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Catalytic Response of Transition metals (Ni, Co & Cu) Doped SiO_2: TiO_2 Nanocomposite Under Natural Sun Light

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Abstract: Catalysis is the acceleration of a photo reaction in the presence of a catalyst. Dye degradation is a process in which the large dye molecules are broken down chemically into smaller molecules. Dye degradation with photo catalysis takes place through photo sensitization and photo oxidation. It depends on the electronic structure, especially band structure of the catalyst and the dye.

- ***According to:***

- ***Degradation efficiency (%) = [1- (C_t/C_0)] X 100***

- ***Where,***

- ***C_t is the concentration after time t***
- ***C_0 is the initial concentration***

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I. INTRODUCTION

The de ionization of MB molecule has major absorption band at λ_{max} = 660 nm. In accordance with the standard spectra of MB, the color of the dispersion was found to have disappeared considerably indicating that at least the chromophoric structure of dye was destroyed.

The molecular structures of Methylene Blue are shown in the figure below.

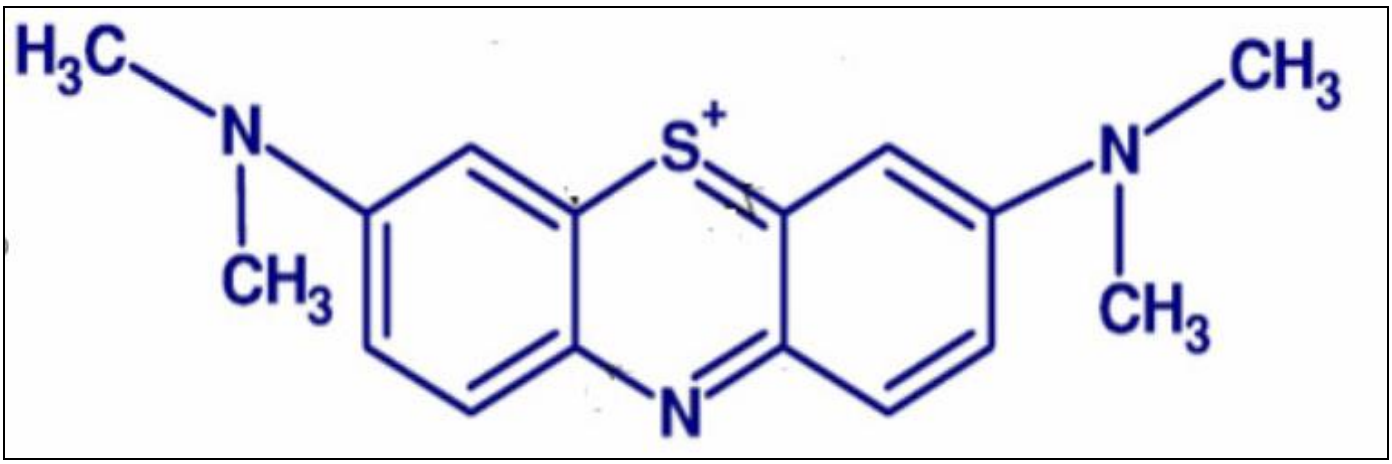

Fig 1 Molecular structure of Methylene Blue

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The enhanced photo catalytic activity of d- block metals (Ni, Co & Cu) doped SiO_2: TiO_2 Nano composites could be due to reduced hydrogen related defects. It is worth note that the photo catalytic activity of Transition metals (Ni, Co & Cu) doped SiO_2: TiO_2 nanoparticles towards dye of MB are higher than it. Therefore the MB from diluted industrial effluents may be easily removed by using these Transition metals (Ni, Co & Cu) doped SiO_2: TiO_2.

- *Photo Catalytic Activity of Bio Residues Derived Bio Silica*

The decreases in MB dye concentration due to reaction between RHS nanoparticles are shown in Fig. 7.2.1 (a). MB dye de colorization was noted that after exposure to the sunlight at different time intervals. There was about 25% degradation in the first 60 minutes and later increase up to 75% in 120 minutes was observed. The highest degradation takes place in the first half an hour but in the second half an hour, slow degradation can be noted. More over approximately 80% of MB degradation was observed at the end of 120 minutes [Nabeel A. Bakr, et al. (2014)]. The degradation study was undertaken for all the three bio silica samples Viz., RHS, MHS, RaHS as a catalyst given in the Fig. 7.2.1 (a-c) respectively. The presence of SiO_2 nano particles as a photo catalyst reveals the intensity of peak which was found to decrease with increasing irradiation time due to photo catalytic activity of bio silica. Moreover, maximum degradation was observed at 120 minutes.

