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A green chemistry approach for synthesis of $CaTiO_3$ Photocatalyst: its effects on degradation of methylene blue, phytotoxicity and microbial Study

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ABSTRACT

Calcium titanate particles in the nanometer size regime have been successfully synthesized by mechanochemical method using green chemistry approach. In this work, the possibility of mechanochemical synthesis of $CaTiO_3$ from CaO and TiO_2 was investigated at 1000 ^{O}C for a period of 20 hours. Intensive mechanochemical grinding of powder containing CaO and TiO_2 under optimal grinding conditions, resulted in synthesis of single phase $CaTiO_3$. The structural and micro structural properties of $CaTiO_3$ material was characterized by various analytical practices like FT-IR, UV-DRS, XRD, SEM and BET. The synthesized material was used for photodegradation of methylene blue dye with respect to various dye concentrations and catalyst amount. $CaTiO_3$ treatment exhibited 93 % degradation. The effect of MB dye degradation products on wheat seed germination were also investigated. The degradation of MB dye removed the toxic effects. This is an evidence for removal of toxicity in degradation products. Antimicrobial activity shows that $CaTiO_3$ photocatalyst was found to be non toxic to the environment.

Keyword: Mechanochemical method, Calcium titanate, Methylene blue, Photodegradation, toxicity.

INTRODUCTION

The textile dying industry needed huge amount of water at its various process of dying and finishing. The Literature survey shows that 15 % of the total world production of dyes were lost during the dyeing process and it released in textile effluents[1]. This effluents is non-biodegradable in nature create environmental problem to their removal. The toxicity have 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]. Conventional methods for the dye removal from waste water and textile industries viz. physical methods, chemical methods, adsorption, absorption, incineration and biological. Each methods has some merits and demerits. For example due to large number of dyes molecules and the stability of modern dyes, conventional biological methods are ineffective for decolorization and degradation.

Last two decades TiO_2 and ZnO has attracted extensive interest to solve the environmental and energy problem[5]. Many researcher work on this metal oxides semiconductors photocatalysis and has become more appealing than conventional oxidation methods. Semiconductors are inexpensive, non-toxic and capable of extended use without substantial loss of photocatalytic activity. It may be easily recovered by filtration and centrifugation. But little attention is given on photocatalyst[6] of the type ABO_3.

Calcium Titanate, $CaTiO_{3,}$ belongs to the important group of compounds with a perovskite. $CaTiO_3$ is well known for its high dielectric, luminescent and semiconductor properties[7-8]. It is also used as photocatalysis on decomposition of water under UV light irradiation[9]. In literature survey, calcium titanate has been prepared by combustion [10], organic–inorganic solution[11], sol–gel[12], polymeric precursor[13], co-precipitation and hydrothermal method[14]. 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 $CaTiO_3$.

In the present study we focus on the synthesis of $CaTiO_3$ by green chemistry approach and its new application for photocatalytic degradation of methylene blue dye, photocatalytic activity and its toxicity study. The scope was extended to cover Methylene Blue (MB) 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 [15]. In this report, the degradation of MB dye was investigated by using $CaTiO_3$ nanocrystalline particles. The effect of various parameters such as pH, initial concentration of dye and amount of catalyst were studied under sunlight. The degradated product also tested for the phytotoxicity studied.

MATERIALS AND METHODS

Synthesis of $CaTiO_3$

The starting material used for the synthesis of calcium titanate, calcium oxide and titanium dioxide used were analytical reagent grade (AR), Methylene Blue dye was purchased from Research Lab Fine Chem. Industries Mumbai, India. $CaTiO_3$ nanocrystalline powder was prepared by using stoichiometric mixture of CaO and TiO_2, this mixture 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 ^oC/ min from one temperature to the subsequent higher temperature. After heating at higher temperature the material was cooled and grinded with gap of 2 hours by using mortar and pestle. Later on, the grinded material was further heated at 1000 ^oC for 20 hours.

Characterization of $CaTiO_3$
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's equation from the full width at half maximum (FWHM) of the XRD pattern. FT-IR spectra 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 and association elemental composition is determined by scanning electron microscopy (SEM) JEOL. BET surface area was performed on Quantachrome autosorb automated gas sorption system.

