in preventing recombination which is one of the desirable characteristics for solar cell applications [14, 15]. Sample annealed for 30 min shows small and spherical particles in their shape. Sample annealed for 45 min showed bigger-sized agglomerates compared to sample annealed for 30 min. Similarly, samples annealed for 60 min show agglomerates formed out of flaky particles. Sample synthesized for 60 min shows the formation of

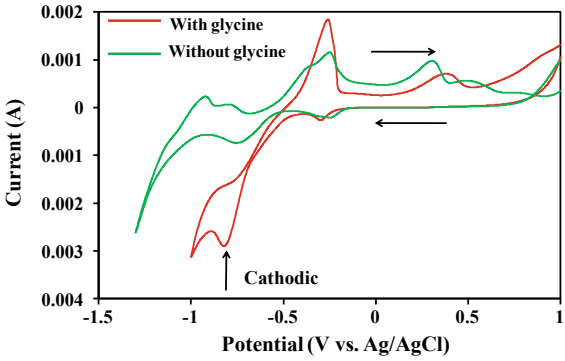

Fig. 1.1 Cyclic voltagrams in the presence and absence of complexing agent

Table 1.1 Effect of annealing time on elemental composition (atomic %)

Element	30 min	45 min	60 min	75 min
Cu	35.9	40.4	28.6	27.7
Zn	7.9	9.3	14.5	12.9
Sn	17.1	11.3	19.1	23.7
S	39.1	38.9	37.9	35.6
S/Cu	1.1	1.0	1.3	1.3
Cu/(Sn + Zn)	1.4	1.9	0.9	0.8

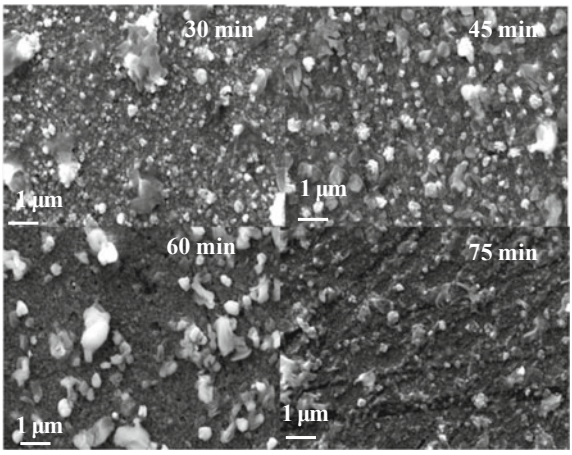

Fig. 1.2 Effect of annealing time on surface morphology

cracks. The samples annealed for 75 min show the presence of lesser agglomerates when compared to other samples.

The effect of different annealing time on elemental composition was also carried out. It can be seen from Table 1.1 that the sulfur concentration is affected to a lesser extent with annealing time. The samples annealed for 60 and 75 min are copper poor. Further, optimization is necessary to achieve desirable stoichiometry.

1.3.3 X-ray Diffraction

The X-ray diffraction patterns of annealed samples for different annealing time are shown in Fig. 1.3. The XRD spectra recorded for sample annealed at 300 °C for 30 and 45 min show the amorphous nature of the deposits. Small diffraction peaks were observed at 28.6° which correspond to (1 1 2) crystal plane of kesterite CZTS [COD (Crystallography Open Database) 96-900-4751]. It is observed that with increase in annealing time, the intensity (1 1 2) of diffraction peak becomes sharp, which indicates that the crystalline nature of CZTS thin film is also improved with increase

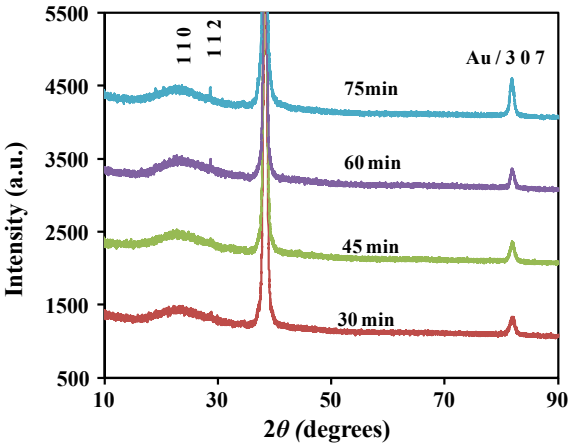

Fig. 1.3 X-ray diffraction patterns of CZTS thin films annealed for different annealing time

in annealing time. The diffraction peak positions are not shifted with annealing time, suggesting that CZTS phase is stable and its formation is independent of annealing time. XRD spectra obtained for all the samples also show that no secondary phases are formed.