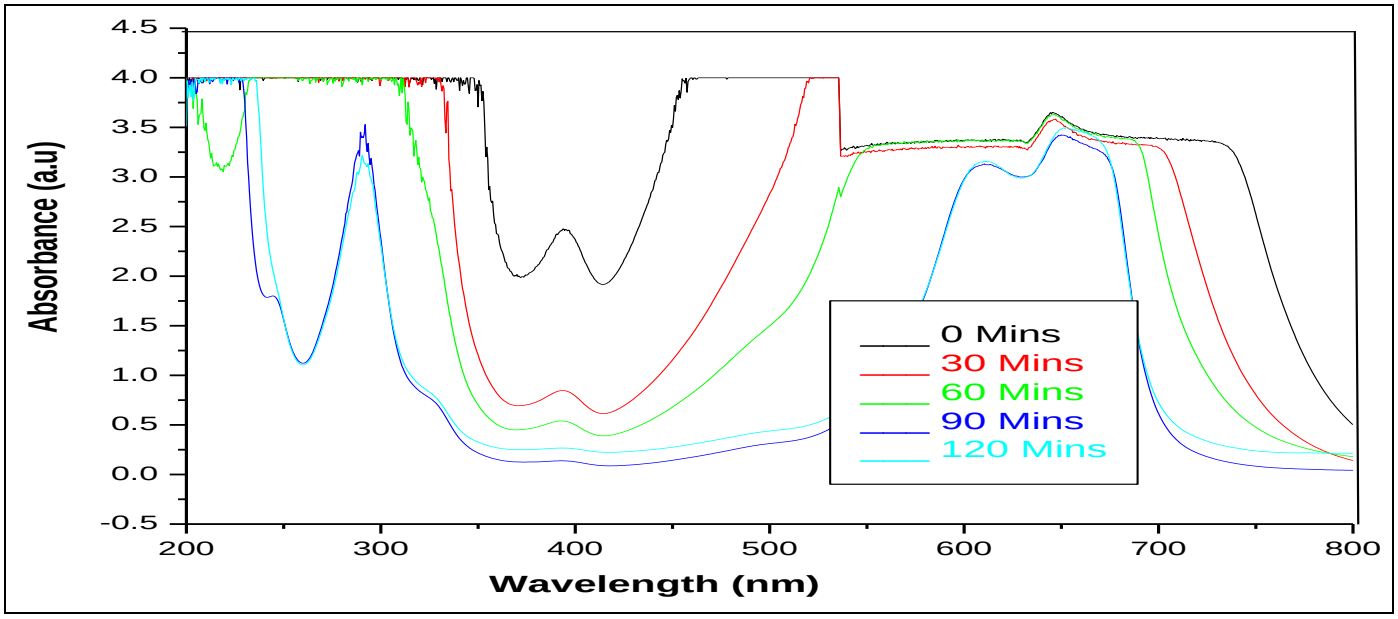

Fig 2 (a) Photo catalytic Degradation of Methylene Blue when 0.5 g of Rice Husk Silica (RHS) under Natural Sun Light at Different Time Intervals

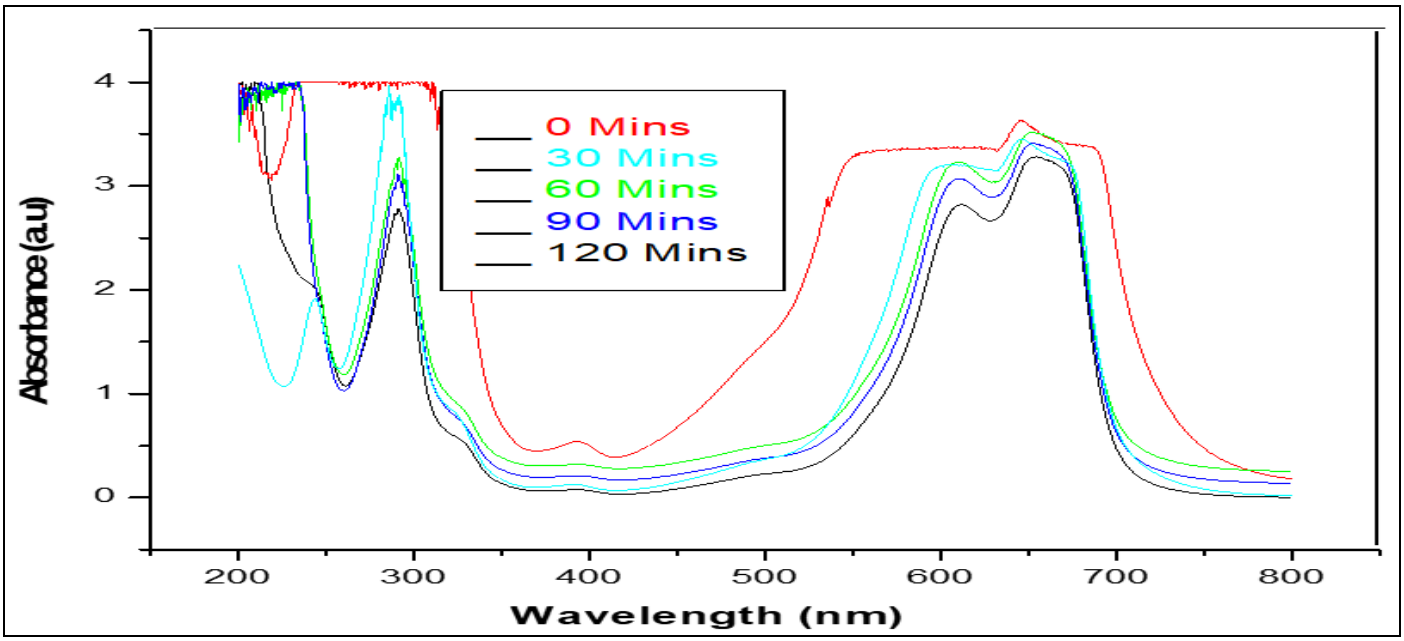

Fig 3 (b) Photocatalytic Degradation of Methylene Blue when 0.5 g of Maize Husk Silica (MHS) under Natural Sun Light at Different Time Intervals

