RESEARCH PAPER

Effective Degradation and Mineralization of Real Textile Effluent by Sonolysis, Photocatalysis, and Sonophotocatalysis Using ZnO Nano Catalyst

Vilas Kailas Mahajan and Gunvant Hari Sonwane *

[1] *Department of Chemistry, Kisan Arts, Commerce and Science College, Parola, Dist- Jalgaon, India*

ARTICLE INFO

Article History:
Received 19 April 2016
Accepted 23 June 2016
Published 1 July 2016

Keywords:
Industrial effluents
Sonophotocatalysis
Total organic carbon
Zinc oxide

ABSTRACT

In this study, the ultrasonic, photocatalytic and sonophotocatalytic degradation of organics in textile industrial effluent was studied using ZnO nano catalyst, ZnO nano catalyst was synthesized by using sol-gel method. The structure and morphology of the catalyst were investigated using scanning election microscopy (SEM), electron dispersive X-ray spectroscopy (EDS) and X-ray diffraction pattern (XRD). The percentage removal of textile influents was determined by using TOC. The effects of various operational parameters such as, contact time, catalyst loading, and solution pH on the degradation efficiency were studied. The increase in degradation efficiency with the increase in catalyst loading, contact time. Neutral pH is suitable for degradation of textile industrial effluents, and comparative study shows that the sonophotocatalyst is effective for degradation technique than ultrasonic and photocatalytic degradation of textile industrial effluent.

How to cite this article
Mahajan VK, Sonawane, GH. Effective degradation and mineralization of real textile effluent by sonolysis, photocatalysis, and sonophotocatalysis using ZnO nano catalyst. Nanochem Res, 2016; 1(2):258-263. DOI: 10.7508/ncr.2016.02.013

INTRODUCTION

Wastewater generated from textile, leather, paper and plastic industries contains toxic dyes, which can make serious damages on water resources and can thus results in severe economic and environmental problems [1-3]. Synthetic dyes are widely used in food products, cosmetics, pharmaceuticals, paper, printing etc. Due to their good solubility, synthetic dyes are also common water pollutants and they may be frequently found in large quantities in industrial wastewater. Meanwhile, many of these dyes are also toxic and even carcinogenic [4]. Then, it is necessary to eliminate dyes from wastewater before it is discharged. However, wastewater containing dyes is very difficult to treat because the existing synthetic dyes are recalcitrant organic molecules, resistant to aerobic digestion, and stable to light, heat and oxidizing agents [5]. During the past decades, several physical, chemical and biological removal methods have been studied for the dyes wastewater purification strategies, like adsorption, filtration, coagulation, biodegradation [6-10]. However, physical methods are limited because further treatment was demanded, where the removed dyes only being transferred from liquid phase to solid phase. Among various techniques of dyes removal, Advanced Oxidation Processes (AOPs) is the procedure of choice and gives the best results as its strong oxidizing property and environmentally benign characters [11, 12].

Photocatalysis is an advanced oxidation technique to use the catalytic activity of the semiconducting metal oxides. This technique produces OH•, which has stronger oxidation power than ordinary oxidants normally used in the oxidation process, and decomposes the organic compounds into harmless compounds, such as CO_2, H_2O, or HCl [13]. Many types of

* Corresponding Author Email: *drgunvantsonawane@gmail.com*

semiconductors have been used as photocatalyst including TiO_2, ZnO, CdS, WO_3, etc. Most of these semiconductor photocatalysts have band gap in the ultraviolet (UV) region, equivalent to or

larger than 3.2eV (λ = 387 nm). When photocatalyst absorbs ultraviolet (UV) radiation from sunlight or illuminated light source, it will produce pairs of electrons and holes. The excess energy of this excited electron promotes the electron to the conduction band therefore creating the negative-electron (e-) and positive-hole (h+) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. The positive-hole of photocatalyst breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. The activation of ZnO by UV light can be represented by the following steps [14, 15]

$$ZnO + h_v \rightarrow e^- + h^+ \quad (1)$$

$$e^- + O_2 \rightarrow O_2^{\cdot -} \quad (2)$$

$$h^+ + \text{Organic compound} \rightarrow CO_2 \quad (3)$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \quad (4)$$

$$OH + \text{Organic compound} \rightarrow CO_2 \quad (5)$$

Present study involves the use of synthesized nano ZnO catalyst for degradation of the industrial effluent and the effect of various parameters like pH, catalyst dose and H_2O_2 addition through ultrasonic, photocatalytic and sonophotocatalytic degradation techniques.

