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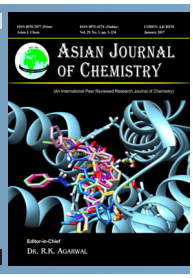

Rapid Visible Light Induced Photocatalytic Degradation of Orange-II Using H_2O_2 Sensitized Cu_2O

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Photocatalytic degradation of orange II has been studied using H_2O_2 sensitized Cu_2O and visible light. Complete degradation of orange II is achieved for 90 min of irradiation. Addition of external oxidant H_2O_2 is found to be enhancing the rate of degradation. Formation of $^{\bullet}OH$ free radicals during irradiation is ascertained with photoluminescence studies using terephthalic acid as probe molecule.

Keywords: Orange II, Photocatalytic degradation, Synergetic effect, Cu_2O.

INTRODUCTION

Azo-dyes constitute a major portion of synthetic organic dyes commonly used in textile industries. Waste water exhausts from these industries contain large amounts of remnant azo-dyes and pose a potential threat to human health due to their toxic nature. Direct exposure to either UV or visible light has been reported to be ineffective in inducing photo degradation of azo dyes [1]. Similarly, biological degradation also is either slow or does not proceed for many of azo dyes [2,3]. Orange II is an azo-dye and degradation of orange II was reported using Fenton process [4], photo assisted Fenton method [5], microwave electrode less photocatalytic degradation [6], photo-catalytic [7] and electrochemically assisted photocatalytic degradation methods [8]. Photocatalytic degradation of orange II was reported by Lucarelli and coworkers [9] using TiO_2 and UV radiation. These investigators reported that when H_2O_2 was initially added as an oxidant to the photo degradation process, the rate of dye removal from solution was accelerated significantly and orange II got degraded more readily over anatase than on rutile. Fernandez *et al*. [10] reported photocatalytic degradation of orange II using Degussa P25 under UV light. Feng *et al*. [11] developed a clay based Fe nano composite for the degradation of orange II in presence of H_2O_2 and UV light. Mu *et al*. [12] investigated degradation of orange II in aqueous dispersions of TiO_2 using UV light as irradiation source. Stylidi and coworkers [13] reported visible light induced degradation of orange II in aqueous TiO_2 suspensions in presence of added H_2O_2 in 47 h. Bessekhouad *et al*. [14] made a comparative study of UV-visible *versus* visible light degradation of orange II in a coupled CdS/TiO_2 suspension and noticed only 40 % degradation under visible light. Bojinova *et al*. [15] studied the influence of anatase to rutile mixing ratio on the photo-catalytic degradation of orange II under UV light. Stengl and Bakardjieva [16] reported that Mo-doped anatase could degrade orange II to an extent of 40 % under visible light. Yang *et al*. [17] reported the photocatalytic performance of BiOCl/ZnO heterojunction for degradation of orange II under UV irradiation. Susmitha and coworkers [18] reported effective catalytic performance of Mn and P-codoped TiO_2 for the degradation of orange-II under visible light.

The above literature reports indicate that the photocatalytic degradation of orange II is more extensively studied under UV irradiation than under visible light that are confined to doped or coupled TiO_2 [14,16,18]. Though TiO_2 mediated photocatalysis has been reported to be potentially advantageous, the main drawback is its wide band gap limiting the absorption to UV region which is hardly < 5 % in solar radiation. In order to exploit 45 % of visible light in solar radiation, search for suitable non-TiO_2 type semiconductor metal oxides has been in progress [19]. Cuprous oxide (Cu_2O) is a p-type semiconductor with a band gap in the region of 2.0 to 2.2 eV. Photocatalytic degradation of several organic dye pollutants like rhodamine-B, methylene blue and methyl orange [20], bromocresol green, rosaniline and eosin blue [21] as well as aromatic derivatives like nitrophenols [22] and nitrobenzene [23] has been recently reported from this laboratory. Present paper describes a simple inexpensive method for 100 % photo-catalytic degradation of orange II using H_2O_2 sensitized Cu_2O under visible light irradiation.

EXPERIMENTAL

As purchased AR grade Cu_2O (99 %) obtained from Sigma Aldrich and Orange-II was obtained from Merck India Ltd.

Phase purity of Cu_2O is ascertained using X-ray diffractometer (PANalytical-X' Pert PRO, Japan) at room temperature with Ni filtered Cu-K_α radiation and a scan rate of 2° min^{-1}.