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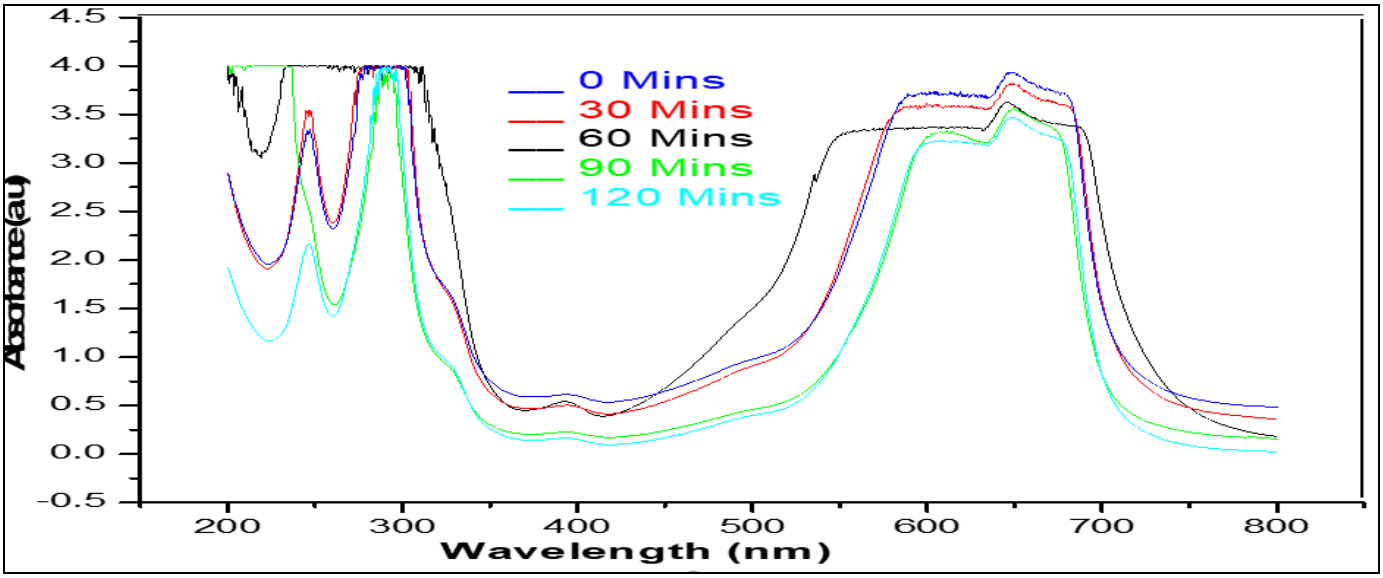

Fig 4 (c) Photocatalytic Degradation of Methylene Blue when 0.5 g of Ragi Husk Silica (RaHS) under Natural Sun Light at Different Time Intervals

➢ *Photo Catalytic Activity of Bio Residues Derived from Bio Silica with Tio₂*

Photo degradation of MB dye was examined using biosynthesized TiO_2 nanoparticles by natural sun light at different time intervals (0, 30, 60, 90 & 120 minutes) as shown in Fig. 7.2.2 (a-c). Firstly, the color of dye was seen by deep blue color changed into light blue after 30 minutes with RHS/TiO_2 nanocomposites while exposed to sun light.

