



Synthesis and Photocatalytic Efficiency of Sunlight Driven Novel Ternary Metal Oxide Nanophotocatalyst

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Effluents from the textile industry usually contain high concentrations of organics and are characterized by deep colour as well as high in chemical oxygen demand and total organic carbon values. Dyes from dyeing operations are the major source of colour in textile effluents. Currently many physical and chemical techniques are available for treatment but these are costly and have disposal problem at industrial level. In the present study co-precipitation method was used to prepare sunlight driven efficient nanophotocatalyst aluminium zinc ferrite ($\text{Al}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$). It was characterized for its structural properties by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis (EDX). The photocatalytic activity was evaluated by degrading reactive black B dye under sunlight irradiation with the help of UV-visible spectrophotometer. The observed photo degradation rate was 91 % in 120 min. Aluminium zinc ferrite photocatalyst was separated from reaction mixture and recycled for 7 cycles of reuse without appreciable loss of activity.

Keywords: Aluminium zinc ferrite, Chemical coprecipitation, Nanophotocatalyst, Reactive Black B degradation.

INTRODUCTION

The main causes of surface water and groundwater contamination are industrial discharges¹. The textile industry has a big pollution problem. According to the estimation of The World Bank 17-20 % of industrial water pollution caused by textile processing industries. Wastewater generated by the textile industries are known to contain considerable amounts of non-fixed dyes and a huge amount of other toxic chemicals. It has been estimated that more than 10 % of the total dye stuff used in dyeing processes are released into the environment². Traditional methods which are still in use to decontaminate polluted water include adsorption^{3,4}, chlorination^{5,6}, coagulation^{7,8}, ion flotation⁹, membrane process^{10,11}, sedimentation¹² and solvent extraction^{13,14}. The end products of these techniques need to be processed further for complete purification. There are newer advanced oxidation processes including biodegradation^{15,16}, Fenton^{17,18}, photo-Fenton^{19,20}, photocatalytic^{21,22} radiation²³⁻²⁵, sonolysis²⁶⁻²⁸, ozonation²⁹ and UV photocatalytic processes^{30,31} can be used to degrade organic pollutants into harmless products, carbon dioxide and water³². Nanotechnology has replaced the previous technologies because the nanomaterials completely mineralize most of organics and are inexpensive³³ and non-toxic³⁴. They are easily available and stable to corrosion in the presence of water and chemicals³⁵.

Nano sized semiconductor photocatalyst materials have become the focus of research to meet the challenges of serious environmental problems³⁶⁻³⁹. Photocatalyst materials having band gap energy below 3 eV and ionic character 20-30 % could be used under visible light for remediation of these problems⁴⁰. Photocatalytic activity can be enhanced by combining different semiconductors with different band gap energies⁴¹. A variety of nanophotocatalysts have been developed for the remediation of environmental issues e.g. Fe^{3+} - TiO_2 ⁴², ZnFe_2O_4 ⁴³, $\text{TiO}_2\text{ZnFe}_2\text{O}_4$ ⁴⁴, Zn-Al-In ⁴⁵, $\text{Fe}_2\text{O}_3\text{-ZrO}_2/\text{Al}_2\text{O}_3$ ⁴⁶ and $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ⁴⁷. However, these are not meeting the commercial requirement of waste water treatment. Scientists are still in search of new nanophotocatalysts which could work under sunlight efficiently and can meet the current commercial challenges.

In present study, the use of new $\text{AlZnFe}_2\text{O}_4$ nanophotocatalyst produced has been proposed first time. This nanophotocatalyst ($\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) exhibited 91 % Reactive black B dye degradation activity under sunlight irradiation. For characterization of highly active sample ($\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$), advanced analytical techniques like XRD, SEM and EDX were used.

