STUDY OF PHOTOCATALYTIC ASSET OF LEAD TITANATE SYNTHESIZED BY ECO-FRIENDLY MECHANOCHEMICAL METHOD

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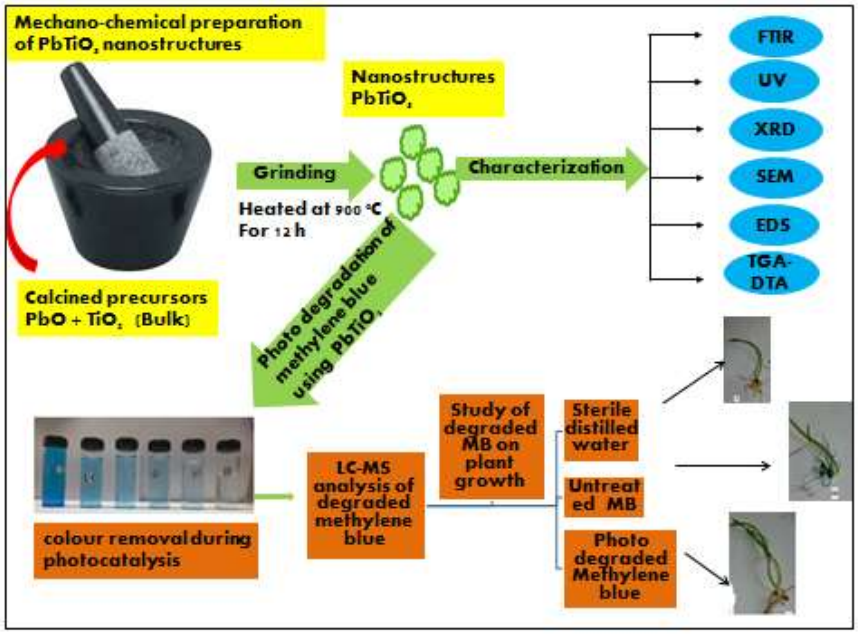
Abstract : Lead titanate particles in the nanometer size regime have been successfully synthesized by mechano-chemical method using green chemistry approach. The structural and micro structural properties of $PbTiO_3$ material was characterized by various investigative techniques like FT-IR, UV-DRS, XRD, SEM, TGA and Electrical Conductivity. The particle size of $PbTiO_3$ was found to be 64 nm by XRD. Electrical properties show semiconducting nature of synthesized lead titanate. The thick films of the material were prepared by screen printing method. The synthesized material was used for photo degradation of methylene blue dye with respect to various dye concentrations and catalyst amount under sunlight. Degradation product analysis was done using the LC–MS technique (Liquid chromatography–mass spectrometry) and the results shows that the dye degradation. The degraded product tested for the phytotoxicity and show good results. Degradation products were less toxic and more similar to pure water compared to methylene blue. $PbTiO_3$ photo catalysts was found to be nontoxic to the environment.

IndexTerms - Ball-milling, Metal Titanate, screen printing, Photo toxicity, Nano crystalline



Graphical abstract

I. INTRODUCTION

A wide variety of dyes, detergents and organic compounds, which are toxic and stable to natural decomposition are nowadays introduced into the water system from various sources, such as industrial effluents, chemical spills and their persistence in the environment [1]. This effluent is non-biodegradable in nature and create environmental problem to their removal. The toxicity has demonstrated that most of these chemicals are harmful and toxic, the colored waste water in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbation in the aquatic life. The dye from textile industries and other commercial dyestuffs have been a focus of environmental remediation in the last few years [2-4]. There are many conventional methods for the dye removal from waste water and textile industries viz. physical methods, chemical methods, adsorption, absorption, incineration and biological. Each method has some merits and demerits.

The past two decades have witnessed intensive studies within light induced mineralization of hazardous pollutant with use of TiO_2 and ZnO photocatalyst and attracted extensive interest to solve the environmental and energy problem [5]. Many researchers work on these metal oxides semiconductors photocatalysis and have become more appealing than conventional oxidation methods[6]. Semiconductor photocatalysis has been intensively studied in recent decades for a wide variety of application such as hydrogen production from water splitting and water and air treatment. Semiconductors are inexpensive, non-toxic and capable of extended use without substantial loss of photocatalytic activity. The majority of photocatalysts are, however, wide band-gap semiconductors which are active only under UV irradiation. In order to effectively utilize visible solar radiation,

here is need to investigates various types of visible-light active photocatalysts including metal ion-doped TiO_2, mixed metal oxides, nanocomposites. It may be easily recovered by filtration and centrifugation. But little attention is given on photocatalyst[7-8] of the type ABO_3 mixed metal oxides.

