

Natural Sunlight Assisted Bentonite-ZnO Mixed Oxide Catalyst for Organic Pollutant Removal in Leather Post Tanning Wastewater with Solar Reactor

by

E. T. Deva Kumar,^a Sathya Ramalingam,^a K. Thirumalai,^b R. Aravindhan,^{c*} M. Swaminathan^{b,d*} and J. Raghava Rao^{*†}

^a*Inorganic and Physical Chemistry Laboratory, CSIR – Central Leather Research Institute, Chennai, India.*

^b*Photocatalysis Laboratory, Department of Chemistry, Annamalai University, Annamalainagar, India.*

^c*Leather Process Technology Division, CSIR – Central Leather Research Institute, Chennai, India.*

^d*International Research Centre(IRC), Kalasalingam University, Krishnankoil, India.*

Abstract

Organic pollutants in leather post tanning wastewater were degraded by the advanced oxidation process using semiconductive photocatalysis technique. A mixed oxide nanocatalyst Bentonite-ZnO was employed for the degradation process and the same has been prepared by hydrothermal method. The morphological and optical characteristics of the nanocatalyst was well characterized by using X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Diffuse Reflectance Spectroscopy (DRS) and Fluorescence Spectrophotometer studies. The diffraction peak of the mixed oxide catalyst confirms the formation of wurzite structure of ZnO with the incorporation of bentonite clay particles. The SEM image displayed the formation of nanosized particles with porous spherical texture. The optical band gap of the bare ZnO (3.3 eV) and Bentonite-ZnO (2.5eV) catalysts were measured by DRS studies. A comparative study of photoluminescence spectra of ZnO and Bentonite-ZnO showed the suppression of charge carrier recombination in case of Bentonite-ZnO than bare ZnO. Existence of suitable charge carriers and vectorial transportation between bentonite and ZnO makes Bentonite-ZnO as an appropriate catalyst for degradation of organic pollutants present in leather post tanning liquor. The semiconductive photocatalysis on leather tannery post tanning wastewater was carried out in a specially designed pilot scale solar light reactor with Bentonite-ZnO, the results are compared with bare ZnO catalyst, where the degradation property with mixed oxide catalyst Bentonite-ZnO is better than bare ZnO. The decrease in COD with Bentonite-ZnO nanocatalyst is found to be 35.3% for three hours of continuous reaction under solar light. Such percentage of COD reduction suggest to offer this nanocatalyst treatment as preliminary step for better performance of further treatment process.

Introduction

Production of leather and leather products from raw skin/hide generate huge amounts of liquid waste containing various pollutant loads in addition with air emissions.¹ Growing demands in the leather products leads to establishment of many tannery units which has increasing risk factors in environmental ecosystem including water bodies, land and air. In general, 30-50 cubic meters of wastewaters discharged for a ton of raw hides/skins.² If the number of tanneries increased to meet the future demands then it will lead to great negative impact worldwide. The process of making leather involves three main steps, pre-tanning, tanning, and post tanning. Each step contributes different percentage of liquid and solid waste based on the chemicals input in that particular step.³ Treatment of tannery wastewater predictable as a serious environmental risk due to high pollution load includes salinity, organic load (chemical oxygen load or demand, biological oxygen demand), inorganic matter, dissolved and suspended solids, ammonia, Total Kjeldahl Nitrogen (TKN), specific pollutants (sulphide, chromium, chloride, sodium and other salt residues) and heavy metals⁴ etc. Amongst all process steps, post tanning contributes major release of organic pollutants because it involves the use of extensive chemical agents like syntan, fatliquors, organic dyes, dye levelling agent, salts and acids in the processing stream.^{5,6} Even though substantial efforts have been made through process modification or chemical replacement to reduce the environmental contaminants, still the wastewater contains large quantity of organic pollutants.

*Authors for correspondence e-mails: (J. Raghava Rao) jr Rao@clri.res.in.; (M. Swaminathan) chemres50@gmail.com; (R. Aravindhan) aravindhan78@gmail.com; Tel: + 91 44 2441 1630; Fax: + 91 44 2491 1589
Manuscript received April 10, 2018, accepted for publication May 10, 2018.

Conventional wastewater treatment methods such as coagulation, adsorption, and membrane separation subjected to high operating costs and generate secondary pollutants⁷, biological methods using microbic cultures in aerobic and anaerobic conditions are also used to treat the wastewater.⁸ On the other hand, electrochemical oxidation methods and advanced oxidation process with the aid of UV/H₂O₂ was also in practice to treat the wastewater.⁹ The conventional processes has drawbacks such as need of large tanks during aerobic oxidation process, moreover the process take long duration of time from hours to several days. In electrochemical oxidation methods, it is necessary to supply external electric potential into the wastewater. In the case of UV/H₂O₂ oxidation process the external chemicals are added into the reaction bath and some time it may lead to the generation of unwanted chemical mixtures. Hence identification of simple methods to treat organic pollutants is need of the time to reduce the environmental constraints caused by present post tanning process.