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 $CaTiO_3$ nanocrystalline powder was added. This mixture was irradiated under 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 and antimicrobial study
Preparation of 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.

Preparation of antimicrobial activity
Antimicrobial activity of $CaTiO_3$ photocatalyst was performed against Gram-positive bacteria like Pseudomonas aeruginosa (ATCC 27853) and Staphylococcus aureus (ATCC 259523) and Germ-negative bacteria like Esherichia Coli (ATCC 25922). For the detection of antimicrobial activity Pour plate method with well diffusion technique (size of well 6 mm) were used. Chloramphinicol was used as standard antibiotic for antimicrobial activity. The diffusion time was 4 ^{o}C for 1 hrs. The zone of inhibition was compared with the standard drug after 24 hrs of incubation at 37 ^{o}C . Inhibitor activity measure in mm as the diameter of observed inhibition zone.

RESULTS AND DISCUSSION

The FTIR spectrum of nanocrystalline $CaTiO_3$ is represented in Fig.1. A band around 688.54 cm^{-1}, 655.75 cm^{-1}, 613.32 cm^{-1}, 459.03 cm^{-1} ,412.74 cm^{-1} and 374.16 cm^{-1} are possibly caused by the stretching vibration due to the interactions produced between the oxygen and the metal bonds. The O-O vibrations of the peroxo group was at 946 cm^{-1} and 906.48 cm^{-1} .The bands at 1483 cm^{-1} and 1413 cm^{-1} are due to the unantisymmetric and symmetric stretching vibrational modes of metal-oxygen bond. There was no peak found in the region of 3400 cm^{-1} that clearly shows that absence of moisture and water molecular.