Lead titanate, $PbTiO_3$, belongs to the important group of compounds with a perovskite. $PbTiO_3$ is well known for it's widely used in optoelectrics, sensors, transducers and non-volatile memory devices due to its remarkable ferroelectric, pyroelectric and pizoelectreical properties. In literature survey, lead titanate has been prepared by combustion, sol–gel[9], polymeric precursor[10] co-precipitation[11] and hydrothermal method. Many of this method are not cost effective and not ecofriendly. Therefore, it is still desirable to develop an alternative method for ecofriendly synthesis of $PbTiO_3$.

In the present study, we focus on the synthesis of $PbTiO_3$ by green chemistry approach and its new application for photocatalytic degradation of methylene blue (MB) dye, its toxicity study and electrical property. The scope was extended to cover Methylene Blue dye usually used in the textile, food, and cosmetics industries. Methylene blue is regarded as a highly toxic dye that may lead to permanent burn to the eyes of human and animals, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia[12-13]. In this report, the degradation of MB dye was investigated by using $PbTiO_3$ nanocrystalline particles under sunlight. The depredated product also tested for the phytotoxicity studied.

II. EXPERIMENTAL

Synthesis of $PbTiO_3$ photocatalyst : The starting material used for the synthesis of lead titanate, lead oxide and titanium dioxide used were analytical reagent grade (AR), Methylene Blue dye was purchased from Research Lab Fine Chem. Industries Mumbai, India. $PbTiO_3$ nanocrystalline powder was prepared by using stoichiometric mixture of PbO and TiO_2, and it was subjected to stepwise calcinations until terminal temperature of the reaction mixture was reached by heating in the muffle furnace with increase in temperature at the rate of 10°C/ min from one temperature to the subsequent higher temperature. After heating at higher temperature the material was cooled and grinded with a gap of 2 hours by using mortar and pestle. Later on, the grinded material was further heated at 900 °C for 10 hours.

Characterization of $PbTiO_3$ photocatalyst: The XRD analysis of the sample was carried out by DX-2000 X-ray powder diffractometer with CuKα monochromatic radiation. The mean particle size of the product was calculated by using Debye Scherrer equation from the full width at half maximum (FWHM) of the XRD pattern. FT-IR spectrum of a powder sample was performed with KBr pellet on Shimadzu Fourier Transform Infrared Spectrophotometer 8400 S model. UV-DRS Spectrum was carried out using JASCO UV-visible diffuse reflectance spectrophotometer. The structural morphology is determined by scanning electron microscopy (SEM) JEOL. Thermogravimetric/differential thermal analysis (TG-DTA) experiments were performed on Shimadzu DTA-60 instrument, in a Pt crucible at heating rate of 10°C / min from 10 to 900°C at nitrogen atmosphere. The degraded product was analysis using Shimadzu LCMS-8030. The electrical properties were studies using the thick film of lead titanate, which was prepared by using some binder and screen printing technique [14].

Photodegradation study: The concentration of methylene blue dye solution was 10 ppm. A 50 ml of dye solution was transferred into the beaker and then 50 mg of $PbTiO_3$ nanocrystalline powder was added. This mixture was irradiated under natural source sunlight, which induced the photochemical reaction to proceed. Every 30 min the reaction mixture was taken and centrifuged to discard other sediment. These solutions were monitored on UV-visible spectrophotometer (Shimadzu 1800) before and after reaction at wavelength 665 nm. An investigation of the effects of reaction conditions was also done by varying conditions and monitors the activity.

***Phytotoxicity activity*:** Phytotoxicity effect was also studied on tested microbial strains in three sets of Petri dishes. One set contain only regular water. In second set degradation product obtained after the photocatalytic reaction and in third set methylene blue dye concentration. Dye concentration solution was used to evaluate on germination and seeding growth of wheat plants. Textile industry located where this type of plants commonly cultivated.

