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Visible Light Induced Photocatalytic Degradation of Victoria Blue by using ZnS and Co Doped ZnS Nano Catalyst

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Abstract: **ZnS and Co doped ZnS were synthesized by chemical precipitation method. Structure and morphology of synthesized Co doped ZnS nano catalyst was investigated using scanning election microscopy (SEM), Electron dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The photocatalytic activity of Co doped ZnS nano catalyst was investigated by degradation of Victoria blue solution under visible light radiation. The effects of various parameters such as the Victoria blue concentration, catalyst dose, effect of pH on the photocatalytic degradation were examined. The kinetics study shows that the reaction follows pseudo first order kinetics. Among the different amounts of dopant like 1, 2, and 5 wt% Co-doped ZnS nanocatalyst, it was observed that 5 wt % Co doped ZnS shows highest degradation rate for Victoria blue. The particle size, surface morphology and photo induced electron–hole pair generation are the key factors which has impact on photocatalytic activity.**

Keywords: Victoria blue, ZnS and Co doped ZnS, photocatalysis.

I. INTRODUCTION

Now-a-days environmental pollution becomes major area of concern worldwide. Nanotechnology could be the possible solution to this problem. The rapid development in the field of nanotechnology with time have gain attentions considerable attentions on the synthesis and manufacturing of ZnS (Xianfu W., et al.,2013; Gang-Juan L.et al.,2017; Sheshtawy H.et al.,2018). The ZnS has been extensively studied because of its potential applications in flat-panel display, light-emitting diodes (LEDs), infrared windows, electroluminescence, sensors, lasers and photocatalysis due to its diverse range of possible structures and morphologies, and superior chemical and thermal stabilities (Rao R., et al.,2005; Leary R. et al., 2011). Due to the stability of present dyes, conventional treatment methods for industrial wastewater are ineffectual, causing frequently in an intensively discharge of colored pollutants from the effluent treatment plants into the nearby water streams. In recent times, a number of researchers are focusing on heterogeneous photocatalytic degradation of variety of dyes (Augugliaro V., et al.,2002; Datta R., et al.,2002; Sarteep Z., et al.,2016). ZnS nanostructures are interesting entities for catalytic activities because of their notable chemical stability against oxidation and hydrolysis. Besides, ZnS is available in abundance and is nontoxic. Therefore, ZnS can play an important role as catalyst in environmental protection through the removal of organic and toxic water pollutants. ZnS is a wide band gap semiconductor with band gap of 3.77 eV which can be used as photocatalyst. It has a good photocatalytic property of generating rapid electron-hole pair by photo excitation (Langjam M., et al.,2015). Therefore, ZnS can play an important role as catalyst in environmental protection through the removal of organic and toxic water pollutants (Xiaosheng F., et al.,2011). However, for such application it would be desirable to extend the band gap excitations towards the visible region, and also to prolong the lifetime of photo generated charge carriers. Doping of Zinc sulphide with transition metal ions provides a relatively well-studied and convenient way of solving both problems described above. Zinc sulphide doped with transition metal ions can demonstrate extended band gaps and significantly higher photocatalytic efficiencies (Rathore P., et al.,2015; Pricilla A., et al.,2017). In such case dopant proportion is an important parameter to be considered, as the amount of dopant influences the processes of charge carrier trapping, separation and recombination (Nayereh S.,et al.,2012).Thus, the amount of

transition metal introduced should be within a so-called optimum concentration, as too low a dopant content does not affect the process of charge carrier generation while too high a content of doping metal results in the formation of extra recombination sites and shortens the lifetime of photogenerated electrons and holes. Consequently, setting the optimum concentration of doping metal is the very important aspect for successful doping. This optimum value may change considerably and it depends on many factors, like the type of dopant, annealing conditions etc. (Hajati S., et al.,2014). Present study involves the synthesis of ZnS and Co doped ZnS nano catalyst which was characterized by XRD, EDS and SEM. The effect of various parameters like pH of dye solution, contact time, dose of catalyst in photocatalytic degradation using visible light and the kinetics of degradation for Victoria blue using ZnS and Co doped ZnS nano catalyst were studied.

