Efficiency of Photodegradation Properties of Nickel Calciate Nanoparticle Synthesized by solution combustion method

A.M. Santhosh1, K. Yogendra1*, K.M. Mahadevan2, I.H. Mallikarjuna3, N. Madhusudhana1

1Department of P.G studies and Research in Environmental Science, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Shivamogga, Karnataka, India
2Department of Chemistry, Kadur P.G Center, Kuvempu University, Kadur, Karnataka, India
3Department of Chemistry, Government Science College Hassan, Karnataka, India

*Corresponding author: yogendraku@gmail.com Tel: +91 9448149461

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Abstract- In the present work, With the intention of removal of colour from Coomassie Brilliant Blue R (CBBR), a triphenylmethane azo dye using the synthesized Nickel Calciate nanoparticles (NiCaO2) in presence of natural sunlight. The nanoparticles were synthesized by using solution combustion method and characterisation was done by Scanning Electron Micrograph (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX), Brunauer Emmett-Teller surface area determination and point zero charge determined by pH drift method. The band gap was determined by using UV-absorption spectroscopy. The rate of degradation efficiency was studied by varying different parameters such as catalyst concentration, solution pH dye concentration. The rate of degradation is highly efficient in 5×10−6 mol/dm³ dye concentration with pH 6 and constant catalyst concentration 0.027g/50ml. Pseudo first-order rate constants and initial rates were determined and the photocatalytic mechanism was proposed. The result proves that NiCaO2 can be used for removal of dyes from CBBR.

Keywords- Catalyst, Coomassie Brilliant Blue R, Nanoparticles, NiCaO2, Photodegradation

I. INTRODUCTION

Water is the vital and basic need of life. Water is highly polluted by the many ways, majorly by the industries. Dyes and pigments are widely used in textiles, paper, plastics, leather, food and cosmetic industry to colour products [1]. Approximately 10,000 different types of dyes and pigments are utilized worldwide, around 10-15% of the dyes are remained in effluent throughout the course of dying process [2]. The various types of dyes used in textile industry, such as direct dyes, reactive dyes, vat dyes sulphur dyes, disperse dyes and naphthol dyes, which are both soluble and insoluble in water and involves a variety of organic chemicals [3]. Dyes and their substitute’s products have found to be dangerous to aquatic life, mutagenic/carcinogenic and genotoxic [4,5,6,7,8]. The Coomassie brilliant blue belongs to the class of triphenylmethane azo dyes family and shows greater solubility in water in the form of its sodium salt [9]. Coomassie brilliant blue R-250 (CBBR-250) widely used in the biological staining, printing and dyeing leather, ink, lithography, etc. Exposure to these dyes can cause irritation to nose, throat and upper respiratory tract, chemical conjunctivitis to eyes and on chronic exposure it may cause skin dermatitis and show some mutagenic effects in the living organisms [10]. Other researchers have investigated the degradation of CBBR-250 by different nanoparticles like Fe3O4 [11] ZnO [10] α-chitin nanoparticles [12] and Copper modified iron oxide nanoparticles [13]. Altikatoglu and Celebi [14] decolorize the CBBR-250 by Dextran Aldehyde-modified Horseradish Peroxidase. Sankar et al. [15] degrade the CBBR-250 by green synthesized copper oxide nanoparticles.

The treatment through the biological methods is efficient to remove COD but not remove colour because of their complex aromatic molecular structures that resist degradation. Chemical and physical treatment is not harmful, but it can transfer pollutants from one phase to another, hence evolving new treatment technologies for eliminating contaminants from wastewater.[16],[17]. More recently, “Advanced Oxidation Process” (AOPs) use chemical procedures based on the use of catalysts or photochemical compounds which generate highly reactive transient species as the hydroxyl radical which possesses high affectivity for the oxidation of organic compounds [18]. Advanced Oxidation Processes (AOP) has been proposed as a substitute method for water purification of dyes and many other organics in wastewater and effluents. These processes usually, imply UV/H2O2, UV/O3 or UV/Fenton’s reagent for
the oxidative degradation of contaminants [19],[20]. Semiconductor photocatalysis is another developed AOP, which has significant among AOP as a predicting tool for enforcing to the large-scale purification of wastewaters at low cost [21]. As per the research works carried out by many researchers in the past, the present work was carried out with the intention of providing a solution to the aquatic pollution and their effects. Here, the nanoparticle will act as a solar catalyst and through photocatalytic activity will remove the color from the dye solution and controls the pollution. With different parameters like dosage, pH, and dye concentration were examined and studied in the present work.

