Green synthesis strategy for producing doped and undoped ZnO nanoparticles: their photocatalytic studies for industrial dye degradation

Ahamed Fazil A., Sheeba Narayanan, Meera S. Begum, G. Manikandan and M. Yuvashree

ABSTRACT

A facile and green method for synthesizing Zinc Oxide nanoparticles (ZnO NPs) was successfully carried out using unutilized sweet lime; i.e., Citrus Limetta rind pulp (U-CLRP) extract. The structural, morphological and optical studies were elucidated to confirm the crystallinity, size, and shape of the synthesized NPs. Copper doping on ZnO NPs (CZnO NPs) was carried out to enhance the optical properties. The as-prepared and doped nanoparticle’s potential for efficient degradation of a commercial dye, Methylene Blue (MB), was tested under Ultraviolet (UV) and visible light radiation. ZnO NPs showed promising results for dye degradation while an improved result was witnessed for CZnO NPs. ZnO NPs showed 74% of degradation of MB dye under UV irradiation and 57% degradation under visible light radiation. CZnO NPs presented 85 and 90% degradation in the UV and visible radiation, respectively. This green reduction method utilizing biological waste sources shows a promising path for photocatalysts to be developed economically as well as efficiently in the future. These CZnO/ ZnO NPs proved their potential for embedding them as efficient catalysts for wastewater treatment plants of textile industries.

Key words: copper doping, green synthesis, Methylene Blue dye, sweet lime rind pulp, textile industry effluent, zinc oxide nanoparticles

HIGHLIGHTS

- Citrus Limetta fruit’s unutilized rind pulp extract is utilized for the green synthesis of ZnO NPs.
- The extract acted both as a reducing and stabilizing agent.
- ZnO and Cu doped ZnO NPs were characterized and tested for their dye degradation potential.
- Cu doping on ZnO NPs enhanced its photocatalytic activity under both UV and visible radiation.
- This extract paves a green-reduction way for many metal oxide nanostructures.

GRAPHICAL ABSTRACT

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (http://creativecommons.org/licenses/by/4.0/).
INTRODUCTION

We are living in a world where automated machines are easily accessible, and clean drinking water resources are hard to find. Rapid urbanization and industrialization, population overgrowth, and lethargic utilisation of natural resources have severely impacted drinking water quality all over the world, especially the developing nations. Numerous toxic compounds present in the water source pose a great threat for the healthy life of human beings. Various industries like food, leather, textile and municipal sewage disposal pollute the water sources in an unimaginable manner.

Textile industries emit almost 20% of total dye produced from all over the world as effluents into water sources (Sajid et al. 2018). Methylene Blue (MB), a toxic cationic dye, is difficult to be degraded because of its stability to light and oxidation reactions (Cai et al. 2013; Ghorai et al. 2014; Guo et al. 2017). Removal of MB dye from textile wastewater streams will be an environmentally important task to assure clean water streams.

Water treatment with the help of light (photons) has emerged as a promising platform since energy from renewable resources could be widely used (Augugliaro et al. 2006). Semiconductor-based photocatalysis is an effective and eco-friendly technique in abating wastewater streams (Chong et al. 2010). Zinc oxide (ZnO), among semiconductor photocatalysts, has a wide bandgap of 3.37 eV and an exciton binding energy of 60 meV (Vaiano et al. 2018). ZnO nanoparticles (ZnO NPs) play a significant role in light emitting devices, solar cells, lasers, piezoelectric transducers, chemical sensors, transparent electronics and photocatalysts (Kumar et al. 2015). ZnO NPs help in generation of hydroxyl radicals, which in turn oxidize pollutants quickly in the presence of light radiation. Recent reports suggest that ZnO NPs have the capability to reduce organic pollutants and efficiently degrade toxic dyes (Daneshvar et al. 2004; Li et al. 2019).

