

Photo-Degradation of Vat Dye by Bimetallic Photo-Catalysts (Cu-Ni/ TiO₂ and Cu-Ni/ ZnO) Under UV and Visible Light Sources

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Abstract: Photocatalytic degradation of Vat Red R1 dye, used in textile industry using different photocatalysts and light sources were experimented on laboratory scale. 10 wt % metals doped with TiO₂ (Cu-Ni/TiO₂) and ZnO (Cu-Ni/ZnO) as photocatalysts were synthesized by three methods viz. complex precipitation (CP), deposition precipitation (DP) and wet impregnation (WI) methods. The raw photocatalysts were activated by calcination at three different temperatures (180⁰C, 200⁰C and 300⁰C) for 1 hour duration. Batch experiments were conducted with the initial concentration 0.002 mg/l to 0.01 mg/l of Vat Red R1 at pH 7 using the above photocatalysts. The extent of dye degradation was determined by UV – VIS spectrophotometry. The Cu-Ni/TiO₂ catalyst prepared by WI method is observed to show maximum dye removal of 97.70% for the initial dye concentration of 0.008 mg/l under UV irradiation. The other catalyst, Cu-Ni/ZnO showed maximum dye removal of 76% for the initial dye concentration of 0.002 mg/l under UV irradiation. The two catalysts found to perform better colour removal after calcination at 180⁰C. In photocatalytic degradation using visible light, the catalyst Cu- Ni/TiO₂ prepared by WI method (calcined temperature at 180⁰C) showed maximum colour removal of 99.20%. The photocatalyst Cu-Ni/ZnO at the same calcinations temperature showed maximum colour removal (95 %) for the concentration of 0.002 mg/l of Vat Red R1. From these results, it is observed that the maximum colour removal was experienced with the use of Cu-Ni/TiO₂ (calcination temperature 180⁰C) in visible light. The increase in initial concentration has resulted in decrease of colour removal for both the photocatalysts.

Keywords: Cu–Ni Bimetallic Photocatalysts, Vat Red R1, TiO₂ and ZnO Photocatalysis

I. Introduction

Various dyes have been used in textile dyeing, paper pulp, plastic, leather, cosmetics and food industries (Gulnaz et al., 2004). Colour dye stuff when discharged from these industries creates health hazards and environmental problems. The photocatalysis is new, fast, convenient and less expensive method for degradation of the dye (Michael et al., 1992, Chin Mei Ling et al., 2004). Among the various oxides of photocatalysts TiO₂ and ZnO are very effective photocatalysts owing to their high band gap (ZnO, 3.17 eV and TiO₂ 3.2 eV). Efforts are on to increase its efficiency by incorporating stable optical sensitizer with changes within the semiconductors system to make it more effective in receiving and utilizing solar energy (Chatterjee et al., 2005). These include: doping TiO₂ and ZnO with various transition metals such as Pt, Au, Ag, Cr, V (Anpo et al., 2003; Bosc et al., 2007), non metals (like N) (Hong et al., 2005) and anchoring an organic dye sensitizer molecule on its surface (Chatterjee et al., 2005). Present works aims at sensitizing bimetallic photo-catalysts, Cu-Ni/ TiO₂ and Cu-Ni/ ZnO using various methods and study their photo-degradation properties on VR1 dye under UV and visible light sources.

II. Materials And Methods

2.1 Materials

Vat Red R1 (VR1) was used as a model dye for photocatalytic degradation study. Copper nitrate trihydrate Cu (NO₃)₂.3H₂O and nickel nitrate hexahydrate, Ni (NO₃)₂.6H₂O were used to dope titanium dioxide and zinc oxide. 10wt% bimetallic Cu-Ni/ TiO₂ and Cu-Ni/ ZnO with 5:5 copper and nickel ratios were prepared using complex precipitation (CP), deposition precipitation (DP) and wet impregnation (WI) method.

2.2 Preparation of photocatalysts by CP DP and WI methods

Calculated amounts of metal salts were weighed and dissolved in distilled water, followed by the addition of glycerol in 2:1 glycerol: metal molar ratio and stirred continuously. TiO₂ and ZnO were then added

with continuous stirring for one hour. For CP method, precipitates formed during the titration of the above mixture with 0.25M NaOH, maintained at a temperature 8-10⁰C were collected until final of pH 14 is reached. The precipitates were then filtered and dried in oven at 75⁰C for 18 hours. The same procedure was used for the deposition precipitation (DP) method except that the precipitation temperature was 25⁰C and the final pH was 8.5 (Chong et al. 2011).