EXPERIMENTAL

All the chemicals ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, NH_4OH) used in the synthesis and characterization of $\text{AlZnFe}_2\text{O}_4$

were purchased from Sigma Aldrich. For the synthesis of $\text{Al}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ [where $x = 0.1$ (S1), $x = 0.3$ (S2), $x = 0.5$ (S3), $x = 0.7$ (S4) and $x = 0.9$ (S5)] coprecipitation technique was used. Appropriate amounts of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were weighed and dissolved in 100 mL of deionized distilled water separately and heated to 65 °C and mixed by slow stirring. Then 30 % NH_4OH solution was added drop wise at high speed stirring at 65 °C in a temperature controlled reactor until reddish brown precipitate of $\text{Al}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ appeared. This process took 120 min. The mixture was stirred for another 60 min and discharged from the reactor. The precipitate were filtered, washed and dried at 100 °C for 90 min and grounded to a fine powder in an agate pastelmortar. This powder was divided into three portions and was further processed as under.

- $\text{Al}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ uncalcined
- $\text{Al}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ calcined at 400 °C for 4 h
- $\text{Al}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ calcined at 600 °C for 4 h.

Crystalline structure of $\text{AlZnFe}_2\text{O}_4$ nanocomposite was investigated by X-ray diffraction analysis [Rigaku Rotaflex D/Max] K_α radiation (1.5418 Å) with a glass sample holder having cavity ($10 \times 10 \times 1$) mm^3 at a scan rate of 1.2 per min and 2θ range (10-80°). The topography and diameter of $\text{AlZnFe}_2\text{O}_4$ was observed using SEM (JEOL JSM-6480).

Photocatalytic activity test: Photocatalytic activity test was performed by degrading reactive black B dye (50 ppm) solution. An amount 60 mg of photocatalyst was dispersed in 100 mL of dye solution and stirred for 0.5 h in dark to complete adsorption-desorption equilibrium. Then the suspension was illuminated by sunlight with constant stirring in oxygen atmosphere for 2 h. An aliquot of 3 mL was taken after each 20 min interval for dye concentration analysis. The absorbance of sample were measured at 594 nm. Effect of calcination temperature was observed by repeating the photocatalytic activity test with $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ uncalcined and calcined at 400 and 600 °C.

Reusability test: Photostability and long term use of $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was evaluated by separating the spent photocatalyst with centrifugation at 4000 rpm and recycling it up to seven reaction cycles, 3 mg of fresh photocatalyst was added at the start of each cycle to compensate the catalyst loses⁴⁸.

Total organic carbon: For the determination of mineralization of dye total organic carbon test was performed. Sulphuric acid, 1.6 mL (98 %) taken in a clean screw-cap vial was mixed with 1 mL of 2N $\text{K}_2\text{Cr}_2\text{O}_7$ and 4 mL sample (for the calculation of standard factor 4 mL of glucose solution was used) and whole mixture was incubated at 110 °C for 1.5 h. After incubation absorbance was measured at $\lambda = 590$ nm using UV-visible recording spectrophotometer⁴⁹.

Standard factor = Concentration of glucose (mg/L)/ absorbance after incubation

Total organic carbon of sample (mg/L) = Standard factor \times absorbance of sample after incubation

RESULTS AND DISCUSSION

XRD analysis: The crystallinity of $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (uncalcined, calcined at 400 and 600 °C) nanophotocatalyst was examined by powder X-ray diffractometry. The XRD pattern

was observed by using Match! 2.0.7 (phase identification software by Crystal Impact) which showed that uncalcined $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ has gahnite phase according to entry number 96-900-6310, 96-900-6314 and 96-900-6309 which are the published patterns of $\text{Al}_2\text{Fe}_{0.4}\text{O}_4\text{Zn}_{0.6}$ (Fig. 1a). After calcination at 400 °C hercynite phase (entry no. 96-900-6311 and 96-900-6315) was observed in addition to gahnite (Fig. 1b) and calcined at 600 °C only hercynite phase was observed (entry no. 96-900-6311) and (96-900-6315) (Fig. 1c). Particle size calculated by Sherrer's formula was 46.82 nm.

