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Efficiency study of photo catalytic degradation of Rhodamine B using CuO and Zn doped CuO nanoparticles of varying composition

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Abstract:Among the transition metal oxides, CuO is a potential candidate for magnetic storage devices, solar energy transfer, sensors, and super capacitors and especially it acts as a good catalyst in some of the chemical reactions. CuO and Zn doped CuO nano particles are prepared by sol gel technique. The CuO Nano particles were characterized for the studying of their structure and composition from X-ray diffraction, Energy Dispersive X-ray analysis and FESEM for morphology and size of the particles. Then all the catalysts synthesized were used for photocatalytic degradation of Rhodamine B under different experimental conditions. Percent degradation of Rhodamine B by Zn doped CuOnanocatalyst after 1st run achieved up to 85.6% in 120 min. The recycle study reveals stability of the catalyst.

IndexTerms **-CuO Nano-particles, Zn doped CuO nanoparticles, photocatalytic degradation of Rhodamine B.**

I. INTRODUCTION

Wastewater disposal is a major problem in most parts of the world today as the west water from many types of chemical and dyeing industry [1]. One of the recalcitrant pollutants in wastewaters dyes are present in west effluent from dyeing industry. Which introduces naturally non degradable hazardous chemicals and intermediates in natural sources of water making it not only unfit to living organisms but hazardous for living kingdoms [2,3]. They are used in a variety of industries, and have been found to be carcinogenic in man [4]. There are more than 3000 known organic dyes, half the number belongs to the class of Azo dyes [5]. Well-known by their characteristic –N=N- (azo) group, [6] these compounds are often preferred due to the relative ease with which they can be synthesized, the wide variety of colors which they offer, their relatively good adherence and long-lasting aesthetics [7,8]. However, they have also been found to comprise mutagenic and carcinogenic compounds when incompletely broken down. Another well-known class of dyes are the Rhodamines. Mostly used in the paper, pharmaceutical and cosmetic industries, the extent of their toxicity to man is yet to be clearly defined. With these dyes often released into the environment in wastewater, it is essential to find appropriate ways of rendering the wastewater harmless prior to its release into the environment [9].

Worldwide there are number of metal oxides available but some of the metal oxides are most useful in accordance with their applications in day-to-day life in science and technology. Metal oxides like ZnO, TiO_2, and Fe_3O_4 etc. proved as potential candidates for so many applications. In the same way CuO is also one of the useful metal oxides and which has range of applications in different fields [10]. The nanostructures of CuO, as a p-type semiconductor with narrow band gaps of 1.2−1.4 eV has generally been used as catalysts ultraviolet and/or visible light-driven photo catalyst. In the present study, a simple and original method for the synthesis of nanosized CuO by sol-gel technique in nano and micro micelles is described [11-13]. The morphology, crystallographic structure, surface properties and size of CuO particles are characterized by means of Field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) which will give much valuable information about these materials. Copper oxide nanoparticles have been of considerable interest due to the role of CuO in catalysis, Due to the potentiality of CuO, it acts as a catalyst; whereas all metal oxides are not useful for the catalytic activity [14,15].

II. EXPERIMENTAL

2.1 MATERIALS

Solution of Rhodamine B of variable concentrations were prepared in distilled water and pH maintain to 8. The 50 ml Rhodamine B, solution mixed with CuO and Zn doped. CuO nano catalyst taken in the photo reactor. The solution was stirred for 2 hours in the dark to allow equilibration of the system so that the loss of the compound due to adsorption can be taken into account. The dye sensitized CuO and Zn doped CuO was subjected to visible light irradiation for the degradation of Rhodamine B. The catalyst was separated from the solution by centrifugation and the solution was analyzed for determining concentration of dye at λ_{max}555 nm. The reaction kinetics was studied by varying different parameters like initial concentration of dye, catalyst dose and effect of pH on the Rhodamine B solution.

2.2SYNTHESIS OF CuO AND Zn DOPED CuO

The CuO nanoparticles and Zn doped CuO nanoparticles were prepared by sol-gel method. In this method 50 ml $CuCl_2 \cdot 2H_2O$ (0.15 M) is added with 2ml Glacial acetic acid and heated to 100^0C with continuous stirring. To control the pH of the previous solution, NaOH is added to the solution till pH reached desired value. The color of the solution changed from sky blue to black with precipitation. For synthesizing Zn Doped CuO nanoparticles stochiometric amount of $ZnCl_2$ was dissolved in procure solution to get desired dope composition [10,16]. The black precipitation obtained was washed 3-4 times with distilled water. Finally, the solution was centrifuged and dried in air for 24 hours and then calcinated at 300^0C in a muffle furnace for three hours. The powder obtained on cooling was finely crushed. The CuO nanoparticles were characterized by studying their structure with X-ray diffraction (XRD) and composition by energy dispersive X-ray analysis (EDS). The morphology of the nanoparticles was estimated by XRD and Field emission scanning electron microscopy (FESEM).

III. RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION ANALYSIS

XRD pattern of as prepared CuO and Zn doped CuO nanoparticles are shown in Fig. 1. It represents a single-phase with a monoclinic structure. Lattice parameters are a = 4.84 Å, b = 3.47 Å, c = 5.33 Å. No peaks of impurities are found in XRD pattern. The XRD pattern exhibit peaks at 2θ 32.56^0, 38.78^0, 49.10^0, 52.33^0, 59.23^0, 62.37^0 and 69.00^0 corresponding to the (002), (111), (111/200), (202), (020), (202), (113) and (311) reflections of the CuO and Zn doped CuO phase.

The intensities and positions of peaks are in good agreement with the reported values (JCPDS file No. 05-661).

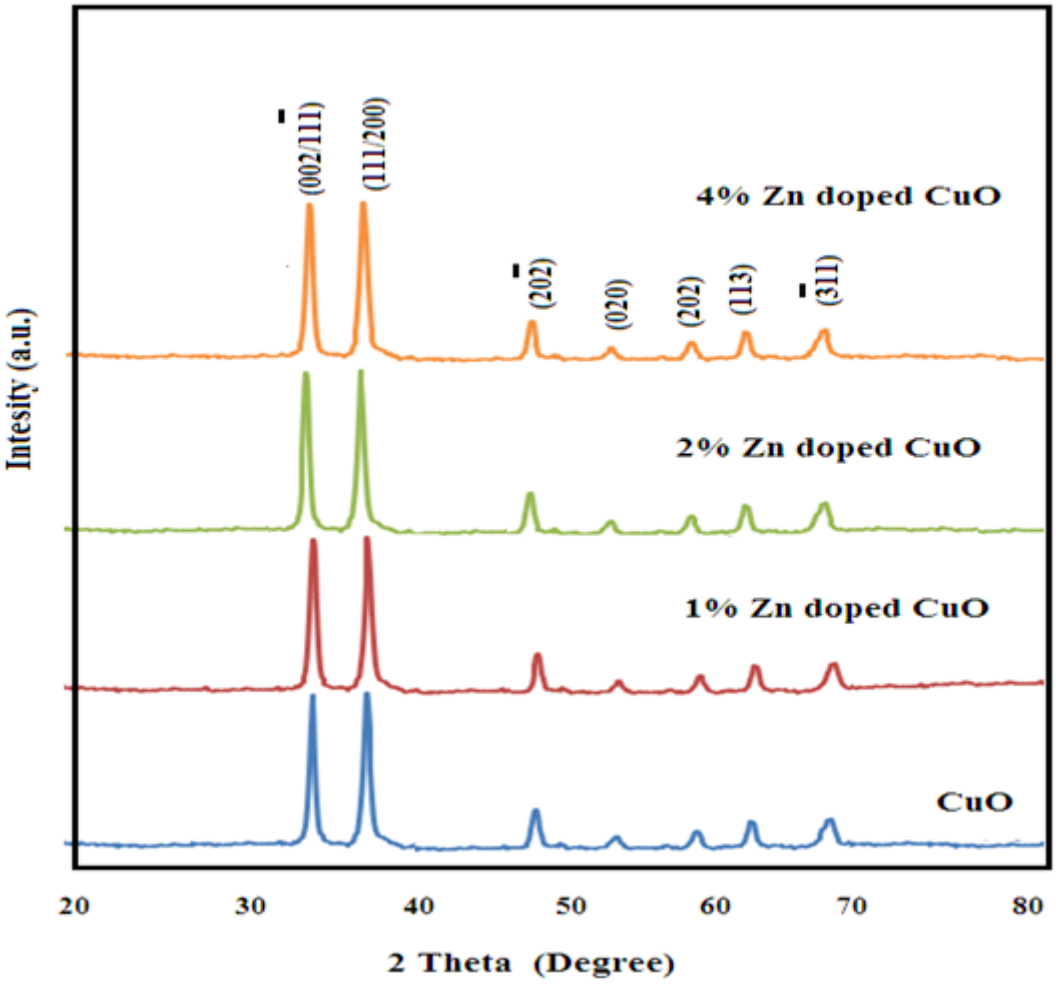

Fig.1 XRD of CuO and Zn doped CuO.