III RESULTS AND DISCUSSION

Structural analysis

The FTIR spectrum of nanocrystalline $PbTiO_3$ is depicted in Fig.1. A band around 439.00 cm^{-1}, 536.00 cm^{-1} , 653.00 cm^{-1} and 757.00 cm^{-1} are possibly caused by the stretching vibration due to the interactions produced between the oxygen and the metal bonds[15]. The O-O vibrations of the peroxo group was at 905.00cm^{-1} .The bands at 1483 cm^{-1} and 1413 cm^{-1} are due to the asymmetric and symmetric stretching vibrational modes of metal-oxygen bond. There was no peak found in the region of 3400 cm^{-1} and it clearly shows that absence of moisture and water molecule.

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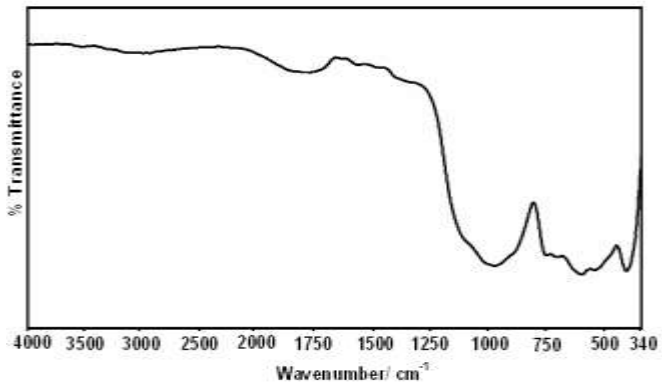


Figure 1. FT-IR spectrum of $PbTiO_3$ nanoparticles

Fig.2. shows UV-visible diffused reflectance spectrum for $PbTiO_3$ with broad reflectance band at 380 nm. The broad shoulder in nanocrystalline material in the UV-visible range probably shows the formation of nano $PbTiO_3$. The band gap was calculated by using equation $E = h\upsilon$ and is found to be 3.35 eV.

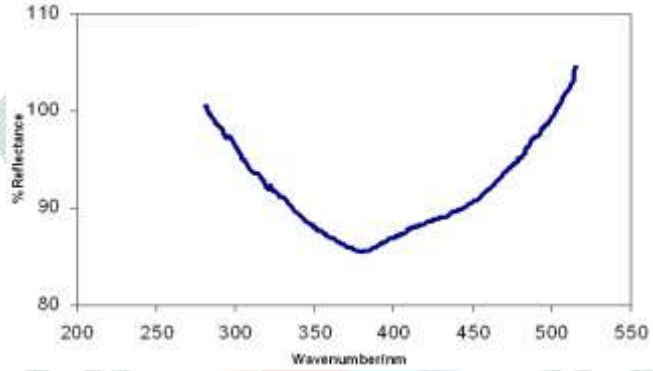


Figure 2. UV- DRS spectrum of $PbTiO_3$ nanoparticles

The XRD pattern of as prepared $PbTiO_3$ nanoparticle is represented in Fig.3. The presence of diffraction peaks can be used to evaluate the structural order at long range or periodicity of the material. $PbTiO_3$ phase was confirmed by the comparison between the XRD patterns with respective JCPDS card no. 06-0452, and no other impurity phases were detected. From Fig.3. it is found that all diffraction peaks of $PbTiO_3$ nanoparticle can be assigned to the tetragonal pervoskite. The crystallite size have been estimated from the X-ray peak broadening of (h,k,l) diffraction using Scherrer formula. The average grain size of sample estimated from strong diffraction (that is, (1 0 0), (1 1 0) and (1 1 1)) half width of the XRD peak and found to be 64 nm for $PbTiO_3$.

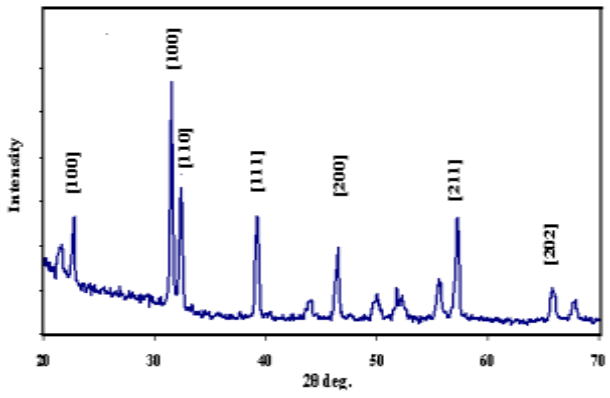


Figure 3. XRD pattern of $PbTiO_3$ nanoparticles.

