

Green chemistry approach for the synthesis of PbSnO_3

An effective photocatalyst for the degradation of dyes under sunlight

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Abstract We report synthesis of light-induced heterogeneous photocatalyst PbSnO_3 by green chemistry approach, using mechanochemical method. The synthesized catalyst was characterized physically by various analytical investigative techniques like UV-DRS, FTIR, XRD, SEM, EDAX, TEM, and TG. The product corresponded to average particle size of 100 nm by TEM images. Photocatalytic activity of PbSnO_3 was studied by photodegradation of Methyl blue, Indigo carmine, and Acid violet dyes under sunlight. The results indicate that the sunlight stimulates a photochemical reaction and successfully complete mineralization of Methyl blue, Indigo carmine, and Acid violet dyes. Antimicrobial activity shows that PbSnO_3 photocatalyst was found non-toxic to the environment.

Keywords Green chemistry · Photocatalyst · Photodegradation · Organic dye · Non-toxic · TG

Introduction

Pervoskites with general formula ABO_3 is a kind of frequently encountered structure in inorganic chemistry. Most of the properties of pervoskite oxides are related to the network of BO_6 octahedra [1] and the state of B-site cations [2, 3], where as brownmillerite ($\text{A}_2\text{B}_2\text{O}_5$) is a kind of oxygen deficient pervoskite like three dimensional framework of corner shearing BO_6 octahedra which are formed by the deficiency of oxygen during the formation of the

structure [4, 5]. Both pervoskite and brownmillerite have been studied widely [6, 7].

Synthetic dyes are toxic refractory chemicals, which can generate intensive color and are hazardous to the environment. Owing to the large degree of organics present in these molecules and stability of modern textile dyes affect aquatic life. Because of their incomplete use and washing operations considerable amount of dyes have been noticed in textile wastewater [8]. The dyes were detected in dissolved or in suspension state in the wastewater [9]. The murky of water has adverse effect on aquatic system due to presence of dyes and pigments.

Mineralization of organic water pollutants using interaction between ultraviolet radiation and semi-conductor catalysts has a strong potential as it has been widely demonstrated in the recent years [10]. Visible light-induced photocatalysts have received considerable attention because visible light occupies the main part of solar light. The development of the future generation of photocatalytic materials is important for the efficient use of solar light. The past two decades have witnessed intensive studies within light-induced mineralization of hazardous organic pollutants with use of TiO_2 photocatalyst [11–15]. Alton and Ferry [16] used SiW_2O_4 as photocatalyst for the photocatalytic degradation of acid orange dye.

There is an urgent need to search for an effective heterogeneous oxide photocatalyst for environmental cleaning purpose and test their efficacy. The uses of conventional methods of treatment used to remove organic matter from the effluents is energy guzzling and lead to excessive emission of CO_2 ; thus abet the global warming. Under such circumstances, we have come to the conclusion that, there is need to find a new material that can work in harmony with nature and will gently restore the natural condition of water bodies by removing the pollutants by using light

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energy. A solution to that problem is use of the photocatalyst. In this article, the structural and microstructural characteristics are determined for purpose of creating an inexpensive and non-toxic photocatalyst. Hence, the efforts are made to synthesize PbSnO₃-light driven photocatalyst by eco-friendly solid state mechanochemical synthesis method and its application for degradation of Methyl blue (MB), Indigo carmine (IC), and Acid violet (AV) dyes in the presence of sunlight.

Experimental

Synthesis of PbSnO₃ photocatalyst

Several methods are used for synthesis of nanocrystalline photocatalytic material, which include co-precipitation [17], sol-gel method [18] and thin film vapor deposition method [19]. These methods are elaborate, expensive and cause water pollution. Hence, in this study, we have synthesized photocatalyst PbSnO₃ by green chemistry approach with mechanochemical process. The mechanochemical procedures are environmentally friendly. The method allows accelerating and facilitating the synthesis processes producing negligible gas emission. It is fast and ecologically pure.

In this method, 1:1 ratio of Analytical Grade PbO and SnO₂ was subjected to stepwise calcinations by heating till terminal temperature. The rise in temperature of muffle furnace was programmed at the rate 10 °C/min from one temperature to the subsequent temperature for 12 h. After heating at 500 °C the material was cooled and grounded with gap of 3 h using mortar and pestle. Later on, the ground material was further heated at 800 °C for another 12 h. Finally, polycrystalline powder of PbSnO₃ obtained was used for further characterization and for degradation of the dyes.