Semiconductive photocatalysis using semiconductive metal oxide is an advanced oxidation process where the organic species are non-selectively oxidised with the aid of light generated hydroxy and peroxy radicals.¹⁰ As UV/solar radiation falls on the semiconductive metal oxide there will be generation of electron-hole pairs at the valence band and the electron is excited to the conduction band.¹¹ The electron-hole pair reacts with the medium and there will be a generation of peroxy and hydroxy radical, this in turn will react with the organic pollutants and convert them into less toxic organic compounds like mineral acid and carbon dioxide.¹² However, there are chances for photo corrosion of the catalyst, loss of efficiency due to electron-hole recombination and other limitations. To address these issues, the current material research dedicated to increase the activity of the catalyst by means of suppressing the recombination of charge carriers and facilitate the electron-hole pair to reach the surface in faster manner.¹³ Research is also focused on the use of naturally available solar radiation in catalysis process for the treatment of wastewater.

Photocatalysis using semiconductive mixed oxide catalysts like CdWO₄-ZnO,¹⁴ BiVO₄-ZnO,¹⁵ Bi₂O₃-ZnO,¹⁶ Flyash-ZnO¹⁷ and etc. for the treatment of organic pollutants has demonstrated better efficiency both in natural sun light and UV radiation, the mixing of two different metal oxides can cause heterojunction at the interface and this can facilitate the vectorial transport of charge carriers¹⁵ and can increase the efficiency of the catalyst, moreover this can help in fine tuning of the band gap of our interest and resist the material from photo corrosion. The action of tuning the band gap and increasing the efficiency of the catalyst was also achieved by mixing industrial by-products like fly ash and clay materials like bentonite.¹⁶ In general clay materials like bentonite are rich in several elements these elements in turn will form heterojunction with the

semiconductive metal oxide materials and create the heterojunction and help in separation of charge carriers.

In this work as supplementary technique to the conventional process, semiconductive photocatalysis using Bentonite-ZnO mixed oxide nanocatalyst has been employed to treat the post tanning wastewater under natural sunlight. Bentonite-ZnO as a catalyst has many advantages includes low cost, good stabilisation, large surface area, and better adsorption performance. To identify the synergetic effect of Bentonite-ZnO mixed catalyst, the degradation rate and efficiency in degrading the pollutants in post tanning wastewater was compared with the bare ZnO catalyst. As compared to bare ZnO catalyst the mixed oxide system showed high photocatalytic activity because of its heterogeneity and suppression in recombination of charge carrier. Harvesting energy from sunlight for catalysis and utilisation of low cost bentonite would make whole system cleaner and cost-effective method for the treatment of post tanning liquor.

Materials and Methods

Materials

Zinc nitrate hexahydrate, oxalic acid, ethanol and sodium hydroxide pellets were obtained from Hi-media chemicals and used as received. Hydrochloric acid from Qualingens, potassium dichromate, silver sulphate, mercurous sulphate and ammonium ferrous sulphate were purchased from Merck and used without further purification. The post tanning wastewater used in this study was collected from the tannery unit of CLRI, Chennai. All the aqueous solutions used in this study were made with double distilled water.

Preparation of Bentonite-ZnO Mixed Oxide Catalyst

The mixed oxide catalyst Bentonite-ZnO was prepared by hydrothermal method at high pressure and temperature. Initially, a 100 mL of Zn(NO₃)₂·6H₂O (0.4 M) solution was taken in a glass beaker stirred till the solution becomes homogenous then 0.6 M oxalic acid solution was added in drop wise and stirred for 30 minutes then 0.243 g of bentonite powder was added and stirred for 8 hours at 95°C then the mixture was transferred to a Teflon coated stainless steel autoclave and treated hydrothermally at 120°C for 6 hours at 18 psi pressure. To remove the unreacted substances, the formed precipitate was centrifuged several times with ethanol-water mixture to remove any unreacted precursors and to wash out the neutral salts. The pure form of Bentonite-ZnO was air dried at 80°C for 12hrs in a hot oven and annealed for 5 hours at 500°C. This procedure resulted in 9% (w/w) Bentonite incorporation in ZnO. Subsequently, for control experiments the bare ZnO catalyst was prepared by following the same procedure without the addition of bentonite.

