Photocatalytic Degradation of Vat Red 13 by Green Synthesized Copper Oxide Nanocatalyst

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Copper oxide nanocatalyst was synthesized by green chemistry approach using *Eichhornia crassipes* leaf extract. The photocatalytic activity of copper oxide nanocatalyst was evaluated using the photocatalytic degradation of C.I. Vat Red 13 under the irradiation of UV light. The maximum photocatalytic activity of the copper oxide photocatalyst was observed at 60 min of irradiation for a catalyst dose of 4 mg at pH 6.6. The degradation of Vat Red 13 was confirmed by comparison of UV and FT-IR studies of the dye solution and copper oxide nanocatalyst treated dye solution.

Keywords: Copper oxide nanocatalyst, Photocatalysis, Vat Red 13, UV irradiation.

INTRODUCTION

Water pollution is one of the major problem worldwide and most important causes of deaths and diseases. The wastewater from textile industry is extremely charged with unconsumed dyes and traces of metals. These discharges cause a major destruction to the environment. So everywhere researchers are looking for proper managements in order to get rid of these pollutants and to achieve degradation of dye house effluents [1-3]. The presence of even very little concentrations of dyes in effluent is very much visible and disagreeable [4]. There are over one lakh commercially accessible dyes with over 7×10^5 ton of dye-stuffs produced annually [5].

Since dyes have complex structure it is difficult to decolourize or degrade the dyes. There are different varieties of dyes such as, basic, acidic, vat, disperse, diazo, azo, anthraquinone based and metal complex dyes. In specific, the liberation of dye-containing emissions into the water location is disagreeable, not only because of their tint, but also for the reason that many of dyes released and their breakdown products are noxious to life forms mainly because of carcinogens, such as naphthalene, benzidine and other aromatic compounds [6]. Without ample management these dyes can persist in the location for a prolonged time. For instance, the half-life of hydrolyzed Reactive Blue 19 at pH 7 and at 25 °C is found to be 46 years [7].

To lessen the perilous effects of dye wastewater, many methods such as microbial degradation, coagulation, incineration, adsorption on activated carbon, bio-sorption, sedimentation and filtration *etc.*, have been devoted [8-10]. On the other hand, these procedures are non-destructive because they simply transport the non-biodegradable substance into slush and provide a new-fangled type of contamination, which requests additional treatment [11-13].

As a result, the hunt for effectual means of removing these compounds has induced many researchers to tackle the ever growing challenges in renewable clean energy and environment where the activity of catalysts can be maintained or improved and thereby the chance of secondary pollution may be restricted. Mainly, semiconducting metal oxides, which act as activators in photocatalysis are capable of extending their efficacy without significant loss in activity. The wide spread use of semiconductor metal oxides increases the opportunity due to their exceptional properties such as superconductivity, high temperature stability, ferromagnetism, ferroelectricity, semiconductivity, piezoelectricity and catalytic activity [14]. Remarkable examples such as SnO_2, TiO_2, ZnO, $SrTiO_3$, ZrO_2, CdS, Fe_2O_3, MOS_2, WO_3 and WS_2 have been accepted as active photocatalysts for the degradation of a number of organic contaminants, synthetic dyes *etc*. Currently photocatalytic degradation is one of the most vital scenarios in pollution control [15-18]. The challenge of photocatalytic degradation is to produce an efficient semiconductor catalyst.

In particular, copper oxide, a *p*-type transition metal oxide semiconductor having a narrow band gap (Eg = 1.2 eV) and an exceptional band structure has received a good deal of attention due to its diverse applications in different fields of solar energy cells [19,20], gas sensing [21,22], electronics [23,24], bio-sensing [25-27], heterogeneous organic catalysis [28-30], super conductors [31], *etc.*

In the present work photocatalytic degradation of a vat dye (Vat Red 13) was carried out by a green synthesized copper oxide nanocatalyst by varying parameters like catalyst dose, dye concentration, pH and irradiation time. The degradation was confirmed by UV-visible and FTIR spectral studies.

EXPERIMENTAL

The chemicals used were of analytical reagent grade and used as received without further purification. Copper sulphate and NaOH were purchased from Merck, India. Vat Red 13 dye (m.f.: $C_{32}H_{22}N_4O_2$, m.w. 494.54 g) was purchased from Chemical company in India and distilled water was used all over the entire experiment.

