Effectiveness of MOU with The Karnatak Cancer Therapy And Research Institute (KCTRI), Hubballi

Introduction

Indian non-communicable diseases, such as cancer, are becoming increasingly prevalent. One of the top causes of death in India is cancer, which is commonly referred to as malignant tumors. Oral cancer is more common in men than in women. In many nations, the prevalence of oral cancer in men ranges from one to ten cases per one lakh people. Oral cancer, one of the most dangerous forms cancers, originates from the mucosal lining of the tongue, buccal mucosa, gingiva, the floor of the mouth, and the floor of the mouth.

Effectiveness

In this context a preliminary study design was conducted in association with KCTRI, Hubballi. A demographic profile (retrospective study) was undertaken at KCTRI covering a period of 10 years from January 2013 till March 2022. This hospital is providing tertiary care to patients in north karnataka and neighbouring areas. After obtaining approval from the institutional ethical committee, the medical record department was approached to obtain case files of all the cancer cases in the hospital.

A convenient sampling method was used and oral cancer patients that fulfilled the inclusion criteria were retrieved and collected on a structured questionnaire. Data were tabulated and statistically analyzed. Statistical analysis for the correlation between the variables, etiological factors and age, gender, histopathological grade, and lymph node metastasis, was performed.

Activities

Demographic study of years 2013,2014,2015,2016.2017,2018,2019,2020,2021 is being done i.e. collection of general information about the patient name, age, sex, income, residence, habbits etc. from a patient file who will be attending OPD of cancer hospital navanagar hubballi. Demographic data of patients collected from KCTRI, was analyzed and interpreted.

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Effectiveness of MOU with Prajna Biosciences Pvt. Ltd., Hubballi

Introduction

Immobilization of enzyme is now a widely accepted technique in biotechnological industries. Immobilized enzymes are preferred over their free counterpart due to their prolonged availability that curtails redundant downstream and purification processes. Immobilized enzymes are nowadays used in detergent industries for the removal of stains as they have good cleaning properties as compared to synthetic detergents. These enzyme based detergents are pollution free as they do not effect environment and used in less amount as compared to synthetic detergents. These enzymes are used as detergents after immobilizing it on suitable substrates to overcome few problems like stability, cost, repeated use, etc.

Effectiveness

In this context, Prajna Biosciences Pvt. Ltd., Hubballi provided Internship Training and Project to 8th sem students of BE biotechnology program for a period of 5 months from January 11th2022 to May 31th2022. Internship project undertaken was "***Optimization of sodium alginate composition for enzyme immobilization and its applications in detergents***"

Activities

In this project enzyme was immobilized using sodium alginate as carrier .Various parameter such as sodium alginate concentration, calcium chloride molarity, pH, temperature, storage and reusability were optimized. It was concluded that the beads were strong with significant and enzyme activity when enzyme was mixed with an optimized % of sodium alginate and dropped in calcium chloride solution. The importance parameters such as, temperature and pH were studied over a range. The beads were stored in different solution to observe the shelf life. By reusability testing it was found that beads could be used for several continuous cycles. This immobilized enzyme has been tested with commercially available detergents to for their ability to remove stain from cloths.

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Effectiveness of Interactions with Indian Institute of Technology, Dharwad

Introduction

The development of recombinant molecules is gaining scientific attention in recent times due to the enormous industrial applications. A strategy for improving the gene expression that encodes novel molecules of interest is gaining lots of research focus. The recombinant approach improves the molecules yield and modifies the chemical and functional attributes. To improvise on better productivity of molecules, several approaches like designing primers, suitable vectors, developing gene cloning and expression strategies are necessary.

Effectiveness

In this context, several interactions and collaborative research activities was undertaken with Department of Chemistry, Indian Institute of Technology, Dharwad and Department of Biosciences and Bioengineering, Indian Institute of Technology, Dharwad. KLE Technological University and Indian Institute of Technology, Dharwad were involved in collaborative research on studies related to gene cloning, molecular expression, biomolecular characterization and functional characterization.

Activities

In this collaborative research project, a lipopeptide encoding gene called iturin A was synthesized. To improvise the yield of the lipopeptide for specific applications, gene cloning and expression studies were undertaken. Iturin A gene sequence was codon-optimized, amplified with gene-specific primers, and ligated into expression vector to achieve high-level protein expression. The highly expressed recombinant iturin A was purified by affinity column chromatography. The purity and molecular mass was determined by SDS-PAGE. This approach of cloning increased the production of the lipopeptide and also revealed the biosurfactant property. The purified recombinant protein was further characterized.

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Outcomes

The collaborative research project led to successful outcome of publication titled "***Gene Expression and Characterization of Iturin A Lipopeptide Biosurfactant from Bacillus aryabhattai for Enhanced Oil Recovery***" authored by Deepak A. Yaraguppi (Research scholar at KLETU), Zabin K. Bagewadi (Principal Investigator, Corresponding author), Nilkamal Mahanta (Principal Investigator, Co-Corresponding author), Surya P. Singh (Collaborator), T. M. Yunus Khan (Collaborator), Sanjay H. Deshpande (Research scholar at KLETU), Chaitra Soratur (Student from KLETU), Simita Das (Student from IITD) and Dimple Saikia (Student from IITD). Published in Gels 2022, 8, 403. https://doi.org/10.3390/gels8070403 with Impact factor of 4.432 indexed in WOS and Scopus.

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polymers

MDPI

Article

Development and Characterization of Biocompatible Membranes from Natural Chitosan and Gelatin for Pervaporative Separation of Water–Isopropanol Mixture

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Abstract: Natural polymers have attracted a lot of interest in researchers of late as they are environmentally friendly, biocompatible, and possess excellent characters. Membranes forming natural polymers have provided a whole new dimension to the separation technology. In this work, chitosan-gelatin blend membranes were fabricated using chitosan as the base and varying the amount of gelatin. Transport, mechanical, and surface characteristics of the fabricated membranes were examined in detail by means of the characterizing techniques such as Fourier transform infrared spectroscopy, differential scanning colorimetry, wide angle X-ray diffraction, scanning electron microscope, and thermogravimetric analysis. In order to analyze the water affinity of the developed blend chitosan-gelatin membranes, the percentage degree of swelling was examined. Out of the fabricated membranes, the membrane loaded with 15 mass% of gelatin exhibited the better pervaporation performance with a pervaporation separation index value of 266 at 30 °C for the solution containing 10% in terms of the mass of water, which is the highest among the contemporary membranes. All the fabricated membranes were stable during the pervaporation experiments, and permeation flux of water for the fabricated membranes was dominant in the overall total permeation flux, signifying that the developed membranes could be chosen for efficient separation of water–isopropanol mixture on a larger scale.

Keywords: chitosan; gelatin; isopropanol; pervaporation; biocompatibility

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1. Introduction

Natural polymers are usually obtained from various sources like an animal (polyhydroxyalkanoates, polylactic acid, polybutylene succinate), bacterial fermentation (chitosan, collagen, chitin), vegetable (alginate, polyisoprene, cellulose-based polymers, starch) [1,2]. These natural polymers are currently used as replacements for synthetic polymers because of their peculiar biodegradable nature. Nowadays, these natural polymers have found applications in various fields like drug delivery, hydrogels, biomedicine, food packaging, water treatment, etc. [3–5]. These materials find extensive applications in membrane-based separation-based technologies such as ultra filtrations, micro filtrations, gas separations, and pervaporation. One of the noteworthy applications of these biopolymers is found in wastewater treatment. López-Maldonado et al. have done extensive work on the removal of hazardous metal ions and heavy metals from water using many natural substances and polymers [6–9].

Among these, pervaporation has identified itself as an important separation technique as it separates several close boiling (azeotropic) liquids, including organic–water and organic–organic liquids [10]. In pervaporation, the separation performance depends on several factors, but one of the most vital factors is the membrane. Intrinsic properties of the Membrane (hydrophilicity, hydrophobicity, free volume) usually decide the separation performance in pervaporation applications. These properties usually depend on the membrane materials. Pervaporation separation of water–organic mixtures requires hydrophilic materials like poly (vinyl alcohol) (PVA), polyvinylidenefluoride (PVDF), etc., which are synthetic polymers [11,12]. However, with these synthetic materials, some natural polymers such as cellulose acetate, sodium alginate, bacterial cellulose, and chitosan are also used as base materials due to their excellent membrane forming ability, hydrophilicity, and eco-friendly nature [13–15]. Among these, chitosan is one of the most abundant biopolymers which is produced from the deacetylation of chitin. Along with the hydrophilic nature and membrane forming ability, it has some of the most important properties like biodegradability, non-toxicity, and biocompatibility [16–18]. Chitosan also has multi-functionality because of the huge number of polar groups present in its structure. Generally, the membrane materials which exhibit good permeability and selectivity factor usually get hampered. The same is observed in the case of chitosan, as it possesses some drawbacks like excessive swelling. The high content of water in the feed will interact with the polar functional groups present on the chitosan, which results in membrane swelling. This leads to higher permeability and lower selectivity [19]. Further, at a lower concentration of water, the driving force of transport across the membrane becomes very low, which leads to the lower flux, which does not serve our purpose as it affects the pervaporation performance.

In order to overcome these drawbacks, M. Vinu et al. prepared chitosan membranes filled with Al-MOF with the intention of studying the effects of defects and structural crystallinity on the pervaporation performance and observed a higher permeation flux of 458 g/m^2 h along with the selectivity of 2741 [20]. Ewelina et al. prepared polyamide-6 supported composite chitosan membranes and examined them for pervaporation separation of water/alcohol mixtures and achieved a higher total normalised permeation flux of 0.5 µm kg m^{-2} h^{-1} in comparison with the pristine chitosan membrane [21]. D. Achari et al. fabricated polystyrene sulfonic acid-co-maleic acid (PSSAMA) incorporated chitosan polyelectrolyte membranes and obtained better membrane performance (highest separation selectivity of 5352 with a flux of 4.145 × 10^{-2} kg/m^2 for water/ter-butanol mixture separation) for different water–organic liquid mixtures separation (water-n-propanol, water-1,4 dioxane, water–isopropanol, water-ter-butanol) in comparison with the pristine chitosan membrane [22].

In order to promote and enhance the properties and membrane performance of chitosan, we tried to blend the chitosan with the natural protein gelatin to incorporate its properties in the fabricated chitosan membranes. The purpose of this work is to develop highly efficient and biocompatible pervaporation membranes for the separation of isopropnaol–water mixtures. Gelatin is produced by partial hydrolysis of collagen and is considered one of the important green polymers. Gelatin contains free amino and carboxylic groups on its skeletal. This increases the perm selectivity of gelatin towards water [23]. Moreover, the flexible chain structure of the gelatin leads to the compact and order chain arrangement in the membrane matrix. Along with these properties, the presence of hydrophilic functional groups on the polymer chain makes it more affinitive towards the water. In this work, we have fabricated membranes using chitosan as the base and varied the content of gelatin. The physical, chemical and morphological characteristics of the developed membranes were characterized using various characterization methods such as FTIR, DSC, WAXD, SEM, and TGA. Further, the fabricated membranes were tested rigorously for the separation of water–isopropanol mixture via pervaporation technique at various temperatures and feed concentrations and discussed thoroughly.

2. Materials and Methods

2.1. Materials

Reagent grade Chitosan (N degree of deacetylation 75–85%, Mw ≈ 200,000) was purchased from Sigma-Aldrich chemicals, St. Louis, MO, USA. Reagent grade gelatin, ethanoic acid, and isopropanol (IPA) were procured from S. D. fine Chemicals Ltd., Mumbai, India. Double distilled deionized water was used in the analysis.

2.2. Membrane Fabrication

A fixed weight (3 g) of chitosan is mixed in 100 cc of 2 weight % of an aqueous solution of ethanoic acid and stirred for 24 h at ambient temperature. The prepared homogenous solution is then filtered to get rid of the undissolved particles; the casting procedure was carried out in the room, which was maintained clean and dust-free. The prepared solution was poured uniformly on the glass plate and spread evenly with the help of a casting knife. The casting plate was then left for drying for two days at room temperature. Subsequently, the membrane was peeled carefully, and the obtained pristine membrane was named M-0.

In order to prepare chitosan-gelatin membranes, 5, 10, 15, and 20 % mass of gelatin with respect to the weight of chitosan was added to the previously prepared homogenous chitosan solution. The mixture was then stirred for 5–6 h at 50–60 °C temperature. Then the obtained solution was cast, and the membranes were obtained by following the same procedure explained above. The obtained membranes were then named M-5, M-10, M-15, and M-20, respectively, based on the mass% of gelatin present in the matrix of the membrane. The pathway of the membrane fabrication is illustrated in Figure 1.

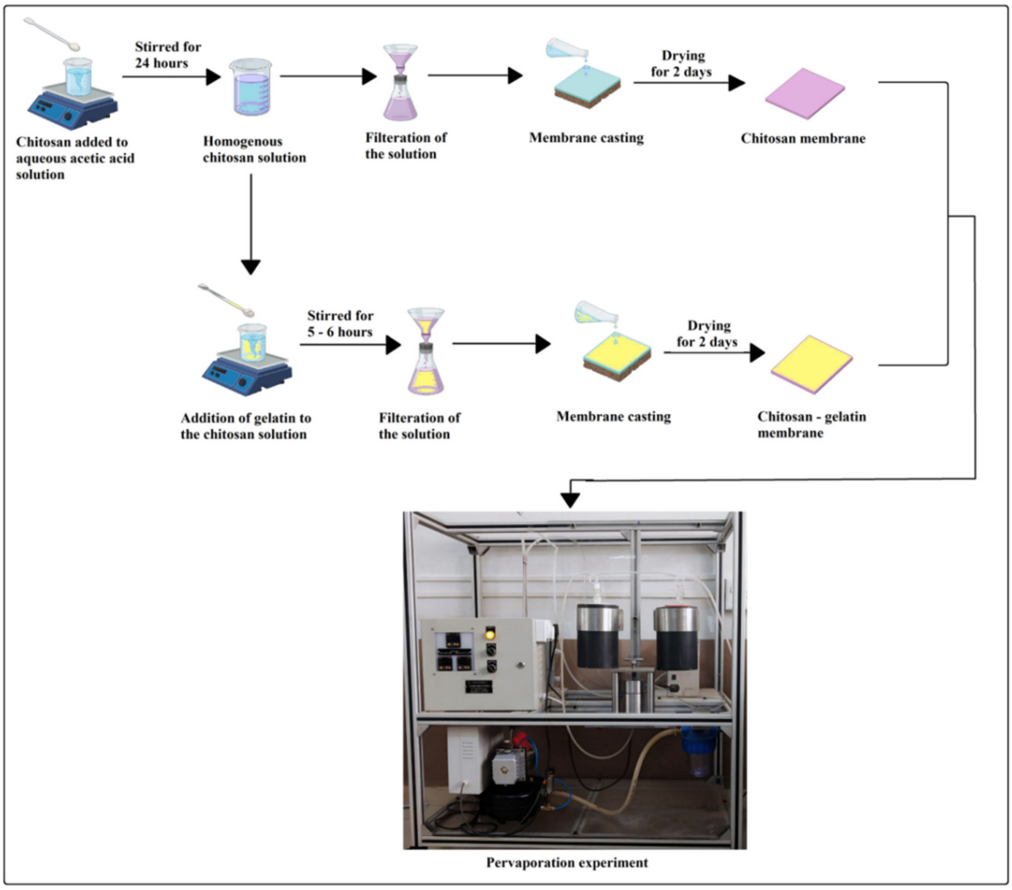

Figure 1. Schematic pathway of the experimental work.

2.3. Membrane Characterization

In order to understand the chemical interaction between the chitosan and gelatin, FTIR analysis was done using a spectrometer named Nicolet, Impact - 410, Madison, WI, USA. Fabricated membranes were properly ground with the applied pressure of 400 kg/cm^2, and pellets were prepared using KBr. The spectrum was reported in the spectral range of 400 to 4000 cm^{-1}. The influence of the gelatin on the solid-state structure of the membrane was analyzed using Philips Analytical X-ray Diffractometer. The range of the analysis was 5° to 50° at the controlled speed of 8°/min. The glass transition temperature (Tg) and thermal behavior of the fabricated membranes are analyzed using thermogravimetric analysis and differential scanning calorimetry techniques by means of DSC Q 20, TA Instruments, Waters LLC, New Castle, DE, USA. The analysis was done in the presence of N_2 at the rate of heating of 10 °C/min. With the intention of analyzing the miscibility of the chemicals and surface morphology, scanning electron microscopic images were taken with JSM-400 Å, Tokyo, Japan. Before the analysis, the properly dried membranes were coated with a sputtered gold layer of the thickness of 400 Å.

2.4. Equilibrium Swelling

Sorption measurements of the fabricated membranes were analyzed at room temperature. Previously weighed ($\mathbf{W_d}$) membranes samples were dipped in the water–isopropanol test solutions having different compositions in an airtight container. The membranes were allowed to soak in the liquid for 48 h. Then the membranes were taken out and wiped with soft tissue paper in order to remove the surface adhered liquid droplets, and then the weight of the wet membranes ($\mathbf{W_s}$) was analyzed. Using the weights, ($\mathbf{W_d}$ and $\mathbf{W_s}$), the percentage degree of swelling was measured using the following expression:

$$\mathbf{DS}\ (\%) = \left[\frac{\mathbf{W_s} - \mathbf{W_d}}{\mathbf{W_d}}\right] \times 100 \tag{1}$$

2.5. Pervaporation Experiments

The pervaporation experiments were conducted in a specially designed pervaporation unit described in our previous research article [8]. The schematic representation of the pervaporation unit is shown in Figure 2. The unit has a feed tank with a volume capacity of 4 L completely sealed from the surrounding inside a heating jacket. The feed tank is also equipped with a stirrer for uniform maintenance of the temperature of the solution mixture, and a circulating pump is also equipped for the continuous circulation of the solution. The heating jacket consists of a heater with 2.5 KW power rating and a temperature sensor Pt-100 for continuous and uniform heat maintenance in the tank. A highly sophisticated TC513BX auto-tuning temperature controller was installed for utility purposes. Membrane holder having a surface area of 15 cm^2 is fabricated from high-quality steel, which is chemically inert. The membrane must be installed in the membrane holder and left for 1 h for equilibrium establishment. Then the vacuum is applied from the permeate side. Permeate vapors are then condensed and collected at uniform time intervals. Further, the mass and the composition of the collected sample of the permeate are determined using the digital microbalance and Karl Fischer titrator named KAFI smart.

In order to achieve higher accuracy of the results, experiments were done three times, and the average data are considered for calculations. Using the data, the efficiency of the fabricated membranes for the water–isopropanol separation using pervaporation technique was analyzed by the calculation of separation selectivity (α_{sep}), total permeation flux *(J)* and pervaporation separation index (*PSI*) using the following equations [24].

$$J = \frac{W}{At} \tag{2}$$

$$\alpha_{sep} = \frac{P_w/P_{IPA}}{F_w/F_{IPA}} \tag{3}$$

$$PSI = J(\alpha_{sep} - 1) \tag{4}$$

where W = mass of permeate (kg), A = effective membrane area (cm^2), t = permeation time (h), P_w = mass percentage of water in the permeate and P_{IPA} = mass percentages of IPA in the permeate. F_w = mass percentage of water in the feed and F_{IPA} = mass percentage of IPA in the feed.

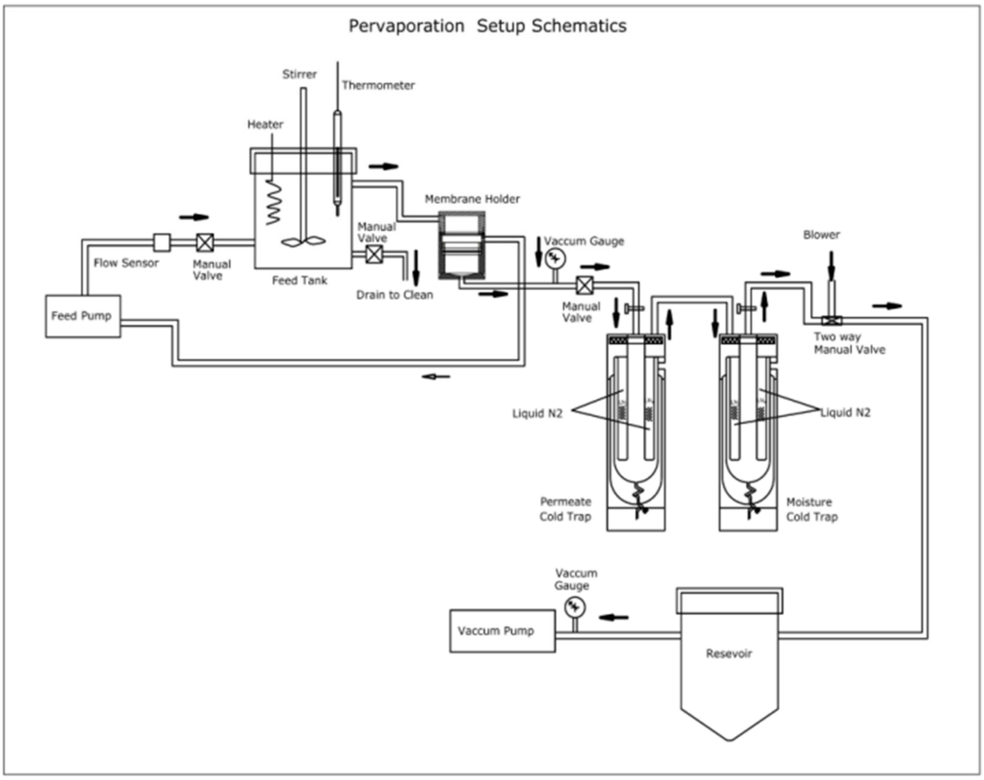

Figure 2. Schematic representation of the pervaporation unit.

Additionally, the permeance (Pi/l) was calculated using the following equation in order to get an unambiguous idea about the inherent properties of fabricated membranes.

$$\frac{P_i}{l} = \frac{D_i K_i}{l} = \frac{j_i}{P_i^f - P_i^p} \tag{5}$$

where D_i = diffusion coefficient of the i^{th} component, K_i = sorption coefficient of the i^{th} component, P_i = permeability of the i^{th} component, P_i^f = feed vapor pressures of the i^{th} component, P_i^P = permeate vapor pressures of the i^{th} component and l = membrane thickness. j_i = molar flux of i^{th} component.

3. Results

3.1. Membrane Characterization

3.1.1. FTIR Studies

In order to understand the molecular fingerprinting of the fabricated membranes, the FTIR analysis was carried out, and the obtained spectra of gelatin, chitosan, and gelatin incorporated chitosan membrane are demonstrated in Figure 3.

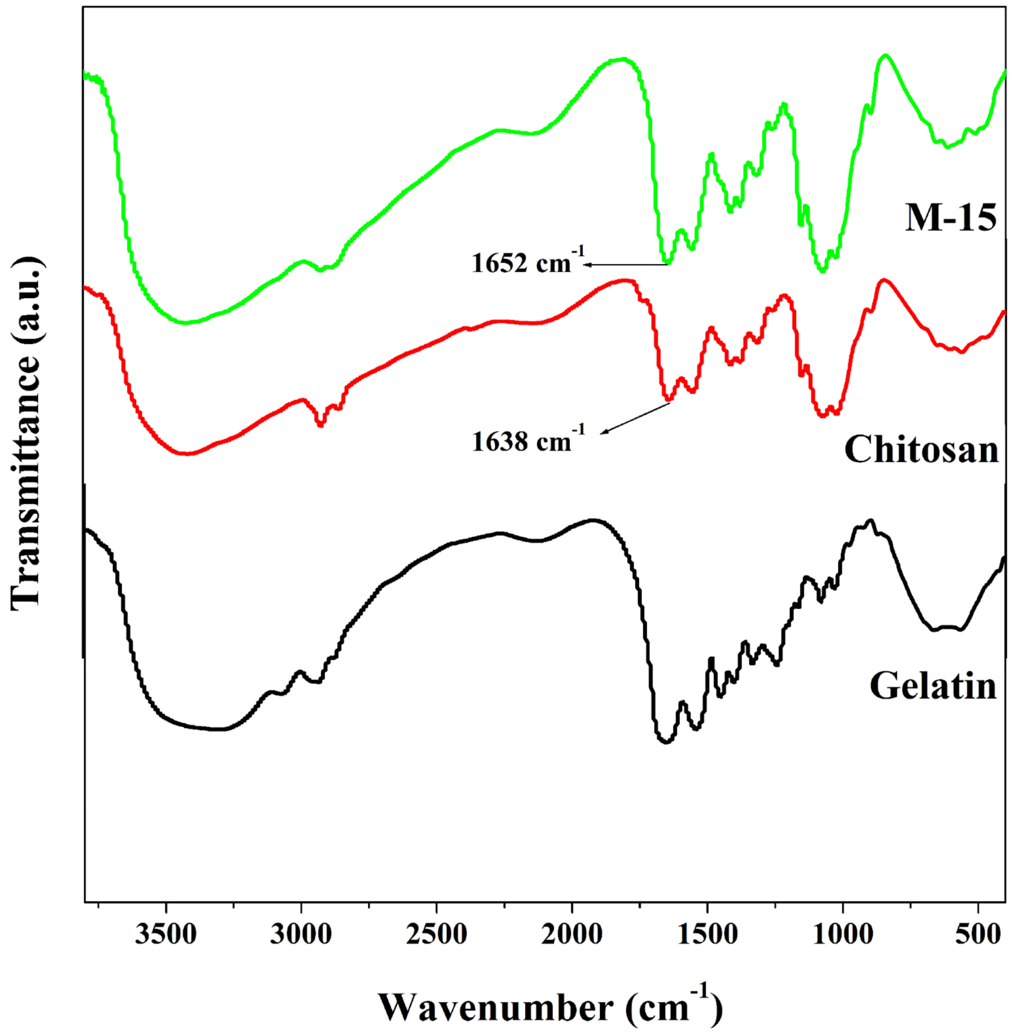

Figure 3. FTIR spectra of plane gelatin, plane chitosan, and chitosan-15 mass% gelatin blend membrane.

In FTIR spectrum of gelatin, a broad peak observed around 3410 cm^{-1} is assigned to the stretching N-H group. The -CH stretching vibration peak has appeared at 2931 cm^{-1}. Peak visible at 1656 cm^{-1} is assigned to the occurrence of C=O and C-N stretching of amide I. The peaks 1544 cm^{-1} and 1238 cm^{-1} represent N-H bending and C-N stretching of amide I and amide II, respectively [25]. Further in the spectrum of chitosan, the peak at 1152 cm^{-1} corresponds to polysaccharides of chitosan. Peak assigned to N-H and C-N vibrations of amide III is exhibited at 1252 cm^{-1}. Peaks at 1560 cm^{-1} and 1638 cm^{-1} are assigned to N-H and C-N group vibrations of amide II and N-H and C=O group vibrations of amide I, respectively. The –CH stretching vibration peak appeared at 2931 cm^{-1}. The broadband between the ranges 3400 cm^{-1} to 3500 cm^{-1} was due to N-H stretching and O-H stretching vibrations [26]. However, for chitosan–gelatin membrane, the peaks of amide I for chitosan at 1638 cm^{-1} were shifted to 1652 cm^{-1} along with the increment in the intensity. This can be attributed to the ionic cross-linking between the -COO^{-} of gelatin and -NH^{3+} of chitosan in these composites [27]. The band for O-H stretching vibration present between 3400 cm^{-1} to 3500 cm^{-1} was also seen broadened, which indicates the enhanced inter and intramolecular hydrogen bonding between the two chemicals. This spectral evidence confirms the miscibility of gelatin in the chitosan matrix and the compatibility between the two chemicals. The interactions between chitosan and gelatin are illustrated in Figure 4.

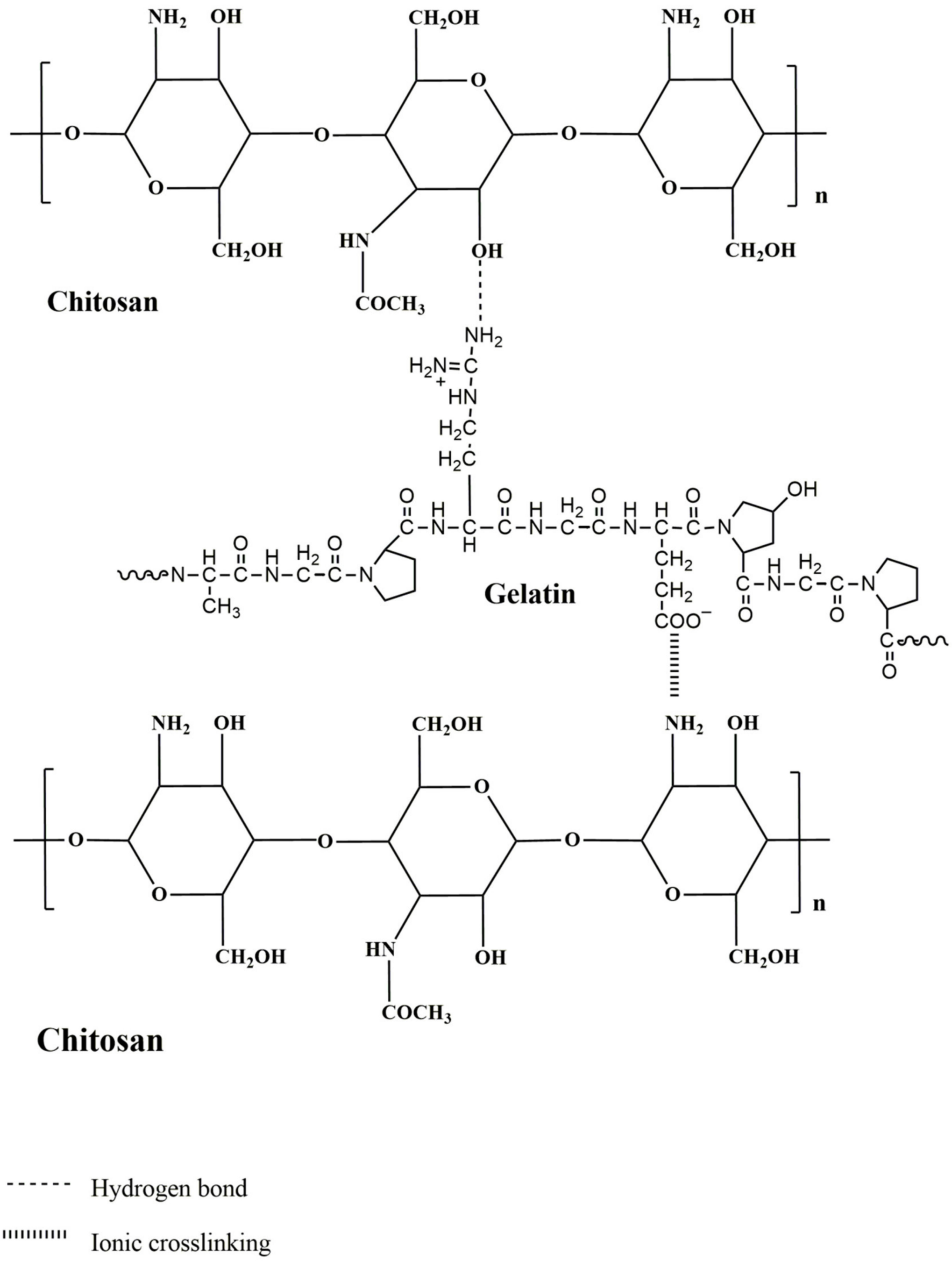

Figure 4. Interactions between chitosan and gelatin.

3.1.2. Wide-Angle X-ray Diffraction Studies (WAXD)

The WAXD studies of the plane gelatin were carried out, and the obtained diffractograms are shown in Figure 5. From the diffractogram, it can be seen that gelatin shows two diffraction peaks at 8° and 18°, respectively [28]. The peak that appeared at 8° corresponds to the diameter of the double helix, and the intensity of that peak is correlated to the triple helix segments of the gelatin. The peak appearing at 18° is characterized by the semi-crystalline nature of the gelatin [23]. In order to analyze the intrinsic nature, the fabricated membranes were tested for WAXD studies, and obtained results are also represented in Figure 5. Plane chitosan membrane (M-0) demonstrated a couple of small and sharp peaks at around $2\theta = 10°$ and 15° along with a broad peak at around $2\theta = 21°$. The broad peak represents the amorphous part, and the small sharp peaks signify the semi-crystalline part of the membranes [29]. The degree of crystallinity for M-0 was 69%, which is almost in accordance with the literature [30]. In the curves of chitosan–gelatin hybrid membranes, the peaks observed prominently in gelatin are absent, which indicates the chemical interaction and compatibility between the two chemicals. After incorporating gelatin in the chitosan matrix, the intensity of the peak appeared at 2θ = 21° gradually decreased along with the increase in the mass% of gelatin up to 10 mass%. This occurs for the reason that at lower concentrations of gelatin, chitosan dominates the complex triple helix structure of the gelatin by the establishment of intermolecular interactions such as ionic cross-linking and hydrogen bonding. This leads to a decrease in the crystalline nature of the membranes (Degree of crystallinity of M-10 = 64%). However, when the concentration of the gelatin increases by more than 10 mass% in the chitosan matrix, the dominant character of chitosan is held back, which leads to the enhancement of the intensity in the diffraction peaks. This leads to a further increase in the crystalline nature of the membranes (Degree of crystallinity of M-20 = 76%).