3.2 FESEM ANALYSIS

Fig. 2 represents the FESEM images of CuO and Zn doped Nano CuO particles prepared by sol-gel method. It shows that higher tendency of agglomerations. We collect the SEM images in different scales most of the images given particle size around 11.9 nm to 43.14 nm. The FESEM image of CuO and Zn doped CuO nano catalyst are shown in Fig. 2 (a, b, c and d). The FESEM image of CuO and Zn doped CuO nano catalyst reveals flakes shape with irregular size and shape. It was observed that the particle size decreases with increasing doping concentration of Zn.

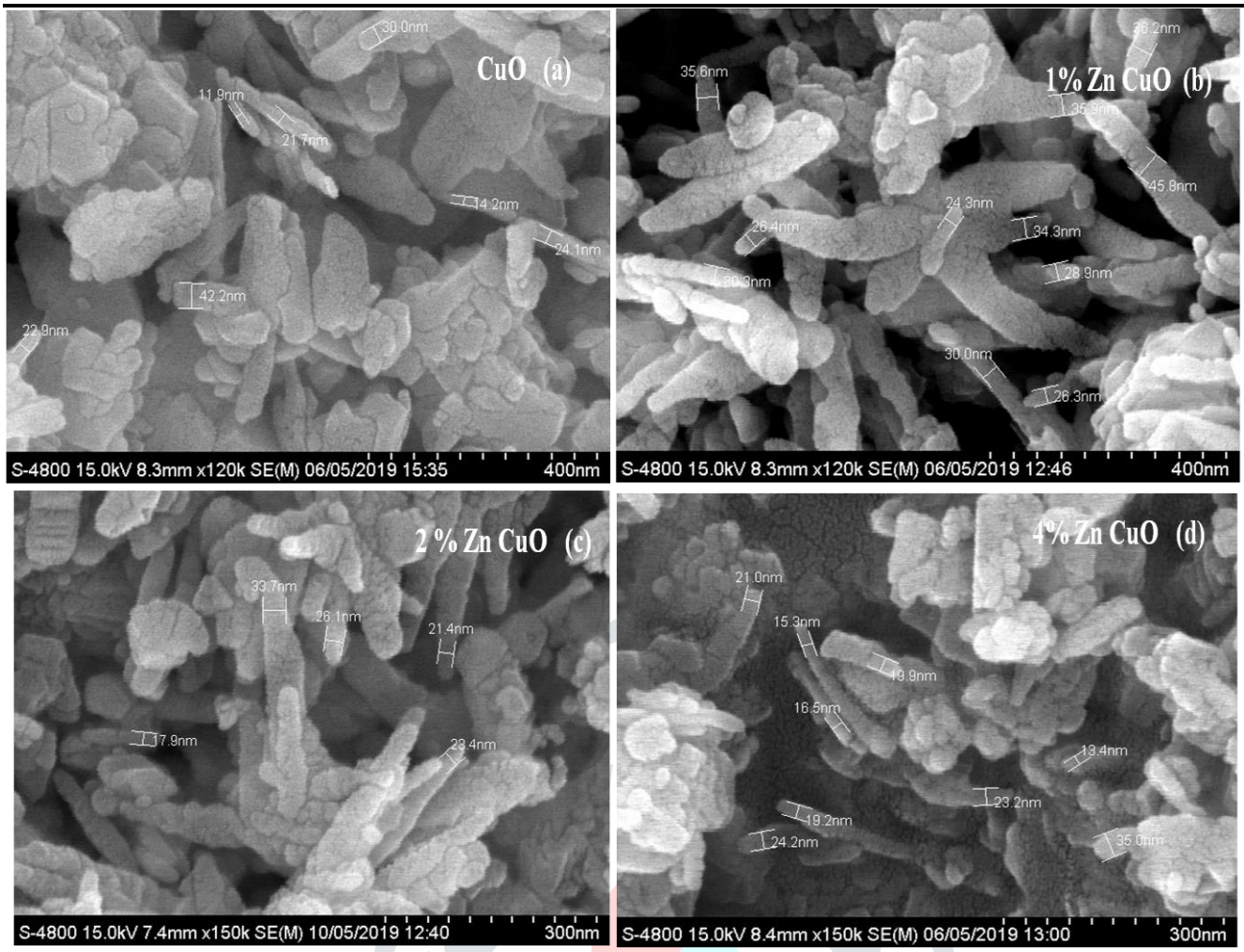

Fig. 2 (a, b, c and d). FESEM image of CuO and Zn doped CuO nano catalyst.