II. MATERIAL AND METHODS

The commercially available water soluble dyes Coomassie Brilliant Blue R (λ<sub>max</sub> 557nm) were obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra (Figure 1). The chemicals like Nickel Nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) (99% A. R.), are obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra Calcium Nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) (99%, A. R.), and Urea (NH<sub>2</sub>CONH<sub>2</sub>) (99.5%), were obtained from Hi-Media Chemicals, Mumbai and used as received without any further purification. The UV-VIS single beam spectrophotometer-119 (Systronics) has been used for recording absorbance.

2.1 SYNTHESIS OF NANOPARTICLES

The Nickel Calcinate nanoparticle was prepared by solution combustion method using Nickel Nitrate, Calcium Nitrate, and Urea as fuel. Stoichiometric compositions of Nickel Nitrate (5.48g), Calcium Nitrate (7.08g), and were dissolved in minimum quantity of water along with Urea (6.05g) was taken in a silica crucible (with volume of 100 cm<sup>3</sup>) using distilled water. Crucible was then introduced into the muffle furnace for calcination which was preheated to 600°C. According to propellant chemistry the reaction is as follows. 3Ni(NO<sub>3</sub>)<sub>2</sub> + 3Ca(NO<sub>3</sub>)<sub>2</sub> + 10NH<sub>2</sub>CONH<sub>2</sub> ------ 3NiCaO<sub>2</sub> + 10CO<sub>2</sub> + 20H<sub>2</sub>O + 16N<sub>2</sub> – (1)

The solution boils and undergoes dehydration followed by decomposition along with the release of certain amounts of gases it froths and swells forming foam which ruptures with a flame and glows to incandescence. The product obtained after calcination is crushed in a mortar to make it amorphous and further used for the photocatalytic degradation study of CBBR aqueous suspensions.

2.2 CHARACTERIZATION OF SYNTHESIZED NANOPARTICLES

Powder X-ray diffraction (XRD) was performed by (Rigaku diffractometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. Specific surface areas (SSA) of all photocatalysts were evaluated at 77 K by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (NOVA-1000 version 3.70 Instrument). Scanning electron microscope (SEM) image was taken with a JEOL (JSM-840A). The UV-visible spectra of the photocatalysts were carried out using a UV-visible spectrophotometer in the λ range from 200 to 1200 nm. The confirmatory presence of elements was carried out using Energy Dispersive X-ray (EDAX).

2.3 POINT OF ZERO CHARGE:

Point of zero charge or isoelectric point is the pH of the solution at which the total charge on the surface of the nanoparticles becomes zero (neutral). The point of zero charge of NiCaO<sub>2</sub> was measured by pH drift method, 50ml of Nacl 0.01M was taken in six separate beakers and bubbled it with Nitrogen gas to expel the dissolved CO<sub>2</sub> for few minutes at room temperature till it gets a stable pH reading. The pH of the solution in each beaker was adjusted between 2 to 12 by adding 0.1N Hcl and 0.1N NaOH after which 50mg of NiCaO<sub>2</sub> nanoparticles were added. This system was kept at room temperature until concurrent pH measured, this was kept for 92hrs for the stabilization of pH. The graph was plot against final pH v/s initial pH, the point which this curve crosses the initial pH=final pH straight line is the point of zero charge.