II. EXPERIMENTAL

A. Materials

A.R. grade Zinc chloride, Sodium sulphide and Cobalt Chloride were purchased from Loba Chemie Pvt. Ltd. Concentration of the Victoria blue was determined by measuring absorbance using UV-VIS double beam spectrophotometer (Systronics model-2203) at the λ_{max} 560 nm. The pH was maintain using 0.1M HCl and 0.1M NaOH with pH meter (model no. EQ - 615.)

B. Method

From stock solution of Victoria blue B at different concentrations were prepared in distilled water. The 50 mL Victoria blue solution mixed with ZnS and Co doped ZnS and taken in the photocatalytic reactor. The solution was stirred in the dark to allow equilibration of the system so that the loss of the compound due to adsorption can be taken into consideration. The dye having ZnS and Co doped ZnS catalyst was subjected to visible light irradiation in order to achieve the degradation of Victoria blue. The catalyst was separated from the solution by centrifugation and the solution was examined for determination of concentration of dye at λ_{max}560 nm.

III. Synthesis of ZnS and Co doped ZnS

ZnS and Co-doped ZnS nanoparticles are prepared by chemical precipitation method. For synthesizing ZnS nanoparticles 50 mL 0.1 M Sodium sulphide solutions was added drop wise to 50 mL 0.1 M Zinc Chloride solution kept stirring on magnetic stirrer at 70^0 C for two hours (Prabu J. et al.,2015). For synthesizing Cobalt doped ZnS of various compositions amount of Cobalt chloride was mixed with Zinc chloride solution before stirring. After stirring for two hours the precipitate was washed by ethanol and then by deionized water and dried in open hot air for four hours. Dry powder formed was calcinated in muffle furnace at 450^0C for three hours then ground to fine size.

IV. Results and discussion

A. Characterization of photocatalyst

1) SEM analysis

The SEM image of ZnS and Co doped ZnS nano catalyst are shown in Fig.1 (a, b, c and d). The SEM image of ZnS and Co doped ZnS nano catalyst shows flower like morphology for small dopent concentration and it get altered on increase in dopent concentration. It was observed that the particle size increases with increasing doping concentration of Co (Bruno L.,et al.,2015).The size of ZnS crystals was observed to be 14 to 51 nm. Accumulation behavior is observed in the crystals to show a bunch of crystals.