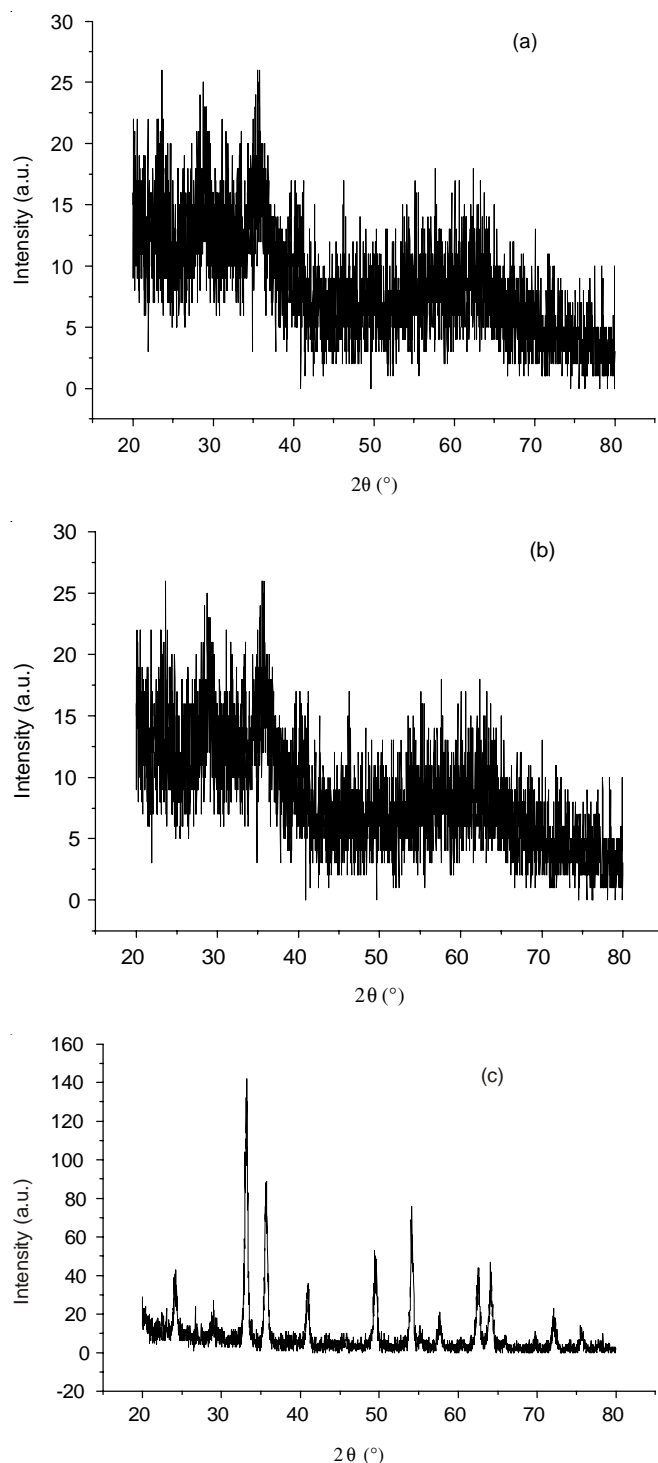


Fig. 1. XRD patterns of $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (a) Uncalcined (b) Calcined at 400 °C and (c) Calcined at 600 °C

Scanning electron microscopic analysis: Scanning electron microscopic analysis of synthesized $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ before and after calcination was carried out and scanning electron microscopy images are given in Fig. 2. There was structural change after calcination at 400 and 600 °C. and particles were not of uniformly separated and there was change in crystal shape with temperature and average diameter observed was 45 nm.