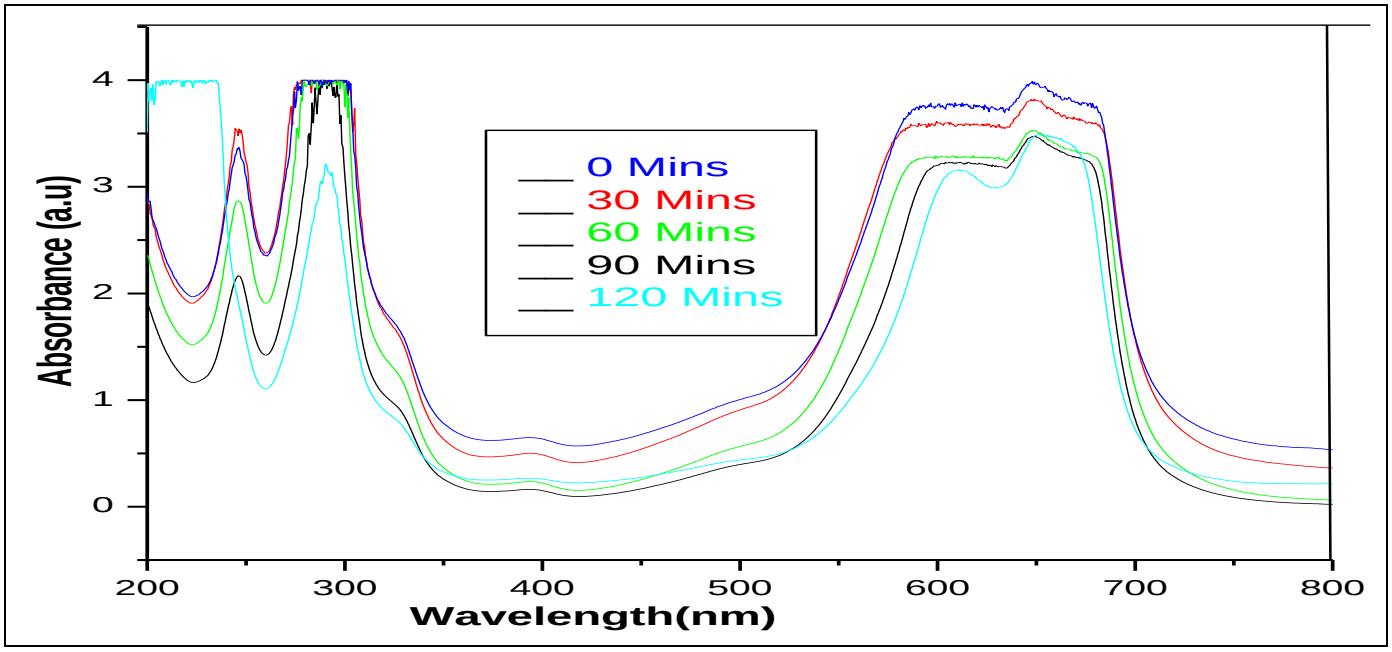

Fig 5 (a) Photocatalytic Degradation of Methylene Blue when 0.5 g of Rice Husk Silica (RHS) and doped 0.2mM TiO_2 under Natural Sun Light at Different Time Intervals

Figure 7.2.2 (a), (b) and (c) shows the UV spectral change of MB at different irradiation times with TiO_2 mediated by RHS, MHS and RaHS. The OH radicals might be responsible for the de colorization of the MB dye**.**The OH radicals may interact with MB dye or the intermediate photoproducts. It intermediates formed during degradation do not absorb at the analytical wavelength. It can be described by the action of silica, which enhances the specific surface area and increases active sites on the surface of the photo catalyst. Besides, the reaction could be controlled by the UV responsive molecular structure Ti - O - Si bonding of the photo catalyst. MB undergoes 75% of degradation in the presence of TiO_2 from ragi husk silica under natural sun light in 120 minutes but TiO_2 from rice husk silica and TiO_2 from maize husk silica produced 62% and 58% of degradations.

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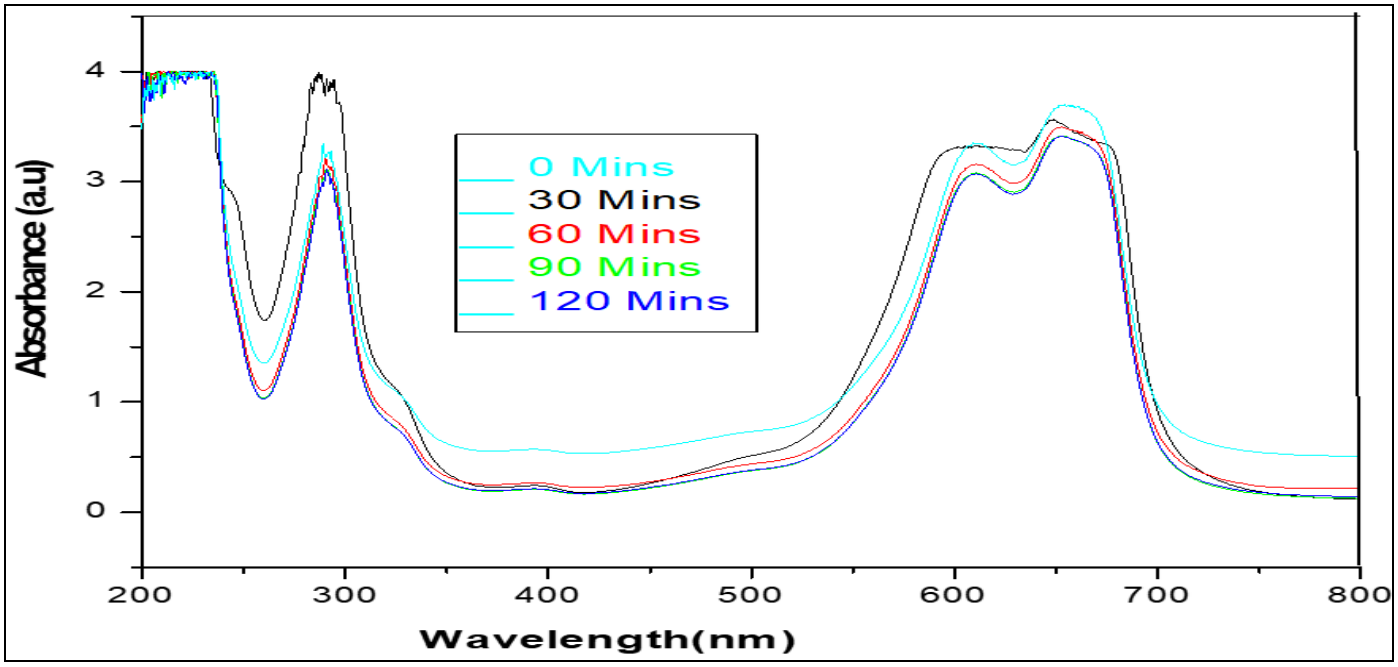

Fig 6 (b) Photocatalytic Degradation of Methylene Blue when 0.5 g of Maize Husk Silica and Doped TiO_2 0.2mM under Natural Sun Light at Different Time Intervals