2.4 PHOTOCATALYTIC EXPERIMENT

A Stock solution of CBBR was prepared by dissolving 0.0412 g of triphenylmethane azo dye with 50mL double
distilled water using a 50ml volumetric flask. The photodegradation of the triphenylmethane azo dye was conducted the batch study under solar light irradiation. Experiments were conducted in 100ml beakers, which were placed on a magnetic stirrer which continuously agitate the solution until the whole experiment was complete. In each experiment, an appropriate amount of triphenylmethane azo dye from stock solution was diluted to 50 ml with double distilled water. The pH of the dye solution was adjusted by adding 0.1N NaOH or 0.1N HCl. In all the experiments, the dye solution of appropriate concentration was taken in the 100ml glass beaker and covered with a glass plate to avoid evaporation of dye solution in the sunlight. Experiments were conducted for 240 min, and 05 mL of samples were taken from beakers with time intervals 30min. The whole experimental set-up was placed in sunlight between 11 a.m. and 4 p.m. and the average intensity of sunlight during this period is 889×100 lux unit using lux meter. The progress of photodegradation of the brilliant blue R was monitored by withdrawing a definite quantity of aliquot at regular intervals and measuring the absorbance in UV-vis spectrophotometer.

2.6 KINETIC STUDIES
The photodegradation of CBBR dye containing NiCaO₂ obeys pseudo-first order kinetics. The rate expression is given by

Rate = -(dC/dt) = kC

(2)

Where C the concentration of dye (milligrams per liter), t the irradiation time, k the reaction rate constant (milligrams per liter hour), and k is the adsorption coefficient of the reactant (liters per milligram). As the initial concentration (Co) of dye is low, the equation can be simplified to an apparent first-order expression.

ln(Co/C) = k ‘t

(3)

Where Co is the equilibrium concentration of the dye and C the concentration at time ‘t’. When a plot of ln (Co/C) versus time results in a straight line; its slope is the pseudo-first-order decolourization rate constant (kapp).

Figure 2: XRD of the synthesized NiCaO₂ Nanoparticles

Figure 3: UV-absorption spectra of synthesized NiCaO₂ Nanoparticles

Figure 4: Scanning Electron Micrographs of synthesized NiCaO₂ Nanoparticles

Figure 5: Energy Dispersive X-ray of synthesized NiCaO₂ Nanoparticles

III. RESULT AND DISCUSSION

3.1 CHARACTERIZATION OF THE NANOPARTICLES
Figure 2 shows, the XRD patterns of NiCaO₂ nanoparticles reveal that, the presence of Rhombo Hedral structure and the 2θ peaks were observed which related to Nickel oxide, (36.67°, 42.72°, 54.00°, 62.26°) (JCPDS card No.01-089-3080) Calitate (28.97°, 39.02°, 46.78°) (JCPDS card No.00-003-0569) and the XRD was performed by powder X-ray diffraction (Rigaku diffractometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. The pattern obtained from the XRD analysis of the prepared NiCaO₂ nanoparticles is presented in figure 2.

According to the Debye Scherrer’s formula: 

$$D = \frac{K\lambda}{\beta \cos \theta}$$

(4)
In the present work, the powdered sample of newly synthesized NiCaO₂ nanoparticle was examined by XRD studies and found that NiCaO₂ nanoparticle size varies from 8 nm to 18 nm and henceforth the average crystallite size was found to be 14 nm. Figure 3 illustrated that, the optical absorption is an important tool to obtain the optical energy band gap of crystalline and amorphous materials. The fundamental absorption corresponds to the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. The absorption spectrum reveals that the NaCaO₂ nanoparticle absorption in the visible light region with a wavelength above 400 nm. The optical energy band gap (Eg) is calculated from the relation:

\[(a h \nu) = B (h \nu - E_g)^n\]  

(5)

Where, ‘hν’ is the photon energy, ‘B’ is the constant and ‘n’ is the power factor and that takes 1/2, 2, 3/2 and 3 allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The optical band gap of the NaCaO₂ nanoparticle found to be 3.05eV [22]. Figure 4 reveals that, the structural morphology of the nanoparticles looks like agglomeration, cluster, and foamy in nature [23]. Figure 5 confirms the presence of nickel, calcium, carbon and oxygen signals of the nickel calcite Nanoparticles. The vertical axis displays the number of x-ray counts although the horizontal axis displays energy in KeV (Figure 5). The weight and atomic percentage of carbon, Oxygen, calcium, and Nickel were found to be 7.79, 51.80, 25.74, 14.67 and 13.57, 67.76, 13.44, 5.23 for NiCaO₂ nanoparticles, these corresponds, the spectrum without impurities peaks. [23-24].