The crystal morphology image of milled powder for $PbTiO_3$ is depicted in Fig.4. The SEM image shows nanoparticles agglomerates with each other. These agglomerates can be soft if they consist of a number of particles held together by weak van der waals forces or hard if the particles inside the agglomerates are held together by strong chemical or sintering bonds[16].

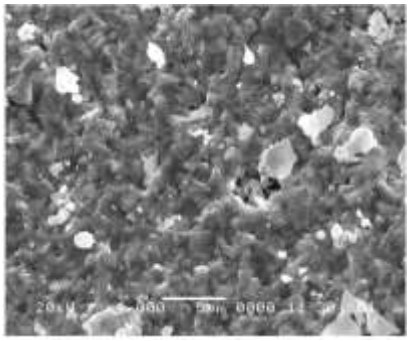


Figure 4. SEM image of $PbTiO_3$ nanoparticles.

Fig.5. shows the TG/ DTA curve of $PbTiO_3$ photocatalyst. There is no significant loss in mass on rise in temperature was observed. Fig.5.didn't show neither exothermic nor endothermic effects because formation of $PbTiO_3$ were almost completely finished during milling and heating. The photo catalyst was found to be stable over the wide range of temperature.

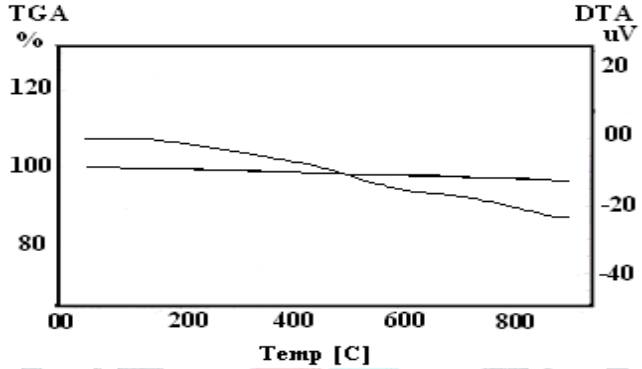


Figure 5. TG-DTA of $PbTiO_3$ nanoparticle

Electrical Properties

I-V Characteristics: Fig.6. shows the I-V characteristics of films at room temperature. Here voltage was continuously varied with constant room temperature and change in conductance was recorded. I-V characteristic are observed to be symmetrical in nature, indicating the ohmic nature of nanocrystalline $PbTiO_3$ materials.

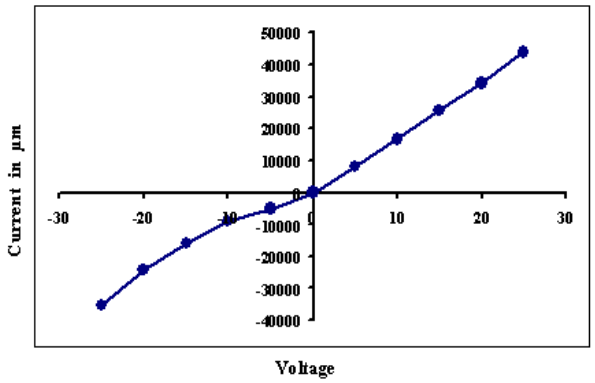


Figure 6. IV characteristic of $PbTiO_3$

Electrical Conductivity

Electrical conductivity for synthesized nanocrystalline material is shown in Fig.7. Electrical performance of the material was studied by measuring change in conductance with temperature. The Fig.7 shows dependence of conductivity of lead titanate film in air ambience. The conductivity of the film goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This confirms the semiconducting nature of the lead titanate. Energy of activation was calculated from the plot of conductivity and temperature. The activation of energy was found to be 1.18 KJ/mol. The film was fired at 550ºC and it shows large conductivity because the temperature increases the adsorption of oxygen species on surface of film are more and hence the conductivity decrease.