Photocatalyst prepared by WI method, TiO₂ and ZnO support was added into the copper and nickel salt solution to prepare 10wt% photocatalysts. The suspension was stirred for 1 hour and the solvent was evaporated in a water bath at 80⁰C until a thick paste was obtained. This paste was then dried in an oven at 120⁰C for 18 hours. The dried catalysts were ground into fine powder and stored in desiccators at room temperature until it is being used (Chong et al.2011).

2.3 Photocatalytic Degradation Study of Vat Red R1

Reaction study was carried out at pH 7 and room temperature (~ 27⁰C). About 1g of Photocatalyst was added to 10 ml of distilled water and sonicated for 10 min at 25⁰C followed by the addition of 1ppm VR1 solution to give a final volume of 30 ml. The suspension was stirred using a magnetic stirrer for two hours in dark and later this suspension was illuminated for 1 hour using 125W UV lamp and 500W halogen lamp (visible light source). Reaction parameters were photocatalysts prepared using different methods and calcination temperatures (180⁰C, 200⁰C, and 300⁰C). After 1 hour reaction time, samples were centrifuged twice prior to monitoring the absorbance of solution at 613nm wavelength using UV/VIS spectrophotometer (Thermo, Helios Zita). Control experiments were also conducted without the addition of photocatalysts.

III. Results and Discussions

3.1 Characterisation of photocatalysts

XRD (XRD – Shimadzu, XRD 6000, made in Japan)

The x-ray diffraction data were recorded by Cu K α radiation (1.5406 Å). The intensity data were collected over a 2 θ range of photocatalysts prepared by complex precipitation method (before and after treatment of Vat Red R1) and wet impregnation method (before and after treatment of Vat Red R1) are 25.327⁰-53.976⁰, 25.1995 - 37.74⁰, 25.208 – 55.012⁰ and 25.314⁰ – 39.097⁰. The average grain size of the samples was estimated with the help of Scherrer equation using the diffraction intensity of four peaks (showed maximum intensity) based on the before and after treatment of Vat Red R1 by complex precipitation and wet impregnation method. The mean grain size (D) of the particles was determined from the XRD line broadening measurement using Scherrer equation (Rita John et al., 2011).

$$D = 0.89\lambda / (\beta \cos\theta) \quad (1)$$

Where λ is the wavelength (Cu K α), β is the full width at the half- maximum (FWHM) of the Cu-Ni/ TiO₂ (before and after treatment of Vat Red R1) line and θ is the diffraction angle. The calculated particle sizes are, at CP method (before treatment of dye) the dimension is 0.99 nm, after treatment of dye by the same method the particle dimension was found that 1.972 nm and the catalyst prepared by WI method , the particle dimension showed that (before and after treatment) 2.90 nm and 3.63 nm respectively. The above result showed that after treatment of dye the particles size are increased.

The peaks appearing at 25.32⁰, 48.09⁰, 53.97⁰(before treatment of dye) can be perfectly indexed to (110), (200), and (210) respectively by wet impregnation method. After treatment of dye the 2 θ values of 25.19⁰, 47.95⁰, 37.69⁰ that correspond to (100), (111) and (100) planes, respectively by the above method. As well as the peaks appeared by complex precipitation method on before treatment of dye, the peaks appearing at 25.2⁰, 47.98⁰ and 55.01⁰ are perfectly indexed to (100), (111) and (220) and after treatment of dye by the above method the peaks appearing at 25.19⁰, 47.98⁰ and 37.74⁰ are indexed to (100), (111), (110) respectively. A number of strong Bragg reflections can be seen which correspond to the (111), (200) and (220) reflections of face centered cubic symmetry (FCC) of copper and nickel. The powder XRD patterns of fresh calcined photocatalysts clearly reveal that the presence of Cu and Ni containing phase detected in all samples. The above result indicates that after photocatalytic degradation particles sizes are increased. The peaks of WI method and CP method of Cu-Ni/ TiO₂ before treatment are 2 θ = 25.32 and 25.20 respectively and after treatment are 2 θ = 25.19 and 25.90 respectively, corresponding to the peak of anatase TiO₂.

FT-IR (FTIR – Shimadzu, Prestige - 21)

The IR spectra of photocatalyst by WI method after calcinations at 180⁰C and dye loaded catalyst is shown in Fig. 1.