General procedure:

Synthesis of nanocatalyst: Copper oxide nanocatalyst was synthesized from *Eichhornia crassipes* leaf extract and copper sulphate using NaOH and characterized by UV-visible absorption spectra, XRD, EDX, FTIR and SEM analysis as reported in previous work [32]. The synthesized copper oxide nanocatalyst was used in the current work.

Photocatalytic degradation: The photocatalytic degradation studies have been carried out in a laminar air flow system. A low-pressure mercury vapour lamp has been used as source of UV irradiation. The lamp emits 8 W of UV radiation with a peak wavelength of 254 nm.

The experimental procedure constitutes of irradiation of dye solution of different concentration (10 to 50 ppm) mixed with different quantity of catalyst powder (1 to 5 mg) at a constant volume of 100 mL. Adsorption equilibrium between the dye molecules and the catalyst surface was established by stirring the mixture for about 20 min in dark. An UV light source of 8 W was used to irradiate the solution. 3 mL samples have been withdrawn at a time interval of 10 min. It was then centrifuged and absorbance measured at 540 nm and returned to the reactor. The studies were carried out at a temperature of 30 °C.

The decolourization efficiency (%) was calculated as follows:

$$\text{Degradation } (\%) = \frac{C_i - C_f}{C_i} \times 100$$

where C_i is the initial dye concentration and C_f is the final concentration of dye after photoirradiation.

RESULTS AND DISCUSSION

Photocatalytic degradability of Vat Red 13: The photodegradability of dye has been found out by exposing the dye solution to UV light with and without copper oxide nanocatalyst.

A sequence of experiments was performed to study the influences of nanocatalyst dose, dye concentration, irradiation time and pH on the photocatalytic degradation under irradiation of UV light. The dye degradation was confirmed by UV-visible and FTIR studies of the dye solution, control solution and copper oxide nanocatalyst treated dye solution.

Effect of copper oxide nanocatalyst dose: The effect of nanocatalyst dose on the dye degradation was found by subjecting dye solution to UV irradiation with different dose of catalyst varying from 1 to 5 mg. A plot of degradation percen-

tage of dye *vs.* catalytic dose is shown in Fig. 1. The degradation percentage increases as the catalytic dose increases because of increase in availability of active sites. At 4 mg catalytic dose, about 90 % of the dye was found to have degraded. Hence 4 mg of catalytic dose was fixed as optimum dose and was used for further studies.
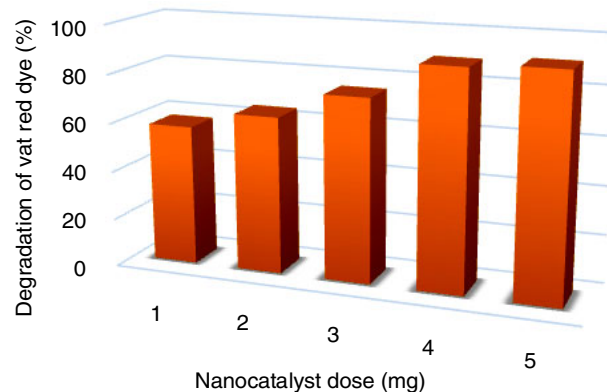

Fig. 1. Amount of nanocatalyst dose against % degradation of dye

Effect of dye concentration: The effect of concentration of dye on the photodegradation of Vat Red 13 was carried out at different dye concentrations ranging from 10-50 ppm. Fig. 2 shows the degradation percentage at various dye concentrations. It was observed that the degradation percentage slowly decreased with increase in dye concentration. The optimum concentration of the dye was found to be 20 ppm and fixed for further studies.
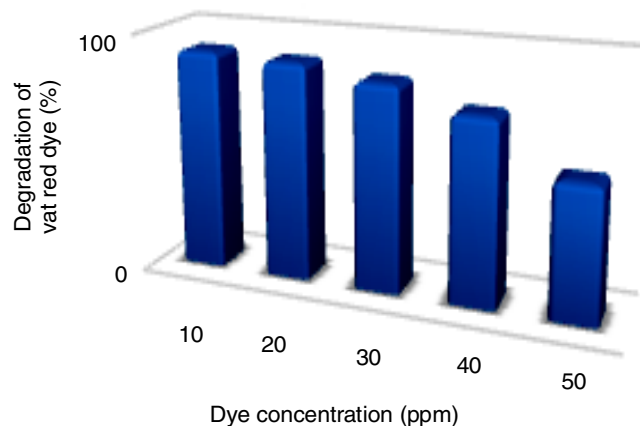