MATERIALS AND METHODS

The set of experiments was conducted using textile industry effluents from dye house of textile industries. The some Physical parameters of textile industrial effluents shown in Table 1. The degradation efficiency of ZnO was determined after treatment with textile effluents from Shyama Trandze Pvt. Ltd, Pandesara, Surat (India). Rate of degradation of textile effluent was determined by using total organic carbon (TOC) analysis. The photocatalytic degradation was carried out in photocatalytic reactor, having 400W mercury lamp. Temperature inside the reactor was maintained by using cooling water jacket. Different nano catalyst doses were added in 100 mL solution and placed in a photocatalytic reactor. Concentration of the effluent was estimated using absorbance recorded on UV-Vis spectrophotometer (Systronics model-2203) at the **λmax** 400 nm. Sonication was performed with ultrasonic Probe Sonicator-20 KHz, 150 W (Dakshin Ultrasound, Mumbai, India) equipped with a titanium probe (10 mm of diameter), a water-circulating unit and a temperature controller. The pH of dye solution is maintained by 0.1M NaOH and 0.1M HCl using pH meter (EQ-615). After certain time intervals, adequate amount of sample is withdrawn and centrifuged to remove the nano catalyst and analyzed for TOC.

% TOC removal can be determined by using the following equation,

$$\%\ TOC\ removal = \frac{(TOC)_0 - (TOC)_t}{(TOC)_0}\ X\ 100$$

where,

$(TOC)_0$ = Initial TOC of industrial effluent

$(TOC)_t$ = TOC of industrial effluent at specific reaction time during treatment with ZnO nano catalyst

Synthesis of ZnO nano catalyst

ZnO nano catalyst was synthesized by using sol-gel method. Zinc nitrate solution was obtained by dissolving 0.05 mole in 500 mL water. NaOH solution was prepared in water by dissolving 0.75 mole in water with the ratio 1:15 (NaOH; water). The prepared NaOH solution was added drop wise to zinc nitrate solution with vigorous agitation at 70 °C. After complete addition of NaOH solution the reaction mixture (precipitate) was agitated for two h. Then, solution was allowed to settle for overnight. Finally supernunt liquid was discarded slowly after centrifugation [36]. The precipitate was thoroughly washed using water and ethanol. Finally filtered precipitate was dried at 75 °C. [16]

RESULTS AND DISCUSSION

SEM and EDX analysis

Morphological characteristics of ZnO nano catalyst was studied by using SEM. SEM micrographs of the ZnO nano catalyst is shown in Fig. 1 (a). SEM micrographs showed that ZnO nano catalyst have oval type shape. The EDX analysis shown in Fig. 2 (b) indicates that ZnO nano catalyst contains Zn K (79.95 %), O K (20.05%).

X-ray diffraction analysis

The XRD pattern of ZnO is shown in Fig. 3. The sample was scanned from 20°to 80° (2θ) at a scanning rate. It shows main peak at 2θ of 30.87°, 33.52°, 35.35°, 46.65°, 55.71°, 61.98°, 65.53°, 67.08°, 68.20°and 76.8° in Fig. 2 corresponding to (1 0 0),