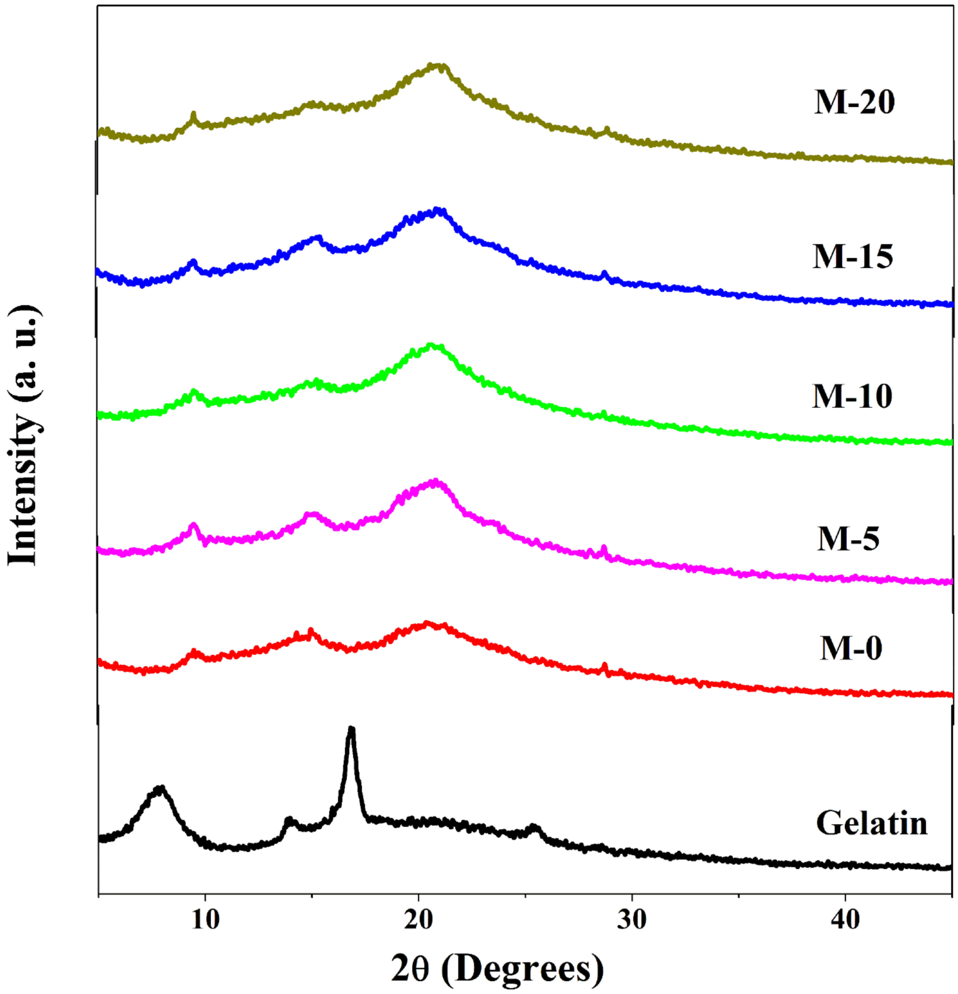

Figure 5. WAXD patterns of gelatin, chitosan, and gelatin incorporated chitosan membranes: pure chitosan; (M); (M-5) 5 mass%; (M-10) 10 mass%; (M-15) 15 mass%; (M-20) 20 mass% of gelatin.

3.1.3. Thermogravimetric Analysis (TGA)

TGA is an important characterizing technique to analyse the thermal stability of the developed membranes [31]. In order to analyze the degradation behavior and thermal solidity of the developed membranes, thermogravimetric analysis was carried out and the thermograms obtained are illustrated in Figure 6. From the results, it was clearly observed that the first degradation process takes place owing to the loss of water molecules (physically absorbed) from the ambient temperature and 126 °C [32]. These molecules of water exist in the bound state but not in free form. The loss of weight due to the removal of water molecules is about 12 to 15%. On careful observation, we found that that the weight loss was more in the case of M-15 and M-20 compared to the other membranes, and M-10 experienced the least weight loss, which indicates the M-15 and M-20 have higher water affinity, and M-10 has the least water affinity among the contemporary membranes. The decomposition of the second stage started from 225 °C in which the major amount of weight loss is observed owing to the polymeric chains decomposition. If we consider 45% weight loss as a reference point, M-0 experiences 45% weight loss at the lower temperature of 303 °C, which is at the lower temperature compared to the other membranes, whereas M-10 experiences the same weight loss at 336 °C. This illustrates the higher thermal stability of M-10 compared to the other membrane due to the higher ionic interactions and hydrogen bonding between chitosan and gelatin.

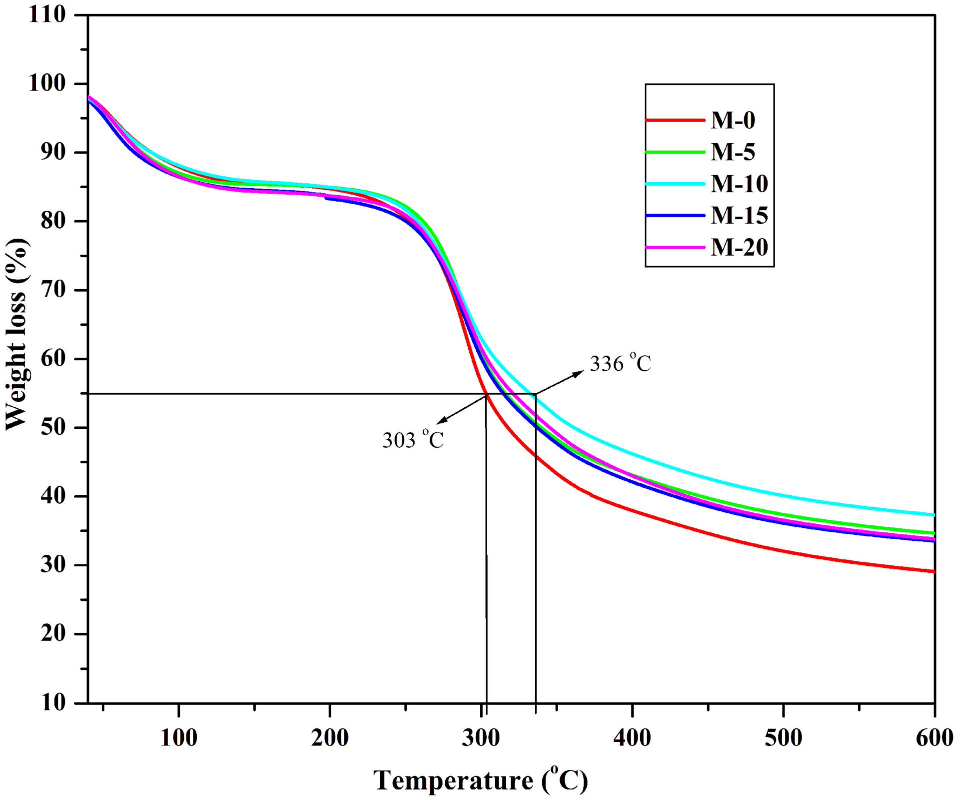

Figure 6. TGA curves of chitosan and gelatin incorporated chitosan membranes: pure chitosan; (M); (M-5) 5 mass%; (M-10) 10 mass%; (M-15) 15 mass%; (M-20) 20 mass% of gelatin.

3.1.4. Differential Scanning Calorimetry (DSC)

The DSC thermograms of plane gelatin, chitosan, and gelatin are illustrated in Figure 7. From the figure, it is noticed that the plane gelatin exhibits an endothermic peak at around 143 °C which may be due to the gelatin denaturation. Further, the intense peak (endothermic) observed at around 288 °C indicates the change of the phase of gelatin as at 320 °C, the melting point of the gelatin is observed [33]. The DSC thermograms of the prepared membranes are also illustrated in Figure 7. In plane chitosan membrane (M), the first endothermic peak appears at around 126 °C, which corresponds to the evaporation of the water molecules (physically absorbed) attached to the internal chains [34]. On careful observation, we see that the area under the curve for M-15 and M-20 is larger compared to the other membranes, which signifies the higher water affinity of the membranes M-15 and M-20. The next peak was observed at around 225 °C with an onset of 175–180 °C, which may be the glass transition temperature of the developed membranes. Here, the weight loss is observed due to the breakage of ionic interactions between the carboxylic group of gelatin and amino groups of chitosan and inter and intramolecular hydrogen bonding between the amino, hydroxyl, and carbonyl groups of chitosan and gelatin. Therefore, for M-0, the decomposition is at a lower temperature compared to the gelatin incorporated chitosan membranes as there are no ionic interactions. However, there is still uncertainty regarding the glass transition temperature as there are different Tg values discussed in the literature [35].

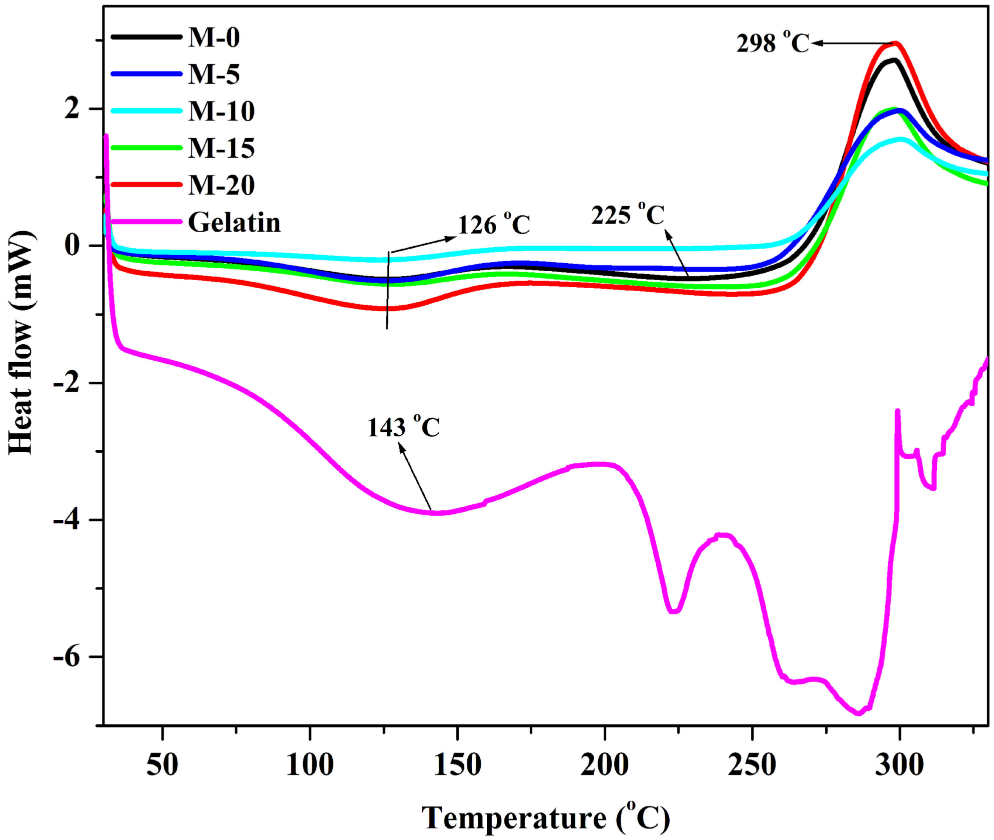

Figure 7. DSC thermograms of gelatin, chitosan and gelatin incorporated chitosan membranes: pure chitosan; (M); (M-5) 5 mass%; (M-10) 10 mass%; (M-15) 15 mass%; (M-20) 20 mass% of gelatin.

This is owing to the discrepancies in the nature of chitosan, such as deacetylation degree and molecular weight. Further, an exothermic peak is observed at around 298 °C, which is due to the depolymerization or decomposition of biopolymers (glycoside bond cleavage, decomposition of the diacetyl and acetyl units, and monomer dehydration). These results are in accordance with the results of TGA for the thermal stability of the developed membranes.

3.1.5. Scanning Electron Microscopy (SEM)

In order to analyze the surface characteristics of the developed membranes, SEM analysis of the developed membranes was carried out, and resultant SEM images are presented in Figure 8. From the surface, it was clearly noticed that the membrane surfaces are even and homogenous up to M-10. However, when the gelatin content is enhanced by more than 10 mass %, the surface becomes rough and irregular with the presence of few small cavities. This indicates that the compatibility between chitosan and gelatin is high up to 10 mass% of gelatin. However, when we observed the cross-sectional views of the membranes, no roughness or porosity is observed. These results are in agreement with the DSC, TGA, and XRD results. Above 10 mass% of gelatin, the compatibility between chitosan and gelatin is slightly reduced as the gelatin just entangles on the surface of the chitosan.

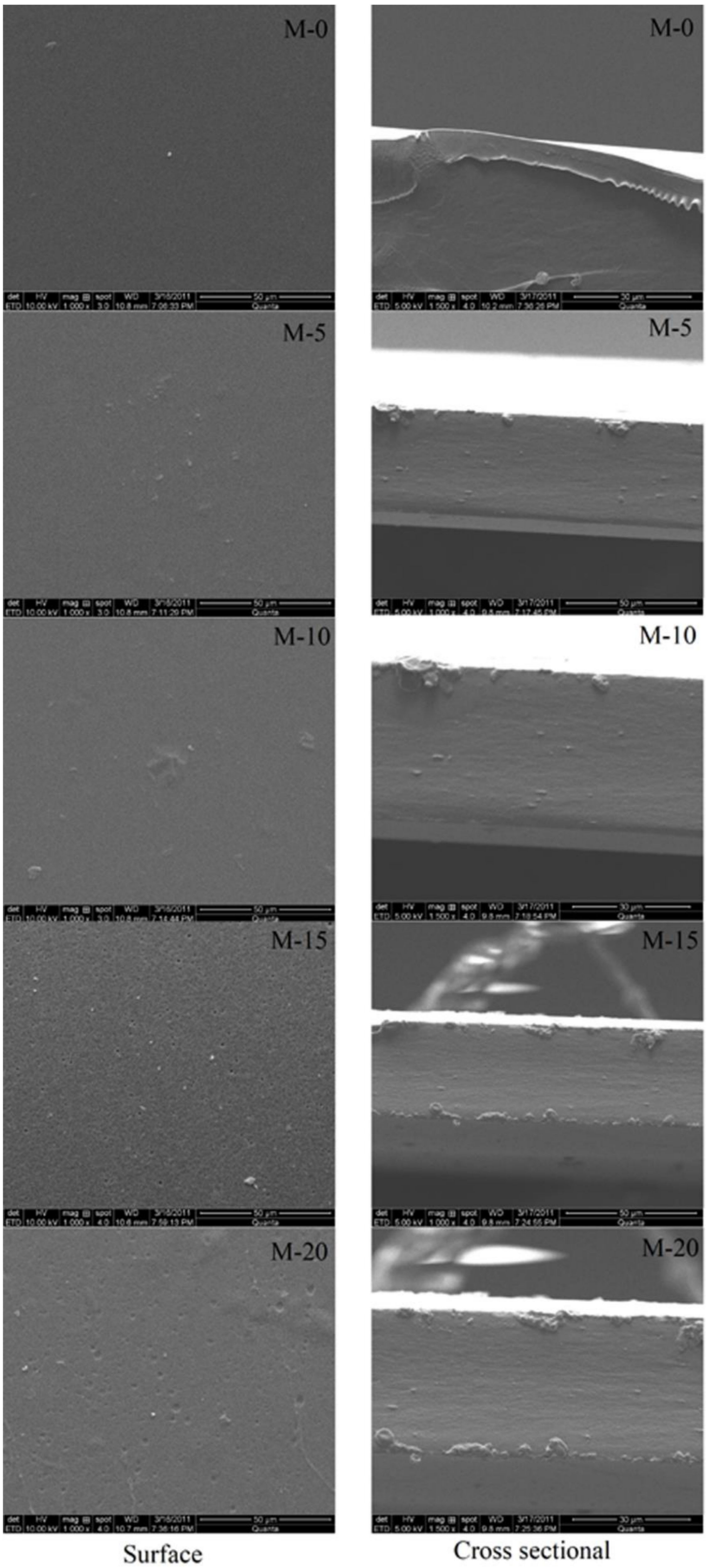

Figure 8. Surface and cross-sectional SEM images of chitosan and gelatin incorporated chitosan membranes: pure chitosan; (M); (M-5) 5 mass%; (M-10) 10 mass%; (M-15) 15 mass%; (M-20) 20 mass% of gelatin.

3.2. Effects of the Amount of Gelatin and Feed Composition on Membrane Swelling

Membrane sorption is an important factor for the membranes as it describes the nature of the membranes [36]. With the purpose of assessing the effect of gelatin content and mixture composition on the wettability of the membranes, the % degree of sorption for the developed membranes at various feed concentrations at 30 °C was plotted in Figure 9. From the plots, it was observed that the sorption % was consistently increased as the content of water increased in the mixture. This behavior was obvious because of the strong interaction that exists between the membrane surface and the water molecules. Water molecules, having higher polarity than isopropanol, interact with the polar groups like carbonyl, hydroxyl, amino and carboxylic groups of the membrane surface. However, the sorption % was decreased from the membrane M-0 to M-10. This is mainly because of the ionic cross-linking between the carboxylic group of gelatin and amino groups of chitosan and inter and intramolecular hydrogen bonding between the carbonyl, hydroxyl, and amino groups chitosan and gelatin, which leads to the stiffness in the complex polymer chains. This also leads to a decrease in the degree of crystallization (64% for M-10). Further, as we move to membranes M-15 and M-20, the % sorption was enhanced. This behavior was observed because the gelatin added more than 10 % in the membrane matrix could not form ionic interactions and hydrogen bonding and instead just remained entangled with the chitosan in the matrix. This brings about an increment in the degree of crystallization (76% for M-20). As a result of this, more and more number of polar groups in the membrane matrix will be accessible for the polar interaction with the water molecules (solvent). These results are in good agreement with the DSC, TGA, and WAXD results.

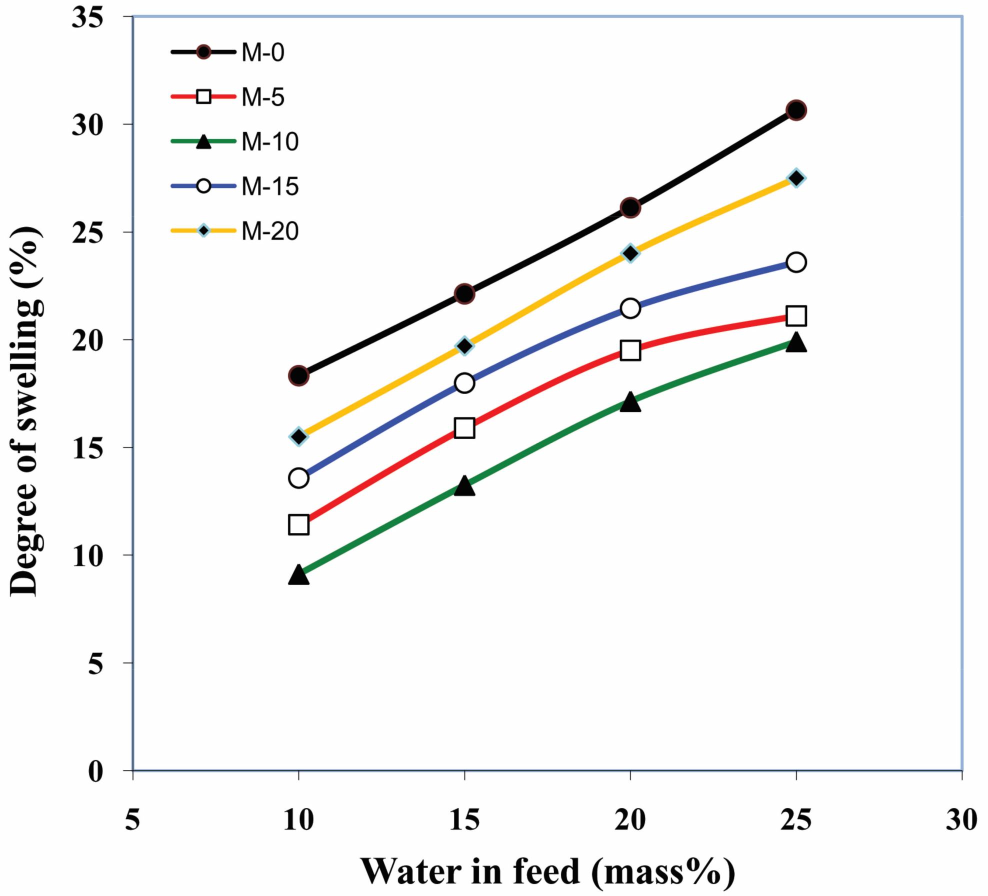

Figure 9. Effect of gelatin and water content on membrane sorption.

3.3. Effects of the Amount of Gelatin and Feed Composition on Pervaporation

The effect of the concentration of water in the separation mixture on the total permeation flux (*J*) and separation selectivity (α_{sep}) was analyzed at 30 °C. The obtained results are depicted in Table 1.

Table 1. Permeation flux and separation selectivity of all the membranes for different mass% of water in the feed at 30 °C.

Mass% of Water	$J \times 10^{-2}$ (kg/m^2 h)					$\alpha_{sep.}$				
	M-0	**M-5**	**M-10**	**M-15**	**M-20**	**M-0**	**M-5**	**M-10**	**M-15**	**M-20**
10	3.733	3.617	3.584	4.201	4.402	848.1	1160	6420	6330	5512
15	6.428	6.350	6.138	6.355	6.605	730.3	879.8	2018	2002	1604
20	9.701	9.076	8.776	9.012	10.21	201.1	412.7	621.0	618.0	405.5
25	14.50	14.01	12.09	12.95	14.59	151.0	174.5	197.0	195.6	134.6

From the results observed, it is clear that as the water content is increased in the mixture to be separated, the permeation flux for all the membranes increased almost linearly. This is owing to the selective interaction of the fabricated membranes with the polar water molecules. In contrast, the total permeation flux was declined from M to M-10. A similar trend is observed in the case of permeance (Table 2).

Table 2. Permeance for all the membranes for different mass% of water in the feed at 30 °C.

Mass% of Water	Pi/l(GPU) *				
	M-0	**M-5**	**M-10**	**M-15**	**M-20**
10	829	803	796	933	978
15	1428	1411	1364	1412	1467
20	2156	2017	1950	2002	2269
25	3222	3113	2687	2877	3242

* GPU = gaspermeationunit = 10^{-6} cc(STP)/cm^2/s/cm Hg.

This is attributed to the ionic interactions between the carboxylic group of gelatin and amino groups of chitosan and inter and intramolecular hydrogen bonding between the amino, hydroxyl, and carbonyl groups of chitosan and gelatin, which leads to the considerable decrease in the polymer chain mobility and the free volume. Moreover, the unavailability of polar groups for the solvent interaction makes the membranes less permeating. However, for the M-15 and M-20, the permeation flux was enhanced substantially throughout the entire range of compositions in the feed. This is expected as the gelatin added beyond 10 mass% in the membrane matrix could not form ionic interactions and hydrogen bonding and instead just remained entangled with the chitosan in the matrix. This makes the gelatin much more free and relaxed, and more interactive groups like -OH$^-$ and -NH^{3+} are available for solvent interactions.

To facilitate the extent of permeation flux for water and isopropanol individually, the Permeation flux of water and isopropanol are calculated individually at 10% aqueous isopropanol mixture and illustrated in Table 3. From the values, it is seen that the permeation flux of water is roughly the same as that of overall permeation flux, and comparatively, the permeation flux of IPA is very small. A similar trend is also seen from Figure 10, which represents overall permeation flux and the individual isopropanol and water permeation fluxes regarded as the function of gelatin content in the membrane for the 10% aqueous isopropanol mixture. These trends clearly depict the selective nature of the developed membranes towards the polar component in the mixture (water).

Table 3. Permeation flux of water and isopropanol for all the membranes for different mass% of water in the feed at 30 °C.

Mass% of Water	J w × 10^{-2} (kg/m^2 h)					J IPA × 10^{-2} (kg/m^2 h)				
	M-0	M-5	M-10	M-15	M-20	M-0	M-5	M-10	M-15	M-20
10	3.694	3.589	3.579	4.194	4.395	0.039	0.028	0.005	0.007	0.008
15	6.378	6.309	6.121	6.337	6.580	0.049	0.041	0.017	0.018	0.024
20	9.512	8.989	8.720	8.954	10.11	0.189	0.087	0.056	0.058	0.100
25	14.14	13.77	11.91	12.77	14.27	0.362	0.236	0.181	0.183	0.318

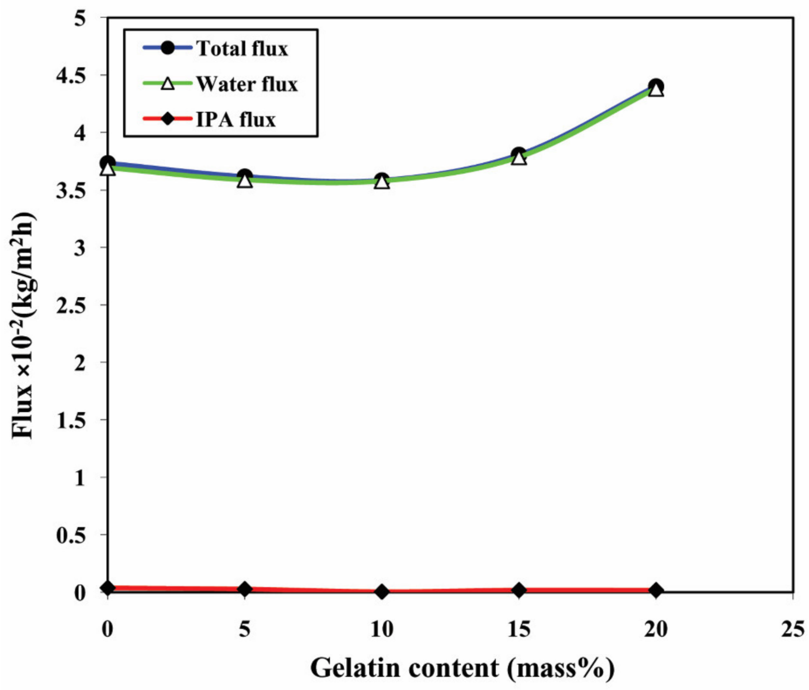

Figure 10. Effect of the content of gelatin on the total permeation flux, permeation flux of water, and permeation flux of isopropanol.

Selectivity of the membrane commonly relies on the interaction of the membrane with the diffusing molecules and the molecular size of the diffusing molecules. From Table 1, it is clearly seen that the separation selectivity of all the developed membranes declined as the ratio of water is enhanced in the separating mixture. This is caused by the higher interaction taking place between the fabricated membranes and the water molecules.

In contrast, the separation selectivity was increasing from M to M-10 for all the compositions of feed. Mainly this occurs because of two factors. First, this is owing to the interionic interactions and hydrogen bonding between the gelatin and the chitosan, which causes a considerable decrease in the polymer chain mobility and the free volume. Secondly, it is due to the difference in the sizes of the two molecules in the mixture. The size of the isopropanol is comparatively larger than water molecules. Further, for M-15 and M-20, the separation selectivity declined radically. This occurs due to the gelatin added beyond 10 mass% in the membrane matrix not being able to form ionic interactions and hydrogen bonding and instead just remaining entangled with the chitosan in the matrix. Consequently, the gelatin augmented the interaction with the liquids under separation with no decrease in the free volume of the membrane, which led to the decrement of separation selectivity. Figure 11 depicts the plots of total permeation flux plus the separation selectivity plotted with respect to various contents of gelatin in the membrane for 10% aqueous isopropanol mixture separation.

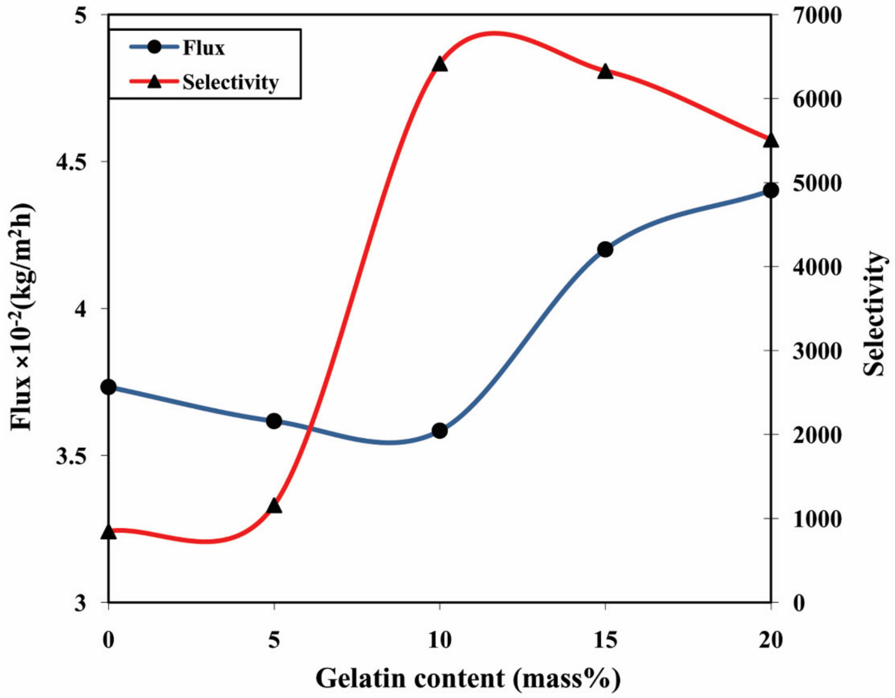

Figure 11. Effect of gelatin on the total permeation flux and separation selectivity of the fabricated membranes.

3.4. Effect of Gelatin on Pervaporation Separation Index (PSI)

PSI is the parameter that considers both separation selectivity and total permeation flux into account and depicts the overall membrane performance in pervaporation. This parameter can be regarded as a tool to design novel membranes and to select the optimal membrane for an overall better PV performance. Figure 12 demonstrates the plot of PSI at various content of gelatin for 10% aqueous isopropanol mixture separation. The plot shows that M-15 exhibits the maximum PSI in comparison with its contemporary membranes as it possesses excellent separation selectivity and decent total permeation flux. This proves that the M-15 has better separation ability compared to the contemporary membranes.

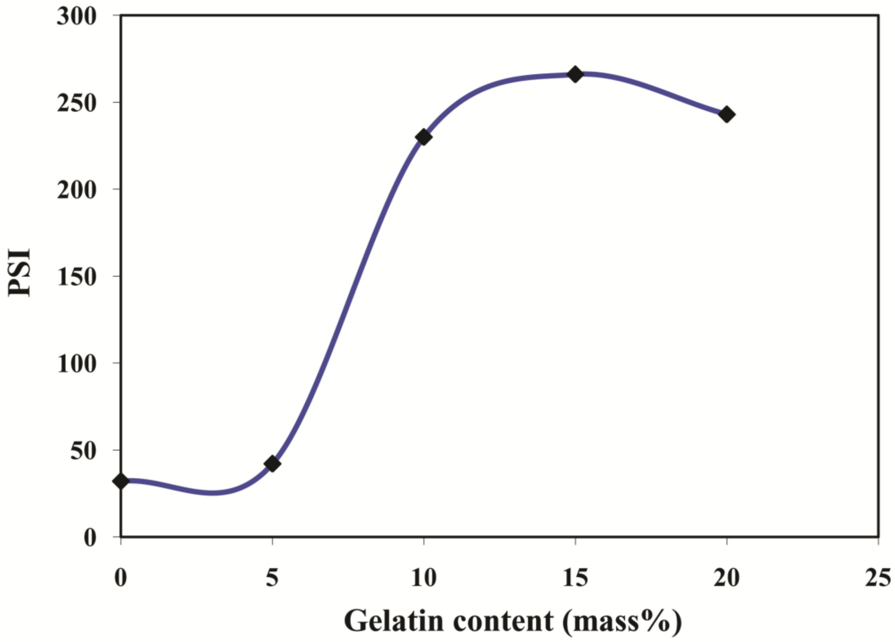

Figure 12. Effect gelatin content on the PSI at 10 mass% of water in the feed.

3.5. Effect of Temperature on Membrane Performance

The influence of temperature during the separation on the membrane performance for 10% aqueous isopropanol mixture separation is analyzed, and the obtained result is depicted in Table 4. From the values, it is seen that the total permeation flux augmented systematically as the temperature increased from 30 °C to 50 °C. Conversely, the separation selectivity declined. This behavior is obvious as higher temperatures will decrease the intermolecular interaction between the membrane and the permeating molecules; in addition, they also decrease the intermolecular interaction in the membrane materials, which leads to the membranes showing plasticizing effect owing to excessive swelling. As a result, the diffusion of associated molecules along with the diffusion molecules turns out to be simple, leading to an enhanced total permeation flux and suppressed selectivity.

Table 4. Permeation flux and separation selectivity of all the membranes for 10 mass% of water in the feed at various temperatures.

Temperature (°C)	**$J \times 10^{-2}$ (kg/m^2 h)**					**$\alpha_{sep.}$**				
	M-0	**M-5**	**M-10**	**M-15**	**M-20**	**M-0**	**M-5**	**M-10**	**M-15**	**M-20**
30	3.733	3.617	3.584	4.201	4.402	848.1	1160	6420	6330	5512
40	5.241	5.180	5.174	5.364	6.129	523.5	722.7	1791	1397	922.7
50	6.640	6.321	6.299	7.299	9.982	452.5	652.7	1159	928.5	723.5

4. Conclusions

In this work, chitosan–gelatin blend membranes were fabricated using chitosan as the base and varying the amount of gelatin using the conventional casting technique. After the fabrication, the membranes were subjected to the separation of an isopropanol–water mixture using the pervaporation technique at various conditions of temperature and concentration of separating mixtures. In the FTIR, the peak of C=O of amide I for chitosan at 1638 cm^{-1} was shifted to 1652 cm^{-1} along with the increment in the intensity. This confirmed the ionic cross-linking between -NH_3^+ of chitosan and the -COO^- of gelatin in three composites. From WAXD, it is confirmed that the crystalline nature of the membrane decreases until the 10 mass% of gelatin and is further enhanced by 15 and 20 mass% of gelatin in the matrix. From the DSC and TGA, it is confirmed that the M-10 membrane exhibited the highest thermal stability among the contemporary membranes. Further, from the SEM analysis, it is clear that the compatibility between chitosan and gelatin is good in all the fabricated membranes. In pervaporation analysis, all the membranes with various content of gelatin in the membrane showed good separation selectivity and decent water permeation flux owing to the considerable improvement in the hydrophilicity and the amorphous nature. Out of the fabricated membranes, the membrane loaded with 15 mass% of gelatin (M-15) exhibited the better pervaporation performance with a pervaporation separation index value of 266 at 30 °C for the solution containing 10% in terms of the mass of water, which is the highest among the contemporary membranes.