Characterization of the Prepared Catalyst

The catalysts prepared were examined for its diffraction planes and crystallinity by X-ray diffraction (XRD) studies using an XPERT-PRO multipurpose X-ray diffractometer procured from the Netherlands, using Cu K α radiation with a wavelength of 1.540 Å and the 2 θ value varied in the range from 10° to 80°. The morphology and size was evaluated by FESEM analysis performed using a Hitachi model S3000-H SEM (Model ULTRA-55). The optical properties of the catalysts were analysed using UV-Vis spectroscopy in diffuse reflectance mode with the wavelength ranging from 200 to 800 nm using a Perkin Elmer Lambda 650 UV-Vis spectrophotometer attached with a 60 mm integrated sphere detector module. The emitting property (PL) of the catalysts was examined with spectrophotometer from SHIMADZU. During photocatalysis the intensity of solar radiation was measured using Light Meter LX-101A from LT Lutron.

Photocatalytic Treatment of Post-tanning Wastewater

The photocatalytic degradation of the post tanning wastewater (composition of the wastewater is given in Table I) were carried out in a specially designed pilot scale solar reactor where the

solar panel is directly exposed to sunlight. The pH of the final wastewater was adjusted to neutral by dilution. The average intensity of solar light was found to be 900×100 ±100 lux. 10 g of the catalyst was mixed with the 10% fevicol solution and brush coated over the acrylic sheet and the sheet was dried under sunlight for one hour, then the sheet was fixed over the solar reactor and the 10% post tanning wastewater was allowed to run over the sheet with the help of a motor pump. The falling waters were collected in a tub and allowed to fall over the reactor in a cyclic manner with the help of pump. Photocatalytic reaction was performed continuously for three hours. After every half an hour of the experiment, 2 mL of the sample was collected to analyse the degradation of organics by determining Chemical Oxygen Demand (COD) as per standard procedure APHA (1998) section 5220. The procedure was repeated with the bare ZnO catalyst to compare the efficiency of the prepared mixed oxide Bentonite-ZnO catalyst with that of bare ZnO.

Results and Discussions

Mixed oxide nanocatalyst containing 9% bentonite in ZnO with good photocatalytic property was prepared by hydrothermal method. The catalytic performance of the prepared mixed oxide catalyst was compared with bare metal oxide and the reduction in COD was found to be higher in mixed oxide catalyst. Hence the present work aimed to develop the mixed oxide catalyst for effective removal of organic pollutant present in the leather processing post tanning liquor.

X- Ray Diffraction Studies

The diffraction pattern and crystalline nature of the prepared bare ZnO and mixed oxide nanocatalyst Bentonite-ZnO were examined using X-ray diffraction analysis. Figure 1 a, b and c showed the diffraction patterns for Bentonite, ZnO, and Bentonite-ZnO respectively. The prominent diffraction peaks observed in plot (b) at the 2 θ values of 31.77°, 34.49°, 36.24°, 56.60°, 62.85°, 66.38°, 69.08°, 72.50° and 76.93° corresponds to the (100), (002), (101), (110), (103), (220), (201), (004) and (220) diffraction planes of ZnO Wurzite structure.¹⁸ The relative higher intensity diffraction peak at 2 θ , 36.24° indicates the preferred orientation of 101 plane in ZnO. The diffraction peaks in plot (a) at 2 θ values of 28.6°, 40.6°, 46.2° and 52.1° corresponds to the (021), (211), (042) and (161) planes of Bentonite structure (JCPDS 14-0688).¹⁷ The diffraction pattern (c) shows the peaks for Bentonite-ZnO mixed oxide, all the diffraction peaks at the 2 θ values corresponding to ZnO and Bentonite confirms the formation of Bentonite-ZnO catalyst. The XRD pattern does not have any other impurity peaks and also the sharp peaks in diffraction pattern indicates the high degree of crystallinity in prepared mixed oxide catalyst of Bentonite-ZnO.

Table I
Composition of the post tanning wastewater.

S.No	Chemicals used	Percentage offered
1	Water	100
2	Acrylic syntan	2
3	Synthetic Fatliquor	2
4	Phenolic replacement syntan	8
5	Melamine resin syntan	3
6	Replacement syntan	8
7	Vegetable tannins	5
8	Dye (Acid Black 210)	3
9	Semi-synthetic Fatliquor	3
10	Neats foot oil	4
11	Fish oil	3
12	Vegetable Fatliquor	4
13	Formic Acid	3