➢ *The photosensitization degradation reaction can be summarized in the following five ways*

$$Dye_{ads} + h\gamma \longrightarrow Dye^{*}_{ads} \quad \text{(excitation reaction)} \quad \text{---------- (1)}$$

$$Dye^{*}_{ads} + TiO_2 \longrightarrow Dye_{ads} + TiO_2 (e_{cb}^{-}) \quad \text{(electron injection reaction)} \quad \text{---- (2)}$$

$$Dye^{*}_{ads} + TiO_2 (e_{cb}^{-}) \longrightarrow Dye_{ads} \quad \text{(charge recombination reaction)} \quad \text{---- (3)}$$

$$TiO_2 (e_{cb}^{-}) + O_2 \longrightarrow O_2^{*} \quad \text{(electron scavenging reaction)} \quad \text{---- (4)}$$

$$Dye^{*}_{ads} + OH^{*} \longrightarrow \text{degradation} \quad \text{---- (5)}$$

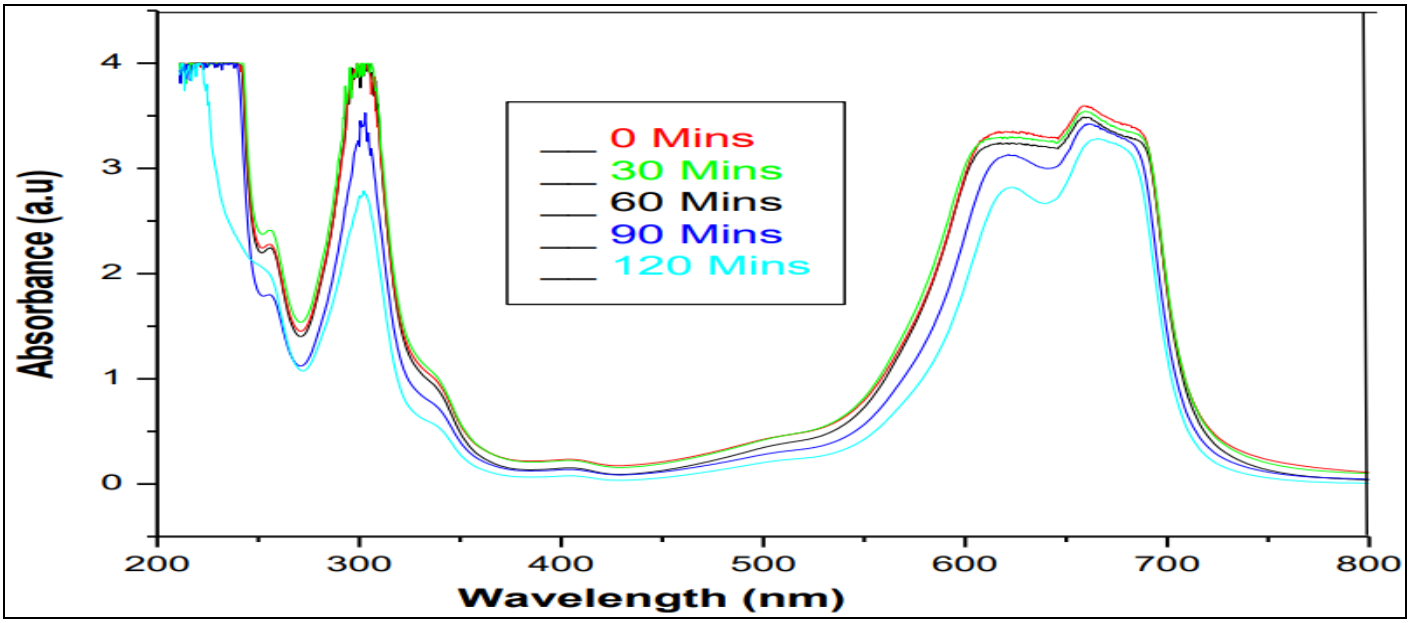

Fig 8 (c) Photo catalytic Degradation of Methylene Blue when 0.5 g of Ragi Husk Silica (RaHS) and Doped TiO_2 0.2mM under Natural Sun Light at Different Time Intervals

ISSN No:-2456-2165 https://doi.org/10.5281/zenodo.14964521

➢ *Photo catalytic activity of nickel doped RHS/TiO_2*

In the sample, introducing doping ions into the pure oxides did not show any change in the crystal structure, but caused a slight change in their particle size and an appreciable increase in their photo catalytic activities. The peak maximum for the absorbance spectra of MB at 665 nm decreases gradually with increasing irradiation time

➢ *According to The Relevant Reactions at the Surface, the Degradation of Dyes Can Be Expressed as Follows: [Lin Et Al., (2012)].*

$$NiO + h\gamma\ (UV) \longrightarrow NiO\ (e^-_{CB} + h^+_{VB}) \quad \text{---- (6)}$$

$$NiO\ (h^+_{VB}) + H_2O \longrightarrow NiO + H^+ + OH^\cdot \quad \text{---- (7)}$$

$$NiO\ (h^+_{CB}) + OH^- \longrightarrow NiO + OH^\cdot \quad \text{---- (8)}$$

$$NiO\ (e^-_{CB}) + O_2 \longrightarrow NiO + O_2 \quad \text{---- (9)}$$

$$O_2^\cdot + H^+ \longrightarrow HO_2^\cdot \quad \text{---- (10)}$$

It is clearly that pre – absorption of the dye on catalytic solid surface is an important phenomenon for an efficient charge transfer. In the photo catalytic processes, one of the main parameters of de coloration of dye solution is the photo catalyst concentration.