1.3.4 UV–Visible Spectroscopy

The absorbance spectra for sample annealed for 30 min are shown in Fig. 1.4. It was found that the sample shows a good absorbance in the entire visible spectrum, thus suitable for solar cell applications. The band gap of the sample was calculated from absorbance data by using the Tauc relation [14]

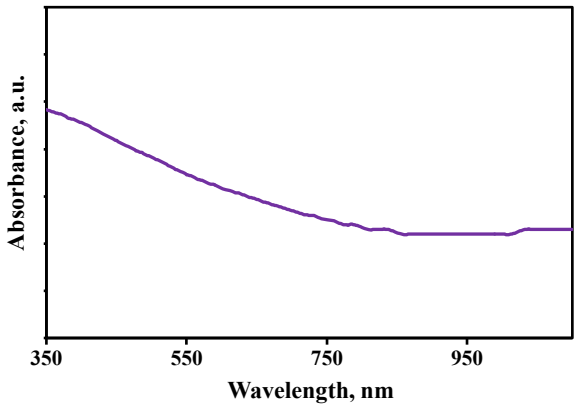

Fig. 1.4 Absorbance spectra of deposited CZTS annealed at 300 °C for 30 min

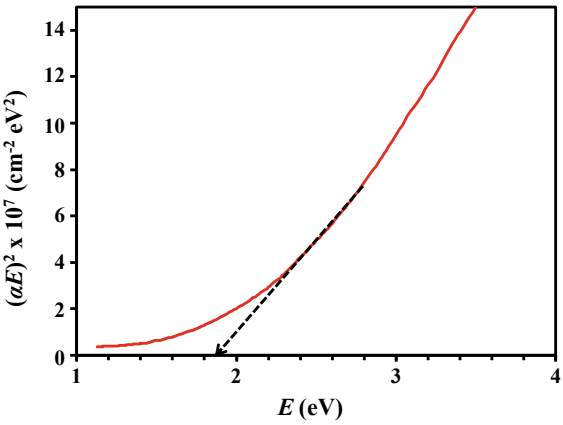

Fig. 1.5 Tauc plot of film annealed at 300 °C for 30 min

$$\alpha = \frac{A\left(E - E_g\right)^n}{E}$$

where

α absorption coefficient.
E photon energy in eV.
E_g band gap energy in eV.
n constant which is assigned values 1/2, 3/2, and 3 for direct allowed, indirect forbidden, and indirect allowed materials, respectively.

The Tauc plot for sample annealed at 300 °C for 30 min is shown in Fig. 1.5. It is observed that the band gap for the sample is 1.85 eV, which is an optimal band gap for the solar cell applications [1–12].

1.4 Conclusion

The effect of different annealing time for the CZTS deposits formed out of single-step electrodeposition was studied. The SEM results show the presence of agglomerates for the samples annealed for 30, 45, and 60 min. The deposits annealed for 60 min showed the presence of cracks. XRD result shows that with increase in annealing time, crystallinity improved slightly. The UV–visible spectroscopy studies show that the deposits exhibit good absorbance in the visible spectrum. The band gap of the particles was 1.85 eV.

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Chapter 2
Production of Bioethanol from Banana Peel Using Isolated Cellulase from *Aspergillus Niger*

Indulekha John, Prasanthi Yaragarla and Arunagiri Appusamy

Abstract In the present work, banana peel, being one of the least investigated biomasses in India, was utilized for the production of bioethanol. Dried and ground banana peel was subjected to ultrasonication at an operating frequency of 20 kHz and 750 W with 2% (v/v) sulphuric acid for 1 h. After the pretreatment, the lignin reduction was 67.50% and the hemicellulose and cellulose recoveries were 45.6 and 69.3%, respectively. *Aspergillus niger* which is capable of producing cellulase enzyme was utilized for the hydrolysis of pretreated banana peel. The activity of isolated crude cellulase enzyme was estimated as 1.712 FPU/ml. The pretreated banana peel was hydrolysed at 50 °C, and the effect of enzyme loading [10–50 FPU] and incubation time [24–96 h] on reducing sugar was determined. Hydrolysate was fermented using 24 h activated *Saccharomyces cerevisiae*, and the effect of fermentation time from 18 to 120 h was investigated. Ethanol concentration was maximum at 24th h of fermentation, and it was 4.24 g/l. The high recovery of cellulose via ultrasonication makes the banana peel suitable for bioethanol production. By providing the in vitro produced enzymes, the usage of commercial enzymes can be eliminated and hence the cost of production of bioethanol might be reduced.

