Photocatalytic Properties of GO-($Cd_{0.8}$-$Zn_{0.2}$)S Nanocomposites Prepared by Chemical Precipitation Method at Different Temperatures

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***Abstract*:- Graphene oxide - ($Cd_{0.8}$-$Zn_{0.2}$)S nanocomposite material was synthesized by the simple and economically viable chemical precipitation method at different temperatures and its photocatalytic properties were investigated. Measurement of photocatalytic degradation of Rhodamine B dye was carried out under visible light. The photocatalytic efficiency of the synthesized nanocomposites was calculated and the effect of bath temperature on the photocatalytic efficiency was studied. The studies suggest that the prepared nanocomposites exhibit reasonably good photocatalytic properties. Better photocatalysis is observed at lower bath temperatures for preparation of the nanocomposites. Photocatalytic efficiency close to 70% has been obtained for the synthesised GO-($Cd_{0.8}$-$Zn_{0.2}$) S nanocomposites which can be further improved by optimizing the preparative conditions.**

***Keywords*:- Rhodamine B dye, nanocomposites, photocatalytic properties**

I. INTRODUCTION

Research on solar energy utilization to tackle energy and environmental issues has gained much attention in recent years. A variety of dyes are widely used in various fields, but their discharge into water cause serious environmental pollution. Therefore, various strategies are being employed for photocatalytic degradation of organic dyes using semiconductor photocatalysts[1].Semiconductor nanocrystals like CdS has a narrower bandgap than TiO_2 making it a competitive candidate as a photocatalyst. Although the photo generated electrons and holes play a vital role in photo catalytic disinfection, their recombination result in low efficiency of photo catalysis. Hybrid of CdS with some support materials like graphene can delay the recombination process as well as adsorb the pollutants. Incorporation of Graphene with appropriate ratio of CdS to ZnS causes improved charge separation and enhanced visible light absorption. .Graphene with atomically thin and two-dimensional conjugated structure, exhibits high conductivity as well as thermal, chemical, mechanical, and optical stability and has a high specific surface area making it suitable as a promising adsorbent supporting material to remove pollutants from aqueous solution. There have been reports that the nanocomposites composed of CdS and graphene showed significantly improved photocatalytic properties as the conjugation net and the conductivity of graphene makes it an efficient electron acceptor [2].Studies have also shown that CdS-ZnS solid solution sensitized nanocomposites have enhanced visible light absorption and also exhibited a red-shift of the band-edge as compared to Graphene -CdS composites [3].

Taking these factors in to account , graphene oxide -($Cd_{0.8}Zn_{0.2}$)S nanocomposite material was synthesised at different temperature (70°C ,80°C and 90°C) and its photocatalytic properties were investigated The existing methods of synthesis of these nano composites are mostly expensive and require high temperature. The proposed materials were synthesized by the simple and economically reliable chemical precipitation method at low temperatures[4-5]. In order to evaluate the adsorption performance and photocatalytic activity, organic dye like Rhodamine B was used.[5] Measurement of photo-catalytic degradation of the dye was carried out under visible light and the absorbance of the of the samples was studied by UV-VIS Spectroscopy. The degradation of the dyes and change in its absorbance was studied with respect to time. The photocatalytic efficiency of the synthesized nanocomposites was calculate.[6].

II. EXPERIMENTAL TECHNIQUES

2.1 Graphene Oxide Synthesis by Modified Hummer's Method [6].

Concentrated H_2S0_4 is added to the graphite powder taken in a beaker followed by the addition of $NaN0_3$.This is placed in an ice bath for continuous stirring for about 10 minutes. Thereafter $KMn0_4$ is slowly added to the mixture and it is allowed to stir for 40 minutes followed by the addition of hot water.H_20_2 is then added to the solution and is allowed to settle for 12 hours. The final mixture is then centrifuged in presence of hot water in order to remove soluble impurities. The obtained mass is allowed to dry in vacuum oven at 60 ^Oc for 5 hours.The obtained material is black powder of Graphene Oxide as shown in figure1.