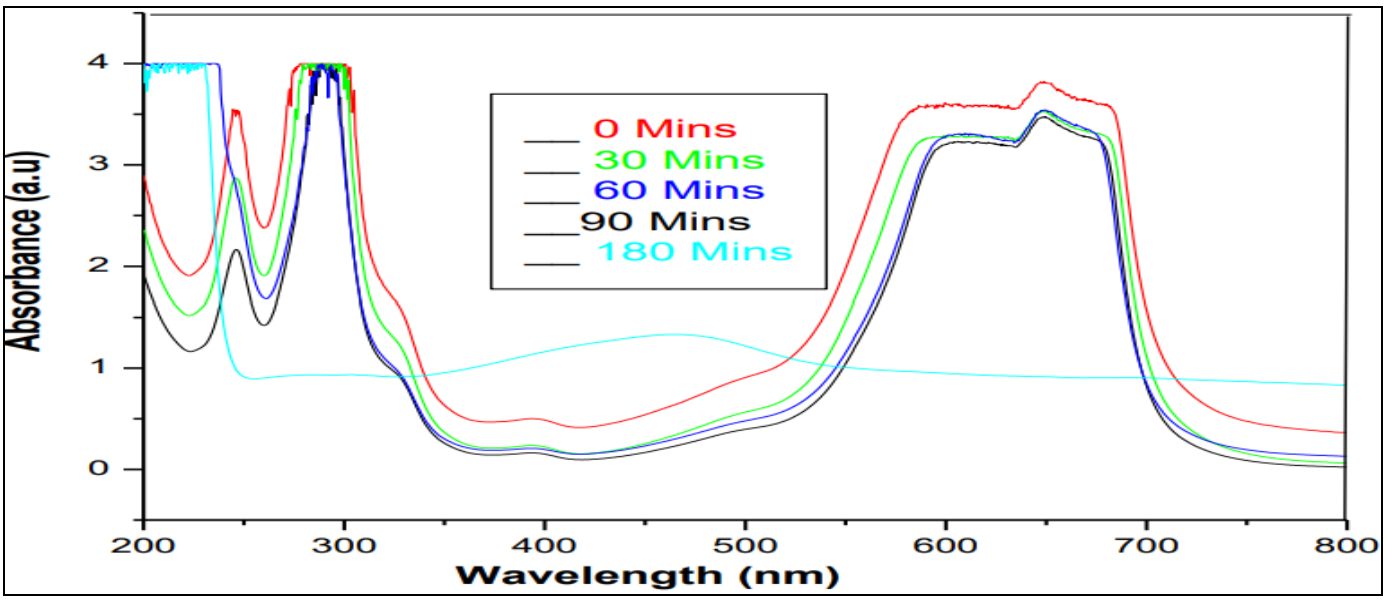

Fig.9 Photocatalytic Degradation of Methylene Blue by RHS/TiO_2/Ni under Natural Sun Light at Different Time Intervals

The degradation efficiency was reached 50% only after 90 minutes. So the increase in the catalyst quantity 30 mg and also time increased up to 180 minutes. Moreover, maximum degradation is achieved.

➢ *Photocatalytic activity of cobalt doped MHS/TiO_2*

This may be due to the high surface area and spherical structure of MHS/TiO_2/Co with highly dispersed cobalt and titanium metal ions on the silica framework

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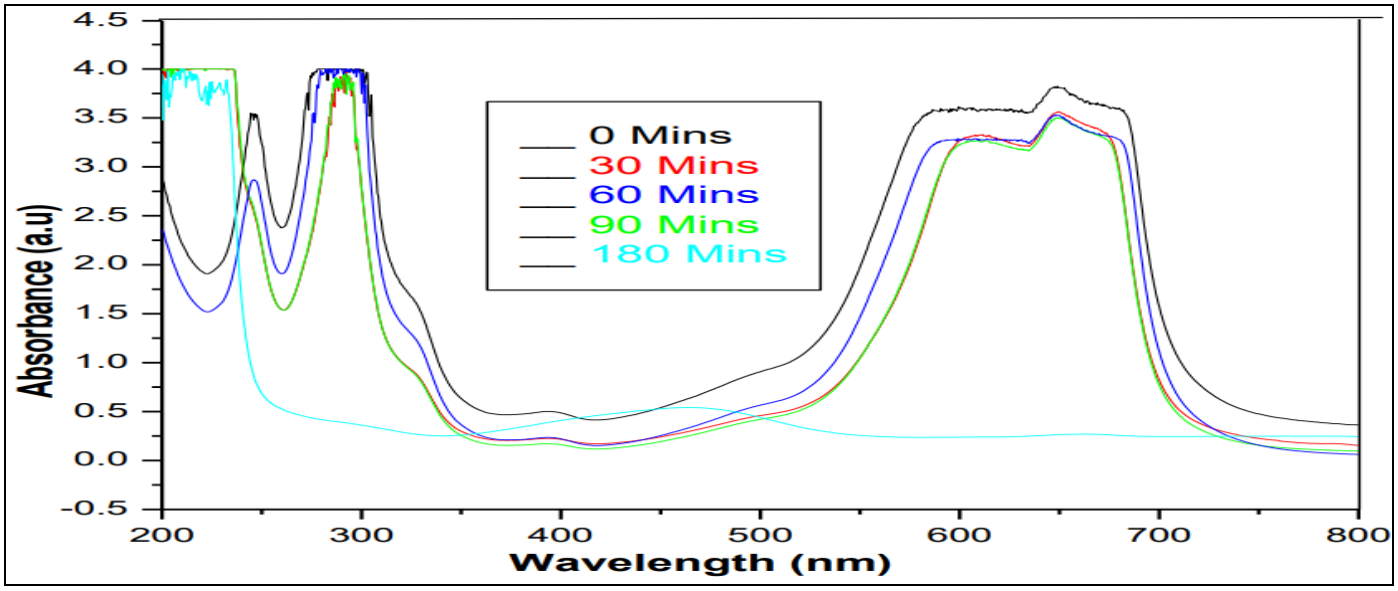