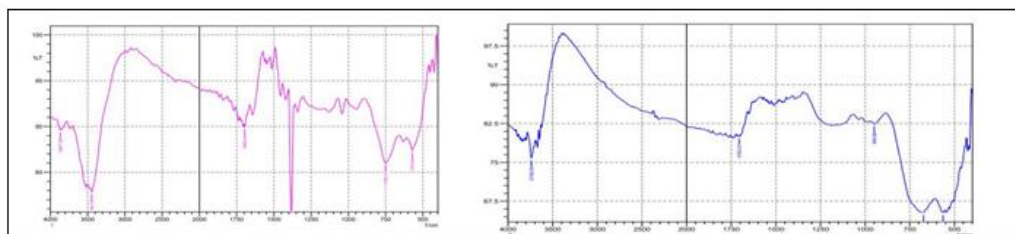


Fig 1: FTIR images of Cu-Ni/ TiO₂ by WI method before and after treatment

The adsorption spectra displayed a number of absorption peaks, indicating the complex nature of the catalysts. FTIR spectrum of Cu-Ni/ TiO₂ by wet impregnation method shows that the peak positions are at 3738.05, 1705.07, 948.98 cm⁻¹. The band at 3738.05 cm⁻¹ is due to NH₂ aliphatic and aromatic group, 1705.07 cm⁻¹ stretch vibration of keto group. 948.98 cm⁻¹ shows bending of O-H carboxylic acid. FTIR spectrum of Cu-Ni/ TiO₂ by WI method with treatment of VR1 shows that the peak positions are at 3867.28, 3446.79, 1695.43, 750.31, 570.93 cm⁻¹. The band at 3867.28 cm⁻¹ is due to NH₂. While 3446.79 cm⁻¹ is an indication of the presence of the stretch vibration of the bonded hydroxyl groups on the catalyst. The strong absorption peak at 1695.43 cm⁻¹ is evidence of stretch vibration of keto group. The IR spectra of photocatalyst by CP method after calcinations at 180⁰C and dye loaded catalyst is depicted in Fig. 2.

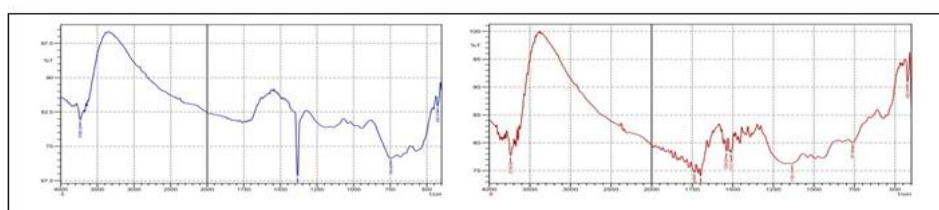


Fig 2: FTIR images of Cu - Ni/ TiO₂ by CP method before and after treatment

FTIR spectrum of Cu-Ni/ TiO₂ by CP method shows that the peak positions are at 3736.12 cm⁻¹, 746.45 cm⁻¹, 426.67 cm⁻¹. The band at 3736.05 cm⁻¹ is due to NH₂ aliphatic and aromatic group, 746.45 show methylene rocking monosubstitution with C-Cl stretch and 426.67 cm⁻¹ shows S-S stretch. FTIR spectrum of Cu-Ni/ TiO₂ by CP method with treatment of VR1 shows that the peak positions are at 3738.05, 1539.20, 1512.19, 1134.14, 761, 424.34 cm⁻¹. The band at 3738.05 cm⁻¹ is due to NH₂ aliphatic and aromatic group, the strong absorption peaks like 1539.20 cm⁻¹ and 1512.19 cm⁻¹ show both are aromatic N-O compound. The band at 1134 cm⁻¹ is due to the presence of sulphonates. 761.88 show methylene rocking monosubstitution with C-Cl stretch and 424.34 cm⁻¹ aryl disulfides (S-S stretch). The results show that, after treatment of catalyst the peaks are increased and it is a good indication for the effective adsorption of VR1.