Photocatalytic studies: 100 mg of catalyst powder was added into 100 mL aqueous solution containing 10 ppm orange II. The suspension was magnetically stirred for 30 min in dark. The suspension was then exposed to 400 W metal halide lamp; 5 mL aliquots were pipetted at periodic time intervals and filtered through 0.45 μ Millipore filters to remove the suspended particles. Extent of degradation was followed by recording the corresponding absorption spectra. All experiments were conducted under ambient conditions. Percent degradation of the dye is calculated by using the formula:

$$\text{Degradation } (\%) = \frac{(A_0 - A_t)}{A_0} \times 100$$

where A_0 and A_t are respectively initial absorbance and absorbance at time 't'.

Photoluminescence study: 50 mg Cu_2O catalyst is added to the beaker containing 100 mL of terephthalic acid (TPA) solution (0.25 mmol L^{-1} in 1 mmol L^{-1} NaOH solution) and 10 μmol H_2O_2. The solution is stirred for 30 min in dark followed by irradiation by 400 w metal halide lamp for 30 min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectroflourometer (Flouromax 4) with the excitation wavelength of 315 nm.

RESULTS AND DISCUSSION

Fig. 1 gives X-ray diffraction pattern of Cu_2O sample used in the present study. The diffraction peaks can be indexed to cubic Cu_2O of JCPDS File No. 78-2076. In the absence of any extra peaks that could not be assigned, the sample is ascertained to be phase pure Cu_2O.

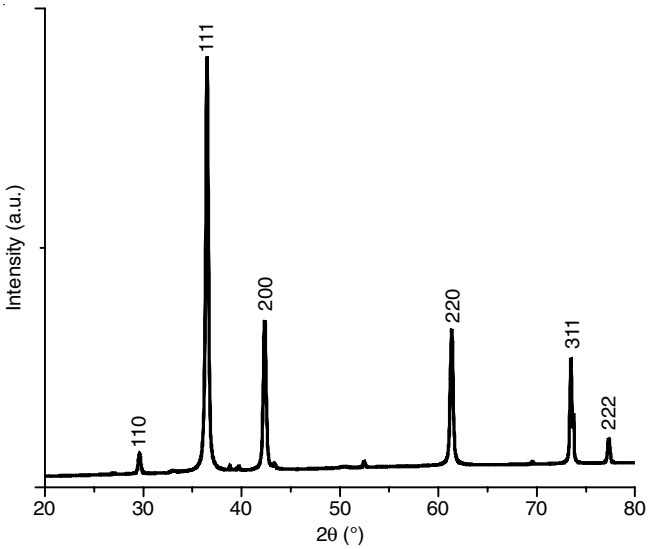
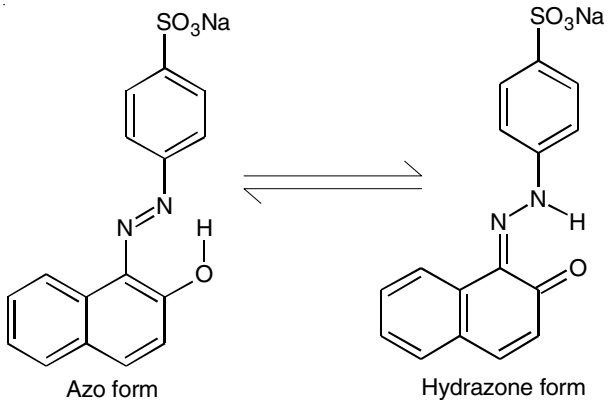


Fig. 1. X-ray diffraction pattern of Cu_2O sample

Fig. 2 shows the UV-visible absorption spectra of aqueous solution of orange II as a function of irradiation time. From the figure, it can be seen that orange II shows two characteristic absorption peaks at λ = 485 and 430 nm which can be attributed to respectively the two tautomeric forms of orange II-hydrazone form and azo form of orange II shown in **Scheme-I**.



Scheme-I: Tautomeric forms of orange II in solutions

Photolysis due to irradiation for 120 min indicated no significant change in the absorption intensity of orange II as seen from Fig. 2a. In presence of H_2O_2, photo degradation to an extent of about 8 % is observable from Fig. 2b. In presence of Cu_2O photo degradation of orange II is effected with progressive irradiation and for irradiation of 180 min nearly 21 % photocatalytic degradation is noticeable from Fig. 2c. However, in presence of both $Cu_2O + H_2O_2$, rapid photo degradation is seen as a function of irradiation time and complete degradation of orange II is achieved for 90 min of irradiation as seen from Fig. 2d.