Characterization of PbSnO₃ photocatalyst

The vibrational frequency of the synthesized catalyst was studied by FTIR-8400S (Shimadzu) in the range of 400–4000 cm⁻¹. The structural properties of the material were studied using X-ray diffractometer-DMAX-2500 (Rigaku) with Cu-K α radiation, having $\lambda = 1.5406 \text{ \AA}$. The optical property of the synthesized product was studied by using UV-visible Spectrophotometer- λ -950 (Perkin-Elmer). PbSnO₃ photocatalyst was scanned over wavelength range of 200–800 nm. The surface morphology and chemical compositions of synthesized catalyst were analyzed using a Scanning Electron Microscope-JSM-6300 (JEOL) coupled with an energy dispersive spectrometer-JED-2300LA (JEOL). TEM images were recorded on

CM-200 (Philips). The effect of temperature on stability of the catalyst was evaluated by thermogravimetric analysis on Thermogravimetric analyzer (Perkin Elmer-TG) using Xenon arc lamp.

Photocatalytic activity

Photocatalytic activity of synthesized nanocrystalline PbSnO₃ was evaluated by studying degradation of Methyl blue, Indigo carmine, and Acid violet dyes. Three types of observations were recorded.

In one set 50 mL 20 ppm solution of a dye was irradiated using 0.3 g of photocatalyst, PbSnO₃, in sunlight. A similar second set was kept in dark. The third set containing only dye solution was exposed to the sunlight. The decrease in absorbance due to mineralization was recorded on double beam UV-visible spectrophotometer (Sytronics) after every 30 min. To study the effect of amount of the photocatalyst on the rate of degradation of dyes, 0.5 g of the photocatalyst was utilized in 50 mL 20 ppm of the dye solution under same environment. Sunlight intensity was monitored by using Lux meter KM-LUX (Kusam-meko).

Antimicrobial activity of PbSnO₃ photocatalyst

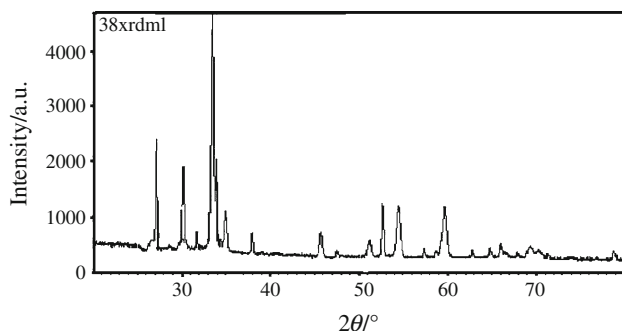
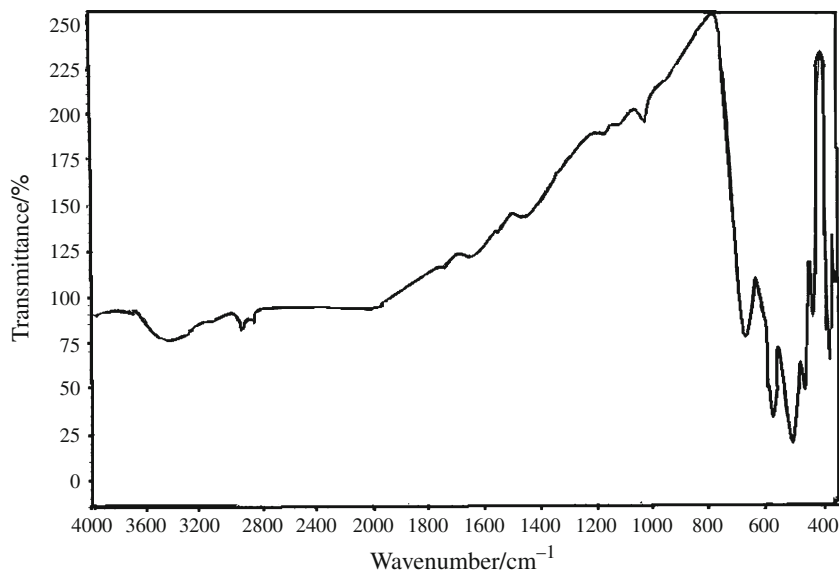
Antimicrobial activity of the PbSnO₃ photocatalyst against bacteria and fungi, was carried out for the detection of the zone of inhibition. Bauer-Kirby method with Mueller-Hinton Agar was used for growing organisms. The inoculum was used as a culture. The test was performed under standardized conditions. The zone of inhibition was measured in millimeters for interpreting the results. Antimicrobial activity of PbSnO₃ photocatalyst was performed against Gram-negative bacteria like *Pseudomonas aeruginosa* (ATCC 27853) and Gram-positive *Staphylococcus aureus* (ATCC 25923) and Germ-negative bacteria *Escherichia coli* (ATCC 25922).