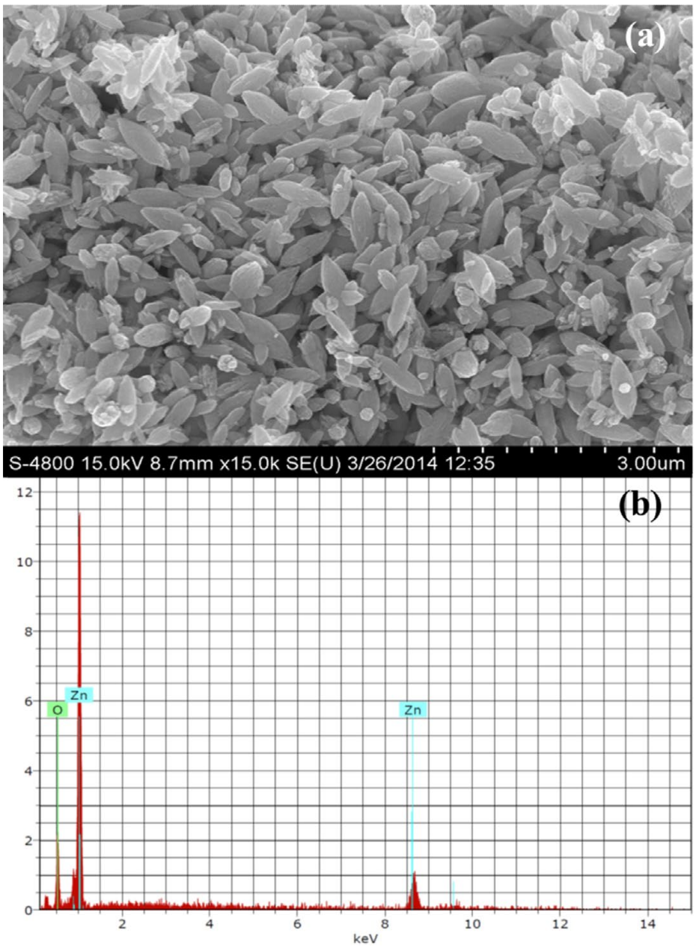

Fig. 1. (a) The SEM image of nano ZnO (b) The EDX spectrum of nano ZnO catalyst

(0 0 2),(1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 2 0), (2 0 0), (1 1 2) and (2 0 2) diffraction planes of oval type shape on nano ZnO. The high intensity of peaks indicates the highly crystalline nature of the ZnO nano catalyst [17].

Effect of pH

The pH value of aqueous solution is a key parameter for ultrasonic, photocatalytic and sonophotocatalytic degradation of wastewater because it affects the degradation of pollutants. The wastewater of textile, dairy and pharmaceutical industries generally have a wide range of pH values.

Table 1. Various parameters of industrial effluent samples

Parameters	Sample
pH	7.5
Electrical conductivity	15.96 X 10^{-3} mhos
TDS	8900 mg/L
TOC	257.2 mg/L
Initial absorbance	2.36 a.u.

In addition, the generation of hydroxyl radicals which is necessary for the ultrasonic, photocatalytic and sonophotocatalytic reaction also depends on pH of the solution. Therefore, pH plays a significant role for both cases, in the chemical nature of wastes and generation of hydroxyl radicals [18, 19]. Hence, many attempts have been taken to investigate

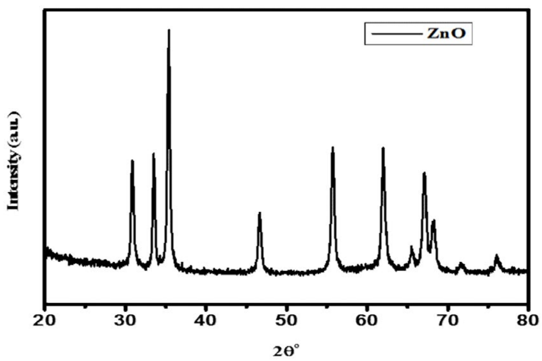

Fig. 2. XRD diagram of ZnO nano catalyst

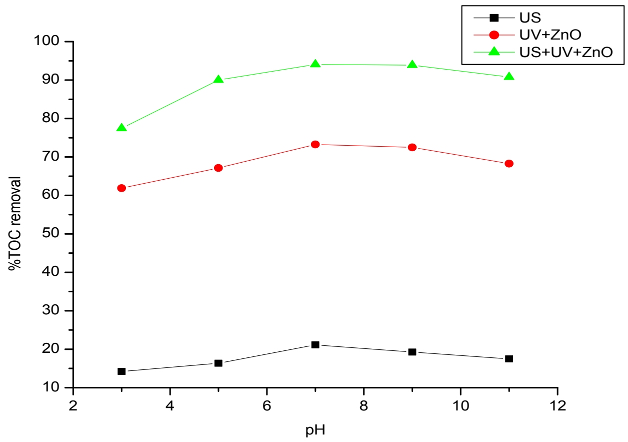

Fig. 3. Effect of pH on textile industry effluent in presence of ZnO nano catalyst (catalyst dose- 1g/L, reaction time 160 min.)