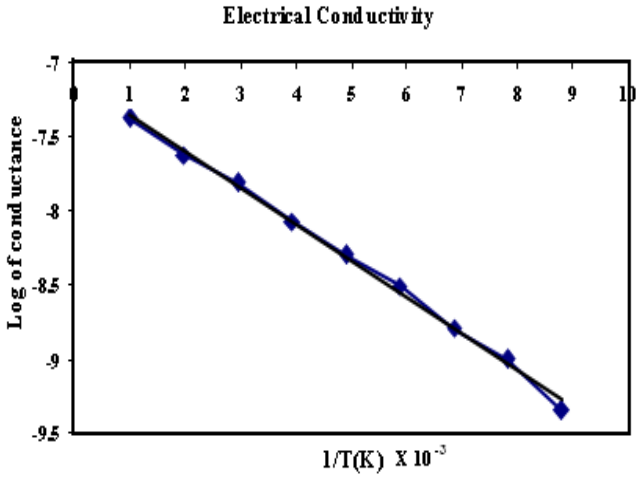


Figure 7. Electrical conductivity of $PbTiO_3$

Photocatalytic activities

Effect of Dye Concentration: The graphical representation of photo degradation of methylene blue dye is represented in Fig.8. The study of initial concentration of methylene blue dye on the photocatalytic efficiency was investigated with concentration of 5, 10, 15 and 20 ppm solution. It was observed that the increase in dye concentration shows decrease in degradation efficiency (Fig. 9). Hence, the photo-oxidation process will work faster at a low concentration of pollutants. These results are in good agreement with previous reports[17-18].that photo degradation of textile dye Reactive Red 2, C.I. Acid Yellow 17 and Direct Yellow 12 decreased with increasing concentrations. At high concentrations of dye, the deeper colored solution would be less transparent to sunlight and the dye molecules may absorb a significant amount of sunlight causing less light to reach the catalyst and thus reducing the OH• radical formation. Since OH• radicals are of prime importance in the attack of the dye molecules, lowering the amount of OH• radicals would cause the photo degradation efficiency to decrease [19]

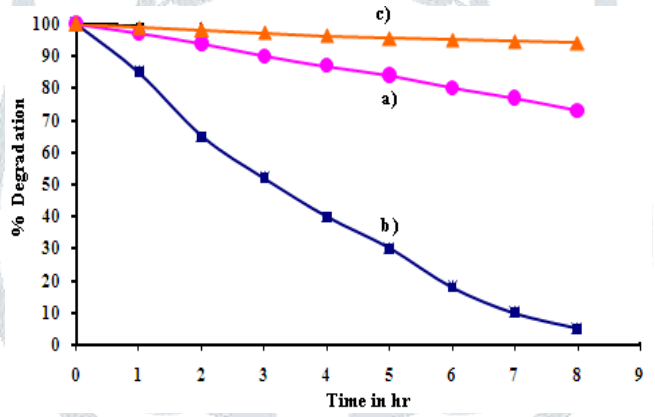


Figure 8. Graphical representation of % degradation of methylene blue a) without catalyst b) with catalyst and c) in dark without catalyst

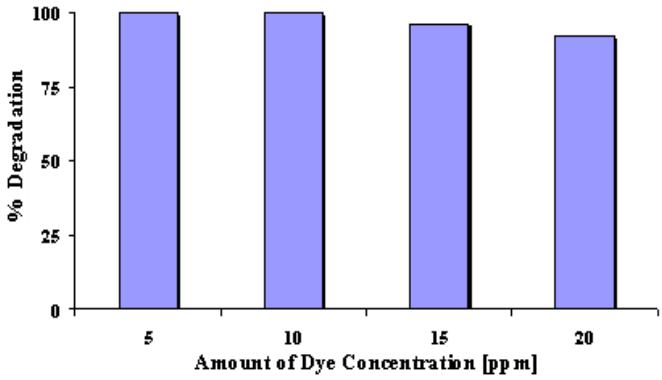


Figure 9. Effect of dye concentration on dye degradation

In the Fig.10, graph a, b, c, d and e represents UV-Visible absorption spectra of MB dye. Chromophoric absorption peaks at 670 nm of the solution before and after exposed to the UV-light and photocatalyst eventually disappeared.

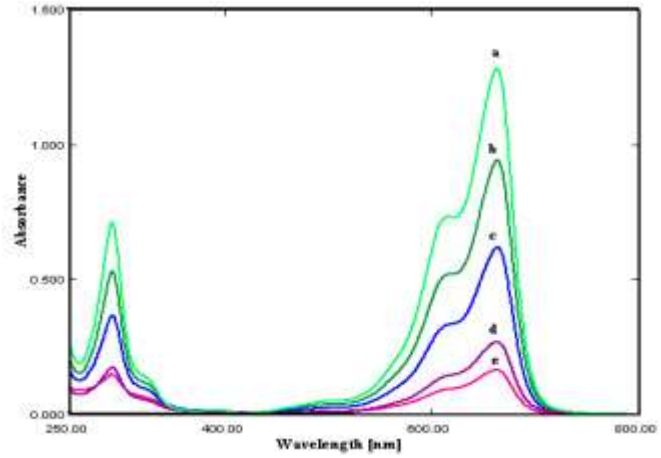


Figure 10. UV- visible Spectra of methylene blue.