Fig1. Graphene Oxide Powder

2.2 GO-(Cd-Zn)S prepared by Chemical Route Method

75mg of Graphene oxide is dissolved in hot triple distilled water which is stirred for one hour. Cadmium acetate and Zinc acetate are added in appropriate ratio followed by TEA ,Thiourea and Ammonia and stirred for 30 minutes. To the entire mixture, mercapthoethanol and methanol are added and the entire solution is stirred for 30 minutes. The solution is kept in water bath at 3 different temperatures namely, 70^0C, 80^0C and 90^0C for 2 hours. The precipitate is then filtered and further dried in oven at 70 ^{O}c for 4 hours to get a yellow powder as shown in figure.2.

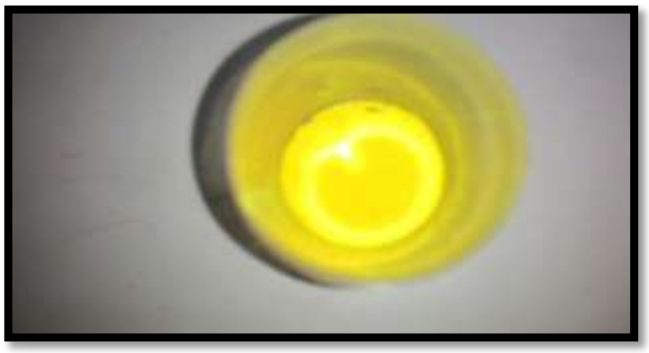

Fig 2. GO-(Cd-Zn)S Powder

2.3 Arrangement for photocatalytic degradation studies:

Figure 3 :Arrangement for photocatalytic degradation of Rhodamine B dye solution.

Figure 3 shows the arrangement for photocatalytic degradation of Rhodamine B (RhB) dye solution. 0.03% Rh.B dye solution is taken to which an appropriate quantity GO-($Cd_{.8}Zn_{.2}$)S is added and mixture is magnetically stirred for 30 minutes to obtain adsorption-desorption equilibrium. The absorbance of the solution is measured before making light incident on the solution and subsequently after every 30 minutes for 2 hours. The degradation of the dye and change in its absorbance was studied with respect to time. The photocatalytic efficiency of the synthesized nanocomposites was calculated.

Calculation of % degradation of dye solution =

$[(C_0 - C)/ C_0]$ x 100 ---------- (1)

where C_0 is the initial concentration and C is the concentration after different times.

III. RESULTS & DISCUSSION

Figure 4 shows the absorbance vs wavelength graph of GO(Cd-Zn)S which is plotted in the 400 to 700nm range. A few absorption peaks in the wavelength range 450-500nm is observed.

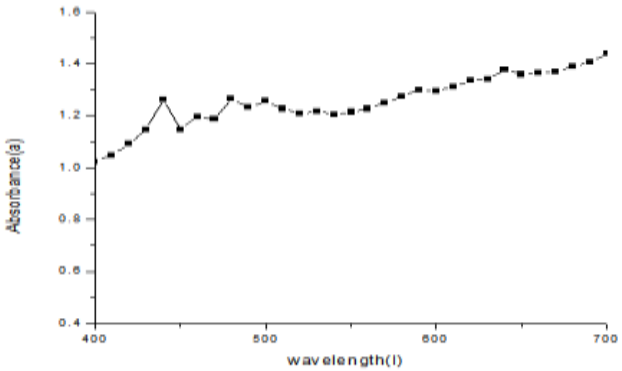

Fig.4: Absorbance vs wavelength plot of GO(Cd-Zn)S

The Rhodamine B dye solution of different concentrations are taken and absorbance is measured as shown in fig.5. It is observed that at different concentrations, the absorbance vary .There is a decrease in absorbance with decrease in the concentration. Also, absorption peak is obtained around 554nm.