Note: % chemical input based on weight of shaved wet blue

Field Emission Scanning Electron Microscope Study

The surface morphology and particle size of mixed oxide Bentonite-ZnO nanocatalyst was examined using Field Emission Scanning Electron Microscope. Figure 2 shows the FESEM images of heterostructured Bentonite-ZnO at two different magnifications 50,000 X (a) and 30,000 X (b). The Figure 2 displayed nano sized spherical morphology with porous structure. The average mean size of particles is found to be around 50 nm with cavities present in between the particle clusters. The porous nature of the catalyst is useful in adsorption of pollutants over the surface of catalyst.¹⁹ During the preparation of polycrystalline materials uniform crystal lattices are not formed, and there will be bulk and surface defects all along the crystal lattices²⁰ These irregular arrangements of particles during crystallization helps in forming surface and bulk electronic states with different energy levels. These points act as charge carrier trapping sites and help in prevention of recombination of charge carriers and facilitate inter phase charge carrier transfer between the catalyst and medium.²¹

UV-Visible Diffuse Reflectance Spectroscopy

The scattering property of bare ZnO and Bentonite-ZnO was studied with UV-Visible Diffuse Reflectance Spectroscopy in the wavelength range of 200 nm – 800 nm. Figure 3 a shows the percentage reflectance of ZnO and Bentonite-ZnO in UV-Visible region. It is obvious from the plots that prepared bare ZnO catalyst has maximum reflectance throughout the visible region in comparison to mixed oxide catalyst Bentonite-ZnO, it

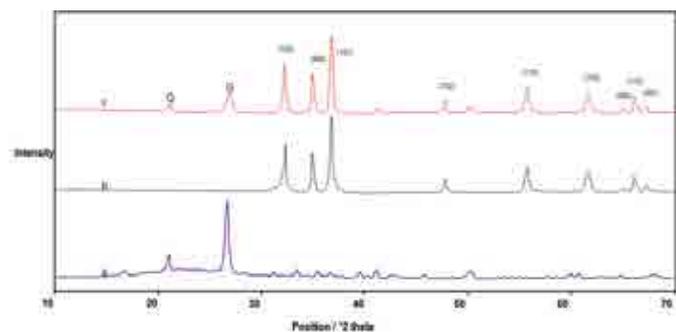


Figure 1. XRD patterns of Bentonite (a), ZnO (b), and Bentonite-ZnO(c).

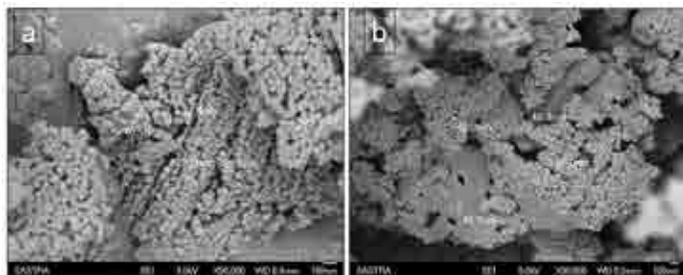


Figure 2. FESEM images of Bentonite-ZnO nanocatalyst at two different magnifications 50,000X (a), 30,000X (b).

represents that Bentonite-ZnO has maximum absorption in visible region than the bare ZnO catalyst. Therefore, this Bentonite-ZnO nanocatalyst will be an efficient catalyst than the bare ZnO in the visible region of the spectrum. The optical band gap for the mixed oxide Bentonite-ZnO nanocatalyst and bare ZnO was determined from the spectra by converting absolute reflection to $h\nu F(R_a)$.¹⁶ The plot (b) is the Tauc plot, where $[h\nu F(R_a)]^2$ in Y axis and energy of radiation in electronic volts along X axis. The tangent meeting the abscissa gives band gap of catalysts. The optical band gap of the prepared ZnO and Bentonite-ZnO were found to be 3.2 eV and 2.5 eV, respectively.

Photoluminescence Study

For a well-efficient catalyst the recombination of the electron and hole pair must be minimum so that the charge carriers can reach the surface of the catalyst and react with the medium.²²

