A COMPARATIVE STUDY ON DYE DEGRADATION BY USING CALCIUM OXIDE NANOPARTICLES

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***Abstract*— Dyes are easily soluble in water by imparting its color, which leads to the water pollution in large sector by the industries to river. Purification of polluted water is not possible in the water bodies which are not economically suitable, with the literature survey series of nanoparticles have used for the degradation, later these nano particles forms toxic to the aquatic system. However to overcome from this issue, the newly synthesized calcium oxide nanoparticles are subjected for photo degradation of different synthetic dyes in lab condition, which are harmless and sediment. The nanoparticles had well calcinated and characterized by SEM and powdered X- ray diffraction. In series some dyes showed good results with complete degradation. The comparative study reveals the complete degradation of dyes.**

***Index Terms*— CaO nanoparticles, dyes, photo catalytic degradation**

INTRODUCTION

Color is an important aspect of human life. Present day there are more than 10,000 dyes which are commercially available and seven lakh tons of dyes are produced annually [1]. Dyes are usually used in textile, plastic, medicine and other industries. These dyes are major group of pollutants which had caused the 15% environmental pollution in dyeing process [2, 3]. Various industries produce large number of dyes which have complex aromatic structure which make them stable and toxic but they are non-biodegradable in nature [4,5].Dyes used in various textile industry are diverse and can be broadly divided into azo, reactive, triphenyl methane, heterocyclic, polymeric structures etc.[6]. Azo dyes represent 70% of total dye stuff produced as they are widely used among synthetic dyes [7].Textile industry consumes water, energy as well as chemicals in large extent. The organic dyes present in the textile waste water are hazardous and toxic to both human and aquatic life, even low concentrations which cause skin irritation, allergy and cancer to humans [8, 9].The removal of these dyes from environment especially from water bodies is a challenging task which we are facing present situation. The treatment of dyes which are let out from the industry has to be treated regularly. The release of dye effluents into water not only changes color but also decreases the sunlight penetration, oxygen content in water and also releases toxic compound during the path of reaction [10]. Discharge of dyes alters the pH, increases the biochemical oxygen demand (BOD), chemical oxygen demand (COD) and gives intense color to the water. Without the improper treatment of these dyes it will remain in the environment for longer period of time [11]. Due to the complexity of dye molecules, the natural process of degradation is not favorable because of incomplete degradation process and transformation of dyes into by-products which may be carcinogenic and mutagenic in nature to human as well as other organisms [12, 13].Methods such as coagulation, flocculation, reverse osmosis, nano-filtration, chlorination and ultra-filtration are used to treat industrial waste water. These methods are very complex and expensive and are not affordable in textile industries [14, 15, 16].Adsorption by activated charcoal is one of the effective methods which is less economic. But it produces large solid disposal waste materials which are hazardous and causes environmental pollution [17]. Photocatalytic degradation is one of promising and effective treatment technique of waste water which involves the removal of water persistent such as dyes, pesticides and has attracted the attention of many researchers these days [18, 19]. Photo catalyst which is developed should be efficient and be able to operate effectively when it is irradiated to visible radiation [20].

To overcome from these aspects of hazardous and toxic materials from water bodies, we had studied photo catalytic degradation by using CaO nano particles. Even calcium oxides are not toxic and hazardous to nature. These nano oxides undergo chemical change eventually with dissolved CO_2 which is converted into $CaCO_3$ in presence of sunlight. The $CaCO_3$ are used for the softening and purification purpose of waterbodies. Hence by keeping in consideration of multipurpose and eco-friendly method, we studied the photo degradation of different types of dyes with CaO nanoparticles.

MATERIALS USED

Chemicals like azo dye, methylene blue, methyl red and methyl orange are produced by AR grade from Merck and Loba chemicals. The instruments like UV visible spectrophotometers by Systronics, the sonicators from labman

instruments. The nano particles were characterized in Central lab facility, Mysore University, Mysore, for scanning electron microscope and X ray diffraction studies.

SYNTHESIS OF NANO PARTICLES

The calcium oxide nano particles were synthesized by dissolving 100mg of $CaCO_3$ in 50mL of distilled water. The reaction was stirred for 30 minutes. The mixture is treated with the surfactant toluene and poly vinyl pyrollidine. The reaction mixture was treated with carbon dioxide by passing through cylinder. Then bubbling of CO_2 with $CaCO_3$ which gives CaOH on hydrolysis. Then it was stirred for 2-3 hours. Then decant the water and was filtered using whatmann's filter paper. Then it was dried in hot air oven. Then it's calcinated for 350°C for 2 hours. Then it was grinded and processed for certain fine particles of nano particles.

RESULTS AND DISCUSSION

The synthesized nano particles are well characterized by SEM, X ray diffraction studies. The size of nano particles were varied with 94nm to 156nm in nano scale. The characterized nano particles were stored and used for degradation of different organic dyes with 1ppm solution.