Keywords Banana peel · Bioethanol · Cellulase · Fermentation · Hydrolysis

2.1 Introduction

The world has been depending on fossil fuels as a major energy source. Despite the fact that fossil fuel overwhelms the energy generation, renewable energy resource like biomass is achieving recognition because of the execution of energy policies and better reception on the significance of green energy [1]. Bioethanol as a fuel has become good alternative to gasoline. Among the liquid biofuels, bioethanol is the most commonly used one [2]. Bioethanol reduces the environmental pollution as

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well as the consumption of crude oil. There is no net increase in carbon dioxide in the atmosphere when bioethanol is burned [3]. For bioethanol production at industrial scale, it is necessary to choose inexpensive and easily available substrates for fermentation [4]. Bioethanol can be produced from agricultural feedstock, forest residues and dedicated crops. Nevertheless, different bioresources should be explored to evade the over-dependency on a single bioresource for energy generation. The conversion of lignocellulosic biomass to bioethanol is a promising methodology due to its low cost, economic benefit, unconsumed biomass, and it does not disturb the land used for agriculture [5]. Lignocellulose consists of polysaccharides such as hemicellulose, cellulose and also aromatic polymer lignin. A variety of lignocellulosic biomass like rice husk, sugar cane bagasse and corn husk are most utilized for second-generation bioethanol production.

Large quantity of unavoidable solid residues are generated during food processing. It is rather difficult to get reliable data on the amount of wastage or by-product fractions. In general, biomass waste from the food processing has been dumped. This is no more a sustainable process since the high amount of carbohydrates, protein, fats and mineral salts present in these residues cause the formation of some other unwanted compounds, foul smell and water browning [6]. The most common solution to their disposal problems is to use them as such for animal feed or as fertilizers. New methods have been introduced in the recovery, bioconversion and utilization of the valuable constituent present in the food processing industries. In recent years, efforts have been taken towards the utilization of cheap renewable agricultural resources as alternative for ethanol production.

Banana is the major foodstuff in the world after rice, corn and milk [7]. India is the world's leading producer nation for bananas, and it records 27% of the overall production worldwide [8]. 30 - 40% of the total weight of banana is wasted as banana peel. In spite of the fact that banana peel is a fruit waste material, it comprises proteins, fibres and carbohydrates in major quantities. The peels of banana are often dumped in landfills, rivers and unregulated dumping grounds. Therefore, the sustainable utilization of banana peel waste would help to diminish the pollution problems caused by their disposal. Production of bioethanol by using banana waste can be an effective utilization of residual biomass mainly in southern part of India. Banana peels are readily available as agricultural waste that can be exploited for bioethanol production since it is rich in carbohydrates.

Bioethanol production from lignocellulose comprises pretreatment, hydrolysis and fermentation processes. Cell wall of lignocellulose is generally disrupted by the pretreatment process, and thus the polysaccharides become accessible for hydrolysis. Polysaccharides such as hemicellulose and cellulose are converted into monosaccharides in the hydrolysis process. In the fermentation process, these monosaccharides are converted to bioethanol with the help of micro-organisms. The selection of appropriate pretreatment method to remove lignin from cell wall and release more polysaccharides without any loss is a challenging step in bioethanol production process [9]. Also, the high cost of commercial enzymes used in the hydrolysis will not make the process economically feasible. Bioethanol production process can be made sus-

tainable and profitable by using cheaper raw materials and cost-effective in house enzyme production.

Cellulase is the most important enzyme used in the enzymatic hydrolysis of bioethanol production. Cellulase is a class of enzyme that catalyses the cellulolysis [10]. The type of micro-organism which can produce cellulase enzymes is mostly fungi. Among various species of fungi, *Aspergillus* sp. are well known for their ability to produce enzymes [11]. In the present study, *Aspergillus niger* was experimented for the production of cellulase using banana peel as substrate. *A. niger* is generally regarded as non-pathogenic fungus that is widely distributed in nature and became an industrially used micro-organism. The main aim of the study was to convert the banana peel waste into bioethanol using in vitro produced cellulase so as to reduce the cost of production of bioethanol.