In recent times, various nanoparticles have been synthesized through green methods, which utilize biological sources for nanoparticle reduction. Different parts of plants, microbes and algae have been utilized for environmentally benign synthesis of nanoparticles (Vidya et al. 2013; Senthilkumar & Sivakumar 2014). Nature has abundant resources even with left-over ingredients, what we generally call ‘wastes’. Fruits of Citrus limetta (Mosambi) are often squeezed for juice and almost 20% of pulp within its rinds is disposed of as solid waste. Peels, which constitute 50% of total fruit weight in most of the citrus fruits, are rich in sugars, insoluble polysaccharides such as pectin and cellulose, and low levels of lignin (Grohmann et al. 1995).

In this study, U-CLRP extract has been used as a green source for synthesizing ZnO nanoparticles to photocatalytically degrade MB dye under Ultraviolet and visible radiation. Copper (Cu) incorporation in ZnO NPs has also been carried out to check for their composite effect. Neutral pH, room temperature and a standard dosage of catalyst was followed for all degradation studies. Detailed structural and optical characterization of the synthesized nanoparticles reveal the photocatalysis of dye and offers the opportunity to explore ‘bio-wastes’ as promising green photocatalysts for textile dye degradation.

MATERIALS AND METHODS

Materials

Zinc acetate dihydrate (Zn(CH₃COO)₂) and copper (II) nitrate (Cu(NO₃)₂) were obtained from SRL chemicals and of analytical grade. Deionized water was procured from NICE chemicals and all the chemicals were used without any further purification. Methylene Blue (MB) dye was from Merck and used with the concentration of 20 ppm.

Photoreactor and light sources

For UV photocatalysis, a batch glass reactor vessel of 500 ml volume was used with a 11 W UV lamp source (253 nm, Philips). The same reactor vessel with an 11 W CFL bulb was utilized for visible photocatalysis.

Synthesis of ZnO nanoparticles (ZnO NPs)

Fruits (Citrus limetta) were procured from a local supermarket available at NIT Trichy campus. After juicing through the manual squeeze method, rind pulp (unutilized) was used for preparing the extract. From the rinds of 4 fruits, approximately 25 ml of extract was derived without dilution. The extract was filtered with 0.22 μm filter and stored at 4 °C until use. Peels obtained after rind pulp and filtrate extraction are still good biomass resources and their utilization is not within the scope of this study.

0.1 M of Zinc acetate dihydrate was added to 40 ml of U-CLRP extract under gentle stirring (Pavithra et al. 2017). Co-precipitated slurry mixture was placed in a household microwave oven maintained at 720 W for 10 minutes. Rapid microwave heating ensured the partial drying of the slurry. Further, the sample was scraped from the flask and dried in a hot air oven.
overnight at 130 °C. Dried powder was calcinated at 400 °C for 2 hours to obtain the crystalline ZnO nanoparticles. After calcination, the powder was ground by mortar and pestle, renamed ZnO NPs, and stored.

**Synthesis of copper doped ZnO nanoparticles (CZnO NPs)**

40 ml of U-CLRP extract was added dropwise to 0.1 M of Zinc acetate dihydrate with stirring and 0.003 M of Copper (II) nitrate was added further under rigorous stirring. The sample was placed in the microwave oven and maintained at 720 W for 10 minutes. Then the sample was scraped from the flask and dried in a hot air oven overnight at 130 °C. The dried powder was calcinated at 400 °C for 2 hours to obtain the copper doped ZnO nanoparticles, brown in colour. The powder sample was named CZnO NPs. Native extract was also dried overnight after microwave treatment and stored for further characterization. Figure 1 illustrates the overall nanoparticle synthesis procedure with dye degradation protocol.

**Characterization of the photocatalysts**

The synthesized ZnO and CZnO NPs were characterized for their structural, optical, morphological and microstructural features through various analytical techniques such as X-Ray Diffraction (Rigaku, Ultima IV), UV-DRS spectrophotometer (Josco, Japan), FE-Scanning electron microscopy (FEI Quanta 400), energy dispersive studies (Oxford Instruments) and HR-Transmission electron microscopy (Tecnai 200).

