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REMOVAL OF BG DYE IN SUNLIGHT AND DARK USING NIO AND ITS COMPOSITES WITH CuO AND ZnO

P. Muhambihai*^{1, 3}, V. Rama², P. Subramaniam³

¹Research Scholar, Reg. no. 11707, Department of Chemistry, Aditanar College of Arts & Science, Tiruchendur, Tamil Nadu, India ²Department of Chemistry, Sarah Tucker College (Autonomous), Tirunelveli, Tamil Nadu, India ³Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli, Tamil Nadu, India *Corresponding authory multiple and amail com

*Corresponding author: muhaselva@gmail.com

ABSTRACT

NiO nanoparticles were synthesized by precipitation method and CuO and ZnO doped NiO nanocomposites were synthesized by co-precipitation method. The synthesized nanomaterials were characterized by UV, FT-IR, XRD and SEM with EDS studies. The photocatalytic properties of synthesized nanocomposites have been evaluated by the photodegradation of Brilliant Green (BG) under Sun light and Dark. In this investigation, the degradation capacities of prepared nanomaterials were analyzed at different catalyst dosage, pH, contact time, electron acceptor, and concentration were determined. The dye removal efficiency of the NiO/CuO nanocomposites is more than that of pure NiO nanomaterials. This enhanced photocatalytic activity can be ascribed to the low recombination probability of photo-induced carriers due to the efficient charge transfer in the nanocomposites. The synthesized NiO/CuO nanocomposite may be a promising candidate for dye photodegradation of wastewaters. The experimental data were best fit for the Langmuir and Freundlich isotherm and it follows pseudo second oder model.

Keywords: Photocatalytic Degradation, Adsorption, NiO, CuO, ZnO, nanocomposites, Brilliant Green (BG).

1. INTRODUCTION

Textile, paint, pharmaceutical and cosmetic industries were the most important resource for pollution of both water and soil over the past decades. In industrial effluents, synthetic dyes were found to be a major environmental intimidation [1, 2]. Synthetic organic dyes are the harmful materials present in water effluents and are carcinogenic to human beings. The dyes present in the water effluents lump the penetration of oxygen and sunlight which are necessary for aquatic life [3, 4]. Release of colored wastewaters from such industries creates severe problems to the environment. Color removal from textile dyeing effluents has been the mark of great attention [5]. Therefore, the efficient removal of dyes from aqueous systems becomes environmentally important. Recent years, a number of chemical, physical and biological methods have been developed for removing dyes from wastewater. Among them, adsorption technique is believed to be one of the most effective and simplest processes [6]. Because of the intractable nature of synthetic dyes, usual biological treatment processes are ineffective and adsorption while coagulation practices result in secondary pollution.

Accordingly, a more hopeful technology based on advanced oxidation processes (AOPs) has been studied extensively for decolorization and degradation of textile dyes. Even though different methods have been attempted, none of the method is proved to be efficient. Hence nano metal oxide was used for the removal of dyes from aqueous solutions. In the presence study, for the removal of Brilliant Green (BG) dye from waste water, efficient adsorbent catalyst like NiO nanoparticles, NiO/CuO and NiO/ZnO nanocomposites were prepared and the structural properties were characterized by spectroscopic and other analytical techniques.

2. MATERIAL AND METHODS

All analytical reagents used in this experiment were of A.R. grade and are obtained from Sigma-Aldrich Chemicals at Chennai, India. The materials include Sodium hydroxide, Zinc nitrate, Copper nitrate, Nickel nitrate, Brilliant Green (BG), Ethanol and Acetone.

2.1. Preparation of NiO nanoparticles, NiO/CuO and NiO/ZnO nanocomposites

To the heated aqueous solution of 0.5M sodium hydroxide, 0.25M Nickel nitrate solution was added

from the burette under high speed stirring. The beaker was sealed at this condition for 2h. The precipitated NiO nanoparticle were filtered and cleaned with deionised water and ethanol, then it is calcinated at 300°C for 2h [7] and to prepare NiO/CuO nanocomposites, the aqueous solution of sodium hydroxide was heated to 55°C and to this, 0.25M aqueous solutions of Nickel nitrate and Copper nitrate prepared in the same beaker are added drop wise from the burette under high speed stirring. The precipitated NiO/CuO nanocomposites were filtered and cleaned with deionised water and ethanol, and then it was calcinated at 300°C for 2h. For the preparation of NiO/ZnO nanocomposites, Zinc nitrate solution was used instead of Copper nitrate and the same procedures were followed as in the preparation of NiO/CuO nanocomposites.

