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Synthesis and characterization of nano zinc peroxide photocatalyst for the removal of brilliant green dye from textile waste water.

Prashant L. Chaudhari*, Pallavi C. Kale

Department of Chemical Engineering, BharatiVidyapeeth University College of Engineering, Pune, India

Abstract: The zinc peroxide nanoparticles were synthesized by using oxidation-hydrolysis-precipitation process.With zinc acetate as a predecessor,Hydrogen peroxide used as a oxidizing agent and polyethylene glycol 200 (PEG 200) was used as a surface modifier. Characterization of zinc peroxide nanoparticles was done by X-ray diffraction [XRD], Fourier transformer infra red [FTIR] and transmission electron microscope [TEM]. The parameters like pH, dye concentration, dosage of nanoparticle catalyst, temperature and contact time were studied for the application of Zinc peroxidenanopaticle as a catalyst for removal of a Brilliant green dye from synthetic sample. Excellent degradation efficiency of brilliant green dye was 86.68% achieved by zinc peroxide with PEG as a catalyst and 84.16% achieved by zinc peroxide without PEG as a catalyst at 120 min of photo catalytic reaction.The maximum degradation efficiency of brilliant green dye (86.68%) was achieved at the optimum operational conditions: initial concentration of dye 9mg/l, catalyst dosage of 200 mg, pH of solution will be in between 6-7.

Keywords : Zinc peroxide nanoparticles, Brilliant green dye, Zinc oxide, Textile waste.

Introduction

The consumption of dyes was highly increased by textile industries in recent years and because of this scenario large amount of coloured wastewater from such industries create serious problems to the environment. From the last few years, colour removal from textile dyeing effluents has been the target of great attention,the reason is not only its toxicity but mainly due to its aesthetic effect and this cause even at lower concentrations, comparing to many other chemicalsfound in wastewater. Because of dyes large amount of surface water get polluted. More than 10000 dyes are available in textile business sector around the world[1].Most of the dyes are not get easily degradable, just only 1 mg/lit dye concentration can also make surface water polluted.

For clean and safe water it is necessary to remove dyes and because of this the quality of all life improved. For all the leaving organisms water is very important part but water is easily get polluted because of the many dyes. Small amount of dye concentration in water also affect surface water, and it is very dangerous to environment. Photocatalyticdecolourizationrequires lightenergy to activate nanoparticles to for decolurizationdyes and it produces less toxic byproducts. The waste water of textile and dye industries are considered to be the most polluting industries and highly hazardous to aquatic living being because they cause serious damage to the surrounding environment[2,3]. So it is very important to treat the waste water. There are many methods techniques for treatment of waste water such as adsorption [4,5],coagulation [6,7],ion flotation[8] and sedimentation[9].All these techniques are versatile and useful, but they all produce secondary waste which needs

treatment further.Many methods widely used for the removal of dyes but adsorption is low in cost but it is not reusable and produce toxic waste.Another set of techniques that are relatively new, more powerful and very efficient called Advance Oxidation Processes (AOPs) has been developed and employed to treat dye-contaminated wastewater effluent[10].

Brilliant green (BG) is a member of triphenyl methane dyes which are extensively used in textile industry for dyeing nylon, wool, cotton, silk as well as for coloring of oils, fats, waxes, plastics and varnishes. BG is considered as highly toxic to both humans and animals since it causes irritation of respiration and gastrointestinal tracts leading to diarrhea and vomiting. Many countries banned on BG due to its carcinogenic nature [11,12,13].Molecular formula of BG is $C_{27}H_{34}N_2O_4S$ (Mol. Wt = 482.62 g/mole) [14]. On the other hand, heterogeneous photocatalysis under visible light offers distinct advantages besides being an energy saving green technology.