The reaction mechanism for the methylene blue photo degradation could be discussed on the basis of semiconductor theory. Illumination of $PbTiO_3$ photocatalyst by photons with energy equal to or greater than its band gap excites electrons (e^-) from valence band to the conduction band and produces holes (h^+) in the valence band. The photogenerated holes (h^+) with strong oxidant capacity can directly oxidize adsorbed organic molecules or react with water molecules or hydroxyl ion (OH^-) to generate hydroxyl radical (•OH). The formed hydroxyl radicals (•OH) also possess strong oxidation ability and can react readily with surface adsorbed organic molecules. Meanwhile, photo generated electrons (e^-) can be trapped by molecular oxygen to from superoxide radical ($^{\bullet}O_2^-$).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, the probable pathway of the degradation was represented by the equations.

$$PbTiO_3 + h\upsilon \rightarrow PbTiO_3 + (h^+ + e^-) \quad [1]$$
$$O_2 + e^- \rightarrow O_2^- \quad [2]$$
$$H^+ + H_2O \rightarrow H^+ + \cdot OH \quad [3]$$
$$\cdot OH + RH \rightarrow H_2O + \cdot R \quad [4]$$
$$\cdot R + O_2 \rightarrow ROO^{\cdot} \rightarrow CO_2 \quad [5]$$

Effect of Amount of Catalyst

The experiments were carried out without and with catalyst (50, 100, 150 and 200 mg) at pH 7 under the sun light (Fig.11.). No degradation was found without catalyst loading dosage. The complete degradation of methylene blue dye was found in 8 hours. With catalyst of 100 mg gave better results than other catalyst dosage when studied under same constant pH condition. The amount has increased from 50 to 200 mg catalyst, this shows that increase in catalyst loading decrease the rate of de-coloration. Therefore 100 mg catalyst loading is considered to be an optimal value. This phenomenon may be explained as, with an increase in catalyst loading the light penetration through the solution becomes difficult. Increase in catalyst concentration decreases photo absorption which in turn reduces the dye adsorption onto the catalyst surface thus reducing the reaction rates.[20-21]The degradation of MB is higher for 100 mg catalyst loading after 8 hour exposure to sun irradiation. Optimal concentration of the catalyst depends on working condition and the incident radiation. The photo catalysts were tested for the reuse and they show that upto 3 times the catalyst work as a normal and then decrease in the reactivity.

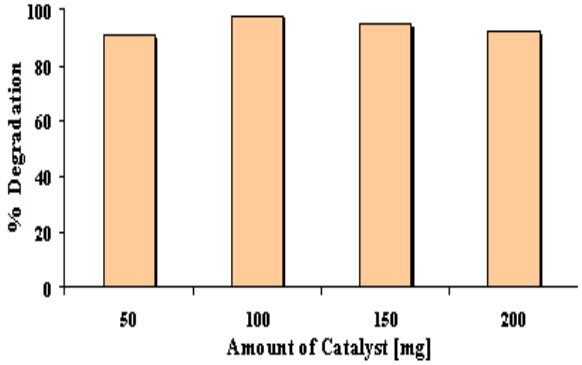
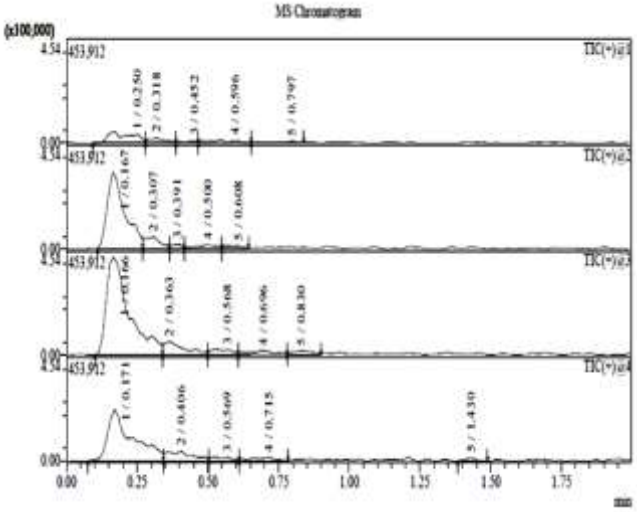