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gels

Article

Fabrication and Characterization of Poly (Vinyl Alcohol)-Chitosan-Capped Silver Nanoparticle Hybrid Membranes for Pervaporation Dehydration of Ethanol

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Abstract: Chitosan-capped silver nanoparticle (CS-capped AgNPs)-incorporated poly (vinyl alcohol) (PVA) hybrid membranes were prepared by a solution-casting technique for ethanol dehydration via pervaporation. The incorporation of CS-capped AgNPs into the PVA membrane and its influence on membrane properties and pervaporation-separation process of azeotropic water/ethanol mixture was studied. The addition of CS-capped AgNPs into the PVA membrane reduced the crystallinity, thereby increasing the hydrophilicity and swelling degree of the hybrid membrane, supported by contact angle (CA) analyzer and swelling degree experiments, respectively. Fourier transform infrared spectroscopy (FTIR) demonstrated the formation of polymeric matrix between PVA and CS and also the binding of AgNPs onto the functional group of CS and PVA, which was also reflected in the microstructure images demonstrated by scanning electron microscopy (SEM) and by 2θ angle of wide-angle X-ray diffraction (WAXD). The effect of CS-capped AgNPs on the thermal stability of the hybrid membrane was demonstrated by differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA). These characteristics of the hybrid membrane positively impact the efficiency of the dehydration of ethanol, as indicated by pervaporation experiments. The best performances in total flux ($12.40 \pm 0.20 \times 10^{-2}$ kg/m^2 h) and selectivity (3612.33 ± 6.03) at 30 °C were shown for CS-capped AgNPs PVA hybrid membrane containing 2 wt.% CS-capped AgNPs (M-4). This confirms that the developed hybrid membranes can be efficiently used to separate water from azeotropic aqueous ethanol.

Keywords: permeation flux; selectivity; hydrophilicity; amorphous; crystallinity

1. Introduction

Ethanol is a versatile natural solvent and is miscible in water and many other organic solvents. [1,2]. Ethanol is produced mostly via fermentation process through the action of microorganisms by using corn or sugar-cane molasses as substrate [3–5]. It is used in the medical field as an antiseptic agent [6] and principally as fuel, as a substitute for petroleum in road-transport vehicles [7]. The ethanol produced by fermentation can be purified by extractive distillation, azeotropic distillation, adsorption, liquid–liquid extraction, and crystallization, which are often inefficient and uneconomical [8,9]. Ethanol separation from the azeotropic composition, which consists of 95.6% (*v*/*v*) concentration of ethanol and 4.4%

(v/v) of water, is carried out by azeotropic distillation, which is an energy-intensive process with a large capital cost and health and safety concerns [10,11]. Instead, the petrochemical and biochemical industries consider pervaporation a potential candidate for separating ethanol from its azeotropic composition. [12].

Pervaporation (PV), in its simplest type, is a combination of membrane permeation and evaporation associated with lower energy consumption and an economical process [13–15]. PV is a membrane-separation process that uses a dense polymeric membrane to selectively permeate one or more components from a liquid mixture. In the process, the liquid mixture is kept in direct contact with one side of the membrane, and the permeated product (pervaporate) is removed in the form of vapor and later condensed. The productivity and success of the pervaporation process largely depend on the fabrication of suitable membranes with high permeability, good selectivity and sufficient mechanical strength [16]. In particular, hydrophilic groups containing new membrane materials are preferred for the dehydration of alcohols. The membranes mainly considered in the PV process for dehydration of alcohols are poly (vinyl alcohol), sodium alginate and chitosan due to their excellent hydrophilicity and good film-forming ability [17–20].

In the PV process, poly (vinyl alcohol) (PVA) is a commonly used polymer for developing membranes. Advantages of using PVA membranes in the PV process are their non-toxic nature, water solubility due to the presence of the hydroxyl group and being biocompatible and biodegradable synthetic polymers [21–23]. The PVA has a high affinity towards water due to the formation of hydrogen bonds between intra- and intermolecular hydroxyl groups [19]. The separation performance of PVA membranes is unsatisfactory due to the swelling phenomenon in the presence of water, high crystallinity restricting from intermolecular hydrogen bonding, and instability. The PVA membrane has been modified to overcome this problem through cross-linking, filling, blending and grafting [24–28]. Despite this, the expected performance was not able to be achieved.

On the contrary, hybrid materials combine the important properties of both inorganic and organic and create new compositions with unique characteristics, which offer specific advantages for fabricating PV membranes exhibiting high selectivity and flux with desirable thermal and chemical strength. Perhaps, this becomes a facile and feasible way to solve the trade-off phenomenon, which generally exists in the PV process [29–31].

Considering this, Wang et al. [32] developed PVA hybrid membranes containing different graphite carbon-nitride nanosheets to dehydrate ethanol by PV. They achieved a separation factor of 57.9 and a total flux of 2.328 $kg.m^{-2}\ h^{-1}$. Jiang et al. [33] had overcome the trade-off phenomena with organic and inorganic hybrid membranes by incorporating graphite into the PVA matrix and increased both flux (0.0913 $kg.m^{-2}\ h^{-1}$) and selectivity (92). Xia et al. [34] developed PVA nanohybrid membranes by incorporating organosilica, and used this membrane for ethanol dehydration by PV and achieved selectivity of 1026 and flux of 0.145 $kg.m^{-2}\ h^{-1}$. Our previous work [35] fabricated B_2SA-grafted poly (vinyl alcohol)–graphene hybrid membranes for ethanol dehydration by PV. Among these, the membrane containing 2 wt.% of graphene exhibited selectivity of 4187 with a flux of 0.1166 $kg.m^{-2}\ h^{-1}$.

Chitosan is the most abundant biopolymer and is deacetylated form of chitin. It exhibits hydrophilicity, degradation and antibacterial properties. It can adsorb metal ions using chelation due to the lone pair of electrons in its amino nitrogen [36–41]. It has better compatibility with PVA due to its hydrogen-bonding interaction [41].

Silver nanoparticles (AgNPs) are used in different fields, including medical, food, health care, consumer and industrial fields, due to their unique physical and chemical properties. These include optical, electrical and thermal properties, high electrical conductivity, biological properties [42–44] and hydrophilic nature [45].

In the present investigation, by understanding the pros and cons of developing hybrid membranes, we attempted to develop hybrid membranes by suitably incorporating CS-capped AgNPs. Different characterization methods are used to examine the physical and chemical properties of the fabricated membranes. Effects of CS-capped AgNPs and temperature on PV performance were systematically studied. The performance of fabricated membranes was evaluated by correlating with their structural properties.

2. Results

2.1. Membrane Characterization

2.1.1. FTIR Studies

Figure 1 shows the FTIR spectra of PVA, CS and CS-capped AgNPs incorporated in PVA membranes; the O-H stretching is visible with a broad peak at 3372 cm^{-1} in the FTIR spectra of the PVA membrane, and multiple brands appeared between 1000 to 1200 cm^{-1} corresponding to –C-O stretching vibrations of the hydroxyl groups. These bands matched those reported by Sajjan et al. [46]. The wide visible peak establishes the occurrence of the hydroxyl functional group at 3444 cm^{-1}, and bands appeared at around 1645 and 1550 cm^{-1} corresponding to NH (amide I) and amide II functional groups of the pure chitosan [47,48].

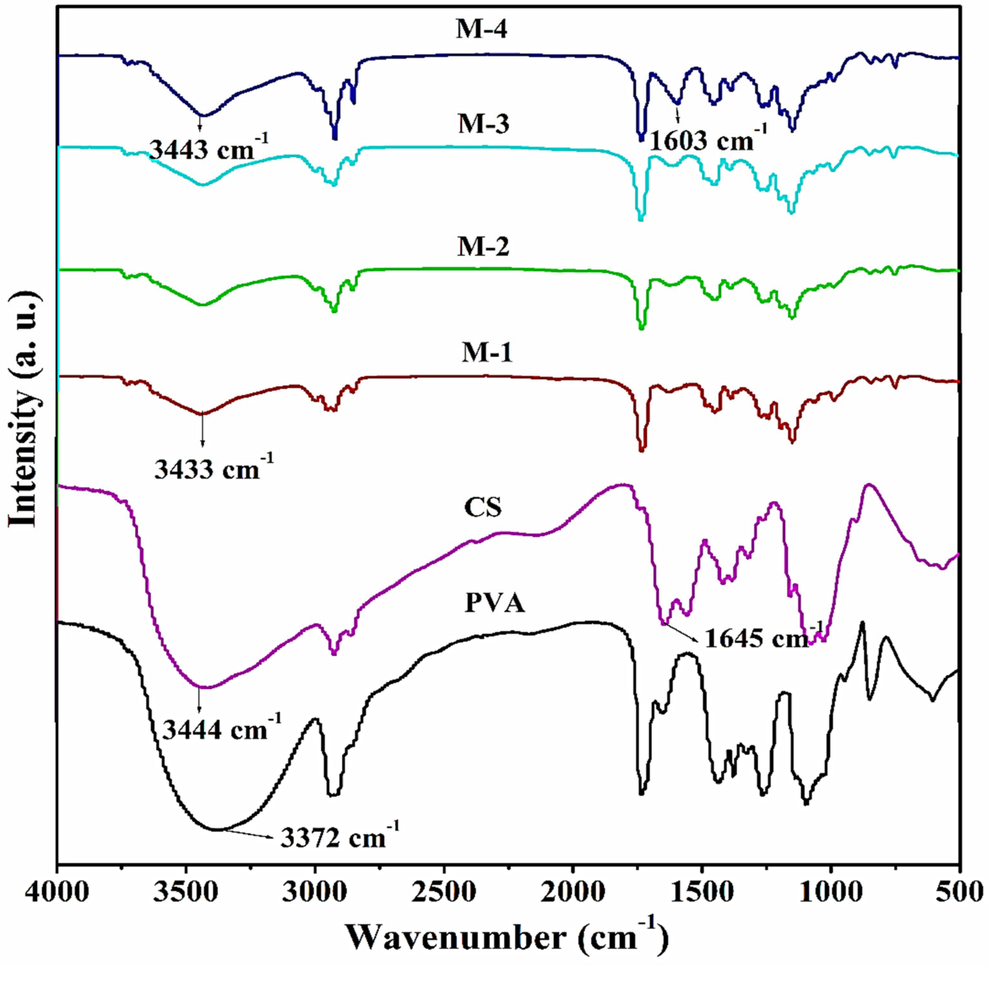
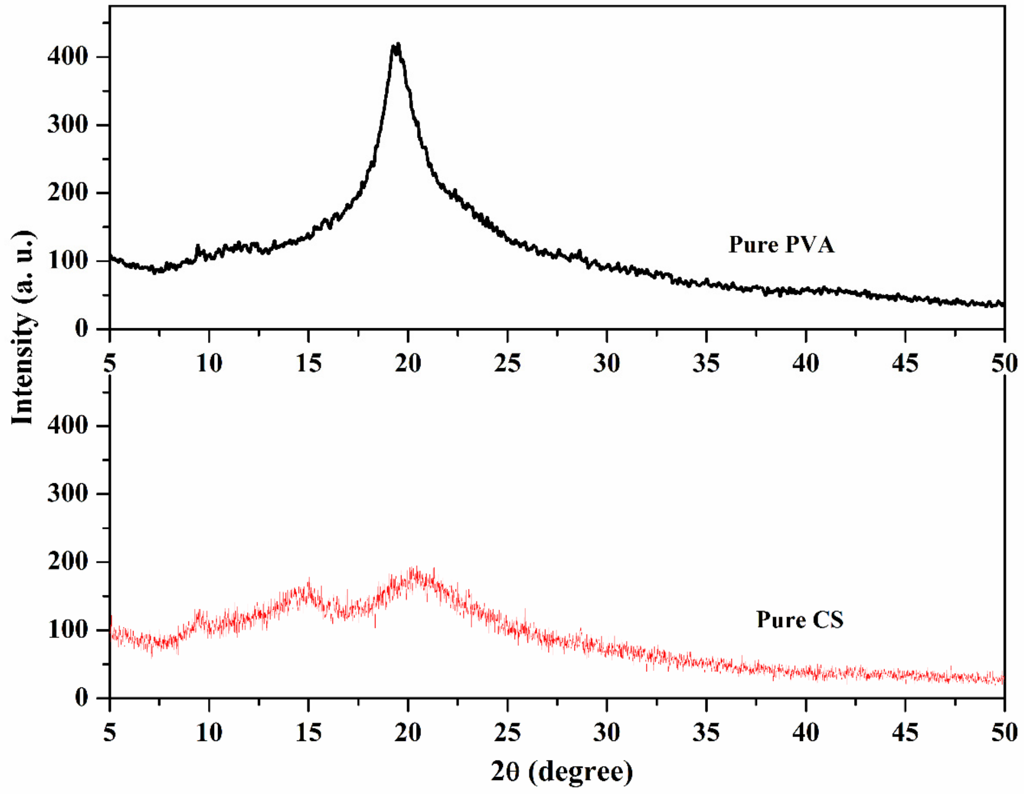


Figure 1. FTIR spectra of pure PVA, Chitosan, CS-capped AgNPs incorporated hybrid PVA membranes: (M-1) 0.5 wt.%; (M-2) 1 wt.%; (M-3) 1.5 wt.%; (M-4) 2 wt.% of CS-capped AgNPs.

In the case of CS-capped AgNPs incorporated hybrid PVA membranes, broadband appeared at 3433 cm^{-1}, showing the movement towards the higher wavenumber along with the increase in the intensity of the band as we progressed from M-1 (0.5% CS-capped AgNPs) to M-4 (2 wt.% CS-capped AgNPs), indicating enhanced hydrogen bonding due to PVA-CS chain interactions [49]. Multiple peaks owing to various amide functional groups that showed in pure chitosan are absent in membranes M-1 (0.5% CS-capped AgNPs) to M-4 (2 wt.% CS-capped AgNPs), demonstrating that these functional groups are involved in AgNP stability. At 1603 cm^{-1}, a new peak appeared. Its peak intensity increased as the wt.% of CS-capped AgNPs increased in the PVA matrix, indicating that silver particles are bound to the functional groups present in chitosan and PVA. The shifting of the peak is due to the formation of a coordination bond between the silver atom and the electron-rich group present in PVA and chitosan [47,49]

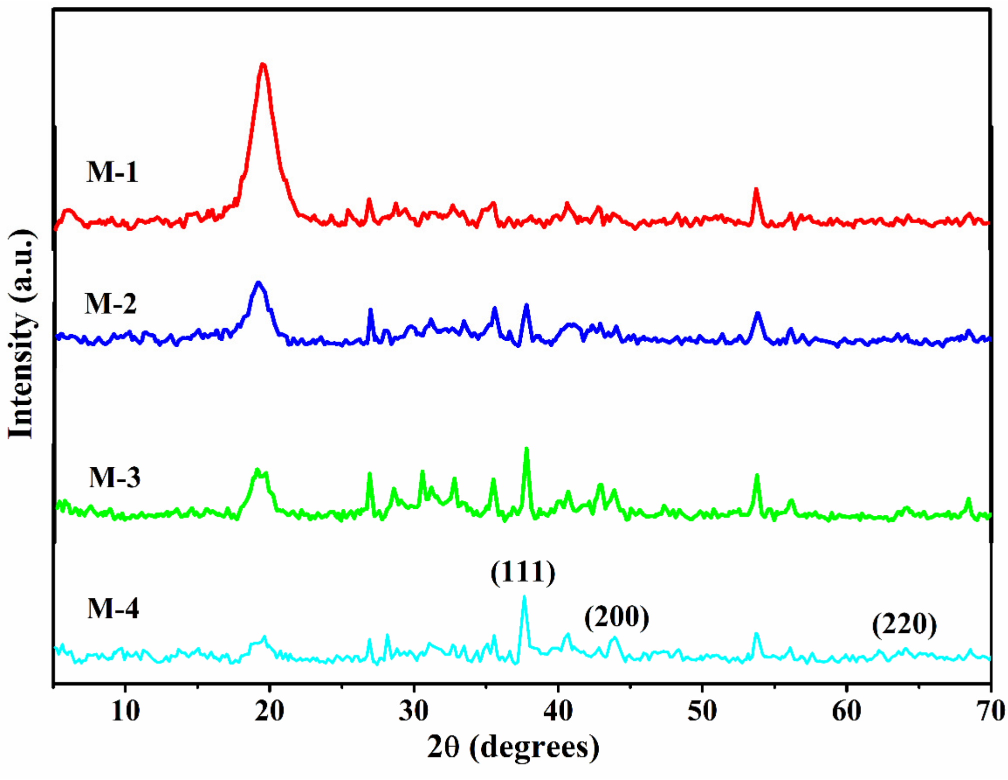
2.1.2. Wide-Angle X-ray Diffraction Studies (WAXD)

The illustrations of the WAXD pattern of PVA and CS-capped AgNPs embedded in PVA membranes are illustrated in Figure 2A,B. The plane PVA membrane exhibited a peak at $2\theta = 20°$, which indicates the presence of crystalline and amorphous regions in the morphology of the membrane [46]. The diffraction-peak intensity of PVA was reduced as the content of CS-capped AgNPs in the PVA matrix increased. This is due to the CS-capped AgNPs, which disorient the PVA chains and enhance the amorphous regions by reducing the crystalline regions. Further, the peak of the M-2 membrane was weaker than that of the PVA membrane, representing strong interaction among PVA and CS-capped NPs. Thus, the XRD results align with the FTIR results, in that some interaction occurred between PVA and CS-capped AgNPs. It implies that the PVA and CS-capped AgNP matrix presents high compatibility with stronger interactions [49]. The peaks that appeared at $2\theta = 27°$, 38° and 55° also confirm the presence of AgNPs. All this evidence suggests that an amorphous nature is predominant in the membranes where CS-capped AgNPs content is present, which supports the selective movement of the molecules through the membranes.



(A)

Figure 2. *Cont.*



(**B**)

Figure 2. (**A**). Wide-angle X-ray diffraction patterns of plane PVA and Chitosan. (**B**). Wide-angle X-ray diffraction patterns of CS-capped AgNP-incorporated PVA membranes: (M-1) 0.5 wt.%; (M-2) 1 wt.%; (M-3) 1.5 wt.%; (M-4) 2 wt.% of CS-capped AgNPs.

2.1.3. Thermogravimetric Analysis (TGA)

Figure 3 exhibits the obtained thermogram of the produced membranes. Thermal degradation of the membranes took place in two phases for all the membranes. Weight loss occurred between ambient temperature and 125 °C, corresponding to the volatilization of water and other volatile molecules in the membrane. The absorbed water molecule exists in the bound rather than the free molecular state [50]. Such a weight loss is about 12% for the PVA membrane, whereas CS-capped AgNP-incorporated PVA hybrid membranes exhibited a higher loss ranging from 17–18%, due to higher water-retention capacity.

Further, incorporated CS-capped AgNPs disturbed the PVA chains due to the intermolecular hydrogen bonding between PVA and CS-capped AgNPs and electrostatic interaction with AgNPs, responsible for decreased crystallinity of the PVA membrane; hence, CS-capped AgNPs membranes have higher water-retention capacity. The second stage of decomposition of the PVA membrane starts from 283–465 °C, attributed to major weight loss due to the decomposition of polymer chains [51]. Compared with PVA in the second stage, the CS-capped AgNP-incorporated PVA hybrid membranes showed 32–35 °C lower than the PVA membrane, which indicates that CS-capped AgNP-incorporated membranes demonstrated lower degradation temperature due to hydrogen bonding and decreased crystallinity. This is well-supported by FTIR and WXRD studies. The CS-capped AgNP-incorporated PVA hybrid membrane demonstrated better thermal resistance since their residue is larger than the PVA membrane.

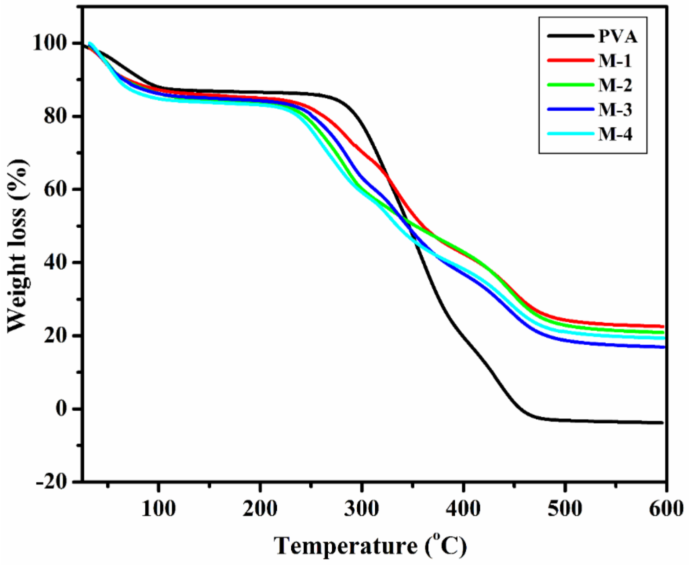


Figure 3. Thermogravimetric analysis patterns of PVA, CS-capped AgNP-incorporated PVA hybrid membranes: (M-1) 0.5 wt.%; (M-2) 1 wt.%; (M-3) 1.5 wt.%; (M-4) 2 wt.% of CS-capped AgNPs.

2.1.4. Differential Scanning Colorimetry (DSC)

The glass-transition-temperature (T_g) investigation was performed to characterize the thermal behavior of the produced membranes. The membrane thermograms (Figure 4) were obtained using DSC analysis at temperatures ranging from 27 to 250 °C. The T_g of the pure PVA membrane, according to these thermograms, was around 85 °C [46]. T_g was then gradually increased from 90 to 101 °C as the amount of CS-capped AgNPs in the PVA matrix grew from M-1 (0.5 wt.% CS-capped AgNPs) to M-4 (2 wt.% CS-capped AgNPs). The interaction between PVA and CS-capped AgNPs causes chain mobility to be hampered, resulting in an increase in T_g. When the proportion of CS-capped AgNPs in the PVA membrane matrix increased, the T_g values increased from M-1 (0.5 wt.% CS-capped AgNPs) to M-4 (2 wt.% CS-capped AgNPs), indicating that the PVA membranes became more stable.

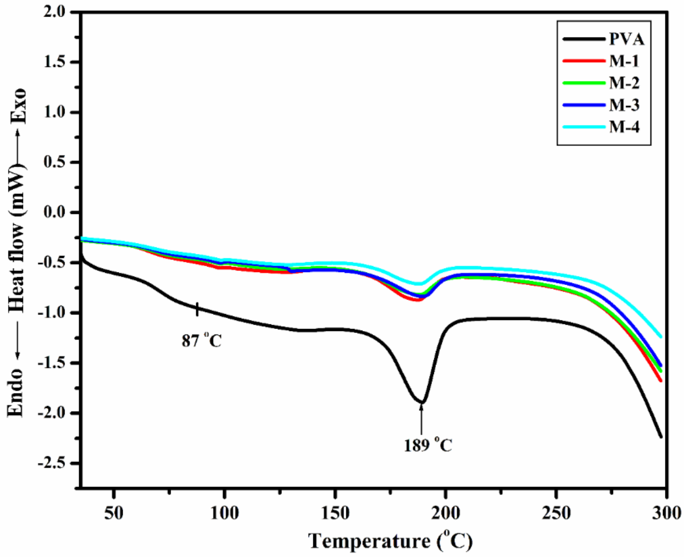


Figure 4. DSC thermograms of PVA and CS-capped AgNP-incorporated PVA hybrid membranes: (M-1) 0.5 wt.%; (M-2) 1 wt.%; (M-3) 1.5 wt.%; (M-4) 2 wt.% of CS-capped AgNPs.

2.1.5. Scanning Electron Microscopy (SEM)

SEM analysis of the fabricated membranes was carried out to investigate the effect of CS-capped AgNPs on the microstructure of the membranes, and the resulting micrographs are shown in Figure 5. The bright patches in the membrane were enhanced as we progressed from M-1 (0.5 wt.% CS-capped AgNPs) to M-4 (2 wt.% CS-capped AgNPs), owing to an increase in the CS-capped AgNP content in the membrane. There was no cluster formation in the membrane matrix when the CS-capped AgNPs were distributed. These images also showed that all of the CS-capped AgNPs were disseminated in the membrane independently and that the membranes were homogeneous and defect-free. Furthermore, these photos demonstrated that the PVA matrix and CS-capped AgNPs are compatible.

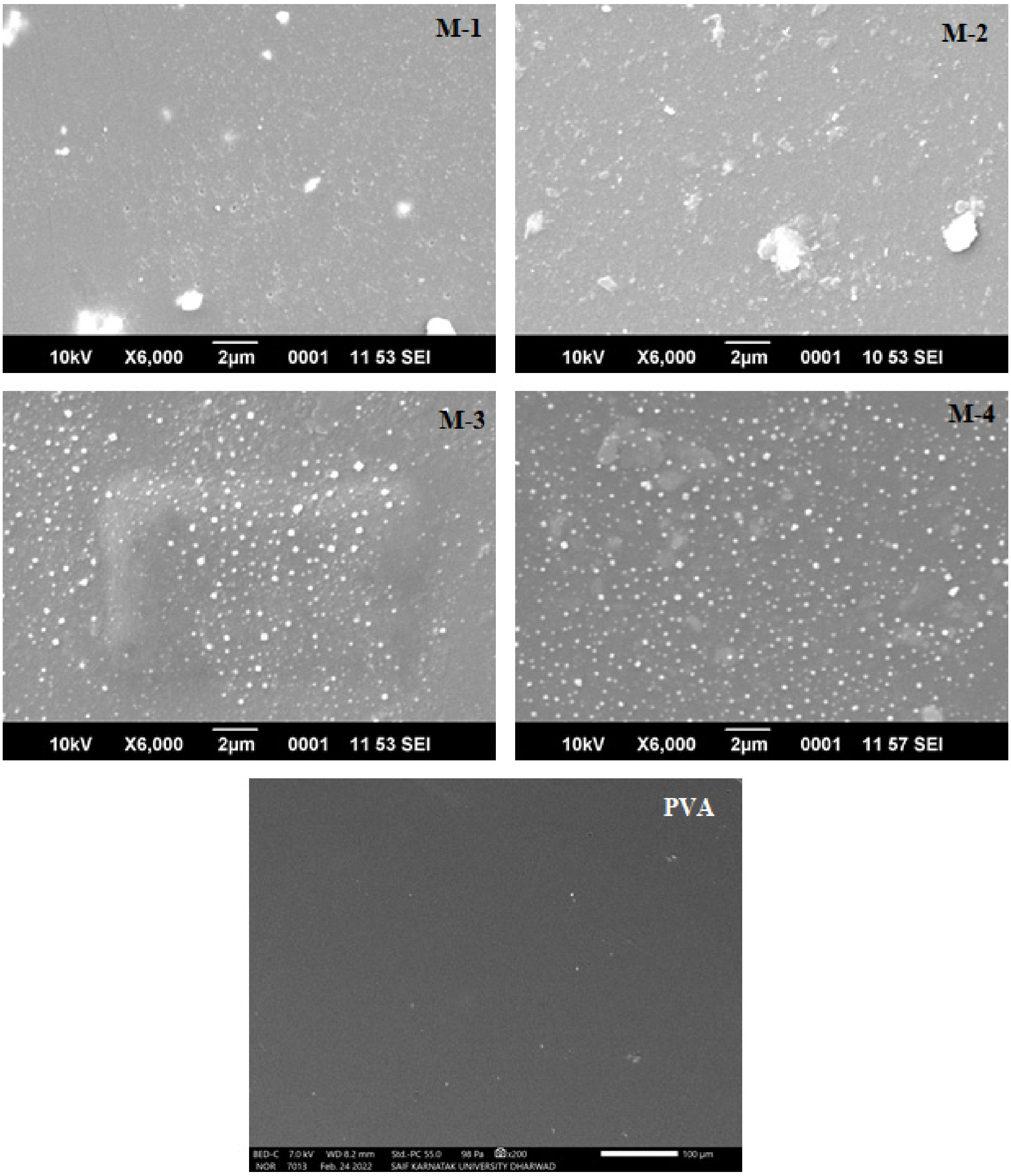


Figure 5. SEM micrographs of PVA and CS-capped AgNP-incorporated PVA hybrid membranes: (M-1) 0.5 wt.%; (M-2) 1 wt.%; (M-3) 1.5 wt.%; (M-4) 2 wt.% of CS-capped AgNPs.

2.1.6. Contact-Angle Analysis

Figure 6 shows the contact angles of PVA and CS-capped AgNPs embedded into PVA membranes. The contact angle of all the membranes was decreased with the increase in the CS-capped AgNP content in the PVA matrix. This demonstrated that incorporating CS-capped AgNPs in the PVA membrane increased the hydrophilicity of the hybrid membrane. This was due to the increased amount of different hydrophilic groups provided by the CS-capped AgNPs, mainly –OH, –NH and AgNPs. Moreover, the disturbance in the regularity of the PVA matrix structure results in lowering the crystallinity of the PVA and hydrogen-bonding network, thus enhancing the availability of the pre–OH groups in the membrane matrix. An increase in the hydrophilicity and decrease in crystallinity of the membrane increases the affinity for the water molecules. As a result, the developed membrane is more effective for pervaporation, especially for the dehydration of low-water-content ethanol [52]. The sorption analysis reflects these findings as well. This illustrates the membrane's improved water affinity with enhancement in the CS-capped AgNPs in the PVA membrane matrix.

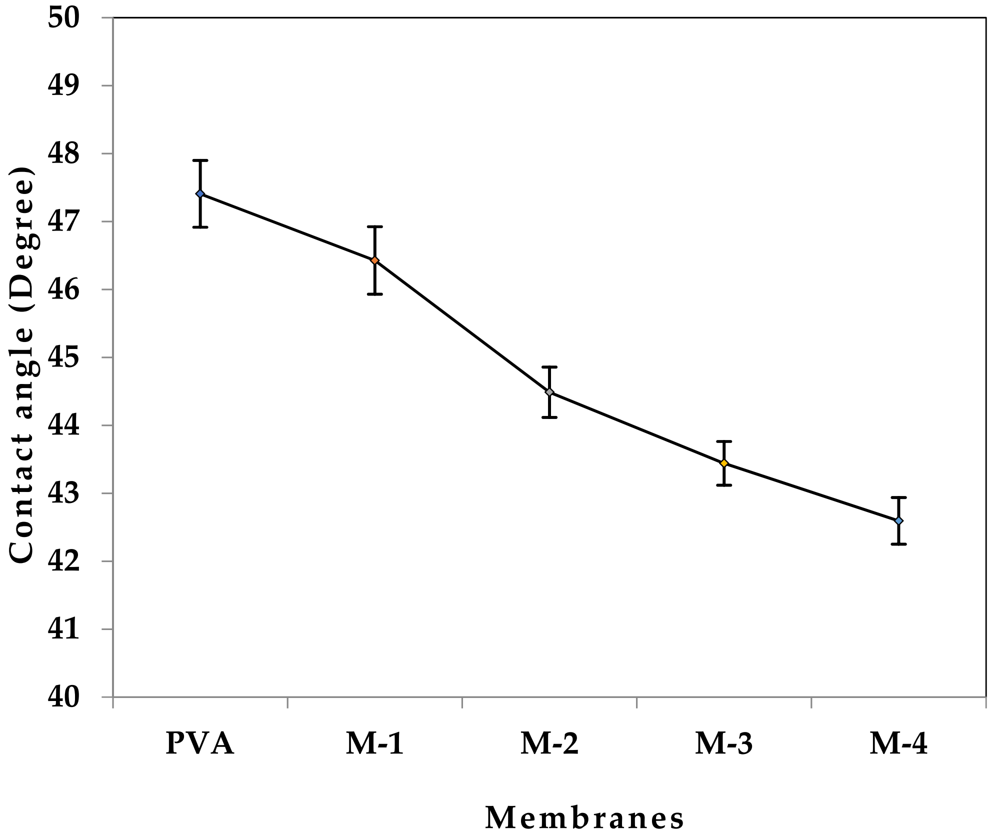


Figure 6. Contact angles of water for all the membranes at 10 s.

2.2. Effect of Amount of CS-Capped AgNPs on Membrane Swelling

Figure 7 shows the observed swelling level of the membranes. From the figure, the extent of swelling increased from membrane M-1 (0.5 wt.% CS-capped AgNPs) to M-4 (2 wt.% CS-capped AgNPs). This is because of the increased amount of different hydrophilic groups provided by the CS-capped AgNPs, mainly –OH, –NH and AgNPs in the PVA membrane matrix, which has a hydrophilic property. This leads to a higher affinity between the fabricated hybrid membranes and the H_2O molecules, and the percentage of the degree of swelling enhances. This enhanced hydrophilic nature of the fabricated hybrid membranes increases the efficiency of PV performance. These results are in line with the contact-angle results.

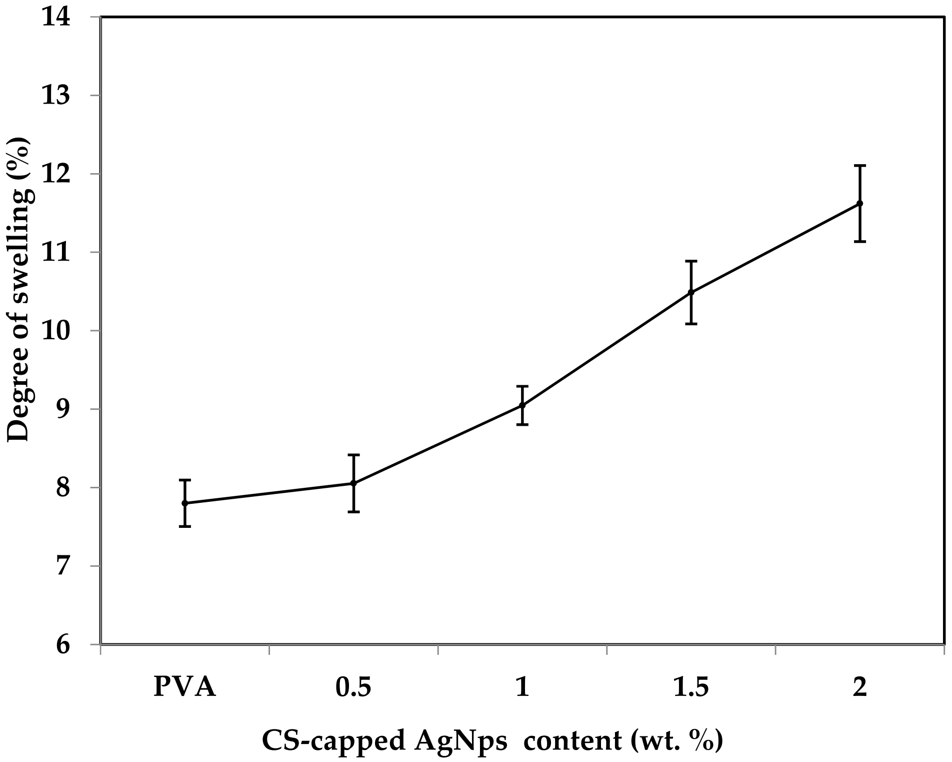


Figure 7. Effect of *CS-capped AgNPs* on membrane swelling degree.