Zinc peroxide is mostly produced by adding one of the following: Zinc oxide; Zinc hydroxide; Zinc nitrate; Zinc chloride, Zinc carbonate in a solution of hydrogen peroxide, with an additional light energy as a source [15,16]. Nanocatalyst of zinc peroxide can be used as predecessor for preparation of nanoparticles zinc oxide. The surface modifier is used as a polyethylene glycol 200 (PEG 200). To analyze the efficiency of the PEG(200) as nanoparticle stabilizer, the nanopartical of zinc peroxide has been produced in two different types: zinc peroxide without PEG200 (ZnO_2WOPEG) and zinc peroxide with PEG200 (ZnO_2WPEG)[17].In present work, synthesis of zinc peroxide had done by using zinc acetate, hydrogen peroxide and polyethylene glycol. It used for degradation of brilliant green dye.

Experimental

Materials:

All the chemicals used in this experiment are A.R. grade and brought from reputed companies.Zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was brought from the High purity laboratory chemicals private limited, Mumbai-400002; 50% hydrogen peroxide aqueous solution(H_2O_2); PEG 200[H(OCH2CH2)*n*OH]; and sodium hydroxide[NaOH]wereprocured from Sigma Life Science. Brilliant green dye was brought frommerckspecialities private limited Mumbai.

Preparation of ZnO_2 nanoparticle solution:

Zinc peroxide nanoparticles were prepared by dissolving 3 gm of elemental Zinc acetate dehydrates in 30 mL of deionized water. To the resulting dispersion 120ml of PEG 200 and 9 ml of H_2O_2 (50%) were added slowly. This complete procedure carried out at room temperature and continuous stirring was kept constant for all the experiments. After the continuous stirring of two hours a clear and colorless solution is converted intoyellow colour[21]. In this process different type of stirring process were used as shown figure 1. It observed that ultrasound sonication stirring got maximum yield as compared to other stirring process.

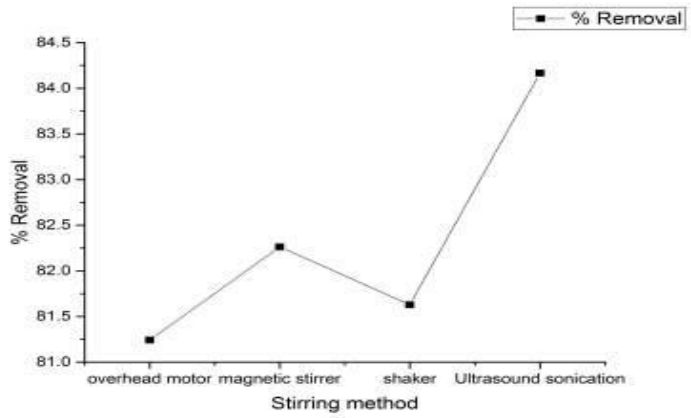


Figure 1: Different type of stirring process

Preparation of ZnO_2 nanoparticle powder:

After continuous stirring of 2 hours, add NaOH solution of 4N wasadded to form a basic medium. After addition of the 4N NaOH, the white color precipitate produced. Add NaOHuptopH value of solution was 11.5 obtained.

Then by centrifuge process, white precipitate was separated from the solution mixture and after the centrifugation process slurry type mixture formed. Then mixture washed at least five to six times by NaOH solution. Finally maintain the pH of the residue water 8.4 by applying 10-12 additional washes of distilled water. The white colored precipitate was dried at 80°C for two hours in anoven[17].

Removal of brilliant green dye:

A stock solution (1,000 mg/l) was prepared by dissolving a 1gm of dye in 1 litredistilled water and was diluted to the required initial concentrations. Batch experiments were carried out tostudy the effect of various parameters such as the pH, adsorbent dose, temperature, contact time and initial brilliant green dye concentration To study the effect of these parameters, initialdye concentration (1 to 15 mg/l), adsorbent dosage (0.1 - 1 g/100 ml), pH (1 to 12), contact time of 10 to 180 min and agitation rate (150 rpm), were considered .The pH of solutions measure by using pHmeter. For each experimental run, 100 ml of dye solutions with different concentration and at a known pH and a known amount of the adsorbent were taken in a 500 ml conical flask. For investigation of the effect of initial dye concentration.The samples were mixed by use of a magnetic stirrer at a constant speed of 150 rpm in presence of UV lamp. In order to separate the adsorbents from the aqueous solutions, all samples were centrifuged and after that the samples was measured by UV spectrophotometer. Ultra violet (UV)-visible spectra have been acquired between 200 and 800 nm with a UV-Visible spectrophotometer. Dye concentration in solutions measured by UV-Visible spectrophotometer at λmax = 720nmfor brilliant green dye. The removal efficiency of dye was calculated using the following equation:

$$\% \text{ Removal} = \frac{(C_0 - C_t)}{C_0} \times 100$$

Where C_0 and C_t (mg/l) are the initial dye concentration and concentration at time (t), respectively[18].

Characterization

X-ray diffraction analysis:

Figure 2a and 2b shows XRD diffraction pattern of Zinc peroxide nanoparticles. Figure 2 shows the crystal structure and phase purity of the ZnO_2. The peaks are indexed as 31.8º (452), 36.2º (626), 47.5º (168), 56.7º (233), 62.8º (196), 66.06º (200), 68º (169) and 69 (109) respectively. From this it is proved that pure nanoparticles of zinc peroxide weresynthesized[19].

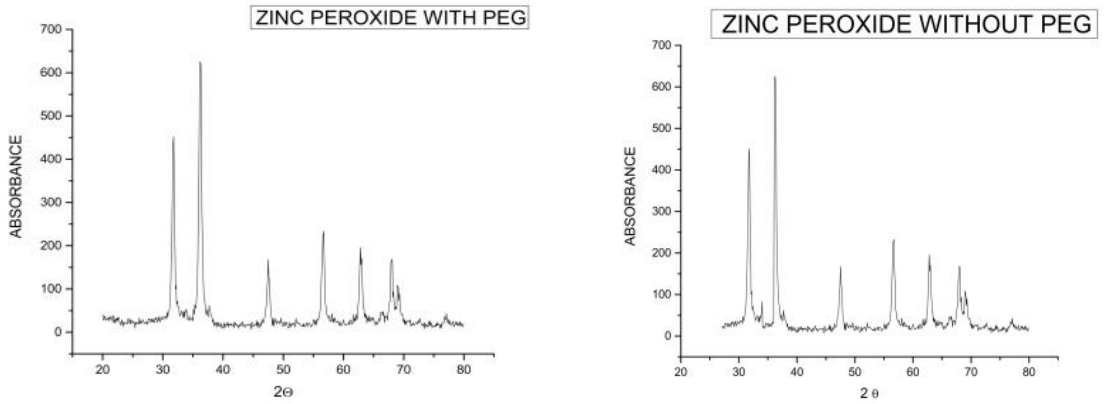


Figure2 (a):XRD patterns of zinc peroxide with PEGnanoparticle Figure2 (b): XRD patterns of zincperoxide withoutPEG nanoparticle

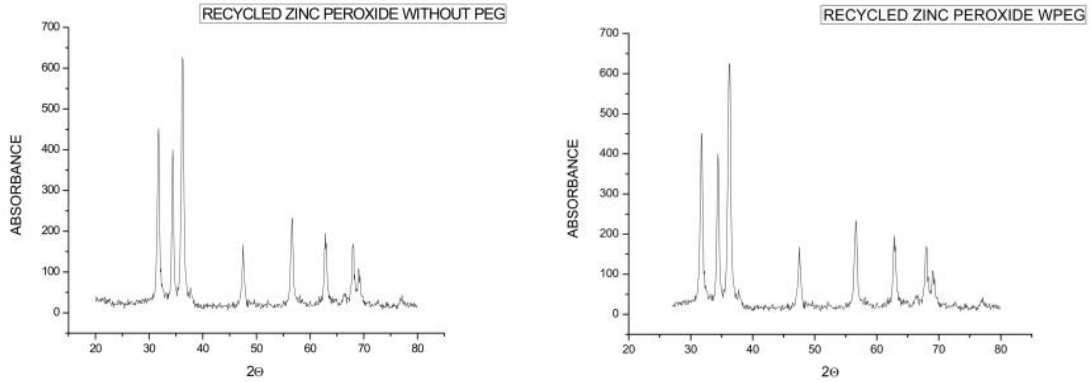


Figure3 (a):XRD patterns ofrecycled(1st cycle)Zincperoxide nanoparticle without PEG Figure3 (b):XRD patterns of recycled(1st cycle) zincperoxide nanoparticle with PEG