Fig. 2. Effect of dye concentration against % degradation of dye

Effect of irradiation time: Irradiation time was evaluated as one of the most important factors affecting degradation efficiency. Absorbance measured at 10 min interval of time and % degradation calculated. A plot of irradiation time against dye degradation is given in Fig. 3. It was seen that 90 % degradation occurred at 60 min and after that no predominant change. Hence an optimum time of 60 min was selected for further studies.

Effect of pH: One of the important factors that affect the photocatalytic degradation was the pH of the solution. Hence experiments were performed to know the effect of pH on the degradation efficiency of Vat Red 13 (Fig. 4). The experiment
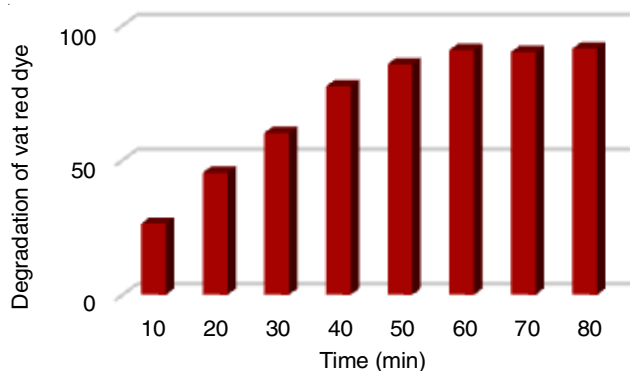
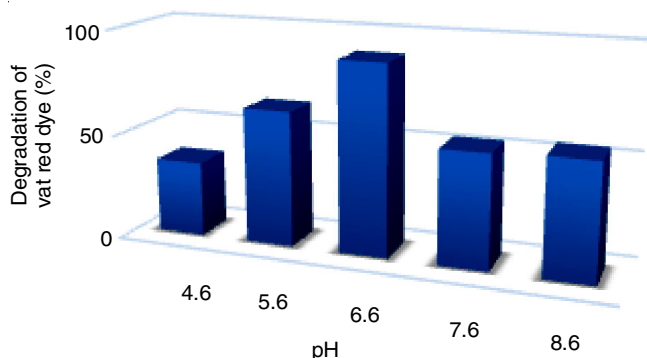Fig. 3. Effect of time against % degradation of dye

Fig. 4. Effect of pH against % degradation of dye

was performed by varying the pH of the dye solution using HCl or NaOH solution. The degradation percentage was maximum at pH 6.6 which is the pH used for further studies.

Spectral studies: UV-visible and FT IR spectral studies were carried out for the confirmation of dye degradation. The spectral analysis was performed for (i) the dye solution and (ii) dye solution of 20 ppm at pH 6.6 irradiated for 60 min without copper oxide nanocatalyst and with copper oxide nanocatalyst of 4 mg.

UV-visible spectroscopy: Fig. 5 presents the UV-visible spectra of the dye solution (A), UV irradiated dye solution without copper oxide nanocatalyst (B), UV irradiated dye solution with copper oxide nanocatalyst (C). No change in the spectra was observed for the dye solution irradiated without copper oxide nanocatalyst. But for the dye solution irradiated with copper oxide nanocatalyst, as the degradation reaction preceded, the main characteristic absorption peak at 540 nm for Vat Red 13 dye disappears, which shows the degradation of the dye.