**Photocatalytic dye degradation**

For photodegradation experiments, 20 ppm concentration of MB dye was prepared. In the 500 ml batch reactor vessel, 10 mg of ZnO NPs were added with 100 ml of dye solution and initially allowed to equilibrate for 30 minutes in the darkness. After attaining adsorption/desorption equilibrium, 11 W UV or visible light source was turned on for the respective experiments to initiate the catalysis reaction. 800 rpm of stirring speed was maintained to make the solution homogenous. The pH value of the test dye solutions was found to be in the range of 6.5–7.5 for all batches. At regular intervals of 30 minutes, 5 ml of suspension was taken out from the reactor vessel and filtered using 0.22 μm filter. Degraded dye concentration after regular time intervals was measured through a UV-Vis spectrophotometer at 665 nm wavelength (Manjunath et al. 2014). For CZnO NPs, the same conditions were used to determine their photocatalytic efficiency and the results were finally compared.

The photodegradation percentage as a function of irradiation time (Daneshvar et al. 2004) was calculated by:

\[
\text{% of dye degradation} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) is the initial Methylene Blue (MB) dye concentration (mg/ml) and \(C_t\) is the concentration of MB (mg/ml) at time \(t\).
RESULTS AND DISCUSSION

Unutilized Citrus limetta rind pulp extract was successfully used for the synthesis of ZnO as well as CZnO NPs. Peels and the extract filtrate were stored for future experiments and will be reported elsewhere. Photocatalysts ZnO NPs and CZnO NPs were analysed for their structural, optical and microstructural characteristics. Finally, dye degradation experiments were carried out for both NPs and the obtained results are discussed in detail.

UV visible spectrum

The UV Visible absorption spectrum is obtained in the range of 200–800 nm. $\lambda_{\text{max}}$ absorbance peaks for ZnO NPs and CZnO NPs are clearly observed between 300 and 400 nm, as depicted in Figure 2. ZnO NPs showed maximum absorbance at 357 nm while CZnO NPs showed at 364 nm. The clear shift of 4 nm for CZnO NPs reveals the reason for the brown colour of the final powder. Earlier studies also confirmed that the maximum absorbance range for ZnO NPs lies between 330 and 380 nm (Lu et al. 2019). Inclusion of Cu within the crystallographic planes of ZnO for CZnO NPs has altered the absorbance maximum towards the blue region.

X Ray diffraction study

The powder XRD spectrum of ZnO and CZnO NPs is presented in Figure 3. The pristine extract showed an amorphous carbon peak, suggesting the presence of only organic compounds. Data obtained for ZnO NPs is in well agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction File (PDF) no. 36–1451, confirming the hexagonal wurtzite structure (Dinesh et al. 2014). The diffraction peaks observed at 2 theta values of 31.79, 34.421, 36.252, 47.51, 56.60, 62.86 and 67.96 correspond to the ZnO lattice planes (100), (002), (101), (102), (110), (103) and (112) respectively. The well-defined diffraction peaks indicate the crystalline nature of ZnO NPs. Crystallite size of NPs are calculated through Scherrer’s Equation (2),

$$D = \frac{K\lambda}{\beta\cos \theta}$$  \hspace{1cm} (2)

where D is the average crystal size, $\lambda$ the X-ray wavelength, $\beta$ the full width at half maximum (FWHM) of the diffraction peak, $K = 0.89$ (dimensionless constant), and $\theta$ the diffraction angle. ZnO NPs crystallite sizes are in the range of 15–20 nm. For CZnO NPs, the crystallite size is ranged between 19–24 nm. CZnO NPs’ data shows two additional characteristic Cu Bragg reflections (111) and (200) at 2$\theta$ 45.86 and 50.90, respectively. No changes on the ZnO Bragg reflections confirm the substitution of Cu ions into the ZnO host lattice without affecting its crystal structure. This proves the successful doping or segregation of Cu ions on the grain boundaries of ZnO NPs (Alim et al. 2005).