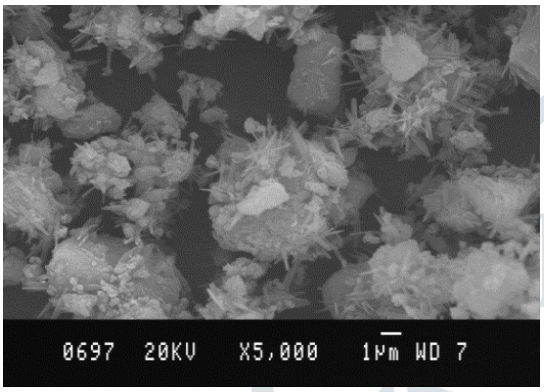


fig showing the SEM image of CaO (×5000)

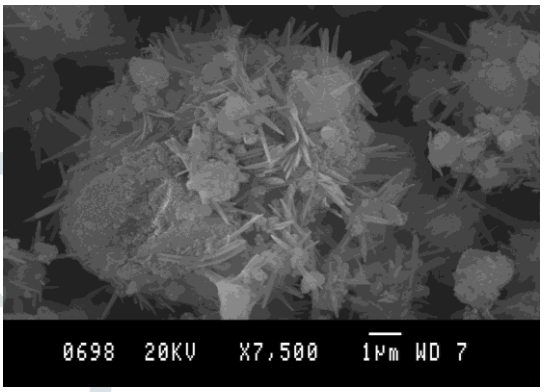


fig showing the SEM image of CaO (×7500)

XRD pattern of calcium nanoparticles exhibits dominant diffraction peaks. The crystallite size of calcium nanoparticles was found to be 94nm, the unit cell volume is 334 $Å^3$, and $\alpha=\gamma=90^0 \neq\beta$, $a\neq b\neq c$, (a=10.39Å, b=5.203Å, c=7.608Å). Accordingly calcium oxide nanoparticle belongs to monoclinic crystal system. The diffraction peaks at 28.15^0, 36.2^0, and 58.2^0 corresponds to Nb phase are seen in XRD pattern of CaO/Nb_2O_5 nanoparticles which confirms the presence of Nb (V) in CaO matrix

All of them can be perfectly indexed to amorphous not only in peak position, but also in their relative intensity. The peaks with 2θ values of 24.6^0, 38.3^0, 50.02^0 and 60.62^0 correspond to the crystal planes of (012), (110), (024) and (214) of crystalline Cr_2O_3, respectively. An average crystalline size, D_{hkl} was estimated using the Debye-Scherrer equation given below for all X-ray diffraction peaks.

$$D_{\text{hkl}}(A0) = \frac{K\lambda}{\beta\, cos\theta}$$

Where K is a shape factor which normally ranges between 0.9 and 1.0 (in our case K=0.9), λ is the X-ray wavelength, and β and θ are the half width of the peak and half of the Bragg angle, respectively. Using the above equation, the crystalline sizes of CaO nanoparticles which were synthesized from Mukia Maderaspatana plant extract found to be 65 nm.

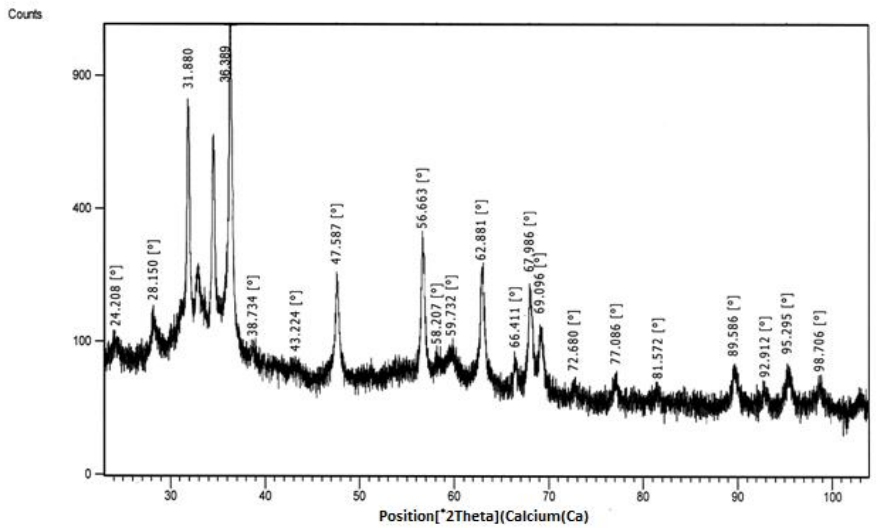
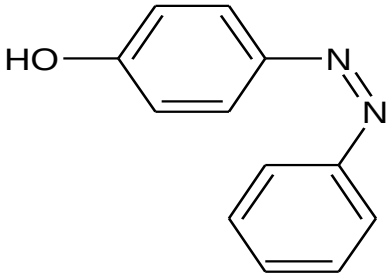


fig showing the XRD image of CaO

DEGRADATION OF AZO DYE

STRUCTURE OF AZO DYE:



The 76mg of azodye which is procured were dissolved in solvent and treated with CaO nano particles under sunlight and room temperature conditions. The decolourisation of the dyes was observed with time, when different concentration of CaO nano particles were added to each test tube containing 2mL of azodye solution which is then diluted with 8mL water. The absorbance had noted with time lapse. The λ_{max} of azo dye was obtained at 420nm. Then each test tube sample was analyzed at 420nm.