In order to establish optimum conditions in terms of the amount of catalyst and the amount of H_2O_2 for the photocatalytic degradation of orange II using Cu_2O, photo degradation studies are performed with different amounts of catalyst. Fig. 3 depicts variation of spectral intensities as a function of irradiation time for varying amounts of catalysts – 50, 100 and 150 mg. Catalytic degradation with 50 mg of catalyst around 90 % degradation is observed. With 100 mg catalyst 100 % degradation is observed for 90 min of irradiation. For the degradation study using 150 mg catalyst, 100 % degradation is observed for 120 min of irradiation.

From these spectra, it is established that 100 mg is the optimum amount of catalyst. Fig. 4 shows variation of spectral intensities as a function irradiation time for differing amounts of H_2O_2, keeping the amount of catalyst (100 mg) and orange-II (10 ppm) constant. With 8 μmol of H_2O_2, photocatalytic degradation is incomplete for 90 min of irradiation. Similarly for 10 μmol of H_2O_2, the observed degradation is not 100 % for 90 min of irradiation. However, with 12 μmol H_2O_2, complete 100 % photocatalytic degradation of orange-II is observed for 90 min of irradiation. The observed spectra therefore suggest that 100 mg catalyst and 12 μmol H_2O_2 are the optimum conditions for the photocatalytic degradation of 10 ppm orange-II.

Present result is significant since effective photocatalytic degradation of orange II has so far been achieved only with modified TiO_2 photocatalysts under UV irradiation only. It is also observed that Cu_2O or H_2O_2 individually did not show any significant photo degradation, but combindly $Cu_2O + H_2O_2$ showed a synergetic effect which may be explained with the possible photocatalytic mechanism indicated below:

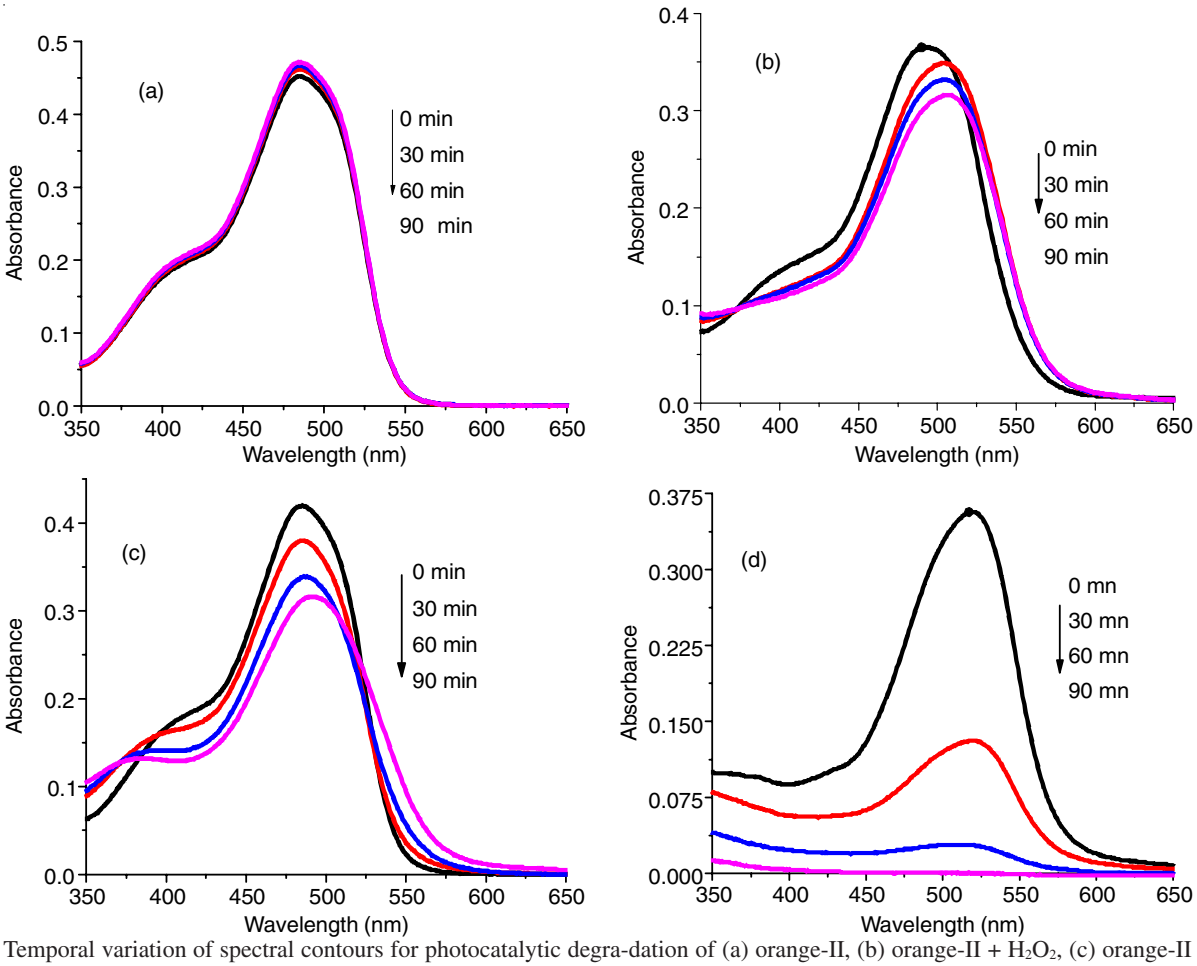


Fig. 2. Temporal variation of spectral contours for photocatalytic degra-dation of (a) orange-II, (b) orange-II + H_2O_2, (c) orange-II + Cu_2O and (d) orange-II + Cu_2O + H_2O_2

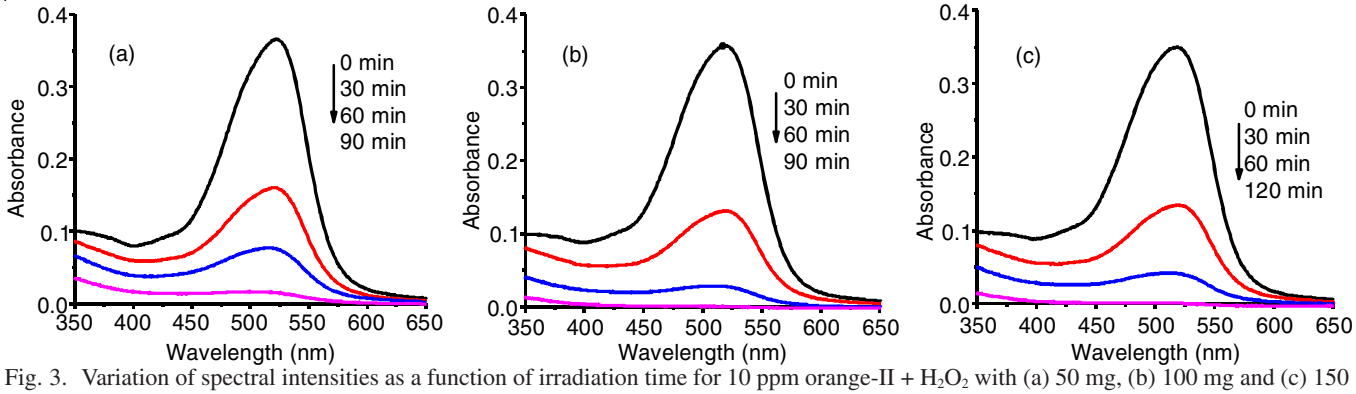


Fig. 3. Variation of spectral intensities as a function of irradiation time for 10 ppm orange-II + H_2O_2 with (a) 50 mg, (b) 100 mg and (c) 150 mg of Cu_2O