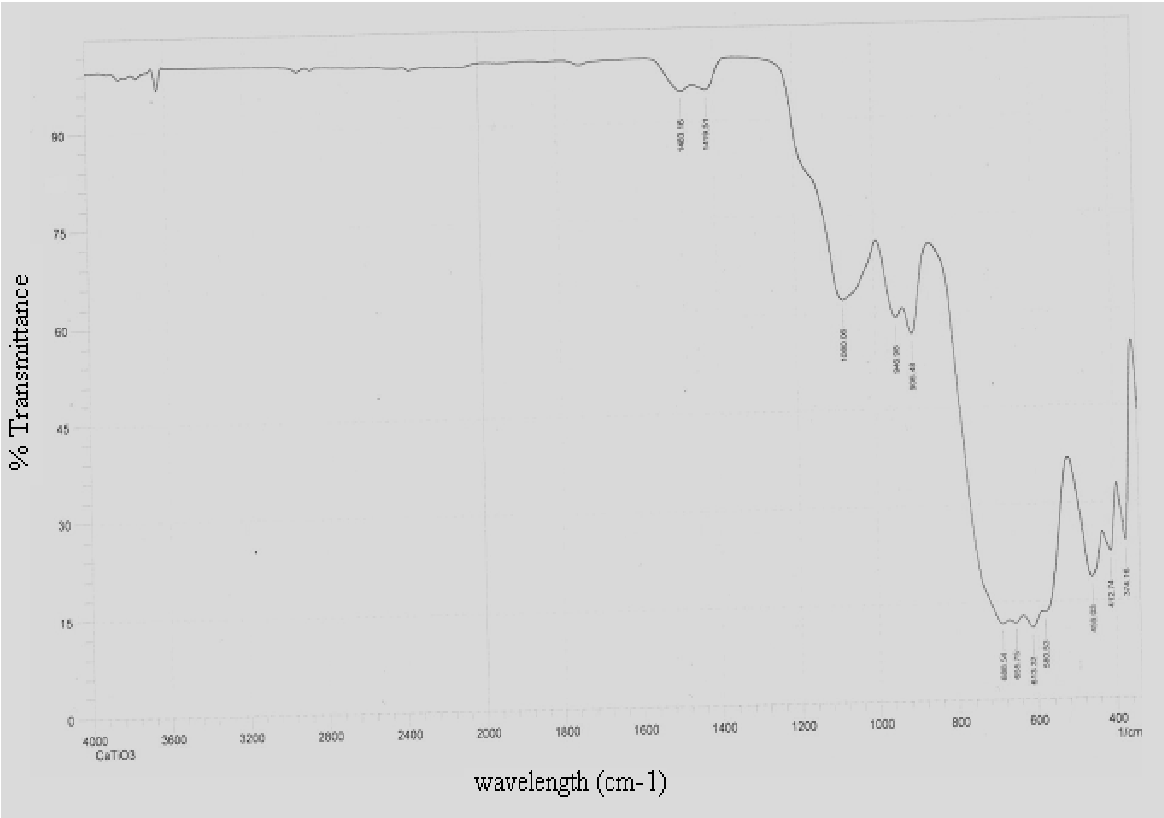

Figure - 1:FT IR spectra of $CaTiO_3$ nanoparticle

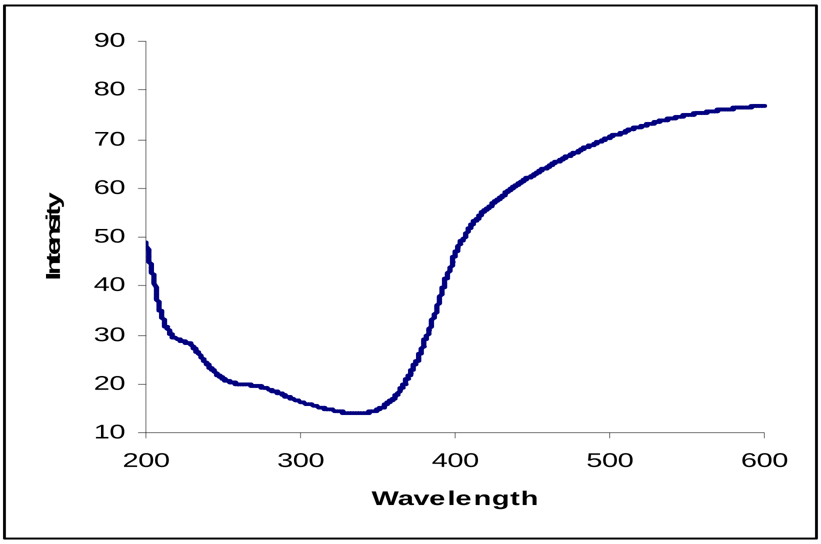

Figure - 2: UV- DRS spectra of $CaTiO_3$ nanoparticles.

The UV-diffused reflectance spectrum for $CaTiO_3$ is depicted in Fig. 2 and show the broad reflectance band at 340 nm. The broad shoulder in nanocrystalline material in the UV-visible range probably shows the formation of nano $CaTiO_3$. The band gap was calculated by using equation E = hυ and is found to be 3.6 eV, which matches with the reported band gap range(3.4 -3.9 eV)[16].

The polycrystalline nature of calcium titanate powder is expressed by XRD pattern as shown in Fig.3, which were identified as an orthorhombic phase. The presence of diffraction peaks can be used to evaluate the structural order at long range or periodicity of the material. Observed X-ray diffraction pattern for $CaTiO_3$ nanoparticles shows high degree of crystallinity. All the peaks in XRD pattern match well with reported characteristic reflection peaks of $CaTiO_3$ (JCPDS Card No.22-0153). 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 half width of the XRD peak and found to below 90 nm for $CaTiO_3$. The XRD peaks correspond to the orthorhombic phase structure of the calcium titanate.