The antifungal susceptibility test was evaluated using plates with Mueller-Hinton agar with glucose, dye and inoculum as a culture. The plates were incubated for the temperature $\pm 35 \text{ }^\circ\text{C}$ for 24 h. Zone of inhibition was recorded to confirm the activity. The antifungal activity was performed against *Candida albicans* (ATCC 90028).

Results and discussion

Characterization of PbSnO₃

The infrared absorption spectrum of the synthesized PbSnO₃ catalyst is depicted in Fig. 1. Vibrational frequency band at 425 and 569 cm⁻¹ indicates the presence of

Fig. 1 IR spectra of PbSnO₃**Fig. 2** XRD pattern of PbSnO₃

Pb–O and frequency around 600 and 685 cm^{-1} indicates the presence of Sn–O vibrations of PbSnO₃. Figure 2 shows XRD pattern of PbSnO₃ powder formed after heating. The crystal structure of PbSnO₃ is tetragonal and all the d-line patterns match with JCPDS data card No-04-055.

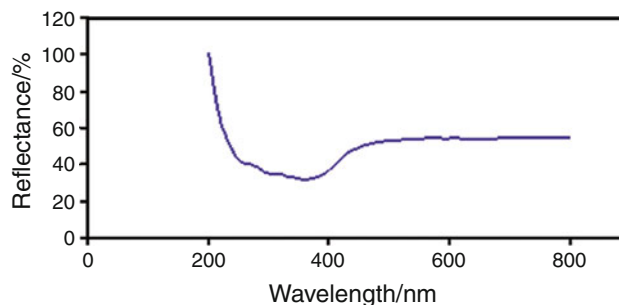
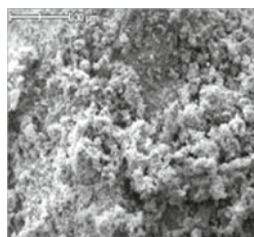
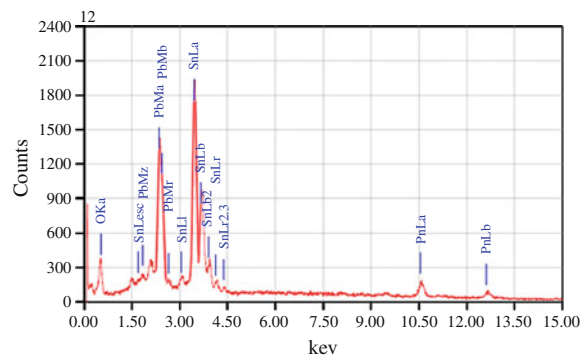
Fig. 4 SEM and EDAX of PbSnO₃**Fig. 3** UV–visible DRS of PbSnO₃

Figure 3 represents the UV–visible diffused reflectance spectra of the synthesized PbSnO₃ photocatalyst. The diffused reflectance spectra depict that absorption goes into UV–visible region. The DRS of the PbSnO₃ has absorption edge cut-off at 350 nm with corresponding band in the



ZAF method standardless quantitative analysis

Fitting coefficient : 0.6116

Element	(keV)	mass%	Error%	At%	k
O K	0.525	14.15	0.94	59.65	10.2103
Sn L	3.442	51.10	0.86	29.03	48.0549
Pb M	2.342	34.75	0.96	11.31	36.8387
Total		100.00		100.00	