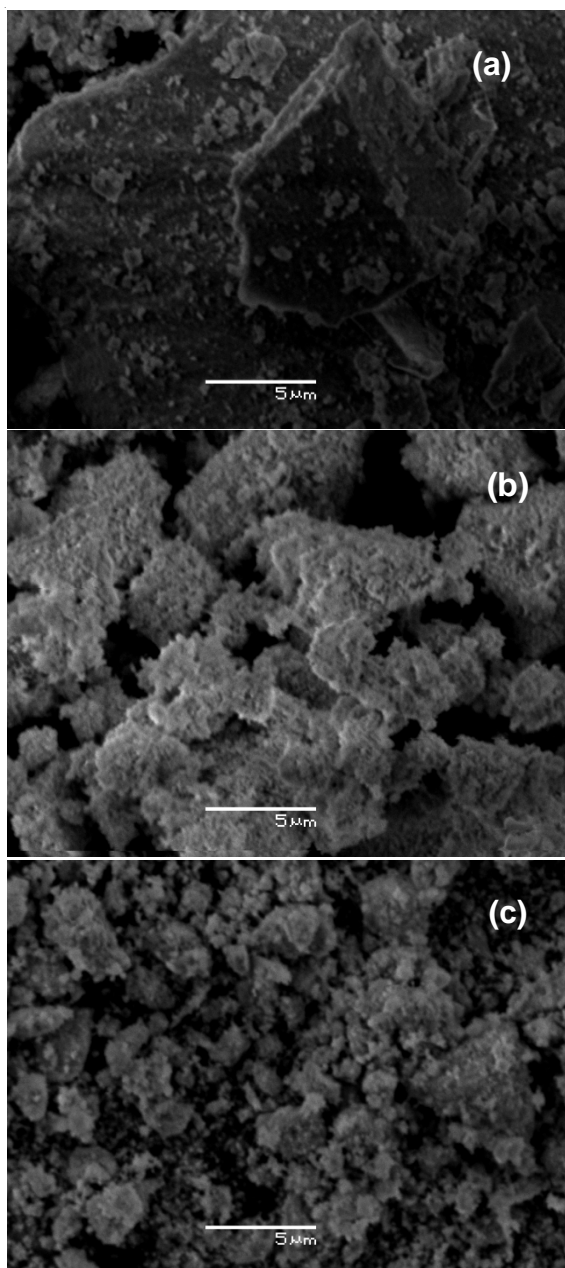


Fig. 2. SEM images of $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (a) Uncalcined, (b) Calcined at 400 °C and (c) Calcined at 600 °C

Energy dispersive X-ray analysis: Energy dispersive X-ray analysis was performed to determine average weight percentage of Al_2O_3 , ZnO and Fe_2O_3 in the composite. Energy dispersive X-ray spectrum of $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ is given below in Fig. 3. Peaks of Al, Zn and Fe are very clear. The presence of Si and Pt peaks are due to Si used as supporting medium and Pt for coating.

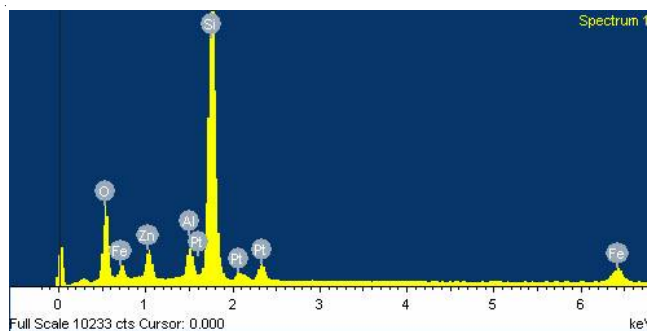


Fig. 3. Energy dispersive X-ray spectrum of $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$

Photocatalytic activity: Photocatalytic activity was determined by studying the degradation rate of reactive black B dye in aqueous solution. Reactive black B dye (50 ppm) was impregnated with 60 mg/100 mL of $\text{AlZnFe}_2\text{O}_4$ and illuminated by sunlight for 120 min with constant stirring in open air. Degradation rates are shown in Fig. 4. $\text{AlZnFe}_2\text{O}_4$ degraded 91 % of reactive black B dye in 120 min. Sample S3 having formula $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ showed the maximum value of degradation. The influence of calcination temperature on degradation of dye *versus* time interval is illustrated in Fig. 5. The results indicated that the degradation of reactive black B dye was increased with the increase in calcination temperature. Degradation percentage of calcined and uncalcined samples differed widely but this difference was much smaller between various calcinized samples at 400 and 600 °C.