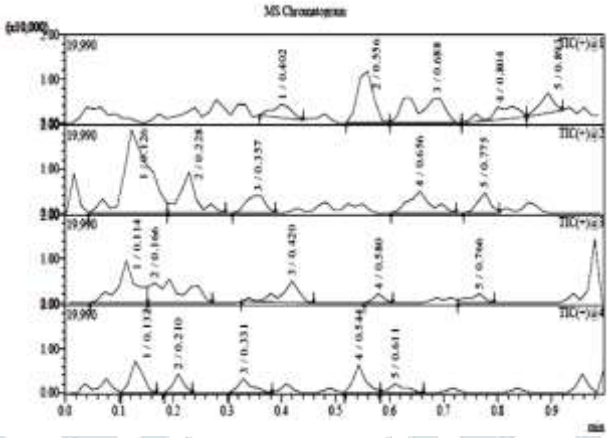
Figure 11. Effect of amount of photocatalyst on degradation of methylene blue.

Fig. 12 (a) and (b) a shows the liquid chromatography mass spectrometry of methylene blue sample before irradiation to sunlight without catalyst and after irradiation to sunlight with catalyst. The result clearly shows that the methylene blue was completely degraded using the photocatalyst. The analysis of degradation intermediate products using $PbTiO_3$ separated at different retention time was done by LC-MS technique and the results are depicted in Fig.13. (a) and (b). The parent molecule of Methylene blue dye elutes at 0.171 min and shows one quasi molecular ions. The m/z = 284 amu corresponds to the singly protonated molecules (Fig

13.a). It shows that before applying any irradiation it is the only one species present as expected. After complete degradation the irradiation peak appear at m/z = 185.



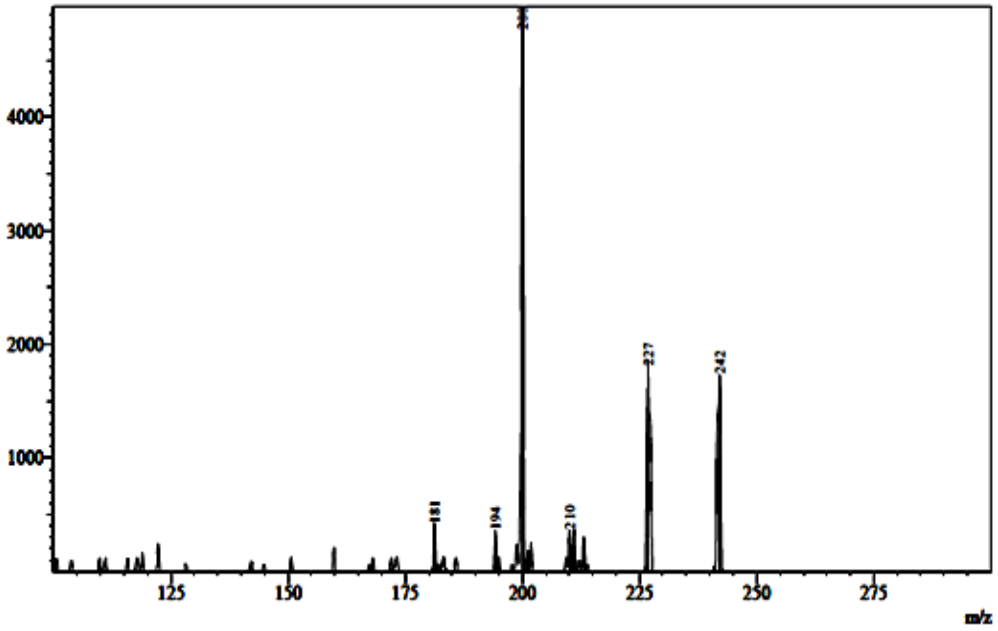
(a)