TO ESTIMATE THE WAVELEGNTH

Figure 1 shows the variation of absorbance for different wavelength and absorption maximum of azo dye was 0.28 at 420nm.

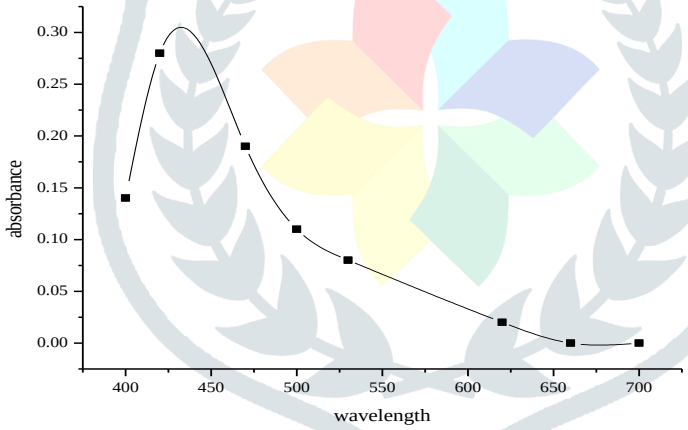


fig.1 shows the plot of absorbance v/s wavelength

DETERMINATION OF ABSORBANCE VALUE

The following data gives the variation of the absorbance with and without sunlight. The initial stage absorbance was more. After the time lapse the absorption gradually decrased which indicated the dye degradation and decoulouration of sample in the test tube. The dye degradation studies was done in different time interval like after 5, 10,15, 20 hours ofinterval.A valuable results were obtained under sunlight condition after 20 hours. The absorbance was completely decreaed. After 20 hours we had significant decrease in absorbance.

Table 1 showing the absorbance values for azo dye solution in presence and absence of sunlight after 5 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.28	0.28
1	0.25	0.29
2	0.18	0.19
3	0.18	0.13
4	0.14	0.20
5	0.16	0.15
6	0.15	0.16

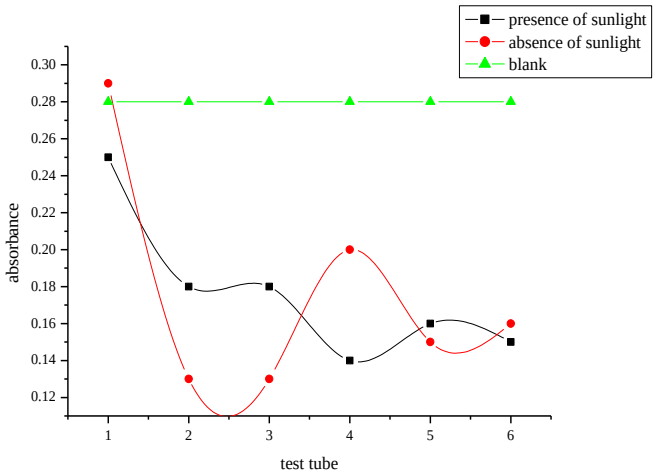


fig. 2 showing plot of absorbance values for different concentration of nano particles

Table 2 showing the absorbance values for azo dye solution in presence and absence of sunlight after 10 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.28	0.28
1	0.02	0.27
2	0.07	0.03
3	0.09	0.14
4	0.12	0.51
5	0.37	0.15
6	0.02	0.15

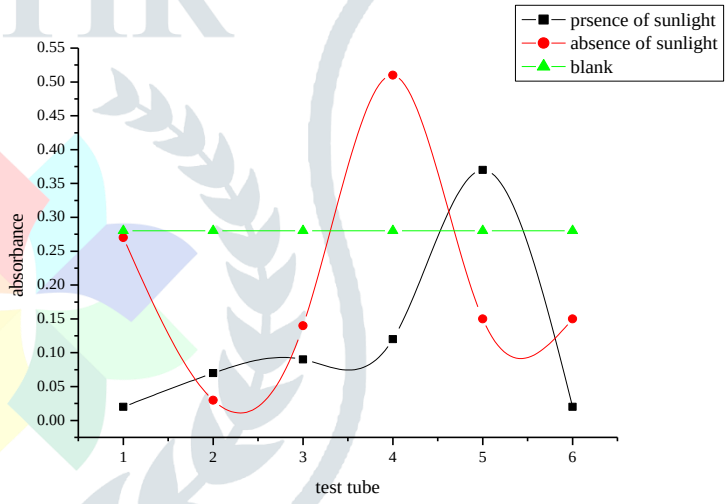


fig. 3 showing plot of absorbance values for different concentration of nano particles

Table 3 showing the absorbance values for azo dye solution in presence and absence of sunlight after 15 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.28	0.28
1	0.25	0.27
2	0.24	0.42
3	1.02	0.82
4	0.42	1.02
5	0.21	0.70
6	1.07	0.05