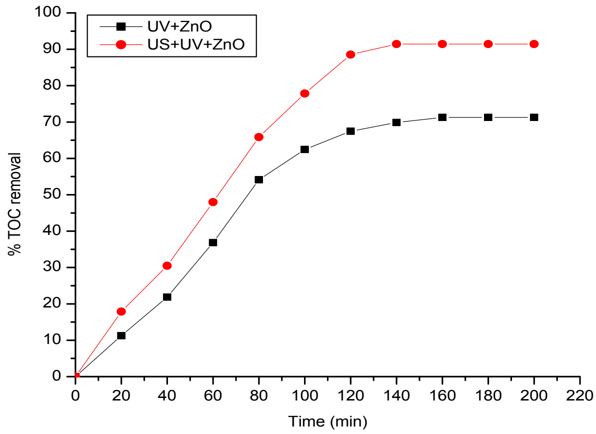

Fig. 4. Effect of contact time on % TOC removal efficiency of textile industry effluent (catalyst dose 1 g/L and pH 7)

the effect of pH in the degradation of wastewater in the visible light irradiations. Effect of pH on degradation efficiency of ZnO nano catalyst on textile industry effluent is shown in Fig. 1. The plot of % TOC removal vs pH (Fig. 3) shows that as pH increases from 3 to 7, % TOC removal increases but further increases in pH up to 11 decreases the % TOC removal . This suggests that pH 7 is suitable pH for % TOC removal for the industrial effluent studies. The % TOC removal for ultrasound (US) is very low (below 21% TOC) for all the pH studied. The photocatalytic (UV+ZnO) study shows an increase in % TOC up to 73 %. The combination of (US+UV+ZnO) that is sonophotocatalyst shows an increase in % TOC removal up to 94%. This suggests that additive of both systems.

Effect of contact time

Effect of contact time on textile industrial effluent in terms of % TOC removal is shown in Fig. 4. The equilibrium time for % TOC removal in photocatalytic and sonophotocatalytic was found to be 160 min. at pH 3. On the basis of % TOC values, as initially as contact time increases % TOC removal also increases rapidly, though it increases slowly after 160 min.

Effect of catalyst on % TOC removal

The effect of catalyst dosage on photocatalytic and sonophotocatalytic % TOC removal is observed by taking different catalyst dosages, while effluent concentration was constant. It is evident that as the amount of ZnO catalyst is increased, the photocatalytic and sonophotocatalytic % TOC removal also increased. On the basis of the experimental results, the % TOC removal increase with increase in amount of catalyst. On increase in photocatalyst and sonophotocatalyst dose from 0.25 mg/L to 1 mg/L, % TOC removal also increases from 22.7 to 71.08% for photocatalyst and

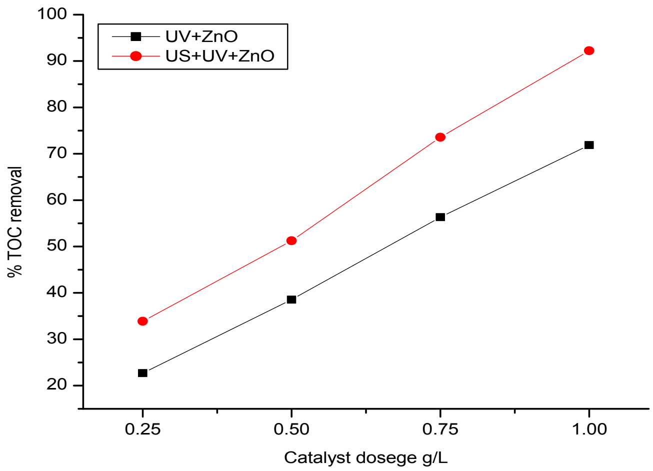

Fig. 5. Effect of catalyst concentration on % TOC removal of textile industry effluent at pH-7 and contact time 160 min

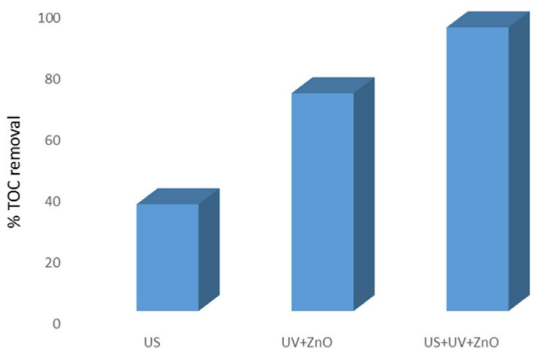

Fig. 6. Comparison of ultrasonic, photocatalytic and sonophotocatalytic processes for degradation of textile industrial effluent at pH 7, ZnO dose 1 g/L, contact time 160 min. and US power 150 W