3.3 EDS ANALYSIS

The elemental analysis of material surface layer is obtained by electron dispersive X-ray spectroscopy (EDS). Fig. 3 (a, b, c and d shows that CuO& Zn doped CuO nano catalyst contains only CuO Cu K 71.94 %, O K 28.06 %. The 1 % Zn doped CuO contains Cu K 71.22 %, O K 27.77 % and Zn 1.22 %. The 2 % Zn doped CuO contains Cu K 70.43 %, O K 27.45 % and Zn 2.12 %. And the 4 % Zn doped CuO contains Cu K 68.97 %, O K 26.91 % and Zn 4.12% in EDS of CuO and Zn doped CuO micrograph proves existence of CuO and Zn doped CuO in the nanocatalyst.

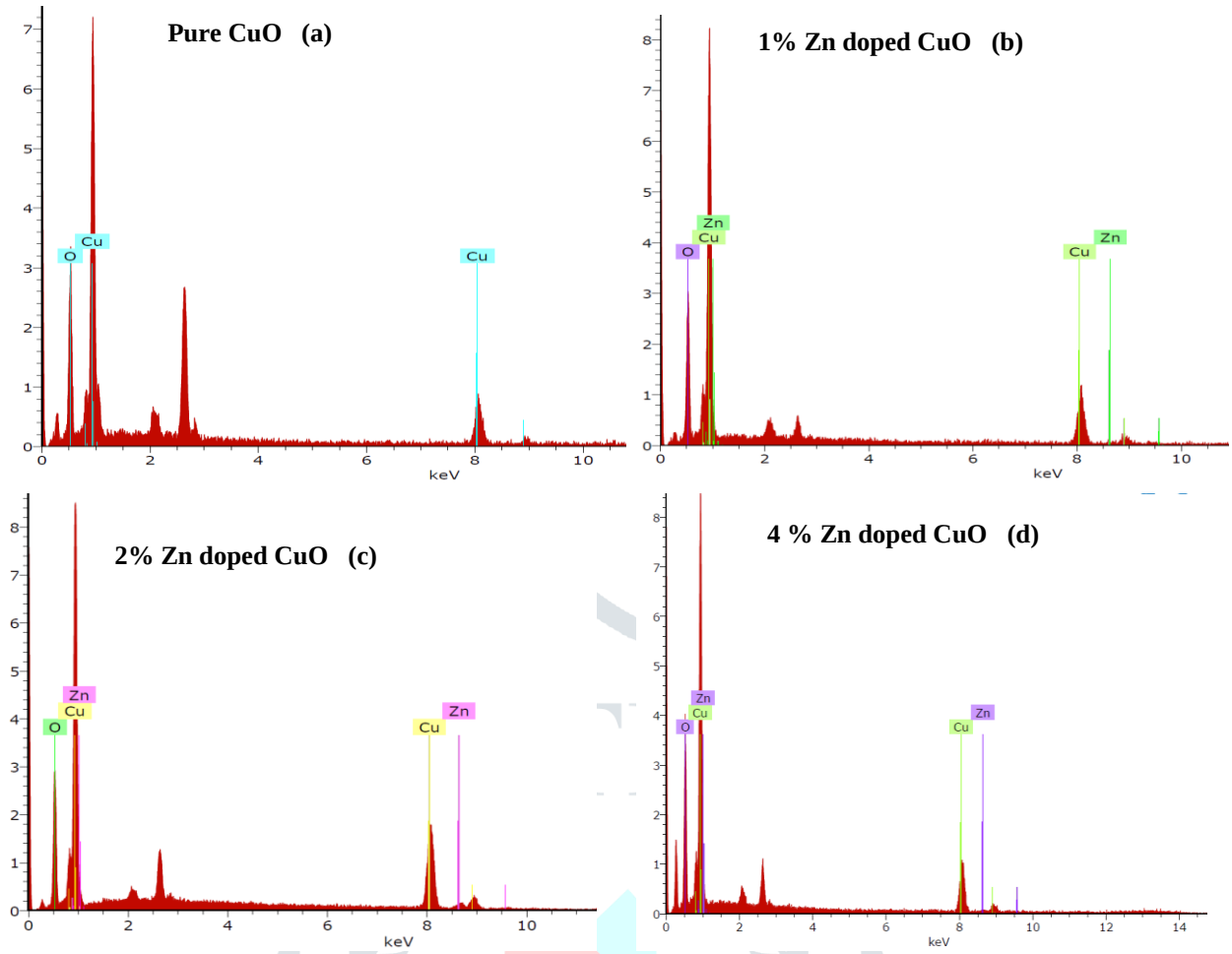

Fig. 3. EDX spectrum of CuO and Zn doped CuONanocatalyst.