Fig. 5 TEM and SEAD image of PbSnO_3 photocatalyst

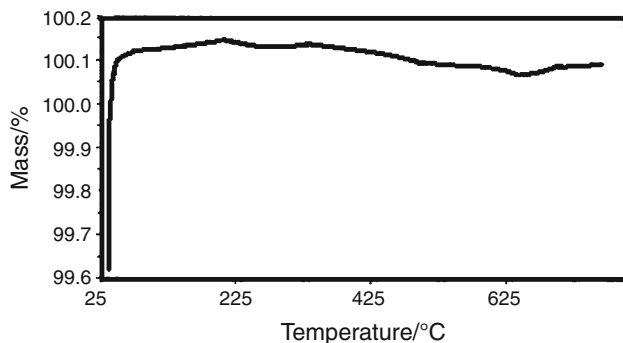
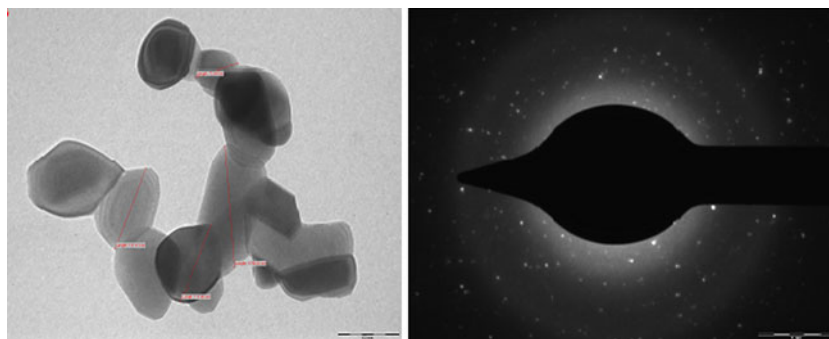


Fig. 6 TG of PbSnO_3 photocatalyst

Fig. 7 Degradation curve of MB, IC, and AC dyes by PbSnO_3 photocatalyst (0.3 g/50 mL)

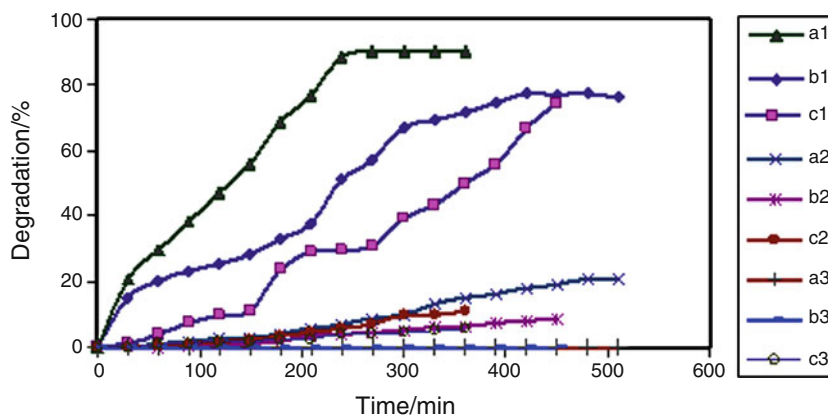
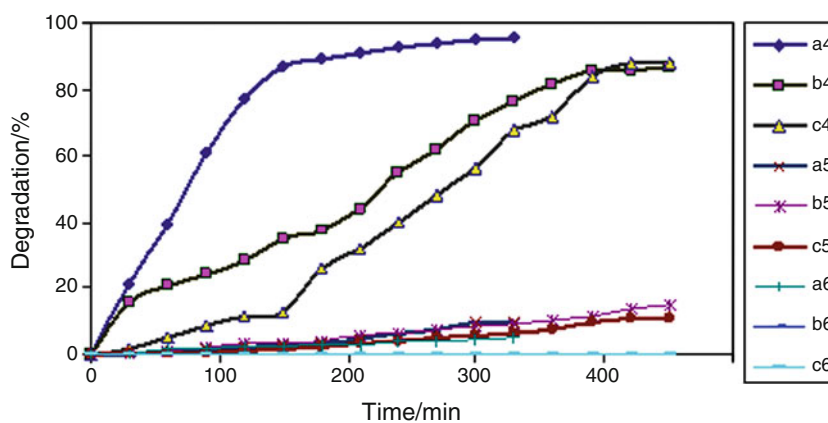


Fig. 8 Degradation curve of MB, IC, and AC dyes by PbSnO_3 photocatalyst (0.5 g/50 mL)



visible region. The band gap energy ($E_g = hc/\lambda$) for the compound was found to be 3.265 eV. The broad absorption edge shoulder in the curve reveals the formation of PbSnO_3 . The presence of uneven shape and size of nanocrystals of PbSnO_3 could be one of the reasons for the broad absorption peak. The result implies that the sample may possess excellent photocatalytic activity.