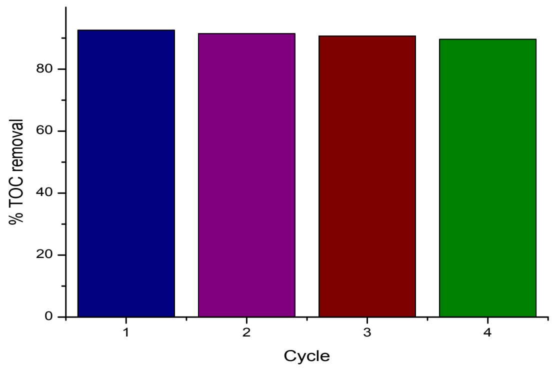

Fig. 7. Reusability of ZnO nanocatalyst

33.88 to 92.55 % for sonophotocatalyst after 160 min reaction time and pH 7.

Comparing the ultrasonic, photocatalytic and sonophotocatalytic degradation of textile industrial effluent

The further experiments were conducted under ultrasonic (US), photocatalytic (UV+ZnO) and sonophotocatalytic (US+UV+ ZnO) processes to study their effect on percentage TOC removal at catalyst dose 1 g/L, pH-7 and contact time 160 min. It is found that after 160 min, 92.55%, 71.08% and 34.83 % textile industrial effluent, % TOC removal takes place under sonophotocatalytic, photocatalytic and ultrasonic processes, respectively. Fig. 6 shows that the sonophotocatalytic % TOC removal efficiency is better than ultrasonic and photocatalytic % TOC removal.

Recycle performance of ZnO nanocatalyst

To find out the stability and efficiency of ZnO nanocatalyst as well as cost effectiveness of the process, the reusability of ZnO nanocatalyst was investigated for the % TOC removal of textile industrial effluents under UV radiation. To study its reusability, the powdered nanocatalyst was centrifuged after completion of each sonophotocatalytic experiment. The recovered sample was reused for 3 times under the same experimental conditions. Fig. 7 shows that % TOC removal of the textile industrial effluents by ZnO nanocatalyst achieves up to 92.55% (160 min) after 1st run. After 4th run it decreases down to 89.62%. The catalytic activity was found to decrease slightly after 4th run. This decrease may be attributed to loss of the reused catalyst during sampling each time and irreversible changes of the sonophotocatalyst surface by pollutants. Fig. 7 shows that ZnO has excellent stability and does not suffer from corrosion during sonophotocatalytic % TOC removal.

CONCLUSION

In present study, the effectiveness of using ZnO nano catalyst by photocatalysis and sonophotocatalysis processes in removing toxic organic pollutants from the selected wastewater influents from textile industries. The collected samples were treated with ZnO nano catalyst and different parameters were analyzed and found that ZnO photocatalyst and sonophotocatalyst have good ability in removing the trace pollutants present in industrial wastewater. The increase in catalyst concentration increases the % TOC removal at neutral pH. Neutral pH is effective for removal of organic pollutants in textile industrial effluent. The comparison for ultrasonic, photocatalytic and sonophotocatalytic treatment of textile industrial effluents for treated wastewater samples using ZnO nano catalyst showed almost constant pH (pH-7). A maximum % TOC removal was observed in 92.55% for sonophotocatalytic, 71.08% for photocatalytic and 34.83 % for ultrasonic in 160 min contact time. All the above results clearly indicate that the sonophotocatalyst is effective for % TOC removal in textile industrial effluents than ultrasonic and photocatalytic process. Furthermore, the ZnO nano catalyst with high mineralization efficiency, high stability and recyclability could be the potential material for the wastewater treatment on an industrial scale

ACKNOWLEDGEMENTS

The authors have gratefully acknowledged to Dr. Shirish Sonawane (NIT Warangal) for providing TOC analysis and for his valuable suggestions. Authors are also thankful to Principal, Kisan Arts, Commerce and Science College, Parola, Dist. Jalgaon (M.S.) for providing necessary laboratory facilities.