3.2 BET SURFACE AREA ANALYSIS

The catalytic activity of the nanoparticles is nearly related to their porous structure helping for contact with the pollutant which favors positively to the photocatalytic activity. Using the BET surface area analysis, the specific surface area and pore volumes obtained for the nanoparticles are reported in table 1. The surface area for NiCaO₂ is 2.44m²/g. This value is analogues to the other nanoparticles [25],[26],[27]. The obtained surface area for NiCaO₂ is suitable to carry out for the photocatalytic activity, as the efficiency of photoelectric conversion is directly proportional to the surface area available [22],[28]

| Catalyst     | Surface area | Pore volume | Average pore diameter |
|--------------|--------------|-------------|-----------------------|
| NiCaO₂ (urea)| 2.4416 m²/g  | 0.01013 cc/g| 165.87Å               |

3.3 NATURE OF POINT OF ZERO CHARGE

It is important to determine the iso-electric point or point zero charge of the nanoparticles. For the determination of PZC of NiCaO₂, NiCaO₂ nanoparticle graph of initial pH against final pH was plotted and the values of pH_pzc was found to be 11.5 (Figure 6). Below this pH_pzc the surface is acidic in nature, positively charged and above this surface is basic in nature and negatively charged. The pH of CBBR is below the pH_pzc, which favors the adsorption of anionic Brilliant Blue R and thus the suitable for Photocatalysis [28],[29].

3.4 EFFECT OF CONTACT TIME

The effect of contact time on the adsorption of BBR was studied to determine the time taken by NiCaO₂ nanoparticles to remove 3×10⁻⁵ mol/dm³ to 7×10⁻⁵ mol/dm³ CBBR solution at pH 6. A 0.027g of NiCaO₂ nanoparticles were added into a 50mL of CBBR solution. Absorbance of the solution at 557nm with time was determined to monitor the CBBR concentration. The results are shown in figure 7. The CBBR concentration decrease with time is due to its adsorption on NiCaO₂ nanoparticles. It can be seen that in about 60 min, almost all the BBR became adsorbed. Agitation time of 60min was selected for succeeding experiments.

3.5 MECHANISM OF THE PHOTOCATALYTIC DEGRADATION

The mechanism of photocatalytic activity of nanoparticles can be predicted. Nanoparticles when exposed to sunlight, molecules get activated and transfer electrons from valence bond to conduction band. Molecular oxygen reduces...
electron present in the conduction band to generate the super oxide radical. The surface of the photocatalyst was adsorb the molecular oxygen to prevent the hole-electron pair recombinant process [30],[31]. Photocatalytic degradation decreases by combining the hole-electron pair. In presence of oxygen and organic molecule may generate the hydrogen peroxyde or organic peroxide and hydrogen peroxyde can be generated in another way. Hydroxyl radicals are powerful oxidizing agents forms by the hydrogen peroxyde and these radicals are capable to degrade the dye molecules.