2.3. Effect of Amount of CS-Capped AgNPs on Pervaporation

Table 1 shows the findings on the pervaporation performance of the fabricated hybrid membranes at various temperatures. As shown in the table, as the quantity of CS-capped AgNPs in the fabricated hybrid membrane increased, the separation selectivity, total permeation flux and permeance were also enhanced. In sorption studies, a similar pattern of increase was seen. The increase in total permeation flux was systematic. The M-4 exhibited the highest total permeation flux of 0.1240 ± 0.0020 kg/m^2 h at 30 °C. According to these results, the addition of CS-capped AgNPs improves the membranes' water affinity. AgNPs are responsible for increased polar nature and decreased crystallinity, which enhances the mechanism of diffusion through the membrane.

Table 1. Permeation flux, separation selectivity and permeance data of the developed membranes at various temperatures.

Membrane	**Temperature (°C)**	**J (kg/m^2 h)**	α_{Sep}	**P_i/l (GPU)**
M	30	0.0844 ± 0.0022	1557.67 ± 11.68	1688.00
	40	0.0891 ± 0.0015	1412.00 ± 8.00	1781.33
	50	0.0922 + 0.0010	1378.67 + 6.11	1843.33
M-1	30	0.0949 ± 0.0008	2238.33 ± 7.64	1897.33
	40	0.1030 ± 0.0010	2028.33 ± 6.51	2060.00
	50	0.1078 ± 0.0003	1912.00 ± 4.00	2155.33
M-2	30	0.1060 ± 0.0005	2425.67 ± 6.03	2077.28
	40	0.1083 ± 0.0005	2192.00 ± 5.29	2123.53
	50	0.1134 ± 0.0004	2045.67 ± 6.03	2222.88
M-3	30	0.1152 ± 0.0004	2807.33 ± 6.43	2259.48
	40	0.1211 ± 0.0005	2407.67 ± 7.64	2374.51
	50	0.1285 ± 0.0003	2258.00 ± 4.00	2519.61
M-4	30	0.1240 ± 0.0020	3612.33 ± 6.03	2384.62
	40	0.1310 ± 0.0036	2937.00 ± 6.24	2519.23
	50	0.1333 ± 0.0050	2449.67 ± 7.09	2564.10

GPU = gas permeation unit = 10^{-6} cc (STP)/cm^2/s/cm Hg.

The membrane's separation selectivity is mostly determined by the molecular size and free volume of the polymer-membrane matrix. The data revealed that separation selectivity was improved as the concentration of CS-capped AgNPs was increased. This is due to the increased amorphous regions in the membrane, which pilots the enhancement of the free volume of the polymer chains. Because of this, the diffusion of the water becomes easier compared to ethanol, owing to its smaller size. Further, polar groups such as –OH and –NH_2 present in PVA and chitosan, respectively, leading to the significant enhancement of hydrogen bonding and electrostatic force of attraction and makes the diffusion of water easier compared to the diffusion of ethanol. Because of the trade-off phenomenon, it is uncommon to see improvements in separation selectivity and total permeation flux. However, this work saw antitrade-off phenomena when CS-capped AgNPs were added to the PVA membrane matrix. A significant enhancement of both hydrophilicity and the amorphous nature of the membrane by incorporating CS-capped AgNPs overcame the trade-off phenomena.

Two-way ANOVA with replication was performed at a 95% ($\alpha = 0.05$) confidence level to see the effect of membrane type and temperature on permeation flux and selectivity, as represented in Table 2. Based on the p-value for membrane type ($p = 9.29 \times 10^{-29}$ & $2.23 \times 10^{-58} < 0.05 = \alpha$), temperature ($p = 1.76 \times 10^{-14}$ & $2.46 \times 10^{-48} < 0.05 = \alpha$), an interaction effect between membrane type and temperature ($p = 0.0432$ & $6.46 \times 10^{-40} < 0.05 = \alpha$) shows that the factors are statistically significant by rejecting the null hypothesis. To see the difference in means of the parameters between membrane type and temperature, a post hoc test using Tukey's HSD was performed after the two-way ANOVA. A Tukey test on membrane type showed a significant effect on total permeation flux and selectivity, as means between all membranes were higher than the mean critical of 0.002576 for total permeation flux and 9.3161 for selectivity, respectively. Similarly, temperature showed a significant effect on total permeation flux and selectivity, as means between all temperatures were higher than the mean critical of 0.001696 for total permeation flux and 6.132 for selectivity, respectively. However, the Tukey test showed no significant effect between membrane type and temperature for total permeation flux and selectivity.

Table 2. Analysis of variance for total permeation flux and selectivity vs. membrane type and temperature.

Source of Variation	Degree of Freedom (df)	Sum of Squares (SS)	Mean Squares (MS)	F	p-Value	F $_{\text{Crit.}}$
Total Permeation Flux						
Type of Membrane (M)	4	0.009358	0.002339	659.0334	9.29×10^{-29}	2.689628
Temperature(T)	2	0.000773	0.000386	108.8769	1.76×10^{-14}	3.31583
Interaction (M × T)	8	6.66×10^{-5}	8.33×10^{-6}	2.346156	0.043261	2.266163
Error	30	0.000106	3.55×10^{-6}			
Selectivity						
Type of Membrane (M)	4	11,681,129	2,920,282	62,906.99	2.23×10^{-58}	2.689628
Temperature (T)	2	2,077,327	1,038,663	22,374.27	2.46×10^{-48}	3.31583
Interaction (M × T)	8	890,847.7	111,356	2398.764	6.46×10^{-40}	2.266163
Error	30	1392.667	46.42222			

Figure 8 shows ethanol, water and total permeation flux as a function of CS-capped AgNP content. The graph clearly shows that the permeation flux curves of total and water overlap very closely. Ethanol, on the other hand, has a low permeation flux. The hydrophilicity and amorphous nature of the fabricated hybrid membranes confirm the nature of the curves.

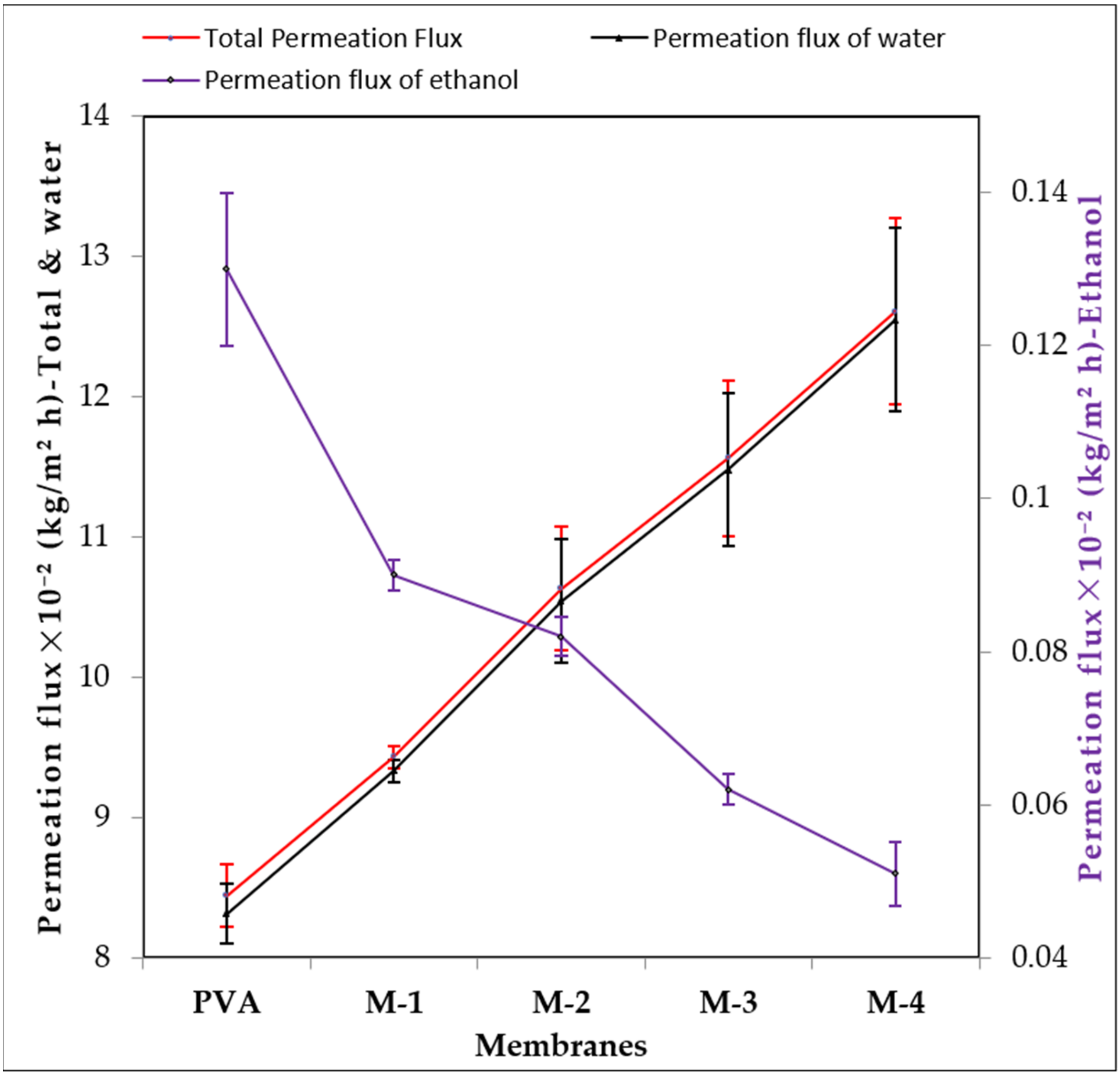


Figure 8. Deviation in total permeation flux and permeation fluxes of water and ethanol at 30 °C.

2.4. Effect of CS-Capped AgNPs on the Pervaporation-Separation Index (PSI)

The pervaporation-separation index (PSI) is the product of total permeation flux and selectivity, which characterizes the membrane-separation ability. This index can be used as a relative guideline for designing new membranes for the pervaporation-separation process and selecting a membrane with an optimal combination of flux and selectivity. To assess the overall performance, the calculated PSI data are plotted as a function of wt.% of CS-capped AgNPs for the azeotropic water-ethanol mixture (Figure 9). It is observed that the PSI values were increased regularly with increasing the CS-capped AgNPs content, signifying that the membranes with a higher amount of CS-capped AgNPs exhibited excellent performance for separation of the azeotropic water-ethanol mixture. This is attributed to the incorporation of CS-capped AgNPs into the PVA membrane matrix, which changes the hydrophilicity of the membranes and their amorphous nature, significantly influencing the diffusion process. Sorption is only the first step, but in the second step of diffusion, the properties of CS-capped AgNPs played a major role in enhancing the overall performance of the membrane.

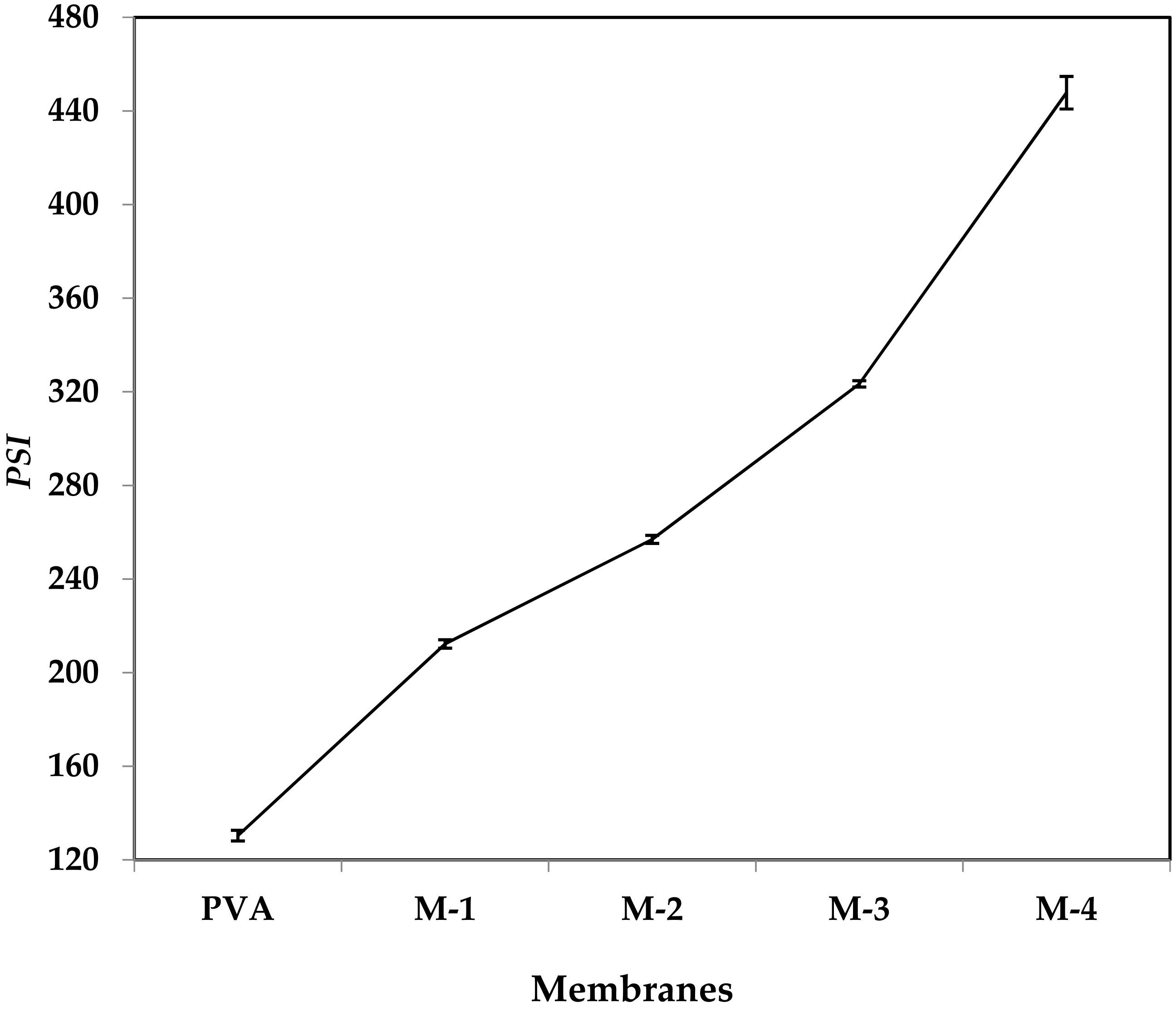


Figure 9. Effect of CS-capped AgNP content on PSI at 30 °C.

2.5. Effect of Temperature on Membrane Performance

The effect of operating temperature on the PV performance for the azeotropic water-ethanol mixture was studied for all the membranes, and the resulting values are presented in Table 1. It is observed that the permeation rate was found to increase from 30 to 50 °C for all the membranes while decreasing the separation factor noticeably. Higher temperature decreases the intermolecular interaction between permeants and decreases the intermolecular interaction within the membrane material, resulting in increased free –OH and $–NH_2$ groups on the membrane. These are responsible for predominating the plasticizing effect on the membrane due to greater swelling. Therefore, the permeation of diffusing molecules and the associated molecules through the membrane becomes easier, increasing total permeation flux while suppressing the selectivity.

3. Conclusions

In this study, new hybrid PVA membranes were prepared by incorporating different wt.% of CS-capped AgNPs for applications in ethanol dehydration from azeotropic water/ethanol mixtures. Increased CS-capped AgNPs content in the membrane matrix resulted in simultaneous permeation flux and selectivity increases. This was explained based on the significant enhancement of hydrophilicity and the amorphous nature of the membrane matrix. The PV separation-index data also indicates that the membrane incorporated with 2 wt.% CS-capped AgNPs (M-4) showed an excellent performance while separating the water-ethanol mixtures because of enhanced hydrophilicity and selective interaction between the membranes and permeate. The membrane M-4 showed the highest total flux ($12.40 \pm 0.20 \times 10^{-2}$ kg/m^2 h) and selectivity (3612.33 ± 6.03) at 30 °C for 10 mass% of water in the feed. Experimental data also revealed that total flux and water flux are almost overlapping for all the CS-capped AgNP-incorporated membranes, suggesting that the developed membranes have higher separation ability. The temperature effect study indicated that permeation flux was increased while decreasing selectivity when the operating temperature was increased. This is mainly because of decreased viscosity of permeating molecules.

4. Materials and Methods

4.1. Materials

The chemicals used in the current study are as follows: Poly (vinyl alcohol), PVA (MW = 85–124 kDa, DH = 86 to 89%), and Acetic acid (purity $\geq$ 99.5%) were purchased from s.d.fine Chemicals Ltd., Mumbai, India. Chitosan, CS (MW = 200 kDa; N-deacetylation degree 75–85%) and silver nanopowder (purity $\geq$ 99.5%, particle size < 150 nm) were purchased from Sigma-Aldrich Chemicals, St. Louis, MO, USA. Rectified ethanol (95.6 vol.%) from Godavari Biorefineries, Karnataka, India. Chemicals purchased were used without further purifications as they are reagent-grade chemicals.

4.2. Preparation of Chitosan-Capped Silver Nanoparticles

The purpose of fabricating CS-capped Ag nanoparticles was to improve the PVA membrane in terms of PV performance. The fabrication procedure was as follows: In 50 mL of water, 2 vol.% acetic acid and 1 g chitosan were added and mixed for 24 h at room temperature. A total of 0.25 g of AgNPs was combined in this homogeneous solution and agitated continuously for 24 h at 60 °C to generate a suspension of CS-capped AgNPs. This dispersion was then sonicated for 30 min at a constant frequency of 38 kHz in an ultrasonic bath (Grant XB6, Shepreth, Cambridgeshire, UK) to break up any possible silver-nanoparticle clumps.

4.3. Membrane Preparation

Poly (vinyl alcohol) (4 g) was dissolved in deaerated water (96 mL) and agitated at 30 °C for 24 h. Further, the solution was filtered, and the undissolved particles were removed. The solution was then gently spread out on a glass plate and allowed to dry for 72 h. The membrane was then carefully peeled away and labeled M.

The development of the CS-capped AgNPs-poly (vinyl alcohol) membrane was carried out according to the procedure mentioned ahead: To uniform PVA solution, a fixed amount of CS-capped AgNPs suspension was mixed and stirred for 24 h. The prepared mixture was then passed through a sonication process maintained at 40 kHz for 2 h for proper distribution of CS-capped AgNPs in the base matrix (PVA). The prepared solution was cast on a clean glass plate. The rest of the procedure is similar to the procedure followed for the fabrication of M. Known amounts (0.5, 1.0%, 1.5%, 2 wt.%) of CS-capped AgNPs were added, and the obtained membranes were named M-1, M-2, M-3 and M-4. The breadth of the fabricated membranes was measured with a thickness gauge at several locations with a precision of 2 μm. (Peacock dial thickness gauge). A constant thickness of 50 ± 2 μm was achieved. The scheme of the fabrication of CS-capped AgNP-incorporated PVA membrane is shown in Figure 10.

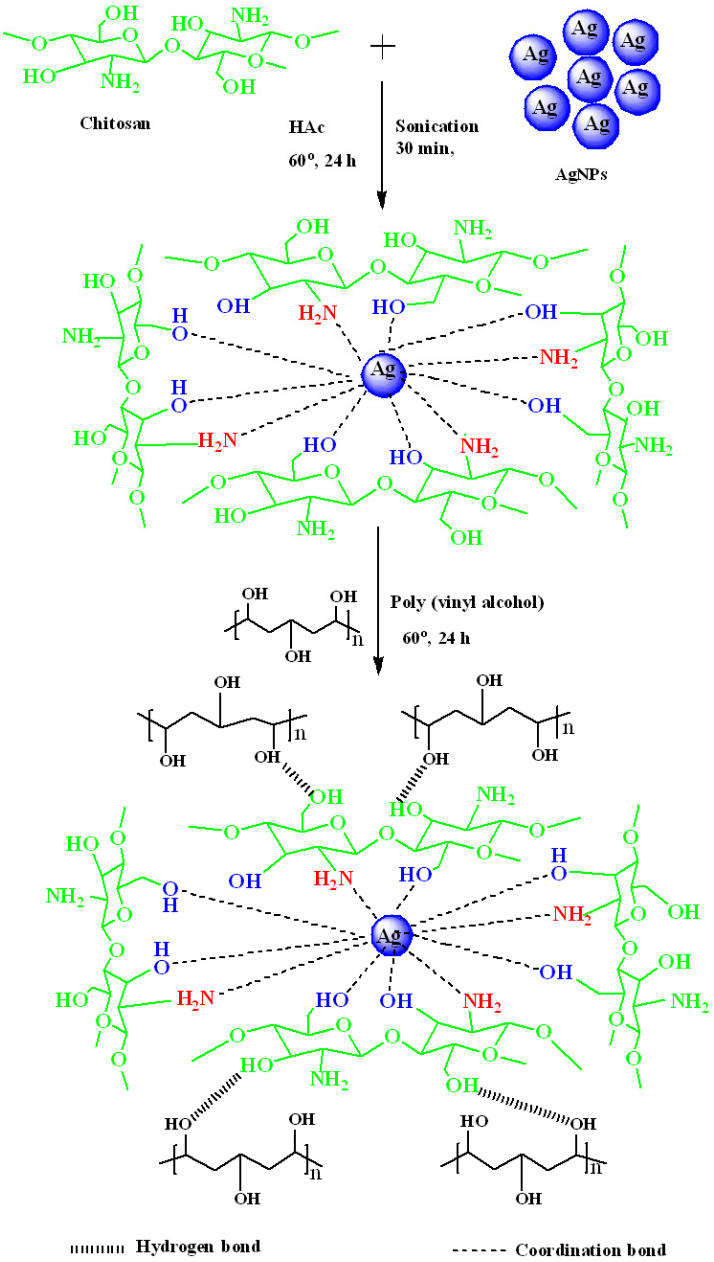


Figure 10. Scheme for the fabrication of CS-capped AgNP-incorporated PVA hybrid membranes.

4.4. Membrane Characterizations

The structural interactions between CS-capped AgNPs and PVA membrane were studied by Spectrum two with Diamond ATR Fourier transform infrared (FTIR) spectroscopy (PerkinElmer Pvt. Ltd., 28, Ayer Rajah Crescent, Singapore). FTIR analysis was recorded in the range of 500 to 4000 cm^{-1} and with a spectral resolution of 4 cm^{-1}.

A wide-angle X-ray diffractometer (Rigaku SmartLab SE, Tokoyo, Japan) was used to identify the solid-state morphology of the membranes developed. Ni-filtered CuKα radiation (30 mA) was used as an X-ray source, and a cathode current of 40 kV was applied. Samples of membranes in the range of 5° to 70° were scanned at the rate of 8°/min for the angle 2θ. Differential scanning calorimetry (DSC) measurements (DSC Q 20, TA Instruments, Waters LLC, New Castle, DE, USA) and Thermogravimetry analyzer (TGA) (DSC Q20, TA Instruments, Waters LLC, New Castle, DE, USA) was used for thermal analysis of the fabricated membranes. Scanning electron microscope (SEM) (JEOL-JSM-IT500, Tokyo, Japan) was used to study the surface morphology of the fabricated membranes.

In order to study the water affinity of the fabricated membranes at 30 °C, the contact angle was measured, employing a contact-angle meter named Acam-series, Apex Instruments Co. Pvt. Ltd., Kolkata, India. In order to further confirm the hydrophilic nature of the developed membranes, membrane-sorption analysis was conducted according to the procedure mentioned in the previous study [16].

4.5. Pervaporation Experiments

For PV experiments, a specifically designed PV apparatus was used, and the photographs of the PV unit are shown in Figure 11. The apparatus was equipped with a heating vessel of 145 mm in diameter with a volume of 3 L used to fill the azeotropic water-ethanol mixture. The tank was isolated from the external surrounding. Insulating material (glass wool) was used in the tank unit. A heater with a power rating of 2.5 kW was employed inside the feed tank to maintain the required temperature. A Pt-100 temperature sensor was also attached to the heater to measure a wide temperature range. Autotuning temperature controller called TC513BX was equipped to maintain the temperature. The membrane holder was made of AISI 304-grade stainless steel with a surface area of 15 cm^2. A circulation pump with adjustable speed was equipped on the feed side. A vacuum of 31.325 kPa was kept on the permeate side using a vacuum pump equipped with a pressure gauge (PN2299 pressor sensor with display). The pressure gauge was also equipped with a pressure sensor to maintain the system pressure constant. The stirrer was fixed in the feed container to keep the same temperature throughout the tank.

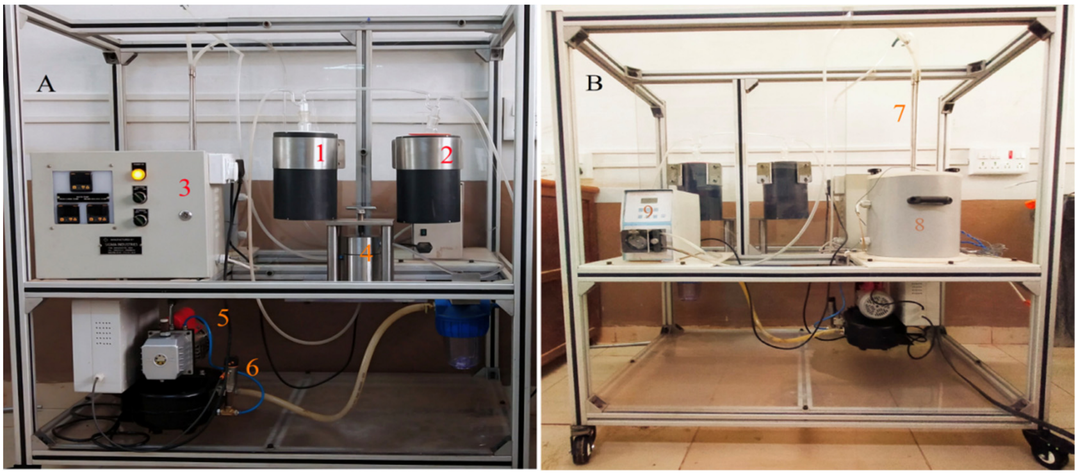


Figure 11. Photographic image of the pervaporation apparatus. (**A**) Front view: (1) permeate cold trap; (2) moisture cold trap; (3) control panel; (4) pervaporation cell; (5) vacuum pump; (6) vacuum control sensor. (**B**) Back view: (7) inlet and outlet of the feed tank; (8) feed tank; (9) circulation pump.

After the membrane reached equilibrium, a fixed vacuum was induced, and on the permeate side, the vapors were accumulated after condensation in the cold traps by inserting liquid nitrogen at uniform intervals. Subsequently, permeate weight was measured by using a digital microbalance, and the permeation flux was calculated. KAFI smart Karl Fischer Titrator measured the composition of the permeate. A minimum of 3 different readings were taken, and the mean value was considered for parameters such as permeation flux, selectivity and PSI. The PV performance of the fabricated hybrid membranes was analyzed by calculating the total permeation flux, separation selectivity and pervaporation-separation index (PSI) using the equations reported in the literature [16,53–57].

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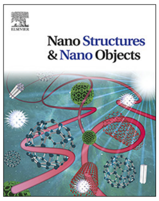

Preparation of bamboo-like carbon nitride nanotubes, spheres, and study of their structural, morphological and optical properties

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ABSTRACT

A large-scale bamboo-like carbon nitride nanotube powder has been prepared on Nichrome60 and quartz substrates at 800 °C by Chemical Vapor Deposition (CVD)-Pyrolysis technique using Triazine as a precursor. X-ray diffraction analysis indicates that the as-prepared powder contains a crystalline alpha carbon nitride (α-C_3N_4) structure with lattice parameters $a = 6.71$ Å, $c = 4.65$ Å and $c/a = 0.69$. The selected area electron diffraction (SAED) pattern, with three diffused circles, confirms the existence of the crystalline α-C_3N_4 phase. High-resolution TEM images depict carbon nanotubes possessing both even and uneven compartments in the nanotube. X-ray photoelectron spectroscopy confirms the presence of both sp^3 and sp^2 bonding between carbon and nitrogen atoms for the formation of the α-C_3N_4 structure. The calculated overall nitrogen content is 17 at. % which is far less than the expected value, but induces compartment formation. The optical bandgap (E_g) of the carbon nitride was evaluated and was found to be 5.5 eV. A mechanism is proposed for the formation of uneven compartment structures in the CNTs. Both even and uneven compartments containing carbon nitride nanotubes (CNNTs) could be ideal for developing hydrogen storage materials.

1. Introduction

Ever since Liu and Cohen predicted a new hard material that is comparable to diamond by replacing silicon with carbon in the β-Si_3N_4 structure, new challenges have opened in material science, chemistry and physics that offer a wide range of applications [1]. So far, five different crystalline structures of carbon nitride, namely α-C_3N_4, β-C_3N_4, cubic-C_3N_4, pseudocubic-C_3N_4 and graphitic-C_3N_4, have been proposed. Among these phases, except for graphitic-C_3N_4, all are predicted to be superhard materials [2]. Carbon nitride has attracted much attention due to its unique properties, such as high hardness, low density and friction coefficient [3], good chemical inertness, thermal stability, nonpoisonous nature and wide-bandgap [4]. Carbon nitride has a broad range of applications, such as optical, hydrogen storage [5], wear-resistant tribological coating [6], electrode in phase change materials [7], dielectric materials [8] and photocatalysis [9]. Apart from the above-mentioned properties, carbon forms multilayers on metals such as Ni and Fe, and under annealing conditions diffuses into metals. With this process, there would be a change in the structure of the metal and the product is useful in preparing magnetic materials [10,11].

There are extensive studies on the synthesis and characterization of hard carbon nitride to achieve phase pure crystals with a rich nitrogen atomic concentration using different techniques, such as ball milling [12,13], CVD-pyrolysis of nitrogen content precursors [14,15], arc-plasma jet chemical vapor deposition [16], solvothermal synthesis [17], ion implantation, microwave plasma-CVD, CVD and the hot melt synthetic reduction method [4]. Among all the above-mentioned techniques, a few techniques have claimed to be promising to prepare single or polycrystalline carbon nitride with less than the expected nitrogen content of 57 at. % for the stoichiometric C_3N_4. However, very few reports are available with annealing treatment to obtain better crystallinity and nanostructures [18]. Defects are inevitable in preparing C_3N_4 as it grows from different intermediates. Besides structural defects, intrinsic defects such as nitrogen and carbon vacancies are generated in carbon nitride. The difficulties in the synthesis of hard carbon nitride is the thermodynamical stability of carbon and nitrogen [18]. Another factor is the tendency for incorporation of a lower amount of nitrogen in the carbon nitride structure due to strong repulsion between nonbonded nitrogen atoms and the consequential partial replacement of C–C bonded dimers [19]. Nitrogen-doped carbon nanotubes with even less than 5.3 at. % show improvement in their photoluminescence

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when compared with pristine CNTs, with two peaks in the UV and blue light range, however, no clear peak shift is identified [20]. In addition, a report explains graphene with free radicals exhibits good magnetic properties. During nitrogen doping, nitrogen carries additional electron density to the pyridinic and graphitic positions which cause the diamagnetic features and magnetic states to disappear [21].

In this article, a bottom-up CVD-pyrolysis technique is adopted in the preparation of α-C_3N_4 phase with bamboo-like CNNTs using Nichrome60 ($Cr_{15}Ni_{60}$) and quartz as substrates. The precursor Triazine ($C_9H_{18}N_6$) is used as both a nitrogen and carbon source for the formation of bamboo-like carbon nitride nanotubes and spheres. The CVD-pyrolysis technique has not been explored much as yet for the production of carbon nitride nanotubes, at the same time, the technique is well suitable for large-scale production, with a low-cost fabrication process.

2. Experimental setup

Carbon nitride was deposited on Nichrome60 and quartz substrates by the CVD technique. The details of the CVD instruments and their specifications are discussed in previous reports [14]. Prior to the deposition process, the quartz substrates were cleaned as reported [14,15]. The cleaned Nichrome60 was rolled to get a spring-like structure and the quartz substrates were placed in between the Nichrome60 wire.

Triazine powder was placed at the bottom zone A of the quartz tube located at the center of the furnace and the substrates at zone B upstream at a fixed distance away from zone A [11]. The quartz tube was connected to a nitrogen (99.99% purity) filled bladder. The quartz tube was evacuated using a vacuum pump and then the nitrogen gas was purged into the quartz tube at least thrice to exhaust all other atmospheric gases present in the quartz tube. A certain amount of nitrogen gas was fed into the quartz tube to ensure an inert atmosphere growth. After this process, the substrates were heated up to the required temperature of 800 °C, stabilized after 60 min. Next, the zone A (precursor side) temperature was raised slowly to 700 °C. The precursor then dissociates into carbon, nitrogen and hydrogen species and deposits on the Nichrome60 and quartz substrates placed at zone B. The time for the growth of carbon nitride is about 60 min. Right after the growth step completed, the quartz tube was immediately taken out from the furnace and allowed to cool to room temperature. The whole process of growth is reported in previous studies [14,15] and work by Ramesh et al. [22–24]. The deposited carbon nitride on Nichrome60 was collected carefully and characterized with no further treatment, such as annealing or acid treatment to improve the crystallinity and remove metal particles respectively.

3. Results and discussions

3.1. XRD analysis

Fig. 1(a) shows the XRD pattern of the prepared carbon nitride nanotube powder. Table 1 lists the *d*-spacing values obtained from the SAED pattern and the XRD analysis, and the present experimental results are compared with the previous theoretical and experimental data. The strong and broad peak observed at a *d*- spacing of 3.32 Å indicates the reflection of α (110). The sharp and intense peak at a *d*-spacing of 2.03 Å belongs to α (211). Other peaks at 2.38, 2.06, 1.76, 1.46, 1.24 and 1.12 Å corresponds to the reflections of (201), (210), (202), (302), and (321) respectively of the alpha phase, though some of the *d*- spacing values match with the beta and graphitic carbon nitride phases. The presence of the graphitic phase is confirmed by a small broad peak at $2\theta = 54.30$, matching with graphitic carbon nitride, which is the most stable state among the carbon nitride phases and is a seed for α-C_3N_4 and other phases.