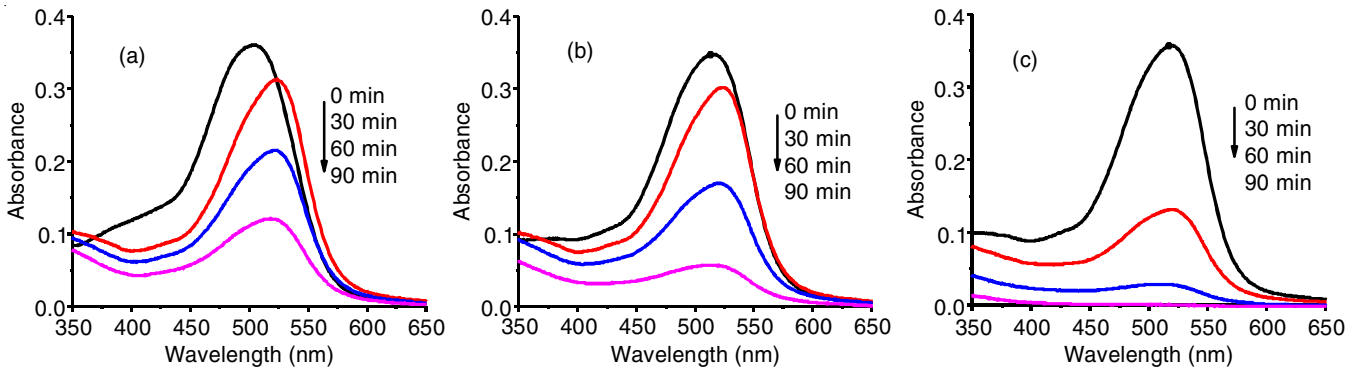


Fig. 4. Time dependent variation of spectral contours for 10 ppm aqueous orange-II solution + 100 mg Cu_2O with (a) 8 µmol, (b) 10 µmol and (c) 12 µmol of H_2O_2

$$Cu_2O + hv \longrightarrow e^-_{CB} + h^+_{VB}$$

$$e^-_{CB} + H_2O_2 \longrightarrow {}^\bullet OH + OH^-$$

$$h^+_{VB} + OH^- \longrightarrow {}^\bullet OH$$

$${}^\bullet OH + \text{orange II} \longrightarrow \text{Degradation products}$$

Formation of $^\bullet$OH free radicals due to addition of external oxidant H_2O_2 during irradiation process is ascertained in terms of photoluminescence studies using terephthalic acid (TPA) as probe molecule. Terephthalic acid is known to react with $^\bullet$OH free radicals to yield 2-hydroxy terephthalic acid (HTPA) which exhibits a characteristic luminescence peak around 420 nm. Fig. 5 depicts photoluminescence spectra of Cu_2O + TPA aqueous suspension with and without addition of H_2O_2 prior to and after irradiation. Intense peak observed for Cu_2O + TPA aqueous suspension in presence of H_2O_2 after irradiation is a clear indication of formation of $^\bullet$OH free radicals from an important part in the photocatalytic degradation of orange II.

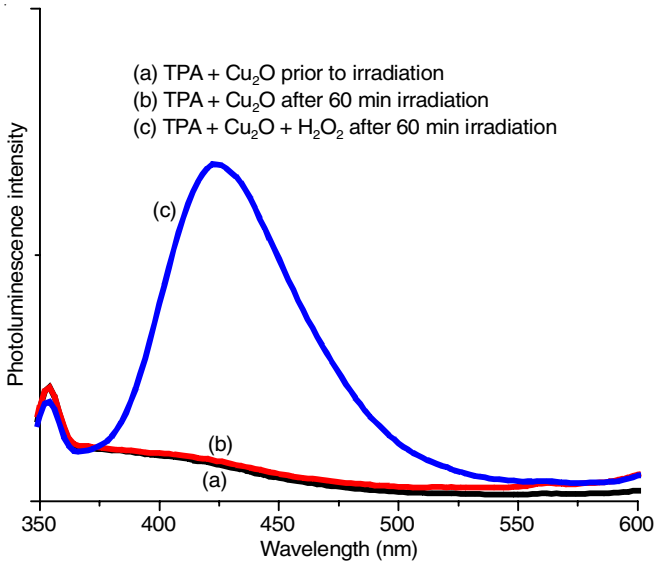


Fig. 5. Photoluminescence spectra of terephthalic acid solutions containing Cu_2O in presence and in absence of H_2O_2 before and after irradiation

Rate constants computed from respective slopes for plots of ln (C_t/C_0) *versus* time for the degradation of orange II under different conditions are given in Table-1.

TABLE-1
CALCULATED RATE CONSTANTS FOR PHOTODEGRADATION OF orange-II, orange-II + H_2O_2, orange-II + Cu_2O AND orange-II + H_2O_2 + Cu_2O

Photodegradation	Rate constant $k_{orange-II}$ (min^{-1})
Dye alone	0.0
Dye + H_2O_2	2.0×10^{-5}
Dye + Cu_2O	3.0×10^{-5}
Dye + Cu_2O + H_2O_2	6.7×10^{-4}

Conclusion

The above experimental results suggest that orange-II can be successfully degraded under visible light using Cu_2O as photocatalyst. Rate of degradation is found to be enhanced in presence of external electron acceptor H_2O_2 which gives rise to $^\bullet$OH free radicals that disintegrate the molecular structure. Formation of $^\bullet$OH free radicals is confirmed by photoluminescence studies using terephthalic acid as probe molecule.