Figure 3a and 3b shows that zinc peroxide sample after thermal treatment convertedinto Zinc oxide nanoparticles. The peaks are indexed as 31.8º (452),34.4º(400), 36.2º (626), 47.5º (168), 56.7º (233), 62.8º (196), 66.06º (200), 68º (169) and 69 (109) respectively. From this it is proved that pure nanoparticles of zinc oxide were synthesized[20].

Transmission Electron Microscopy:

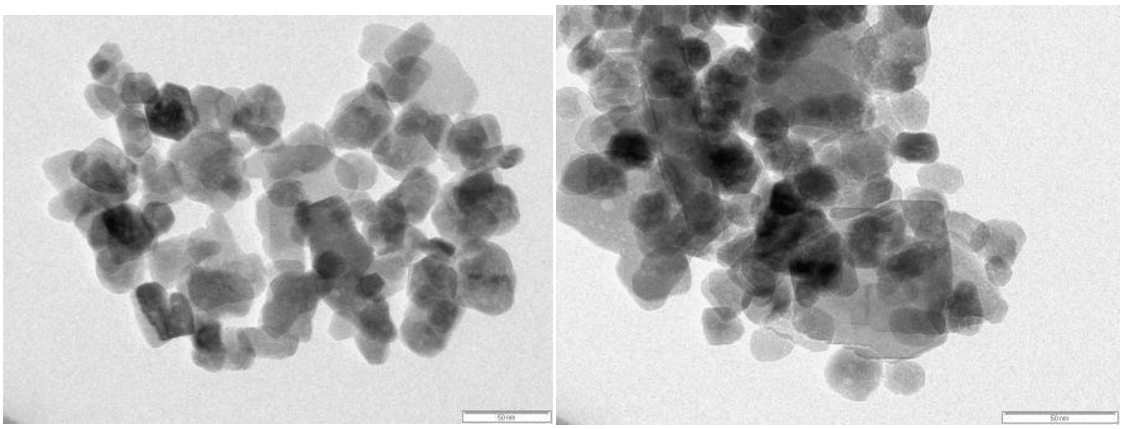


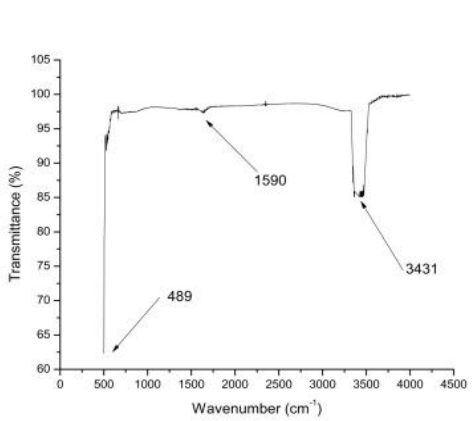
Figure4 (a):TEM of ZnO_2 without PEG Figure4(b): TEM of ZnO_2 with PEG

Figure 4 (a & b) show the TEM images of ZnO_2 nanoparticles. TEM analysis was done at IIT, Powai using TEM CM 200 of the PHILIPS company. The morphology and microstructure of the zinc peroxide nanoparticles was obtained by using TEM analysis.

TEM observations of the Zinc peroxide without PEG and zinc peroxide with PEG, examine a slight difference between the agglomeration shapes as shown infigure 4a.Zinc peroxide without PEG formed dense agglomerates, whereas infigure 4b.zinc peroxide with PEG created smaller size agglomerates.