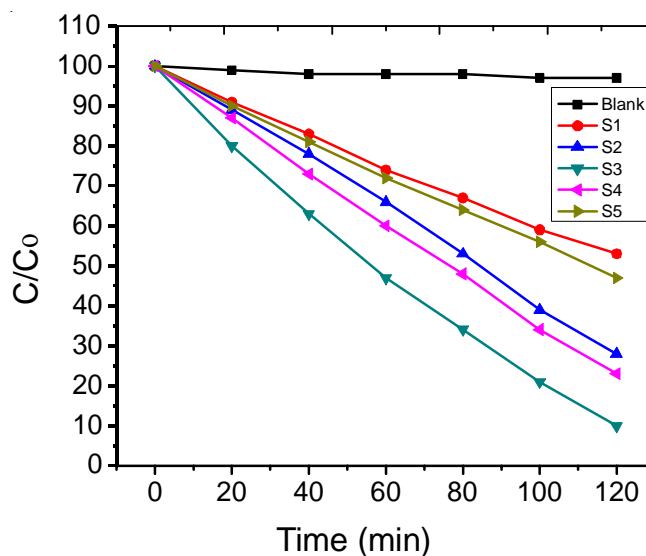


Fig. 4. Photocatalytic degradation of reactive black B by sunlight irradiation calcined at 600 °C

Stability and reusability of photocatalyst: At the end of degradation experiment the catalyst was separated from suspension by centrifugation, washed and dried. Catalyst did not change its colour indicating that adsorbed dye had been degraded completely. Stability of catalyst against light and chemicals was evaluated by reusing it in seven cycles of reaction. Catalyst had maintained its activity. Only 5 % recovery loss of catalyst took place during separation and there was 4 % loss in activity during 7 cycles of reuse. Results are shown in Fig. 6.

TABLE-1
COMPARISON OF $\text{AlZnFe}_2\text{O}_4$ WITH PREVIOUSLY USED NANOPHOTOCATALYSTS

Photocatalyst	Pollutant	Degradation (%)	Light irradiation	Time (min)	References
$\text{AlZnFe}_2\text{O}_4$	Reactive black B	91	Sun light	120	Present study
$\text{Fe}_2\text{O}_3\text{-ZrO}_2/\text{Al}_2\text{O}_3$	Phenol	90	UV	120	50
$\text{Ag-AgBr}/\text{Al}_2\text{O}_3$	Phenol	65	Visible (≥ 420 nm)	60	51
BiOI/TiO_2	Methyl orange	80	Visible	120	52
$\text{ZnO}/\text{Mg-Al-CO}_3\text{-LDH}$	Acid red G	98	Mercury lamp	120	53
ZnAlInMMO	Methylene blue	73	Visible light	240	54

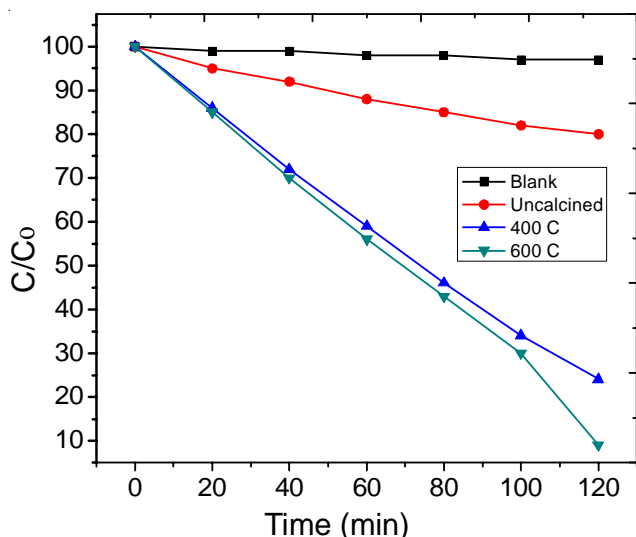


Fig. 5. Photocatalytic degradation of reactive black B by sunlight irradiation of blank, uncalcined, calcined at 400 and 600 °C for 4 h