Fig 10 Photocatalytic Degradation of Methylene Blue by MHS/TiO_2/Co under Natural Sun Light at Different Time Intervals

➢ *The Relevant Reactions at the Coo Surface Causing the Degradation of Dyes Can Be Expressed as Follows [Lin, Et Al. (2012)]:*

$$CoO + h\nu\ (Sunlight) \longrightarrow CoO\ (e^-_{CB} + h^+_{VB}) \quad \text{---- (11)}$$

$$CoO\ (h^+_{VB}) + H_2O \longrightarrow CoO + H^+ + OH^\cdot \quad \text{---- (12)}$$

$$CoO\ (h^+_{CB}) + OH^- \longrightarrow CoO + OH^\cdot \quad \text{---- (13)}$$

$$CoO\ (e^-_{CB}) + O_2 \longrightarrow CoO + O_2^\cdot \quad \text{---- (14)}$$

$$O_2^\cdot + H^+ \longrightarrow HO_2^\cdot \quad \text{---- (15)}$$

$$Dye + OH^\cdot \longrightarrow \text{Degradation products} \quad \text{---- (16)}$$

$$Dye + h^+_{VB} \longrightarrow \text{Oxidation products} \quad \text{---- (17)}$$

$$Dye + e^-_{CB} \longrightarrow \text{Reduction} \quad \text{---- (18)}$$

➢ *PHOTOCATALYTIC ACTIVITY of COPPER DOPED RAHS/TIO₂*

There is no red shift in the case of TiO_2 implanted with Si and the time increased to half an hour, the degradation started. Moreover, the maximum de colourization was observed at 180 minutes. Temporal variation of spectral changes as a function irradiation of time is shown in Fig. 8.1.5 for MB $^+$ RaHS/TiO_2/Cu nanocomposites. From the change in intensity as observed, it can be seen that the nano composites could reach maximum degradation for 180 minutes of sun light irradiation.

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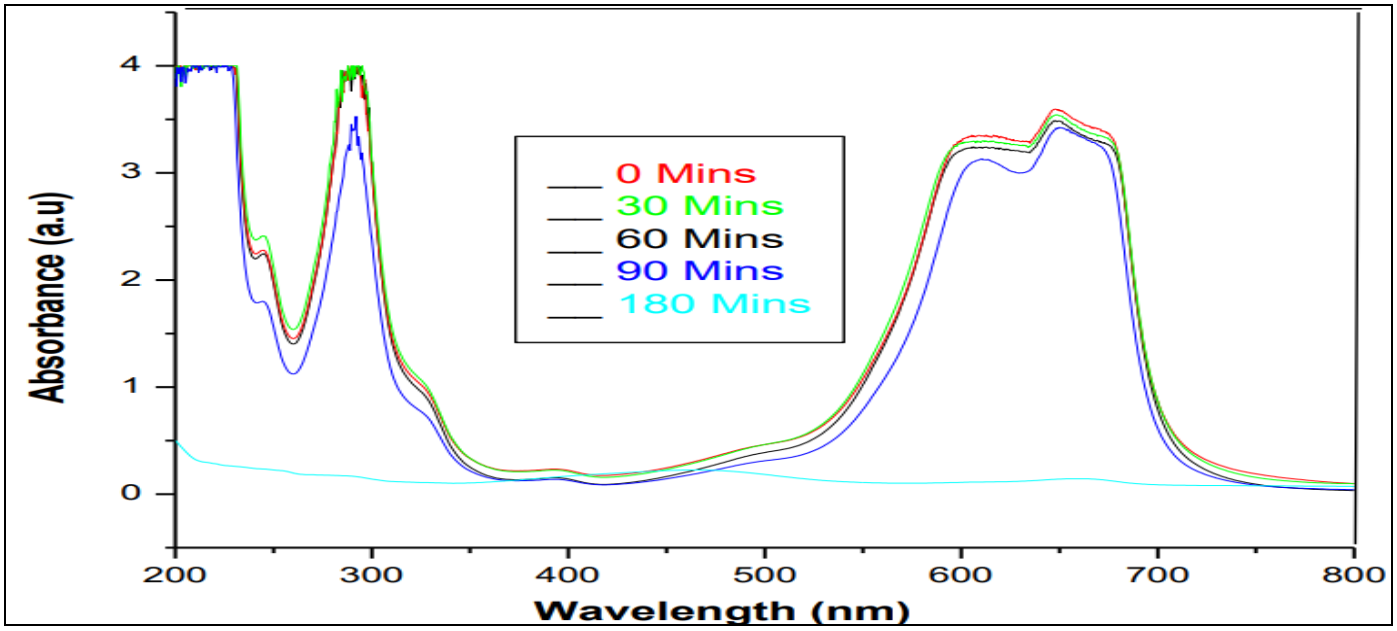