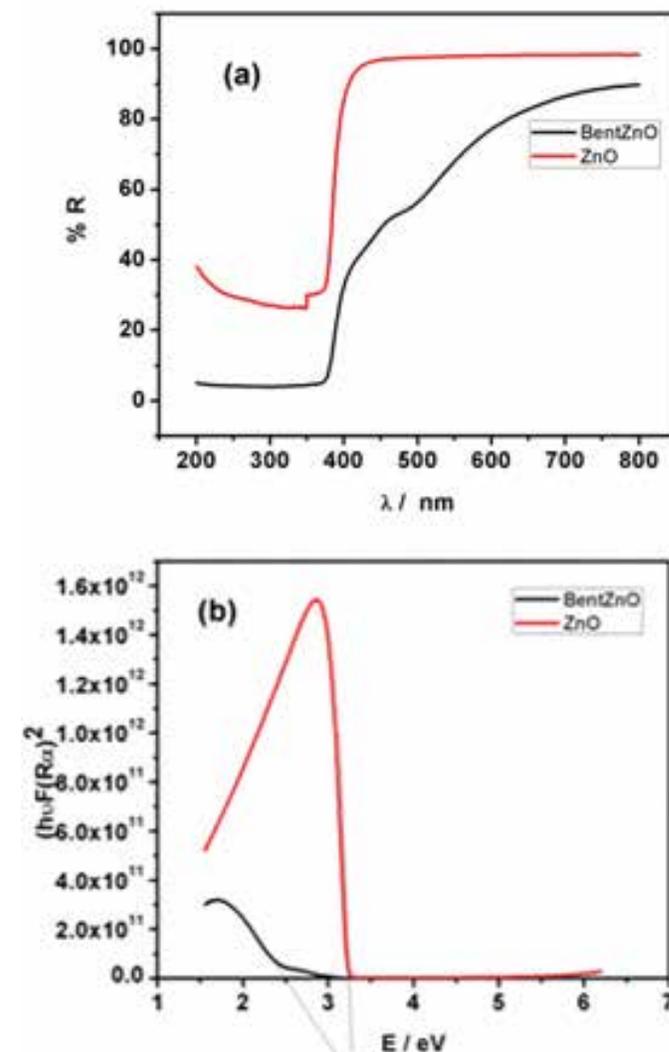


Figure 3. UV-Visible Diffuse Reflectance Spectra for the Bentonite-ZnO nanocatalysts and bare ZnO (a), Tauc plot by converting the %R to $h\nu F(R_a)^2$ and wavelength to energy, indicating the band gap of Bentonite-ZnO and bare ZnO catalysts (b).

The recombining property of the charge carriers is directly related to the intensity of the peak in PL spectra, hence photoluminescence study has been carried out for the bare ZnO and Bentonite-ZnO catalysts. Figure 4 show the PL spectra of ZnO (a) and Bentonite-ZnO (b). There is a decrease in photoluminescence intensity with Bentonite-ZnO in comparison with that of bare ZnO, which confirms the suppression of electron-hole recombination. This will eventually facilitate the fast charge carrier transfer at the interface to the surface medium and to the pollutant adsorbed over the surface. Thus, the Bentonite-ZnO acts as a better catalyst than the ZnO.

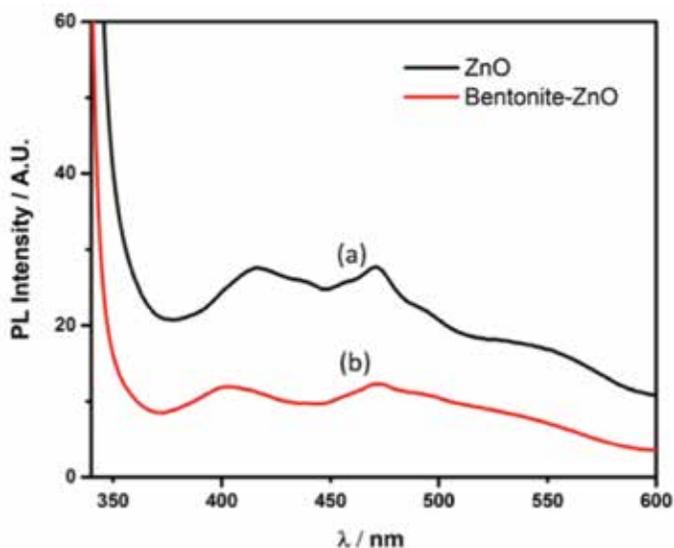


Figure 4. Photoluminescence spectra of ZnO (a), Bentonite-ZnO (b) at excitation wavelength of 320 nm showing the emission of charge carriers from conduction band to valence band.

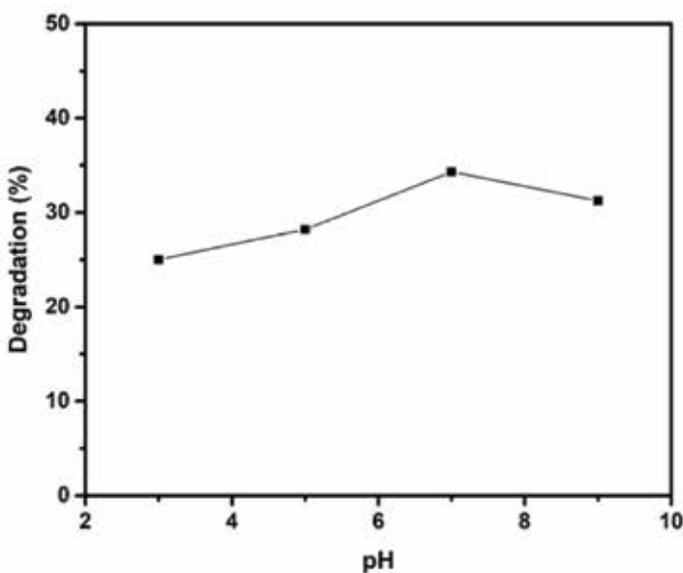


Figure 5. Degradation profile of the post tanning liquor with Bentonite-ZnO catalyst at various pH.