The surface morphology and associated chemical composition of synthesized photocatalyst was analyzed using a scanning electron microscope (SEM) coupled with EDAX and is shown in Fig. 4. The SEM image shows that the particles are agglomerating with each other. The EDAX

data furnishes elemental composition in conformity with the respective molar proportions taken.

The TEM image along with the selected area of the diffraction pattern (SAED) recorded for the sample corresponding to PbSnO₃ is shown in Fig. 5. The TEM reveals that, the nanoparticles are elliptical; however, there are several hexagonal-shaped crystallites. The dark spot in the TEM micrograph can be alluded to PbSnO₃ nanoparticles as SAED pattern associated with such spots reveals occurrence of tetragonal PbSnO₃ is in total agreement with the XRD data. The average size of the PbSnO₃ nanocrystallites was found to be 100 nm.

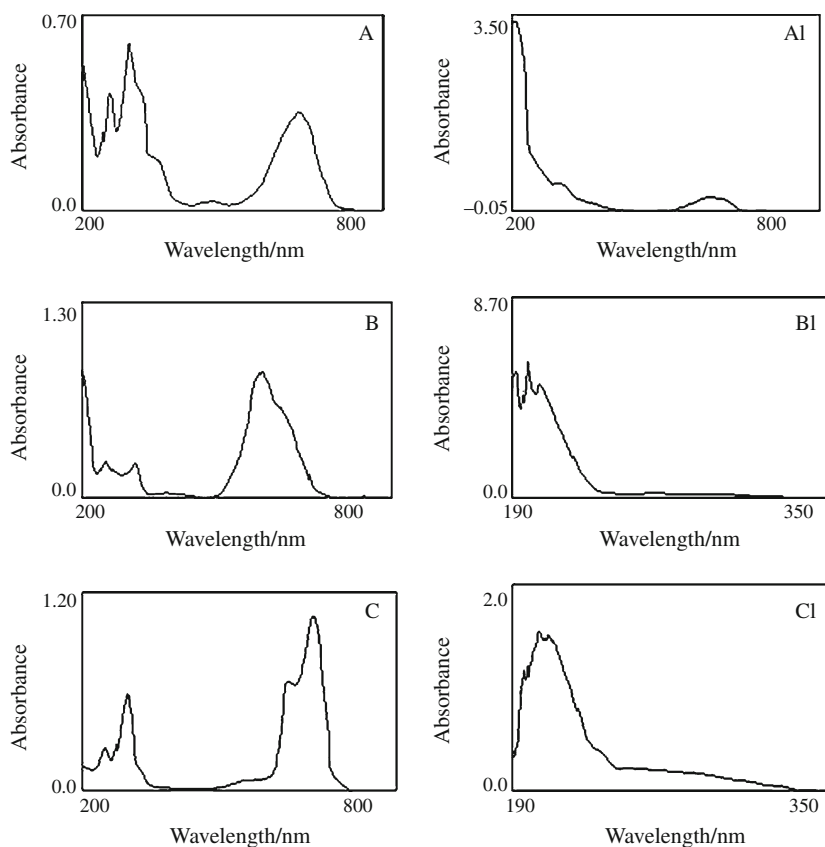
Figure 6 shows TG curve for the PbSnO₃ photocatalyst. Heating rate of the furnace was maintained at 10 °C per minute. No significant loss in mass on rise in temperature was observed up to 700 °C. The photocatalyst was found to be very stable over a wide range of temperature.

Photocatalytic property of PbSnO₃

Photocatalytic property was evaluated by photodegradation of Methyl blue, Indigo carmine, and Acid violet dyes. The photodegradation of the dyes were studied by measuring the absorbance after every 30 min on double beam spectrophotometer (Systronics). Figure 7 indicates graphical representation of percentage degradation of dyes, the

degradation of MB is indicated by series-a, degradation of IC is indicated by series-b, and degradation of AV is indicated by series-c in the graph, respectively. In the figure curve a1, b1, and c1 of the graph represent the decrease in the absorbance of the dye solution in presence of PbSnO₃ photocatalyst when irradiated under sunlight. The sunlight intensity was 980 × 50000 to 700 × 50000 lux. The curve a2, b2, and c2 of the graph indicate very minute decrease in absorbance when the dye solution was irradiated under sunlight in the absence of photocatalyst and the curve a3, b3, and c3 indicate that there was no measurable change in the absorbance in the presence of photocatalyst when kept in dark. This proves that, the degradation and color removal take place only in the presence of photocatalyst (PbSnO₃) in the presence of sunlight. Figure 8 correspondingly reveals that, on increased amount of photocatalyst enhances the degradation of MB, IC, and AV dyes. In the Fig. 8, curve a4, b4, and c4 indicate the rapid degradation of dyes. This may be due to increase in amount of the photocatalyst, which increases ejection of number of photons and electrons in the conduction band and in the valence band, respectively. Figure 9 reveals that the degradation of dyes before and after exposure to the sunlight and photocatalyst. In the Fig. 9, graph A, B, and C represent UV–visible absorption spectra of MB, IC, and AV dyes, respectively, before exposure to the sunlight and