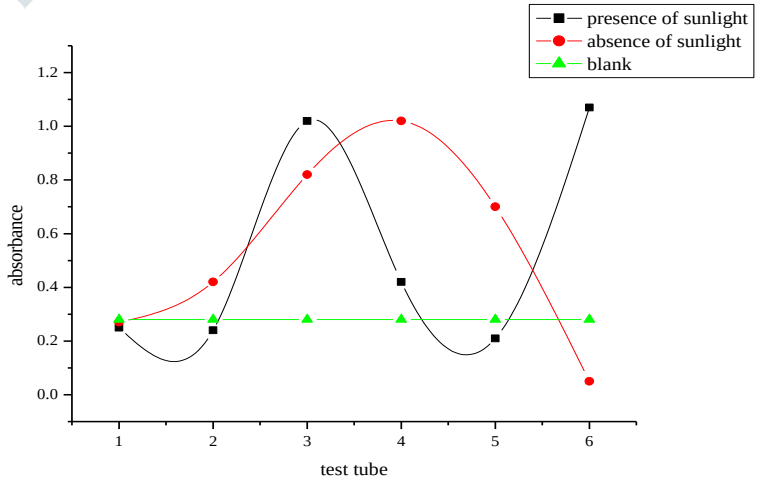


fig. 4 showing plot of absorbance values for different concentration of nano particles

Table 4 showing the absorbance values for azo dye solution in presence and absence of sunlight after 20 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.28	0.28
1	0.24	0.24
2	0.34	0.50
3	1.06	0.95
4	0.30	1.06
5	0.91	1.05
6	0.98	0.26

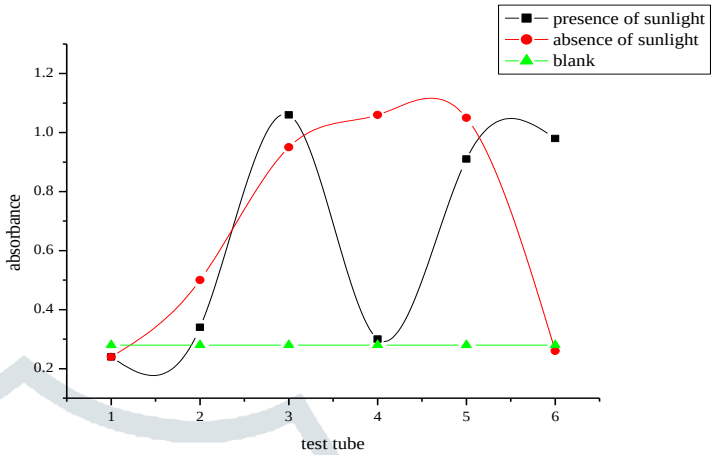


fig. 5 showing plot of absorbance values for different concentration of nano particles

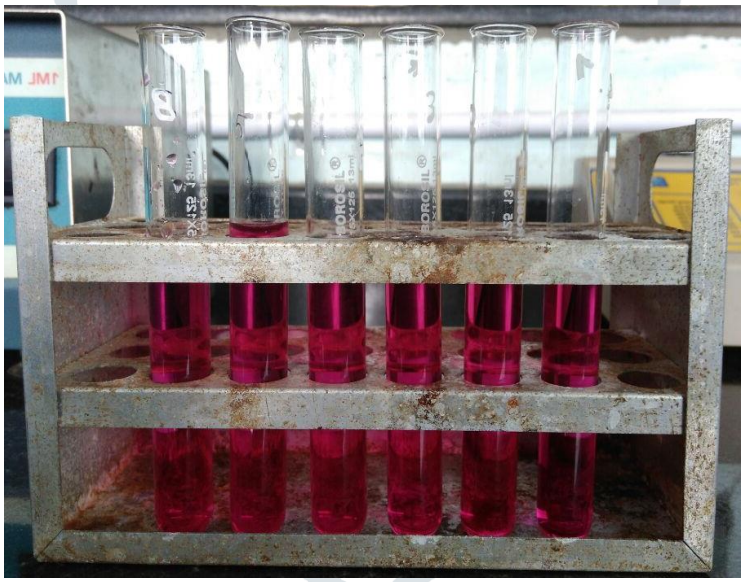
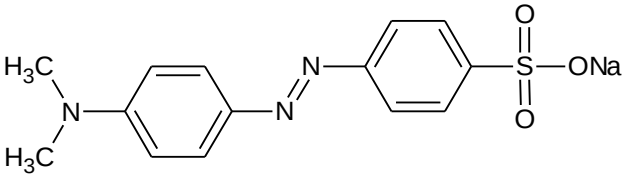


fig 6 showing the degradation of azo dye

The dyes which were used did not show the complete degradation. No much difference in the color was seen even after 24 hours and we concluded that CaO nano particles were not very much suitable for the breaking down of larger dye molecules.

DEGRADATION OF METHYL ORANGE

STRUCTURE OF METHYL ORANGE:



About 240mg of methyl orange was weighed and dissolved using solvent in a standard flask.10mL of this solution was pipetted out into 100mL standard flask and was made up to the mark. 1mL of this solution was diluted with 9mL of water. Different concentration of nanoparticles were added to each of test tube and shaken well. One batch was studied in presence of sunlight and other in absence of sunlight. An absorbance value for decolouration of dye with time was recorded. λ_{max} of a methyl orange was found to be at 420nm with absorbance value 0.45. Each test tube was analysed at 420nm.

TO ESTIMATE WAVELENGTH

Figure 7 shows the variation of absorbance for different wavelength and absorption maximum of methyl orange dye was 0.45 at 420nm.