Figure 8: Mechanism of Photodegradation of CBBR dye

3.6 EFFECT OF INITIAL DYE CONCENTRATION

The effect of initial dye concentration on the rate of degradation of CBBR by varying the dye concentration from 3×10⁻⁴ mol/dm³ to 7×10⁻⁴ mol/dm³ with pH 6, constant catalyst loading 0.027g/50ml and the results are present in table 2 and figure 9 shows the relationship between the dye concentration and NiCaO₂ nanoparticles with respect to the irradiation time on photocatalytic degradation of CBBR dye. The results depict that, the rate of degradation increases with increase in the dye concentration up to 5×10⁻⁴ mol/dm³ and gradually decreases and due to the equilibrium adsorption of the dye on the catalyst surface which results in the decrease in the active sites of the NiCaO₂ nanoparticles and the generation of the hydroxyl radicals are constant. The decolourisation rate relates to the formation of •OH radical, critical species in the decolourisation process. Reactions of hydroxyl radicals decrease by increasing the dye concentration [32]. Similarly, this kind of study reported in [33],[34]. Hence k can be expressed as follows

\[ k = k_o P_{OH} P_{dye} \]

where \( k \) is the overall rate constant, \( k_o \) is the reaction rate constant, \( P_{OH} \) is the probability of generation of the ‘OH radicals on the catalyst surface, \( P_{dye} \) is the probability of the ‘OH radicals reacting with dye molecules. The reaction rate constant \( k_o \) is independent of the initial dye concentration by \( P_{OH} \) and \( P_{dye} \) will depend on the dye concentration implicitly. The previous works show that, the photocatalytic aromatic compound is through hydroxylation of hydroxyl radicals [34]. Sakthivel et al. (2003) [34] point out the rate-determining reaction may be the formation of ‘OH since they react with aromatic ring compounds. Thus, the formation of hydroxyl radicals by the reaction of holes with adsorbed \( \text{OH} \) and \( \text{H}_2\text{O} \). If we accept the adsorbed \( \text{OH} \) places are replaced by dye ions (dye”) which are produce from the dissociation of the sodium salt of dye molecules, (Dye-Na) → (dye”) +Na⁺ then the production of ‘OH will be reduces the active surfaces for producing OH radicals. Therefore, \( P_{OH} \) is adversely affected by the catalyst site, coverage fraction of dye and its oxidation intermediates. Hence the photon passes through the solution decreases by the increase in dye concentration, and reduces the light penetration resulting in lower production of \( \text{O}_2^- \) species and hydroxyl radicals in low concentration the reverse effect is observed [35],[36],[37].

From this study, it is concluded that as the initial concentration of dye increases, the amount of dye absorbed on the catalyst surface increased up to optimum dye concentration and further increase in the dye concentration there is a decrease in photons passes through the solution. Since illumination time and optimum catalyst concentration remains constant, the attacking of \( \text{OH} \) and \( \text{O}_2^- \) species molecules decreases by increasing the dye concentration [38],[39].

3.7 EFFECT OF pH

The release of industrial effluents had varied pH. In this study, the effect of pH is a very significant parameter in the photodegradation of dyes and also characteristics of

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wastewater. In this study pH was varying from the 2 to 10 with constant loading of catalyst (0.027g/50ml) and constant dye concentration 5×10⁻⁴ mol/dm³, the results are shown in table 3 and figure 10. The result illustrated that, the rate of degradation is increasing with increase in pH and shows maximum degradation at pH 6 and increase in pH the rate of degradation was gradually decreased in alkaline pH. Many researchers have reported this kind of work reported in [39],[40],[41]. The rate of degradation depends on the dye adsorbed on the surface of the catalyst. The adsorption was highly influenced by pH of the solution. So it can be suggested that, the dye adsorbed on NiCaO₂ nanoparticles influences the photocatalytic activity [42].

| pH  | k   | r   |
|-----|-----|-----|
| 2   | 1.7 | 1.2 |
| 4   | 1.9 | 2.0 |
| 6   | 3.4 | 2.9 |
| 8   | 2.3 | 2.3 |
| 10  | 1.7 | 2.0 |

Table 3: Influence of pH on the rate of degradation of CBBR, k pseudo first-order rate constant (×10⁻³, mol/dm³), CBBR= 5×10⁻⁴ catalytic amount = 0.027g/50ml, R-Initial, rate constant (×10⁻⁴, mol/dm³).