Fig 11 Photocatalytic Degradation of Methylene Blue by RaHS/TiO_2/Cu under Natural Sun Light at Different Time Intervals

➢ *The Relevant Reactions at the Cuo Surface Causing the Degradation Of Dyes Can Be Expressed As Follows:*

$$CuO + h\nu\ (Sunlight) \longrightarrow CuO\ (e^-_{CB} + h^+_{VB}) \quad (19)$$

$$CuO\ (h^+_{VB}) + H_2O \longrightarrow CuO + H^+ + OH^\cdot \quad (20)$$

$$CuO\ (h^+_{CB}) + OH^- \longrightarrow CuO + OH^\cdot \quad (21)$$

$$CuO\ (e^-_{CB}) + O_2 \longrightarrow CuO + O_2^\cdot \quad (22)$$

$$O_2^\cdot + H^+ \longrightarrow HO_2^\cdot \quad (23)$$

$$Dye + OH^\cdot \longrightarrow \text{Degradation products} \quad (24)$$

$$Dye + h^+_{VB} \longrightarrow \text{Oxidation products} \quad (25)$$

$$Dye + e^-_{CB} \longrightarrow \text{Reduction products} \quad (26)$$

II. CONCLUSIONS

MB dye was degraded using SiO_2/TiO_2 and metal doped SiO_2/TiO_2 nanocomposites under natural light irradiation. It reveals that the catalysts depend on the metal doping (Ni, Co and Cu) on SiO_2/TiO_2. The highest degradation efficiency was noted that Nickel doped rice husk silica, cobalt doped maize husk silica and copper doped ragi husk silica. In comparison of all the prepared catalysts, maximum degradation occurred in copper doped ragi husk silica.

The catalytic activity of these transition metal doped SiO_2/TiO_2 nanocomposites for the elimination of methylene blue was analyzed at its low concentration. The photo degradation of MB took place within 120 minutes; this suggests that transition metal doped SiO_2/TiO_2 nanocomposites are more effective for the photo degradation of MB. It was found that the transition metal doped SiO_2/TiO_2 nanocomposites prepared by sol gel method played a vital role in photocatalytic performance through studying the degradation efficiency of transition metal doped SiO_2/TiO_2 nanocomposites catalyst.

REFERENCES

[1]. Umeda J, Kondoh K and Michiura Y. Process parameters optimization in preparing highpurity amorphous silica originated from rice husks. *Materials Transactions.* (2007) 48(12):3095- 3100.

[2]. Shen J, Liu X, Zhu S, Zhang H and Tan J. Effects of calcination parameters on the silica phase hydrolysis:

ISSN No:-2456-2165 https://doi.org/10.5281/zenodo.14964521

effect so foriginal and leachedricehuskash. *Materials Letters*. (2011)65(8):11791183

[3]. WangW,GuB,LiangL,HamiltonWA, Wesolowski DJ. Synthesis of rutile nanocrysttalswith controlled size and shape by low temperature hydrolysis: effects of solvents composition.J.Phys.Chem.B. (2004)108, 14789-92

[4]. BakT,NowontyJ,RekasM,andSorrellC.C., Review article: Photo electrochemical hydrogen generation from water using solar energy. Materials related aspects, International journal of hydrogen energy, (2002), 991-1022.

[5]. Gole J.L., Prokes, S.M., GlembockiO.J,WangJ, Qiu X and Burda C, study of concentrationdependent cobaltiondopingoftio2andtio22-xNxat the nanoscale, Nanoscale, (2010), 11341140.

[6]. Lin, Y.J, Chang Y.H., Yang W.D., and Tasi B.S., synthesis and characterization of ilmenite $NiTiO_3$and $CoTiO_3$ prepared by a modified by pechini method, journal of non – crystalline solids, (2006), 789-794.

[7]. Devi L.G., Kottam.N., Kumar S.G., andRajashekhar K.E., preparation and enhanced photocatalyticactivity of Ni2+ doped titania under solar light, Central European journal of chemistry, (2010), 142- 148.

[8]. Bengum N.S., AhmedH.M.F., Gunasekhar.g., effects of Ni doping on photocatalytic activity of TiO_2 thhinfilms prepared by liquid phase deposition technique, Bulletin of materials science, (2008), 747-751.

[9]. Nozik A.J., photochemical diodes, U S patent No. 4,094,751, (1976), 150-153.

[10]. [10]. Shu X, He J, Chen D, Visible light induced photocatalyst based on the nickel titanate nanoparticles, Industrial and engineering chemistry research, (2008), 4750-4753.

[11]. .Kalapathy U, A. Proctor, J. Shultz, A simple method for production of pure silica from rice hull ash, M. Chareonpanich, Bioresour.Technol.73(2000)257–262.

[12]. SelvarajVentakeswaran, Ratinamyuvakumar and Venkatachalamrajendran, Nano silicon from nano silica using natural resource (Rha) for solar cell fabriciation, Phosphorus, sulphur and silicon and the related elements, (2013), 1178-1193.

[13]. Nabeel A. Bakr*, Sabah A. Salman, Ahmed M.Shano,Effect ofCoDopingonStructuralandOptical Properties of NiO Thin Films Prepared By Chemical Spray Pyrolysis Method**,** *International Letters of Chemistry, Physics and Astronomy, 11, 2014, 15-30.*