Figure 2 | UV Visible absorbance spectrum for ZnO and CZnO NPs with $\lambda_{\text{max}}$ values.
SEM analysis

Field Emission Scanning Electron Microscope (FE-SEM) images of ZnO NPs are presented in Figure 4. Hexagonal crystallites are clearly visible and lie in the range of 20 nm. This is in good agreement with that of Scherrer’s data from XRD. The images reveal that the hexagonal nanostructures, which cover the entire surface, are of self-assembled ZnO crystallites formed during the calcination process. Further increasing the calcination temperature might have led to the enhancement of crystallite size, resulting in agglomeration. 400 °C calcination used in this study allows us to obtain fine crystallites with proper porosity for efficient dye degradation. EDS elemental mapping also confirms the presence of Zn and O in the NPs without any other phases.

**Figure 3** | Powder X-Ray diffraction spectrum of extract, ZnO NPs and CZnO NPs (respective inset images are the final powders after calcination).

**SEM analysis**

Field Emission Scanning Electron Microscope (FE-SEM) images of ZnO NPs are presented in Figure 4. Hexagonal crystallites are clearly visible and lie in the range of 20 nm. This is in good agreement with that of Scherrer’s data from XRD. The images reveal that the hexagonal nanostructures, which cover the entire surface, are of self-assembled ZnO crystallites formed during the calcination process. Further increasing the calcination temperature might have led to the enhancement of crystallite size, resulting in agglomeration. 400 °C calcination used in this study allows us to obtain fine crystallites with proper porosity for efficient dye degradation. EDS elemental mapping also confirms the presence of Zn and O in the NPs without any other phases.

**Figure 4** | FESEM images of ZnO NPs (a,b) and EDS mapping images (b).
Figure 5 shows the morphological characteristics of CZnO NPs. The change in the ZnO NPs’ morphology after Cu doping is distinctively visible with the appearance of rose-petal shaped crystallite structures. From hexagonal shapes to petal shapes, these crystallite structures will tend to move to needle-like structures, confirming the presence of Cu substitutions (Suryawan-shi et al. 2015). EDS mapping images of CZnO NPs also confirm the presence of Cu within the ZnO crystal lattice. 0.15 weight percentage of Cu substitution obtained from the EDS spectrum also aligns with the initial molar concentration used for the synthesis. The incorporation of Cu at ZnO lattice sites seemed to influence the surface morphology of CZnO NPs and resulted in the rose petal formation of crystals shifting from hexagonal crystal shapes of ZnO NPs. Doping even at micromolar level plays a crucial role in the shape dependency of crystals.

**TEM analysis**

To infer the microstructure features of the nanoparticles, TEM analysis was carried out and the results are presented in Figure 6. Figure 6(a) and 6(b) are Bright Field (BF) images and (c) is the SAED pattern of ZnO NPs, whereas (d)-(f) belongs to CZnO NPs. Figure 6(a) and 6(d) are the low magnification BF images of ZnO and CZnO NPs, respectively. Figure 6(b) depicts the high magnification image of ZnO NPs, and the average crystallite size is ∼14 nm, which is in good agreement with the approximated XRD values calculated earlier as 15–20 nm. Similarly for CZnO NPs, from Figure 6(e), the average crystallite size is calculated to be ∼17 nm. This marginal increase in size for CZnO NPs is due to the substitution of Cu atoms in the grain boundaries of ZnO. The SAED pattern for both NPs is polycrystalline in nature with a defined ring pattern, and the planes are identified. There is no major change in the electron diffraction pattern and this confirms the presence of ZnO phase alone without any impurities.