3.4 Effect of pH

The pH of solution plays vital role in photocatalysis. Therefore, the influence of pH on photocatalytic degradation of Rhodamine B was performed and results are shown in Fig. 4. The natural pH of Rhodamine B is 8.4. The percentage degradation of Rhodamine B higher in basic media that is increase in pH, the percentage degradation decreases and higher degradation is observed in acidic medium. The pH 8 is suitable for degradation of Rhodamine B in presence of CuO nano catalyst for photocatalytic degradation. This is because of zero-point charge for CuO is at pH 8.0. CuO surface is positively charged above pH 8 and above this pH, the surface is negatively charged due to adsorbed OH^- ions. The presence of large quantities of OH^- ions on the particle surface as well as in the reaction medium favors the formation of $OH^{\bullet}$, which is responsible for enhancement in photocatalytic activity [18].

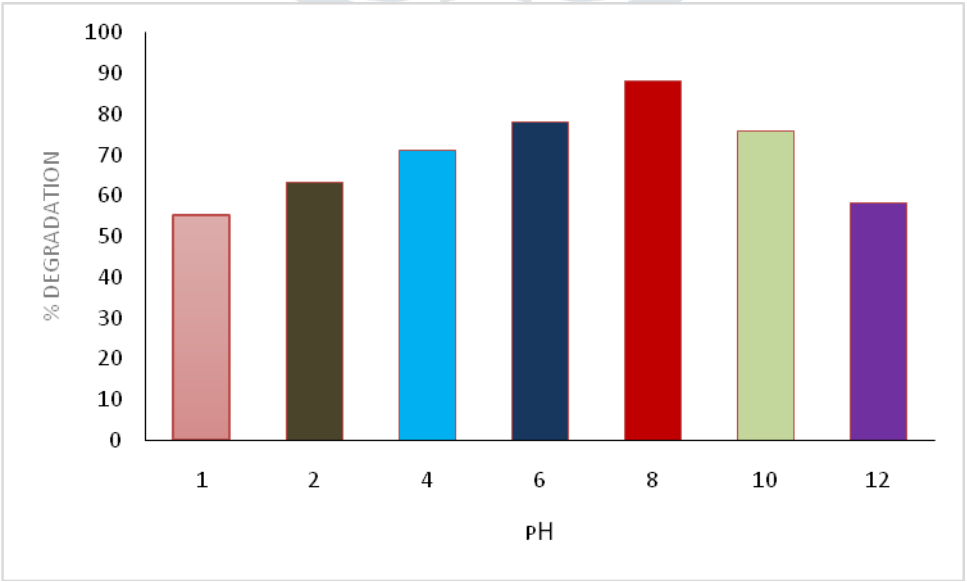

Fig.4 Effect of pH on photocatalytic degradation of Rhodamine B (Conc. 20 mg/L, catalyst dose 1.0 g/L and reaction time 120 min).

3.5 Effect of catalyst on initial Dye Concentration

The effect of catalyst on initial dye concentration of Rhodamine B was investigated by changing the doping amount Zn in CuO as 1%, 2% and 4% using 2 g/L of CuO and Zn doped CuO nano catalyst at pH 8. The results showed that dye concentration decreases from 20 mg/L to 4.2 mg/L with increasing in doping concentrations from CuO, 1 % Zn doped CuO 20 mg/L to 3.0 mg/L, 2% Zn doped CuO 20 mg/L to 2.1 mg/L, 4% Zn doped CuO 20 mg/L to 1.7 mg/L, (Fig. 5). As doping concentration increases the concentration of unabsorbed dye in the solution decreases which lead to excess penetration of light through the solution on to the surface of CuOand Zn doped CuO. Hence the concentration of ·OH radicals on the catalyst surface increases and finally increases the percentage degradation [13].