Fig. 9 UV–Visible absorption spectra of dyes before and after degradation



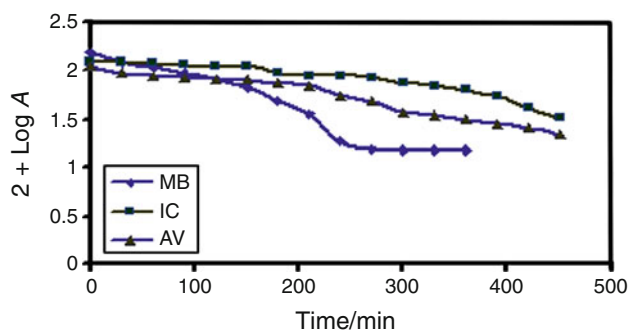


Fig. 10 Study of kinetics of degradation of dyes

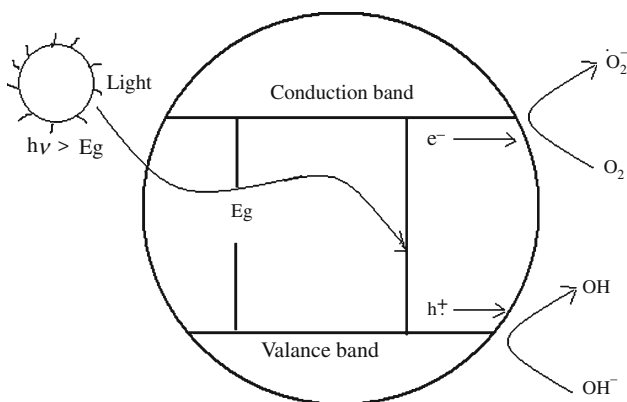
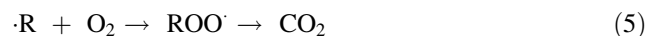
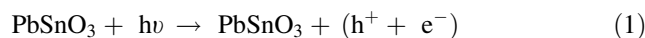


Fig. 11 Schematic pathway of photocatalysis

photocatalyst. The chromophoric absorption peaks at 670, 690, and 685 nm of the solution before exposed to the sunlight and photocatalyst eventually disappeared, and new peaks at 287, 217, and 230 nm appeared due to the mineralization after exposure to the sunlight and photocatalyst, which is shown in figure A1, B1, and C1, respectively. Figure 10, shows the degradation process follows first order kinetics with the rate constant 0.0014, 0.0042, and 0.00263 min^{-1} for MB, IC, and AV dyes, respectively.

When aqueous suspension of the photocatalyst PbSnO_3 was irradiated with light energy greater than the band gap energy of the semiconductor oxide, conduction band electrons (e^-), and valance band holes (h^+) are formed. The photogenerated electrons react with absorbed molecular O_2 reducing it to superoxide radical anion O_2^- , and photogenerated holes can oxidize organic molecules directly or the $\cdot\text{OH}$ and the H_2O molecule adsorbed at catalyst surface to $\cdot\text{OH}$ radical. These will act as strong oxidizing agent and can easily attack on organic molecule or those located close to the surface of the catalyst, thus leading to complete mineralization, Eqs. 1–5, Fig. 11 represent the probable pathway of the degradation.



The study of the antimicrobial activity test showed that the photocatalyst PbSnO_3 was non-toxic to the Gram-positive, Gram-negative bacteria and fungi as there was the absence of zone of inhibition. The PbSnO_3 photocatalyst was found to be non-toxic to the environment.