3. RESULTS AND DISCUSSION

3.1. Characterization of the nanomaterials

In the UV Vis spectrum for NiO nanoparticles, it is noted that the absorption edge values for NiO samples lie in the wavelength range of 356 nm [8] and the UV-visible absorption spectra of NiO-CuO nanocomposites, two new peaks appeared at 245 nm and at 320 nm for NiO-CuO nanocomposites. NiO and CuO nanoparticles have better efficiency in UV region (200-380nm) and it drastically decrease in visible region whereas in NiO-CuO nanocomposite, the spectra shows increase in absorption when it goes from UV region to visible region [9] and the UV-Vis spectra of NiO-ZnO nanocomposites, two new peaks appeared at 336 nm and at 624 nm for NiO-ZnO nanocomposites. NiO and ZnO nanoparticles have better efficiency in UV region (200-380nm) and it drastically decrease in visible region whereas in NiO-ZnO nanocomposites the spectra shows increase in absorption when it goes from UV region to visible region [10]. The band gap energy (Eg) of the prepared nanomaterials can be evaluated from the UV-Vis spectra by Tauc plot of $(\alpha h\nu)^2$ versus (h ν) and extrapolation of the linear portions of the curves to the energy axis according to [11]:

$$\alpha h\nu = B(h\nu - E_{g})^{1/2}$$

where, α is the absorption coefficient, hv is the photon energy, E_g is the direct band gap energy, and B is a constant. The absorption coefficient (α) was determined from the relation A = $I/I_0 = e^{(-\alpha_d)}$ or it can be calculated using the well-known relation deduced from Beer-Lambert's relation, $\alpha = 2.303$ A/d, where d is the path length of the quartz cuvette and A is the absorbance determined from the UV-visible spectrum. UV-Vis absorption spectra and the Tauc plot of the prepared nanomaterials are shown in Fig. 1. From the curve, the band gap of the NiO sample has been found to be 3.47 eV, which is in agreement with value (3.55 eV) reported by Boschloo and Hagfeldt [12]. The E_{σ} of the photocatalyst NiO-ZnO was found to be 3.69 eV. Band (E_{σ}) of the synthesized NiO-CuO energy gap nanocomposites photocatalysts was found to be 5.06 eV.



Fig.1: UV Spectra and Tauc plot for (a) NiO (b) NiO/ZnO (c) NiO/CuO nanomaterials

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In the FTIR spectra of NiO nanoparticles, the peak observed at 3440.39 cm⁻¹ are may be due to O-H stretching and deformation and peak at 1630.62 cm⁻¹ assigned to the bending vibrations of water molecules adsorption on the metal surface. The peaks at 429.08 cm⁻¹ are corresponding to Ni-O stretching vibration [13]. The strong peak in the spectrum of NiO/CuO nanocomposite at 3417.86 cm⁻¹ is attributed to isolated hydroxyl groups and at 1649.14 cm⁻¹ indicates the bending vibration of the water molecule which is on the

surface of NiO/CuO nanocomposite. Ni-O stretching band is observed at 482.20 cm⁻¹ while the Cu-O stretching band is observed at 597.93 cm⁻¹ [14]. In the FT-IR spectra of ZnO/NiO nanocomposite, the broad band at 3417.86 cm⁻¹ corresponds to OH group of isolated water molecule and band at 1629.55cm⁻¹ is assigned to bending vibration of water molecule. The weak peaks at 671.23 cm⁻¹ and 422.41cm⁻¹ correspond to the stretching frequencies ZnO [15] and NiO respectively.



Fig.3: XRD pattern of (a) NiO, (b) NiO/ZnO and (c) NiO/CuO nanomaterials

In the X-ray diffraction patterns of NiO nanoparticles all the diffraction peaks are well indexed to the cubic phase NiO with the rock salt structure [16] (JCPDS file no: 78-0429). The average particle size in the present precipitation method calculated is found to be in the range of 26.3 nm [17] and the XRD pattern of ZnO/CuO nanocomposite, the diffraction peaks are well defined and in good agreement with JCPDS card numbers 78-0429 and 89-5899 for NiO based cubic phase with the rock salt structure and CuO based

monoclinic structure respectively. The sharp peaks represents that the obtained nanocomposite is having high crystallinity nature. The average crystallite size was measured as 16.2 nm [9] and the X-ray diffraction pattern of NiO/ZnO nanocomposite, some of the diffraction peaks like 35.62°, 38.71°and 48.84° can be indexed to ZnO as per the JCPDS file 80-0075 and some other diffraction peaks are indexed to NiO as per the JCPDS file 78-0429. The NiO/ZnO nanocomposite is a mixture of two phases such as a ZnO-based hexagonal wurzite structure and a NiO-based cubic phase with the rock salt structure [18]. The average particle size has been found to be in the range of 22.6 nm.

The SEM image of NiO nanoparticle shows that, it is spherical, aggregated and compressed and the SEM image

of NiO/CuO nanocomposite have been found to be needle shaped and snow flaked structure and the SEM image of NiO/ZnO nanocomposites have been found to be spherical and porous structure.