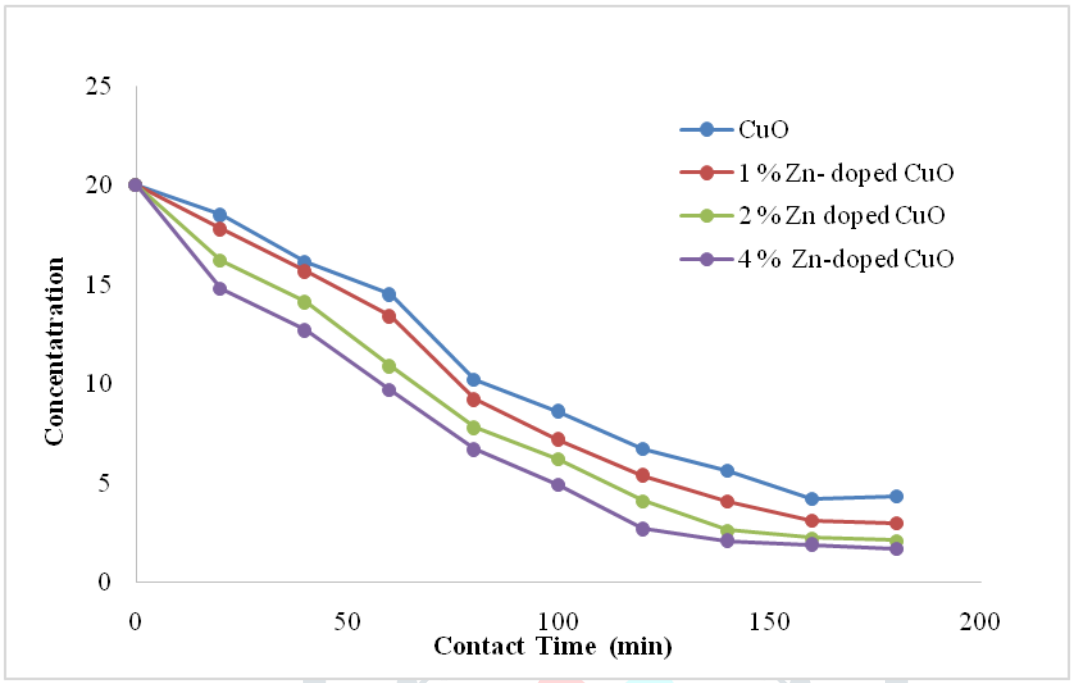

Fig.5 Effect of catalyst on initial dye concentration (Rhodamine B conc. 20 mg/L, pH 8, Catalyst dose =1.0 g/L, reaction time 180 min.)

3.6 Effect of doping percentage

Fig. 6 shows the effect of different doping ratios on the photocatalytic degradation of Rhodamine B at optimum conditions viz., catalyst dose 1 g/L, pH 8 and Rhodamine B concentration were 20 mg/L, respectively. As shown in Fig. 6, during the progress of degradation with contact time, initially the Rhodamine B degradation efficiency (%) was increases up to 120 min then after that it attains equilibrium. As shown in Fig. 6, during degradation of Rhodamine B with contact time, degradation efficiency (%) was increased slightly with the increase of doping ratio from 1 to 4 %. Photocatalytic activity of doping concentration increases with decreasing the band gap energy [10]. In addition, rapid transfer of the electrons from the CuO to the Zn may cause increase in the photocatalytic activity and increase the efficacy of photo degradation [17].

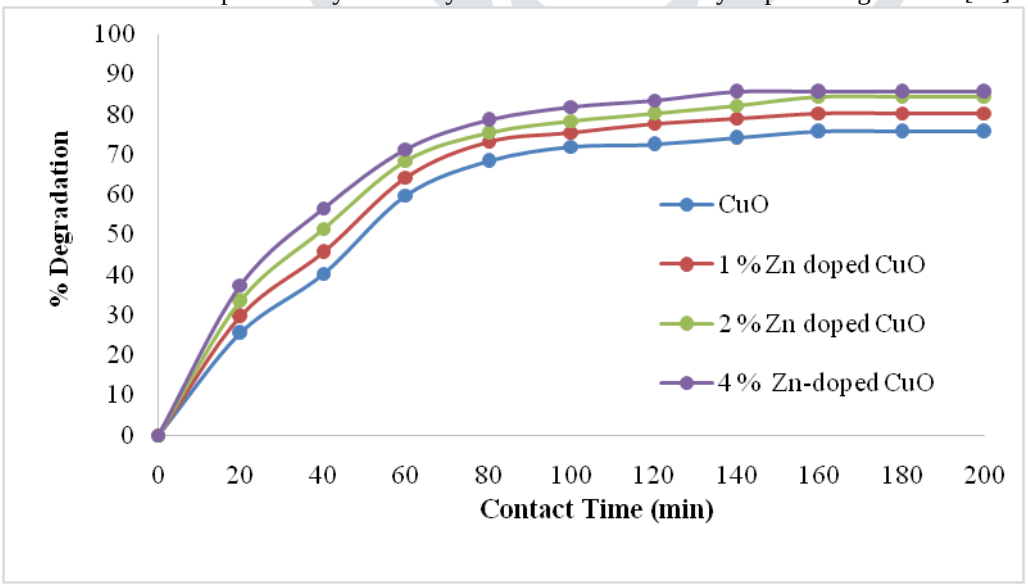

Fig. 6. Effect of doping percentage on percentage degradation of Rhodamine B (undoped CuO, 1% Zn doped CuO, 2% Zn doped CuO and 4% Zn doped CuO= 1.0 g/L, pH=8 Rhodamine B conc. = 40 mg/L).