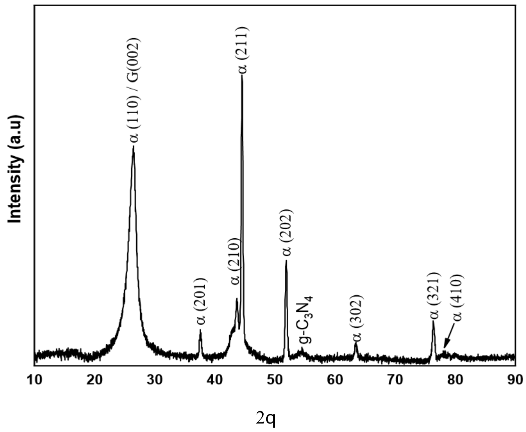

Fig. 1(a). XRD pattern of the carbon nitride (α-C_3N_4) nanopowder.

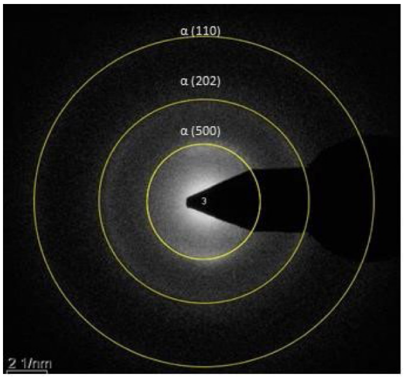

Fig. 1(b). SAED pattern of carbon nitride (α-C_3N_4).

The SAED pattern of the as-prepared carbon nitride nanotubes is shown in Fig. 1(b). Three diffraction rings are observed at 3.22, 1.8 and 1.12 Å, and match exactly with the α-C_3N_4 phase for reflections of the (110), (202), and (500) planes, respectively. Both the XRD and SAED *d*- spacing values confirm the existence of α-C_3N_4. To support this, the lattice constants values were calculated and these are a = 6.71 Å, c = 4.65 Å and $c/a = 0.69$. They agree with the reported lattice parameters as presented in Table 1. A comparison of the intensities and *d*- spacing values suggests the existence of α-C_3N_4 in the prepared nano-powder. The dominance of α-C_3N_4 over β-C_3N_4 implies that the alpha phase is thermodynamically more stable than the crystalline beta phase. A report is available on how to change the crystalline nature of CNTs to amorphous using 2 MeV protons irradiation [27].

3.2. FESEM and HRTEM analysis

The morphology of the as-prepared powder on a quartz substrate was investigated using FESEM. The microstructure of the carbon nitride nanotube was observed by using High-Resolution TEM. 2a shows the FESEM image of the CNNTs with sphere structures. The substrate Nichrome60 plays an important role in the synthesis of nanostructures. The highly reactive chromium acts as a catalyst for the growth of CNNTs and nickel assists the growth. The diameter of the CNNT lies around 90 nm and the length varies up to a few microns. Apart from CNNTs, carbon nitride spheres are also formed with a diameter of around 500 nm. The presence

Table 1
Comparison of the present experimental XRD and SAED data with those from previous reports. The lattice constants calculated from our data are: a = 6.71 Å, c = 4.65 Å, c/a = 0.69 for (α-C_3N_4).

Present report (α-C_3N_4)			S. Matusumoto [25]		Qiang Lv [17]		J.Wang [26]	
SAED (d (Å))	XRD d (Å)	hkl	d_{Theo} (Å)	hkl (α-C_3N_4)	d_{Exp} (Å)	hkl (α-C_3N_4)	d_{Theo} (Å)	hkl (α-C_3N_4)
3.22	3.34	(110)	3.23	(110)	3.23	110	3.23	110
	2.38	(201)	2.4	(201)	2.41	201	2.40	201
	2.07	(210)	2.1	(210)	2.12	210	2.11	210
	2.03	(211)	1.93	(211)			1.9	211
1.80	1.76	(202)	1.8	(202)	1.80	202	1.8	202
	1.46	(103)	1.51	(103)			1.5	103
	1.24	(321)	1.23	(321)	1.2	321	1.23	321
	1.23		1.2	410				
1.12		(500)	1.12	(500)				

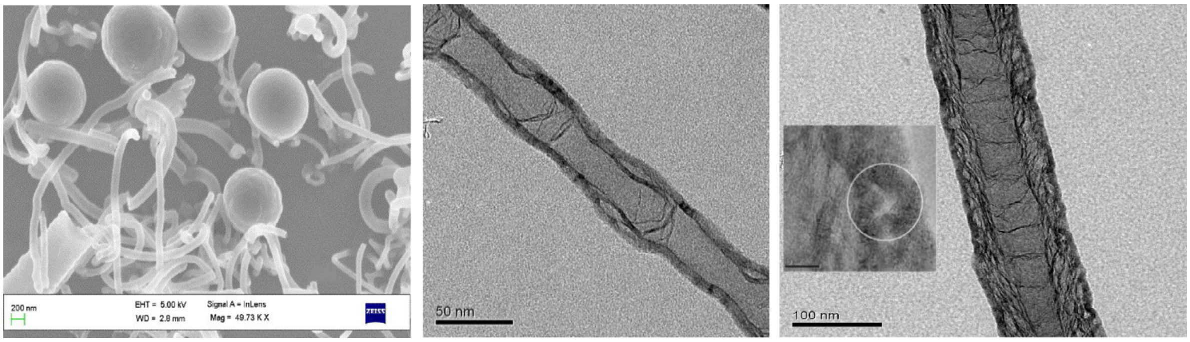

Fig. 2. (a) FESEM image of carbon nitride containing CNNTs and spheres. (b, c) HRTEM images of ultrafine bamboo-like CNNTs of α-C_3N_4 powder with different structures..

of carbon nitride spheres may be due to the carbonization process at high temperatures [28]. It is noticed that the nanotubes have open ends on both sides. HRTEM imaging (2b) confirms that the tube has uneven thin compartments rather than a complete hollow. The wall thickness varies from 30 nm to 38 nm with distortion within the wall (insert 2b) and the compartment size is not uniform. The HRTEM image (2c) shows the bamboo structured CNNTs having a wall thickness of 8 nm and the diameter of the tube is 36 nm with a 20 nm inner diameter. The distance between the compartments is around 90 nm and it is uniform.

There was no identification of any metal particles on or at the edges of the nanotube, though the substrate is a metal. From the literature, a uniform compartment is observed only for very thin wall CNNTs [29,30]. The uneven growth mechanism of CNNTs is not yet clear. The substrate is of an alloy nature and possibly it has different atomic arrangements and *d*- spacings. The carbon atoms as a network form a graphitic layer on the metal alloy particles (incoherent particles) at a high temperature. Therefore, the graphitic layer experiences dislocation due to atomic vibrations or movements. The graphitic layer starts growing up on incoherent particle face dislocations, causing defects at the walls of the nanotubes, and the introduction of nitrogen again reduces the system energy and forms transverse layers with uneven compartments. The uneven compartment formation occurring in CNNTs with a larger outer diameter, unlike the smaller diameter CNTs, indicates that particle size is higher due to incoherent large particles. For any metal catalyst to produce CNTs, it should be in a quasi liquid state with poor wettability against the carbon materials. Apart from the catalyst method, the solution process is also reported to produce nanotubes using an ionic self-assembly process, however nanotubes produced this way do not possess any special structures, such as compartments [31].

In the case of bamboo-like CNNTs with an even compartment, the growth mechanism can be explained as follows. The catalyst acts as a seed for the growth of hollow CNTs when the light element nitrogen atoms are introduced into the graphitic layer, which tends to reduce the system energy and causes the bending of the graphene layers to form a transverse layer. This process forms compartment containing CNNTs rather than hollow CNTs. The distance between compartments mainly depends on the nitrogen atomic concentrations [5,30]. With an increase in the nitrogen percentage, the crystallinity and the compartment length are decreased. Also, no transverse layer is observed out from the CNNT's wall.

Selected-area electron diffraction (SAED) patterns of CNNTs displayed three weakly diffused rings, as shown in Fig. 1(b). From the diffused three circled rings, the *d*- spacing was calculated and discussed in the structural analysis section.

3.3. X-ray photoelectron spectroscopy

The nature of the bonding between the carbon and nitrogen atoms as well as their atomic ratio were obtained using X-ray photoelectron spectroscopy. Fig. 3 shows an XPS survey spectrum of the prepared carbon nitride powder. The XPS spectrum shows a pronounced C *1s* peak, along with N *1s* and O *1s* peaks. There are no traces of other peaks to represent chromium and nickel. The O 1s peak arises mainly from physically adsorbed oxygen, since graphitic carbon is known to be susceptible to oxygen adsorption even at low pressures (10^{-8} to 10^{-10} Torr) [32].

The core-level spectra of C *1s* and N *1s* for carbon nitride powder are shown in Figs. 4(a) and 4(b) respectively. The core spectra of carbon and nitrogen were deconvoluted using Gaussian peak fit into various lines and are associated with different binding energies. As the nitrogen atoms intercalate into the carbon network, this induces charge transfer from low electronegative carbon atoms to the more electronegative nitrogen atoms. This process causes the binding energy of carbon to shift to a higher energy state.

Whereas, the nitrogen core spectrum shows charge transfer from nitrogen to carbon. As a result, the nitrogen binding energy decreases to lower binding energies.

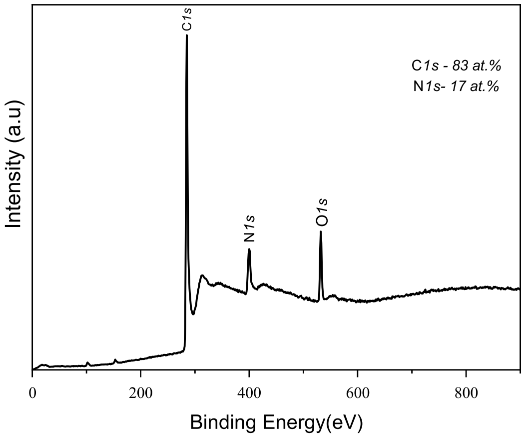

Fig. 3. XPS wide spectrum of the carbon nitride (α-C_3N_4) powder.

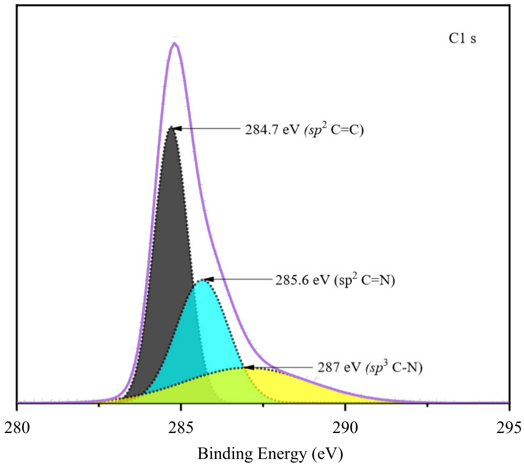

Fig. 4(a). Deconvoluted core spectrum of C-1s.

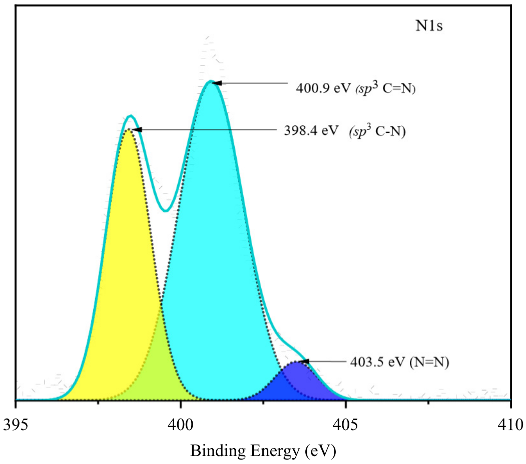

Fig. 4(b). Deconvoluted core spectrum of N-1s.

The carbon peak was deconvoluted into three major peaks. The first and sharp peak at 284.7 eV is due to the presence of adventitious carbon or unreacted carbon, which appears for any carbon containing compounds with an sp^2 bonding state [33,34]. Another carbon peak at 285.65 eV is due to carbon associated with nitrogen via sp^2 bonding [4]. The small and broad peak at 287 eV indicates the existence of sp^3 bonding between carbon and nitrogen as the primary bonding for the formation of α or β-C_3N_4 structure [35,36].

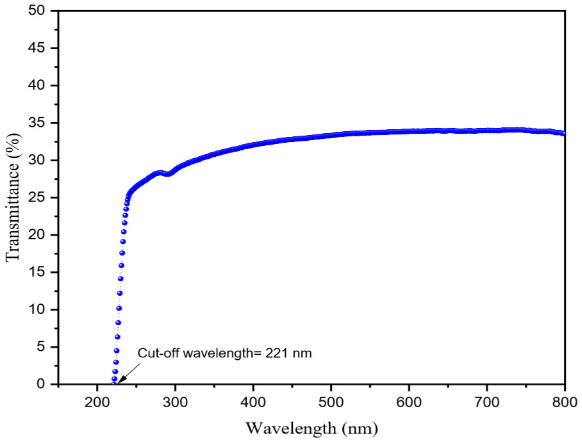

Fig. 5(a). UV–Visible–IR transmittance spectrum of α-C_3N_4.

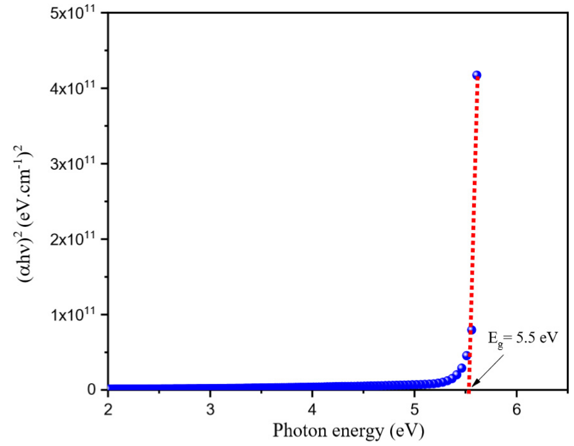

Fig. 5b. Optical bandgap of α-C_3N_4 ($(\alpha h\nu)^2$ vs. photon energy (hv)).

The deconvoluted core-level spectrum of nitrogen shows three peaks at 398.4, 400.9 and 403.5 eV. The higher binding energy at 403.5 eV corresponds to the N=N bond [37]. The lower binding energy peaks at 400.9 and 398.4 eV are due to electron exchange between carbon and nitrogen, from sp^2 and sp^3 bonding, respectively [4,34,38]. The binding energy at 398.4 eV originates from the C-N bond, the only type expected in α or β-C_3N_4 phases. The core spectra of carbon and nitrogen bonding indicate no sp^1 bonding state between carbon and nitrogen, and therefore confirm the formation of a good organic structure.

The atomic percentages of carbon and nitrogen were calculated using the nominal formula [12]. The overall carbon and nitrogen contents are 83 and 17 at. % respectively. As carbon and nitrogen are much more stable and the pyrolysis temperature is high, this causes a reduction in the nitrogen percentage, which is less in the prepared nanostructures [39].

3.4. UV-visible spectroscopy

The optical properties of the prepared carbon nitride were investigated using UV–Visible–IR spectroscopy. The optical bandgap of the α-C_3N_4 phase can be predicted to be in the range between 3 and 7 eV, as a wide bandgap material [4]. The carbon nitride spheres and CNNTs containing the quartz substrate film has been used to investigate the light transmittance behavior. Fig. 5(a) shows the transmittance of a film, ranging from 30 to 35% in the 300 to 800 nm wavelength range. The cut-off wavelength occurred at 221 nm and the optical bandgap is estimated to be 5.5 eV, as shown in Fig. 5b. The bandgap was calculated using the Tauc plot method and is equal to the G_oW_o calculation made by Shang-Peng Gao of 5.49 eV for α-C_3N_4 [40]. Previous experimental reports show a maximum bandgap of 4.38 and 4.13 eV for α and β-C_3N_4 mixed phases and β-C_3N_4 respectively [4,41]. After a very careful literature survey, the present work shows an indirect optical bandgap of 5.5 eV, which is higher than the previous experimental reports.

4. Conclusion

This study facilitates the simple and cost-effective preparation of crystalline carbon nitride with nanostructures such as bamboo-like carbon nitride nanotubes (CNNTs) with even and uneven compartments, and carbon nitride spheres using an organic compound by CVD on Nichrome60 and quartz substrates. Both SAED and XRD analyses confirm the existence of α-C_3N_4 and their *d*-spacing values match the reported theoretical and experimental results. The XPS analysis confirms that a significant amount of hexagonal networks of tetrahedral-bonded C atoms (sp^3) are connected to trigonal N atoms (sp^2) for the formation of crystalline α-C_3N_4. A comprehensive study has been performed to characterize the inner structure of the nanotubes. It was found that the carbon nitride nanotubes have both even and uneven compartment structures with open ends on both sides. This open end has many graphitic layers, which could be useful in field emission applications. The bamboo-like CNNTs have a porous structure, open-ended graphitic layers and edges along with nitrogen, which helps in the hydrogen adsorption and desorption process. So, it could be useful as a hydrogen storage material. The nitrogen percentage of the prepared powder is around 17 at. %, which is far less than the expected value of 57 at. %, however, the prepared carbon nitride shows the presence of α-C_3N_4. The calculated optical bandgap is 5.5 eV, which is the largest bandgap reported experimentally for α-C_3N_4 to date.

CRediT authorship contribution statement

R. Venkatesh: Conceptualization, Methodology, Investigation, Data curation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Prashantha Murahari:** Investigation, Data curation, Writing – review & editing. **N.R. Banapurmath:** Writing – review & editing. **K. Ramesh:** Conceptualization, Methodology, Investigation, Data curation, Validation, Writing – original draft, Visualization, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Growth of spherical carbon nitride with crystalline alpha and beta phases

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ABSTRACT

Carbon is a versatile element, and its allotropes play a center role in both science and technology. Further, doping of nitrogen into carbon network has been of great interest as it leads to superior properties such as chemical, mechanical and electronic properties. Though the preparation of ultrahard β-carbon nitride remains challenging one, it owes great attention due to its superior properties. This work reports preparation and characterization of crystalline carbon nitride on silicon (100) substrate. The X-Ray diffraction revealed that the deposited film- have α and β carbon nitride crystalline phases. The calculated lattice parameters are found to be $a = 6.26$ Å, $c = 2.38$ Å for β-C_3N_4 and $a = 6.8$ Å, $c = 4.6$ Å for α-C_3N_4. The X-Ray photoelectron spectroscopy study confirms that carbon atom is bonded tetrahedrally (sp^3) with nitrogen atoms as expected for the formation of crystalline C_3N_4, and also the presence of $C = N$ trigonal (sp^2) bond. The surface morphology of the film examined by field emission scanning electron microscopy shows the formation of carbon nitride spheres.

1. Introduction

In 1989, Liu and Cohen reported a local density approximation pseudopotential calculation on hypothetical beta carbon nitride (β-C_3N_4) by replacing silicon atom from β-Si_3N_4 structure. The β-C_3N_4 structure consisting of tetragonally bonded sp^3 carbon and trigonal planar sp^2 nitrogen that have short bond length (1.47 Å) and strong bonds with low ionicity (7%), which leads to extreme hardness comparable or greater than that of diamond. The prediction of ultrahard β-C_3N_4 received an immense attention among research community [1]. A considerable research on theoretical and experimental carbon nitride reveals properties such as high hardness, variable bandgap, chemical inertness, high thermal conductivity, and low friction coefficient [2, 3]. All these unique properties make carbon nitride suitable for wide range of applications such as cutting tool, heat dissipative substrates, wear resistant hard coatings [4], photocatalytic agent [5] etc.

Different techniques have been employed to prepare crystalline carbon nitride (C_3N_4) thin films and powders with expected stoichiometric ratio of 1.33. However, due to strong repulsion of nitrogen to the nitrogen in the C–N containing bonds lead to a lower nitrogen content than the expected 57 at.% of Nitrogen [6]. Till now, most of the reports show only a small amount of crystalline carbon nitride embedded in the amorphous matrix [7]. Also, the prepared crystalline carbon nitride samples contain nanostructures such as carbon nitride nanotubes [8], hexagonal crystalline rods [9], fullerene like [10], nano-onion [11], nanoflake [5] and spherical nanospheres [12]. Among, these structures, the fullerene like carbon nitride called as “super hard rubber” shows extreme elasticity and high resistance against plastic deformation. This superior resiliency with low coefficient of friction could be a promising material for the wear resistant coatings when compared to DLC (diamond-like coatings) and amorphous CN_x [13].

In the present work, Triazine (C9H18N6) was used as a precursor since it has the required bonding between carbon and nitrogen for the formation of carbon nitride. For the film preparation, nitrogen gas was used as inert atmosphere and carrier gas. The prepared film was analysed for the nanostructure formation, elemental composition and subsequent bonding occurring between elements.

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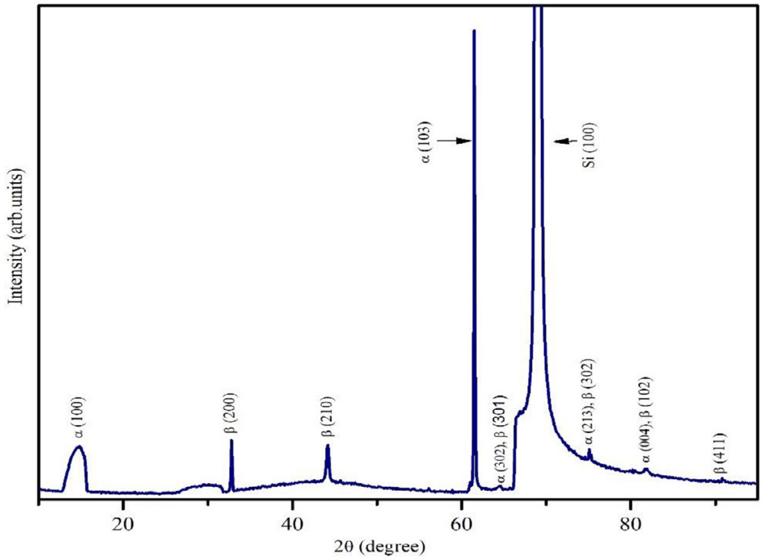

Fig. 1. XRD pattern of the as-deposited carbon nitride film on Si (100) substrate.

2. Experimental details

Carbon nitride film was deposited on silicon (100) substrate by pyrolysis assisted chemical vapor deposition (PVCD) using a two-zone furnace. The experimental setup and the details concerning deposition are reported in our previous work [14]. Triazine ($C_9H_{18}N_6$) powder of 96% purity procured from Sigma Aldrich was used as the precursor. About 0.5 g of the precursor was transferred to closed end of the quartz tube. The oxide layer on the surface of Si was removed by immersing in Hydrofluoric acid for 1 min and washed with deionized water thrice. After that the substrate was cleaned ultrasonically using solvents such as acetone and isopropanol bath. Then the substrate was dried and cleaned with high pure (99.999%) nitrogen gas before loading into the pyrolysis zone. The quartz tube was also purged by the high pure N_2 gas, and evacuated thrice before deposition. After this procedure, the quartz tube was filled with nitrogen gas and then the setup would be ready for the deposition process. Initially temperature of the pyrolysis zone was increased to 800 °C and the temperature was controlled and stablished using a PID temperature controller. Then the temperature of the precursor zone was slowly increased to 400 °C at a rate of 2 °C/min even though the boiling temperature of the precursor is 175 °C. The triazine then would evaporate and dissociates into carbon, nitrogen and hydrogen species entering the pyrolysis zone; and then, deposits on the silicon substrate maintained at 800 °C. After 60 min of deposition, the furnace was allowed to cool down to room temperature. The deposited carbon nitride film was found to well adhered to the crystalline silicon substrate.

The crystal structure of the film was determined by XRD ((Rigaku, Cu K_α radiation ($\lambda = 1.54$ Å)). The optical spectroscopic analysis probed using Raman spectroscopy (LabRAM HR) using visible wavelength of 514 nm and CCD detector at room temperature. The nature of the bonding between the elements were analyzed using XPS (AXIS ULTRA, monochromatic X-ray source (Al Kα, 1486.6 eV, line width 0.5 eV, under a vacuum environment of 2×10^{-9} Torr) and the surface morphology features were investigated by FESEM (Gemini Ultra 55).

2.1. XRD analysis

The XRD pattern of the as-prepared film given in Fig. 1 clearly displays the presence of sharp peaks with considerable background and humps indicating the presence of both the crystalline and amorphous nature. The obtained XRD result is compared with previously reported theoretical and experimental results, as listed in table 1. Peaks observed at d-spacing of 5.92, 2.73, 2.05, 1.50 and 1.08 Å are indexed to carbon nitride of α (100), β (200), β (210), α (103) and β (411) respectively. Other d-spacings at 1.44, 1.26 and 1.17 Å show mixed phase of α and β-C_3N_4 as mentioned in the table 1. A very strong peak observed at $2\theta = 61.56$ corresponds to α-C_3N_4 (103). The secondary phase strong peak observed at $2\theta = 44.20$ (2.05) corresponds to (210) of β- C_3N_4. Apart from sharp peaks, the presence of broad humps clearly illustrates the presence of amorphous matrix in the deposited film**.** The amorphous carbon nitride is the starting material and the application of temperature induces the formation of more tetrahedral bonded crystalline carbon nitride [1]. The prepared film shows the presence of both α and β phases as the total energy for α-C_3N_4 is lower than for β phase and differs only by 277 meV/ unit cell [15].

The calculated lattice parameters for β-C_3N_4, $a = 6.26$ Å, $c = 2.38$ Å and $c/a = 0.38$; and for α-C_3N_4, $a = 6.8$ Å, $C = 4.6$ Å and $c/a = 0.67$. The calculated parameters are in close agreement with previous reports [19, 20]. There is no peak observed for graphene or diamond phases of carbon allotropes. A high intense sharp peak at $2\theta = 69.5$ is due to silicon (100) substrate and no other evidence for the formation SiC, SiN and SiCN found.

2.2. FESEM

The surface morphology features of the prepared carbon nitride film was obtained by FESEM. The FESEM images show the formation of spherical structures with branches. The size of the spheres ranges from nanometer to micron as shown in Fig. 2. Initially, the dissociated carbon and nitrogen species from the precursor side travel and deposits on silicon substrates maintained at 800 °C in the pyrolysis zone. All the carbon atoms with sp^2 bonding nature form hexagonal rings and grow as basal planes on the substrate. The upcoming nitrogen atoms incorporated into the hexagonal network of carbon basal planes, changes the carbon-sp^2 to reactive carbon sp^3 sites. This reduces the barrier energy for the formation of pentagon structures which leads to the curvature of basal planes of graphene sheets. This process could ultimately evolve as a spherical structure. An illustration of basal plane formation and curvature induced in the basal planes to spherical structure formation are depicted stepwise in Fig. 3. Carbon sites adjacent to

Table 1
d-spacing and hkl values from the present work compared with the values reported in the literature.

S. Matsumoto et al. [16]				J. Wang et al. [8]		Yin et al. [17]		D.J. Johnson et al. [18]		Present work		
β-C_3N_4		α-C_3N_4		β-C_3N_4		β-C_3N_4		α, β-C_3N_4		α, β-C_3N_4		
d (Å)	hkl	d (Å)	hkl	d (Å)	hkl	d (Å)	hkl	d (Å)	hkl	d(Å)	hkl	Phase
5.54	100	5.600	100	–	–	–	–	–	–	5.92	100	α-C_3N_4
2.77	200	2.800	200			2.765	200	2.70	200	2.73	200	β-C_3N_4
2.095	210	–	–	2.069	(210)	2.09	210	2.043	210	2.05	210	β-C_3N_4
1.538	310	1.512	103	–	–	–	–	1.499	310	1.50	103	α-C_3N_4
1.465	301	1.463	302	1.465	(301)	1.46	301	1.423	301	1.44	mixed phase	α (302), β (301)
1.272	302	1.261	213	–	–	1.27	320	1.263	311	1.26	mixed phase	α (213), β (302)
1.175	102	1.177	004	1.197	(002)	1.175	102	–	–	1.17	mixed phase	α (004), β (102)
1.08	411	–	–	–	–	1.10	002	–	–	1.08	411	β (411)

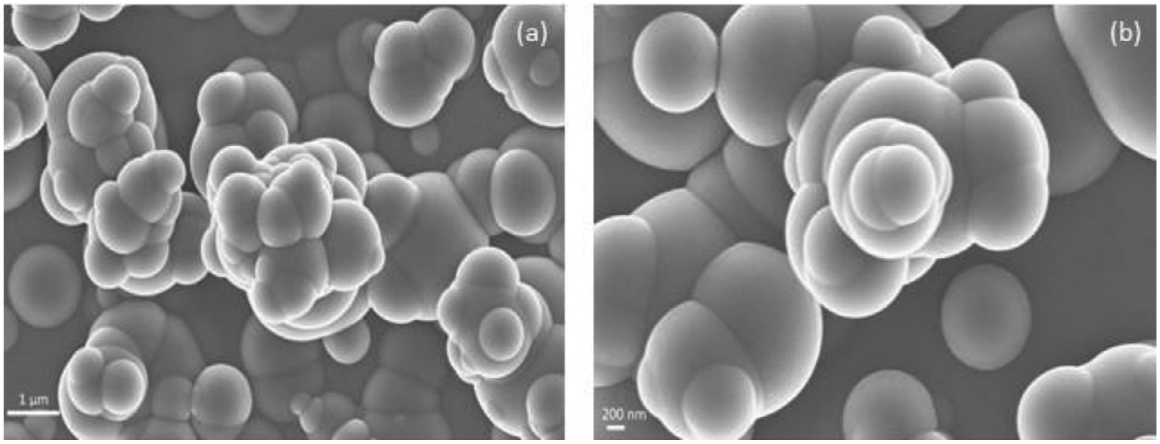

Fig. 2. FESEM images of the carbon nitride spheres prepared at 800 °C with different magnifications are (a) 1 μm and (b) 200 nm.

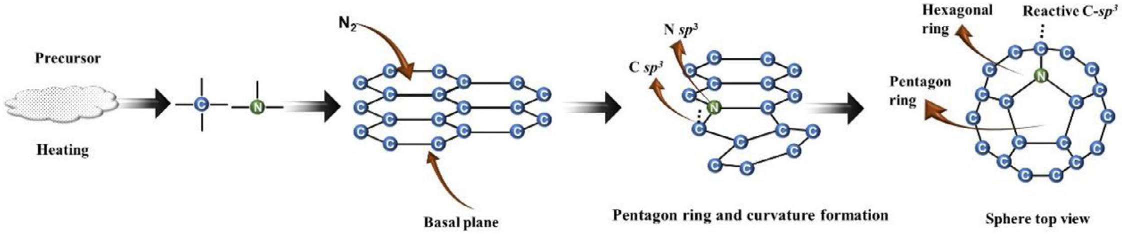

Fig. 3. Possible representation of the formation of basal planes, nitrogen substitution and pentagon formation, induction of curvature and formation of spherical structure respectively.

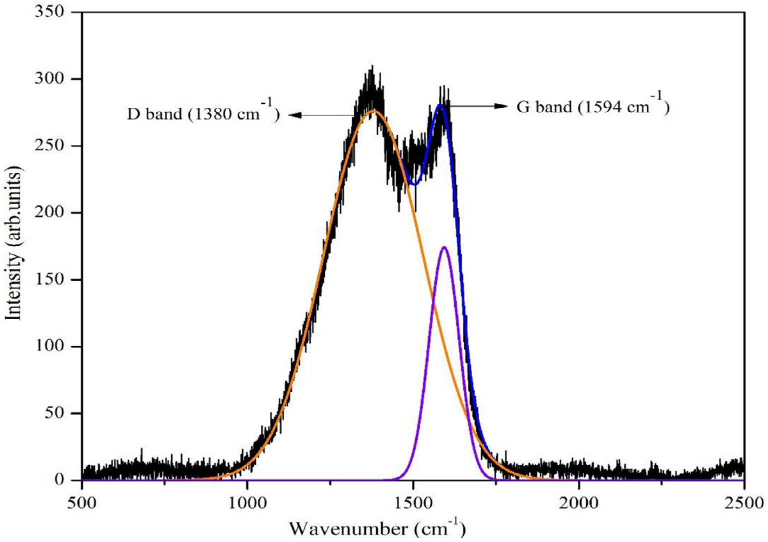

Fig. 4. Raman spectrum of the carbon nitride thin film on silicon substrate.

nitrogen are highly reactive. These reactive sites can directly bond with the already formed adjacent domes of a spherical structure. These spherical structures which are already present can also act as nuclei for the growth of new spheres. The spheres grow vertically up and their size and growth decreases as they grow vertically up from the substrate. This implies that the nucleation started from the substate covers a greater number of carbon and nitrogen molecules, and consequently, grow wider compared to that of the top. These domes grow vertically from the substrate and perpendicular from the initial dome, thus form microscopic tree like structures [11, 13]. The cross-sectional measurement gives a thickness value of about 2 micrometer for the film matrix above which nanostructures are grown.

2.3. Raman spectroscopic analysis

Fig. 4 shows the Raman spectrum measured between 500 cm^{-1} and 2500 cm^{-1} for the carbon nitride thin film deposited on silicon substrate. The appearance of D and G band are the fingerprints of any carbon material. The spectrum shows the presence of D (1380 cm^{-1}) and G (1594 cm^{-1}) band as observed in previous reports [14, 15].