The chemical composition of NiO nanoparticle, NiO/CuO and NiO/ZnO nanocomposites were investigated by EDS analysis. The chemical analysis of the NiO nanoparticle shows that only Ni and O signals have been detected. The EDS spectrum of NiO/CuO nanocomposites shows Ni, Cu and O signals as well as NiO/ZnO nanocomposites shows Ni, Zn and O signals. In all the cases, there is no signals of secondary phase are impurity has been detected. This suggested the high purity of prepared nanomaterials.



Fig. 4: The SEM and EDS for (a) NiO (b) NiO/ZnO and (c) NiO/CuO nanomaterials

3.2. Mechanism of photocatalytic reaction

In a typical photocatalytic system, photo reaction or photoinduced molecular transformation occurs on the photocatalyst surface. The basic mechanism of photocatalytic reaction [19] is governed by the generation of electron-hole pair into the semiconductor and its transportation to destination (*i.e.*, reaction with organic pollutants). Semiconductor photocatalysts generally absorb different color light depending on their band gap energy and used as photocatalysts because of their interesting electronic configurations, light absorption ability, charge carrier transport property, and excitedstate life times. When a photocatalytic surface is exposed by a radiation, it creates a positively charged hole in the valance band and negatively charged electron in the conduction band by exciting the electrons in the valance band to the conduction band.

Photocatalysts + $hv \rightarrow e^- + h^+$ $h^+ + H_2O \rightarrow H^+ + OH^$ $h^+ + OH^- \rightarrow OH^$ $e^- + O_2 \rightarrow O^{2^-}$ $2e^- + O_2 + 2H^+ \rightarrow H_2O_2$ $e^- + H_2O_2 \rightarrow OH^- + OH^-$ Dye + OH^+ + $O_2 \rightarrow CO_2 + H_2O$ + Other degradation product

The conduction band electron reduces oxygen (into O²⁻) adsorbed to photocatalyst surface whereas the positively charged hole oxidizes either organic pollutants directly or

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indirectly by water to produce hydroxyl free radicals (HO[•]). In the photocatalysis of the organic pollutants, the oxidation of pollutants and the reduction process of oxygen do not occurs concurrently, there is an accumulation of electrons in the conduction band of the photocatalyst, thus helping a recombination of negatively charged electron and positive hole. Therefore, efficient utilization of electrons is necessary to encourage photocatalytic oxidation process. Semiconductors can also be used as photocatalysts for environmental remediation. Here, the photon-induced electron-hole pairs helps in redox reactions at the semiconductors catalyst surface and produces hydroxyl free-radicals (OH') and superoxide ions (O^{2}) . These generated species act as powerful oxidizer to disintegrate harmful organic pollutants in wastewater and convert them into CO₂ and H₂O. The most significant and fundamental components for a proficient photocatalytic system are the photocatalyst, the light source are the reactor configuration.

3.3. Degradation studies in Dark and Sunlight

3.3.1. Effect of photocatalyt loading and varying concentration of dye

The effect of photocatalyst loading on the percentage degradation of dyes has been studied by varying its amount from 0.01g - 0.09 g / 50 ml of dye solution. The % of degradation efficiency increases by increasing the amount of catalyst for the removal of Brilliant Green (BG) dye using the prepared nanomaterials. The increase in the efficiency seems to be due to the increase in the total surface area (namely number of active sites) available for the photocatalytic reaction as the dosage of photocatalyst increased. Also the degradation of dye was studied by varying the initial concentrations from 20 to 100 ppm. Generally the percentage degradation of dye decreases with increase in the amount of dye concentration. Due to the fact that as the concentration of dye molecule increases, more molecules get adsorbed on the photocatalyst surface, the substrate concentration can influence the extent of adsorption and rate of reaction at the surface of the photocatalyst. It will be an important remitter for optimization between high degradation rate and efficiency found the optimum propoxur concentration. Above this concentration, the rate decrease due to insufficient quantity of OH' radicals, as the formation of 'OH radicals is a constant for a given amount of the catalyst. From the result obtained, it is found that NiO/CuO nanocomposites have better ability to remove Brilliant Green (BG) dye compared to other two nanomaterials. This is due to the fact that the particle size of NiO/CuO nanocomposites is low compared to NiO and NiO/ZnO.

3.3.2. Effect of pH and Contact time

The removal of Brilliant Green (BG) is found to be maximum at higher pH. Since it is a cationic dye, at higher pH, there exists a reaction between OH^- ions and BG molecule with the disruption of conjucation. At pH \leq 2 BG dye solution became almost colourless. This is due to the nucleophilic attack of H_3O^+ . H_3O^+ destroyed the conjucation between the aromatic rings and a colorless compound was formed at low pH. The degradation of Brilliant Green (BG) dye using different nanomaterials reached equilibrium within 60 mins.