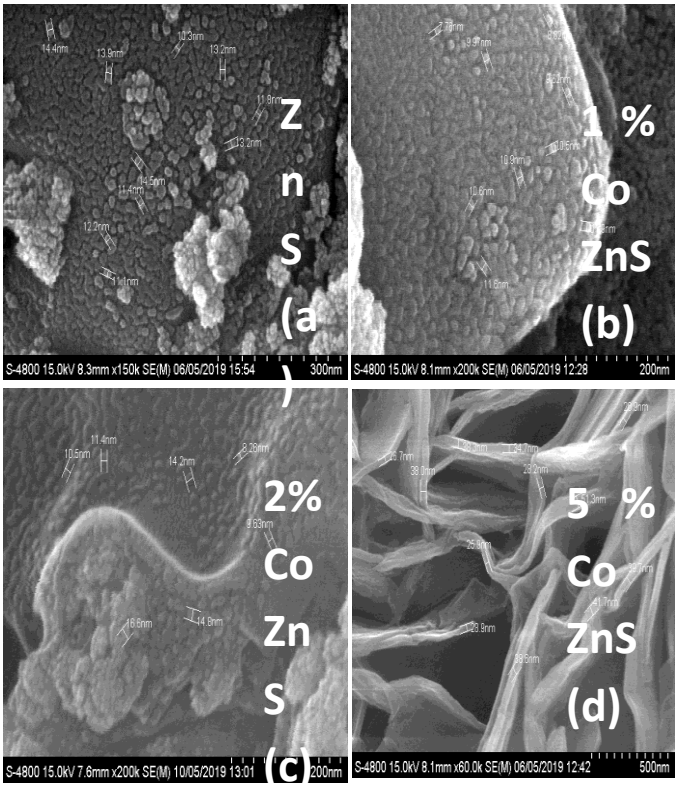

Fig.1 SEM image of ZnS and Co doped ZnS

2) EDS analysis

The elemental analysis of ZnS and Co doped ZnS surface is carried out by EDS. Fig. 2 (a, b, c and d shows that ZnS and Co doped ZnS nano catalyst contains ZnS Zn K 58.48 %, S K 41.52 %. The 1 % Co doped ZnS contains Zn K 51.59 %, S K 45.98 % and Co .41 % , The 2 % Co doped ZnS contains Zn K 51.59 %, S K 46.91 % and Co 1.39 %. And the 5 % Co doped ZnS contains Zn K 71.07 %, S K 25.88 % and Co 3.05% in EDS of ZnS and Co doped ZnS micrograph evidences existence of ZnS and Co doped ZnS in the nanocatalyst.

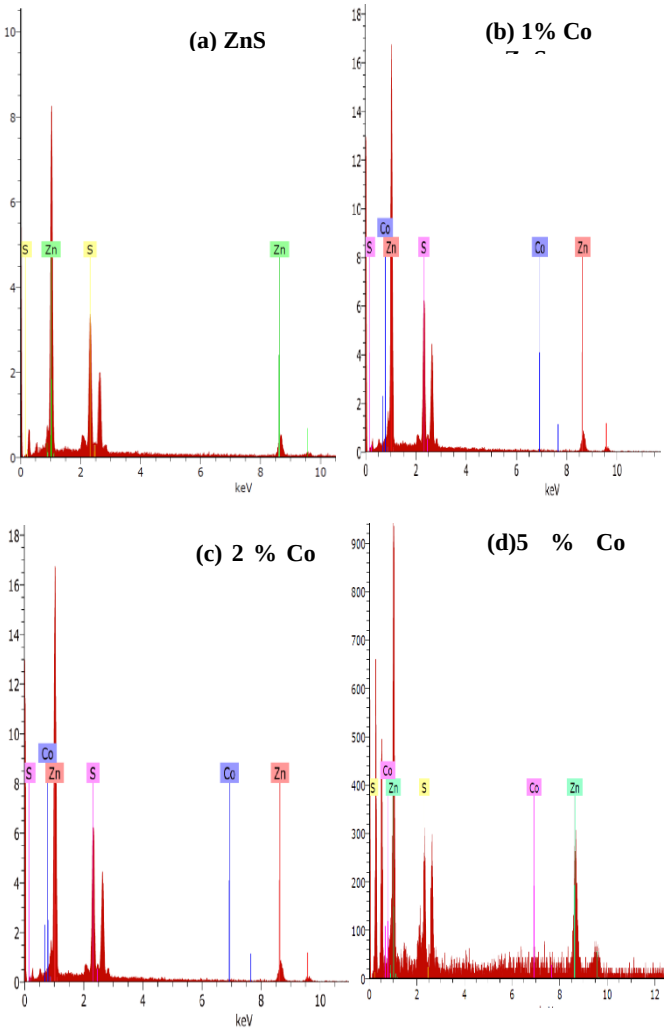

Fig.2 EDX spectrum of ZnS and Co doped ZnS.