**Effect of UV irradiation on dye degradation**

Methylene Blue (MB) dye of 20 ppm concentration is correlated with the respective time interval and plotted. 10 mg catalyst dosage was used for 100 ml of dye solution. To test the efficacy of these two NPs, the dosage concentration is kept the same for all batch experiments in both radiation sources. UV-Vis spectrophotometer data at 665 nm wavelength was taken for all the degradation analysis for both radiation sources. It can be observed from Figure 7 that in the sole presence of UV light (11 W Philips) and in the absence of photocatalysts, there is a less significant degradation of ∼9% obtained through photolysis. Negligible reduction percentage is obtained by photocatalyst addition to the reactor and in the absence of the UV radiation.

![Figure 5](http://iwaponline.com/wst/article-pdf/84/10-11/2958/968899/wst084102958.pdf)
MB photocatalysis with the presence of both ZnO NPs and UV radiation resulted in 74% dye degradation after 210 minutes (~3.5 hours). CZnO NPs with UV radiation presented a better efficiency of 85% degradation after 3 hours. CZnO NPs initially showed ~50% reduction within 30 minutes and slow degradation follows. This exemplifies the dye molecule occupying the available surface sites rapidly during the initial hour; then, oxidation of dye molecules occurs with the help of electron hole-pair action.

Since CZnO NPs showed maximum absorbance in the ‘blue’ region, they have performed better than the ZnO NPs. This phenomenon might also give high activity in the visible region as well. At the end of 4 hours, the dye solution attained equilibrium and no more reduction was witnessed. This could be enhanced by increasing the catalyst loading.

**Effect of visible radiation on dye degradation**

Figure 8 gives information that in the sole presence of visible light (11 W Philips) and in the absence of photocatalysts, there is a mere ~2.5% degradation obtained through photolysis. When the experiment is conducted in the absence of light and with catalysts, negligible reduction is witnessed.
MB photocatalysis in the presence of both ZnO NPs and visible radiation resulted in 57% dye degradation after 210 minutes, whereas CZnO NPs provided an improved efficiency of 90% degradation after 3 hours. With a visible light source, CZnO NPs initially showed around >60% reduction within 30 minutes. Dye molecules occupy the available surface sites rapidly during the initial hour, giving rise to degradation. Later, after 240 minutes, the reduction becomes stable due to the full occupancy of active sites and lack of more catalyst dosage.

These experiments demonstrated that both light source and photocatalysts are essential to degrade dye molecules. The reaction initiates with the photoexcitation of the semiconductor photocatalysts, followed by the generation of electron-hole pairs on the catalyst’s surface. Catalyst dosages play a critical role in bringing higher active sites to degrade more dye compounds. Therefore, the availability of active sites on the surface and penetration of light source in the suspension decides the speed of degradation (Goncalves et al. 1999).

Kinetics of photocatalytic degradation of Methylene Blue

The linear plot of log[dye] vs irradiation time of CZnO NPs under visible radiation is plotted in Figure 9, which suggests that the photodegradation of MB approximately follows the pseudo-first order reaction kinetics (Langmuir-Hinshelwood model).

Rate constant \( K = 0.015 \text{ min}^{-1} \) is calculated (Jawad et al. 2016) from the slope according to Equation (3).

\[
\ln \frac{C_0}{C_t} = Kt
\]  

(3)

where \( C_0 \) is the initial MB dye concentration (mg/ml) and \( C_t \) is the concentration of MB (mg/ml) at irradiation time \( t \).

Figure 8 | Effect of visible light and photocatalysts on Methylene Blue (MB) degradation; changes observed in the dye concentration during different time intervals.

Figure 9 | Kinetics plot for CZnO NPs under visible radiation.
In summary, green biomass resources that are dumped as ‘wastes’ could be effectively turned into photocatalysts. This work demonstrates such an effort. The synthesized nanoparticles’ potential catalytic activity towards MB dye degradation was tested under two different light irradiations and compared. Future studies involving catalyst dosage variation, pH effects, high power radiation source, and peroxide addition could bring detailed understanding of the degradation chemistry and sunlight source-mediated dye degradation would help to elucidate the economical photocatalysis approaches.