FTIR spectroscopy:

Figure 5 (a& b) shows FTIR spectra of nanoparticles zinc peroxide. Metal oxides generally give absorption bands in fingerprint region i.e. below 1000 cm^{-1} arising from inter-atomic vibrations. Absorption peaks are obtained at 3431 and 1590 cm^{-1} to the stretching vibration of the O-H bond and the bending vibration of H-O-H from water moleculesrespectively. The peak at 489 cm^{-1} shows the absorption band of the samples.[21]



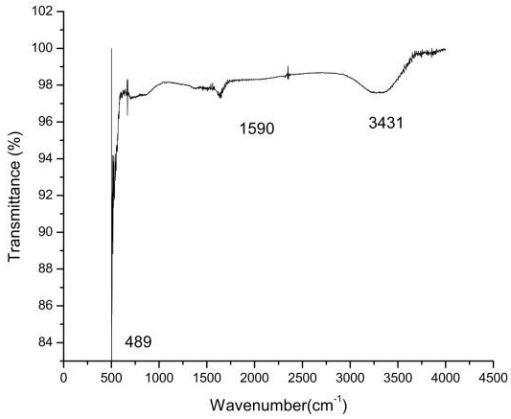


Figure5(a):FTIR of $ZnO_2$with PEG Figure5(b): FTIR of ZnO_2without PEG

Result and Discussions:

Effect of doses and time:

The effect of contact time on % removal of Brilliant green dye (5 mg/litre) at differentdosageof nanoparticles of zinc peroxide as shown in figure.6 and 7. The plots proves that as the dosage of nanoparticles zinc peroxide with PEG and zinc peroxide without PEG increased from 100 to1000 mg ,the maximum % decolourization of brilliant green dye was83.6028% and 82.17198% respectively shown in figure 7. Thus, maximum decolourization achieved at 120 min as shown in figure 6[22]

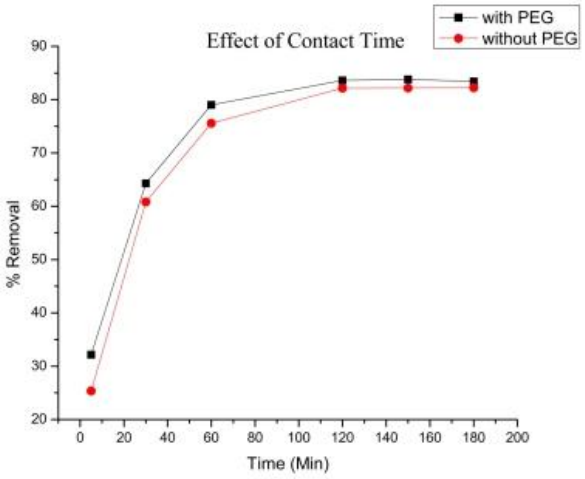


Figure6:Effect of contact time on removal of BG dye by using nanocatalyst as zinc peroxide with PEG and zinc peroxide without PEG (Dye concentration= 5 mg/lit, Temperature-30^{o}C,pH-6.5, Catalyst dose-200mg)

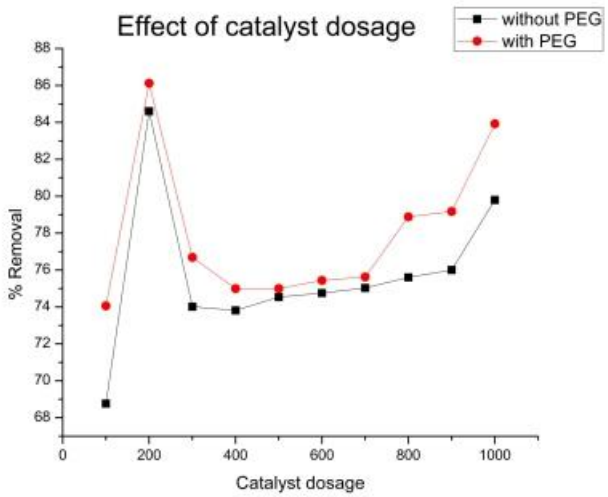


Figure7:Effect of catalyst dosage on removal of BG dye by using nanocatalyst as a zinc peroxide with PEG and zinc peroxide without PEG(Dye concentration-5 mg/lit, Temperature-30^{o}C,pH-6.5, Time- 120 min)