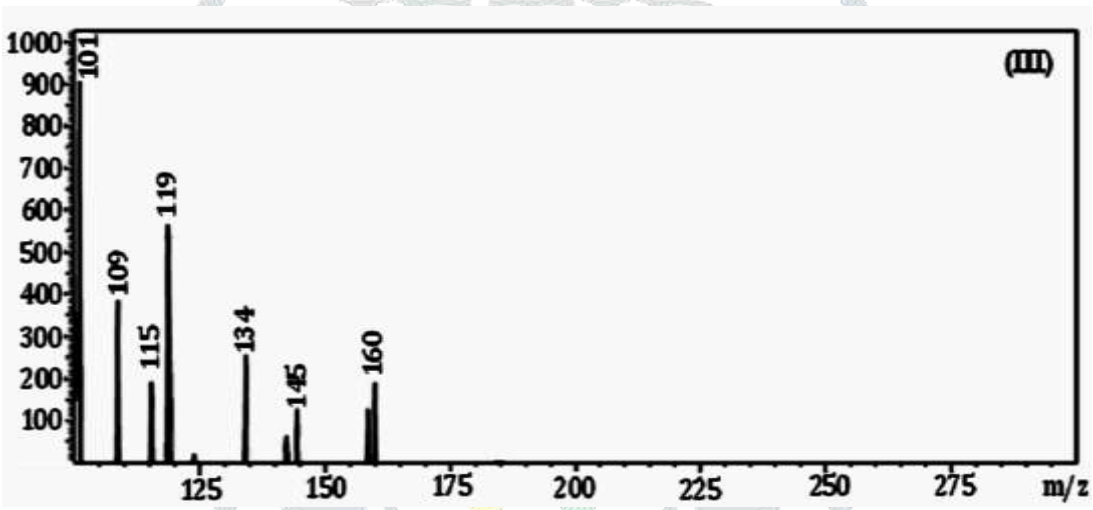
(b)

Figure 12. Liquid chromatography mass spectroscopy graph of a) before degradation and b) after degradation

Many peaks of different intensities were observed in addition to the peak of Methylene blue dye, which indicate the variation in the composition and concentration of the degradation products. Some of these intermediate masses and predicting their structures by the cleavage of one or more groups lead to intermediate products that agree in their masses with the eluted intermediates.



(a)



(b)

Figure 13 Chromatogram of a) before degradation and b) after degradation of methylene blue.

Phytotoxicity study: In phytotoxicity study, the wheat seeds were germinated in sterile 10 cm Petri dishes, layered with sterile filter paper. Seeds were sterilized before transferring to the surface of the paper in Petri dishes.[28] Seeds of wheat were irrigated with 1 ml of solution for each Petri dish. The selection of concentration was based on the actual concentrations used in textile industry, which is usually around 10 ppm. The concentration covers possible dye discharge into water streams, 1 ml of the same solution was applied every day to the surface of the filter paper. Each treatment was replicated three times. Seeds germinated in water irrigated Petri dishes were used as a control. All dishes were kept at room temperature for 7 days. Germination of seeds was recorded daily. The shoot and root lengths of seedlings were measured after 7 days. The effects of dye and photocatalytic degradation dye products on seed germination are shown in Table1. The dye degradation products obtained after photocatalytic degradation show that the degradation of dye with catalyst removed the dye toxic effect and the germination of wheat grains as well as the shoot and root elongation throughout the experiment . However, after seven days, the shoot and root length increased to the comparable value as in the control. Thus the photocatalytic degradation products improved the germination, shoot as well as root elongation as compared to normal wheat seeds using tap water.

	Control [Regular water]	Methylene Blue Dye	Degraded Product
Root [cm]	3.2	1.3	3.0
Shot [cm]	8.4	3.4	7.8

Table 1: Phytotoxicity study data.

IV CONCLUSION

The $PbTiO_3$ synthesis was carried out under ecofriendly, easily and cheap solid state mechano-chemical method. The prepared material, $PbTiO_3$ was successfully employed in the degradation of Methylene Blue dye under sunlight. The optimization studies revealed the dependence of the degradation of methylene blue on initial dye concentration and amount of the catalyst. The degraded products also tested for phytotoxicity study and the results showed that the degraded products were less toxic as compared to methylene blue and similar to that with pure water. $PbTiO_3$ also shows electrical properties and confirm semiconductor. Thus the $PbTiO_3$ photocatalyst is non-hazardous to soil and aquatic microbial systems and hence ecofriendly. The catalyst was recovered and reusable.

V ACKNOWLEDGMENT

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