CONCLUSIONS

The current study explores the possibility of utilizing the rind pulp extracts of *Citrus limetta* for the green synthesis of zinc oxide as well as copper-doped zinc oxide nanoparticles. The NPs were tested for their potential to degrade the cationic dye, Methylene Blue. Compared to ZnO NPs, CZnO NPs could degrade the dye both in UV and visible radiation. ZnO NPs performed better in UV radiation while CZnO NPs degraded 85% of dye concentration in 210 minutes. The results indicated that the degradation potential was affected by low wattage radiation source and fixed catalyst dosage.

Enhancing the above parameters and optimizing them are currently under study. After final optimization it is believed that the complete removal of dye could be achieved within an hour. It is hence concluded that the mechanism of degradation predominantly lies with active hydroxyl radicals, but positive holes might also have enhanced the degradation reaction.

ACKNOWLEDGEMENTS

Authors M G and Y M gratefully acknowledge the support of NIT Tiruchirappalli (NIT-T) for the internship tenure. XRD and FE-SEM facility of MME department of NIT-T and TEM facility of STIC-CUSAT are also acknowledged.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Alim, K. A., Fonoberov, V. A., Shamsa, M. & Balandin, A. A. 2005 Micro-Raman investigation of optical phonons in ZnO nanocrystals. *Journal of Applied Physics* 97 (12), 124313.

Augugliaro, V., Litter, M., Palmisano, L. & Soria, J. 2006 The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 7 (4), 127–144.

Cai, T., Yang, Z., Li, H., Yang, H., Li, A. & Cheng, R. 2013 Effect of hydrolysis degree of hydrolyzed polyacrylamide grafted carboxymethyl cellulose on dye removal efficiency. *Cellulose* 20 (5), 2605–2614.

Chong, M. N., Jin, B., Chow, C. W. K. & Saint, C. 2010 Recent developments in photocatalytic water treatment technology: a review. *Water Research* 44 (10), 2997–3027.

Daneshvar, N., Salari, D. & Khataee, A. R. 2004 Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO2. *Journal of Photochemistry and Photobiology A: Chemistry* 162 (2–3), 317–322.

Dinesh, V. P., Biji, P., Ashok, A., Dhara, S. K., Kamruddin, M., Tyagi, A. K. & Raj, B. 2014 Plasmon-mediated, highly enhanced photocatalytic degradation of industrial textile dyes using hybrid ZnO@Ag core–shell nanorods. *RSC Advances* 4 (103), 58930–58940.

Ghorai, S., Sarkar, A., Raoufi, M., Panda, A. B., Schönherr, H. & Pal, S. 2014 Enhanced removal of methylene blue and methyl violet dyes from aqueous solution using a nanocomposite of hydrolyzed polyacrylamide grafted xanthan gum and incorporated nanosilica. *ACS Applied Materials & Interfaces* 6 (7), 4766–4777.

Goncalves, M. S. T., Oliveira-Campos, A. M. F., Pinto, E. M. M. S., Píasencia, P. M. S. & Queiroz, M. J. R. P. 1999 Photochemical treatment of solutions of azo dyes containing TiO2. *Chemosphere* 39 (5), 781–786.

Grohmann, K., Cameron, R. G. & Buslig, B. S. 1995 Fractionation and pretreatment of orange peel by dilute acid hydrolysis. *Bioresource Technology* 54 (2), 129–141.

Guo, Z., Yang, M. & Huang, X. J. 2017 Recent developments in electrochemical determination of arsenic. *Current Opinion in Electrochemistry* 3 (1), 130–136.

Jawad, A. H., Mubarak, N. S. A., Ishak, M. A. M., Ismail, K. & Nawawi, W. I. 2016 Kinetics of photocatalytic decolourization of cationic dye using porous TiO2 film. *Journal of Taibah University for Science* 10 (3), 352–362.