3.7 Effect of initial dye concentration

The effect of initial dye concentration on photocatalytic degradation of Rhodamine B was studied by varying the dye concentration from 10 to 40 mg/L (Fig. 7) at 1 g/L catalyst concentration. From the outcome of the results of study of initial dye concentration on degradation it is observed that, as the dye concentration increases percent degradation decreases.

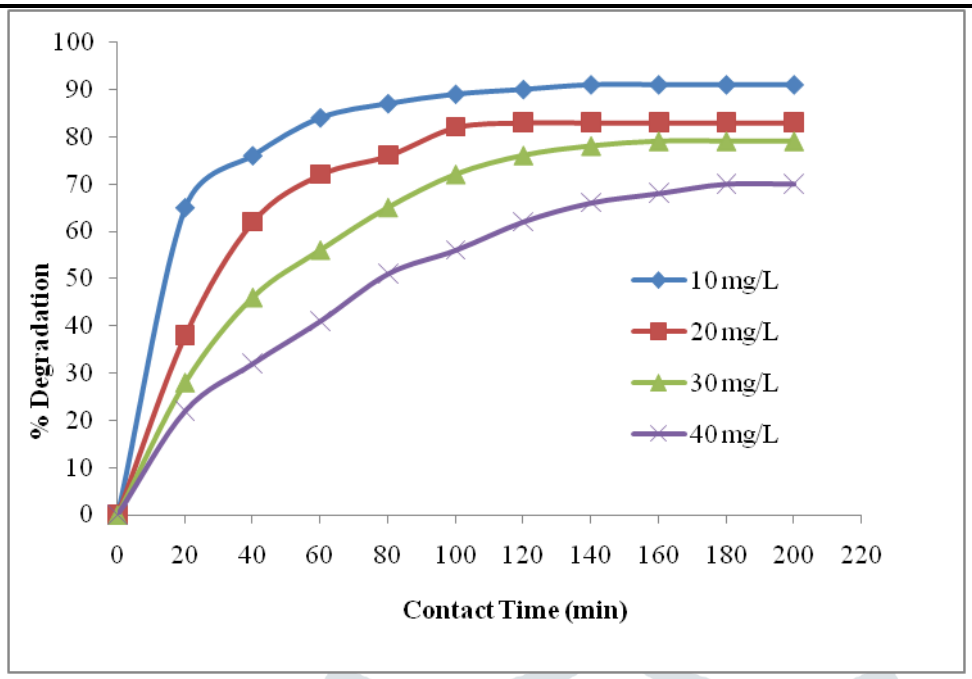

Fig. 7. The effect of initial dye concentration on photocatalytic degradation of Rhodamine B was studied by varying the dye concentration from 10 to 40 mg/L conc. Using 1 g/L 4% Zn doped CuO).

3.8 KINETICS OF DEGRADATION

The photocatalytic degradation of Rhodamine B by CuO nano catalyst obeys pseudo-first-order kinetics. It is expressed as follows,

$$\ln(C_o/C) = k_{app}t \qquad (1)$$

Where C and C_o are the reactant(dye) concentration at time t = t and t = 0, respectively, and k_{app} and t are the apparent reaction rate constant and time, respectively. According to the equation, a plot of $\ln(C_o/C)$ versus t will yield a slope of k_{app}. The results are displayed in Fig. 8. The linearity of the plot suggests that the photocatalytic degradation reaction approximately follows pseudo-first-order kinetics [18].