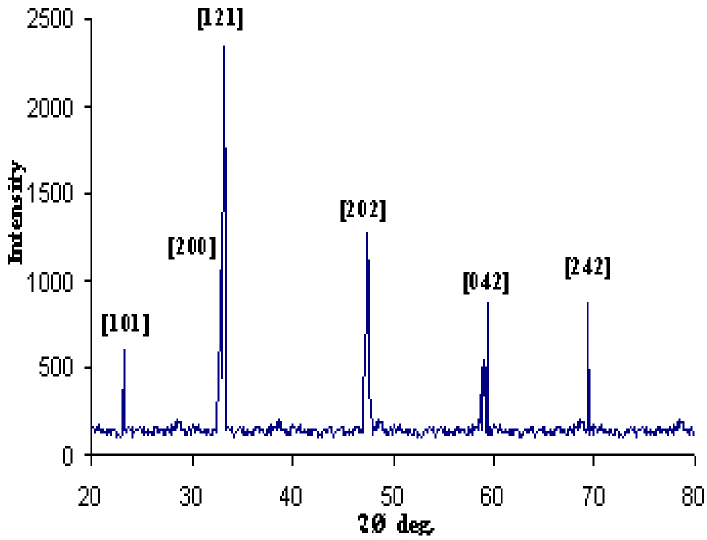

Figure - 3: XRD pattern of $CaTiO_3$ nanoparticles

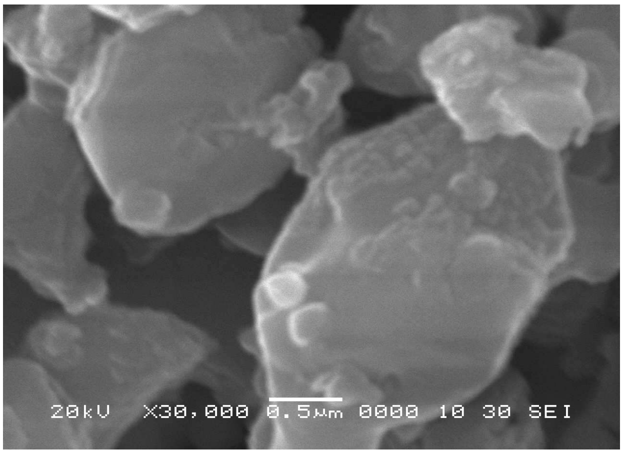

Figure - 4: SEM images of $CaTiO_3$ nanoparticles

The crystal morphology with elemental detection of milled powder for $CaTiO_3$ is depicted in Fig.4. A careful inspection of Fig. 4 shows that some of crystals show hexagonal structure. The SEM image shows nanoparticles with good uniformity and crystallinity.

The surface area of nanocrystalline $CaTiO_3$ photocatalyst was calculated by N_2 adsorption-desorption method. It reveals that the sample have IV, N_2 adsorption desorption isotherm with H1 hysteresis. The BET surface area of $CaTiO_3$ was found to be 301.1 m^2/g.

The degradation of dye was carried out at pH -7 (natural pH range). As per the effluents from factories may cover a wide range of pH. To carry the efficiency of degradation by $CaTiO_3$ solution of several pH value (3,5,7 and 8) were investigated. In general it is known that the metal oxide particles in water exhibit amphoteric behavior and readily reacts with dye. Fig.5 shows the graphical representation of degradation of methylene blue dye under sunlight .

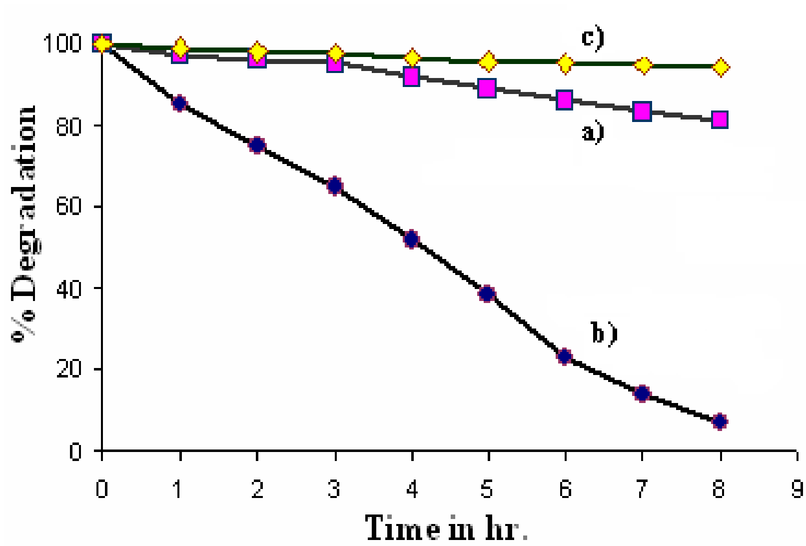

Figure – 5: Graphical representation of % degradation of methylene blue. a) without catalyst and b) with catalyst c) in dark without catalyst

Effect of Dye Concentration

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 (Figure 6). Hence, the photo-oxidation process will work faster at a low concentration of pollutants. These results are in good agreement with previous reports[17-19] that photodegradation 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 coloured 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 photodegradation efficiency to decrease[20].