FT-IR spectroscopy: Fig. 6 shows the FTIR spectra of the dye solution whereas Fig. 7 gives the FTIR spectra of the dye solution after photocatalytic degradation. The results in Fig. 7 exposed that the ring structures were certainly degraded which was confirmed by disappearance of peaks at the wavenumber between 540 and 420 cm^{-1}, which denote aromatic rings, after photocatalytic degradation. In particular, the connecting bond between anthraquinone rings was broken which was shown by disappearance of the peak ranging from 1335 to 1380 cm^{-1}. Apart from the demolition of the aromatic structures, the functional groups attached to them were also transformed.
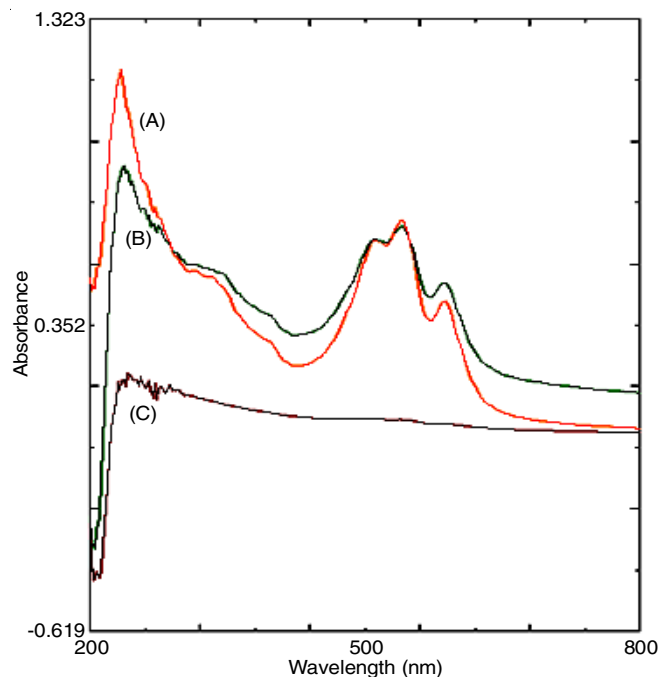

Fig. 5. UV-visible absorption spectra of dye solution (A), UV irradiated dye solution (B) and UV irradiated dye solution with copper oxide nanocatalyst (C)
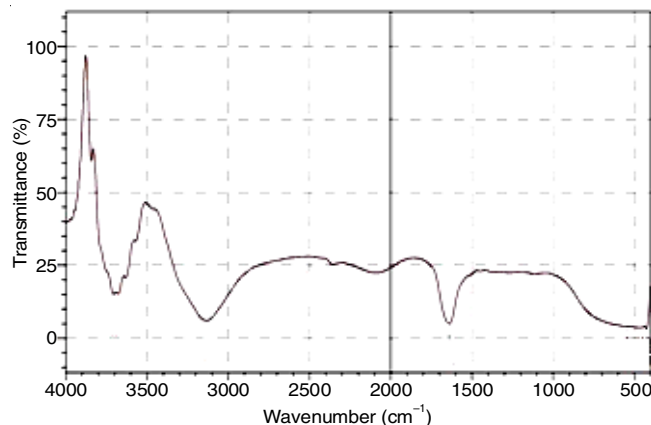

Fig. 6. FTIR spectra of dye solution
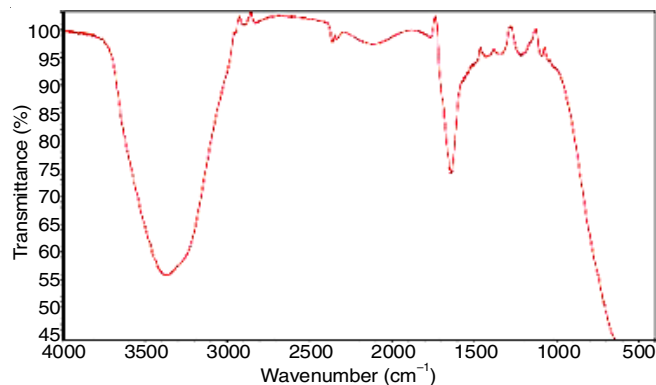

Fig. 7. FTIR spectra of UV irradiated dye solution with copper oxide nanocatalyst

Table-1 gives a comparative analysis of degradation of various dyes by copper oxide nanocatalysts and also other nanocatalysts. From the table it is observed that maximum degradation of dyes is obtained with minimum time using copper oxide nanocatalysts when compared with other nanocatalysts.