The effect of pH can be explained on the basis of zero point charge (ZPC) of NiCaO₂ nanoparticles, where zero point charge of NiCaO₂ was 11.5 shown in figure 6. NiCaO₂ nanoparticles surface is positively charged with below the 11.5 pH. The CBBR is an anionic in nature, it can easily combine with cationic charged nanoparticles and forms ionic bonds and it gets easily degraded. When the solution containing dye and nanoparticles expose to sunlight its hydroxyl anions increases the production of hydroxyl radicals. The result table 3 and figure 10 illustrated that, the rate of degradation shows higher in the acidic pH and adsorption of dye molecules was low at the alkaline pH. Increase in the hydroxyl radicals, they combine with the hole of the semiconductor and the ‘OH radicals are critical oxidizing species responsible for photodegradation on the greater the optimum pH [43],[44]. The decrease in the rate of degradation explained in terms of amphoteric nature of the catalyst, because the catalyst surface becomes negatively charged for the higher pH value, which causes the electrostatic repulsion between the catalyst and negatively charged dyes [35].

3.8 EFFECT OF CATALYST CONCENTRATION
A series of the experiment was carried out to assess the optimum catalyst loading by varying the amount of catalyst from 0.020g to 0.050g with constant dye concentration 5×10⁻⁴ mol/dm³ and constant pH 6. The rate of degradation is shown in table 3 and figure 11. Increase in the amount of photocatalyst, there is an increase in the number of active sites on the surface of the NiCaO₂ nanoparticle which turns to increases the number of OH⁻ and OH₂⁺ radicals [45]. The table 4 and Figure 11 illustrated that, the increase in the photocatalyst loading up to 0.027g/50ml the rate of degradation also increase, further the increase in the catalyst loading the rate of degradation was decreases due to excess loading of catalyst leads to turbidity of the solution and reduces the light penetration through the solution [46].

| Dosage  | k   | r   |
|---------|-----|-----|
| 0.020g  | 1.1 | 1.4 |
| 0.025g  | 1.7 | 1.9 |
| 0.027g  | 3.4 | 2.9 |
| 0.030g  | 1.9 | 1.8 |
| 0.040g  | 1.7 | 1.5 |
| 0.050g  | 1.3 | 1.2 |

Table 4: Effect of catalyst loading on the degradation of CBBR, k pseudo first-order rate constant (×10⁻³, mol/dm³), CBBR= 5×10⁻⁴ pH=6, R-Initial, rate constant (×10⁻⁴, mol/dm³).

The effect of pH can be explained on the basis of zero point charge (ZPC) of NiCaO₂ nanoparticles, where zero point charge of NiCaO₂ was 11.5 shown in figure 6. NiCaO₂ nanoparticles surface is positively charged with below the 11.5 pH. The CBBR is an anionic in nature, it can easily combine with cationic charged nanoparticles and forms ionic bonds and it gets easily degraded. When the solution containing dye and nanoparticles expose to sunlight its hydroxyl anions increases the production of hydroxyl radicals. The result table 3 and figure 10 illustrated that, the rate of degradation shows higher in the acidic pH and adsorption of dye molecules was low at the alkaline pH. Increase in the hydroxyl radicals, they combine with the hole of the semiconductor and the ‘OH radicals are critical oxidizing species responsible for photodegradation on the greater the optimum pH [43],[44]. The decrease in the rate of degradation explained in terms of amphoteric nature of the catalyst, because the catalyst surface becomes negatively charged for the higher pH value, which causes the electrostatic repulsion between the catalyst and negatively charged dyes [35].
below the level, it assumes that the catalyst surface and adsorption of the light by the catalyst are limiting factor [51],[52].

3.9 REUSE OF CATALYST
The NiCaO nanoparticles were used to test the reusability under similar condition solar light irradiation, the efficiency of NiCaO nanoparticle gets decreases first and second reuse. The efficiency decreased from 86% and 77% respectively due to the surface leaching of nanoparticles during separation [22],[28],[53],[54].