The observed peaks are analogous to amorphous carbon (D band (1360 cm^{-1}) and G (1575 cm^{-1})) signal of Raman spectrum [21]. The incorporation of nitrogen into the carbon matrix makes shift in the peak positions and broadening of the peaks. The shift of the G band above 1580 cm^{-1} indicates an increase in the crys-

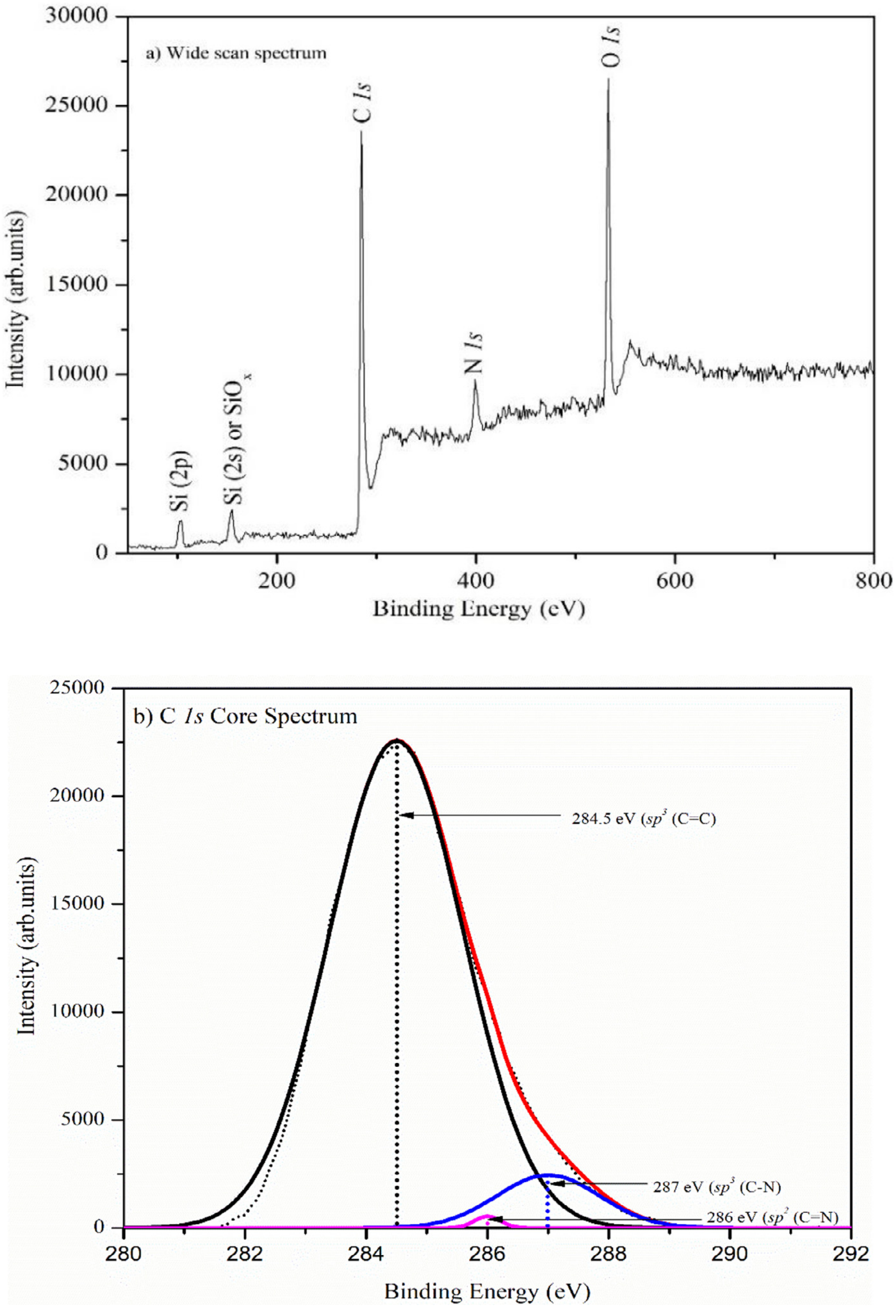

Fig. 5. X-Ray photoelectron spectra of the carbon nitride thin film on Si substrate, a) Wide scan spectrum, b) Carbon 1 s core spectrum and c) Nitrogen 1 s core spectrum.

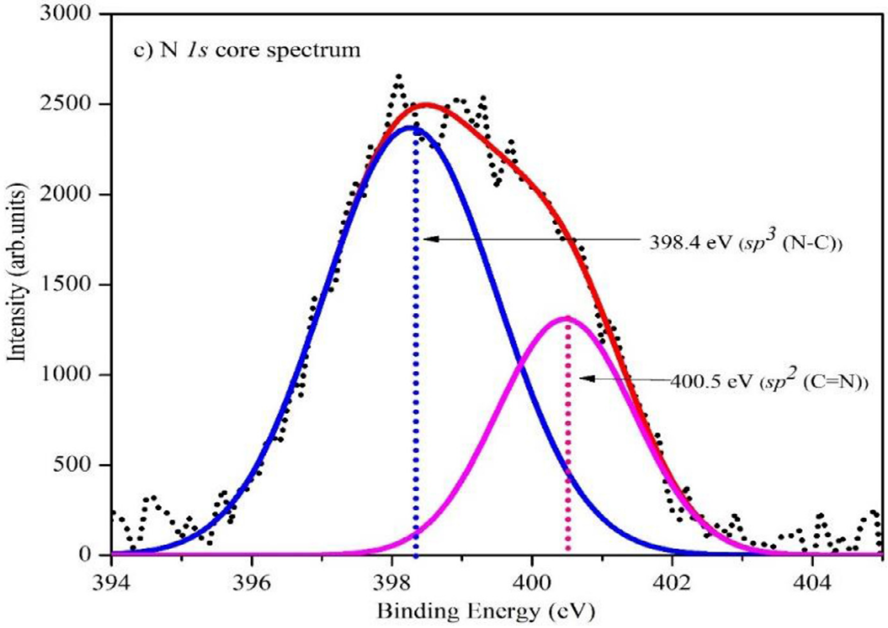

Fig. 5. Continued

tallinity of the film. The shift of the D band indicates an increase in the number of sp^3 bonds between carbon and nitrogen [22]. The increased FWHM of D band is 355 cm^{-1} clearly indicates that the sp^3 bonded C–N crystallites are embedded in the amorphous sp^2 bonded $C = N$ [23]. All these observations favor the formation of crystalline C_3N_4. The calculated intensity ratio of I_D/I_G value is 1.5 indicates the possibility of growth of the large number of microdomains of sp^2 bonded carbon nitride [24].

Theoretically, the Raman vibration frequencies for beta and alpha carbon nitride are calculated using Hooke's law since tetrahedrally bonded C–N is similar to Si-N [25]. However, very rarely Raman peaks have been observed for crystalline carbon nitride phases prepared experimentally [9, 26-28]. Most of the prepared crystalline samples showed pattern similar to amorphous carbon in Raman spectra [29, 30]. From these reports, it is understood that still there are no tentative or universally accepted Raman peaks available even though there are a few reports with Raman peaks apart from D and G peaks for carbon nitride.

2.4. XPS analysis

X-ray photoelectron spectroscopy is employed to identify elements present, composition, and the chemical bonding states of the elements in the thin film developed. Fig. 5(a) shows the wide spectrum of the film. The wide spectrum shows that the thin film contains carbon, nitrogen, oxygen and traceable amount of Si (2p) and Si (2 s) or SiO_x due to the substrate effect. The intense peak of oxygen is due to air exposure of the film [31]. The inclusion of nitrogen into carbon matrix induces charge transfer from less electronegative carbon atoms to high electronegative nitrogen atoms. Consequently, the electron density in the carbon atom reduces and moves towards higher binding energy and replace the homopolar bonds (C–C) with heteropolar bonds (C–N) [7]. It is very essential to identify the types of bonding state of nitrogen to carbon and also to estimate the N/C ratio of the film and phases. The XPS of the core spectra of carbon and nitrogen are most effectively deconvoluted as a sum of two Gaussian components. The deconvoluted C 1 s spectrum is comprised of two peaks (Fig. 5(b)). The major peak at 284.5 eV [32] is originating from sp^2 bonding of $C = C$. The peak centered at 287 eV [5] with low intensity is due to the presence of sp^3 bonded of C–N bonds which is reported to be the source for the formation of β-C_3N_4. The low intensity peak at 286 eV is identified as originating from sp^2 bonding ($C = N$) [32-34]. Another core spectra N1s is shown in Fig. 5(c), is deconvoluted into two peaks centered at 398.4 eV [14, 35] and 400.5 eV [35] which are identified to be originating from sp^3(N–C) and sp^2 ($C = N$) bonding respectively. Those binding energies obtained from those two species at 287 eV and 398.4 eV are favorable for the formation of crystalline α/β-C_3N_4. Apart from sp^2 and sp^3, the binding energy corresponds to sp^1 bonding between C and N is not observed and none of the Si-C and Si-N bonding formation is observed.

The atomic fraction of nitrogen ($f = N/[N + C]$) in the sp^3 bonded carbon and nitrogen is calculated by dividing the area under corresponding peaks by appropriate relative sensitivity factors of carbon (1) and nitrogen (1.8). The calculated at.% of nitrogen and carbon are 59 and 41 respectively, and the corresponding stoichiometric value of 1.4 for carbon nitride, are higher than the theoretical value of 1.33. Though the overall N/C is little away from stoichiometric value, the film area where α/β-C_3N_4 exists, nitrogen is in well agreement with the stoichiometric ratio.

3. Conclusions

In summary, crystalline C_3N_4 thin film was successfully prepared by CVD technique on silicon substrate using Triazine ($C_9H_{18}N_6$) as a precursor. The film contains both α and β-C_3N_4 crystalline phases. Silicon substrate found to be favorable for the growth of both α and β-C_3N_4 crystalline phases. The Raman peak shifts confirm the presence of nitrogen in the carbon matrix. The XPS analysis confirms the presence of tetrahedral bonding between carbon and nitrogen favoring the formation of crystalline C_3N_4 and also the sp^2 bonding between them. The surface morphology analyses show the formation of tree like spherical structures due to nitrogen incorporation into carbon network. This causes sp^3 bonding between carbon and nitrogen to form curvature in the basal planes and cross linkage to form tree like spherical structures. A further research to obtain purely single-phase carbon nitride is worth expecting. Also, this nitrogen incorporated carbon nitride spheres are a promising coating material for mechanical and tribological application.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Venkatesh Ramasamy: Conceptualization, Methodology, Data curation, Investigation, Writing – original draft. **Prashantha Murahari:** Investigation, Data curation. **N.R. Banapurmath:** Investigation. **K. Ramesh:** Conceptualization, Methodology, Investigation, Writing – review & editing, Supervision, Project administration.

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MEMORANDUM OF UNDERSTANDING

THIS MEMORANDUM OF UNDERSTANDING ('MOU') is made at KLE Technological University Hubballi, Karnataka, India on this 21st day of November 2019 by and between:

VICE CHANCELLOR
KLE Technological University
HUBBALLI-580 031. India

General Manager (Tech.)
Company Office, HESCOM,
HUBBALLI-580 025.

The General Manager (Tech.) represents **HESCOM, Hubballi**

and

The Vice-Chancellor representing **KLE Technological University Hubballli - 580031** witnesses as follows:

The **Hubli Electricity Supply Company Limited**, Hubballi, hereinafter referred to as HESCOM (which form shall mean and include unless repugnant to the context and meaning of the same to mean and include the assigns and successors) of the one part

And

KLE Technological University, Hubballi-580031, herein after referred to as **KLETU** (which form shall mean and include unless repugnant to the context and meaning of the same to mean and include the assigns and successors) of the other part further witnesses as follows:

HESCOM:

The Government of Karnataka as part of reforms in power sector has unbundled the transmission and distribution activities in the state of Karnataka. As a result, the HESCOM Limited was incorporated on 30.04.2002 under the Companies Act, 1956 (No. 1 of 1956) and HESCOM started operation w.e.f. 01.06.2002. HESCOM came into existence with geographical jurisdiction of 7 Districts comprising of Dharwad, Belagavi, Gadag, Haveri, Uttar Kannada, Bagalkot & Vijayapur with an objective to carry on the business of distribution and supply of electricity more efficiently and economically. HESCOM today is functioning as a commercial entity in pursuance of power sector reforms undertaken by Government of Karnataka, duly represented by its Managing Director hereinafter referred to as "**HESCOM**" which expression shall, unless repugnant to the context or meaning thereof, be deemed to mean and include its successors and permitted assigns;

And WHEREAS

VICE CHANCELLOR
KLE Technological University
HUBBALLI-580 031. India

General Manager (Tech.)
Company Office, HESCOM,
HUBBALLI-580 025.

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KLE Technological University, Hubballi-580031:

KLE Technological University (KLE Tech) has its roots in one of the premier engineering institution of Karnataka, B. V. Bhoomaraddi College of Engineering and Technology (BVB), a prestigious engineering college in Hubli. The founding organization KLE Society, Belgaum, established BVB College in 1947 with an aspiration of creating an institution that would lay the foundation of modern engineering education in northern region of Karnataka. Over the years, it evolved to reach and hold a unique position of pride in the technical education system of India. As we entered into the 21st century, the college undertook comprehensive reform process to adapt to the challenging global engineering education scenario. In pursuit of academic excellence, the college attained academic autonomy from University Grant Commission (UGC) in the year 2007. As an autonomous college, BVB established its distinctive character in the academic space through its curriculum and outstanding student experience.

Over the time it gained tremendous credibility with the industries and employers and emerged as a brand to reckon with. The Alumni of the Institute have done exceedingly well in all spheres of life at both national and international levels and brought name and fame for themselves as well as to their Alma Mater.

The times have changed, and the higher educational institutions need to continually innovate to maintain and enhance their relevance to meet the ever changing demands of global economies. Apart from delivering good quality education, the institutions are expected to develop their capacity in research and innovation. They also need to undergo a fundamental transformation in terms of their role in the society, mode of operation, and economic structure and the scale at which they operate

Keeping the above challenges in mind BVB College of Engineering and Technology undertook strategic initiative of transforming itself into a University of national distinction. In 2014 the college was recognized as a state private University by Government of Karnataka. The rich heritage of BVB College as one of the best engineering college in Hubli combined with brand equity of KLE Society are the starting points for KLE Technological University to emerge as a University with a national distinction.

Department Profile

The Electrical and Electronics Engineering program prepares professionals with the capacity to apply their knowledge, skills, attitudes, and the most recent technological developments to the solution of problems in our society. The profile of the EEE graduate states the following:

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Graduates from the Electrical and Electronics Engineering program are instrumental in planning, designing, implementing and evaluating products, services, and systems which integrate people, materials, equipment's, and information for the progress and improvement of the quality of life of humankind. They ensure that these products, services, or systems can be provided economically with the required level of quality necessary for satisfying society's needs. The Electrical Engineer draws upon knowledge and skills mostly from the areas of mathematics and physics, social, physiological and computer sciences, together with principles and methods of engineering analysis and design.

The Understanding aims:

Both the parties are interested in having a MOU in Capacity Building/Training Initiatives for officers of HESCOM and R&D, DSM activities in KLETU. To introduce and train students and practicing engineers on the emerging trends related to distributed generation, smart grid and activities of Power Distribution System for next 5 years from the above mentioned date.

Now, this Memorandum of Understanding witnesses as follows:

IT IS HEREBY MUTUALLY AGREED BY AND BETWEEN THE PARTIES AS FOLLOWS:

This collaboration between KLETU and HESCOM will create cooperation to initiate PACE (Program for Academic Connect and Engagement) in KLETU and R&D (Research & Development)/ DSM (Demand side Management) activities of HESCOM.

Further to provide a platform to build a strong and ongoing relationship between the HESCOM and KLETU.

The goals of PACE are:

1. To develop and foster strategic linkages between the KLETU and the technical departments of HESCOM.
2. To understand the needs and expectations of both the institute and the organization and to execute relevant identified activity required to meet the needs and expectations therein.

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3. Offering courses of mutual interest to the students and issuing the students certificates jointly, upon successful completion of the course.
4. Identify the area of research and development in Engineering of mutual interest and work on the identified proposals jointly on agreed terms.
5. HESCOM will permit their Engineers and Experts to tender their expertise for the benefit of the students when they are requested for specially focused programs
6. HESCOM will mentor UG/PG students for projects of mutual interest and convenience.
7. HESCOM will promote various activities for overall development of students with present trends.
8. HESCOM will advise institute for achieving program for educational objectives and outcomes to Department of Electrical and Electronics Engineering
9. Exploring and carrying out any other academic activity with mutual consent.
10. Provide exposure to students & faculty members to emerging technologies
11. Help bridge the gap between academia and industry and contribute to education eco system
12. Participate in enhancing knowledge of niche technologies and domain education by partnering.
13. As per the PACE, HESCOM provides its speakers to participate and deliver technical presentations and talks on topics as shall be, jointly, decided by KLETU and HESCOM. Such lectures shall either be a part of the curriculum or a value-added knowledge for the students. Further faculties of KLETU shall deliver technical presentations to HESCOM engineers on topics jointly decided.

The goal of Research & Development (R&D) of HESCOM is,

1. KLETU will design and implement the R&D Projects with HESCOM.
2. KLETU will support in Research & Development activities and provide platform for students and HESCOM interaction.

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HESCOM will make provision for funding the cost of HESCOM approved R&D project activities and extend similar funding support in HESCOM approved joint activities.

The goal of Demand Side Management (DSM) of HESCOM is,

1. KLETU will design and implement the DSM Projects with HESCOM.
2. KLETU will support and propagate Energy saving and safety awareness programs and activities in HESCOM geographical areas.

HESCOM will make provision for funding the cost of HESCOM approved DSM activities and extend similar funding support in HESCOM approved joint activities.

Internships to students:

In order to impart practical training under PACE, HESCOM shall identify, encourage and support in evolving technical competence in students by providing internships to students during their vacation period between successive semesters. HESCOM shall deploy such interns on specific technical works at their development centers. HESCOM shall evaluate the quality of the work carried out by the interns and award them with a certificate at the end of the internships. Industry-Institute coordinator shall co-ordinate with HESCOM throughout the process including initiation of the internship request at the appropriate time, selection of students for the internship, overseeing the technical work carried out by the interns and the evaluation of the work carried out by the interns as might be required by HESCOM.

Nurturing Exchange programs:

HESCOM shall foster the industry-institute exchange program with respect to the faculty and industry executives to serve in the organizations on an exchange basis. This shall provide the associates of HESCOM and Institute with cross-learning opportunities. Additionally, PACE will imbibe HESCOM culture amongst students and they will understand HESCOM practices.

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Contd... Pg. 6/8

INDEMNITY:

Neither Party will be liable to indemnify the other Party, and/or its employees from and against all costs, claims, demands, liabilities, expenses, damages or losses arising while executing the activities defined in this Agreement or in connection with a Party's negligence or breach of the terms of this Agreement.

CONFIDENTIALITY:

The Parties acknowledge that, in the course of their negotiations under this MoU, it may be necessary for one Party to provide documentation, technical and business information and/or intellectual property, in whatever form recorded (collectively, "Confidential Information") to the other Party. All Confidential Information provided or disclosed by either Party hereunder shall remain the property of the furnishing party, and shall be held in strict confidence by the receiving Party, unless the furnishing Party otherwise consents in writing or unless disclosure of such Confidential Information is required by the applicable laws. Confidential Information furnished by any Party hereunder.

GOVERNING LAW:

This **MoU** shall be governed by laws of India and the parties submit themselves to the jurisdiction of the courts in Hubballi, Karnataka, India.

This **MoU** is entered into for a period of 5 years between HESCOM, Hubballi and KLE Technological University, Hubballi-580031. The period would thereafter be extendable on mutual satisfaction and consent. Further this **MoU** could be terminated with one month's prior notice by either party at any point of time without giving reasons.

In witness where of the following parties have signed the MoU on this day 21st November 2019 at KLE technological University, Hubballi and the same would come into effect from 21st November 2019.

VICE CHANCELLOR
KLE Technological University
HUBBALLI-580 031. India

General Manager (Tech.)
Company Office, HESCOM,
HUBBALLI-580 025.

Contd... Pg. 7/8

KLE Technological University, Hubballi-580031.	**Hubli Electricity Supply Company Limited (HESCOM)**
By signing this MOU, I also confirm that I am authorized to sign on behalf of **KLE technological University – 580031.** **Signature:** VICE CHANCELLOR KLE Technological University HUBBALLI-580 031. India	By signing this MOU, I also confirm that I am authorized to sign on behalf of **HESCOM**, Hubballi **Signature:** General Manager (Tech.) Company Office, HESCOM, HUBBALLI-580 025.
Name: **Dr. Ashok Shettar**	Name: **Er. Jagadeesha L Belagali**
Designation: **Vice Chancellor**	Designation : **General Manager (Tech.)**
Date: **21-11-2019**	Date: **21-11-2019**
Place: **Hubballi**	Place: **Hubballi**

Contd... Pg. 8/8

Department of Electrical and Electronics Engineering

Collaboration Activities with HESCOM in academic year 2021-22

In order to impart practical training under HESCOM, 23 identified students have completed their Internship Training and Internship project in their curriculum of 8th semester, academic year 2021-22. Department of Electrical and Electronics Engineering has encouraged and supported these students to upgrade their technical competence in HESCOM. HESCOM has deployed these interns on specific technical works at their development centres. HESCOM has also evaluated their quality of the work carried out awarded them with a certificate after the completion of internship (training and project).

This process helped in developing and fostering the strategic linkages between the KLETU and the technical departments of HESCOM. Some of the needs were identified executed by the students by collecting the real time data in the Department of Electrical and Electronics Engineering in collaboration with experts of HESCOM by using modern software tools. HESCOM has mentored our UG students for internship projects of mutual interest and convenience.

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Website : www.shirkegroup.com **CIN :** U45201PN1994PTC077340

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ISO 9001 ISO 14001
ISO 45001

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Kelageri, Chikkamalligewad Village,
Pune-Bengaluru Road, Opp. High Court,
Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/272
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Ms. Vinayalaxmi Shanbhag bearing USN 01FE18BCV102** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed her internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022 to 28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

She was very sincere & hard working in her internship-based project work and was up to the expectations. We wish her all the best for her future endeavors.

For **B.G. Shirke Construction Technology Pvt Ltd.,**

B G Sangale
Dy. Chief Executive.

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Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2022-23/268
Date: 1st April 2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Vishal Patil bearing USN 01FE18BCV428** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For B.G. Shirke Construction Technology Pvt Ltd.,

B G Sangale
Dy. Chief Executive.

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Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/269
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Prasad Hiremath bearing USN 01FE19BCV402** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For B.G. Shirke Construction Technology Pvt Ltd.,

B G Sangale
Dy. Chief Executive.

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Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/276
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Yashkumar Patil bearing USN 01FE19BCV413** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For **B.G. Shirke Construction Technology Pvt Ltd.,**

B G SHIRKE CONST. TECH. PVT. LTD.
IIT-PROJECT
DHARWAD

B G Sangale
Dy. Chief Executive.

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Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/271
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Sayed Sufiyan Ahmed Betgeri bearing USN 01FE19BCV421** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022 to 28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For B.G. Shirke Construction Technology Pvt Ltd.,

B G Sangale
Dy. Chief Executive.

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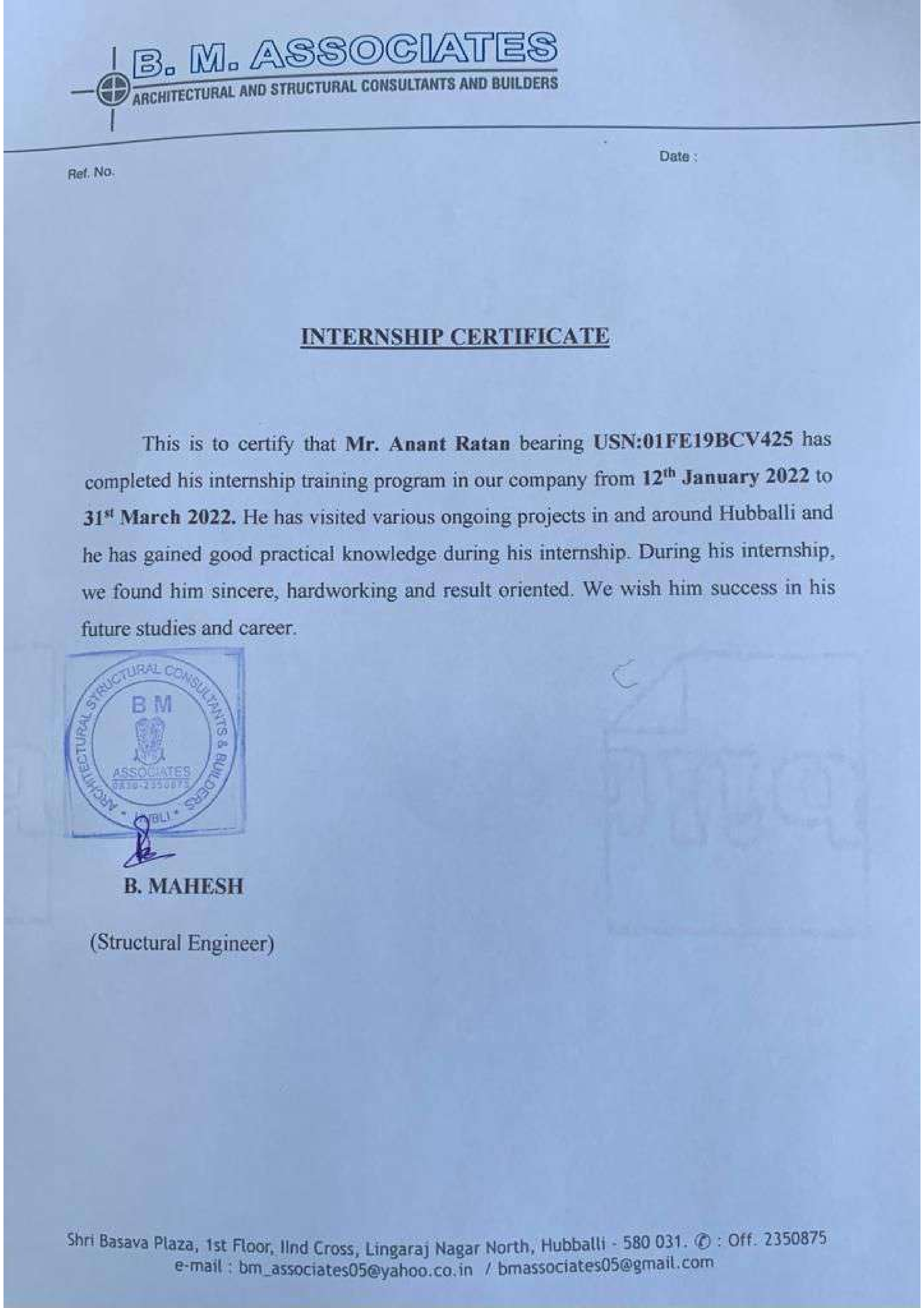

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No.

Date :

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Anant Ratan** bearing **USN:01FE19BCV425** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

0836-2350875

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off. 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Ajay Kabadi** bearing **USN:01FE19BCV406** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B M ASSOCIATES
HUBLI

B. MAHESH

(Structural Engineer)

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e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No.

Date :

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Abhay Bewoor** bearing **USN:01FE19BCV401** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

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e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

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ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Parasaraddi T. A** bearing **USN:01FE19BCV409** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

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HUBLI

B. MAHESH

(Structural Engineer)

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e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

Shapoorji Pallonji
Real Estate

01st April, 2022.

TO WHOM IT MAY CONCERN

CERTIFICATE OF SUMMER INTERNSHIP

Ms. Srireshma A student of KLE Technological Univeristy, Hubbali did internship at Shapoorji Pallonji Real Estate, Bengaluru for the period from 20th January 2022 to 28th March, 2022.

We wish all the very best in future endeavors.

Yours sincerely,

For Shapoorji Pallonji Real Estate Private Limited,

Jayasimha Haresmudram,
Assistant General Manager – HR & Admin.

Shapoorji Pallonji Real Estate Private Limited
(Formerly known as Shapoorji Pallonji Construction Private Limited)

Regd. Office: SP Centre, 41/44,
Minoo Desai Marg, Colaba,
Mumbai 400005

Tel: +91 22 6749 0000
Fax: +91 22 6633 8176
CIN: U45309MH2017PTC293758

Constantly Committed

Shapoorji Pallonji
Real Estate

01st April, 2022.

TO WHOM IT MAY CONCERN

CERTIFICATE OF SUMMER INTERNSHIP

Ms. Zaheen Fatima Kittur student of KLE Technological Univeristy, Hubbali did internship at Shapoorji Pallonji Real Estate, Bengaluru for the period from 20th January 2022 to 28th March, 2022.

We wish all the very best in future endeavors.

Yours sincerely,

For Shapoorji Pallonji Real Estate Private Limited,

H J

Jayasimha Haresmudram,
Assistant General Manager – HR & Admin.

Shapoorji Pallonji Real Estate Private Limited
(Formerly known as Shapoorji Pallonji Construction Private Limited)

Regd. Office: SP Centre, 41/44, Minoo Desai Marg, Colaba, Mumbai 400005

Tel: +91 22 6749 0000
Fax: +91 22 6633 8176
CIN: U45309MH2017PTC293758

Constantly Committed

Shapoorji Pallonji
Real Estate

01st April, 2022.

TO WHOM IT MAY CONCERN

CERTIFICATE OF SUMMER INTERNSHIP

Ms. Sahana Patil student of KLE Technological Univeristy, Hubbali did internship at Shapoorji Pallonji Real Estate, Bengaluru for the period from 20th January 2022 to 28th March, 2022.

We wish all the very best in future endeavors.

Yours sincerely,

For Shapoorji Pallonji Real Estate Private Limited,

Jayasimha Haresmudram,
Assistant General Manager – HR & Admin.

Shapoorji Pallonji Real Estate Private Limited
(Formerly known as Shapoorji Pallonji Construction Private Limited)

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Fax: +91 22 6633 8176
CIN: U45309MH2017PTC293758

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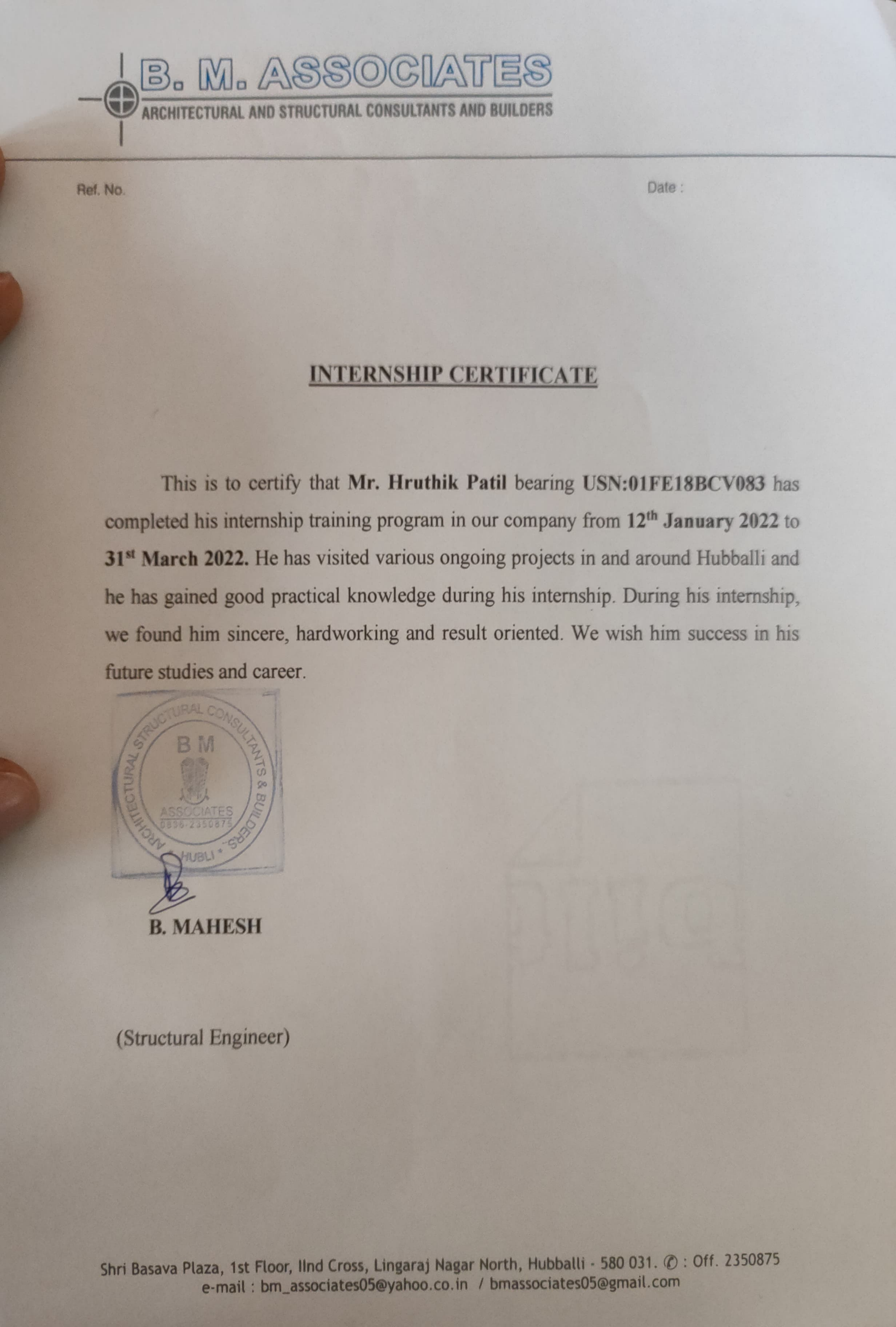

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ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No.