Conclusions

The nanocrystalline photocatalyst PbSnO_3 was synthesized by green chemistry approach using mechanochemical method. Synthesis of PbSnO_3 and degradation of different dyes were carried out without affecting aquatic life. The band gap energy of the photocatalyst was 3.265 eV with average particle size 100 nm. The TEM micrograph and SAED pattern associated with spots reveals occurrence of tetragonal PbSnO_3 in total agreement with the XRD data. PbSnO_3 photocatalyst was effectively used for degradation of Methyl blue, Indigo carmine, and Acid violet dyes. Antimicrobial activity of PbSnO_3 was performed against Gram-positive, Gram-negative bacteria as well as fungi and it was found non-toxic.

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References

1. Kuzushita K, Morimoto S, Nasu S. Charge disproportionation and magnetic properties in perovskite iron oxides. *Phys B Cond Matter*. 2003;329:736–7.
2. Misono M. A view on the future of mixed oxide catalysts: the case of heteropolyacids (polyoxometalates) and perovskites. *Catal Today*. 2005;100:95–100.
3. Snijkers FM, Buekenhoudt A, Luyten JJ. Proton conductivity and phase composition in $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$. *Scr Mater*. 2004;50: 655–9.
4. Shin S, Yonemura M, Ikawa H. Order-disorder transition of $\text{Sr}_2\text{Fe}_2\text{O}_5$ from brownmillerite to perovskite structure at an elevated temperature. *Mater Res Bull*. 1978;13:1017–21.
5. Tanasescu S, Totir ND, Marchidan DI. Thermodynamic properties of the $\text{SrFeO}_{2.5}$ and $\text{SrMnO}_{2.5}$ brownmillerite-like compounds by means of EMF-measurements. *Solid State Ion*. 2000;134:265–70.
6. Zhang GB, Smyth DM. Defects and transport of the brownmillerite oxides with high oxygen ion conductivity— $\text{Ba}_2\text{In}_2\text{O}_5$. *Solid State Ion*. 1995;82:161–72.

- Libby WF. Promising catalyst for auto exhaust. *Science*. 1971. doi:10.1126/171.3970.499.
- Chakrabarti S, Dutta BK. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. *J Hazard Mater*. 2004;112(3):269–78.
- Xu Y, Jia J, Zhong D, Wang Y. Degradation of dye wastewater in a thin-film photoelectrocatalytic (PEC) reactor with slant-placed TiO₂/Ti anode. *Chem Eng J*. 2009;150:302–7.
- Haque MM, Muneer M, Bahnemann DW. Semiconductor-mediated photocatalyzed degradation of a herbicide derivative, chlorotoluron, in aqueous suspensions. *Environ Sci Technol*. 2006;40:4765–70.
- Chen YS, Crittenden JC, Hackney S, Sutter L, Hand DW. Preparation of a novel TiO₂-based p–n junction nanotube photocatalyst. *Environ Sci Technol*. 2005;39:1201–8.
- Yamashita H, Harada M, Tanii A, Honda M, Takeuchi M, Hirao T. Preparation of efficient titanium oxide photocatalysts by an ionized cluster beam (ICB) method and their photocatalytic reactivities for the purification of water. *Catal Today*. 2000;63:63–9.
- Rashed MN, El-Amin AA. Photocatalytic degradation of methyl orange in aqueous TiO₂ under different solar irradiation sources. *Int J Phy Sci*. 2007;2:073–81.
- Paola AD, López EG, Ikeda S, Palmisano L. Photocatalytic degradation of organic compounds in aqueous systems by transition metal doped polycrystalline TiO₂. *Catal Today*. 2002;75:87–93.
- Konstantinou IK, Albanis TA. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review. *Appl Catal B Environ*. 2004;49:1–14.
- Alaton LA, Ferry JL. Near-UV–VIS light induced acid orange 7 bleaching in the presence of SiW₁₂O₄₀⁴⁻ catalyst. *J Photochem Photobiol A*. 2002;152:175–81.
- Saylikan F, Asilturk M, Şener S, Erdemoglus S. Hydrothermal synthesis, characterization and photocatalytic activity of nano-sized TiO₂ based catalysts for Rhodamine B degradation. *Turk J Chem*. 2007;31:211–21.
- Preoana L, Malic B, Zaharescu M. LaCO₃ Formation from precursors obtained by water based sol-gel method with citric acid. *J Therm Anal Calorim*. 2011. doi:10.1007/s10973-009-0315-x.
- Heine JR, Rodriguez, Bawend MG, Jensen KF. Synthesis of CdSe quantum dot-ZnS matrix thin films via electrospray organometallic chemical vapor deposition. *J Cryst Growth*. 1998;195:564–8.