REFERENCES

1. M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995); https://doi.org/10.1021/cr00033a004.
2. G. Helz, R. Zepp and D. Crosby, Aquatic and Surface Chemistry, Lewis Publishers: Boca Raton, FL (1995).
3. M. Halmann, Photodegradation of water pollutants; CRS Press: Boca Raton, FL (1996).
4. J. Bandara, C. Morrison, J. Kiwi, C. Pulgarin and P. Peringer, *J. Photochem. Photobiol. Chem.*, **99**, 57 (1996); https://doi.org/10.1016/1010-6030(96)04339-0.
5. J. Fernandez, J. Bandara, A. Lopez, Ph. Buffat and J. Kiwi, *Langmuir*, **15**, 185 (1999); https://doi.org/10.1021/la980382a.
6. X. Zhang, G. Li, Y. Wang and J. Qu, *J. Photochem. Photobiol. Chem.*, **184**, 26 (2006); https://doi.org/10.1016/j.jphotochem.2006.03.021.
7. M. Stylidi, D.I. Kondarides and X.E. Verykios, *Int. J. Photoenergy*, **5**, 59 (2003); https://doi.org/10.1155/S1110662X0300014X.
8. G. Li, J. Qu, X. Zhang, H. Liu and H. Liu, *J. Mol. Catal. Chem.*, **259**, 238 (2006); https://doi.org/10.1016/j.molcata.2006.06.038.
9. L. Lucarelli, V. Nadtochenko and J. Kiwi, *Langmuir*, **16**, 1102 (2000); https://doi.org/10.1021/la990272j.
10. J. Fernandez, J. Kiwi, C. Lizama, J. Freer, J. Baeza and H.D. Mansilla, *J. Photochem. Photobiol. Chem.*, **151**, 213 (2002); https://doi.org/10.1016/S1010-6030(02)00153-3.
11. J. Feng, X. Hu, P.L. Yue, H.Y. Zhu and G.Q. Lu, *Chem. Eng. Sci.*, **58**, 679 (2003); https://doi.org/10.1016/S0009-2509(02)00595-X.
12. Y. Mu, H.Q. Yu, J.C. Zheng and S.J. Zhang, *J. Photochem. Photobiol. Chem.*, **163**, 311 (2004); https://doi.org/10.1016/j.jphotochem.2003.08.002.
13. M. Stylidi, D.I. Kondarides and X.E. Verykios, *Appl. Catal. B*, **47**, 189 (2004); https://doi.org/10.1016/j.apcatb.2003.09.014.
14. Y. Bessekhouad, N. Chaoui, M. Trzpit, N. Ghazzal, D. Robert and J.V. Weber, *J. Photochem. Photobiol. Chem.*, **183**, 218 (2006); https://doi.org/10.1016/j.jphotochem.2006.03.025.
15. A. Bojinova, R. Kralchevska, I. Poulios and C. Dushkin, *Mater. Chem. Phys.*, **106**, 187 (2007); https://doi.org/10.1016/j.matchemphys.2007.05.035.
16. V. Stengl and S. Bakardjieva, *J. Phys. Chem. C*, **114**, 19308 (2010); https://doi.org/10.1021/jp104271q.
17. K. Yang, C.L. Yu, L.N. Zhang and J.M. Yu, *J. Synth. Cryst.*, **41**, 171 (2012).
18. T. Susmitha, T. Siva Rao and B. Sreedhra, *J. Environ. Chem. Eng.*, **2**, 1505 (2014).
19. A.V. Prasada Rao, A.M. Umabala and P. Suresh, *J. Appl. Chem.*, **4**, 1145 (2015).
20. T. Narasimha Murthy, P. Suresh, A.M. Umabala and A.V. Prasada Rao, *J. Appl. Chem.*, **4**, 1751 (2015).
21. T. Narasimha Murthy, K. Deepthi, A.M. Umabala, A.V. Prasada Rao, *Der Pharma Chem.*, **8**, 140 (2016).
22. T. Narasimha Murthy, P. Suresh, A.M. Umabala, A.V. Prasada Rao, *Der Pharma Chem.*, **8**, 228 (2016).
23. T. Narasimha Murthy, P. Suresh, A.M. Umabala and A.V. Prasada Rao, *Int. J. Recent Sci. Res.*, **7**, 10895 (2016).