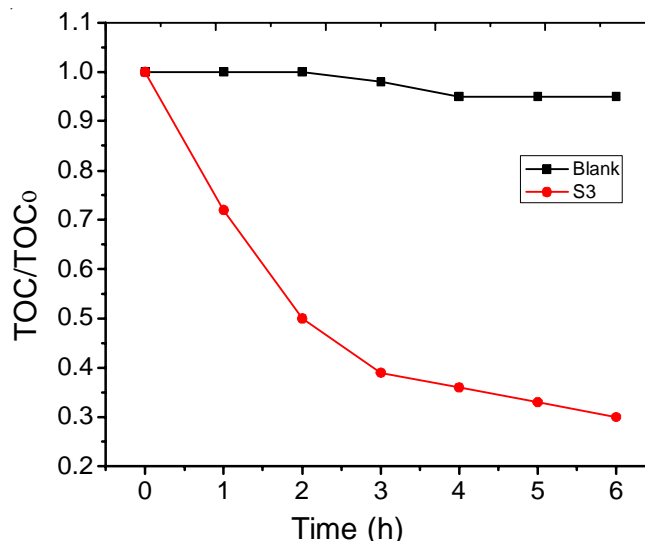


Fig. 7. Mineralization rate of sample S3 calcined at 600 °C

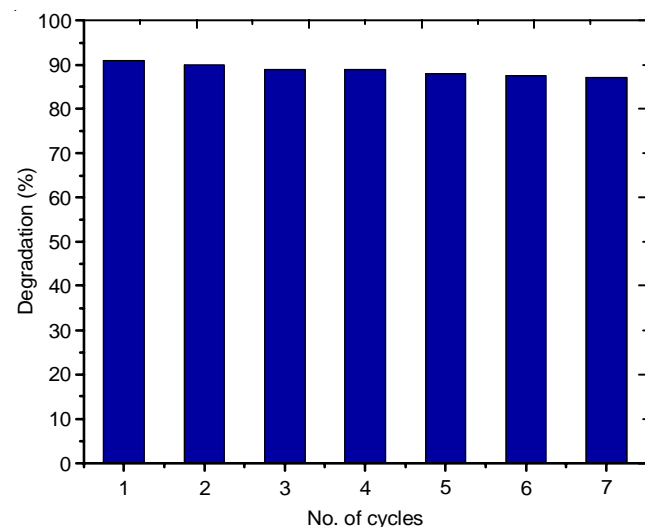


Fig. 6. Photodegradation of reactive black B in seven cycles of reuse under similar experimental conditions by sample S3

Mineralization of dye: Mineralization of reactive black B dye with $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was measured by total organic carbon values of illuminated mixture by sunlight after every 1 h of reaction time. When the dye concentration was 0.05 mM and catalyst load was 600 mg L^{-1} , 70 % mineralization of dye took place in 6 h (Fig. 7).

$\text{AlZnFe}_2\text{O}_4$ degraded reactive black B upto 91 % under sunlight irradiation in 120 min, so it can be use for the removal of dyes from textile effluents. Degradation of organic pollutants by $\text{AlZnFe}_2\text{O}_4$ is not reported in literature however we are

giving some photocatalyst with enhanced activity for comparison in Table-1.

Conclusion

A novel nanophotocatalyst $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with enhanced activity working on sunlight was synthesized which degraded 91 % reactive black B dye in aqueous solution in 120 min. Catalyst can be reused several times without an appreciable loss of activity. Reactive black B dye was also mineralized upto 70 % in 6 h. It is suggested that $\text{Al}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ is potential nanophotocatalyst for wastewater treatment.