2.2 Experimental

2.2.1 Materials

Banana peel was collected from canteen located at NIT Tiruchirappalli campus. Peel was washed and then sun-dried for 3 days. Dried peel was powdered and particle size in the range of 0.5–1 mm was chosen for further studies.

2.2.2 Production of Cellulase

2.2.2.1 Inoculum Preparation of *A. niger*

A. niger was purchased from Microbial Type Culture Collection (MTCC), Chandigarh. Czapek yeast extract (CYA) broth medium was used for the inoculation of *A. niger.* Czapek concentrate was made up of $NaNO_3$: 30 g, KCl: 5 g, $MgSO_4.7H_2O$: 5 g, $FeSO_4.7H_2O$: 0.1 g and 100 ml of distilled water. CYA medium was comprised of yeast extract: 5 g/L, K_2HPO_4: 1 g/L, sucrose: 30 g/L and Czapek concentrate: 10 ml/L. Few drops of sterile distilled water was provided to the freeze-dried culture of *A. niger*, and this suspension was streaked on CYA broth medium. *A. niger* was subcultured onto CYA slants, and the slants were incubated for 7 days at 30 °C.

2.2.2.2 Cellulase Production by Solid-State Fermentation

The mineral salt medium used for cellulase production had a composition in g/100 g of substrate: $CoCl_2$, 0.1; $CuSO_4.5H_2O$, 0.5; KH_2PO_4, 5; corn steep liquor, 50; and yeast extract, 0.5. A pH of 7.0 was preferred for the growth of micro-organism.

Banana peel was used as substrate for cellulase enzyme under solid-state fermentation. To a 250-ml Erlenmeyer flask, 30 ml of mineral salt medium and 10 g of substrate were added. The flask was sterilized for 15 min at 121 °C. After sterilization, the flask was cooled down to room temperature and then inoculated with 5 ml of culture. The contents were mixed well and incubated at 30 °C under static conditions for 5 days. The flask was mixed periodically by gentle shaking.

At the end of solid-state fermentation, the enzyme was extracted from the banana peel by mixing homogenously with 50 ml of distilled water. The extract was kept in an orbital shaker rotating at speed of 120 rpm for 1 h. The extract was centrifuged at 6000 rpm for 20 min at 4 °C to remove the debris and the supernatant was used as extracellular cellulase enzyme. The activity of cellulase was assayed according to filter paper assay. Cellulase activity was determined as filter paper hydrolysing activity using a Whatman No.1 filter paper strip of 1 × 6 cm. Enzyme sample was supplemented with 1 ml of 50 mM of sodium citrate buffer of pH 4.8, 50 mg of filter paper strip was immersed in the mixture and then the mixture was incubated at 50 °C for 1 h. After that, 3 ml of dinitrosalicylic acid (DNS) solution was added to the enzyme sample, blank and enzyme blank, and boiled for 5 min; 20 ml of distilled water was added to all the test tubes and the mixture was allowed to settle down by keeping it at room temperature for 20 min. Supernatant liquid was measured against 540 nm for estimation of glucose concentration.

$$\text{FPU} = \frac{0.37}{\text{Enzyme concentration to release 2 mg of glucose}}$$

2.2.3 Production of Bioethanol from Banana Peel

2.2.3.1 Pretreatment of Banana Peel by Acid-Assisted Ultrasonication

Powdered banana peel was pretreated by acid-assisted ultrasonication. Ultrasonication experiments were conducted in a jacketed glass vessel. Cold water is distributed through the jacket of the vessel to endure the temperature of the process. Ultrasonic processor used in the present study was probe-type processor (VCX 750, Sonics and Material Inc, USA) which operates at 750 W and 20 kHz. The powdered banana peel was sonicated with 2% (v/v) of sulphuric acid at a solid-to-liquid ratio of 1:10 for 60 min. After cooling down the contents to room temperature, it was filtered. The solid contents attained after filtration were washed repeatedly with distilled water to get a neutral pH for the contents. It was then dried at 45 °C. The composition of the untreated and pretreated banana peel was evaluated to know the effectiveness of pretreatment. The cellulose and hemicellulose contents were estimated using Van Soest fibre analysis, and lignin content was determined using NREL method.