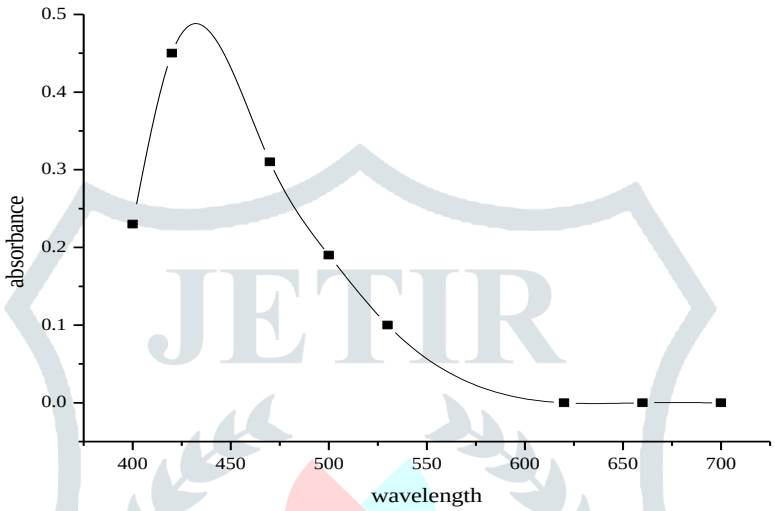


fig.7 shows the plot of absorbance v/s wavelength.

DETERMINATION OF ABSORBANCE VALUE:

The following data gives the variation of the absorbance in presence and absence of sunlight, after the addition of nano particles. Initially the absorbance was more and as time lapses there is gradual decrease in absorbance value. The decoluration of the sample was seen which indicated the dye degradation.

Table 5 showing the absorbance values for methyl orange dye solution in presence and absence of sunlight after 5 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
blank	0.45	0.45
1	0.45	0.44
2	0.43	0.38
3	0.43	0.36
4	0.43	0.40
5	0.45	0.37
6	0.45	0.42

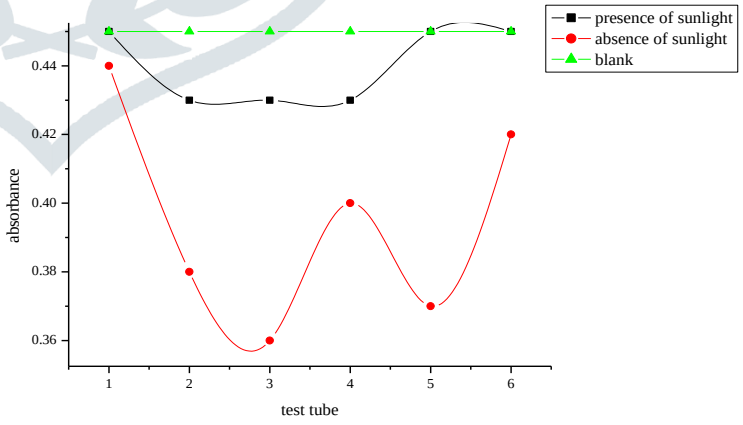


Fig. 8 showing plot of absorbance values for different concentration of nano particles

Table 6 showing the absorbance values for methyl orange dye solution in presence and absence of sunlight after 24 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.45	0.45
1	0.45	0.41
2	0.32	0.33
3	0.31	0.33
4	0.32	0.33
5	0.32	0.33
6	0.32	0.31

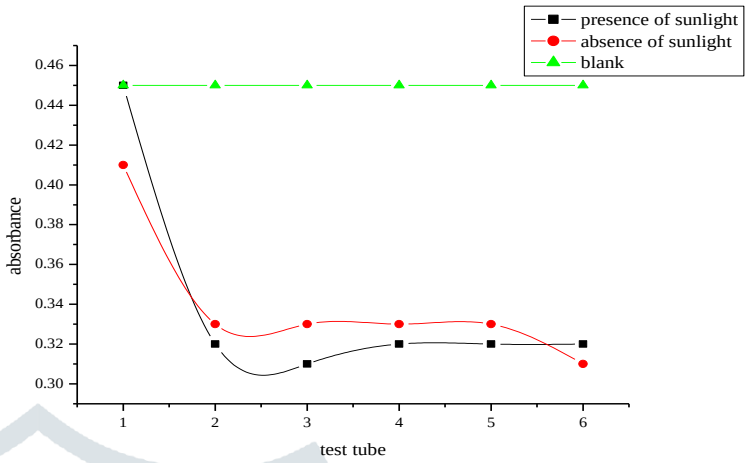
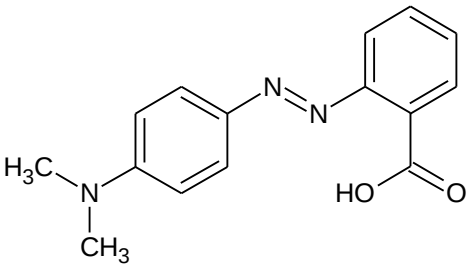


fig. 9 showing plot of absorbance values for different concentration of nano particles

fig. 10 degradation of methyl orange

The dye under study showed a no much changes in their absorbance value when it was subjected to photo degradation. On addition of nano particles, the dye started to degrade slowly as a result of which we observed the gradual decrease in the absorbance values. From this we concluded that the CaO was suitable to break down the dye but the reaction is very slow.