3) X-ray diffraction analysis

Fig. 3 shows XRD pattern of ZnS and Co doped ZnS nanoparticles. The crystalline nature of the prepared nano size ZnS and Co doped ZnS powder is evident from the x-ray diffraction pattern. The phase identification carried out with help of standard JCPDS data base the three different peaks 29.0^0, 48.1^0 and 57.0^0 corresponds to (111), (220) and (311) planes of cubic crystalline ZnS respectively, which indicates that the prepared nano crystals belongs to the cubic zinc blende structure. The broadening of peak of nano crystal is due to their small size. Position of diffraction peaks is in well agreement with standard JCPDS No. 05-0566.

The typical broadening of the three diffraction peaks is also observed implying that the size of ZnS and Co doped ZnS nanoparticles is very small.

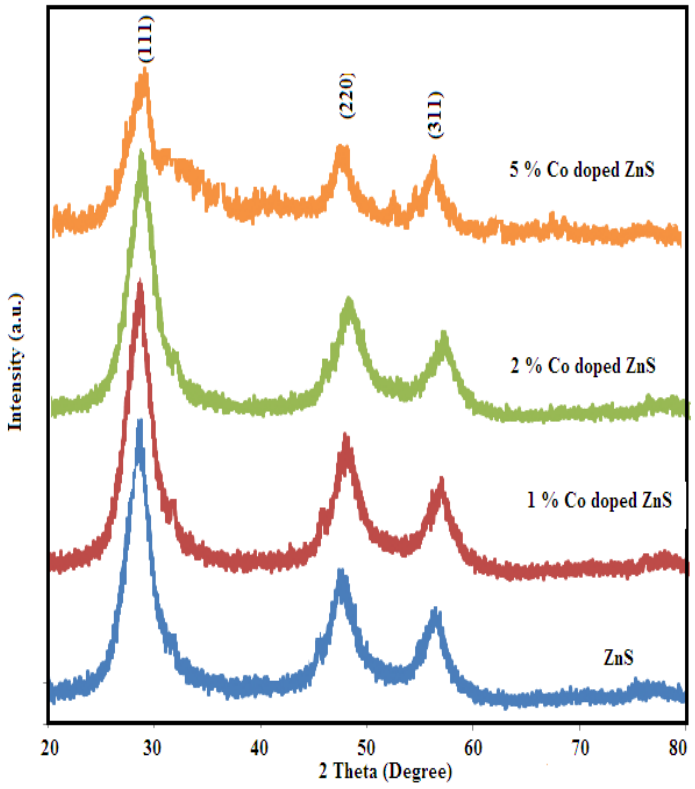

Fig.3 XRD of ZnS and Co doped ZnS

B. Photocatalytic study

1) Effect of pH

The influence of pH on photocatalytic degradation of Victoria blue was performed under UV-visible light source and results are shown in Fig. 4. The percentage degradation of Victoria blue increase with increase in pH up to 8 and higher degradation is observed in alkaline media. The pH 8 is favorable for degradation of Victoria blue in presence of ZnS nano catalyst for photocatalytic degradation.

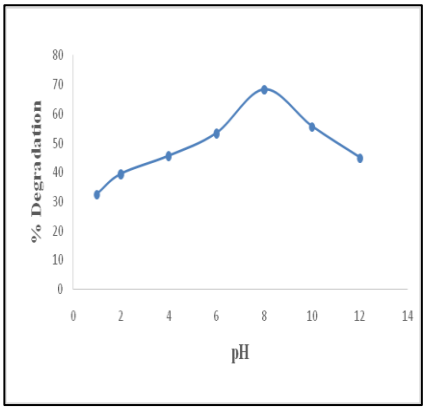

Fig. 4 Effect of pH on photocatalytic degradation of Victoria blue (Conc. 20 mg/L, catalyst dose 1.0 g/L and contact time 120 min).