Date :

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Hruthik Patil** bearing **USN:01FE18BCV083** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

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ASSOCIATES
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* HUBLI *

B. MAHESH

(Structural Engineer)

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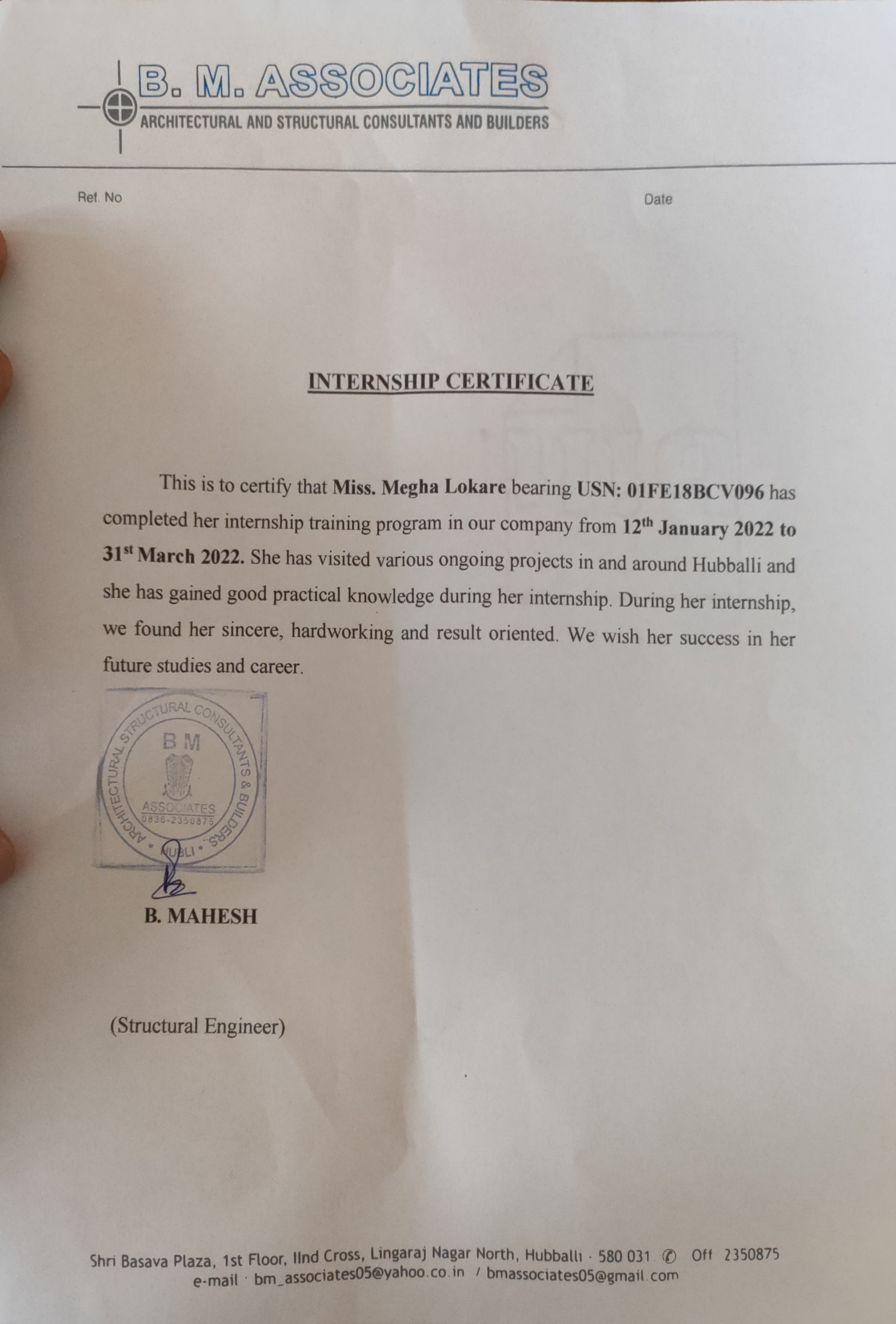
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com



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Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Miss. Megha Lokare** bearing **USN: 01FE18BCV096** has completed her internship training program in our company from **12th January 2022 to 31st March 2022.** She has visited various ongoing projects in and around Hubballi and she has gained good practical knowledge during her internship. During her internship, we found her sincere, hardworking and result oriented. We wish her success in her future studies and career.

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0836-2350875

B. MAHESH

(Structural Engineer)

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Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Prashant Kali** bearing **USN:01FE18BCV086** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

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B. MAHESH

(Structural Engineer)

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ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Malatesh Balami** bearing **USN:01FE18BCV100** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

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B. MAHESH

(Structural Engineer)

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ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Lingaraj Bandiwad** bearing **USN:01FE18BCV096** has completed his internship training program in our company from **12th January 2022 to 31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

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B. MAHESH

(Structural Engineer)

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e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

SOBHA
PASSION AT WORK

18th April 2022

To Whomsoever It May Concern

Mr. Sawan V. Navale (01FE18BCV055) from **K. L. E. Technological University, Karnataka** has successfully completed his internship training at Sobha Limited for the duration from **10th January 2022 to 10th April 2022**

We wish him all the best for his future endeavors.

Thanking you,

For Sobha Ltd.

Srinivas Shetty
General Manager HR.

SOBHA LIMITED
REGD & CORPORATE OFFICE : 'SOBHA', SARJAPUR - MARATHAHALLI OUTER RING ROAD, BELLANDUR POST, BANGALORE - 560103, INDIA
CIN: L45201KA1995PLC018475 | TEL : +91-80-49320000 | FAX : +9180 49320444 | www.sobha.com

SOBHA
PASSION AT WORK

18th April 2022

To Whomsoever It May Concern

Mr. Shishir A.R (01FE18BCV056) from **K. L. E. Technological University, Karnataka** has successfully completed his internship training at Sobha Limited for the duration from **10th January 2022 to 10th April 2022**

We wish him all the best for his future endeavors.

Thanking you,

For Sobha Ltd.

Srinivas Shetty
General Manager HR.

SOBHA
PASSION AT WORK

18th April 2022

To Whomsoever It May Concern

Mr. Pravez Alalam Dharwad (01FE18BCV421) from **K. L. E. Technological University, Karnataka** has successfully completed his internship training at Sobha Limited for the duration from **10th January 2022 to 10th April 2022**

We wish him all the best for his future endeavors.

Thanking you,

For Sobha Ltd.

Srinivas Shetty
General Manager HR.

SOBHA LIMITED
REGD & CORPORATE OFFICE : 'SOBHA', SARJAPUR - MARATHAHALLI OUTER RING ROAD, BELLANDUR POST, BANGALORE - 560103, INDIA
CIN: L45201KA1995PLC018475 | TEL : +91-80-49320000 | FAX : +9180 49320444 | www.sobha.com

SOBHA
PASSION AT WORK

18th April 2022

To Whomsoever It May Concern

Mr. Ashish B.V (01FE18BCV405) from **K. L. E. Technological University, Karnataka** has successfully completed his internship training at Sobha Limited for the duration from **10th January 2022 to 10th April 2022**

We wish him all the best for his future endeavors.

Thanking you,

For Sobha Ltd.

Srinivas Shetty
General Manager HR.

SOBHA LIMITED
REGD & CORPORATE OFFICE : 'SOBHA', SARJAPUR - MARATHAHALLI OUTER RING ROAD, BELLANDUR POST, BANGALORE - 560103, INDIA
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B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Nutan Sankpal** bearing **USN:01FE18BCV040** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031 ✆ Off 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Prateek D Patil** bearing **USN:01FE18BCV042** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Prateek S Guddad** bearing **USN:01FE18BCV043** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off. 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Shridhar Mundargi** bearing **USN:01FE18BCV060** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ Off 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

H.P. MADHUKAR AND CO.
Engineers & Class I PWD Contractors
Water Supply Projects on Turnkey Basis
& N.H. Road Works etc.

HEAD OFFICE :
No. 41, 'Prashant',
Vijaynagar Extn.,
HUBLI - 580 032.
Tel : 0836-2351805
E-mail : hpmhubli@gmail.com
hpmadhukar@gmail.com

PAN No.: AANFH2771G
GST No.: 29AANFH2771G1Z2

Certificate of Internship

To,
The Head of the Department,
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING,
KLE Technological University,
Vidyanagar,
HUBBALLI-580021.

Dear Sir,

This is to certify that **Mr.Sidram K B** , has completed his Internship training in our company i.e. H P MADHUKAR & CO for a duration of 70 days i.e. from 10-01-2022 to 20-03-2022 in pavement construction.. His performance is highly appreciated and is certified with the marks for the same.

For H. P. MADHUKAR AND Co.

PARTNER

Date:28.03.2022

Place: HUBLI

H.P. MADHUKAR AND CO.
Engineers & Class I PWD Contractors

Water Supply Projects on Turnkey Basis
& N.H. Road Works etc.

HEAD OFFICE :
No. 41, 'Prashant',
Vijaynagar Extn.,
HUBLI - 580 032.
Tel : 0836-2351805
E-mail : hpmhubli@gmail.com
hpmadhukar@gmail.com

PAN No.: AANFH2771G
GST No.: 29AANFH2771G1Z2

Certificate of Internship

To,
The Head of the Department,
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING,
KLE Technological University,
Vidyanagar,
HUBBALLI-580021.

Dear Sir,

This is to certify that **Mr.Shivarajagoud M Patil** has completed his Internship training in our company i.e. H P MADHUKAR & CO for a duration of 70 days i.e. from 10-01-2022 to 20-03-2022 in pavement construction.. His performance is highly appreciated and is certified with the marks for the same.

For H. P. MADHUKAR AND Co.

PARTNER

Date:28.03.2022

Place: HUBLI

H.P. MADHUKAR AND CO.
Engineers & Class I PWD Contractors

Water Supply Projects on Turnkey Basis
& N.H. Road Works etc.

HEAD OFFICE :
No. 41, 'Prashant',
Vijaynagar Extn.,
HUBLI - 580 032.
Tel : 0836-2351805
E-mail : hpmhubli@gmail.com
hpmadhukar@gmail.com

PAN No.: AANFH2771G
GST No.: 29AANFH2771G1Z2

Certificate of Internship

To,
The Head of the Department,
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING,
KLE Technological University,
Vidyanagar,
HUBBALLI-580021.

Dear Sir,

This is to certify that **Mr.Manish Kulkarni** has completed his Internship training in our company i.e. H P MADHUKAR & CO for a duration of 70 days i.e. from 10-01-2022 to 20-03-2022 in pavement construction.. His performance is highly appreciated and is certified with the marks for the same.

Date:28.03.2022
Place: HUBLI

For H. P. MADHUKAR AND Co.
PARTNER

H.P. MADHUKAR AND CO.
Engineers & Class I PWD Contractors

Water Supply Projects on Turnkey Basis
& N.H. Road Works etc.

HEAD OFFICE :
No. 41, 'Prashant',
Vijaynagar Extn.,
HUBLI - 580 032.
Tel : 0836-2351805
E-mail : hpmhubli@gmail.com
hpmadhukar@gmail.com

PAN No.: AANFH2771G
GST No.: 29AANFH2771G1Z2

Certificate of Internship

To,
The Head of the Department,
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING,
KLE Technological University,
Vidyanagar,
HUBBALLI-580021.

Dear Sir,

This is to certify that **Mr.Vaibhav M Sannakki** has completed his Internship training in our company i.e. H P MADHUKAR & CO for a duration of 70 days i.e. from 10-01-2022 to 20-03-2022 in pavement construction.. His performance is highly appreciated and is certified with the marks for the same.

Date:28.03.2022
Place: HUBLI

For H. P. MADHUKAR AND Co.
PARTNER

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Ms. AISHWARYA YADAV** bearing **USN 01FE19BCV424** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical College
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Ms. SHREEDEVI VADDODAGI** bearing **USN 01FE19BCV416** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During her training she was exposed to Building Construction site and worked on Building planning, drawing, estimation and Quality issues.

During the training period she was found to be obedient and exhibited quest for learning.

for

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical College
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr. Md HUZAIFA S HULLUR** bearing **USN 01FE18BCV036** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical College
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr. ROHIT V HOSAMANI** bearing **USN 01FE18BCV051** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical College
Gabbur road, Hubballi

ISO 9001-2000 Certified

Public Works Department

Government of Karnataka
(Public Works Department)

SL No PWDNVL/INTERN/2021-22 / 618

Date: 31/3/2022

Office of the
Assistant Executive Engineer
Public Works Department
Sub-Division, Navalgund

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr. Rahul S Chougala, a student of Bachelor of Engineering (Civil) bearing USN: 01FE18BCV048 from KLE Technological University has satisfactorily completed the Internship Training as the Quality Control intern and Site Engineer on various construction works for a period of 80 days from 10th January 2022 to 31st March 2022 in Karnataka Public Works Department, Sub-Division, Navalgund.

During the period of his internship program with us he had been exposed to different processes and was found perceptive, punctual, hardworking and inquisitive.

Assistant Executive Engineer
Public Works Department
Sub-Division Navalgund

ISO 9001-2000 Certified

Public Works Department

Government of Karnataka
(Public Works Department)

SL No PWDNVL/INTERN/2021-22 6·18

Date: 31/3/2022

Office of the
Assistant Executive Engineer
Public Works Department
Sub-Division, Navalgund

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr. Chetan Managooli, a student of Bachelor of Engineering (Civil) bearing USN: 01FE18BCV016 from KLE Technological University has satisfactorily completed the Internship Training as the Quality Control intern and Site Engineer on various construction works for a period of 80 days from 10th January 2022 to 31st March 2022 in Karnataka Public Works Department, Sub-Division, Navalgund.

During the period of his internship program with us he had been exposed to different processes and was found perceptive, punctual, hardworking and inquisitive.

Assistant Executive Engineer
Public Works Department
Sub-Division Navalgund

ISO 9001-2000 Certified

Public Works Department

Government of Karnataka
(Public Works Department)

SL No PWDNVL/INTERN/2021-22 618

Date: 31/3/2022.

Office of the
Assistant Executive Engineer
Public Works Department
Sub-Division, Navalgund

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr. Prashant S Chalageri, a student of Bachelor of Engineering (Civil) bearing USN: 01FE18BCV041 from KLE Technological University has satisfactorily completed the Internship Training as the Quality Control intern and Site Engineer on various construction works for a period of 80 days from 10th January 2022 to 31st March 2022 in Karnataka Public Works Department, Sub-Division, Navalgund.

During the period of his internship program with us he had been exposed to different processes and was found perceptive, punctual, hardworking and inquisitive.

Assistant Executive Engineer
Public Works Department
Sub-Division Navalgund

ISO 9001-2000 Certified

Public Works Department

Government of Karnataka
(Public Works Department)

SL No PWDNVL/INTERN/2021-22
618

Date: 31/3/2022.

Office of the
Assistant Executive Engineer
Public Works Department
Sub-Division, Navalgund

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr. Manu R Handral, a student of Bachelor of Engineering (Civil) bearing USN: 01FE18BCV353 from KLE Technological University has satisfactorily completed the Internship Training as the Quality Control intern and Site Engineer on various construction works for a period of 80 days from 10th January 2022 to 31st March 2022 in Karnataka Public Works Department, Sub-Division, Navalgund.

During the period of his internship program with us he had been exposed to different processes and was found perceptive, punctual, hardworking and inquisitive.

Assistant Executive Engineer
Public Works Department
Sub-Division Navalgund

6th April 2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr.Dhirajkumar G Patil S, BE Civil student of K L E Technological University, Hubbali has successfully undergone Internship in this organisation from 10th January 2022 to 31st March 2022.

For Shapoorji Pallonji And Company Private Limited

SUMIT VIREN
DEPUTY GENERAL MANAGER - HR

ISO 9001:2015
ISO 14001:2015
BS OHSAS 18001:2007
BUREAU VERITAS
Certification
UKAS MANAGEMENT SYSTEMS 0008

SHAPOORJI PALLONJI AND COMPANY PRIVATE LIMITED

Registered Office:
70, Nagindas Master Road,
Fort, Mumbai - 400023
(T) +91-22-22624530
www.shapoorji.in

Regional Office:
7th Floor, Surya Chambers,
No. 124, HAL Airport Road,
Bangalore - 560017
(T) +91-80-66213500

Corporate Office:
SP Centre, 41/44,
Minoo Desai Marg,
Colaba, Mumbai - 400005
(T) +91-22-67490000

Shapoorji Pallonji
ENGINEERING & CONSTRUCTION

Corporate Identification No (CIN): U45200MH1943PTC003812

6th April 2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr.Samarth Shyadaguppi, BE Civil student of K L E Technological University, Hubbali has successfully undergone Internship in this organisation from 10th January 2022 to 31st March 2022.

For Shapoorji Pallonji And Company Private Limited

SUMIT VIREN
DEPUTY GENERAL MANAGER – HR

SHAPOORJI PALLONJI AND COMPANY PRIVATE LIMITED

Registered Office:
70, Nagindas Master Road,
Fort, Mumbai - 400023
(T) +91-22-22624530
www.shapoorji.in

Regional Office:
7th Floor, Surya Chambers,
No. 124, HAL Airport Road,
Bangalore - 560017
(T) +91-80-66213500

Corporate Office:
SP Centre, 41/44,
Minoo Desai Marg,
Colaba, Mumbai - 400005
(T) +91-22-67490000

Corporate Identification No (CIN): U45200MH1943PTC003812

Shapoorji Pallonji
ENGINEERING & CONSTRUCTION

6th April 2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr.Shreyas Astagi, BE Civil student of K L E Technological University, Hubbali has successfully undergone Internship in this organisation from 10th January 2022 to 31st March 2022.

For Shapoorji Pallonji And Company Private Limited

SUMIT VIREN
DEPUTY GENERAL MANAGER – HR

ISO 9001:2015
ISO 14001:2015
BS OHSAS 18001:2007
BUREAU VERITAS
Certification
UKAS
0008

SHAPOORJI PALLONJI AND COMPANY PRIVATE LIMITED

Registered Office:
70, Nagindas Master Road,
Fort, Mumbai - 400023
(T) +91-22-22624530
www.shapoorji.in

Regional Office:
7th Floor, Surya Chambers,
No. 124, HAL Airport Road,
Bangalore - 560017
(T) +91-80-66213500

Corporate Office:
SP Centre, 41/44,
Minoo Desai Marg,
Colaba, Mumbai - 400005
(T) +91-22-67490000

Corporate Identification No (CIN): U45200MH1943PTC003812

Shapoorji Pallonji
ENGINEERING & CONSTRUCTION

6th April 2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr.Thejas B Shettar, BE Civil student of K L E Technological University, Hubbali has successfully undergone Internship in this organisation from 10th January 2022 to 31st March 2022.

For Shapoorji Pallonji And Company Private Limited

SUMIT VIREN
DEPUTY GENERAL MANAGER - HR

SHAPOORJI PALLONJI AND COMPANY PRIVATE LIMITED

Registered Office:
70, Nagindas Master Road,
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www.shapoorji.in

Regional Office:
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(T) +91-80-66213500

Corporate Office:
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Minoo Desai Marg,
Colaba, Mumbai - 400005
(T) +91-22-67490000

Corporate Identification No (CIN): U45200MH1943PTC003812

Shapoorji Pallonji
ENGINEERING & CONSTRUCTION

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr. ARVIND M PATILKULKARNI** bearing **USN 01FE18BCV073** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **05-02-2022 to 31-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H NRamadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr. D ABHISHEK CHOUDHARY** bearing **USN 01FE17BCV023** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **05-02-2022 to 31-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H NRamadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

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Date: 31.02.2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certified that, Mr. **VISHWANATH REDDY** a student of **KLE TECHNOLOGICAL UNIVERSITY (USN No: 01FE18BCV071)** worked under our supervision during her internship period from **17.01.2022 to 17.03.2022** he posted at site project **"SHRIYA LUMBINI"**. We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr. **VISHWANATH REDDY** possesses a good moral character and pleasing personality. We wish him every success in future.

Thanking you

580030

13, Arjun Vihar, Gokul Road,
HUBBALLI - 580030 (Karnataka)
+91 888 448 3111
+91 903 674 7492
sales@shriyaproperties.com
www.shriyaproperties.com

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Date: 31.02.2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certified that, Mr. **BASAVARAJ S KOTTARGI** a student of **KLE TECHNOLOGICAL UNIVERSITY (USN No: 01FE18BCV109)** worked under our supervision during her internship period from **17.01.2022 to 17.03.2022** he posted at site project **"SHRIYA LUMBINI"**. We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr. **BASAVARAJ S KOTTARGI** possesses a good moral character and pleasing personality. We wish him every success in future.

Thanking you

SHRIYA PROPERTIES ★ HUBLI ★ 580030

13, Arjun Vihar, Gokul Road,
HUBBALLI - 580030 (Karnataka)
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+91 903 674 7492
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REAL ESTATE INVESTMENT • RESIDENTIAL APARTMENT • COMMERCIAL SPACES

Date: 31.02.2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certified that, Mr. **AMRUT R PUTHANI** a student of **KLE TECHNOLOGICAL UNIVERSITY (USN No: 01FE18BCV 112)** worked under our supervision during her internship period from **17.01.2022 to 17.03.2022** he posted at site project **"SHRIYA LUMBINI"**. We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr. **AMRUT R PUTHANI** possesses a good moral character and pleasing personality. We wish him every success in future.

Thanking you

SHRIYA PROPERTIES
HUBLI
580030

13, Arjun Vihar, Gokul Road,
HUBBALLI - 580030 (Karnataka)
+91 888 448 3111
+91 903 674 7492
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www.shriyaproperties.com

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Date: 31.02.2022

INTERNSHIP CERTIFICATE

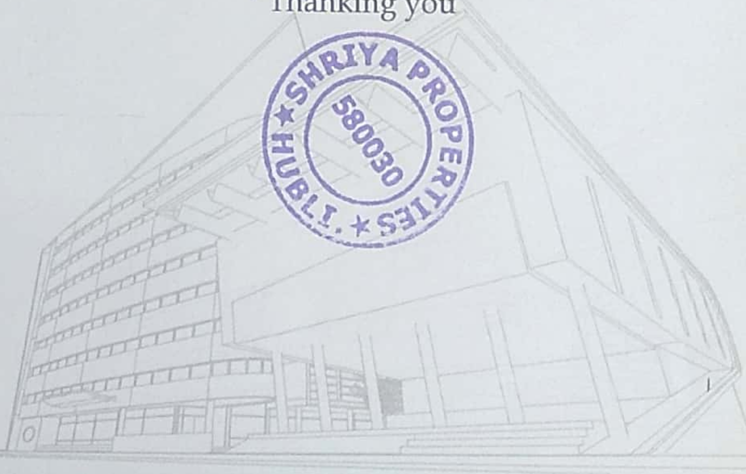
TO WHOMSOEVER IT MAY CONCERN

This is certified that, Mr. **ABHISHEK C NEGALUR** a student of **KLE TECHNOLOGICAL UNIVERSITY (USN No: 01FE18BCV089)** worked under our supervision during her internship period from **17.01.2022 to 17.03.2022** he posted at site project **"SHRIYA LUMBINI"**. We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr. **ABHISHEK C NEGALUR** possesses a good moral character and pleasing personality. We wish him every success in future.

Thanking you

SHRIYA PROPERTIES
HUBLI
580030



13, Arjun Vihar, Gokul Road,
HUBBALLI - 580030 (Karnataka)
+91 888 448 3111
+91 903 674 7492
sales@shriyaproperties.com
www.shriyaproperties.com

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Date: 06-04-2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certify that, **Mr. ROSHAN CHAVAN (01FE18BCV099)** a student of **KLE Technology University** worked under our supervision during his internship period from 17-01-2022 **to 17-03-2022** he posted at site project **"Shreya Lumbini , "Stellar" "Shriya Riddi Siddi** We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr . ROSHAN CHAVAN a possesses a good moral character and pleasing personality. We wish her every success in life.

Thanking you

SHRIYA PROPERTIES
580030
★HUBLI.★

13, Arjun Vihar, Gokul Road,
HUBBALLI - 580030 (Karnataka)
+91 888 448 3111
+91 903 674 7492
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Date: 06-04-2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certify that, Mr. **T S BASAVARAJ (01FE18BCV094)** a student of **KLE Technology University** worked under our supervision during his internship period from 17-01-2022 **to 17-03-2022** he posted at site project **"Shreya Lumbini , "Stellar" "Shriya Riddi Siddi |** We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr . T S BASAVARAJ a possesses a good moral character and pleasing personality. We wish her every success in life.

Thanking you

SHRIYA PROPERTIES
580030
HUBLI.

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SHRIYA PROPERTIES
REAL ESTATE INVESTMENT • RESIDENTIAL APARTMENT • COMMERCIAL SPACES

Date: 06-04-2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certify that, **Mr. KARTIK S AGADI (01FE18BCV097)** a student of **KLE Technology University** worked under our supervision during his internship period from 17-01-2022 **to 17-03-2022** he posted at site project **"Shreya Lumbini , "Stellar" "Shriya Riddi Siddi** We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr . KARTIK S AGADI a possesses a good moral character and pleasing personality. We wish her every success in life.

Thanking you

580030

13. Arjun Vihar, Gokul Road, HUBBALLI - 580030 (Karnataka)
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+91 903 674 7492
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Date: 06-04-2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certify that, **Mr. SUMIT S KOKATANUR (01FE18BCV095)** a student of **KLE Technology University** worked under our supervision during his internship period from 17-01-2022 **to 17-03-2022** he posted at site project **"Shreya Lumbini , "Stellar" "Shriya Riddi Siddi** We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr . SUMITH S KOKATANUR a possesses a good moral character and pleasing personality. We wish her every success in life.

Thanking you

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Date: 06-04-2022

INTERNSHIP CERTIFICATE

TO WHOMSOEVER IT MAY CONCERN

This is certify that, **Mr. SOHAN KEMPANNAVAR (01FE18BCV0120)** a student of **KLE Technology University** worked under our supervision during his internship period from 17-01-2022 **to 17-03-2022** he posted at site project **"Shreya Lumbini , "Stellar" "Shriya Riddi Siddi** We are pleased to state that he worked hard and he has been able to present a good picture of the concerned works.

Mr . SOHAN KEMPANNAVAR a possesses a good moral character and pleasing personality. We wish her every success in life.

Thanking you

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MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Ms. AMRUTA HEMANNAVAR** bearing **USN 01FE18BCV114** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During her training she was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period she was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr. HARISHA T** bearing **USN 01FE19BCV417** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr. RAMESH CHALAWADI** bearing **USN 01FE19BCV428** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Ms. SANJANA T S** bearing **USN 01FE19BCV427** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During her training she was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period she was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr. TAMMANNA M MADANAMATTI** bearing **USN 01FE19BCV414** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

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No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

This is to certify that ***Mr. Gagandeep B.*** *bearing* ***USN: 01FE18BCV021*** *of 8th semester during the year 2021-2022 from School of Civil Engineering,* ***KLE Technological University-Hubballi*** *has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our* ***"HUBBALLI-DHARWAD SMART CITY LIMITED"*** *from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

This is to certify that ***Mr. Amoghvarsh J Patil*** *bearing* ***USN: 01FE18BCV006*** *of 8th semester during the year 2021-2022 from School of Civil Engineering,* ***KLE Technological University-Hubballi*** *has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "****HUBBALLI-DHARWAD SMART CITY LIMITED****" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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Website: www.hubballidharwadsmartcity.com E-mail: smartcityhubballidharwad@gmail.com

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No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

This is to certify that ***Mr. Jay Shrikant Kotyal*** *bearing* ***USN: 01FE18BCV027*** *of 8th semester during the year 2021-2022 from School of Civil Engineering,* ***KLE Technological University-Hubballi*** *has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "****HUBBALLI-DHARWAD SMART CITY LIMITED****" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

This is to certify that ***Mr. Chinmay J Pattanshetty*** *bearing* ***USN: 01FE18BCV352*** *of 8th semester during the year 2021-2022 from School of Civil Engineering,* ***KLE Technological University-Hubballi*** *has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "****HUBBALLI-DHARWAD SMART CITY LIMITED****" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

This is to certify that ***Mr. Chetan Hospeti*** *bearing* ***USN: 01FE19BCV415*** *of 8th semester during the year 2021-2022 from School of Civil Engineering, KLE Technological University-Hubballi has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "****HUBBALLI-DHARWAD SMART CITY LIMITED****" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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No: HDSCL/IC/2022-23
Date: 13-04-2022

CERTIFICATE

*This is to certify that **Mr. Prateek Ginimav** bearing **USN: 01FE18BCV075** of 8th semester during the year 2021-2022 from School of Civil Engineering, **KLE Technological University-Hubballi** has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "**HUBBALLI-DHARWAD SMART CITY LIMITED**" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors

.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

*This is to certify that **Mr. Kiran Shejawadkar** bearing **USN: 01FE18BCV031** of 8th semester during the year 2021-2022 from School of Civil Engineering, **KLE Technological University-Hubballi** has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "**HUBBALLI-DHARWAD SMART CITY LIMITED**" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

This is to certify that ***Mr. Shivprasad Badiger*** *bearing* ***USN: 01FE18BCV090*** *of 8th semester during the year 2021-2022 from School of Civil Engineering,* ***KLE Technological University-Hubballi*** *has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "****HUBBALLI-DHARWAD SMART CITY LIMITED****" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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HUBBALLI DHARWAD SMART CITY LIMITED
Special Purpose Vehicle for Implementation of Smart City Project
(Registered Company No. CIN : U74999KA2017 PLC 101265)

No: HDSCL/IC/2022-23 Date: 13-04-2022

CERTIFICATE

This is to certify that ***Mr. Manu Hiremath*** *bearing* ***USN: 01FE18BCV035*** *of 8th semester during the year 2021-2022 from School of Civil Engineering,* ***KLE Technological University-Hubballi*** *has successfully undergone "INDUSTRY INTERNSHIP TRAINING" at our "****HUBBALLI-DHARWAD SMART CITY LIMITED****" from 10-01-2022 to 10-04-2022.*

During the Period of internship, he has worked in Redevelopment of "OLD CITY BUS STAND", Hubballi.

During the training we found him punctual, and his performance was found to be satisfactory. We wish him all the best for his future endeavors.

Deputy General Manager
Hubballi-Dharwad Smart City Limited
Hubballi

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Jalavahini Management Services (P) Ltd.,
CIN No. U74140KA2003PTC032960

Jalavahini

Ref: JMSD/DWD/Internship/2021-2022/208 Date: 31/03/2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Miss. Spurthi Chimmalagi USN no: 01FE18BCV354 has completed satisfactorily the internship from 18th Jan 2022 to 17th March 2022 at our Company.

This Certificate is issued at the specific request of the trainee, without any commitment on our part.

Place: Dharwad
Date: 31-03-2022

DHARWAD

(Managing Director)
For Jalavahini Management Services Pvt Ltd,
Dharwad

ENGINEERING AND PROJECT MANAGEMENT CONSULTANTS
AN ISO 9001-2015 CERTIFIED COMPANY
JALAVAHINI TECH PARK, 9th Cross, Dodda Nayakankoppa,Dharwad-580 008. Ph. : 0836-2775052
e-mail : Jalavahini@gmail.com Website : www.jmspl.in

Jalavahini Management Services (P) Ltd.,
CIN No. U74140KA2003PTC032960

jalavahini management services pvt. ltd

Ref: JMSD/DWD/Internship/2021-2022/42 Date: 31/03/2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Miss. Sahana Bannad USN no: 01FE18BCV082 has completed satisfactorily the internship from 18th Jan 2022 to 17th March 2022 at our Company.

This Certificate is issued at the specific request of the trainee, without any commitment on our part.

Place: Dharwad
Date: 31-03-2022

(Managing Director)
For Jalavahini Management Services Pvt Ltd,
Dharwad

Jalavahini Management Services (P) Ltd.,
CIN No. U74140KA2003PTC032960

Ref: JMSD/DWD/Internship/2021-2022/1420 Date: 31/03/2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr. Sagar S A USN no: 01FE18BCV080 has completed satisfactorily the internship from 18th Jan 2022 to 17th March 2022 at our Company.

This Certificate is issued at the specific request of the trainee, without any commitment on our part.

Place: Dharwad
Date: 31-03-2022

(Managing Director)
For Jalavahini Management Services Pvt Ltd,
Dharwad

ENGINEERING AND PROJECT MANAGEMENT CONSULTANTS
AN ISO 9001-2015 CERTIFIED COMPANY
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e-mail : Jalavahini@gmail.com Website : www.jmspl.in

Jalavahini Management Services (P) Ltd.,
CIN No. U74140KA2003PTC032960

Ref: JMSD/DWD/Internship/2021-2022/1224 Date: 31/03/2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mr. Pavankumar D R USN no: 01FE18BCV423 has completed satisfactorily the internship from 18th Jan 2022 to 17th March 2022 at our Company.

This Certificate is issued at the specific request of the trainee, without any commitment on our part.

Place: Dharwad
Date: 31-03-2022

(Managing Director)
For Jalavahini Management Services Pvt Ltd,
Dharwad

Jalavahini Management Services (P) Ltd.,
CIN No. U74140KA2003PTC032960

Ref: JMSD/DWD/Internship/2021-2022/422 Date: 31/03/2022

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Miss. Poornima P Hugar USN no: 01FE18BCV101 has completed satisfactorily the internship from 18th Jan 2022 to 17th March 2022 at our Company.

This Certificate is issued at the specific request of the trainee, without any commitment on our part.

Place: Dharwad
Date: 31-03-2022

(Managing Director)
For Jalavahini Management Services Pvt Ltd,
Dharwad

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Ms. Adarsha shiragur** bearing **USN: 01FE18BCV108** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During her training she was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period she was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N [illegible]
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Ms. Deepa Dharmasing Rathod** bearing **USN: 01FE18BCV110** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During her training she was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period she was found to be obedient and exhibited quest for learning.

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Ms. Deepa** bearing **USN: 01FE18BCV111** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During her training she was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period she was found to be obedient and exhibited quest for learning.

H N Rautadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

CERTIFICATE

This is to certify that **Mr.Mahantesh Kalawad** bearing **USN: 01FE19BCV411** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

H N Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.