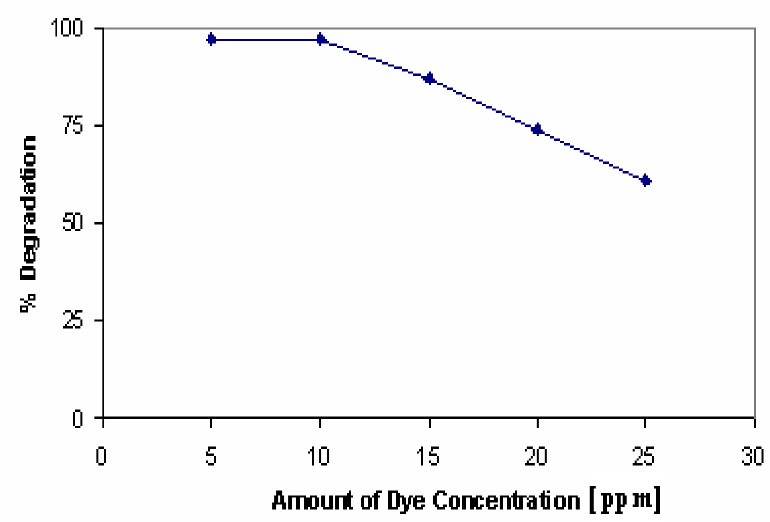

Figure – 6:Effect of amount of dye concentration on dye degradation

In the Figure 7, graph a, b, c and d 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.

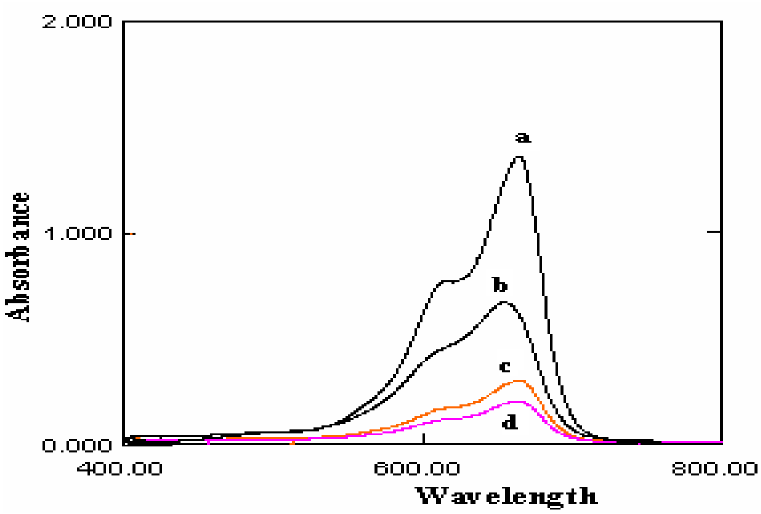

Figure - 7: UV-visible Spectra of methylene blue.

When aqueous suspension of the photocatalysts $CaTiO_3$ 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 molecule directly or the OH· ions and the H_2O molecule adsorbed at catalyst surface to ·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, equation 1-5 represent the probable pathway of the degradation.