2) Effect of catalyst

The effect of catalyst on initial dye concentration of Victoria blue was examined by varying the doping amount Co in ZnS as 1%, 2% and 5% using 2 g/L of ZnS and Co doped ZnS nano catalyst at pH 8. The results showed that dye concentration decreases with increasing in doping concentrations. For undoped ZnS initial concentration 20 mg/L was decreased to 3.90 mg/L, for 1% Co doped ZnS 20 mg/L dropped to 3.11 mg/L, for 2 % Co doped ZnS 20 mg/ dropped to 2.24 mg/L, and for 5% Co doped ZnS initial concentration 20 mg/L fall down to 1.61 mg/L. (Fig. 5). The reason behind this is as doping percentage increases the concentration of unabsorbed dye in the solution decreases which causes more penetration of light through the solution on to the surface of ZnS and Co doped ZnS. It increase the concentration of $^{\bullet}OH$ radicals on the surface and hence increases the degradation rate (Mahajan V. ,et al.,2015).

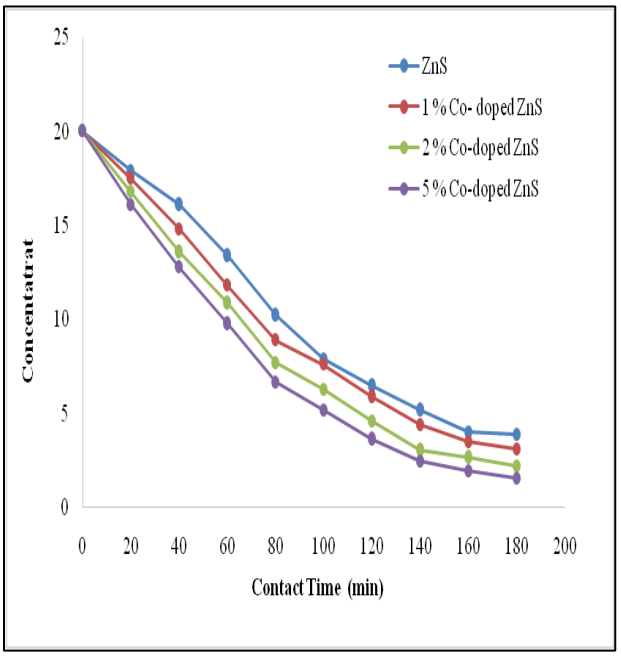

Fig. 5 Effect of catalyst on initial dye concentration Victoria blue pH 8, catalyst dose 2.0 g/L, and reaction time 180 min.

3) Effect of Dose

To avoid the excess use of catalyst, the optimum dose was determined by varying the dose of ZnS and Co doped ZnS. For this purpose 20 mg/L concentration of dye was used for degradation purpose. It was observed initially that rate of degradation increases with the increase in catalyst dose, upto certain limit but beyond that level it remained almost constant. In present case 1g/L was found to be the optimum catalyst dose. It was observed that as percentage of Co in ZnS increases percentage degradation of Victoria blue was increased. The increase in catalyst concentration causes increase in the number of photons absorbed and number of dye molecules adsorbed. It further improves the rate of dye degradation. Beyond certain catalyst concentration, the numbers of substrate molecules are insufficient to fill the active sites of ZnS. Hence, further addition of catalyst does not cause the improvement in degradation rate. This is may be due to the reduction in the light penetration with excess amount of ZnS. The excess addition of the catalyst makes the solution more turbid and penetration of light is inhibited from the sample (Kaur S.., et al.,2007).

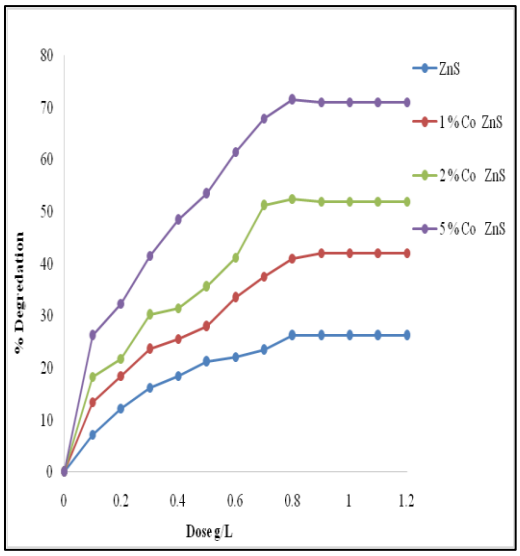

Fig. 6 Effect of dose on percentage degradation of Victoria blue.