Effect of pH on the Activity

In general, pH of the medium influences the band edge position of the photocatalyst. In order to examine the effect of pH on the activity of photocatalyst the photocatalytic reaction was carried out at four different pH. This reaction was performed under natural sunlight in a borosilicate tube with 50 ml of the post tanning liquor and 100 mg of catalyst dispersed in it. The pH of post tanning liquor is around 3.2. It is used as such and three more reaction solutions adjusted to pH of 5, 7 and 8 by the addition of sodium hydroxide solution were used for the study. The degradation profile for the Bentonite-ZnO catalyst at various pH is shown in the Figure 5. It is clear from the profile that the activity of the Bentonite-ZnO nano catalyst is found to be best at neutral pH. The degradation efficiency of the catalyst in acidic medium of pH 3 and 5 are found to be increasing order



Figure 6. The photograph of the a) solar photoreactor used for degradation of post tanning wastewater using semiconductive Bentonite-ZnO mixed oxide catalyst and b) Visual assessment of colour change during before (C) and after (E) catalytic treatment.

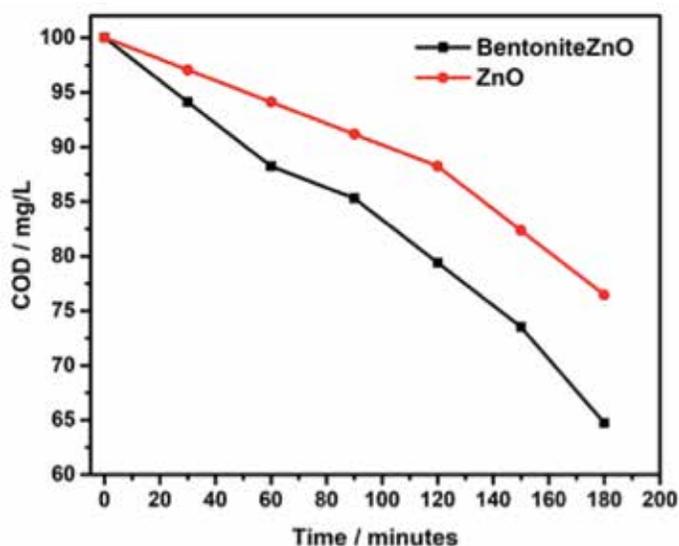


Figure 7. Plot showing the degradation profile of post tanning liquor in terms of reduction in COD in three hours under sunlight for Bentonite-ZnO and ZnO catalysts.

form 28% and 31% respectively then it reaches the maximum degradation efficiency of 36% at neutral pH then after in basic pH of 9 the degradation efficiency found to be decreased due to the dissolution of the catalyst in basic medium.

Photocatalytic Degradation Under Solar light.

Photocatalytic degradation of post tanning wastewater was carried out by employing bare ZnO and mixed oxide Bentonite-ZnO as photocatalyst. The degradation reaction was carried out for continuous three hours in a pilot scale solar reactor shown in Figure 6 (a), with 10 g of catalyst coated over the acrylic sheet mixed with 10% fevicol solution.

The degradation of pollutants (mineralization) in wastewater was analysed by the estimation of reduction in COD which is directly related to the amount of organics in post tanning wastewater. The plots of COD versus time for bare ZnO and Bentonite-ZnO are presented in Figure 7.

It is evident from the plots that the reduction in COD for 150 mg of ZnO is 23.6% and for Bentonite-ZnO it is found to be 35.3% for three hours of continuous reaction. While comparing the photocatalytic degradation of ZnO and Bentonite-ZnO the activity of mixed oxide catalyst is found to be higher than the bare ZnO. This is because the elements present in the bentonite clay material involve in the formation of heterojunction with ZnO. The heterojunction will lead to alignment of their Fermi levels and further results in temporary electric field at the interface. These altogether prevent the recombination of photo induced charge carriers and facilitate charge carrier transport to the surface of the catalyst followed by the redox reaction with the pollutants, leading to higher degradation efficiency. In addition to COD reduction, the visible change in colour of the wastewater was monitored and photograph of the same has been shown in the Figure 6 (b).