TABLE-1
COMPARISON OF CuO CATALYZED DYE
DEGRADATION WITH OTHER NANOPARTICLES

Dye	Nanocatalyst	Degradation (%)	Time	Ref.
Methylene Blue	TiO_2	100	60 min	[33]
	Mn-doped ZnO	100	120 min	[34]
	CuO	95	30 min	[35]
Rhodamine-B	TiO_2	96	30 min	[36]
	ZnO	95	70 min	[37]
	CuO	98	120 min	[38]
Reactive Black	TiO_2	93	60 min	[39]
	ZnO	100	60 min	[40]
	CuO	80	10 min	[41]
Congo Red	TiO_2	~100	210 min	[42]
	ZnO	95	60 min	[43]
	CuO	100	14 min	[44]
Crystal violet	CdS	80	20 min	[45]
	ZnO	~96	80 min	[46]
	CuO	100	16 min	[47]
Methyl orange	Ag	~100	12 h	[48]
	ZnO	~100	5 h	[49]
	CuO	90	180 min	[50]
Alizarin Red	Bi doped TiO_2	80	90 min	[51]
	ZnO	77	90 min	[52]
	CuO	100	95 min	[53]
Vat Red 13	CuO	90	60 min	Current work

Since copper oxide nanoparticles proved to be best nanocatalysts for various dyes, attempts were made for degradation of vat dyes using copper oxide nanoparticles. The copper oxide nanocatalyst efficiency is better compared with Mn^{2+} and Ag^+ for the degradation of Vat Blue BO [54]. In the present work maximum degradation of Vat Red 13 was achieved with copper oxide nanocatalyst.

From the above results it was clear that copper oxide nanoparticles acts as a best photocatalyst.

Conclusion

In this work, photocatalytic degradation of Vat Red 13 was carried out by UV irradiation using copper oxide nanocatalyst. By increasing the time of UV irradiation for a dosage of 4 mg copper oxide nanocatalyst, the degradation efficiency increases and at a time of irradiation of 60 min, maximum degradation is observed. UV-visible spectral studies and FT-IR studies confirmed that the photocatalytic degradation process is an effectual method for the degradation of Vat Red 13.