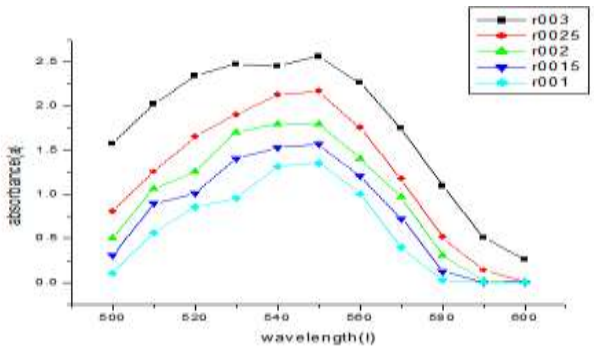

Fig.5 Absorbance vs wavelength plot of Rh B (different concentrations)

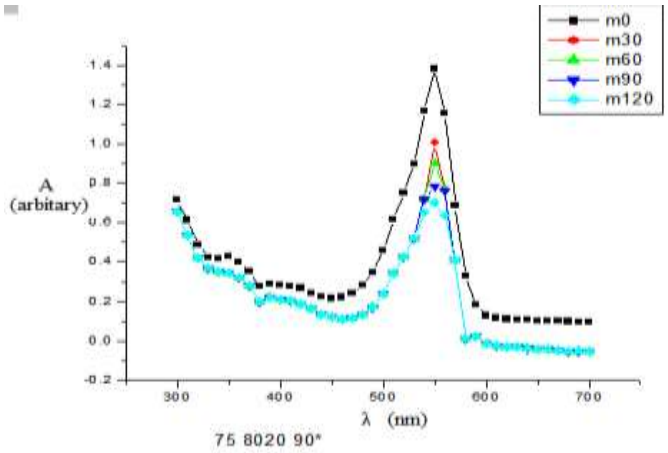

Fig.6 Absorbance vs wavelength plot of degraded dye solution after different time intervals with GO-($Cd_{.8}Zn_{.2}$)S prepared at 90^0C.

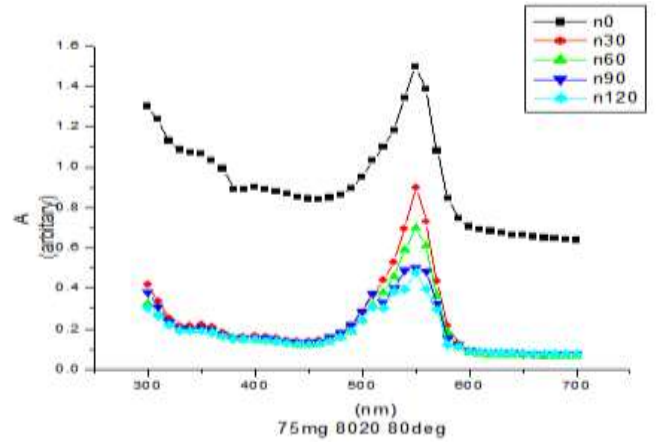

Fig.7 Absorbance vs wavelength plot of degraded dye solution after different time intervals with GO-($Cd_{.8}Zn_{.2}$)S prepared at 80^0C.

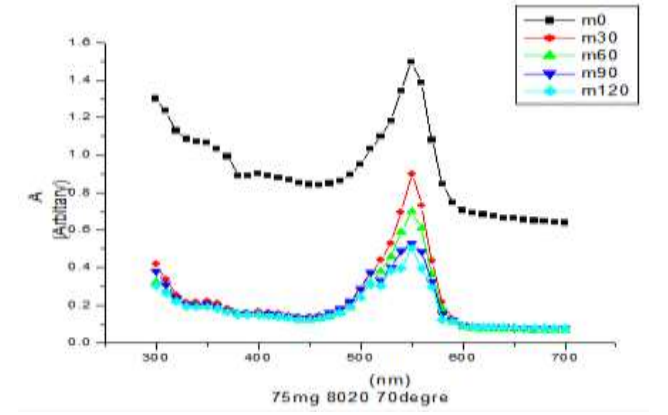

Fig.8 Absorbance vs wavelength plot of degraded dye solution after different time intervals with GO-($Cd_{.8}Zn_{.2}$)S prepared at 70^0C

Figures 6, 7 and 8 show the absorbance vs wavelength graph after different time intervals of degraded dye solution with GO-($Cd_{.8}Zn_{.2}$)S prepared at 90^0C, 80^0C and 70^0C respectively. In all the cases, the absorption peak is obtained at around 554 nm. At 0 minutes, that is before placing the solution in visible light the absorbance is high but as the concentration of dye decreased, the absorbance also decreased suggesting the photocatalytic degradation of the dye by GO-($Cd_{.8}$ -$Zn_{.2}$)S. It can also be observed that the photocatalytic efficiency is higher in the case of the nanocomposites prepared at lower temperatures (80^0C and 70^0C).