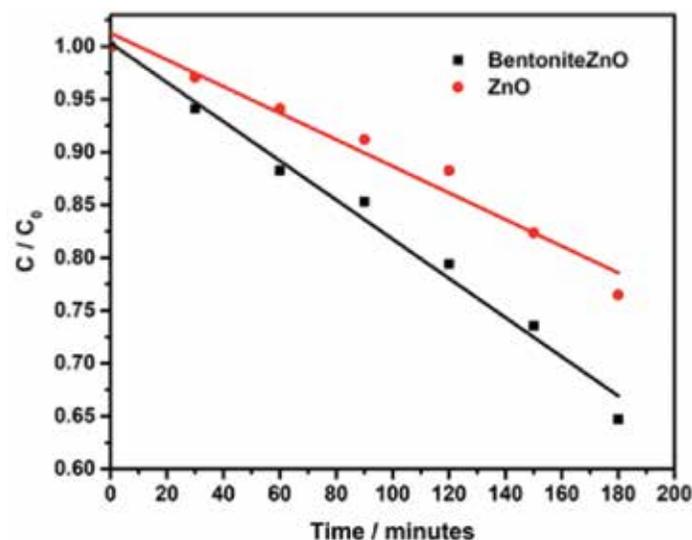


Figure 8. Zero order plot of C/C_0 versus time for degradation of post tanning liquor with Bentonite-ZnO and ZnO catalysts.

Compared to control catalyst (bare ZnO) wastewater treated by mixed oxide catalyst showed almost complete decoloured solution indicate the photodegradation of coloured organic pollutants exist in the wastewater. Hence it was proven that the uses of mixed oxide catalyst Bentonite-ZnO found to be suitable for reduction in organic pollutants in tannery wastewater with higher efficiency. To determine the kinetics of the degradation reaction with the Bentonite-ZnO and ZnO catalyst a graph of plotted between C/C_0 and time as shown in Figure 8. The degradation reaction obeys $C/C_0 = 1 - (K/C_0) t$ and follows zero order reaction as most of the photocatalytic degradation reaction. The rate constant for Bentonite-ZnO and ZnO is found to be $18.5 \times 10^{-2} \text{ mg L}^{-1} \text{ S}^{-1}$ and $12.6 \times 10^{-2} \text{ mg L}^{-1} \text{ S}^{-1}$. This also confirms that the photocatalytic degradation reaction does not depend on the concentration of the pollutants but on the light generated electron-hole pair which generate hydroxy and peroxy radicals and degrade the pollutants by redox reaction. To find the reusability of the catalyst the same catalyst coated PVC plate was used in further three cycles of consecutive degradation reactions. However, even after the fourth cycle the efficiency of the degradation reaction with the Bentonite-ZnO catalyst found to be more or less same, this reflects the stability of the prepared catalyst.

Conclusions

A mixed oxide catalyst, Bentonite-ZnO nanocatalyst, was prepared by blending bentonite clay material with ZnO by hydrothermal method. The surface morphology of the nanocatalyst was found to be spherical and porous texture with many active sites. The band gap of the prepared Bentonite-ZnO catalyst was determined to be 2.50 eV which make the catalyst suitable for visible region. The mixed oxide nanocatalyst was employed to degrade the post tanning liquor in a specially designed solar reactor under natural sunlight. The reduction in COD with Bentonite-ZnO is found to be 35.3% for three hours of reaction. The activity of the catalyst is enhanced when compared to the bare ZnO metal oxide due to formation of heterojunction and suppression of charge carrier recombination in Bentonite-ZnO nanocatalyst. The mixed oxide catalyst can actively degraded the pollutants in the leather tannery post tanning wastewater to a greater extent if the reaction is continued for long hours and it can be a great added advantage if the photocatalytic degradation reaction is combined with the conventional leather wastewater treating processes.

Acknowledgement

Financial support from the Council of Scientific and Industrial Research (CSIR), India, under Extra Mural Research (EMR-II) scheme holding the sanction number 02(0144) / 13 / EMR-II, dt.08/07/2013 and the project number GAP - 1401 towards this research work is highly acknowledged. CLRI Communication number 1279.