REFERENCES

1. C. Galindo, P. Jacques and A.J. Kalt, *Photochem. Photobiol. A Chem.*, **130**, 35 (2000); https://doi.org/10.1016/S1010-6030(99)00199-9.
2. B.I. Akmehmet and I. Arslan, *J. Adv. Oxid. Technol.*, **4**, 189 (1999).
3. T. Porada, R. Gade, D. Fabler and K. Gu¨nther, *J. Adv. Oxid. Technol.*, **4**, 203 (1999).
4. P. Nigam, G. Armour, I.M. Banat, D. Singh and R. Marchant, *Bioresour. Technol.*, **72**, 219 (2000); https://doi.org/10.1016/S0960-8524(99)00123-6.
5. H. Zollinger, Colour Chemistry-Synthesis, Properties of Organic Dyes and Pigments, VCH, New York, pp. 92-100 (1987).
6. D. Suteu, C. Zaharia, A. Muresan, R. Muresan and A. Popescu, *Environ. Eng. Manag. J.*, **8**, 1097 (2009).
7. O.J. Hao, H. Kim and P.-C. Chiang, *Crit. Rev. Environ. Sci. Technol.*, **30**, 449 (2000); https://doi.org/10.1080/10643380091184237.
8. A.N. Rao, B. Sivasankar and V. Sadasivam, *J. Mol. Catal. A*, **306**, 77 (2009); https://doi.org/10.1016/j.molcata.2009.02.028.
9. Z.S. Seddigi, *Contam. Toxicol.*, **84**, 564 (2010); https://doi.org/10.1007/s00128-010-9995-y.
10. M.A. Rauf and S.S. Ashraf, *J. Hazard. Mater.*, **166**, 6 (2009); https://doi.org/10.1016/j.jhazmat.2008.11.043.
11. I. Arslan, I.A. Balcioglu, T. Tuhkanen and D. Bahnemann, *J. Environ. Eng.*, **126**, 903 (2000); https://doi.org/10.1061/(ASCE)0733-9372(2000)126:10(903).
12. S.K. Chaudhuri and B. Sur, *J. Environ. Eng.*, **126**, 583 (2000); https://doi.org/10.1061/(ASCE)0733-9372(2000)126:7(583).
13. N. Stock, J. Peller, K. Vinodgopal and P.V. Kamat, *Environ. Sci. Technol.*, **34**, 1747 (2000); https://doi.org/10.1021/es991231c.
14. H. Liu, S.P. Gong, Y.X. Hu, J.Q. Liu and D.X. Zhou, *Sens. Actuators B Chem.*, **140**, 190 (2009); https://doi.org/10.1016/j.snb.2009.04.027.
15. Z. Zhang, Y. Yuan, G. Shi, Y. Fang, L. Liang, H.C. Ding and L. Jin, *Environ. Sci. Technol.*, **41**, 6259 (2007); https://doi.org/10.1021/es070212x.
16. S. Bharathi, D. Nataraj, D. Mangalaraj, Y. Masuda, K. Senthil and K. Yong, *J. Phys. D: Appl. Phys.*, **43**, 015501 (2010); https://doi.org/10.1088/0022-3727/43/1/015501.
17. H.R. Pouretedal, A. Norozi, M.H. Keshavarz and A. Semnani, *J. Hazard. Mater.*, **162**, 674 (2009); https://doi.org/10.1016/j.jhazmat.2008.05.128.
18. M. Sathish, B. Viswanathan and R.P. Viswanath, *J. Hydrogen Energy*, **31**, 891 (2006); https://doi.org/10.1016/j.ijhydene.2005.08.002.
19. E. Alonso, C. Pérez-Rábago, J. Licurgo, E. Fuentealba and C.A. Estrada, *Sol. Energy*, **115**, 297 (2015); https://doi.org/10.1016/j.solener.2015.03.005.
20. M.I. Hossain, F.H. Alharbi and N. Tabet, *Sol. Energy*, **120**, 370 (2015); https://doi.org/10.1016/j.solener.2015.07.040.
21. M. Yang, J. He, M. Hu, X. Hu, C. Yan and Z. Cheng, *Sens. Actuators B Chem.*, **213**, 59 (2015); https://doi.org/10.1016/j.snb.2015.02.055.
22. K. Akhtar, I.U. Haq and K. Malook, *Powder Technol.*, **283**, 505 (2015); https://doi.org/10.1016/j.powtec.2015.06.023.
23. S.-T. Bee, L.T. Sin, C.T. Ratnam, K.J.S. Haraveen, T.-T. Tee and A.R. Rahmat, *Nucl. Instrum. Methods Phys. Res. B*, **360**, 36 (2015); https://doi.org/10.1016/j.nimb.2015.07.105.
24. E. Park, H.W. Park and J. Lee, *Colloids Surf. A Physicochem. Eng. Asp.*, **482**, 710 (2015); https://doi.org/10.1016/j.colsurfa.2015.07.029.
25. P. Moozarm Nia, W.P. Meng, F. Lorestani, M.R. Mahmoudian and Y. Alias, *Sens. Actuators B Chem.*, **209**, 100 (2015); https://doi.org/10.1016/j.snb.2014.11.072.
26. P. Gao and D. Liu, *Sens. Actuators B Chem.*, **208**, 346 (2015); https://doi.org/10.1016/j.snb.2014.11.051.
27. T. Alizadeh and S. Mirzagholipur, *Sens. Actuators B Chem.*, **198**, 438 (2014); https://doi.org/10.1016/j.snb.2014.03.049.
28. C. Jeong, M.J. Hyun and Y.-W. Suh, *Catal. Commun.*, **70**, 34 (2015); https://doi.org/10.1016/j.catcom.2015.07.011.
29. S. Induja and P.S. Raghavan, *Catal. Commun.*, **33**, 7 (2013); https://doi.org/10.1016/j.catcom.2012.12.016.
30. S.J. Ahmadi, S. Sadjadi, M. Hosseinpour, M. Outokesh and R. Hekmatshoar, *Catal. Commun.*, **10**, 1423 (2009); https://doi.org/10.1016/j.catcom.2009.03.009.
31. J.H. Schön, M. Dorget, F.C. Beuran, X.Z. Zu, E. Arushanov, C. Deville Cavellin and M. Laguës, *Nature*, **414**, 434 (2001); https://doi.org/10.1038/35106539.
32. S. Hemalatha and M. Makeswari, *Rasayan J. Chem.*, **10**, 838 (2017).
33. S. Naskar, S. Arumugom Pillay and M. Chanda, *J. Photochem. Photobiol. Chem.*, **113**, 257 (1998); https://doi.org/10.1016/S1010-6030(97)00258-X.

34. M. Khaksar, M. Amini and D.M. Boghaei, *J. Exp. Nanosci.*, **10**, 1256 (2015);
     https://doi.org/10.1080/17458080.2014.998300.