3.3.3. Effect of electron acceptors

In the present study, there are two electron acceptors have been used for the degradation of Brilliant Green (BG) (i.e. H_2O_2 and $K_2S_2O_8$). In heterogeneous photocatalytic reaction, molecular oxygen (air) has been used for this purpose as an electron acceptor for prevention of electron hole recombination. One approach used to prevent electron hole recombination is to add electron acceptors into the reaction media. The presence of H_2O_2 as electron acceptor can serve as electron scavengers to prevent the recombination and enhance photodegradation efficiency. H_2O_2 has several effects including: (a) avoid recombination of electronhole by accepting the conduction band electron and (b) increase the concentrations of the hydroxyl radical [20-23].

 $\begin{aligned} H_2O_2 + h\upsilon &\rightarrow 2 \text{`OH} \\ h^+ + OH^- &\rightarrow \text{`OH}^- \\ e^- + O_2 &\rightarrow O_2^{-} \\ e^- + H_2O_2 &\rightarrow \text{HO'} + OH^- \end{aligned}$

Dye molecules + 'OH \rightarrow H₂O + dye' \rightarrow further oxidation

Peroxydisulphate anion $(S_2O_8)^{2^-}$ is considered as a strong oxidizing agent ($E^0=2.01V$) and can be activated by means of UV/Solar irradiation, heat energy, transition metal ions or ultrasound irradiation to produce sulphate radicals (SO_4^+) as a stronger oxidizing agent with a redox potential of 2.6 V [24, 25]. As can be seen from the above tables and graphs, it indicates that the increasing the concentration of $K_2S_2O_8$, the decolorization efficiency increases with in 60 min. This result can be explained by the following mechanisms. Firstly, sunlight irradiation can activate the $S_2O_8^{2^2}$ ions. In the next step, hydroxyl radicals may be formed through sulphate radicals. Furthermore, produced sulphate radicals can contribute in the degradation of organic dyes.

$$S_2O_8^{2^2} + hv \rightarrow 2SO_4^{\bullet^-}$$

 $SO_4^{\bullet^-} + H_2O \rightarrow H^+ + SO_4^{2^2} + OH^{\bullet}$
 $SO_4^{\bullet^-} + Dye \text{ molecules} \rightarrow SO_4^{2^2} + Intermediates + H$

 $SO_4^{\bullet^*}$ + Intermediates $\rightarrow SO_4^{2^*}$ + CO_2 + H_2O + Other degradated products

From the results obtained, it is found that the degradation of BG dye increases by increasing the concentration of H_2O_2 as well as $K_2S_2O_8$ using the prepared nanomaterials. This is because of the fact that both are acting as electron acceptors.



Fig.5: Effect of variable parameters for the degradation of BG using the prepared nanomaterials

3.4. Comparative Study

Keeping all the factors identical, the effect of photocatalyst on photo catalytic degradation of BG was studied by using different photocatalysts such as NiO Nanoparticle, NiO/ZnO Nanocomposite, NiO/CuO Nanocomposite. The overall photo degradation extent increased, over the composite systems is in the order: NiO $\leq NiO/ZnO \leq NiO/CuO$

NiO < NiO/ZnO < NiO/CuO.

The NiO/CuO nanocomposite has shown the maximum activity exhibiting above 85 % dye degradation under investigation; its activity was noticeably higher than the other catalysts. The comparative study has been carried out for the degradation of dye solution in sunlight and dark. The aqueous suspensions of photocatalyst 0.05g/50ml containing BG dye (60ppm) was exposed to

sunlight and dark at neutral pH. The rate of degradation was found to be slightly more in the sun light in comparison to dark. This is due to sunlight have all type of radiation. So the solar light can be efficiently used for the photocatalytic degradation of waste water. In tropical countries like India, enough amount of sunlight is available throughout the year and hence it could be efficiently used for Photocatalytic degradation of pollutants in waste water. Also in the absence of sunlight, the prepared nanomaterial are adsorbed the dye molecules on its surface whereas in the presence of sunlight the removal of BG dye is maximum because, under Sunlight both adsorption and Photocatalytic degradation can takes place.

4. CONCLUSION

The NiO nanoparticle, NiO/CuO and NiO/ZnO nanocomposites are effective photocatalysts for the removal of Brilliant Green (BG) dye. The degradation was found to be highly dependent on pH. Alkaline conditions favor the removal of Brilliant Green (BG) dye. The percentage removal decreased with increasing concentration of dye. The degradation process was also dependent on dosage of adsorbent, initial concentration, pH and contact time. The optimum adsorbent dosage and contact time are 0.05g/50ml and 60 minutes.

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