Effect of initial dye concentration:

As shown in figure 8, the effect of Brilliant green dye concentration was studied by varying concentration from 1 to 15 mg/L, the % removal of dye efficiency got decreased for the same amount of nanoparticle zinc peroxide concentration. The dye decolourizationstudy was performed using 200 mg/100ml nanoparticle by taking 9 mg/litre of the dye for 120 min and pH of solution was 6. Figure 8shows the % removal of the dye solution after decolourization. The absorbance of the dye solution has remained constant after 9 mg/litre at wavelength (622.4 nm) disappearing completely. The maximum % decolourization was observed at 9mg/L for zinc peroxide with PEG it was 86.68623% and for zinc peroxide without PEG it was 84.16476% (for 120 min).

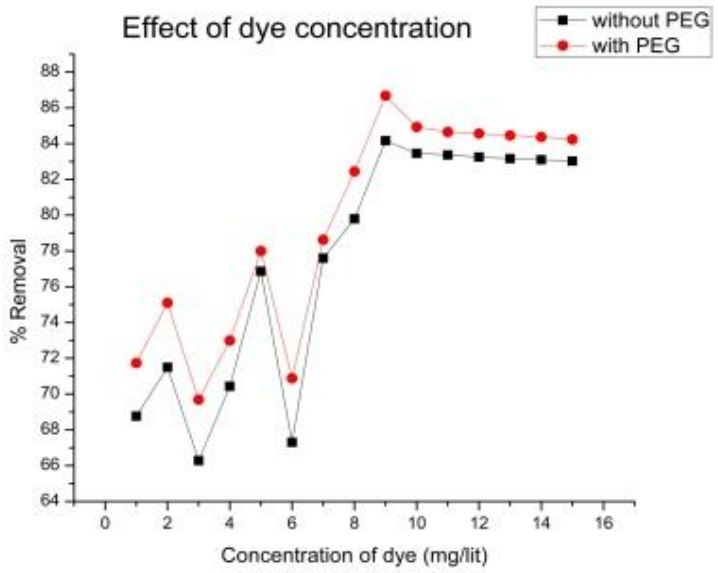


Figure8:Effect of dye concentration on removal of BG dye using nanocatalyst as a zinc peroxide with PEG and zinc peroxide without PEG (Temperature-30^{o}C,pH-6.5, Catalyst dose-200mg, Time- 120 min)

Effect of pH:

In this work, we studied the effect of pH on dye degradation in the range of 3–12 pH Solutions were prepared with a dye concentration of 9 mg/l and their pH was adjusted using 0.1 N HCl and 0.1 N NaOH. .The used catalyst dose was 200mg and maximum time was 120 min. Figure. 9shows % removal of the dye at different pH values. It can be seen that maximum % removal with zinc peroxide with PEG was observed at pH 6 (85.43041 % in 120 min) and zinc peroxide without PEG was observed at pH 6 (83.25879 % in 120 min)