35. A. Farrouji, A. Eddine, S. Bouzit, B. Boualy, A. Mehdi, L. Firdoussi and M. Ali, *Int. Res. J. Pure Appl. Chem.*, **8**, 190 (2015);
     https://doi.org/10.9734/IRJPAC/2015/18057.

36. B. Wang, G. Zhang, Z. Sun and S. Zheng, *Powder Technol.*, **262**, 1 (2014);
     https://doi.org/10.1016/j.powtec.2014.04.050.

37. Q.I. Rahman, M. Ahmad, S.K. Misra and M. Lohani, *Mater. Lett.*, **91**, 170 (2013);
     https://doi.org/10.1016/j.matlet.2012.09.044.

38. B. Shaabani, E. Alizadeh-Gheshlaghi, Y. Azizian-Kalandaragh and A. Khodayari, *Adv. Powder Technol.*, **25**, 1043 (2014);
     https://doi.org/10.1016/j.apt.2014.02.005.

39. M.S. Lucas, P.B. Tavares, J.A. Peres, J.L. Faria, M. Rocha, C. Pereira and C. Freire, *Catal. Today*, **209**, 116 (2013);
     https://doi.org/10.1016/j.cattod.2012.10.024.

40. S. Laohaprapanon, J. Matahum, L. Tayo and S.-J. You, *J. Taiwan Inst. Chem. Eng.*, **49**, 136 (2015);
     https://doi.org/10.1016/j.jtice.2014.11.017.

41. N. Anandhavalli, B. Mol, S. Manikandan, N. Anusha, V. Ponnusami and K.S. Rajan, *Asian J. Chem.*, **27**, 2523 (2015);
     https://doi.org/10.14233/ajchem.2015.17966.

42. H. Guo, K. Lin, Z. Zheng, F. Xiao and S. Li, *Dyes Pigments*, **92**, 1278 (2012);
     https://doi.org/10.1016/j.dyepig.2011.09.004.

43. Elaziouti, N. Laouedj and B. Ahmed, *J. Chem. Eng. Process. Technol.*, **2**, 106 (2011);
     https://doi.org/10.4172/2157-7048.1000106.

44. P. Narasaiah, B.K. Mandal and N.C. Sarada, *Mater. Sci. Eng.*, **263**, 0022012 (2017);
     https://doi.org/10.1088/1757-899X/263/2/022012.

45. A. Nezamzadeh-Ejhieh and Z. Banan, *Desalination*, **284**, 157 (2012);
     https://doi.org/10.1016/j.desal.2011.08.050.

46. S. Ameen, M.S. Akhtar, M. Nazim and H.-S. Shin, *Mater. Lett.*, **96**, 228 (2013);
     https://doi.org/10.1016/j.matlet.2013.01.034.

47. S. Sonia, S. Poongodi, P.S. Kumar, D. Mangalaraj, N. Ponpandian and C. Viswanathan, *Mater. Sci. Semicond. Process.*, **30**, 585 (2015);
     https://doi.org/10.1016/j.mssp.2014.10.012.

48. P. Kumar, M. Govindaraju, S. Senthamilselvi and K. Premkumar, *Colloids Surf. B Biointerfaces*, **103**, 658 (2013);
     https://doi.org/10.1016/j.colsurfb.2012.11.022.

49. R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng and J. Ding, *Powder Technol.*, **189**, 426 (2009);
     https://doi.org/10.1016/j.powtec.2008.07.004.

50. X. Liu, Z. Li, Q. Zhang, F. Li and T. Kong, *Mater. Lett.*, **72**, 49 (2012);
     https://doi.org/10.1016/j.matlet.2011.12.077.

51. S. Sood, S.K. Mehta, A. Umar and S.K. Kansal, *New J. Chem.*, **38**, 3127 (2014);
     https://doi.org/10.1039/C4NJ00179F.

52. S.K. Kansal, R. Lamba, S.K. Mehta and A. Umar, *Mater. Lett.*, **106**, 385 (2013);
     https://doi.org/10.1016/j.matlet.2013.05.074.

53. N.P. Mohabansi and A.K. Satone, *J. Nanosci. Technol.*, **4**, 320 (2018);
     https://doi.org/10.30799/jnst.099.18040106.

54. X.-R. Xu, H.-B. Li, W.-H. Wang and J.-D. Gu, *Chemosphere*, **57**, 595 (2004);
     https://doi.org/10.1016/j.chemosphere.2004.07.030.