KAHER's JAGADGURU GANGADHAR MAHASWAMIGALU
MOORUSAVIRMATH MEDICAL COLLEGE
Gabbur Cross, Hubballi-580028.
(A Constituent unit of KLE Academy of Higher Education & Research Deemed-to-be-University)

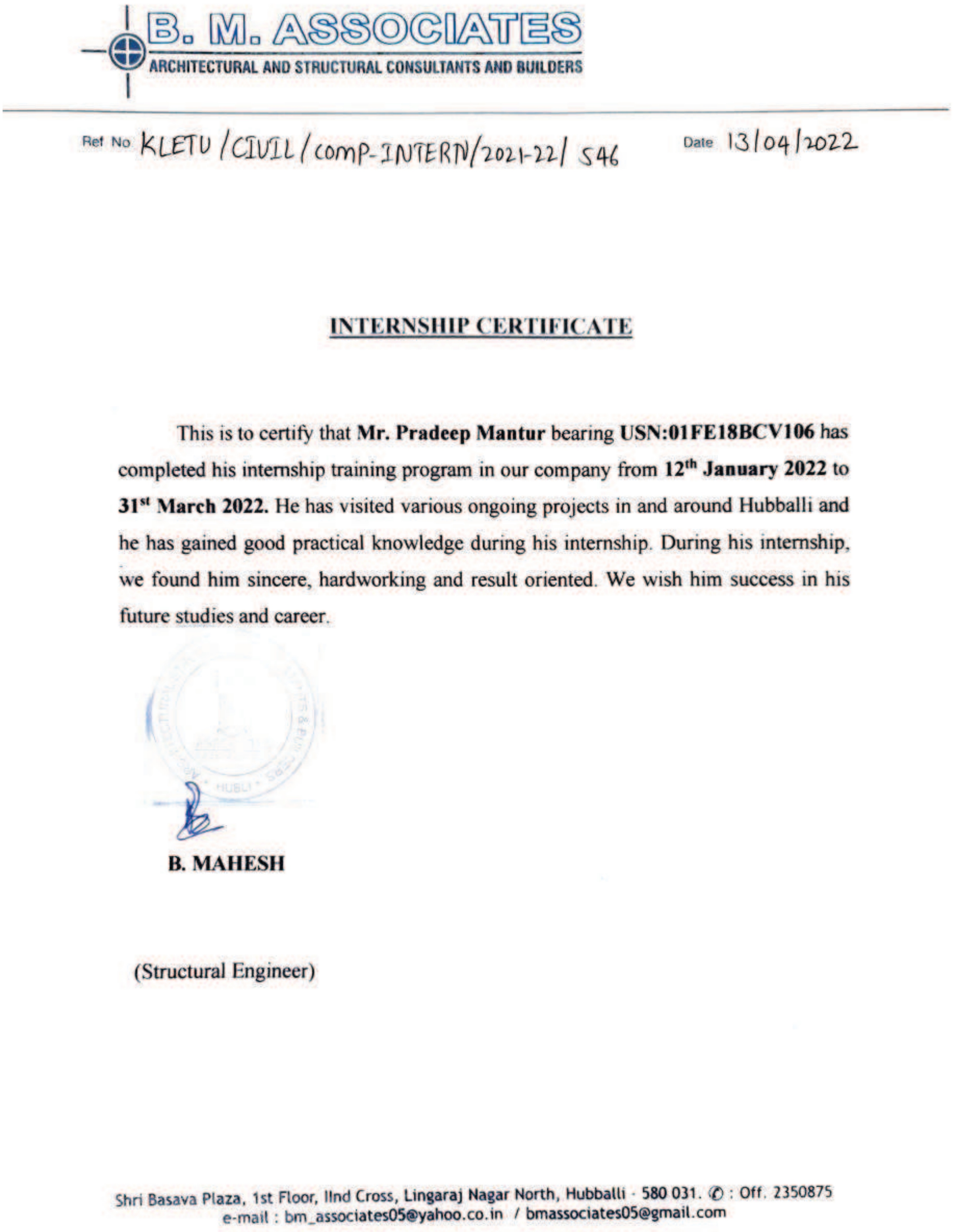
CERTIFICATE

This is to certify that **Mr. Iranna Tukaram Kunigeri** bearing **USN: 01FE19BCV419** of 8th semester **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial internship training at our organization from **25-01-2022 to 28-03-2022**. During his training he was exposed to Building Construction site and worked on Building planning, drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

H [illegible] Ramadas
Project Manager
KLE society's JGMM Hospital & Medical college
Gabbur road, Hubballi

Project Manager
KAHER's JGMM Medical College
Gabbur Cross, HUBBALLI-580 028.



B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref No KLETU /CIVIL / COMP-INTERN/2021-22/ 546 Date 13/04/2022

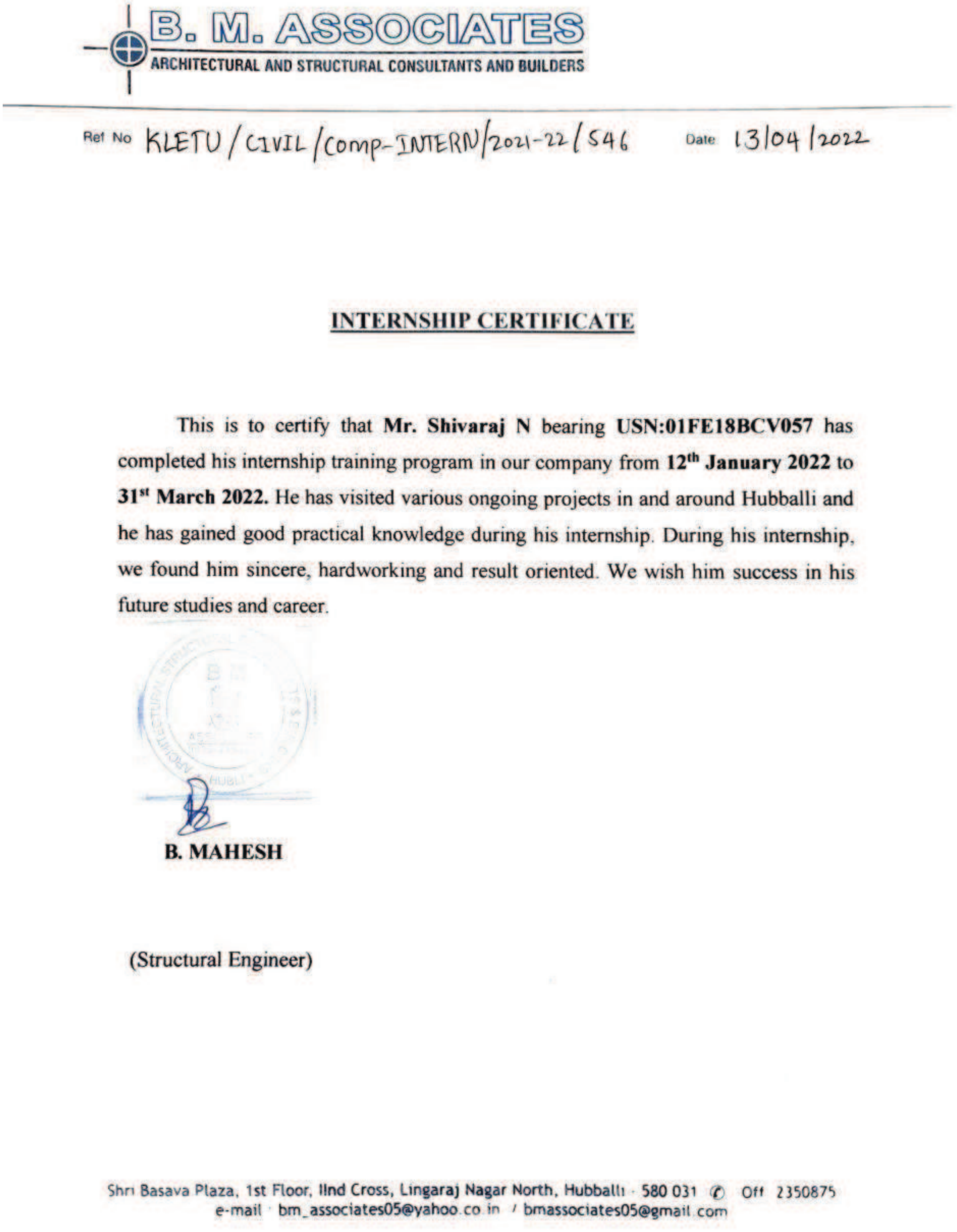
INTERNSHIP CERTIFICATE

This is to certify that **Mr. Pradeep Mantur** bearing **USN:01FE18BCV106** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off. 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com



B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref No KLETU / CIVIL / Comp-INTERN/2021-22 / 546 Date 13/04/2022

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Shivaraj N** bearing **USN:01FE18BCV057** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031 ✆ Off 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No KLETU/CIVIL/ COMP-INTERN/2021-22/546 Date 13/04/2022

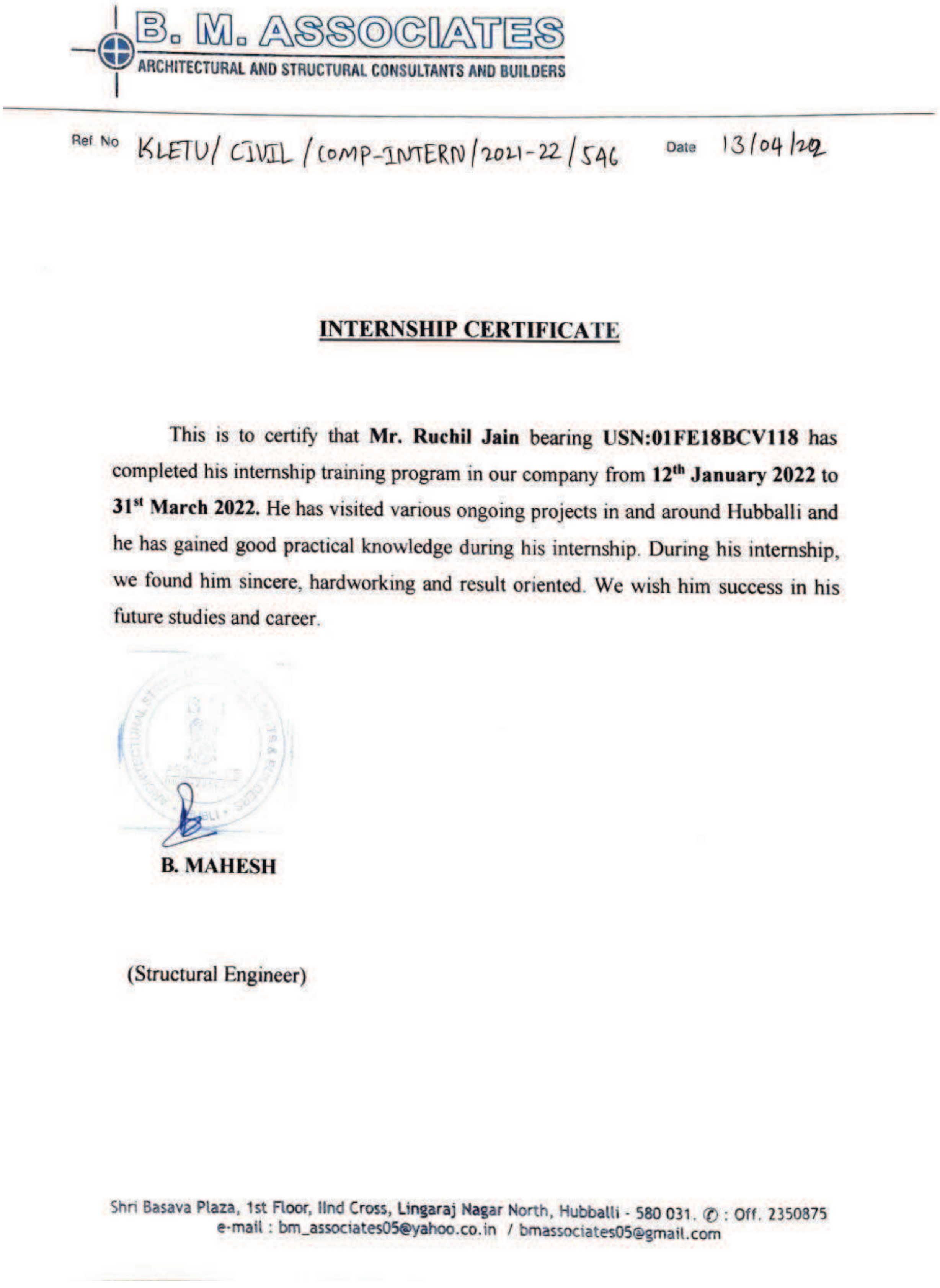
INTERNSHIP CERTIFICATE

This is to certify that **Mr. Vijay Gokak** bearing **USN:01FE18BCV116** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off. 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com



B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No KLETU/ CIVIL / COMP-INTERN/2021-22/ 546 Date 13/04/22

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Ruchil Jain** bearing **USN:01FE18BCV118** has completed his internship training program in our company from **12th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off. 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

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Website : www.shirkegroup.com **CIN :** U45201PN1994PTC077340

MANAGEMENT SYSTEM CERTIFICATION
DNV·GL
ISO 9001 ISO 14001
ISO 45001

Address of the Site:
IIT-Dharwad Project,
Kelageri, Chikkamalligewad Village,
Pune-Bengaluru Road, Opp. High Court,
Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/266
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Ajinkya Ainapure bearing USN 01FE19BCV403** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For **B.G. Shirke Construction Technology Pvt Ltd.,**

B G Sangale
Dy. Chief Executive.

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IIT-PROJECT
DHARWAD

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MANAGEMENT SYSTEM CERTIFICATION
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ISO 9001 ISO 14001
ISO 45001

Address of the Site:
IIT-Dharwad Project,
Kelageri, Chikkamalligewad Village,
Pune-Bengaluru Road, Opp. High Court,
Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/267
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Akash N.S bearing USN 01FE19BCV404** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For **B.G. Shirke Construction Technology Pvt Ltd.,**

B G Sangale
Dy. Chief Executive.

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MANAGEMENT SYSTEM CERTIFICATION DNV·GL
ISO 9001 ISO 14001
ISO 45001

Address of the Site:
IIT-Dharwad Project,
Kelageri, Chikkamalligewad Village,
Pune-Bengaluru Road, Opp. High Court,
Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/275
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. K.Vishal bearing USN 01FE19BCV430** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For B.G. Shirke Construction Technology Pvt Ltd.,

B G SHIRKE CONST. TECH. PVT. LTD.
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DHARWAD

B G Sangale
Dy. Chief Executive.

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ISO 45001

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Pune-Bengaluru Road, Opp. High Court,
Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/273
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Shivakumar G bearing USN 01FE18BCV115** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For B.G. Shirke Construction Technology Pvt Ltd.,

IIT-PROJECT
DHARWAD

B G Sangale
Dy. Chief Executive.

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HOD, Department of Civil Engineering, KLE Technological University, Hubballi – 31

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ISO 45001

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Pune-Bengaluru Road, Opp. High Court,
Dharwad 580 011
Email: bgs1425@shirke.co.in / bgs531@shirke.co.in

Ref: BGSCTPL/IIT-D/INTERNSHIP/HR/2021-22/270
Date: 28th March'2022

TO WHOMSOEVER IT MAY CONCERN

INTERNSHIP COMPLETION CERTIFICATE

This is to certify that **Mr. Sanjeev Madiwalar bearing USN 01FE19BCV412** studying in **VIII Semester, Department of Civil Engineering of KLE Technological University, Vidyanagar, Hubballi – 580 031** has successfully completed his internship-based project work in **B. G. Shirke Construction Technology Pvt. Ltd.** from **15th January'2022** to **28th March'2022** at our Construction of **CPWD - Indian Institute of Technology Dharwad** at Dharwad.

This is done in fulfilment of the requirements for the degree of Bachelor of Engineering in Civil Engineering.

He was very sincere & hard working in his internship-based project work and was up to the expectations. We wish him all the best for his future endeavors.

For **B.G. Shirke Construction Technology Pvt Ltd.,**

B G Sangale
Dy. Chief Executive.

IIT-PROJECT
DHARWAD

Copy to:
HOD, Department of Civil Engineering, KLE Technological University, Hubballi – 31

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Karthikay Santaba** bearing **USN:01FE18BCV098** has completed his internship training program in our company from **24th January 2022 to 31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B M
ASSOCIATES
0836-2350875

B. MAHESH

(Structural Engineer)

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No.   Date :

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Lankesh P Koujalagi** bearing **USN:01FE18BCV105** has completed his internship training program in our company from **24th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Amit Rawal** bearing **USN:01FE18BCV084** has completed his internship training program in our company from **24th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B M ASSOCIATES
0836-2350875
HUBLI

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031 ✆ Off 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

B. M. ASSOCIATES
ARCHITECTURAL AND STRUCTURAL CONSULTANTS AND BUILDERS

Ref. No

Date

INTERNSHIP CERTIFICATE

This is to certify that **Mr. Gururaj Anandashetti** bearing **USN:01FE18BCV103** has completed his internship training program in our company from **24th January 2022** to **31st March 2022.** He has visited various ongoing projects in and around Hubballi and he has gained good practical knowledge during his internship. During his internship, we found him sincere, hardworking and result oriented. We wish him success in his future studies and career.

B M
ASSOCIATES
0836-2350875
HUBLI

B. MAHESH

(Structural Engineer)

Shri Basava Plaza, 1st Floor, IInd Cross, Lingaraj Nagar North, Hubballi - 580 031. ✆ : Off 2350875
e-mail : bm_associates05@yahoo.co.in / bmassociates05@gmail.com

Galagali Associates
STRUCTURAL ENGINEERS, BRIDGE DESIGNERS
& PROJECT MANAGEMENT CONSULTANTS

AN ISO 9001:2008
CERTIFIED COMPANY

1st Floor, Anand Complex, Opp. Kotambri Science College, Vidyanagar, Hubballi -580031. ☎ 0836 2277437 E-mail : galagali.associates@gmail.com Web : www.galagali.org

CERTIFICATE

This is to certify that **Mr. KISHOREKUMAR KALAL** bearing **USN 01FE19BCV429** of 8th semester, **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial training at our organization from **24-01-2022 to 29-03-2022** . During his training he was exposed to some of the Building Construction sites and worked on Building Planning, Drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

A APatil

Akhila Patil
HR Manager
M/s Galagali Associates
Hubballi.

HUBLI
Tel. : 2277437

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CERTIFICATE

This is to certify that **Ms. BHAGYASHREE HUGAR** bearing **USN 01FE19BCV410** of 8th semester, **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial training at our organization from **24-01-2022 to 29-03-2022** . During her training she was exposed to some of the Building Construction sites and worked on Building Planning, Drawing, Estimation and Quality issues.

During the training period she was found to be obedient and exhibited quest for learning.

AAPatil
Akhila Patil
HR Manager
M/s Galagali Associates
Hubballi.

Galagali Associates
STRUCTURAL ENGINEERS, BRIDGE DESIGNERS
& PROJECT MANAGEMENT CONSULTANTS

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CERTIFICATE

This is to certify that **Mr. NAVEEN HULLAMBI** bearing **USN 01FE19BCV418** of 8th semester, **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial training at our organization from **24-01-2022 to 29-03-2022** . During his training he was exposed to some of the Building Construction sites and worked on Building Planning, Drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

A APatil

Akhila Patil
HR Manager
M/s Galagali Associates
Hubballi.

Galagali Associates
ARCHITECTURAL & STRUCTURAL CONSULTANTS
HUBLI
Tel. : 2277437

Galagali Associates
STRUCTURAL ENGINEERS, BRIDGE DESIGNERS
& PROJECT MANAGEMENT CONSULTANTS

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CERTIFICATE

This is to certify that **Mr. PRASANNA KALKOTI** bearing **USN 01FE19BCV408** of 8th semester, **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial training at our organization from **24-01-2022 to 29-03-2022** . During his training he was exposed to some of the Building Construction sites and worked on Building Planning, Drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

AAPatil

Akhila Patil
HR Manager
M/s Galagali Associates
Hubballi.

Branch Office : A-503, Pride Pavilion No: 2/1,1st Stage, 6th Phase West of Chord Road Rajajinagar, Bengaluru - 560010 Cell : +91 9448113737

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- Bridge design
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- Proof Checking
- Soil / Geotechnical Investigation

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1st Floor, Anand Complex, Opp. Kotambri Science College, Vidyanagar, Hubballi -580031. ☎ 0836 2277437 E-mail : galagali.associates@gmail.com Web : www.galagali.org

CERTIFICATE

This is to certify that **Mr. SHIVAKUMAR N. Y** bearing **USN 01FE19BCV407** of 8th semester, **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial training at our organization from **24-01-2022 to 29-03-2022** . During his training he was exposed to some of the Building Construction sites and worked on Building Planning, Drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

AAPatil
Akhila Patil
HR Manager
M/s Galagali Associates
Hubballi.

HUBLI
Tel. : 2277437

Branch Office : A-503, Pride Pavilion No: 2/1,1st Stage, 6th Phase West of Chord Road Rajajinagar, Bengaluru - 560010 Cell : +91 9448113737

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CERTIFICATE

This is to certify that **Mr. SURESH R.B** bearing **USN 01FE19BCV422** of 8th semester, **School of Civil Engineering, KLE Technological University Hubballi,** has successfully undergone industrial training at our organization from **24-01-2022 to 29-03-2022** . During his training he was exposed to some of the Building Construction sites and worked on Building Planning, Drawing, Estimation and Quality issues.

During the training period he was found to be obedient and exhibited quest for learning.

Akhila Patil
HR Manager
M/s Galagali Associates
Hubballi.

HUBLI
Tel. : 2277437

STIN:29ADAFS3950J1ZS
WD REG NO.:CNB/C1/CIVIL/4863/2020
M/s. S.S.Alur Construction Co.
ENGINEERS & CLASS-1 CONTRACTORS

||Shri Sangameshwar Krupa||

Vaishnavi heights,Second floor,
Near Ibrahimpur railway gate,
Opp. KSFC, Vivek nagar(east),
Vijayapura-586109
tel:08352-298495
E-mail:ssalur123@gmail.com
accounts@alurconstructions.co.in

Ref. no.

Date:

INTERNSHIP CERTIFICATE

This is to certify that **INDUSTRY INTERNSHIP TRAINING AND PROJECT PROGRAM** by **MISS. KEERTHI M ANGADI USN: 01FE18BCV029** a bonafide student of **KLE TECHNOLOGICAL UNIVERSITY, HUBBALLI,** in partial fulfillment for the award of Bachelor of Civil Engineering degree for 8th Semester has successfully completed internship Training in our company **from 15/01/2022 to 27/03/2022**.

She has thoroughly studied INTERNSHIP PROGRAM in our company, as required for her project and copy of report has been submitted to us.

During this period of internship program we found her to be Punctual, Hardworking, Disciplined, Sincere and Obedient.

For. M/s. S.S.Alur Construction Co.

Partner.

M/s. S.S. Alur Construction Co.
Vijayapur
*

|| Shri Sangameshwar Kripa ||

GSTIN:29ADAFS3950J1ZS
PWD REG NO.:CNB/C1/CIVIL/4863/2020
M/s. S.S.Alur Construction Co.
ENGINEERS & CLASS-1 CONTRACTORS

Vaishnavi heights,Second floor,
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tel:08352-298495
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accounts@alurconstructions.co.in

Ref. no.

Date:

INTERNSHIP CERTIFICATE

This is to certify that **INDUSTRY INTERNSHIP TRAINING AND PROJECT PROGRAM** by **Mr. PRAVEEN D SAVALAGI USN: 01FE18BCV045** a bonafide student of **KLE TECHNOLOGICAL UNIVERSITY, HUBBALLI**, in partial fulfillment for the award of Bachelor of Civil Engineering degree for 8th Semester has successfully completed internship Training in our company **from 15/01/2022 to 27/03/2022** .

He has thoroughly studied INTERNSHIP PROGRAM in our company, as required for his project and copy of report has been submitted to us.

During this period of internship program we found him to be Punctual, Hardworking, Disciplined, Sincere and Obedient.

For. M/s. S.S.Alur Construction Co.

Partner.

M/s. S.S.Alur Construction Co.
Vijayapur

alurgroupofcompanies.com

|| Shri Sangameshwar Krupa ||

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M/s. S.S.Alur Construction Co.
ENGINEERS & CLASS-1 CONTRACTORS

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Vijayapura-586109
tel:08352-298495
E-mail:ssalur123@gmail.com
accounts@alurconstructions.co.in

Ref. no.

Date

INTERNSHIP CERTIFICATE

This is to certify **that INDUSTRY INTERNSHIP TRAINING AND PROJECT PROGRAM** by **Mr. VISHWA V PATIL USN: 01FE18BCV070** a bonafide student of **KLE TECHNOLOGICAL UNIVERSITY, HUBBALLI,** in partial fulfillment for the award of Bachelor of Civil Engineering degree for 8th Semester has successfully completed internship Training in our company **from 15/01/2022 to 27/03/2022** .

He has thoroughly studied INTERNSHIP PROGRAM in our company, as required for his project and copy of report has been submitted to us.

During this period of internship program we found him to be Punctual, Hardworking, Disciplined, Sincere and Obedient.

For. M/s. S.S.Alur Construction Co.

Partner.

M/s. S.S. Alur Construction Co.
Vijayapur

|| Shri Sangameshwar Krupa ||

GSTIN:29ADAFS3950J1ZS
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Ref. no.

Date:

INTERNSHIP CERTIFICATE

This is to certify that **INDUSTRY INTERNSHIP TRAINING AND PROJECT PROGRAM** by **Mr. RUTIK M HALLIMANI USN: 01FE18BCV052** a bonafide student of **KLE TECHNOLOGICAL UNIVERSITY, HUBBALLI**, in partial fulfillment for the award of Bachelor of Civil Engineering degree for 8th Semester has successfully completed internship Training in our company **from 15/01/2022 to 27/03/2022** .

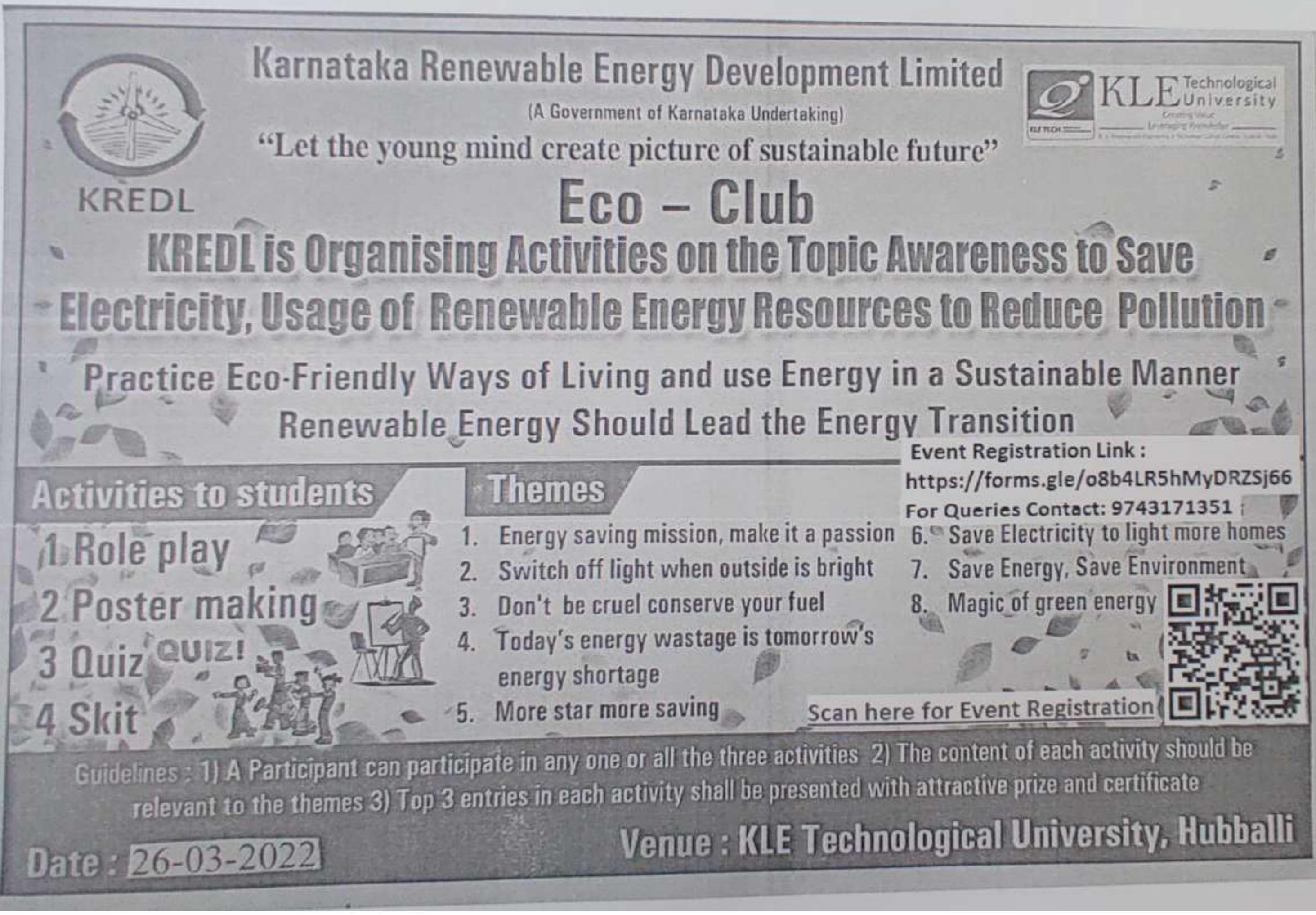
He has thoroughly studied INTERNSHIP PROGRAM in our company, as required for his project and copy of report has been submitted to us.

During this period of internship program we found him to be Punctual, Hardworking, Disciplined, Sincere and Obedient.

For. M/s. S.S.Alur Construction Co.

Partner.

M/s. S.S. Alur Construction Co.
Vijayapur



KREDL

Karnataka Renewable Energy Development Limited

(A Government of Karnataka Undertaking)

KLE Technological University

"Let the young mind create picture of sustainable future"

Eco – Club

KREDL is Organising Activities on the Topic Awareness to Save Electricity, Usage of Renewable Energy Resources to Reduce Pollution

Practice Eco-Friendly Ways of Living and use Energy in a Sustainable Manner

Renewable Energy Should Lead the Energy Transition

Event Registration Link :
https://forms.gle/o8b4LR5hMyDRZSj66
For Queries Contact: 9743171351

Activities to students

1 Role play
2 Poster making
3 Quiz
4 Skit

Themes

1. Energy saving mission, make it a passion
2. Switch off light when outside is bright
3. Don't be cruel conserve your fuel
4. Today's energy wastage is tomorrow's energy shortage
5. More star more saving
6. Save Electricity to light more homes
7. Save Energy, Save Environment
8. Magic of green energy

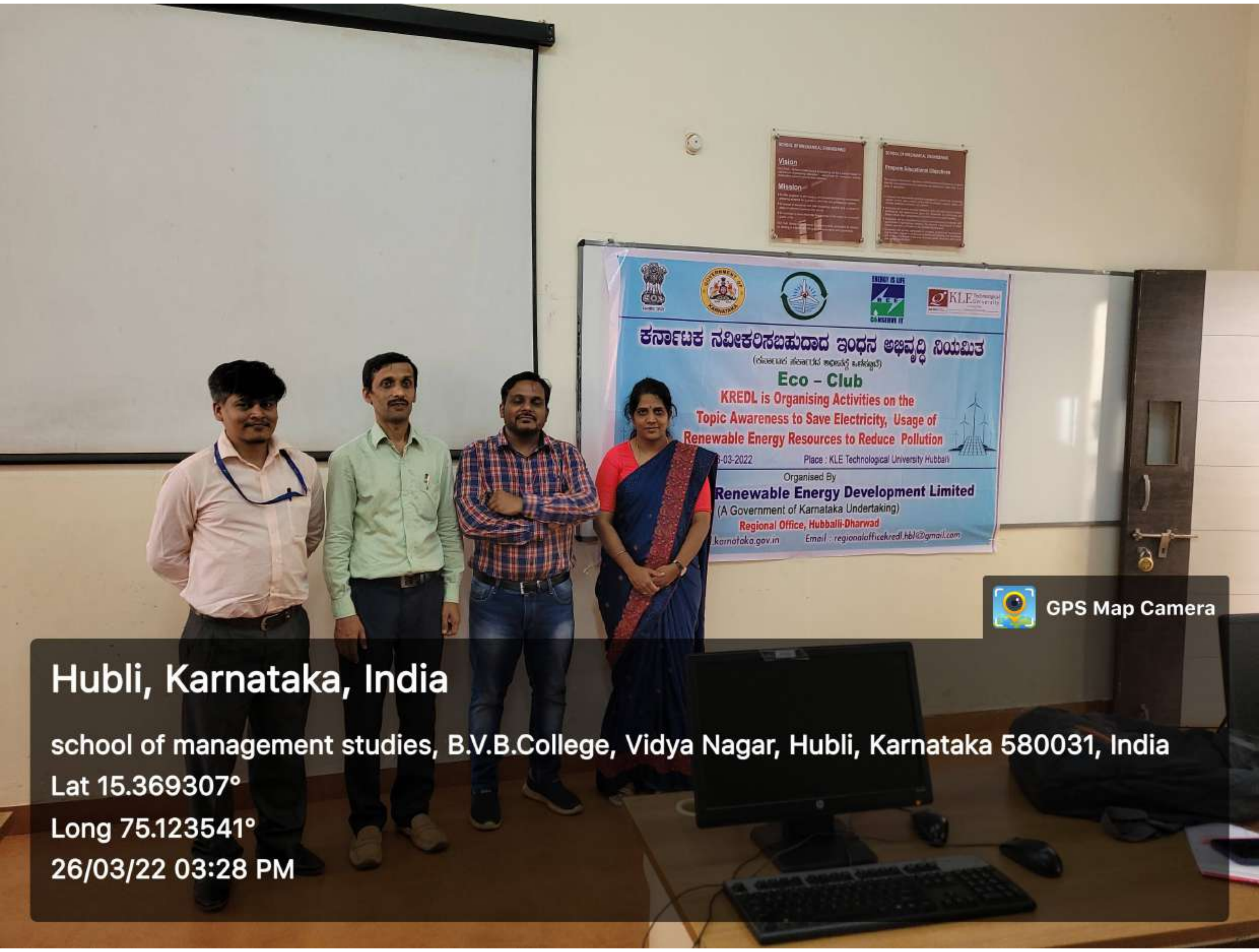
Scan here for Event Registration

Guidelines : 1) A Participant can participate in any one or all the three activities 2) The content of each activity should be relevant to the themes 3) Top 3 entries in each activity shall be presented with attractive prize and certificate

Date : 26-03-2022

Venue : KLE Technological University, Hubballi


ಕರ್ನಾಟಕ ನವೀಕರಿಸಬಹುದಾದ ಇಂಧನ ಅಭಿವೃದ್ಧಿ ನಿಯಮಿತ
Eco – Club
KREDL is Organising Activities on the
Topic Awareness to Save Electricity, Usage of
Renewable Energy Resources to Reduce Pollution
Organised By
Karnataka Renewable Energy Development Limited
(A Government of Karnataka Undertaking)
Regional Office, Hubballi-Dharwad
GPS Map Camera
Hubli, Karnataka, India
school of management studies, B.V.B.College, Vidya Nagar, Hubli, Karnataka 580031, India
Lat 15.369307°
Long 75.123541°
26/03/22 02:37 PM

ಕರ್ನಾಟಕ ನವೀಕರಿಸಬಹುದಾದ ಇಂಧನ ಅಭಿವೃದ್ಧಿ ನಿಯಮಿತ
Eco – Club
KREDL is Organising Activities on the
Topic Awareness to Save Electricity, Usage of
Renewable Energy Resources to Reduce Pollution
6-03-2022
Place : KLE Technological University Hubballi
Organised By
Renewable Energy Development Limited
(A Government of Karnataka Undertaking)
Regional Office, Hubballi-Dharwad
karnataka.gov.in
Email : regionalofficekredl.hbl@gmail.com
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26/03/22 03:28 PM