SEM ((SEM – JOEI - JSM 6390)

SEM images showing the shapes and morphology of the Cu-Ni/ TiO₂ prepared by WI and CP methods before and after treatment of VR1 are depicted in Figure 3a and 3b

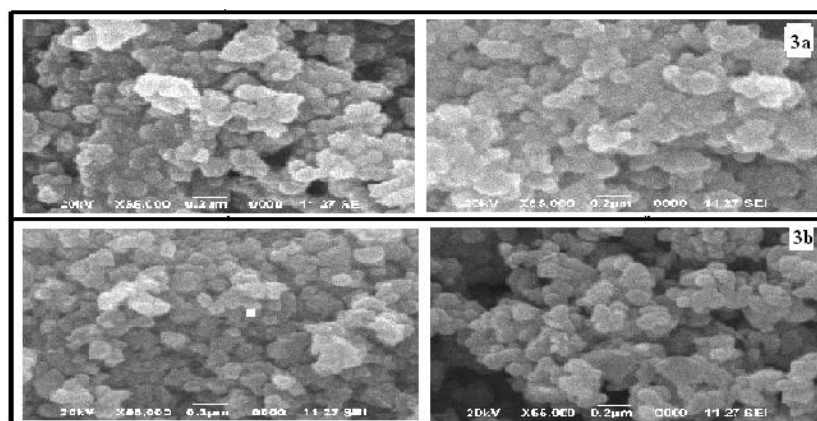


Fig.3a & 3b SEM images of photocatalysts (WI & CP) before and after treatment

The SEM photographs showed that particle size was increased after degradation. The surface structure was found rough and heterogeneous porous nature before and after treatment. After degradation of dye the catalyst Cu-Ni/ TiO₂ has considerably number of pores where there is good possibility for dye to be trapped and adsorbed onto these pores and it is a good sign for effective adsorption of dye Vat Red R1

EDX (EDX -JOEI - JSM 6390)

EDX Analysis is providing an elemental map of the sample that can be compared to the electron micrographs. Chemical characterizations of the Cu-Ni/ TiO₂ before and after treatment of vat red R1 by wet impregnation and complex precipitation methods shown in the figure 4 and 5. To stimulate the emission of characteristic x- rays from a specimen, a high energy beam of charged particle such as electrons or photons or a beam of x-rays, is focused into the sample being studied of the Cu-Ni/ TiO₂ film coated on the glass substrate. It is clearly displayed that materials contained Cu, Ni, Ti and O. Weight percentage and atomic percentage elements where shown in table 1 and 2. No other peak related with any impurity has been detected in the EDX.

Table1: EDX data of Wet impregnation method of Cu-Ni/ TiO₂

Wet impregnation method of Cu-Ni/ TiO ₂ (Before treatment of vat red R1)			Wet impregnation method of Cu-Ni/ TiO ₂ (After treatment of vat red R1)		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
O	56.33	80.48	O	44.14	71.79
Ti	30.87	14.73	Ti	37.30	20.26
Cu	6.42	2.50	Cu	10.37	4.59
Ni	6.38	2.29	Ni	8.19	3.35

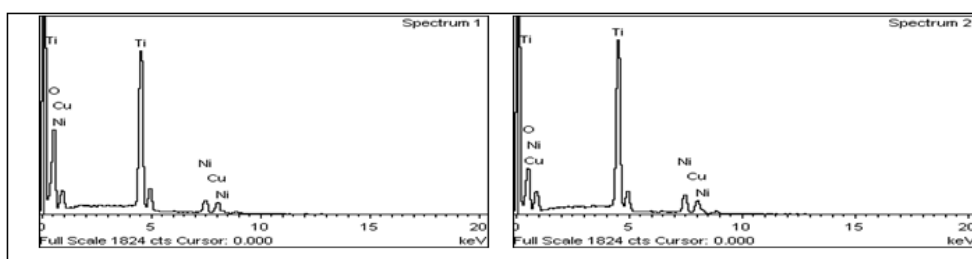


Fig 4: EDX images of photocatalysts (WI & CP) before and after treatment

Table 2: EDX data of Wet impregnation method of Cu-Ni/ TiO₂

Complex precipitation of Cu-Ni/ TiO ₂ (Before treatment of vat red R1)			Complex precipitation method of Cu-Ni/ TiO ₂ (After treatment of vat red R1)		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
O	46.53	73.05	O	50.58	76.39
Ti	43.79	22.96	Ti	37.21	18.77
Cu	4.81	2.06	Cu	6.24	2.57
Ni	4.87	1.93	Ni	5.97	2.27