PHOTO DEGRADATION OF METHYL RED
STRUCTURE OF METHYL RED



About 201.9mg of methyl red was weighed and transferred to a standard flask and was made up to the mark with distilled water.10mL of this solution was pipetted out into 100mL standard flask and was made up to the mark. 1mL of this solution was taken in test tube and was diluted with distilled water to 10 mL.CaOnano particles of different concentration were

added to each test tube containing methyl red dye solution and were shaken well. Absorbance was noted and λ_{max} was found to be 500nm at absorbance value of 0.92.

TO ESTIMATE WAVELENGTH:

Figure 11 shows the variation of absorbance for different wavelength and absorption maximum of methyl red was 0.92 at 500nm.

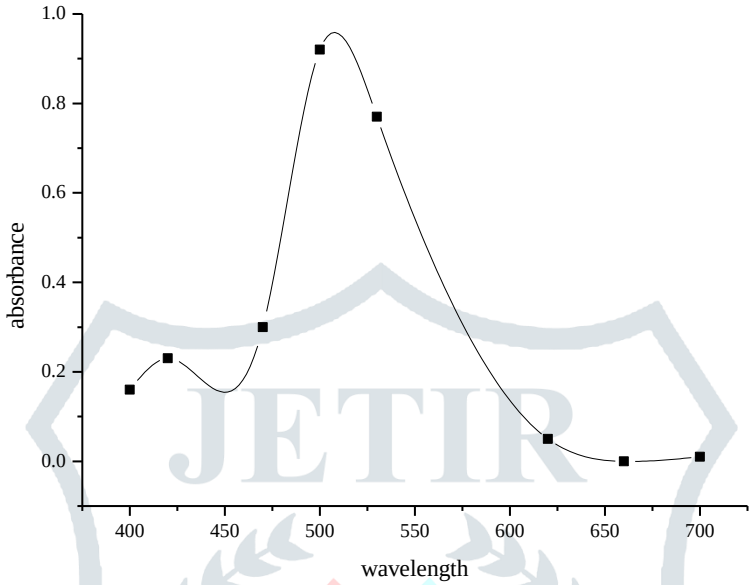


fig.11 shows the plot of absorbance v/s wavelength.

DETERMINATION OF ABSORBANCE VALUE:

The following data gives the variation of the absorbance in presence and absence of sunlight after the addition of CaO nano particles. Gradual decrease in the absorbance value was seen after 5,10 and 15 hours . The decolorisation of the sample indicates the degradtion . The absorbance values were completely decreased after 15 hour.

Table 7 showing the absorbance values for methyl red dye solution in presence and absence of sunlight after 5 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
blank	0.92	0.92
1	0.79	0.91
2	0.52	0.68
3	0.58	0.68
4	0.47	0.65
5	0.41	0.66
6	0.10	0.36

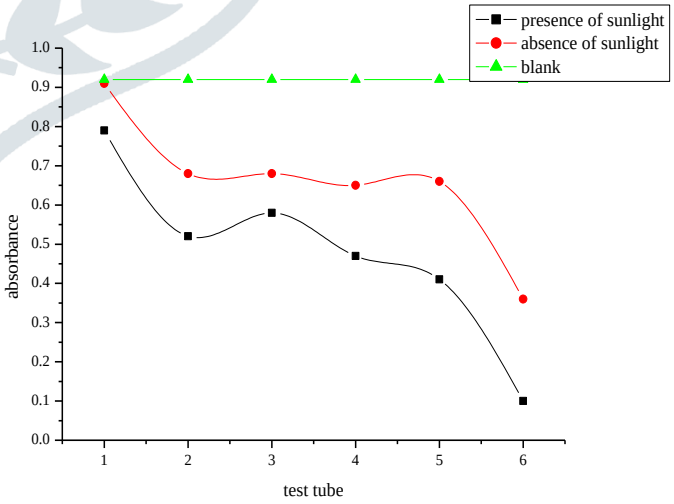


fig. 12 showing plot of absorbance values for different concentration of nano particles

Table 8 showing the absorbance values for methyl red dye solution in presence and absence of sunlight after 10 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.92	0.92
1	0.89	0.96
2	0.51	0.60
3	0.53	0.67
4	0.43	0.63
5	0.30	0.58
6	0.01	0.27

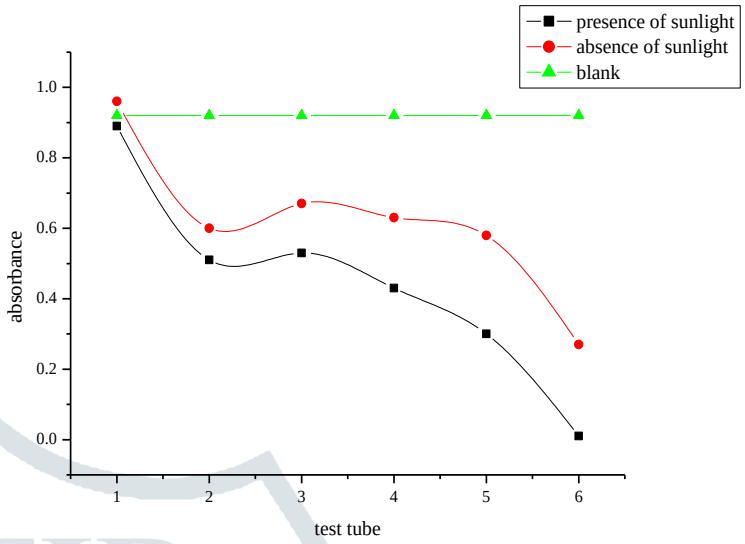


fig. 13 showing plot of absorbance values for different concentration of nano particles