REFERENCES

[1] Asfaram A, Ghaedi M, Hajati S, Goudarzi A, Dil EA. Screening and optimization of highly effective ultrasound-assisted simultaneous adsorption of cationic dyes onto Mn-doped Fe_3O_4-nanoparticle-loaded activated carbon. Ultrason. Sonochem. 2017; 34: 1-12.

[2] Pourjavadi A, Doulabi M, Doroudian M. Adsorption characteristics of malachite green dye onto novel kappa-carrageenan-g-polyacrylic acid/TiO_2–NH_2 hydrogel nanocomposite. J. Iran. Chem. Soc. 2014; 11 (4): 1057-65.

[3] Zolgharnein J, Bagtash M, Shariatmanesh T. Simultaneous removal of binary mixture of Brilliant Green and Crystal Violet using derivative spectrophotometric determination, multivariate optimization and adsorption characterization of dyes on surfactant modified nano-γ-alumina. Spectrochim. Acta Mol. Biomol. Spectrosc. 2015; 137: 1016-28.

[4] Kyzas GZ, Fu J, Matis KA. The change from past to future for adsorbent materials in treatment of dyeing wastewaters. Materials. 2013; 6 (11): 5131-58.

[5] Zhao K, Zhang M, Huang M. Heterogeneous Degradation of Dyes in Industrial Effluent over Fenton-Like Nano-Fe_2O_3/ Goldmine Complex. GEP. 2015; 3 (10): 24.

[6] Gungor O, Yilmaz A, Memon S, Yilmaz M. Evaluation of the performance of calix [8] arene derivatives as liquid phase extraction material for the removal of azo dyes. J. Hazard. Mater. 2008; 158 (1): 202-7.

[7] Muthuraman G, Palanivelu K. Selective extraction and separation of textile anionic dyes from aqueous solution by tetrabutyl ammonium bromide. Dyes Pigm. 2005; 64 (3): 251-7.

[8] Muthuraman G, Teng TT. Solvent extraction of methyl violet with salicylic acid from aqueous acidic solutions. Desalination. 2010; 263 (1): 113-7.

[9] Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technol. 2001; 77 (3): 247-55.

[10] Bes-Piá A, Mendoza-Roca J, Alcaina-Miranda M, Iborra-Clar A, Iborra-Clar M. Reuse of wastewater of the textile industry after its treatment with a combination of physico-chemical treatment and membrane technologies. Desalination. 2002; 149 (1): 169-74.

[11] Kar A, Smith YR, Subramanian V. Improved photocatalytic degradation of textile dye using titanium dioxide nanotubes formed over titanium wires. Environ. Sci. Technol. 2009; 43 (9): 3260-5.

[12] Zheng H, Pan Y, Xiang X. Oxidation of acidic dye Eosin Y by the solar photo-Fenton processes. J. Hazard. Mater. 2007; 141 (3): 457-64.

[13] Lee S-Y, Park S-J. TiO_2 photocatalyst for water treatment applications. J Ind Eng Chem. 2013; 19 (6): 1761-9.

[14] Banu JR, Anandan S, Kaliappan S, Yeom I-T. Treatment of dairy wastewater using anaerobic and solar photocatalytic methods. Sol Energy. 2008; 82 (9): 812-9.

[15] Kaneva N, Dushkin C. Preparation of nanocrystalline thin films of ZnO by sol-gel dip coating. Bulg Chem Commun. 2011; 43: 259-63.

[16] Patil S, Raut S. Synthesis and Characterization of ZnO Nanoparticles and 50% ZnO-Bentonite Nanocomposite. Int J Chem Sci. 2012;10 (2): 1124-32.

[17] Meshram S, Limaye R, Ghodke S, Nigam S, Sonawane S, Chikate R. Continuous flow photocatalytic reactor using ZnO–bentonite nanocomposite for degradation of phenol. Chem. Eng. J. 2011; 172 (2): 1008-15.

[18] Neppolian B, Choi HC, Sakthivel S, Arabindoo B, Murugesan V. Solar/UV-induced photocatalytic degradation of three commercial textile dyes. J Hazard Mater. 2002; 89 (2–3): 303-17.

[19] Chiron S, Fernandez-Alba A, Rodriguez A, Garcia-Calvo E. Pesticide chemical oxidation: state-of-the-art. Water Res. 2000; 34 (2): 366-77.