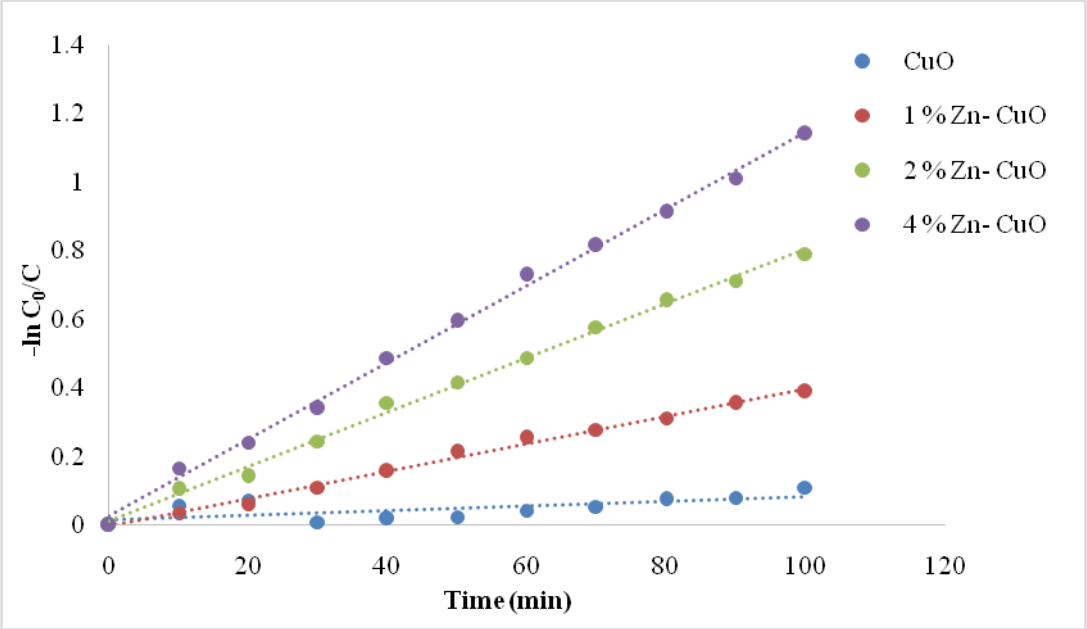

Fig. 8. First order kinetics plot of Rhodamine B degradation with CuO, Zn doped CuOphotocatalyst (Rhodamine B conc. = 20 mg/L, CuO conc. = 1 g/L, pH = 8).

3.9 RECYCLE PERFORMANCE OF Zn DOPED CuONANOCATALYST

Stability and proficiency of Zn doped CuOnanocatalyst as well as cost effectiveness of the process is investigated by studying the reusability of Zn doped CuOnanocatalyst for the % degradation of Rhodamine B. To study its reusability, the powdered nanocatalyst was centrifuged after completion of each photocatalytic degradation experiment. Then recovered sample was reused for 3 times under similar experimental conditions. Fig. 9 shows % that degradation of Rhodamine B by Zn doped CuOnanocatalyst after 1st run is achieved up to 85.6% (120 min). After 4th run it decreases down to 81.55%. The catalytic activity was found to decrease marginally after 4th run. This decrease may be attributed to loss of reused catalyst during sampling each time and irreversible changes of the surface of the photo catalyst by pollutants. Fig. 9 shows that Zn doped CuO have excellent stability and do not alter photocatalytic degradation capability.

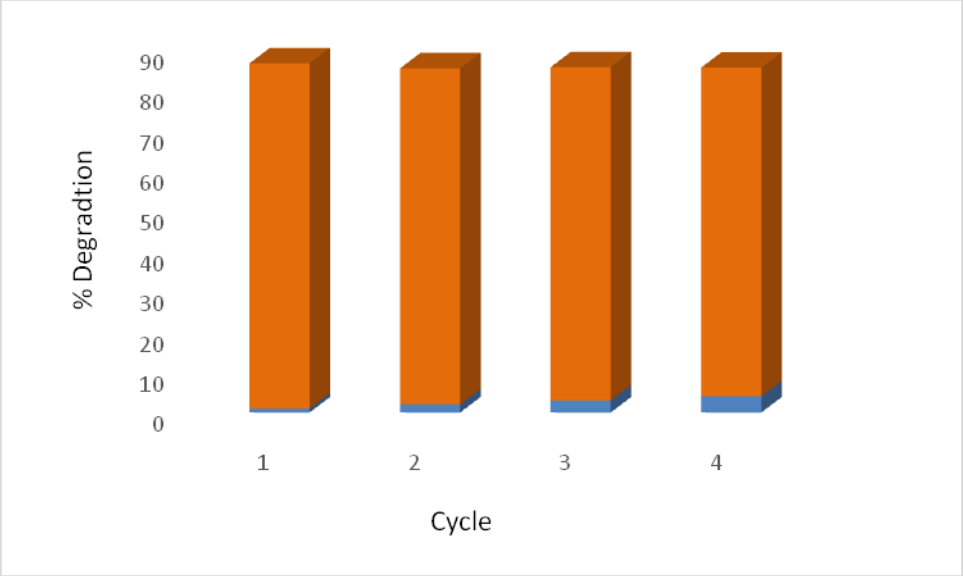

Fig. 9. Reusability study of Zn doped CuO nano catalyst.

IV. CONCLUSION

The photocatalytic degradation of Rhodamine B in the presence of nano CuO and nano Zn-doped CuO were carried out. The photocatalytic degradation followed first order kinetics with respect to Rhodamine B and the percentage degradation increased with an increase in catalyst loading and decrease with increase in pH in alkaline media, initial concentration of dye. pH 8 is suitable for photocatalytic degradation of Rhodamine B. A comparative study shows that 4 % Zn doped CuOphotocatalyst degradation of Rhodamine B is effective degradation technique than CuO, 1 %Zn doped CuO, 2% Zn doped CuO photocatalytic degradation. The recycle study up to 4 cycles shows the excellency of the catalyst towards degradation capability.

V. ACKNOWLEDGMENT

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