REFERENCES

- M.N. Rashed and A.A. El-Amin, *Int. J. Phys. Sci.*, **2**, 73 (2007).
- R.J. Maguire, *Water Sci. Technol.*, **26**, 265 (1992).
- S. Parsons, *Advanced Oxidation Processes for Water and Wastewater*, IWA Publishing, London, UK (2004).
- M.Z. Alam, S. Ahmad, A. Malik and M. Ahmad, *Ecotox. Environ. Saf.*, **73**, 1620 (2010).
- C. O'Neill, A. Lopez, S. Esteves, F.R. Hawkes, D.L. Hawkes and S. Wilcox, *Appl. Microbiol. Biotechnol.*, **53**, 249 (1999).
- N. Nasuha, B.H. Hameed and A.T.M. Din, *J. Hazard. Mater.*, **175**, 126 (2010).
- M.A. Rauf, S.M. Qadri, S. Ashraf and K.M. Al-Mansoori, *Chem. Eng. J.*, **150**, 90 (2009).
- V.K. Sharma, G.A.K. Anquandah, R.A. Yngard, H. Kim, J. Fekete, K. Bouzek, A.K. Ray and D. Golovko, *J. Environ. Sci. Health Part A*, **44**, 423 (2009).
- F. Ge, L. Zhu and J. Wang, *Desalination*, **225**, 156 (2008).
- M. Riera-Torres, C. Gutiérrez-Bouzán and M. Crespi, *Desalination*, **252**, 53 (2010).
- A.L. Ahmad and S.W. Puasa, *Chem. Eng. J.*, **132**, 257 (2007).
- K. Shakir, A.F. Elkafrawy, H.F. Ghoneimy, S.G. ElrabBeheir and M. Refaat, *Water Res.*, **44**, 1449 (2010).