![Figure 12: Reusability of NiCaO nanoparticles against CBBR dye](image)

**Figure 12:** Reusability of NiCaO nanoparticles against CBBR dye

### IV. CONCLUSION

In the present work, as per the result, the synthesized nanoparticles have proved to be more consistent and efficient photocatalysts. The maximum degradation was achieved at $5 \times 10^{-3}$ mol/dm$^3$ dye concentration with constant catalyst concentration (0.027g/50ml) and constant pH 6. The photodegradation of the dye with NiCaO nanoparticles obeyed pseudo-first-order kinetics and it is recommended for industrial application. Hence, further research work can be carried out in a bigger scale and can be applied at industrial sectors to control aquatic pollution. Also, there is a scope for further improvement in the quality of the nanoparticles.

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AUTHOURS PROFILE

A.M. Santhosh has finished his M.Sc. degree in Environmental science in the year 2015 from the Department of Environmental Science, Kuvempu University, Karnataka State, India and currently working as a Research Scholar in Department of postgraduate studies and research in Environmental Science, Kuvempu University Shankaraghatta. He published 8 papers in international and national reputed journals. His research focuses on the synthesis, characterization of nanoparticles and its application to the degradation of dyes and industrial effluents. He is a member of Indian Science Congress Association (ISCA), Kolkata and International Journal of Scientific Research in Science and Technology, Gujarat.

Dr. K. Yogendra has finished his M.Sc. and Ph.D. in Environmental science. Currently, he is working as Assistant Professor in the Department of Post-graduate studies and research in Environmental science, Kuvempu University, Karnataka State, India. He was also worked as Research Associate in a research project sponsored by National River Conservation Directorate, Ministry of Environment and Forests, Government of India. He has published more than 50 research articles in national and international reputed journals. His interest is in the areas of environmental chemistry particularly in the field of colour degradation of dyes by using nano-sized semiconductor metal oxides. Dr. Yogendra is a member for International Association for Ecology (INTECOL), senior member for APCBEES, Bangkok and member for Indian Science Congress Association (ISCA), Kolkata.

K.M. Mahadevan has finished his M.Sc. degree from the University of Mysore in 1997 with distinction, qualified CSIR-JRF in 1997, and obtained Ph.D., degree in 2003 from Kuvempu University. He carried out post-doctoral research work at KRICT South Korea and a visiting scientist to the University of Sunderland, London, UK. He is presently working as Professor and head of the department of chemistry. And also a Director P.G Centre Kadur, Kuvempu University. His research interest includes synthetic chemistry and medicinal chemistry. He received the Distinguished Industrial Research Scientist Award for recognition of his research contribution in chemistry from Bio-Organic and Applied Material Pvt. Ltd., Bangalore. He has been published more than 200 research papers and edited 8 books. 38 students have already completed their Ph.D degree and another 17 students are working at present. He has been a Scientific Advisory Board Member of Bio-Organics and Applied Material Pvt. Ltd., Bangalore. He has completed over 5 research projects funded by DDT, DST, CSIR and UGC. Identification of new drugs for malaria and tuberculosis in collaboration with CDRI, and investigation of new organic solar cells and OLED materials funded by DST are currently in progress. Some of his research investigations are referred in foreign textbooks, which attribute high-quality research work being done in his lab.

I.H. Mallikarjuna obtained Ph.D from Karnatak University Dharwad in 2006. Presently, He is working as Assistant Professor in Chemistry at Department of Post Graduation Studies in Chemistry, Government Science College, Hassan, Karnataka. India. Recently He is honoured “Emerald Who’s who”. His research area of interest is Reaction Kinetics, Electrochemistry and Surface chemistry.

N. Madhusudhana has finished his Ph.D. in Environmental science. He is currently working as Post-Doctoral Fellow in the Department of post-graduate studies and research in Environmental science, Kuvempu University, Karnataka State, India. He published 25 papers in international and national reputed journals. His current research focuses on synthesis, characterizations of Nanoparticles and its application to Industrial Dyes and colored effluents. He is a member of Indian Science Congress Association (ISCA)