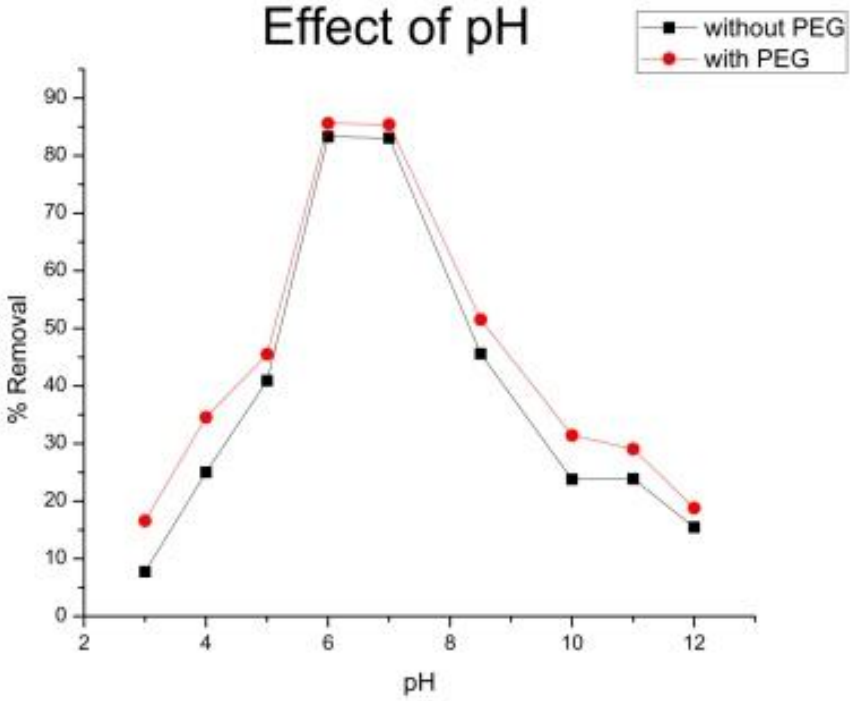


Figure9:Effect of pH on removal of BG dye by using nanocatalyst as a zinc peroxide with PEG and zinc peroxide without PEG (Dye concentration-5 mg/lit, Temperature-30^{o}C, Catalyst dose-200mg, Time- 120 min)

Effect of temperature:

Effect of temperature on the photocatalytic removal of brilliant green dye was investigated in the range of temperatures 25^0C to 55^0C.The used catalyst dose was 200mg, and the pH value of solution was kept 6 and dye concentration 9 g/ litre. The photocatalyticdye removal were increased with as increase of the reaction temperature to approach 91.84871% for the used dye aqueous solution at temperature 55^0C, and the obtained results are shown in Figure 10.

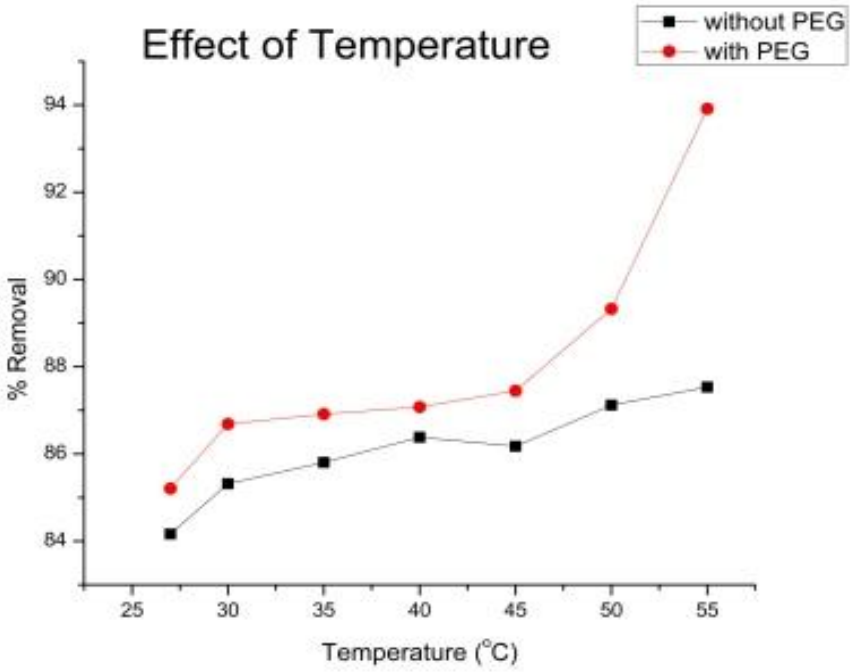


Figure10: Effect of temperatureon removal of BG dye by using nanocatalyst as zinc peroxide with PEG and zinc peroxide without PEG (Dye concentration-5 mg/lit,pH-6.5, Catalyst dose-200mg, Time- 120 min)