13. M.S. Lee, C. Huang, K.R. Lee, J.R. Pan and W.K. Chang, *Desalination*, **234**, 416 (2008).
14. H. Jirankova, J. Mrazek, P. Dolecek and J. Cakl, *Water Treat.*, **20**, 96 (2010).
15. V.M. Egorov, S.V. Smirnova and I.V. Pletnev, *Sep. Purif. Technol.*, **63**, 710 (2008).
16. R.S. Juang, W.C. Huang and Y.H. Hsu, *J. Hazard. Mater.*, **164**, 46 (2009).
17. M.A. Rauf and S.S. Ashraf, in ed.: A.R. Lang, Application of Advanced Oxidation Processes (AOP) to Dye Degradation-An Overview, Dyes and Pigments: New Research, Nova Science Publishers, Inc. (2009).
18. L. Ayed, K. Chaieb, A. Cheref and A. Bakhrouf, *Desalination*, **260**, 137 (2010).
19. Ö. Çinar, S. Yasar, M. Kertmen, K. Demiröz, N.Ö. Yigit and M. Kitis, *Process Saf. Environ. Prot.*, **86**, 455 (2008).
20. C. Bouasla, M.E.H. Samar and F. Ismail, *Desalination*, **254**, 35 (2010).
21. A. Masarwa, S. Rachmilovich-Calis, N. Meyerstein and D. Meyerstein, *Coord. Chem. Rev.*, **249**, 1937 (2005).
22. J.M. Monteagudo, A. Duran, I.S. Martin and M. Aguirre, *Appl. Catal. B*, **95**, 120 (2010).
23. N. Modirshahla, M.A. Behnajady and F. Ghanbary, *Dyes Pigments*, **73**, 305 (2007).
24. M.A. Rauf, M.A. Meetani, A. Khaleel and A. Ahmed, *Chem. Eng. J.*, **157**, 373 (2010).
25. R. Xu, J. Li, J. Wang, X. Wang, B. Liu, B. Wang, X. Luan and X. Zhang, *Sol. Energy Mater. Sol. Cells*, **94**, 1157 (2010).
26. A. Vahdat, S.H. Bahrami, M. Arami and A. Motahari, *Radiat. Phys. Chem.*, **79**, 33 (2010).
27. K.M. Mohamed, A.A. Basfar and A.A. Al-Shahrani, *J. Hazard. Mater.*, **166**, 810 (2009).
28. Y.P. Chen, S.Y. Liu, H.Q. Yu, H. Yin and Q.R. Li, *Chemosphere*, **72**, 532 (2008).
29. S. Merouani, O. Hamdaoui, F. Saoudi and M. Chiha, *Chem. Eng. J.*, **158**, 550 (2010).
30. H. Ghodbane and O. Hamdaoui, *Ultrason. Sonochem.*, **16**, 455 (2009).
31. G. Wang, Y. Qin, J. Cheng and Y. Wang, *J. Fuel Chem. Technol.*, **38**, 502 (2010).
32. I. Ullah, S. Ali, M.A. Hanif and S.A. Shahid, *Int. J. Chem. Biochem. Sci.*, **2**, 60 (2012).
33. A.R. Tehrani-Bagha, N.M. Mahmoodi and F.M. Menger, *Desalination*, **260**, 34 (2010).
34. F.H. Alhamedi, M.A. Rauf and S.S. Ashraf, *Desalination*, **239**, 159 (2009).
35. M. Styliadi, D.I. Kondarides and X.E. Verykios, *Appl. Catal. B*, **40**, 271 (2003).
36. W. Choi, *Catal. Surv. Asia*, **10**, 16 (2006).
37. J.F. Zhu, J.L. Zhang, F. Chen and M. Anpo, *Mater. Lett.*, **59**, 3378 (2005).
38. M. Addamo, M. Bellardita, D. Carriazo, A. Di Paola, S. Milioto, L. Palmisano and V. Rives, *Appl. Catal. B*, **84**, 742 (2008).
39. H. Park, H.S. Jie, B. Neppolian, K. Tsujimaru, J.-P. Ahn, D.Y. Lee, J.-K. Park and M. Anpo, *Top. Catal.*, **47**, 166 (2008).
40. I. Shakir, M. Shahid and D.J. Kang, *Chem. Commun.*, **46**, 4324 (2010).
41. M. Shahid, I. Shakir, S. Yang and D.J. Kang, *Mater. Chem. Phys.*, **124**, 619 (2010).
42. M. Daturi, A. Cremona, F. Milella, G. Busca and E. Vogna, *J. Eur. Ceram. Soc.*, **18**, 1079 (1998).
43. C. Wang, H. Shi and Y. Li, *Appl. Surf. Sci.*, **257**, 6873 (2011).
44. S. Srinivasan, J. Wade and E.K. Stefanakos, *J. Nanomater.*, Article ID 45712 (2006).
45. G. Fan, W. Sun, H. Wang and F. Li, *Chem. Eng. J.*, **174**, 467 (2011).
46. W.-J. Liu, F.-X. Zeng, H. Jiang, X.-S. Zhang and W.-W. Li, *Chem. Eng. J.*, **180**, 9 (2012).
47. X.C. Yang, W. Riehemann, M. Dubiel and H. Hofmeister, *Mater. Sci. Eng. B*, **95**, 299 (2002).
48. H.R. Pouretedal, Z. Tofangsazi and M.H. Keshavarz, *J. Alloys Comp.*, **513**, 359 (2012).
49. A.E. Greenberg, L.S. Claesceri and A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington DC (1998).
50. W.-J. Liu, F.-X. Zeng, H. Jiang, X.-S. Zhang and W.-W. Li, *Chem. Eng. J.*, **180**, 9 (2012).
51. X. Zhou, C. Hu, X. Hu and T. Peng, *J. Hazard. Mater.*, **219-220**, 276 (2012).
52. Z. Liu, X. Xu, J. Fang, X. Zhu, J. Chu and B. Li, *Appl. Surf. Sci.*, **258**, 3771 (2012).
53. S. Yuan, Y. Li, Q. Zhang and H. Wang, *Colloids Surf. B*, **348**, 76 (2009).
54. G. Fan, W. Sun, H. Wang and F. Li, *Chem. Eng. J.*, **174**, 467 (2011).