Table 9 showing the absorbance values for methyl red dye solution in presence and absence of sunlight after 15 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.92	0.92
1	0.90	0.98
2	0.45	0.94
3	0.49	0.60
4	0.38	0.54
5	0.23	0.52
6	0.03	0.23

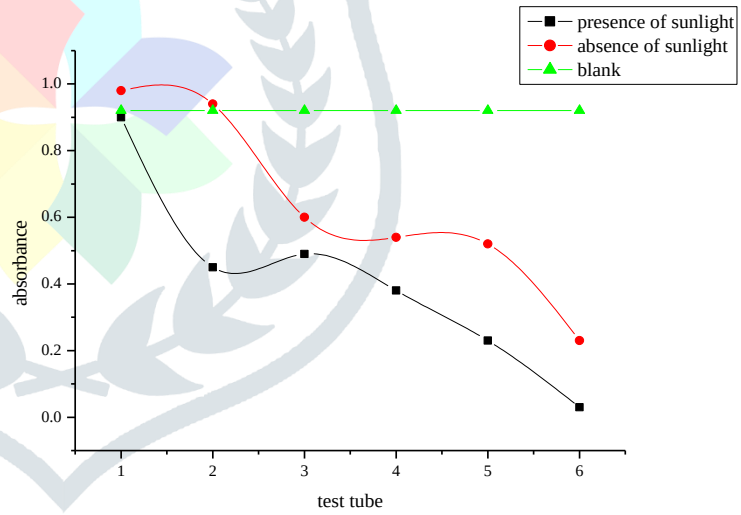


fig. 14 showing plot of absorbance values for different concentration of nano particles

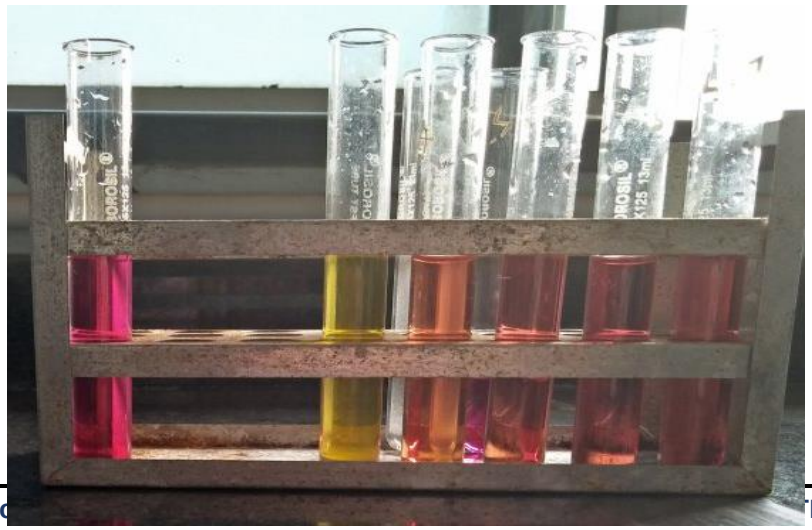
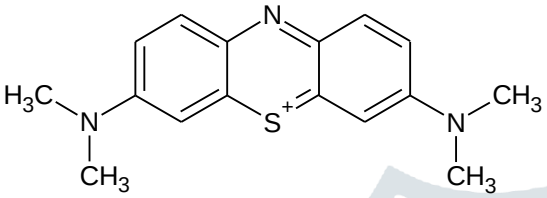


fig. 15 showing degradation of methyl red

Methyl red dye showed remarkable changes in the absorbance values. As the time lapsed the colour changes in the solution was seen which indicated the dye degradation. Dye which was under study was broken down successfully by CaO nano particles and the absorbance value significantly explained the decreased concentration of the dyes in the solution.

DEGRADATION OF METHYLENE BLUE

STRUCTURE OF METHYLENE BLUE



About 240mg of methylene blue was weighed and transferred to a standard flask and its solution was made. 10ml of this solution was pipetted out into 100ml standard flask and was made up to the mark. 1ml of this solution was taken in test tube and 9ml of water was added. Different concentration of CaOnano particles were added to each test tube. Test tubes were studied in presence of sunlight and in absence of sunlight. The $\lambda_{max}$was 660nm with absorbance 0.21.