Kumar, N., Mittal, H., Reddy, L., Nair, P., Ngila, J. C. & Parashar, V. 2015 Morphogenesis of ZnO nanostructures: role of acetate (COOH-) and nitrate (NO3-) ligand donors from zinc salt precursors in synthesis and morphology dependent photocatalytic properties. *RSC Advances* 5 (48), 38801–38809.
Li, J. F., Rupa, E. J., Hurh, J., Huo, Y., Chen, L., Han, Y., Ahn, J. C., Park, J. K., Lee, H. A., Mathiyalagan, R. & Yang, D. C. 2019 *Cordyceps militaris* fungus mediated Zinc Oxide nanoparticles for the photocatalytic degradation of Methylene blue dye. *Optik* **183**, 691–697. https://doi.org/10.1016/j.ijleo.2019.02.081.

Lu, J., Bajikha, I., Hurh, J., Han, Y., Ali, H., Mathiyalagan, R., Ling, C., Ahn, J. C. & Yang, D. C. 2019 Photocatalytic degradation of methylene blue using biosynthesized zinc oxide nanoparticles from bark extract of *Kalopanax septemlobus*. *Optik* **182**, 980–985.

Manjunath, K., Ravishankar, T. N., Kumar, D., Priyanka, K. P., Varghese, T., Naika, H. R., Nagabhushana, H., Sharma, S. C., Dupont, J. & Ramakrishnappa, T. 2014 Facile combustion synthesis of ZnO nanoparticles using *Cajanus cajan* (L.) and its multidisciplinary applications. *Materials Research Bulletin* **57**, 325–334.

Oberoi, H. S., Vadlanii, P. V., Madl, R. L., Sauida, L. & Abeykoon, J. P. 2010 Ethanol production from orange peels: two-stage hydrolysis and fermentation studies using optimized parameters through experimental design. *Journal of Agricultural and Food Chemistry* **58** (6), 3422–3429.

Pavithra, N. S., Lingaraju, K., Raghu, G. K. & Nagaraju, G. 2017 *Citrus maxima* (Pomelo) juice mediated eco-friendly synthesis of ZnO nanoparticles: applications to photocatalytic, electrochemical sensor and antibacterial activities. *Spectrochimica Acta – Part A: Molecular and Biomolecular Spectroscopy* **185**, 11–19. http://dx.doi.org/10.1016/j.saa.2017.05.032.

Sajid, M. M., Khan, S. B., Shad, N. A., Amin, N. & Zhang, Z. 2018 Visible light assisted photocatalytic degradation of crystal violet dye and electrochemical detection of ascorbic acid using a BiVO 4/FeVO 4 heterojunction composite. *RSC Advances* **8** (42), 234989–234989.

Senthilkumar, S. R. & Sivakumar, T. 2014 Green tea (*Camellia sinensis*) mediated synthesis of zinc oxide (ZnO) nanoparticles and studies on their antimicrobial activities. *International Journal of Pharmacy and Pharmaceutical Sciences* **6** (6), 461–465.

Suryawanshi, S. R., Singh, A. K., Deo, M., Late, D. J., Sinha, S. & More, M. A. 2015 3D Hetero-architecture of GdB 6 nanoparticles on lessened cubic Cu2O nanowires: enhanced field emission behaviour. *CrystEngComm* **17** (21), 3936–3944.

Vaiano, V., Matarangolo, M., Murcia, J. J., Rojas, H., Navío, J. A. & Hidalgo, M. C. 2018 Enhanced photocatalytic removal of phenol from aqueous solutions using ZnO modified with Ag. *Applied Catalysis B: Environmental* **225**, 197–206.

Vidy, C., Hiremath, S., Chandraprabha, M. N., Antonyraj, M. A. L., Gopal, I. V., Jain, A. & Bansal, K. 2013 Green synthesis of ZnO nanoparticles by *Calotropis gigantea*. *International Journal of Current Engineering and Technology* **1** (1), 118–120.

First received 9 May 2021; accepted in revised form 16 July 2021. Available online 30 July 2021.