$CaTiO_3 + h\upsilon \rightarrow CaTiO_3 + (h^+ + e^-)$ (1)
$O_2 + e- \rightarrow O_2^-$ (2)
$H^+ + H_2O \rightarrow H^+ + \cdot OH$ (3)
$\cdot OH + RH \rightarrow H_2O + \cdot R$ (4)
$\cdot R + O_2 \rightarrow ROO^\cdot \rightarrow CO_2$ (5)

Effect of Amount of Catalyst

The experiment was carried out without and with catalyst (50 , 100 , 150 and 200 mg) at pH 7 under the sun light. No degradation was found without catalyst loading dosage. Fig.8 show that the % of untreated methylene blue with time at pH 7. The complete degradation of methylene blue dye was found in 8 hours. With catalyst of 100 mg gave a 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 decoloration. 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[21-23]. 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[24-25]. The photocatalyst were tested for the reuse and they show that upto 3 times the catalyst work as a normal and then decrease in the reactivity.

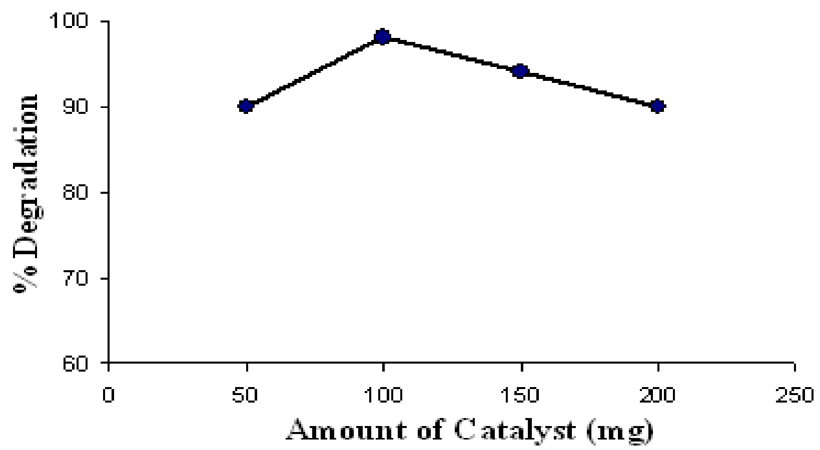

Figure - 8: Effect of amount of Photocatalyst on degradation of methylene blue

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[14]. Seeds of wheat was 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 effect of dye and photocatalytic degradation dye products on seed germination 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 campaired to normal wheat seeds using tap water.

Table.1. Phytotoxicity study data

	Control [Regular water]	Methylene Blue Dye	Degraded Product
Root [cm]	3.2	1.3	2.8
Shot [cm]	8.4	3.4	7.2

Antimicrobial study

The study of the antimicrobial activity showed that zone of inhibition is not detected or absence of zone as compared with the control standard Fig.9. This shows that the $CaTiO_3$ photocatalysts was found to be non toxic and not harmful to the environment.

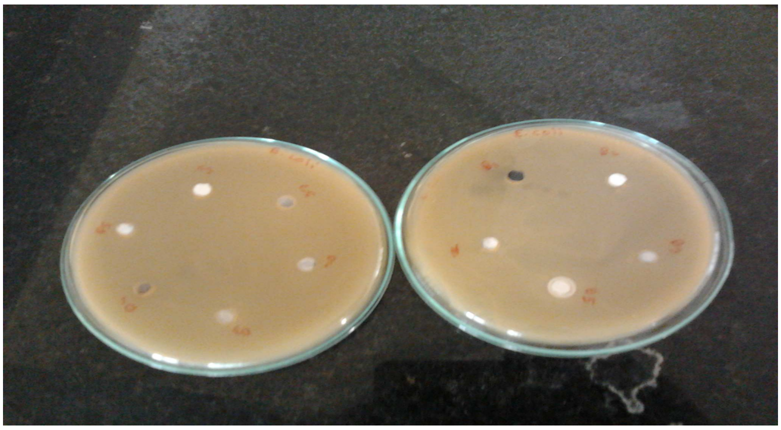

Figure -10: Antimicrobal study.

CONCLUSION

The $CaTiO_3$ synthesis was carried out under ecofriendly, easily and cheap solid state mechanochemical method. The prepared material, $CaTiO_3$ 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 degradated 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. Antimicrobial activity shows that the no zone of inhibition. Thus the $CaTiO_3$ photocatalyst is non-hazardous to soil and aquatic microbial systems and hence ecofriendly. The catalyst was recovered and reusable.

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