References

1. Chowdhury, M., Mostafa, M. G., Biswas, T. K., Saha, A. K.; Treatment of leather industrial effluents by filtration and coagulation processes. *Water Resources and Industry* **3**, 11-22, 2013.
2. Kanagaraj, J., Velappan, K. C., Babu, N. K. C., Sadulla, S.; Solid wastes generation in the leather industry and its utilization for cleaner environment - A review. *J. Sci. Ind. Res.* **65** (7), 541-548, 2006.
3. Saravanabhavan, S., Thanikaivelan, P., Rao, J. R., Nair, B. U., Ramasami, T.; Reversing the Conventional Leather Processing Sequence for Cleaner Leather Production. *Environ. Sci. Technol.* **40** (3), 1069-1075, 2006.
4. Dixit, S., Yadav, A., Dwivedi, P. D., Das, M.; Toxic hazards of leather industry and technologies to combat threat: a review. *J. Clean. Prod.* **87**, 39-49, 2015.
5. Tang, Y. L., Zhou, J. F., Zeng, Y. H., Zhang, W. H., Shi, B.; Effect of Leather Chemicals on Cr(III) Removal from Post Tanning Wastewater. *JALCA* **113** (3), 74-80, 2018.
6. Mahesh, M., Arivizhivendhan, K. V., Nivetha, K., Swarnalatha, S., Sekaran, G.; Anaerobic digestion of sulphate-rich post-tanning wastewater at different COD/sulphate and F/M ratios. *3 Biotech* **8**, 15, 2018.
7. Chowdhury, M., Mostafa, M. G., Biswas, T. K., Saha, A. K.; Treatment of leather industrial effluents by filtration and coagulation processes. *Water Resour. Indus.* **3**, 11-22, 2013
8. Durai, G. and Rajasimman, M.; Biological Treatment of Tannery Wastewater - A Review. *J. Environ. Sci. Technol.* (4), 1-17, 2011.
9. Naumczyk, J. H., Kucharska, M. A.; Electrochemical treatment of tannery wastewater Raw, coagulated, and pretreated by AOPs. *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.* **52** (7), 649-664, 2017.
10. Subash, B., Krishnakumar, B., Velmurugan, R., Swaminathan, M.; Photodegradation of an azo dye with reusable SrF₂-TiO₂ under UV light and influence of operational parameters. *Separation and Purification Technology* **101**, 98-106, 2012.
11. Chan, S. H. S., Wu, T. Y., Juan, J. C., Teh, C. Y.; Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye waste-water. *J. Chem. Technol. Biotechnol.* **86** (9), 1130-1158, 2011.
12. Chan, S. H. S., Wu, T. Y., Juan, J. C., Teh, C. Y.; Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye waste-water. *J. Chem. Technol. Biotechnol.* **86** (9), 1130-1158, 2011.
13. Kudo, A., Omori, K., Kato, H.; A Novel Aqueous Process for Preparation of Crystal Form-Controlled and Highly Crystalline BiVO₄ Powder from Layered Vanadates at Room Temperature and Its Photocatalytic and Photophysical Properties. *J. Am. Chem. Soc.* **121** (49), 11459-11467, 1999.
14. Kumar, E. T. D., Thirumalai, K., Aravindhan, R., Swaminathan, M., Rao, J. R.; Nair, B. U.; Visible light photocatalytic degradation of wattle extract: effect of mixing CdWO₄ over a semiconductive ZnO photocatalyst. *RSC Adv.* **5** (75), 60926-60937, 2015.
15. Kumar, E. T. D., Thirumalai, K., Balachandran, S., Aravindhan, R., Swaminathan, M., Raghava Rao, J.; Solar light driven degradation of post tanning water at heterostructured BiVO₄-ZnO mixed oxide catalyst interface. *Surf. Interface* **8**, 147-153, 2017.
16. Thirumalai, K., Kumar, E. T. D., Aravindhan, R., Rao, J. R., Swaminathan, M.; Hierarchically structured bentonite loaded Bi₂O₃-ZnO and its multiple applications. *Surf. Interface* **5**, 30-38, 2016.
17. Thirumalai, K., Balachandran, S., Swaminathan, M.; Superior photocatalytic, electrocatalytic, and self-cleaning applications of Fly ash supported ZnO nanorods. *Mater. Chem. Phys.* **183**, 191-200, 2016.
18. Balachandran, S., Swaminathan, M.; Facile Fabrication of Heterostructured Bi₂O₃-ZnO Photocatalyst and Its Enhanced Photocatalytic Activity. *J. Phys. Chem. C* **116** (50), 26306-26312, 2012.
19. Rouquerol, F., Rouquerol, J., Sing, K.; CHAPTER 11 - Adsorption by Clays, Pillared Layer Structures and Zeolites. In *Adsorption by Powders and Porous Solids*, Academic Press: London, pp 355-399, 1999.
20. Liu, D., Lv, Y., Zhang, M., Liu, Y., Zhu, Y., Zong, R., Zhu, Y.; Defect-related photoluminescence and photocatalytic properties of porous ZnO nanosheets. *J. Mater. Chem. A* **2** (37), 15377-15388, 2014.
21. Linsebigler, A. L., Lu, G., Yates, J. T.; Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **95** (3), 735-758, 1995.
22. Sakthivel, S., Geissen, S. U., Bahnemann, D. W., Murugesan, V., Vogelpohl, A.; Enhancement of photocatalytic activity by semiconductor heterojunctions: α-Fe₂O₃, WO₃ and CdS deposited on ZnO. *J. Photochem. Photobiol. A: Chemistry* **148** (1), 283-293, 2002.