4) Effect of doping percentage

The effect of different doping percentage on the photocatalytic degradation of Victoria blue at 20 mg/L concentration, catalyst dose 1g/L and pH 8 was shown in Fig 7. From Fig. 7 it has been observed that as contact time increases, percentage degradation increases and after 100 min it is almost constant. As % of Co in ZnS increases from 1 to 5 % degradation increases. Photocatalytic activity of doping concentration increases with decreasing the band gap energy (Khataee A., et al.,2015). The rapid transfer of the electrons from the ZnS to the Co may improve the photocatalytic activity and increase the competence of photocatalysis.

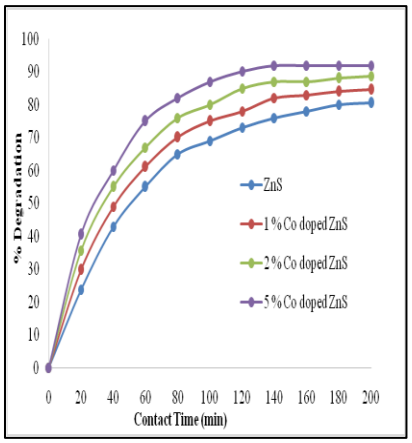

Fig. 7 Effect of doping percentage on percentage degradation of Victoria blue (catalyst dose = 1.0 g/L, pH=8, dye conc. = 20 mg/L and reaction time 200 min.)

5) Effect of Initial Dye Concentration

The degradation of Victoria blue at different concentrations (10,20,30 and 40 mg/L) for a catalyst dose of 1 g/L of 5 % Co doped ZnS nano catalyst and pH=8 was investigated. Fig. 8 shows that the maximum degradation 94% was found to at 10 mg/L for Co doped ZnS nano catalyst and 67% was found to at 40 mg/L for Co doped ZnS nano catalyst it indicates that as concentration of dye increases the percentage degradation decreases. The degradation efficiency was observed to be inversely proportional to the increase in concentration. This is because, as the dye concentration increases, the equilibrium adsorption of the dye on the catalyst surface active sites increases, therefore resulting in the lower formation rate of •OH radicals which is the principle oxidant in this process (Chen X., et al.,2017; Khan M., et al.,2017).

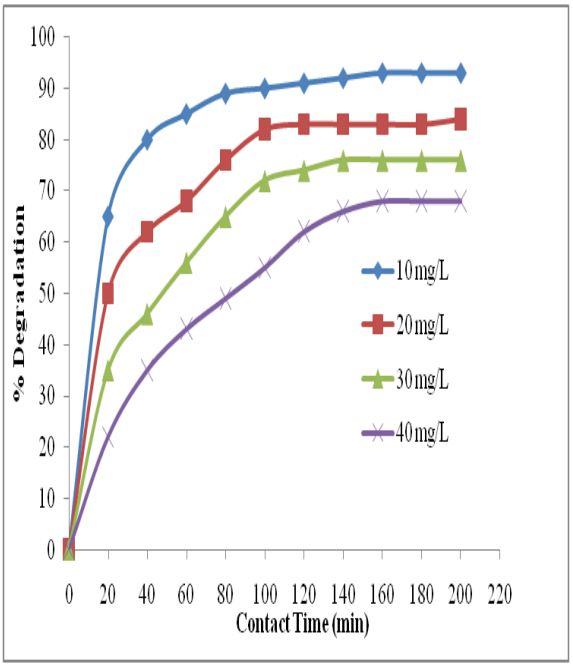

Fig. 8 Effect of initial dye concentration on Victoria blue (pH 8, Catalyst dose 1 g/L, 5% Co doped ZnS).