Recycle of the used catalyst zinc peroxide:

Reuse of the catalyst which wasused in the removal of Brilliant green from the wastewater was performed using solvents to wash the used catalyst with distilled water many times, thenit was dried at 300^oC in oven for ten hours to remove the sticking molecules of dye[17].

$$ZnO_2 \xrightarrow{} ZnO_{(s)} + \frac{1}{2}O_{2\,(g)}$$

The obtained material was converted from zinc peroxide to zinc oxide and it was characterized by XRD test as shown in figure. 3.a. and 3.b.then obtained zinc oxide was used in the removal of brilliant green dye using the same optimum conditions that were used for zinc peroxide and the obtained results are shown in Figure 11. From these figure it was found that the first use catalyst and the second use gave the removal efficiency for this dye 86.68623 and 74.29609 respectively. After fifth time of use, the efficiency of % removal was decreased upto 47.2202%. The % removal of recycled catalyst goes on decrease as per the every cycle.

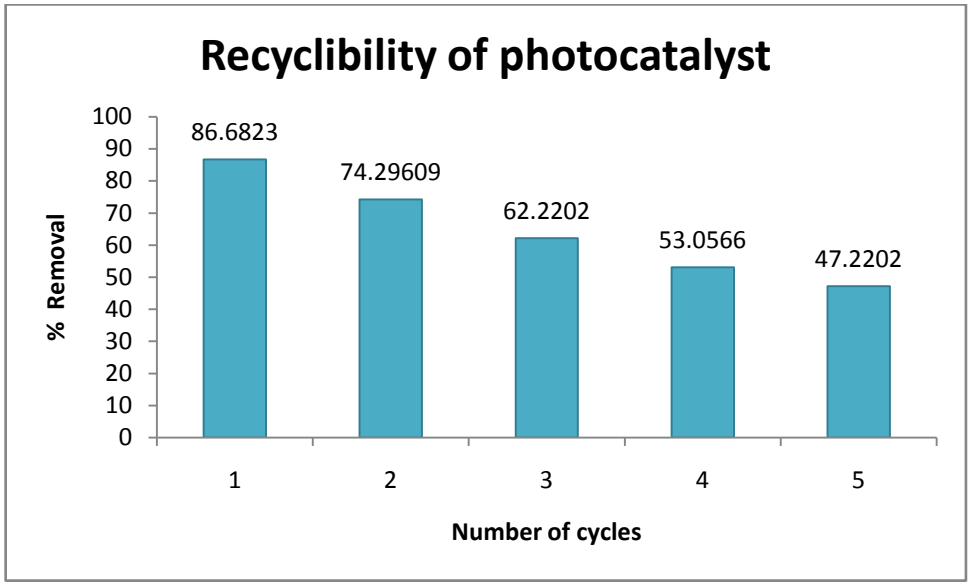


Figure11: Recyclibilty of photocatalyst

Conclusion:

StabillisedZnO_2 nanoparticles were synthesized by using ultrasound sonication process. For characterization different techniques were applied(XRD, TEM, FTIR). The photocatalyicdecolourization of Brilliant green was achieved successfully by two catalyst i.e. zinc peroxide with PEG and zinc peroxide without PEG.From the result we come to know that the photocatalyticdecolourization of dye with nanoparticles of catalyst zinc peroxide depend on the concentration of dye, dosage of photocatayticnanopaticles ,Contact time,pH of solution, Temperature of solution. It was found that the optimal amount of catalyst used was 200mg/lit. It has been observed that at 10 mg/lit maximum decolourization occurs. The decolourization is favored in neutral solution. The optimal time to be required was found 120 min.

The recycling of zinc peroxide can be performed up to five cycles. After use of first cycle the heat treatment was done on used zinc peroxide and after that zinc peroxide was converted into zinc oxide.

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