Fig.9 shows the concentration vs time graph of degraded dye solution. It is observed that the concentration of the dye is reduced to around 0.3 after 2 hours which suggests that an efficiency of about 70% could be achieved for GO-($Cd_{.8}Zn_{.2}$)S samples prepared at 80^0C and 70^0C. At a further higher temperature, efficiency falls to about 50%.

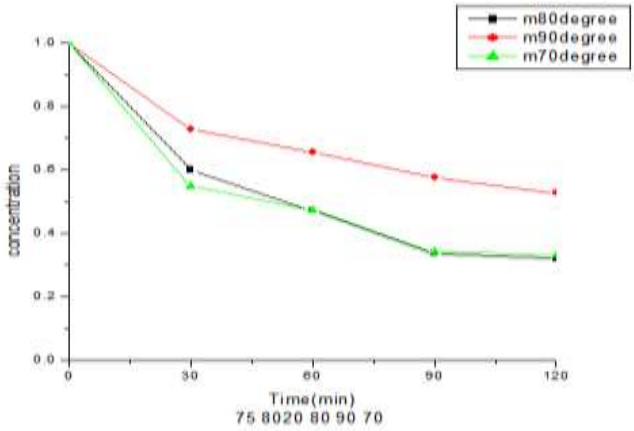

Fig.9 : Concentration vs time graph of degraded dye solution with GO-($Cd_{.8}Zn_{.2}$)S prepared at different temperatures.

The mechanism of photo degradation that may have occurred could be summarized as below:

Under visible light irradiation, the valence electrons of the semiconductor are excited to the conduction band creating holes in valence band thereby forming photogenerated electron hole pairs. Since the conduction band of CdS and graphene are at close levels, the photogenerated electrons can easily transfer from the semiconductor to graphene [2]. Graphene thus acts as an electron trap inhibiting the recombination and photo induced electron can be consumed by the dissolved oxygen atom to form peroxide ions. These ions and holes in the valence band oxidize the pollutants into CO_2 and water. Thus good photocatalytic activity under visible light can be obtained. In the process of charge transfer from (Cd-Zn)S to graphene ,separation of electron hole pairs also occur which improves the photocatalytic activity[7].

Possible reaction of photocatalysis can be as follows—

$$(Cd\text{-}Zn)S + h\upsilon \longrightarrow (Cd\text{-}Zn)S\ (e^- + h^+)$$

$$(Cd\text{-}Zn)S\ e^- + \text{graphene} \longrightarrow CdS + \text{graphene}\ (e^-)$$

$$(Cd\text{-}Zn)S + h^+ + \text{dye} \longrightarrow (Cd\text{-}Zn)S\ CO_2 + H_2O$$

$$O_2^- + \text{dye} \longrightarrow CO_2 + H_2O$$

IV. CONCLUSION

GO($Cd_{.8}Zn_{.2}$)S nanocomposite material was synthesised by chemical route method and its photocatalytic properties were investigated. Measurement of photo-catalytic degradation of Rhodamine B was carried out under visible light and the absorbance of the samples was studied by UV-VIS Spectroscopy. The adsorption performance and photocatalytic activity of the nanocomposite material was evaluated. The degradation of the dyes and change in its absorbance was studied with respect to time. The photocatalytic efficiency of the synthesized nanocomposites was calculated and an efficiency of about 70% was observed. The effect of bath temperature on the photocatalytic efficiency was studied and it was observed that a better adsorption capacity is observed in the case of GO-($Cd_{.8}Zn_{.2}$)S prepared at lower temperatures.

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