C. Kinetic of degradation

The kinetics of photocatalytic degradation of Victoria blue by ZnS nano catalyst was studied by pseudo-first-order kinetics model (Fig. 9). The linearity of the plot -ln C_0/C vs contact time suggests that the photocatalytic degradation reaction follows pseudo first order kinetics.

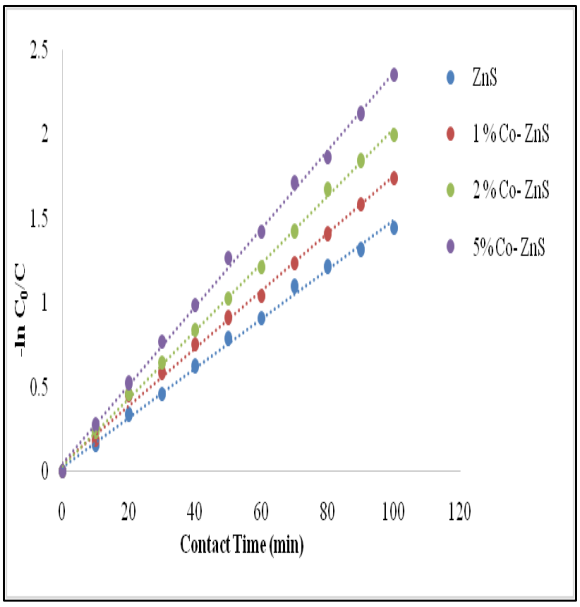

Fig.9 Pseudo First order kinetics plot for degradation of Victoria blue (conc. = 20 mg/L, ZnS conc. = 1 g/L, pH = 8, and reaction time 100 min.).

D. Recycle study of Co doped ZnS nanocatalyst

To find out the stability and efficacy of Co doped ZnS nanocatalyst as well as cost effectiveness of the process, the reusability of 5%Co doped ZnS nanocatalyst was investigated for the degradation of Victoria blue. For this purpose, the powdered nanocatalyst was centrifuged after completion of each photocatalytic cycle. The recovered catalyst sample was reused for 3 times under identical experimental conditions. Fig. 12 shows that % degradation of Victoria blue achieved at the end of 1st cycle and 4th cycle is 92.52% and 84.67% after 120 min. The catalytic activity was found to decrease marginally after 4th run. This decrease may be due to loss of reused catalyst during sampling every time and irreversible changes on the surface of the photocatalyst by pollutants. Fig. 10 shows that Co doped ZnS have admirable stability and do not suffer from corrosion.

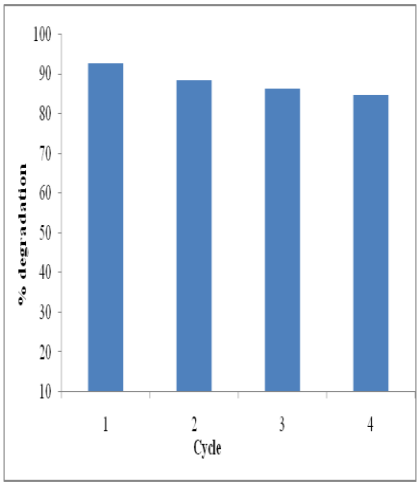

Fig.10 Recycle study of Co doped ZnS nano catalyst.

CONCLUSION

Co doped ZnS have been successfully synthesized by chemical precipitation method. The results point out that it could be promising photocatalyst, exhibits improved photodegradation efficacy in Victoria blue removal as compare to bare ZnS. The photocatalytic results indicated that the catalyst dose and pH values significantly influences the degradation efficiency of Co doped ZnS. Secondly; the photodegradation efficiency might be improved with the increase of catalyst loading. The photocatalytic decomposition of Victoria blue was most efficient at pH 8 and 1 g/L catalyst dose within 120 min.

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