TO ESTIMATE WAVELENGTH:

Figure 11 shows the variation of absorbance for different wavelength and absorption maximum of methylene blue was 0.21 at 660nm

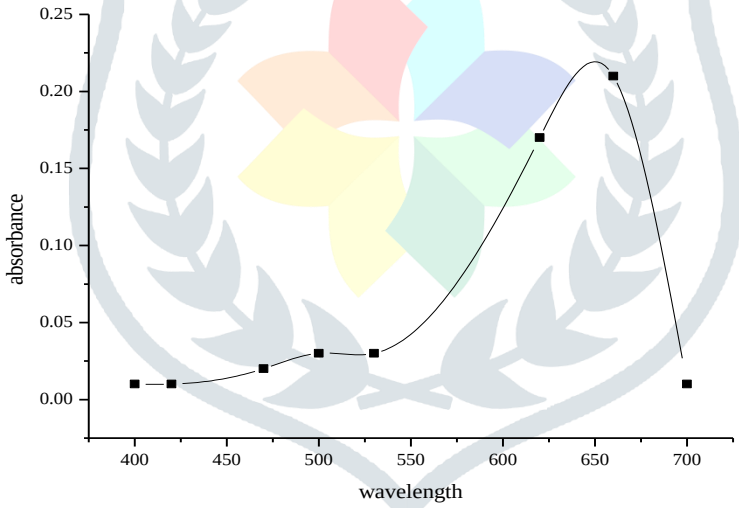
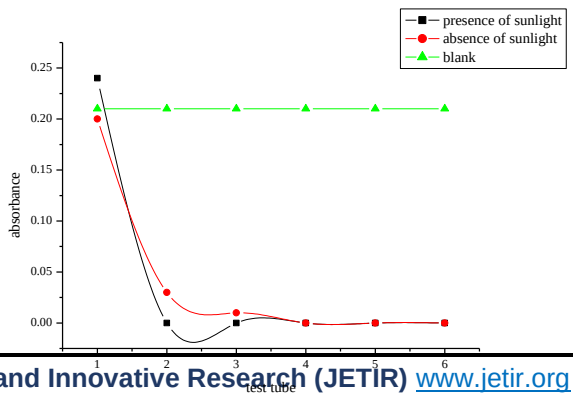


fig.16 shows the plot of absorbance v/s wavelength.

DETERMINATION OF ABSORBANCE VALUE:

The following data gives the variation of the absorbance in presence and absence of sunlight after the addition of nano particles .CaO nano particles has degraded this methylene blue dye completely. The absorbance values were completely decreased to zero. This was an remarkable result which was obtained. The study was done at 5 and 10 hours and absorbance values were noted down.

Table 10 showing the absorbance values for methylene blue dye solution in presence and absence of sunlight after 5 hours



Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.21	0.21
1	0.24	0.20
2	0.00	0.03
3	0.00	0.01
4	0.00	0.00
5	0.00	0.00
6	0.00	0.00

fig. 17 showing plot of absorbance values for different concentration of nano particles

table 11 showing the absorbance values for methylene blue dye solution in presence and absence of sunlight after 10 hours

Test tube	Absorbance in presence of sunlight	Absorbance in absence of sunlight
Blank	0.21	0.21
1	0.24	0.20
2	0.00	0.00
3	0.00	0.00
4	0.00	0.00
5	0.00	0.00
6	0.00	0.00

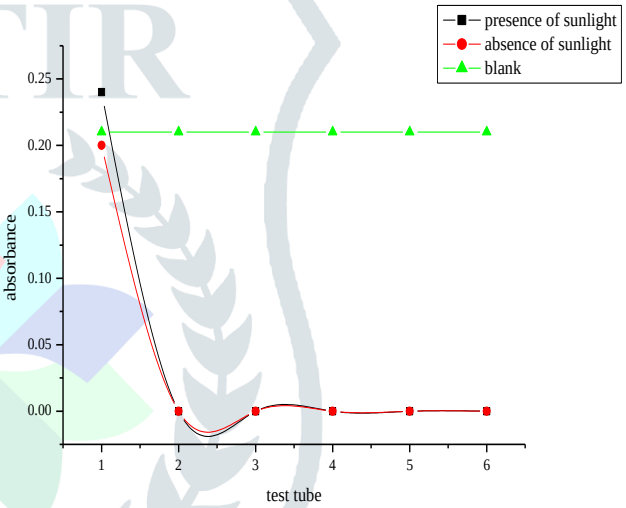


fig. 18 showing plot of absorbance values for different concentration of nano particles

fig. 19 showing degradation of methylene blue

The best result for the present study was seen in methylene blue dye. The dye was completely degraded both under the presence and absence of sunlight. There was no trace of colour seen in the dye solution and the resulting solution showed zero absorbance which concluded the complete degradation of the dye solution.

CONCLUSION

Nanotechnology is gaining importance due to the elimination of harmful particles and provides effective synthesis of expected products in an economical manner. Cao nano particles which were used in this study showed keen difference in the absorbance values in presence and absence of sunlight. Some of the dyes showed the remarkable decrease in the optical density and reached zero absorbance value. Whereas some dyes should gradual decrease which included the slow degradation of dyes. The overall conclusion that could be drawn is CaO nanoparticales which are used in the present study has got a great economic use in the field of industry as it degrades the dye within the short period of time and yields remarkable results which are satisfactory. The study revealed the catalytic action of CaO in breaking down of organic dyes into nontoxic form. The overview of this study was that CaO was a standard tool in degrading many toxic dyes. Because of this one can reduce the water pollution and safeguard the environment for the better future.

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