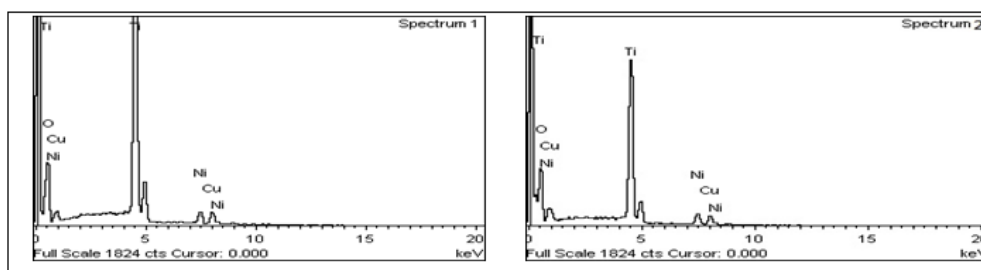


Fig.5: EDX images of photocatalysts (WI & CP) before and after treatment

3.2. Photocatalytic degradation studies

3.2.1 UV light source:

The result obtained for Photocatalytic activity of Cu-Ni/TiO₂ and Cu-Ni/ZnO prepared by CP, DP, and WI methods observed that the photocatalyst of Cu-Ni/TiO₂ at CP methods showed maximum removal of VR1 at 180°C of calcined temperature. It was observed that 90% removal of 0.0002 mg/l VR1. The DP and WI methods showed maximum removal was found at 180°C calcined temperature and 0.002 mg/l and 0.004 mg/l of VR1. In DP method 85 % of colour removal was found at 0.002 mg/l of VR1 and WI method the maximum removal was

showed at 97.74% of 0.004 mg/l of VR1. In photocatalytic degradation with UV lamp, the catalyst Cu-Ni/ZnO showed maximum removal of 66.5% (at 0.008 mg/l), 68.75 % (at 0.008 mg/l) and 76% (at 0.008 mg/l) respectively using the CP, DP, WI method.

3.2.2 Visible light sources:

The photocatalyst prepared by CP, DP, WI methods showed better activity at 180⁰C and 200⁰C of calcined temperatures. It was observed that the photocatalyst prepared by using Cu-Ni/TiO₂ at calcined temperature 180⁰C by WI method showed maximum colour removal. It found that 99.20 % of 0.002 mg/l of Vat Red R1 was removed. The comparison of photocatalyst prepared by using Cu-Ni/ZnO was found that maximum removal 95 % at 180⁰C calcined temperature of 0.002 mg/l of vat red R1. The reference experiments under similar conditions without the presence of photocatalysts were also carried out. Under the same concentration of Vat Red R1 (0.002 mg/l), 20% dye removal under UV and 25% dye removal under visible light sources were observed (Fig. 6.). Similarly experiments were carried out by adding the catalysts in the absence of light sources to same concentration of Vat Red R1. The results showed 35% and 31% dye removal respectively by the Cu-Ni/TiO₂ and Cu-Ni/ZnO catalyst.

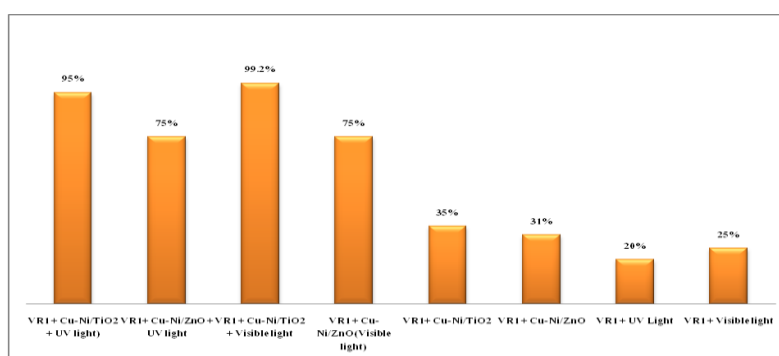


Fig 6: Comparison study graph of Vat Red R1

IV. Conclusions

Photocatalytic degradation studies of vat Red R1 dye were carried using different photocatalysts and UV and visible light sources. 10 wt % metals doped TiO₂ (Cu-Ni/TiO₂) and ZnO (Cu-Ni/ZnO) as photocatalysts were synthesized by three methods Viz. complex precipitation, deposition precipitation and wet impregnation methods. The study showed that among the three methods of preparation, the WI method is the best method for VR1 degradation. Comparison of calcinations temperature (180⁰, 200⁰, and 300⁰) revealed that photocatalyst calcined at 180⁰C showed best photocatalytic activity for dye removal. Also Cu-Ni/TiO₂ is proved more efficient catalyst than Cu-Ni/ZnO in the removal of Vat Red R1. In this system studied, total removal of dye was possible in a practical time scale. According to XRD and SEM analysis, after degradation of dye the catalyst Cu-Ni/ TiO₂ has considerably number of pores where there is good possibility for dye to be trapped and adsorbed onto these pores and it is a good sign for effective adsorption of dye Vat Red R1.

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